

THERMODYNAMIC PROPERTIES OF NONSTOICHIOMETRIC NICKEL  
TELLURIDES AND OF TELLURIUM

BY

Robert E. Machol

A dissertation submitted in partial fulfillment  
of the requirements for the degree of  
Doctor of Philosophy in The  
University of Michigan  
1957

Doctoral Committee:

- Associate Professor Edgar F. Westrum, Jr., Chairman
- Associate Professor Richard B. Bernstein
- Professor Joseph O. Halford
- Professor Joseph J. Martin
- Associate Professor Charles L. Rulfs
- Dr. O. Lyle Tiffany

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## PREFACE

The time has passed when a Faraday, working with a ball of wax and a piece of string, could make prodigious scientific discoveries. To obtain that all-important extra decimal place, the modern investigator must construct highly sophisticated apparatus, and this makes him dependent on a host of supporters and technicians. I wish to thank the U. S. Atomic Energy Commission, the U. S. Veterans Administration, The University of Michigan Engineering Research Institute, and The University of Michigan Chemistry Department for financial support. I wish to thank D. I. Myers, Jr., for Pyrex glass blowing; J. A. Mannlein for machining innumerable materials to exacting specifications; P. D. Barakauskas for carpentry; F. Grønvold for preparation of nickel telluride samples; and many others for procurement of materials, for instrumentation, for translations, for bibliographic aid, for data reduction, for optical equipment design, for aid in spectroscopic analyses and x-ray analyses, etc. I wish to express especial appreciation to Gunther Kessler, glassblower for The University of Michigan Physics Department, who undertook all of the extremely difficult silica glassblowing required in this research although it was outside his normal responsibility.

I would also like to take this opportunity to thank Professors R. W. Parry, L. O. Case and the members of my research committee, and in particular Prof. E. F. Westrum, Jr., the chairman of that committee, for their sympathetic guidance and their extraordinary patience in listening to, and answering, my innumerable questions.

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## I. INTRODUCTION

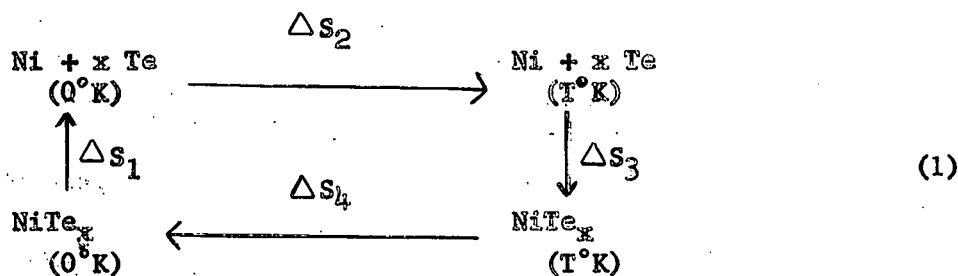
The interesting nature of the nickel/tellurium system was first indicated\* by Tengner<sup>1</sup>, who asserted that there was a continuous and homogeneous transition between the stoichiometric compounds NiTe and NiTe<sub>2</sub>. More recent work<sup>2</sup>, has indicated that the single-phase region extends only from NiTe<sub>2.00</sub> to about NiTe<sub>1.08</sub> at room temperature, although at higher temperature it apparently<sup>3</sup> goes to NiTe or beyond. Certainly the region of homogeneity is unusually wide, and exhibits an unusual continuous transition from one crystal structure (NiTe of NiAs type<sup>4</sup>) to another (NiTe<sub>2</sub> of CdI<sub>2</sub> type<sup>1</sup>). In proceeding from NiTe to NiTe<sub>2</sub>, nickel atoms are removed from alternate (0,0,1/2) planes, while the positions of the remaining nickel atoms (in 0,0,0 and 0,0,1 planes) and of the hexagonal-close-packed tellurium atoms (in 2/3, 1/3, 1/4 and 1/3, 2/3, 3/4) are affected very little, so that the basic structure and the lattice constants undergo very little change (the c-axis--the distance from 0,0,0 to 0,0,1  $\psi$ --contracts by only 2%).

Whether the intermediate compositions are solid solutions or non-stoichiometric chemical compounds is a question of semantics only. They are unusual and poorly understood, and for both these reasons are of interest. Furthermore, they are apparently free from magnetic complication, making them particularly suitable for thermodynamic studies. It is of interest to know whether the holes in the 0,0,1/2 plane are ordered, and if so whether there is a second order transition accompanying their disorder; whether at higher temperatures there might be disordering accompanying transfer of some of these holes to the 0,0,0 and 0,0,1 planes; and so forth.

\* The literature on the nickel/tellurium system is summarized in Appendix 1.

For these reasons a study of this system was undertaken, and as a point of departure, an attempt was made to collect data which would determine zero-point entropy as a function of composition; if this entropy could be determined with sufficient accuracy it could be correlated with the degree of randomness of the holes at 0°K. The present thesis is concerned with the collection of some of this data, and with certain other phenomena concerning tellurium and the nickel tellurides which appeared to be related or of interest. As a by-product of this effort was developed the major contribution of this work: an apparatus and technique for the measurement of vapor pressures at high temperatures which is widely applicable and believed capable of greater accuracy than any other method described in the literature.

Zero-point entropy is determined by consideration of the following cycle:



$\Delta S_1$  is determined by measuring  $\Delta S_2$ ,  $\Delta S_3$ , and  $\Delta S_4$  experimentally and taking their sum; on the reasonable assumptions that the zero-point entropy of nickel<sup>5</sup> is zero and the zero-point entropy of crystalline tellurium<sup>6</sup> is zero, this entropy change is equal to the entropy of the compound.  $\Delta S_2$  and  $\Delta S_4$  are determined by

$$\Delta S = S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} \frac{C_p}{T} dT = \int_{T_1}^{T_2} C_p d \ln T \quad (2)$$

where  $C_p$  is the heat capacity at constant pressure, and is determined experimentally for each element and for the various compositions of the compounds. Heat capacities are discussed in Section II of this report.

There are many thermodynamic relations connecting entropy with other quantities, but the number of methods which are practically capable of giving sufficient accuracy for "third-law determinations" at the high temperatures necessary (see below) is small, and as applied to this problem was soon reduced to two basic relationships:

$$\Delta S_3 = \frac{\Delta H - \Delta G}{T} \quad (3)$$

$$\Delta S_3 = - \left( \frac{\partial \Delta G}{\partial T} \right)_p = - \left( \frac{\partial \Delta F}{\partial T} \right)_v \quad (4)$$

where  $G$  is the Gibbs free energy,  $F$  the Helmholtz free energy,  $H$  the enthalpy, and  $T$  the absolute temperature.

Attention was first directed to (3), and some study was made of the possibility of determining the heat of reaction at or near room temperature; this abortive study is reported in section 4A. However, it appeared that the necessary accuracy would be difficult to obtain. Furthermore, after the measurements on enthalpy of reaction had been made, it would still be necessary to determine the free energy of reaction; since these measurements must be made in any case, it seemed simpler to make them at different temperatures and use (4), and so the investigation of enthalpy measurements was dropped.

Two basically different methods are available for measuring the free energy of the reaction between nickel and tellurium: electrochemical measurements, and measurement of the pressure of some volatile

material directly or indirectly involved in the reaction. The same basic difficulty plagues both methods: the reaction being measured takes place at the interface between a solid phase of variable composition (the nickel telluride) and a fluid phase (the electrolyte, or the vapor), thus altering the composition of the surface layer of the solid, and therefore its chemical potential (which is ultimately the quantity being measured). To avoid errors it is therefore necessary that the reaction be carried out at a sufficiently high temperature that self-diffusion is rapid enough to effect homogeneity (and therefore make possible the measurement of true equilibrium) within a reasonable time interval. Furthermore, it is highly desirable that the nature of the experiment be such that it is possible to prove that true equilibrium had indeed been established.

At the time when these experiments were started, no adequate prediction was available from solid-state physics as to the temperature which must be achieved to obtain sufficiently rapid diffusion. In general, solid-state diffusion follows an expression of the form  $C \exp(E/RT)$ , where  $C$  is a constant,  $E$  an energy of activation,  $R$  the gas constant, and  $T$  the absolute temperature. However, there are many exceptions to this rule, and there is no good way to predict either  $C$  or  $E$ . "Tammann's rule"<sup>7</sup> states that self-diffusion becomes "appreciable" at 0.52 to 0.57 times the melting point; a recent article in an electrochemical journal<sup>8</sup> states: "experience has shown that operating temperatures not lower than 0.3 or 0.4 of the absolute melting temperature of the alloy are suitable." The latter statement seems unduly optimistic, and the former is difficult to apply when the solidus and liquidus temperatures are far apart, as in this case, and it is not clear which is to be taken as the "melting point". At the start of these experiments

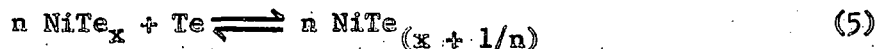
it was known<sup>3</sup> that the solidus temperatures for these compounds was in the neighborhood of 900°C, and it was therefore guessed that the minimum temperature for equilibrium might be as low as 400° or as high as 700°, and the apparatus was designed for a maximum operating temperature of 750°C (it has actually been operated at considerably higher temperatures). It has turned out that no lag in vapor pressure could be measured corresponding to a small change in the temperature of any of the nickel tellurides, and this was at first taken to mean that solid state diffusion was rapid at all the temperatures at which vapor pressures were high enough to be measured. Subsequently it was discovered that this experimental result merely meant that homogenization of a thin layer at the surface of the various crystallites was sufficient to give this apparent equilibrium; but when a great excess of tellurium was present, it required some hours at 700°C to diffuse homogeneously into the center of every crystallite. This is in agreement with Grönvold's qualitative observation<sup>9</sup> that equilibrium requires several hours at 700° and a month at 450°.

High-temperature electrochemical measurements always introduce the possibility of systematic errors; for example, there must be several interfaces in the cell, and thermoelectric potentials may be set up at any of them. The volatility of the tellurium would be a complicating factor, especially in view of the very poisonous and corrosive nature of tellurium vapor. The tellurium vapor would be certain to attack any metal which it contacted, thus altering the concentration of the nickel tellurides. Some of these problems have presumably been solved (although one cannot be sure about systematic errors) for some tellurides, since experimental electrochemical measurements have been reported<sup>10</sup> for the

free energy of formation of ZnTe, CdTe, SnTe, and PbTe. However, these metals do not form nonstoichiometric compounds, as nickel does; the article states that the emf's were not affected by the presence of excess metal, while the free energy of formation of the nickel tellurides is a very sensitive function of concentration in the single-phase region. In the vapor pressure measurements which were made, the accuracy was sufficient to detect a change in concentration of less than 0.01%.

Attention was therefore turned to pressure measurements. A number of indirect methods are available; for example, the reduction of water vapor to produce hydrogen, and subsequent measuring of the total pressure. All such methods, however, are complicated by the presence of tellurium vapor, and it seemed best, therefore, simply to measure the pressure of that vapor. The method finally chosen for this measurement is described in Section 3. It is characterized by a constant pressure error of approximately 0.1 mm Hg, and is therefore extremely accurate at high pressures; however, it is considerably less accurate at lower pressures. Furthermore, the reduction in vapor pressure with addition of nickel was more rapid than expected, so that no measurements at all were possible below  $\text{NiTe}_{1.5}$ , and measurements of any accuracy were not possible below  $\text{NiTe}_{1.7}$ , and at that concentration only at temperatures above about  $750^\circ$ . This means that specific heat measurements will have to be extended to about  $750^\circ$ , and every slight rise in temperature in this region means additional experimental difficulties and errors in specific heat measurement. However, such measurements will allow some overlap in the region around  $\text{NiTe}_{1.9}$ , which will allow a desirable check, since  $d \Delta S/dT$  can be determined independently by the two methods.

The reaction being observed when one measures the pressure (dissociation pressure) of tellurium vapor over nickel telluride can be expressed in the following way:



In making measurements at equilibrium, one attempts to make the sample size sufficiently large and the vapor space sufficiently small that the concentration of the  $\text{NiTe}_x$  is not appreciably changed. In the limit of such an experiment,  $n$  may be considered infinite, and (5) describes the addition of one mole of tellurium to an infinite amount of  $\text{NiTe}_x$ . If the tellurium is in its standard state (which is liquid at all temperatures of interest in this experiment), then the free energy change is the sum of three terms: the free energy of converting one mole of liquid tellurium to vapor at the equilibrium pressure  $p_0$  (free energy change equals zero); the free energy of expanding one mole of tellurium vapor from  $p_0$  to  $p$ , for which the free energy change is given by

$$\Delta G = RT \ln \frac{p}{p_0} \quad (6)$$

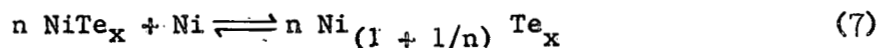
and the free energy of converting one mole of tellurium vapor at the equilibrium pressure  $p$  to nickel telluride (free energy change equals zero). Hence the free energy change corresponding to (5), which is called the partial molal free energy of tellurium in  $\text{NiTe}_x$ , and denoted by  $\Delta G_{\text{Te}}$ , is given by (6); this applies to two gram-atoms of tellurium.

All of the equations given thus far are thermodynamically rigorous with the exception of (6), which would be rigorous if the pressures were replaced by fugacities. The error involved in this substitution



appears to be negligible insofar as imperfection of the gas is concerned, because of the high temperature and low pressure involved. A serious error would be made if the number of atoms per molecule were variable, since the ratio of pressure to fugacity would be a function of pressure. However, there is strong evidence<sup>41,72</sup> that the number of atoms per vapor molecule is not appreciably greater than two at temperatures well below the triple point, and not appreciable less than two at temperatures well above 1000°C, and so it seems safe to assume that it is invariant with pressure in the temperature range of interest here, namely 600 to 800°C.

Corresponding to (5) is a similar expression for nickel:



for which the free energy is  $\Delta \bar{G}_{\text{Ni}}$ . If we now add  $x$  gram-atoms of tellurium and one gram-atom of nickel to an infinite quantity of  $\text{NiTe}_x$ , we have formed exactly one new mole ( $1 + x$  gram-atoms) of  $\text{NiTe}_x$ , and the free energy is given by

$$\Delta G = \frac{1}{(1 + x)} \Delta \bar{G}_{\text{Ni}} + \frac{x}{2(1 + x)} \Delta \bar{G}_{\text{Te}} \quad (8)$$

where  $\Delta G$  is the integral free energy of formation per gram-atom, and is the quantity in equation (4). There are also equations corresponding to (4) for partial molal quantities, and one corresponding to (8) for adding partial molal entropies to obtain the integral entropy of formation, the  $\Delta S_3$  of (1); this method of computation would of course yield the same result.

Partial molal free energies of tellurium have been determined at temperatures from about 550° to 780°C for all concentrations from

100% to 60% tellurium. No data have been obtained on the partial molal free energy of nickel. The two partial molal free energies are related by a Gibbs-Duhem equation of the form

$$C_{Ni} \left( \frac{\partial \Delta \bar{G}_{Ni}}{\partial C_{Ni/T}} \right) = C_{Te} \left( \frac{\partial \Delta \bar{G}_{Te}}{\partial C_{Te/T}} \right) \quad (9a)$$

where  $C_{Ni}$  is the concentration (atomic fraction) of nickel,  $C_{Te}$  is the concentration (atomic fraction) of tellurium, and the sum of the two concentrations is unity. Writing  $C = C_{Te} = 1 - C_{Ni}$ , this equation can be rewritten as follows:

$$\Delta \bar{G}_{Ni} = \int_{C_1}^{C_2} \frac{C}{1-C} \left( \frac{\partial \Delta \bar{G}_{Te}}{\partial C} \right)_T dC + K \quad (9b)$$

so that the partial molal free energies of the nickel can be obtained from the partial molal free energies of the tellurium, provided a boundary condition is available to determine the constant K. At 100% tellurium, the partial molal free energy of tellurium is zero (as is evident from equation (6)) and the partial molal free energy of nickel is infinite; from (9) it is clear that the slope of  $\Delta \bar{G}_{Ni}$  must be infinite at this point. Thus, to obtain the partial molal free energies of nickel it is necessary either to extend the vapor pressure measurements to 0% tellurium (where K is known to be zero), which is impossible by several orders of magnitude with the present apparatus, or to obtain the partial molal free energy of nickel at one concentration at various temperatures.\* This has not been done. As indicated in

\* With the data at hand, (9b) can be solved except for the unknown K, and (4) could then be solved except for the unknown  $dK/dT$ . There appears to be no way to estimate these unknowns at the present time.

Section 2, the high-temperature specific heats are also lacking. Both of these sets of data must be obtained before the zero-point entropies can be computed.

## II. HEAT CAPACITIES

As discussed in the previous section, it is necessary to know the heat capacities of nickel, tellurium, and the nickel tellurides from 0° to about 1000° K in order to determine the zero-point entropies. The heat capacity of nickel is known over this entire range. The heat capacity of tellurium has been determined up to about 800° K, but much of this data is uncertain. The heat capacity of the nickel tellurides was of course unknown at the start of this research.

It is convenient and conventional to consider such heat-capacity data under two headings: low temperature (from 0°K to about 300°K), and high temperature (above 300°K).

Two basic methods of calorimetry for measurement of thermal properties are available: adiabatic, and drop. In the first, a known, small amount of energy is supplied to the sample, and its temperature rise noted. The temperature rise is small enough that the actual heat capacity ( $dH/dT$ ) can be accurately computed from the observed mean heat capacity ( $\Delta H / \Delta T$ ). If the observed heat capacity shows high curvature (as a function of temperature), smaller temperature intervals can be used, trading accuracy in temperature-interval measurement for accuracy in curvature correction. The important point is that the sample can be maintained approximately in thermal equilibrium at all times.

In drop calorimetry, the total enthalpy difference between some variable temperature,  $t$ , and some fixed temperature, usually 0°C, is measured; then

$$\Delta H (t_2 \rightarrow t_1) = \Delta H (t_2 \rightarrow 0) - \Delta H (t_1 \rightarrow 0)$$

and the heat capacity,  $C = dH/dT$ , is computed as before. Although the enthalpy increments thus computed are small differences between large numbers, the total enthalpies and the temperature increments may be measured with great accuracy, so that the results are good where the method is applicable. The disadvantage of drop calorimetry for the present purpose is that high-temperature phenomena (such as disorder) may be frozen in when the sample is quenched, and true specific heats are therefore not in general obtained if there are any first or second order transitions or similar anomalies in the interval. This objection does not apply to low-temperature specific heats, and the method is capable of high accuracy<sup>\*</sup>; but adiabatic calorimetry is also capable of high accuracy below room temperature and is more convenient for collection of large amounts of data. At high temperatures, in addition to the many difficulties which plague any precision measurements, the fourth-power increase in radiation makes temperature drifts larger and more difficult to correct for, and therefore makes drop calorimetry the most accurate when it is applicable.

## 2A. LOW TEMPERATURE

2.A.1 Nickel. The low-temperature heat capacity of nickel has been measured many times. In particular, measurements of exceedingly high

\* It is interesting to note that Busey and Giauque<sup>5</sup>, in reporting their own very accurate measurements on the low-temperature specific heat of nickel, discuss all of the preceding work except the very old measurement by Tilden<sup>17</sup> of the mean specific heat of nickel between the boiling point of oxygen and 15°C, determined by drop calorimetry. Nevertheless, Tilden's result, when appropriately corrected, is more accurate than any of the intervening work when compared with the results of Busey and Giauque.

accuracy on very pure samples are available in the range 15°K to room temperature<sup>5</sup> and 1.7° to 4.2°K<sup>11</sup>. Data of slightly less accuracy are available in the intermediate ranges 1° to 20°K<sup>12</sup> and 10° to 26°K<sup>13</sup>. The entropy of nickel at room temperature may be assumed known with an error so small as to be quite negligible in comparison with the other data involved.

2.A.2. Tellurium. The low-temperature heat capacity of tellurium has been measured down to liquid nitrogen temperature<sup>14</sup> and to liquid helium temperature<sup>15</sup>. Recently, very accurate measurements on very pure samples have been made over the range 4.5 to 350°K,<sup>6</sup> and 1.5° to 4.5°K<sup>20</sup>. The entropy of tellurium at room temperature may therefore also be considered known with adequate accuracy.

2.A.3. Nickel Tellurides.<sup>\*</sup> Heat capacity measurements in the range 4.5 to 350°K were run on three compositions of nickel tellurides, namely NiTe<sub>1.1</sub>, NiTe<sub>1.5</sub>, and NiTe<sub>2.0</sub>. The samples were especially prepared for this purpose and were thoroughly annealed at temperatures down to 450°C. They were cooled slowly from this temperature to room temperature, but it is not believed that any changes in structure take place in reasonable periods of time at temperatures below 450°. The samples are believed to be 99.99% pure, and to have the stated compositions within 0.01%.

\* Although the author cooperated in the operation of the calorimeter, the reduction of the data, and the interpretation of the results, most of the work reported in this section was performed by E. F. Westrum, Jr., C. Chou, and F. Grønvd.

Sample sizes for the calorimetry were approximately 170 grams each for  $\text{NiTe}_{1.1}$  and  $\text{NiTe}_{1.5}$  and 120 grams for  $\text{NiTe}_{2.0}$ . The smaller weight of the latter was due to its smaller bulk density, which is due to its mica-like cleavage which in turn is due to its layered crystalline lattice. Care was taken not to force the soft flakes of  $\text{NiTe}_{2.0}$  into the calorimeter, since this might have altered the heat capacity through cold-working.

The calorimeter and cryostat have been described elsewhere.<sup>16</sup> The samples were cooled to liquid-helium temperature over a period of about two days, and the heat capacity measured by noting the temperature rise produced by a known input of electrical energy. The temperature increments can be adjudged from the adjacent mean temperatures of the data in Table I which are given in chronological order. The heat capacities are expressed in terms of the defined thermochemical calorie, equal to 4.1840 absolute joules; the ice point is taken to be 273.15°K; the atomic weights of nickel and tellurium are taken to be 58.69 and 127.61 respectively. The data are expressed in terms of one total gram-atom of substance--i.e. 94.79 grams of  $\text{NiTe}_{1.1}$ , 100.04 grams of  $\text{NiTe}_{1.5}$ , and 104.64 grams of  $\text{NiTe}_{2.0}$ --which is equivalent to using the formula  $\text{Ni}_{0.4}\text{Te}_{0.6}$  for  $\text{NiTe}_{1.5}$ , for example. The heat capacities ( $C_p = dH/dT$ ) were determined by adding to the experimentally observed value of  $\Delta H/\Delta T$  for each temperature interval an analytically determined curvature correction, and are plotted on Fig. 1.

The heat capacities of Table I were plotted on a large graph and a smooth curve drawn through them. This curve had the usual sigmoid shape and no singularities or inflections other than the major inflection predicted by Debye theory, except for an unexplained increase in the heat capacity of  $\text{NiTe}_{1.1}$  of about 0.01 calories per gram-atom which occurred in the neighborhood of room temperature.

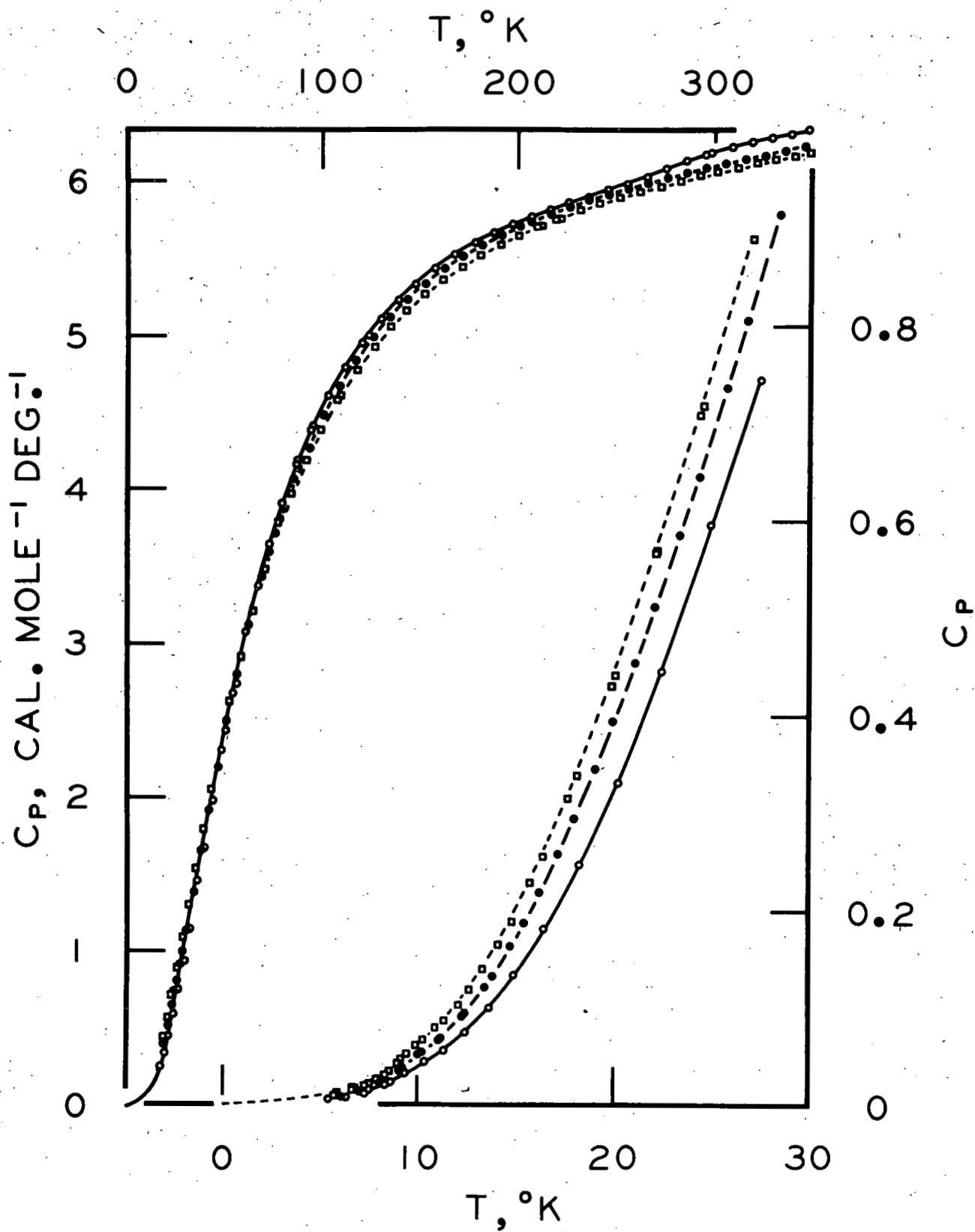


FIGURE 1

215 021

HEAT CAPACITY OF NICKEL TELLURIDES



TABLE I. HEAT CAPACITY OF NICKEL TELLURIDES  
(in cal/"mole" deg)

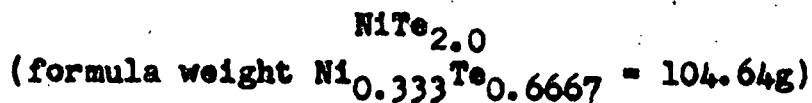
T, °K	C <sub>p</sub>	T, °K	C <sub>p</sub>	T, °K	C <sub>p</sub>
NiTe <sub>1.1</sub> (formula weight Ni <sub>0.4762</sub> Te <sub>0.5238</sub> = 94.79g)					
Series I		27.44	0.7470	138.62	5.229
		30.08	0.9234	147.64	5.334
5.44	0.0065	33.18	1.143	157.35	5.435
6.44	0.0099	36.60	1.393	167.52	5.523
7.56	0.0154	40.37	1.670	177.63	5.598
8.65	0.0240	44.61	1.974	187.57	5.665
		49.47	2.308	197.10	5.721
Series II		55.05	2.674	206.52	5.771
		51.25	2.433	216.13	5.817
5.41	0.0064	56.11	2.740	225.83	5.860
6.38	0.0093	61.85	3.079	235.58	5.903
7.33	0.0140	67.67	3.381	245.31	5.941
8.34	0.0209	73.54	3.647	255.16	5.982
9.36	0.0302	79.97	3.916	265.11	6.026
10.34	0.0427	87.07	4.175	275.09	6.081
11.34	0.0576	94.38	4.391	285.08	6.132
12.44	0.0765	87.69	4.196	295.18	6.174
13.63	0.1018	95.21	4.414	298.82	6.181
14.93	0.1356	103.23	4.613	308.92	6.217
16.44	0.1829	111.74	4.796	318.95	6.248
18.23	0.2493	120.27	4.957	328.91	6.274
20.20	0.3369	123.47	5.006	338.80	6.294
22.43	0.4482	129.99	5.110	347.16	6.321
24.95	0.5910				

TABLE I (continued)

$\text{NiTe}_{1.5}$   
(formula weight  $\text{Ni}_{0.4}\text{Te}_{0.6} = 100.04\text{g}$ )

Series I		11.13	0.0690	117.37	4.836
		12.43	0.0963	126.07	4.990
6.33	0.0108	13.82	0.1343	134.78	5.121
7.29	0.0167	15.41	0.1892	143.56	5.235
8.34	0.0240	17.18	0.2605	152.66	5.337
9.28	0.0382	19.03	0.3479	162.16	5.432
10.24	0.0556	21.08	0.4564	171.91	5.514
11.20	0.0702	23.32	0.5880	181.61	5.586
12.27	0.0923	25.71	0.7394	191.29	5.652
13.44	0.1231	28.36	0.9164	200.90	5.708
14.72	0.1654	31.53	1.135	206.43	5.735
16.22	0.2205	35.12	1.386	216.26	5.785
17.97	0.2968	38.88	1.649	226.08	5.828
19.95	0.3967	42.83	1.915	235.89	5.871
22.06	0.5143	47.10	2.197	245.75	5.912
24.30	0.6480	51.87	2.494	255.65	5.949
26.75	0.8084	57.19	2.803	265.60	5.986
29.50	0.9943	63.15	3.125	275.68	6.021
		69.84	3.440	285.61	6.055
Series II		76.60	3.723	295.57	6.084
		73.70	3.603	305.64	6.114
6.18	0.0104	78.72	3.807	315.65	6.139
7.12	0.0153	85.34	4.053	325.63	6.160
8.14	0.0233	92.54	4.272	335.65	6.188
9.11	0.0355	100.77	4.488	345.72	6.217
10.07	0.0504	109.14	4.676		

TABLE I (continued)



Series I		8.26	0.0313	118.18	4.775
		9.23	0.0475	126.70	4.925
5.86	0.0120	10.26	0.0648	135.20	5.054
6.79	0.0169	11.38	0.0887	143.73	5.169
7.56	0.0230	12.66	0.1206	152.58	5.267
8.53	0.0357	14.11	0.1671	161.71	5.363
9.48	0.0515	15.76	0.2313	171.18	5.444
		17.68	0.3179	180.91	5.519
Series II		19.89	0.4337	190.65	5.589
		22.17	0.5710	200.27	5.648
5.75	0.0113	24.51	0.7212	209.80	5.700
6.86	0.0172	24.37	0.7119	219.36	5.749
7.91	0.0270	26.99	0.8904	212.33	5.711
8.98	0.0434	29.82	1.091	221.75	5.756
9.94	0.0601	32.83	1.302	231.53	5.808
10.94	0.0800	36.19	1.538	241.59	5.853
12.08	0.1055	39.95	1.792	251.78	5.893
13.36	0.1421	44.06	2.054	262.05	5.928
14.82	0.1929	48.63	2.336	272.32	5.967
16.40	0.2581	53.72	2.623	282.57	6.001
18.15	0.3414	59.32	2.918	292.75	6.035
20.05	0.4461	65.36	3.212	302.97	6.062
22.14	0.5693	71.74	3.481	301.49	6.062
		78.15	3.732	311.64	6.087
Series III		84.81	3.972	321.43	6.114
		92.01	4.196	330.87	6.140
5.90	0.0123	99.89	4.391	340.47	6.158
6.76	0.0164	108.39	4.583	348.23	6.177
7.40	0.0216	109.78	4.614		

Above 30°K most of the points deviated from the smooth curve by less than 0.001 calories per gram-atom per degree (the curve was stretched out to a total length of almost 15 meters and plotted with a pencil sufficiently sharp so that deviations of 0.2 mm would be plainly evident; no deviations could be seen for most of the points). The deviations were not normally distributed, and in a few cases were close to 0.01 calories per gram-atom per degree. Experience indicates that these deviations are not reproducible and presumably not significant. Below 30°K the measurements become increasingly inaccurate, due to the smaller absolute heat capacity, the smaller temperature intervals (necessitated by the increasing curvature), and the decreased sensitivity of the thermometer. Fortunately the specific heat of all three compounds had reached a  $T^3$  dependency at the lowest temperatures reached, so that the extrapolation to 0°K could be made with considerable confidence.

Values of  $C_p$ ,  $H^\circ - H_0^\circ$ , and  $S^\circ - S_0^\circ$  at rounded temperatures are shown in Table II. The enthalpy and entropy increments were computed by numerical integration, using values of heat capacity at rounded temperatures and rounded logarithms of temperatures which were read from the smooth curve. The values of entropy are considered to be accurate to  $\pm 0.02$  calories per gram-atom per degree, and the enthalpy values are considered accurate to  $\pm 0.2\%$  except at the lowest temperatures; relative accuracies (e.g. comparison of entropies or enthalpies of different compositions at the same temperature) are somewhat better. The temperatures given in Tables I and II are believed to correspond with the thermodynamic scale within 0.03° from 10° to 90°K and within 0.04° from 90° to 350°K; relative temperature accuracy is better by a factor of almost 100 (the error of measuring the temperature intervals is probably less than 0.001°):

TABLE II. Thermodynamic properties of nickel tellurides  
(in cal/"mole" deg)

T, °K	NiTe <sub>1.1</sub>			NiTe <sub>1.5</sub>			NiTe <sub>2.0</sub>		
	(formula weight Ni <sub>0.4762</sub> Te <sub>0.5238</sub> =94.79g)			(formula weight Ni <sub>0.4</sub> Te <sub>0.6</sub> =100.04g)			(formula weight Ni <sub>0.3333</sub> Te <sub>0.6667</sub> =104.64g)		
	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> -S <sub>0</sub> <sup>o</sup>	$\frac{H^o-H_0^o}{T}$	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> -S <sub>0</sub> <sup>o</sup>	$\frac{H^o-H_0^o}{T}$	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> -S <sub>0</sub> <sup>o</sup>	$\frac{H^o-H_0^o}{T}$
10	0.038	0.013	0.010	0.049	0.016	0.012	0.061	0.020	0.015
15	0.138	0.044	0.033	0.175	0.056	0.043	0.200	0.068	0.051
20	0.327	0.108	0.081	0.400	0.135	0.102	0.442	0.156	0.116
25	0.594	0.208	0.156	0.692	0.255	0.190	0.754	0.287	0.212
30	0.918	0.345	0.256	1.029	0.411	0.301	1.103	0.455	0.331
35	1.276	0.513	0.376	1.380	0.596	0.430	1.455	0.652	0.466
40	1.643	0.707	0.511	1.726	0.803	0.571	1.795	0.869	0.612
45	2.001	0.921	0.657	2.060	1.025	0.718	2.114	1.099	0.761
50	2.347	1.150	0.809	2.379	1.259	0.868	2.415	1.337	0.912
60	2.974	1.635	1.118	2.961	1.745	1.170	2.953	1.826	1.208
70	3.490	2.134	1.422	3.447	2.240	1.461	3.412	2.317	1.491
80	3.917	2.628	1.708	3.858	2.727	1.736	3.799	2.799	1.756
90	4.266	3.111	1.973	4.198	3.202	1.991	4.133	3.266	2.002
100	4.540	3.575	2.217	4.469	3.659	2.226	4.400	3.716	2.229
110	4.764	4.018	2.438	4.694	4.096	2.440	4.617	4.146	2.436
120	4.950	4.441	2.640	4.885	4.512	2.636	4.809	4.556	2.626
130	5.110	4.843	2.824	5.052	4.910	2.816	4.978	4.947	2.801
140	5.246	5.227	2.992	5.191	5.290	2.980	5.120	5.322	2.961
150	5.360	5.593	3.146	5.309	5.652	3.132	5.243	5.679	3.109
160	5.459	5.942	3.288	5.411	5.998	3.271	5.347	6.021	3.246

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TABLE II (continued)

170	5.543	6.276	3.418	5.498	6.329	3.400	5.436	6.348	3.372
180	5.615	6.595	3.538	5.575	6.645	3.518	5.514	6.660	3.489
190	5.680	6.900	3.649	5.643	6.949	3.628	5.584	6.960	3.597
200	5.737	7.193	3.752	5.703	7.240	3.731	5.646	7.248	3.698
210	5.788	7.474	3.848	5.755	7.519	3.826	5.701	7.525	3.792
220	5.834	7.744	3.937	5.802	7.788	3.915	5.752	7.791	3.880
230	5.878	8.005	4.020	5.846	8.047	3.998	5.801	8.048	3.963
240	5.919	8.256	4.099	5.888	8.297	4.076	5.846	8.296	4.040
250	5.960	8.498	4.172	5.928	8.538	4.149	5.886	8.535	4.113
260	6.002	8.733	4.242	5.966	8.771	4.218	5.924	8.767	4.182
270	6.052	8.960	4.308	6.002	8.997	4.283	5.959	8.991	4.247
280	6.106	9.181	4.371	6.036	9.216	4.345	5.992	9.208	4.309
290	6.153	9.396	4.432	6.067	9.428	4.404	6.024	9.420	4.368
300	6.191	9.606	4.490	6.096	9.634	4.460	6.054	9.624	4.423
350	6.327	10.571	4.743	6.223	10.584	4.703	6.183	10.567	4.666
273.15	6.069	9.030	4.328	6.013	9.066	4.303	5.970	9.060	4.267
298.15	6.184	9.567	4.479	6.091	9.597	4.450	6.049	9.586	4.413

T, °K

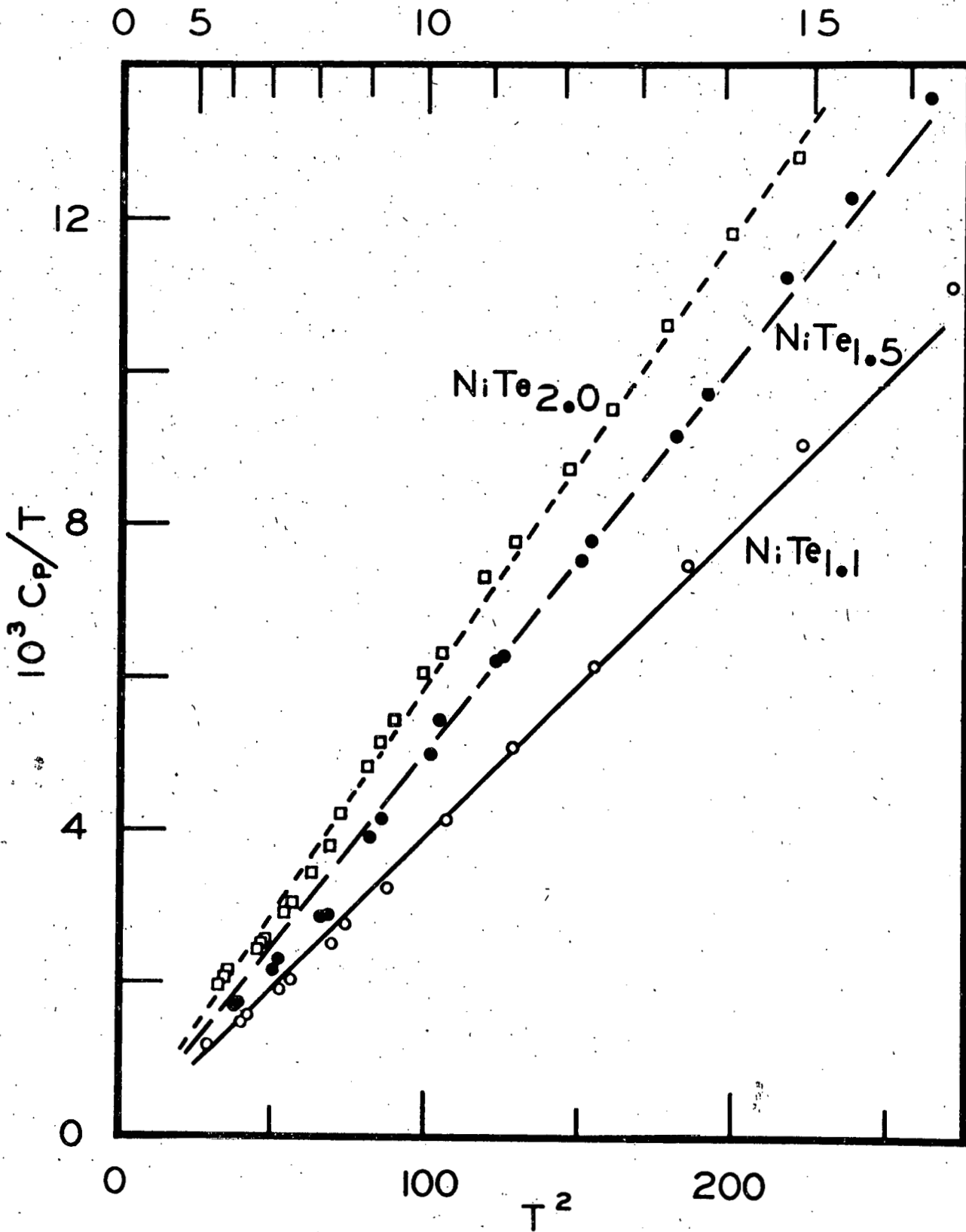


FIGURE 2

DEPENDENCE OF HEAT CAPACITY ON TEMPERATURE AT LOW TEMPERATURE

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Plots of  $\log C_p$  against  $\log T$  and plots of  $C_p/T$  against  $T^2$  (Fig. 2) show that all three compositions had reached a  $T^3$  dependency at the lowest temperatures measured, and the latter plots give no indication of a linear term in  $T$  (such as might be due to an electronic contribution). These results are particularly interesting in the case of  $\text{NiTe}_2$  because of the widespread investigations, both experimental and theoretical, of the heat capacity of layered lattices at low temperatures.

The present data also permit an experimental test of the so-called Kopp-Neumann rule which says that the heat capacity of an alloy is an additive function of the heat capacities of the elements of which it is composed. There is, in fact, little theoretical justification for this rule, although it has often been used in practical metallurgy in the absence of any better method of estimating certain thermodynamic quantities (for example, if the heat of formation of an alloy is known at one temperature and wanted at some other temperature, one often estimates that it is the same). In the light of our modern understanding of crystals, their heat capacity is not a function of the individual atoms, but of the crystal as a whole, particularly at low temperatures. From the viewpoint of Debye theory, there is no reason to expect the characteristic temperature of an alloy to be the appropriate weighted average of the characteristic temperatures of its constituents.

The heat capacity of  $\text{NiTe}_{1.5}$  was computed by means of the Kopp-Neumann rule by adding 0.4 times the atomic heat capacity of nickel to 0.6 times the atomic heat capacity of tellurium, and this was compared with the experimental values of the heat capacity of  $\text{NiTe}_{1.5}$ . The heat capacity of tellurium was taken from the older data<sup>14,15</sup>. The heat capacity of nickel was corrected for the electronic



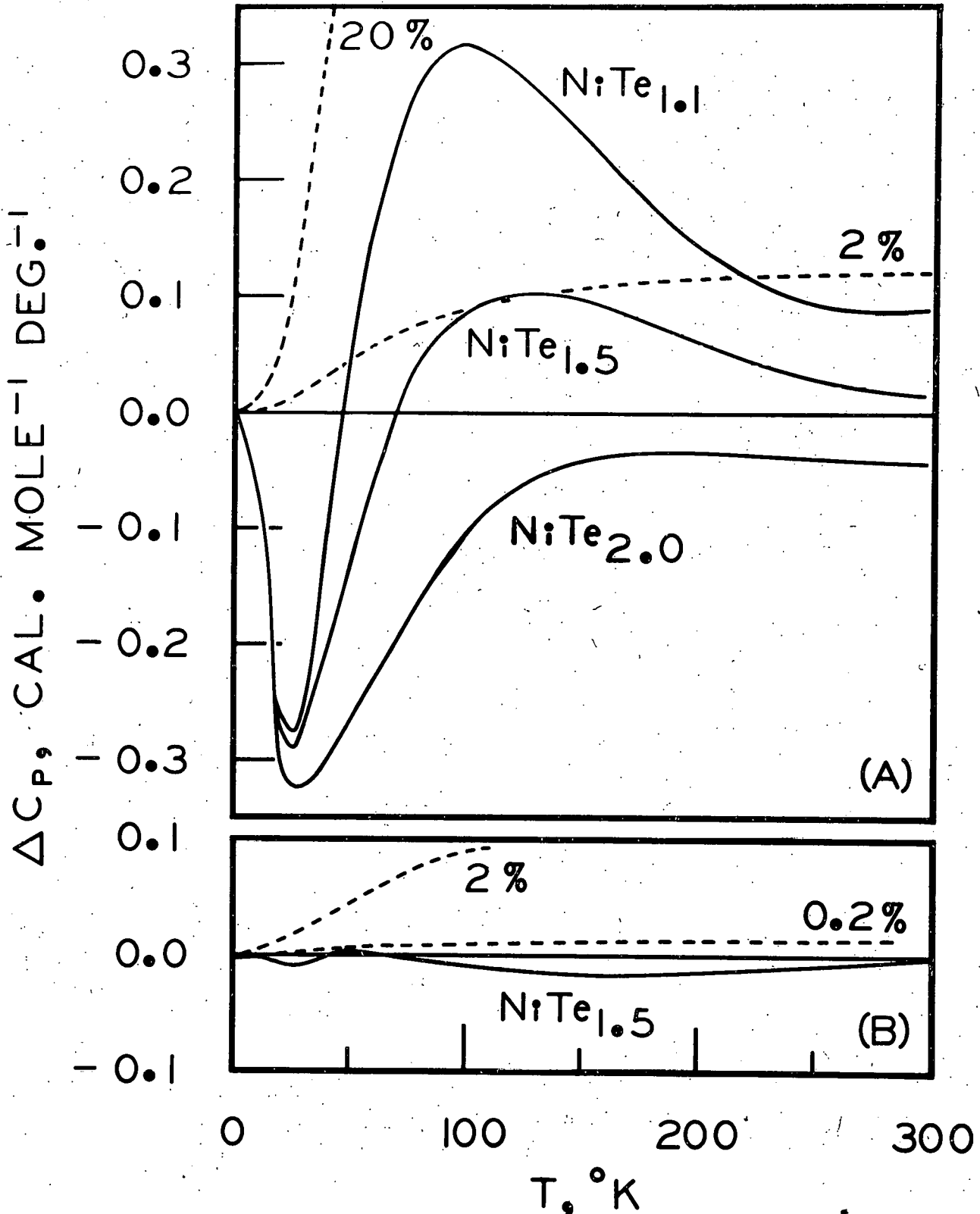


FIGURE 3

DEVIATIONS FROM ADDITIVITY OF THE HEAT CAPACITY OF NICKEL TELLURIDES

contribution, other corrections<sup>73</sup> being negligible. The results, shown in Fig. 3a, show appreciable deviations, especially at low temperatures; at higher temperatures all of the substances involved show approximately the same (i.e. Dulong and Petit) value. The deviations are not surprising, especially when it is considered that the crystal structure of the  $\text{NiTe}_{1.5}$  is quite different from that of the elements.

On the other hand, the heat capacity (and other thermodynamic functions) are indeed additive functions if one considers the constituents to be nickel tellurides of the same phase. Thus, the heat capacity of  $\text{NiTe}_{1.5}$  can be computed by adding 0.4667 times the heat capacity of  $\text{NiTe}_{1.1}$  to 0.5333 times the heat capacity of  $\text{NiTe}_{2.0}$ ; and the deviations of these values from the experimental heat capacities, as shown in Fig. 3b, are comparatively small (the anomalous increase in the heat capacity of  $\text{NiTe}_{1.1}$  above room temperature has been omitted for this comparison).

Debye characteristic temperatures are presented as a function of temperature for the three experimental compositions in Fig. 4. The Debye  $\theta$  for each of the three compositions becomes negative (i.e., the heat capacity exceeds the Dulong and Petit limit) above the ice point, presumably because of electronic contributions. The electrical conductivity<sup>66</sup> at room temperature is about  $10,000 \text{ ohm}^{-1} \text{ cm}^{-1}$ , intermediate between that of typical semiconductors and typical conductors. This fact and the general metallic natures of these substances have been noted<sup>3</sup> to give "an alloyic character" to these compositions. The only available heat of formation data<sup>56</sup> is on the stoichiometric compound  $\text{NiTe}$ ; its heat of formation ( $-9 \text{ kcal/mole}$ ) is higher than that of

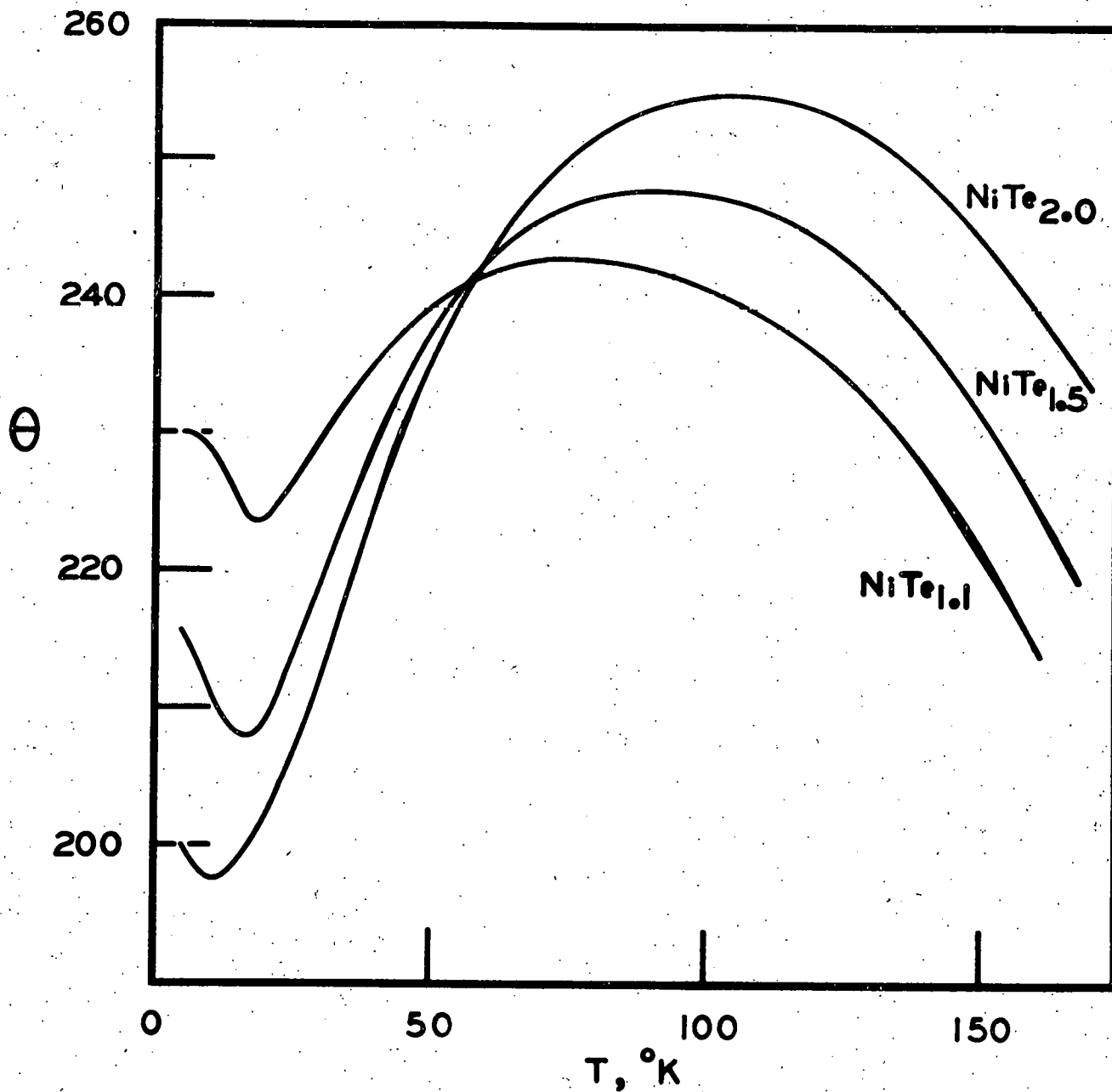


FIGURE 4

DEBYE CHARACTERISTIC TEMPERATURES OF NICKEL TELLURIDES

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typical alloys. However, free energy data (Section 3) seem to indicate that the heat of formation of tellurium-rich compositions is smaller.

## 2.B. HIGH TEMPERATURE

### 2.B.1 Nickel

Because of the interest in the magnetic transition in nickel, as well as for other reasons, the high-temperature specific heat of nickel has been measured many times, including two recent and apparently very accurate series of adiabatic measurements<sup>21,76</sup>.

### 2.B.2. Tellurium

The high-temperature specific heat of tellurium has been measured twice, both times by drop calorimetry and to temperatures only slightly above the melting point. The first series<sup>22</sup> is highly suspect because it indicates a transition at 350°C which has been proven (in this research and, less conclusively, elsewhere) not to exist. The second series<sup>23</sup> gives only a few points. It appears that the specific heat will have to be run at temperatures above the melting point (450°C) in any case; that a check on the latent heat of fusion is highly desirable; and that the specific heat from room temperature to the melting point should probably be checked. In the liquid region a correction will have to be made for heat of vaporization, but the molal heat of vaporization and vapor pressures are known with ample accuracy for this purpose.

### 2.B.3. Nickel Tellurides

Since one of the principal reasons for measuring the specific heat was to investigate the presence of disorder phenomena at the various

temperatures, conventional drop calorimetry is out of the question. The measurement of specific heats of these substances at high temperatures by adiabatic methods involves considerable difficulties. The construction of an adiabatic calorimeter for temperatures up to 700° or 800°C is a project of enormous difficulty, and only two or three good ones exist in this country.

An idea, believed to be original, was considered for a type of unconventional drop calorimetry. Instead of dropping the sample into a mixture of ice and water and determining the amount of ice melted, the sample could be dropped into a mixture of, say, liquid and solid aluminum and the amount of aluminum frozen (or melted if the original sample temperature were above 660°C) could be determined. There appear to be no objections to this method on the grounds of lack of equilibrium, but it was the unanimous opinion of experimental thermodynamicists who were consulted that such an apparatus would present forbiddingly difficult experimental problems.

Permission was therefore tentatively obtained to make the specific heat measurements on one of the best high-temperature adiabatic calorimeters in existence, namely that constructed by Prof. E.E. Stansbury of the University of Tennessee<sup>76</sup>. However, the nature of the nickel tellurides made this impossible. This calorimeter is of such a nature that the sample must have a maximum outside diameter of one inch, with a re-entrant well to carry the heater. For the nonvolatile metals with which Stansbury has worked, this small sample size is feasible, but the nickel tellurides are volatile and the tellurium vapor given off is highly corrosive. The samples would therefore have to be kept in a vessel of vitreous silica, but because of the low thermal conductivity of this

material it would be necessary to enclose the silica vessel in a metal vessel which would have a uniform exterior temperature which could be kept the same as that of the adiabatic shield. This would result in a minuscule space for the sample, so that the heat capacity of the container would be excessive compared to the heat capacity of the sample. Furthermore, the temperature lags getting through the metal container, the intervening space, the silica container, the intervening space, and the sample, would probably be excessive. The spaces could be filled with helium, but little can be done about the temperature lags across the silica. The corrosiveness of tellurium is such that the nickel tellurides probably cannot be contained in any material of higher conductivity than silica, although graphite might be possible.

Thus the high-temperature heat capacities remain undetermined, and constitute a major block in the determination of zero-point entropies.

### III. VAPOR PRESSURES

Of the many methods available for the measurement of vapor pressure<sup>18a, 19a</sup>, few are capable of being applied with accuracy at high temperatures. Dynamic\* methods in general are indirect, and therefore subject to systematic errors; it is worthy of note that the first two measurements of the vapor pressure of tellurium<sup>24, 25</sup> were by dynamic methods, and while each was self-consistent (the log p vs 1/T plots were straight and the scatter around them small), both have been proved (by this research and elsewhere<sup>26, 72</sup> as well as by intercomparison) to have large systematic errors. Dynamic methods are also difficult to apply to multicomponent substances (such as the nickel tellurides) where the pressure changes as the material is progressively vaporized. Effusion methods have been used with considerable accuracy, but are limited to pressures lower than about 0.1 mm, which would restrict their use in the nickel tellurides to compositions richer in nickel than about NiTe<sub>1.3</sub> or NiTe<sub>1.4</sub>. Static methods, on the other hand, are subject to errors from minute amounts of impurities, particularly those which are volatile and insoluble in the sample. In both cases, there are other "difficulties and sources of error which increase exponentially with the temperature"<sup>19b</sup>.

\* The terms "dynamic" and "static" as applied to methods of measuring vapor pressure refer to the type of equilibrium between vapor and condensed phase. Thus, effusion and transport methods are dynamic, while the method employed in this research is static. The boiling-point method is often called dynamic because the criterion of equilibrium is evident ebullition at a known temperature under known pressure of inert gas. However, the author prefers to consider this method static, reserving the term dynamic for those methods in which there is continuous removal of volatilized material from the condensed sample.

The method chosen for this research is a static method whose general outlines are indicated in Fig. 5. The sample (S) is placed in a glass tube which connects to a glass bourdon gage (G). When the sample is heated, its vapor exerts pressure in the gage, and tends to force the pointer (P) to the right. An inert gas is then admitted through the valving system (V) until the pointer is returned to its original position, and the pressure of this inert gas is measured on a manometer (M). The sample-containing tube is inserted in a large metal block (B) whose temperature is measured and assumed to be the same as that of the sample. The entire apparatus is inserted in a furnace, indicated on the figure by the dotted lines.

This method was chosen because it had been previously used, apparently with good accuracy, to determine the vapor pressure of tellurium,\* and because it was believed that the precision could be improved. This did, in fact, turn out to be the case; the pressure measurements are self-consistent, and believed accurate, with a probable error of 0.1 mm. At the highest temperatures, temperature errors are more significant than pressure errors; these amount to about 0.1 to 0.2° on a relative basis, and perhaps 0.3° on an absolute basis.

Vapor pressure measurements were made on nickel tellurides of compositions  $\text{NiTe}_{1.5}$ ,  $\text{NiTe}_{1.7}$ ,  $\text{NiTe}_{1.9}$ , and  $\text{NiTe}_{2.0}$ , and on a mixture of 90 atomic percent tellurium and 10 atomic percent nickel (referred to hereinafter as  $\text{NiTe}_9$ ), up to 780°C, and on pure tellurium up to 855°C.

\* Previous investigations of the vapor pressure of tellurium are summarized in Appendix 2.



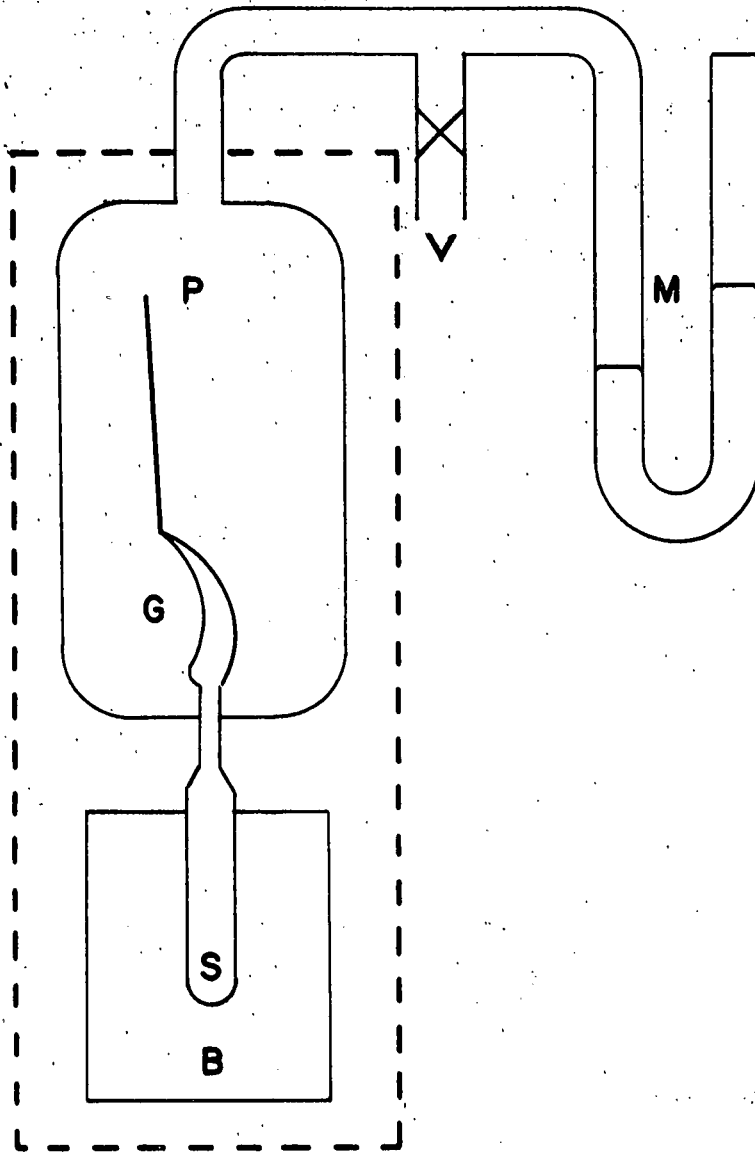


FIGURE 5

METHOD OF MEASURING PRESSURE (schematic)

### 3.A. The Furnace

The design temperature of the furnace was 750°C, but it soon became apparent that the data at higher temperatures would be of considerable interest. In most of the experiments, outgassing was done at about 800°, and the measurements were taken up to 780°, with the gage kept about 20° hotter than the sample. At the conclusion of the experimental work, an attempt was made to take data on the vapor pressure of tellurium up to the maximum temperature attainable. The experiment was actually terminated at a sample temperature of 855°C (with the gage at 880°C), due to a fortuitous circumstance. It is believed that the furnace would have failed at a temperature only slightly higher than this.

The furnace consists of a black-iron can, 15" i.d., 41" high, placed on a four-legged iron stand with adjustable legs for leveling. Resting on the center of the bottom of the can is a 5" layer of Silocel brick, on top of which is a vertical Alundum tube 14" long (the lower furnace); on top of this is another Alundum tube 17" long (the upper furnace). Silocel is a trade-mark name of the Johns-Manville Co., for diatomaceous earth (almost pure silica, of organic origin); Alundum is a trade-mark name of the Norton Co. for aluminum oxide with a silicate binder. The Alundum tubes were of 3" i.d., and pre-grooved by the manufacturer with a pitch of .1731". The pregrooving permitted winding with absolute uniformity, which makes the attainment of isothermality in the furnace considerably easier. The tubes were unfortunately neither perfectly round nor perfectly straight.

The tubes were wound with 14 gage Chromel A wire (Chromel is a trade-mark name of the Hoskins Co; A is 80% nickel, 20% chromium); the ends were brought out through the furnace through porcelain

insulators and attached to 12-gage copper wires; the copper wires were also brought in in parallel and attached to the resistor wires close to the Alundum cores. The measured resistances of the windings were 14 ohms for the upper furnace and 12 ohms for the lower furnace at 600°C (the resistance of Chromel A wire changes very little with temperature). 68 volts on the lower furnace and 79 volts on the upper, for a total input of about 900 watts, maintained the lower furnace at 855° and the upper at 880°. The furnaces were almost never operated at more than 80 volts on the lower and 90 volts on the upper, which is less than 7 amperes in each winding and a total input of just over 1100 watts, although they would probably have withstood a great deal more, especially for short periods. Power was supplied to each furnace from a Variac connected directly to the 110V supply.

Because of the excellent insulation, cooling of the furnaces, and particularly of the lower furnace with its large heat capacity, was very slow. To cool from operating temperature to 420° (the temperature at which null readings were made--see Sec. 3.E.3.) took about seven hours. If the furnace were to be rebuilt it would be desirable to include some method for rapid cooling.

The two furnaces were separately wound and powered, but abutted in such a way that there was no appreciable gap between the windings (which would lead to a cold spot); it was not felt necessary to supply a third winding<sup>26</sup> to cover this region. Each furnace, after winding, was covered with a thin layer of Alundum high-temperature cement which acted as an electrical insulator and also protected the windings (from reducing gases). The two furnaces were then cemented together and to the Silocel brick and fastened firmly in place with

14-gage Chromel wire. The annular space between the cemented cores and the iron can (about 5-1/2") was filled with Santocel (Santocel is a trade-mark name of the Monsanto Co., for a finely divided silica aerogel). The gel structure of Santocel is supposed to break down between 750° and 850°C, and it was anticipated that this might set an upper limit on the temperature of the furnace. In fact, no such effect was noted. However, if the furnace were to be rebuilt for higher-temperature operation, it would be desirable to wrap the cores with a layer of some more refractory material.

Within the lower furnace was an isothermal block, described in Sec. 3.B., containing two platinum vs. platinum-rhodium thermocouples, described in Sec. 3.C.1. Each furnace was also equipped with a Chromel-Alumel thermocouple imbedded in the cement. These thermocouples were made of 18-gage wire--unusually thick--since they could not be replaced if they burned out after the furnace was assembled. They did in fact burn out, but it turned out that they were not necessary for the operation of the apparatus. An additional Chromel-Alumel thermocouple was suspended in the air inside the upper furnace, about half way up; this also burned out, and was replaced by a platinum vs. platinum-rhodium thermocouple.

A horizontal Alundum tube, 3/4" o.d., passed through the can and the upper part of the upper furnace to provide a view of the pointers inside the furnace during operation. A piece of Pyrex glass was cemented in the middle of this tube to act as a convection barrier. This tube was inserted before the furnace was wound, since the windings had to be spaced around it. After the furnace had been in operation for some time another Alundum tube was inserted, at the same height but 90°

away, in order to permit light to be thrown on the pointers. This tube was 1/2" o.d., and also had a Pyrex barrier. The wiring gap necessitated by these tubes undoubtedly created a cold spot in the upper furnace which, however, did not harm the operation. At the maximum temperature of the furnace, these glass windows were probably near their softening point; they should have been made of Vycor.

After the glass apparatus was inserted into the furnace, it was necessary to cover the open top of the upper furnace to keep out the Santocel (which flowed almost like a fluid). It was covered with a sheet of asbestos or a piece of Silocel brick, and then the iron can was filled to the top with Santocel and covered with a sheet of transite. Before removing the glass apparatus from the furnace, the top several inches of Santocel had to be shoveled out each time.

### 3.B. THE ISOTHERMAL BLOCK

It is necessary that the temperature of the sample be accurately known, uniform, and constant during a measurement. The maximum  $dp/dT$  observed in any of these experiments was about 2 mm Hg/ $^{\circ}C$  (for tellurium at  $855^{\circ}C$ ) and so the errors in temperature measurement exceeded in some cases the errors of pressure measurement, and it was vital to keep them as small as possible. Of the three requirements listed, that of knowing the temperature is the most difficult, and makes it unnecessary to have the temperature uniform within much less than  $0.1^{\circ}$  or constant within much less than  $0.02^{\circ}$  per minute (since successive measurements could be made, at constant temperature, within five minutes or less).

To achieve such uniformity and constancy of temperature, it is common to use a large metal block, the high heat capacity of the block making rapid temperature changes unlikely while the high thermal conductivity ensures uniformity of temperature. Three points about such a block appear not to have been generally noted. First, since the block is circular in section and surrounded by a helical winding, difficulties in attaining temperature homogeneity will be entirely axial, radial uniformity being assured. Second, uniformity of environment of the metal block is of considerable importance. And third, since the heat conduction phenomenon is dynamic rather than static, thermal diffusivity rather than thermal conductivity is the pertinent parameter. Because of the last point, silver is the best possible material for the block; while its thermal conductivity is not very different from that of copper, its thermal diffusivity is 50% greater. (Copper is also undesirable because of its tendency to oxidize). Because of the second point, it is not necessary to use a large block of silver, but is better to use a small block, surrounded by a larger block of some other metal. Aluminum bronze has been recommended<sup>27</sup> for isothermal blocks, and was used for this purpose. Although its thermal diffusivity is only about 20% that of copper, this is sufficient for this environmental purpose. Because of the first point, the silver block should be in good thermal contact with its environment radially, but well insulated axially.

The construction of the isothermal block is indicated in Fig. 6. The central block was made of pure silver; the outer block was made of centrifugally cast aluminum bronze (85.7% Cu, 10.7% Al, 3.6% Fe) and was 2.94 o.d. (the largest size which would fit in the nominally 3" aluminum furnace tube). The 0.1 annular space between the silver and

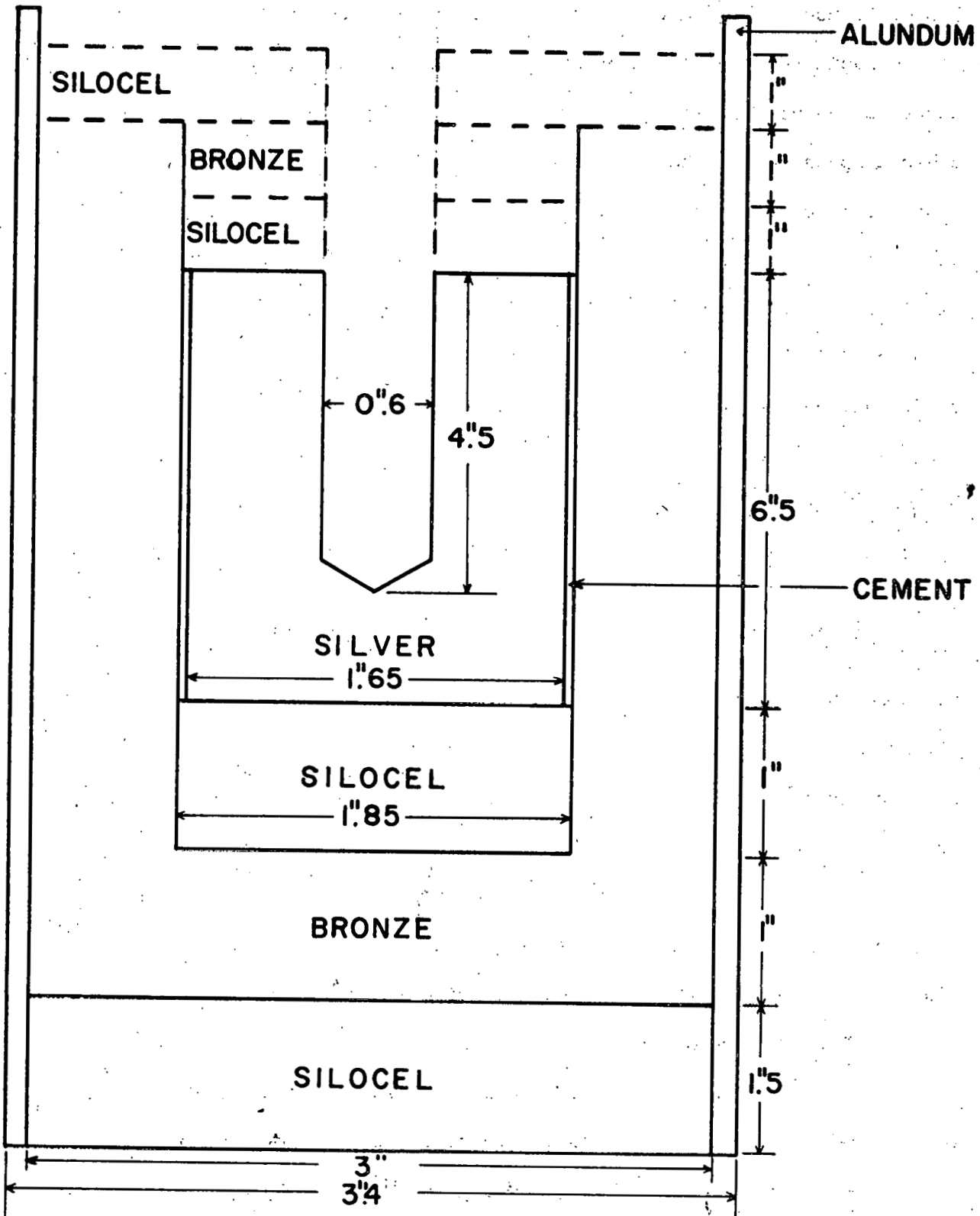


FIGURE 6  
THE ISOTHERMAL BLOCK

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bronze was filled with Alundum cement, to keep the two metals from diffusing into one another, or melting together, at high temperature. A plug of aluminum bronze one inch thick was shrunk-fit into the bottom of the bronze cylinder so that the bronze was essentially a single piece. On top of this plug was a layer of Silocel on which the silver rested. The entire assembly rested on a layer of Silocel 1"-5/16 thick, which was inside the bottom of the bottom furnace. The top should have been finished off in the same way, as indicated by the dotted lines in Fig. 6, with layers of Silocel, bronze, and Silocel, but these spaces were instead filled merely with two thin sheets of "superalloy" which acted as radiation and convections' shields.

Five 1/8" diameter holes were bored through all of the bottom layers of this isothermal block, and also through the Silocel brick below and the bottom of the can. One of these holes was exactly at the center, and the centers of the other four were 0".565 off center and symmetrically placed around it. Through two of these holes were passed platinum vs. platinum-rhodium thermocouples in two-hole porcelain insulators. The central thermocouple came to within 1/2" of the bottom of the large hole in the silver block, and the other thermocouple was 1".5 higher; both thermocouples were capable of probing downward. Through the other three holes were passed thin-walled monel tubes filled with Santocel which served to stabilize the positions of the various parts and keep them lined up so that no forces might be created which would crack the delicate porcelain insulators.

This isothermal block fulfilled its function adequately. No variations in temperature (within 0.1°, the limit of measurement) could be detected in the region surrounding the sample space when the



block was at constant temperature, and the variation is believed to have been much less than  $0.1^\circ$ , the minimum detectable difference. Furthermore, the heat capacity of the block was so great that if the voltage was approximately correct the temperature could not change very fast. This made automatic temperature control unnecessary.

The following thermal relaxation time figures, theoretically computed, are of some interest: radially from the center of the silver block to its periphery, less than 1 second; through the 0.1 Alundum cement, 3 seconds; through the bronze cylinder, 2 seconds; axially, through the length of the silver cylinder, one minute; through the bronze cylinder, 15 minutes.

While the temperature of the silver block in the neighborhood of the sample is known to be uniform, there is still the possibility that the temperature of the sample may be affected from some other source. In particular, it was necessary when making some measurements to keep the upper furnace hotter than the lower. This upper furnace might conceivably affect the temperature of the sample by radiation (conduction through the tellurium vapor is too small by orders of magnitude to have any effect, and convection was not possible since the upper furnace was hotter). However, the sample can only "see" the upper furnace through the 12-mm i.d. hole in the glass sample tube at a distance of 170 mm (the distance to the upper radiation shield). This corresponds to  $1/200$  steradian, or less than  $1/1000$  of the total area seen. Thus if the upper furnace temperature differs from that of the lower furnace by less than  $50^\circ$ , even accounting for the fourth-power effect in radiation and ignoring conduction from the silver to the sample, the difference in temperature between the

sample and the silver would be less than  $0.1^{\circ}$ .

### 3.C. TEMPERATURE MEASUREMENT

As stated earlier, it took four to five minutes to make and record an observation of temperature and pressure. At least two such observations were always made sequentially, and agreement in temperature between them ensured that the isothermal block had come to constant temperature\*. As indicated in the previous section, it could then be assumed that the temperature of the thermocouple was the same as that of the sample. It is then further necessary to determine accurately the temperature of the thermocouple.

The establishment of an absolute temperature scale at these temperatures is difficult; for example, it is indicated in Sec. 4B that several investigators have made errors of one to two degrees, and in one case more than four degrees, in a simple measurement at  $450^{\circ}\text{C}$ . At the beginning of this research it was felt that no accurate absolute scale was needed; that is, for application of equation (6) it was necessary that the two pressures be measured at the same temperature within  $0.1^{\circ}$ , but it would be adequate to know that temperature within about  $1.0^{\circ}$ . In fact, there is no reason to believe even today that the international and thermodynamic temperature scales coincide within better than  $0.2$  or  $0.3^{\circ}$  in some parts of the temperature region here investigated. However, after the vapor pressure of tellurium was measured it became apparent that these measurements were

\* When  $dp/dT$  was small, as at lower temperatures or with nickel-rich mixtures, it was permissible to allow considerable temperature change between readings; but where  $dp/dT$  was high, at least two readings within  $0.1^{\circ}$  were always required.

better than any in the literature, and in order to make these measurements valid, it was necessary to correlate the temperatures with the international temperature scale.

The thermocouple consists of a pair of wires, one of platinum and the other of an alloy of 90% platinum with 10% rhodium, with both ends welded together. One end--the "hot junction"--is maintained at the unknown high temperature while the other end--the "cold junction"--is maintained at a known low temperature, and the voltage between these ends is measured, without drawing current. This voltage is a smooth, strictly monotone function of the temperature of the hot junction, with a slope of approximately  $1\mu\text{V}/0.1^\circ\text{C}$  at all temperatures of interest in this research, and may therefore be used unequivocally to determine the temperature of the hot junction, providing: there are no sources of voltage in the system other than the thermoelectric potential; there are no mechanical or chemical inhomogeneities in the wires in regions where there are thermal inhomogeneities; the voltage is determined with sufficient accuracy; and the relationship between voltage and temperature is accurately known at all temperatures. These points are now considered in order.

Stray voltages may be picked up by induction, through contact potential, or by thermal emf's in the platinum-copper circuits involved in the potentiometer and switches. It is difficult to avoid stray voltage pick-up of one microvolt magnitude when there is a good deal of electrical equipment about. Moderate caution can minimize these effects, but their elimination in this research was based primarily on the method of calibration, which was done under conditions so nearly identical with those of the measurements that it could be assumed that such stray voltages would cancel out.

3.C.1. The Thermocouples The original thermocouples were made of 15 feet of wire of each composition, of 30 gauge (0.010 diameter). Six feet were used for each hot junction and three feet for the cold junction common to both couples. The cold junction after welding was passed through spaghetti and inserted in a glass tube which was filled with paraffin and inserted in a Dewar flask filled with ice with a little water. Such an arrangement maintains the cold junction at 0°C with an error of less than 0.001° for many hours. Fresh ice was put on the cold junction every morning at least an hour before any precise temperature measurements were made.

Each pair of wires for a hot junction was passed through a two-hole porcelain insulator about 16" long. It is highly desirable that there be no discontinuities in the insulator in the regions of high or inhomogeneous temperatures. Appropriate insulators which were exactly straight, had two uniform holes, and were of 3/32" o.d., were finally procured from the McDanel Refractory Porcelain Co. The end of each insulator was first counterbored with a dental drill\*. The wires were then passed through, torch welded, and pulled back so that the welded joint was recessed within the counterbored end, which was then covered with Alundum cement to provide electrical insulation between the thermocouple junction and the metal of the isothermal block. Spaghetti was then passed over the room temperature portion of the wires and they were soldered to the switch connections. A special Leeds & Northrup rotary thermocouple switch was used which was warranted free

\* Literally. None of the tools in the scientific shops could effect the necessary machining on the very hard, narrow, and fragile porcelain, and the work was done by Homer Faust, D.D.S., to whom thanks are hereby expressed.

from contact potentials. The switch was inside a wooden box which was presumably at uniform temperature, all copper-to-precious-metal connections being made within this box; thermal heterogeneity elsewhere would presumably be of no consequence, since it cannot create thermal emf's in homogeneous metal.

Through ignorance, these thermocouple wires were installed as received from the manufacturer. As a result, they contained serious inhomogeneities and the resulting calibrations were very low compared to the standard tables<sup>28</sup> (emf about 1% low, or a correction of, for example, 58 microvolts at the melting point of aluminum (660°C)). Furthermore, the emf was not independent of the temperature distribution in the furnace, so that the calibration was slightly different after the furnace had been hot for some hours than when it was first heated. Some of the early measurements were therefore in doubt by perhaps several tenths of a degree.

One of the hot junctions was therefore replaced with a new one made of 26 gage wires (0.016 diameter). These wires were first welded, then thoroughly annealed by heating them electrically for five minutes to 1200°C, as determined by an optical pyrometer with the appropriate emissivity correction<sup>77</sup> (about 125°). After annealing, the wires are extremely soft, and the slightest strain creates new inhomogeneities which can affect the temperature measurements. To pass them through the porcelain and spaghetti insulators without strain, they were butt-welded to 26 gage manganin wires and pulled through. Calibration procedures showed this thermocouple to have corrections about one third that of the others (e.g., 19 microvolts at the melting point of aluminum). Since the wires are warranted to have corrections no greater

than 8 microvolts at 960°C, it must be presumed that some strains were inadvertently introduced after the annealing procedure. It would probably have been better to use somewhat heavier wires, but this would have involved greater expense, and also a larger diameter insulator, and hence a larger hole in the isothermal block, which might have interfered with its isothermality.

Depth of immersion of a thermocouple is often critical, since heat conduction along the wires may alter the temperature of the junction. The cold junction was immersed about six inches in an environment constant within 0.1°, and beyond that the ambient temperature deviated by only about 30°. The hot junction was immersed more than six inches in the isothermal block, and any deviations due to insufficiency of this depth should presumably be taken care of by the calibration procedure.

3.C.2. Voltage Measurement Voltage was measured with a Rubicon portable potentiometer. The guarantee on this potentiometer was  $\pm 5$  microvolts plus 0.1% of the reading, which amounts to almost exactly 1.0° at temperatures from 550° to 850°C. The potentiometer is actually more precise than this. It was checked periodically by reading voltages on both ends of the slide wire (e.g. 6.073 mv can be read as 6 mv on the dial and 0.073 mv on the slide wire or 5 mv on the dial and 1.073 mv on the slide wire) and never deviated by more than one microvolt. It was checked once against an auto-and absolutely-calibrated White potentiometer (known to be accurate to 0.1 microvolts) and found to be in error by 5 microvolts at 780° and 2 microvolts at 420°. Absolute deviations of this magnitude are quite negligible considering the method of calibration used; the only question is

one of consistency in the readings. A test of this consistency is given by the frequent calibrations of the thermocouples, described below. These did show some inconsistencies, but it is not known whether these are due to the potentiometer or to some other cause. It is concluded that the potentiometer is probably not the principal source of error in the temperature-measuring system, but that it would have been desirable to have a more precise instrument.

3.C.3. Calibration The usual procedure in calibrating thermocouples is to remove them from the furnace and insert them in another furnace with some comparison standard. Often, for "accurate" calibrations, they are removed from their connections and shipped to another laboratory for comparison with a standard. In the opinion of the author, such calibration procedures are exceedingly dangerous and introduce many possible sources of systematic error.

In the present research the thermocouples were repeatedly calibrated in situ, using the same connections, potentiometer, etc., under conditions identical to those in the actual measurement. A standard sample of known melting point was melted and frozen in a crucible 7" long and 0.600 o.d., in the sample space in the silver block. A platinum vs. platinum-rhodium reference thermocouple in a two-hole porcelain insulator, 0.2 diameter and 36" long, was placed in a suitable protection sheath inside the metal, and the halt was observed on this thermocouple. This thermocouple also was recessed into a counter-bored hole in the insulator and covered with Alundum cement to insulate it electrically from the sheath. The furnace was then stabilized at a temperature 2° away from the melting point and the reference thermocouple and thermocouples being calibrated were both read. Since the

variation of emf with temperature of the thermocouples could be assumed identical over this short temperature range, and since the melting point of the standard sample was now known in terms of the voltage of the reference thermocouple, this yields the melting point of the standard sample in terms of the thermocouple being calibrated. As a check, the furnace was always stabilized and readings taken both  $2^{\circ}$  above and  $2^{\circ}$  below the melting point.

After some abortive attempts with vitreous silica the crucibles and protection sheaths were made of graphite. They were machined out of Acheson spectroscopic rods which is of exceedingly high purity, with the walls made as thin as possible (crucible wall thickness 0.089, sheath wall thickness 0.053) consistent with strength requirements. The melting point sample was machined (all machining on melting point samples was done without lubrication) to an annular cylinder 2" high of such thickness (0.049) as to fill the remaining available space. The entire crucible was then filled with graphite powder (the machinings from making the crucibles were saved) to protect the sample of metal from oxidation and incidentally to supply thermal conductivity between the porcelain and graphite.

Standard metals for calibrating thermocouples in the range of interest are zinc, aluminum, and silver. Samples of zinc (sample #43e, freezing point  $419.50^{\circ}$ ) and aluminum (sample dated 2-18-43, freezing point  $660.15^{\circ}$ ) were obtained for this purpose from the National Bureau of Standards. Unfortunately silver could not be used, since the center of the isothermal block is itself made of silver, and the bronze around it would have melted at even a lower temperature. A suitable substance was finally found for a third calibration point in the copper-silver



eutectic (71.9% Ag. 28.1% Cu by weight), which melts at 779.2°C on the international temperature scale of 1947. Since this material could not be procured, it was synthesized as follows. A 3" cylinder, of 0.5 i.d., and 0.6 o.d., was machined out of spectroscopic graphite rod, and placed in a Vycor crucible in which it fitted snugly, and which was fitted with a snug Vycor cover with a large handle. OFHC copper was machined to a cylinder 0.5 diameter and 0.6 long; high-purity silver was machined to a cylinder of 0.5 diameter and length 1.291, which gave the proper weight (actually a small error in composition would have made no difference, since the phase diagram of Ag/Cu is very simple, containing only a single eutectic with liquidus lines of moderate slope). The copper, which is less dense, was placed on the bottom of the crucible and the silver on top of it, all remaining spaces filled with graphite powder, and the cover put in place. It was placed in a furnace which was raised to 1050°C. This is slightly below the melting point of copper, but apparently ample to melt the mixture, and it was feared that a higher temperature might soften the Vycor. After 30 minutes at 1050° the crucible was removed from the furnace, opened, and stirred with a thin graphite rod (held in a long monel tube) which had been preheated in a hydrogen flame. Because of the rapid cooling this operation had to be performed very quickly, and took four hands (i.e., two men). After a few seconds freezing commenced, and the crucible was quickly returned to the furnace before it could be completed, since remelting would be expected to crack the graphite crucible. After another 30 minutes at 1050° the stirring was repeated and the sample then allowed to cool. When cold, the Ag-Cu alloy slipped out of the graphite crucible. When it was machined to the appropriate annular cylinder, the machinings

appeared perfectly uniform in color, as did the bulk material, which indicated that there were no gross inhomogeneities. Since the annular cylinder was a vertical cross-section of the material, and inhomogeneities if present were probably vertical, the final sample was thus probably of the desired composition. This conclusion was supported by the sharpness of the freezing point observed.

No difficulties were encountered in calibrations at the zinc point. A single graphite crucible survived nine calibrations, in each of which the temperature was about  $420^{\circ}$  for one to two hours, without any protection from atmospheric oxidation. At the aluminum point, however, the crucible was only good for about three calibrations, despite a protective atmosphere of carbon dioxide (nitrogen seemed inadvisable because of the possible formation of AlN). At  $779^{\circ}$  the crucible top was completely burned through at the end of one calibration despite a blanket of nitrogen, and the crucible had to be recovered from the bottom of the furnace with a long-handled forceps of the type used in handling radioactive materials. No supercooling of the zinc or eutectic occurred, but with aluminum, if the sample were cooled through the freezing point at  $0.3^{\circ}$  to  $0.4^{\circ}$  per minute, it always supercooled three to five degrees, which gave a rounded halt rather than a flat one. This was finally obviated by cooling the furnace down to two degrees below the melting point and then holding it there until freezing commenced. With the eutectic there was a problem of segregation; as the freezing commences, the silver crystals tend to settle to the bottom. This can be obviated by stirring. The melting point observed on the eutectic was not very sharp, but the freezing point varied by only  $0.1^{\circ}$  over fifteen minutes.

The consistency of the calibrations was unsatisfactory. With the early (unannealed) thermocouple, there were variations of  $0.5^{\circ}$ , and even with the final thermocouple there were inconsistencies of  $0.2$  to  $0.4^{\circ}$  not only between successive calibrations, but between the supposedly equivalent readings taken two degrees above and two degrees below the melting point. Fortunately, the calibrations deviated from the standard tables<sup>28</sup> by approximately the same fraction ( $1/300$ ) at each of the three fixed points, so that a linear interpolation and use of the tables could be effected with confidence. It is hoped that by taking average values, the temperature error resulting is not greater than  $0.2^{\circ}$ , but it seems possible that it is as large as  $0.4^{\circ}$  on an absolute basis, at the highest temperatures. The smoothness of the vapor pressure data obtained, and its reproducibility, are good guarantees that the random errors in temperature measurement are less than  $0.2^{\circ}$ , and perhaps less than  $0.1^{\circ}$ . However, errors in temperature measurement are certainly the principal sources of error at high pressure in the present measurements. It is believed that by use of a better potentiometer and heavier thermocouple wires, and by greater care in preparing and calibrating the thermocouples, these errors could be reduced to a maximum of  $0.1^{\circ}$  without any basic change in the techniques here described.

### 3.D. PRESSURE MEASUREMENT

A glass tube connected the gage to a conventional mercury manometer. This consisted of three limbs, each made of 16-mm Pyrex tubing and approximately 90 cm high. The central limb was evacuated, and the two outer limbs were connected to the system. Since the mercury never moved down in the central limb, its lower portion was made of capillary

tubing, which conserved mercury, lightened the manometer, and acted as a brake on the motion of the mercury in case something broke while the system was under vacuum. The use of two independent limbs exposed to the system gave two advantages: it left one good meniscus in case one of the tubes became contaminated; and it eliminated any questions of lack of plumbness (whether or not the manometer limbs are plumb is of secondary importance; the use of two outer limbs at the same pressure corrects for improper leveling of the cathetometer).

After the manometer had been made, it was thoroughly cleaned with chromic acid, distilled water, ammonia, distilled water, nitric acid, and distilled water. It was then placed in a large wooden box closed in front with a sheet of methyl methacrylate plastic and sealed to the system. It was dried by evacuation, and fairly pure mercury was distilled into it in vacuum. Despite these precautions, the meniscus shape and height were not always constant, and for a while readings were made of the top and bottom of the meniscus, and corrections<sup>29</sup> applied for meniscus height. Later it was discovered that if the manometer were tapped or shaken (the glass connections were sufficiently well annealed to make this possible), the meniscus would come to a shape which was sufficiently uniform, at least within any one limb, to make the meniscus corrections vary by less than 0.02 mm--a negligible amount. Since a null correction, determined on the same manometer, was subtracted from every reading (Sec. 3.E.3.), consistent differences in meniscus height between limbs did not cause errors.

A meter stick placed behind the manometer was used only to facilitate gross pressure adjustments. Height of the mercury columns was read by means of a cathetometer calibrated against a standard

meter bar. Height of the telescope was read, after adjustment of the hairline to the top of the meniscus, with a small magnifying glass; readings to the millimeter were direct, and with a vernier to 0.05 mm. To obtain a sharp image of the meniscus in the telescope, a brass plate was mounted directly behind the manometer, on which was fixed a piece of black velvet. The lower half of this velvet was covered with a white card. This plate was raised and lowered from outside of the manometer box by means of a string. It was found that the reading was dependent on the height of the plate, and so a black line was drawn across the card 1 mm below the velvet, and the plate was always adjusted so that the apparent top of the meniscus was between the black line and the top of the card.

At the top and bottom of the manometer box were mounted two test tubes made of 16-mm Pyrex which contained mercury, inside each of which was a thermometer. It could safely be assumed that the temperature of these thermometers was the same as that of the mercury in the manometer, since they never differed between themselves by more than 1°. These thermometers were read and recorded after every group of pressure measurements at a single sample temperature, and the readings were then converted to those which would be obtained from mercury at 0°C. This correction was quite appreciable; at the highest pressure measured (206 mm at 27°C), it amounted to 1.01 mm.

Gravity in southeastern Michigan is sufficiently close to standard gravity that no correction for this deviation was necessary.

The central limb of the manometer was connected through a stopcock to a high-vacuum system and pumped down whenever necessary. At the start of each day when measurements were taken, this central limb was tested

with a Tesla coil to ascertain that it did not create any discharge visible in a brightly lighted room. This criterion ensured that the pressure in the central limb was always lower than about 0.01 mm.

Reading of the height of a single column of mercury on the manometer was a highly subjective operation, but since differences only were involved, it was only necessary to make sure that the criterion for setting the hairline was constant, and to make sure that the hairline had been moved by an unknown amount since the last reading. The corresponding operation in reading the vernier was more difficult, since it was impossible to forget the last reading. For this reason, although interpolation on the vernier to 0.025 mm was possible, readings were usually taken only to the nearest 0.05 mm. It is believed that the over-all accuracy in reading pressure (i.e., column height difference) on the manometer was better than 0.1 mm, and perhaps as good as 0.05 mm. All pressure computations were carried to the nearest 0.01 mm.

### 3.E. THE GAGE AND AUXILIARY GLASS APPARATUS

Because it is difficult to measure accurately the pressure of a gas which is at a high temperature, the method chosen in this research involved the use of a null instrument at high temperature to equilibrate the pressures of the tellurium vapor and an inert gas; the pressure of the inert gas is then measured by conventional manometry, as described above. The null instrument is a Bourdon gage made of glass (which shows no elastic after effect). Because of the high temperature, only pure (vitreous) silica or nearly pure (Vycor) would serve as the glass; silica was chosen because there was the possibility that Vycor might have had a greater tendency to anneal at

high temperature, to react with the tellurium (oxidation-reduction reaction), or with the nickel telluride (Lewis acid-Lewis base reaction), or to be porous to the inert gas.

Silica is virtually the only fabricatable material in which tellurium can be contained at high temperatures. Tellurium is one of the most corrosive substances known at these temperatures\*, reacting vigorously, for example, with all metals. It could be contained in graphite<sup>38</sup> or perhaps some of the refractory oxides, but it is not obvious how a vacuum-tight container could be made of such materials.

Silica is by no means inert at high temperatures. At about 1300°C, for example, it is reduced by hydrogen<sup>19b</sup>, and at much lower temperatures it reacts vigorously with certain metals--e.g., aluminum at its melting point. It must be kept scrupulously clean, because if it is touched with a finger and then heated, the grease from the invisible fingerprint reacts with the silica to produce glasses with appreciable coefficients of expansion, causing cracks which may weaken and destroy the entire piece. For this reason the silica apparatus was always carefully cleaned with organic solvents before inserting in the furnace, with the portion through which the pointers were seen being given special attention with several solvents. Silicone grease was never used and other greases were removed with care. In spite of all this, the silica always became cloudy in some spots, including the entire surface which was in contact with the

\* It is of interest to note that the element gold is sufficiently inert that it occurs naturally only as the native element, with the exception of a series of rare minerals all of which consist of tellurides.

silver in the isothermal block, whenever it was a high temperature for long periods.

Such silica bourdon gages have been frequently used before to measure vapor pressure<sup>18b,19c</sup>. There are several types, since many differently shaped hollow objects will tend to change shape if the differential pressure between the inside and the outside is changed. Best known are the "spiral" gage, consisting of a hollow helix, and the "spoon" or "sickle" gage. Brooks<sup>26</sup> had measured the vapor pressure of tellurium in both, and reported that the sickle gage was more satisfactory, and on that basis the sickle gage was chosen, although it may be true that the spiral type (which adds the effects of the change of shape of many turns of the helix) can be made less fragile for the same sensitivity.

The construction of such sickle gages has been amply described<sup>19c, 26,30</sup>, and the author can add only the following comments. The blowing of a sensitive gage is very difficult, beyond even the capabilities of some professional glassblowers. Furthermore, it seems to be more of an art than a science, and many gages are generally blown before one of adequate sensitivity appears. Rounding off the sharp edges of the gage has the surprising effect of reducing the tendency to vibration without reducing the sensitivity. The thickness of a sensitive and usable gage, as measured on fragments with a machinist's micrometer calipers, varies between 0.0014 and 0.0020.

The sensitivity\* of the gage is measured by the number of millimeters of motion of the pointers corresponding to a change of pressure

\* The term "sensitivity" is used herein always in the sense of this sentence, the word fragility being used for the other possible meaning of sensitivity.



of one millimeter of mercury. The gages used in most of the present research had sensitivities of about 0.25, which meant about 0.001 motion of the pointer for a change of pressure of 0.1 mm Hg. As discussed in Sec. 3.E.3., this proved adequate for detecting such pressure changes. Gages have been described in the literature with sensitivities of 1 or more; some or all of these very sensitive gages employed fancy mechanical linkages or optical-lever magnification of the pointer motion. The author feels that all such devices increase the possibilities of zero-point drift or other types of error.

The gage and auxiliary glass apparatus are shown in Fig. 7, as originally used. The 15-mm tube on the bottom fits snugly in the hole in the isothermal block and contains the sample; the small opening near the top of this tube is for inserting the sample, and for connection to vacuum. After the gage is evacuated, this tube is sealed off. The tube at the top projects out of the furnace and is connected to the manometer. A reference pointer is supplied for precise determination of null position.

Sensitivity of the gages was tested before they were installed in this apparatus by means of a water manometer, open to the atmosphere at one end, and connected to the gage and to a blowing tube at the other end. These tests showed that the motion was linear with pressure, at least up to 10 mm Hg; some investigators<sup>26</sup> have actually used such gages as deflection instruments, but in this research the gage was used only as a null indicator. Late in the research it became possible to check the sensitivity after installation and at high temperature, since the width of the pointers was accurately known, and the pressure required to move one pointer width could be determined. Sensitivity was

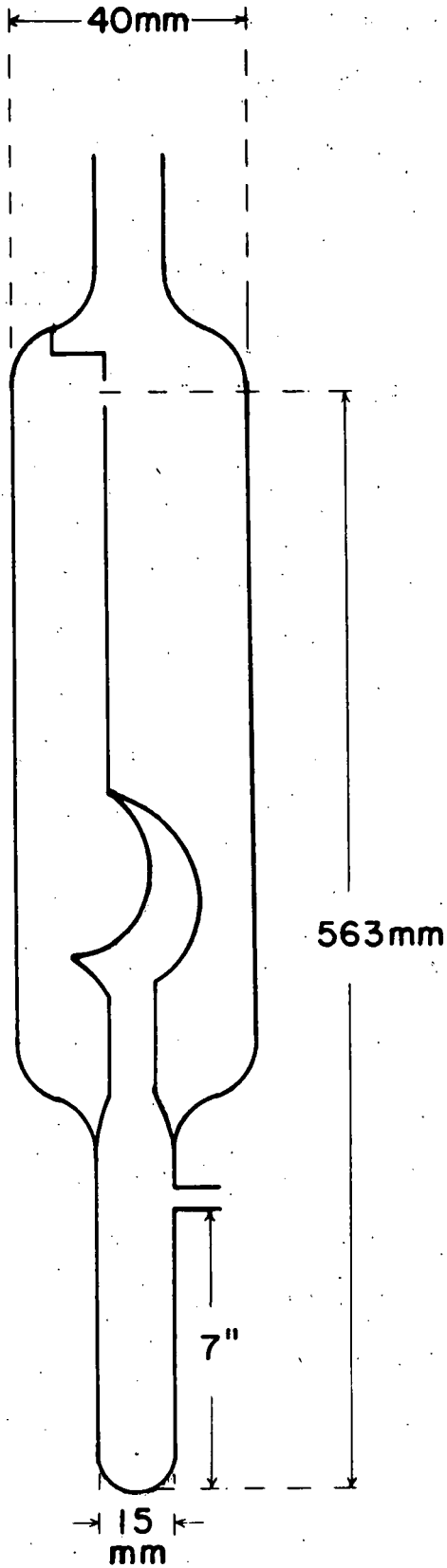


FIGURE 7

BOURDON GAGE AND AUXILIARY GLASS APPARATUS--ORIGINAL DESIGN

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entirely independent of temperature, as determined both in this way and by the lack of dependence, at least on some occasions, of the null correction on temperature. In the sensitivity tests, the gage was always tested at 10 mm Hg positive and negative. During actual measurements the gage was never subjected to a differential pressure of more than 2 or 3 mm, but during installation and sealing it was subjected to unknown pressures perhaps of the order of 10 or 20 mm. At the conclusion of the measurements, the final apparatus (containing tellurium) was heated until the gage was at 850°C and the sample a little below 700°, so that the pressure inside the gage was about 23 mm, while the outside was evacuated. It was left overnight in this strained condition; during the night the sample temperature increased so that the pressure inside was 34 mm, and at some time in this interval the gage ruptured. The author would guess that 30 mm was typical of the fragility of the sensitive silica gages used, and that at temperatures less than 900°C, no strain would result in these gages under stresses less than those required to break the gage.

Before the silica glass apparatus was constructed, a Pyrex glass apparatus was constructed and the vapor pressure of sulfur measured in it to check out all the techniques. In the course of the entire research, three Pyrex and nine silica apparatuses were constructed; each time any change in the gage or pointers had to be made, the entire apparatus had to be rebuilt (although it was sometimes possible to salvage the expensive 40-mm envelope). On four of the occasions the apparatus had to be rebuilt to improve it (change in materials from Pyrex to silica; increase in sensitivity; change to tungsten pointers (Sec. 3.E.3.); and change to rhodium pointers); on one occasion the reference pointer fell

out; on six occasions the gage was accidentally broken; and on the twelfth occasion the gage was purposely broken, as described above. The glassblowing work involved a minimum of eight to ten hours, and the median delay in waiting for a new gage was about a week.

Of the accidental breakages: two were in attempting to open the gage (to insert a new sample); one was due to faulty outgassing procedure; one was due to hydrogen leaking into the gage and exploding while sealing on connections; one was due to a failure of inadequately annealed connecting Pyrex; and one was from causes still unknown. The manipulations being now well understood and practiced many times, it seems likely that the above causes would not generate new failures frequently if the experiments were repeated. Nonetheless, the gages are fragile, and the author guesses that in a new series of experiments, even with the present experience, one should anticipate a breakage about once for every three compositions run.

### 3.E.1. Outgassing

The difficulty of outgassing, which was grossly underestimated at the start of this research, was one of the principal problems. Initially outgassing was done under high vacuum (about  $10^{-6}$  mm) by flaming the glass. This proved inadequate, and as it was assumed the gas was coming from the sample, this was heated to  $100^{\circ}\text{C}$  during the outgassing. The next step was to heat to  $230^{\circ}$  during outgassing. Further heating was thought impossible, since it would distill tellurium out of the sample. The next step was to outgas at  $800^{\circ}\text{C}$ , distilling much of the tellurium out of the sample and then, after sealing off, distilling it back. After each such attempt, a complete series of vapor pressure measurements was made. Pressure up to about 2 mm still

developed in the apparatus, and it seemed that this gas must either be coming from the sample, or from the silica, or through the silica, though each seemed impossible.

At the conclusion of one experiment, therefore, the "evacuated" apparatus, now cold and with about 1 mm of gas at room temperature, was placed in front of a spectroscope, the gas excited by a Tesla coil, and a fifteen-minute exposure taken on #33 film. The resulting spectrogram showed a number of lines in the ultraviolet and a few in the visible violet, and every line was identified as being due to carbon monoxide. A search of the literature then turned up an old paper<sup>31</sup> which indicated that it was almost impossible to maintain a static vacuum in hot silica, and guessed that the difficulty was caused by a carbonaceous gas introduced into the silica when the silica was worked with an oxy-acetylene flame.

With this information in hand, the solution to the outgassing problem was comparatively easy. The silica, which had previously been frequently worked with oxygen-gas flames, was worked only with oxy-hydrogen flames. Furthermore, the outgassing was performed with all of the silica in contact with the sample space at a temperature of 800°C and under high vacuum until actual measurement showed the silica to be completely outgassed. The criterion for outgassing was to close the stopcock connecting the vacuum pump to the system, and watch the rise in the system pressure as measured by an ionization gage. The system was considered outgassed if the pressure did not rise above  $10^{-5}$  mm in five minutes while the apparatus was at 780°C. Outgassing was performed at 800°C, and required from 24 to 48 hours. The measurements were then taken up to 780° on all samples except the final tellurium sample, in which there may have

been a little outgassing during the highest-temperature measurements.

3.E.2. Operation To perform the outgassing as described above, and make the subsequent measurements, the glass apparatus was built as shown in Fig. 8. The silica connecting tube, from ball joint ( $B_1$ ) to butt joint (J), was removed and the apparatus tried in the furnace to be sure that it fit and that the pointers would be visible. It was then removed, and the weighed sample inserted through (J). Since it was found that nickel tellurides tended to adhere to silica, it was introduced directly to the bottom of the sample space (S) through a thin-walled polyethylene tube. With the stopcock (St) open, the connecting tube was put in place, and the joint (J) sealed with a torch. Since the sealing operation introduced water, it was desirable to evacuate as soon as possible, and the apparatus was therefore connected through the ball joint ( $B_2$ ) to the low-vacuum line and slowly evacuated. The resistance of the 2-mm vacuum stopcock was approximately the same as that of the connecting tube, with its two constrictions ( $C_1$  and  $C_2$ ), but a sudden application of suction would probably have ruptured the gage. After the apparatus was evacuated and tested for leaks, it was filled with inert gas, disconnected at ( $B_2$ ), inserted in the furnace, connected through ( $B_2$ ) to the ion gage and high-vacuum system, and pumped down. After a good vacuum had been achieved, all of the glass connections were flamed, except close to the greased joints ( $B_1$ ,  $B_2$ , and St). The silica tubing to the left of ( $C_2$ ) was heated to the maximum temperature attainable with an air-gas torch for a long period of time, since this portion would have to be heated after the pump had been disconnected, but would not be outgassed by being immersed in the furnace. Finally the upper furnace was turned

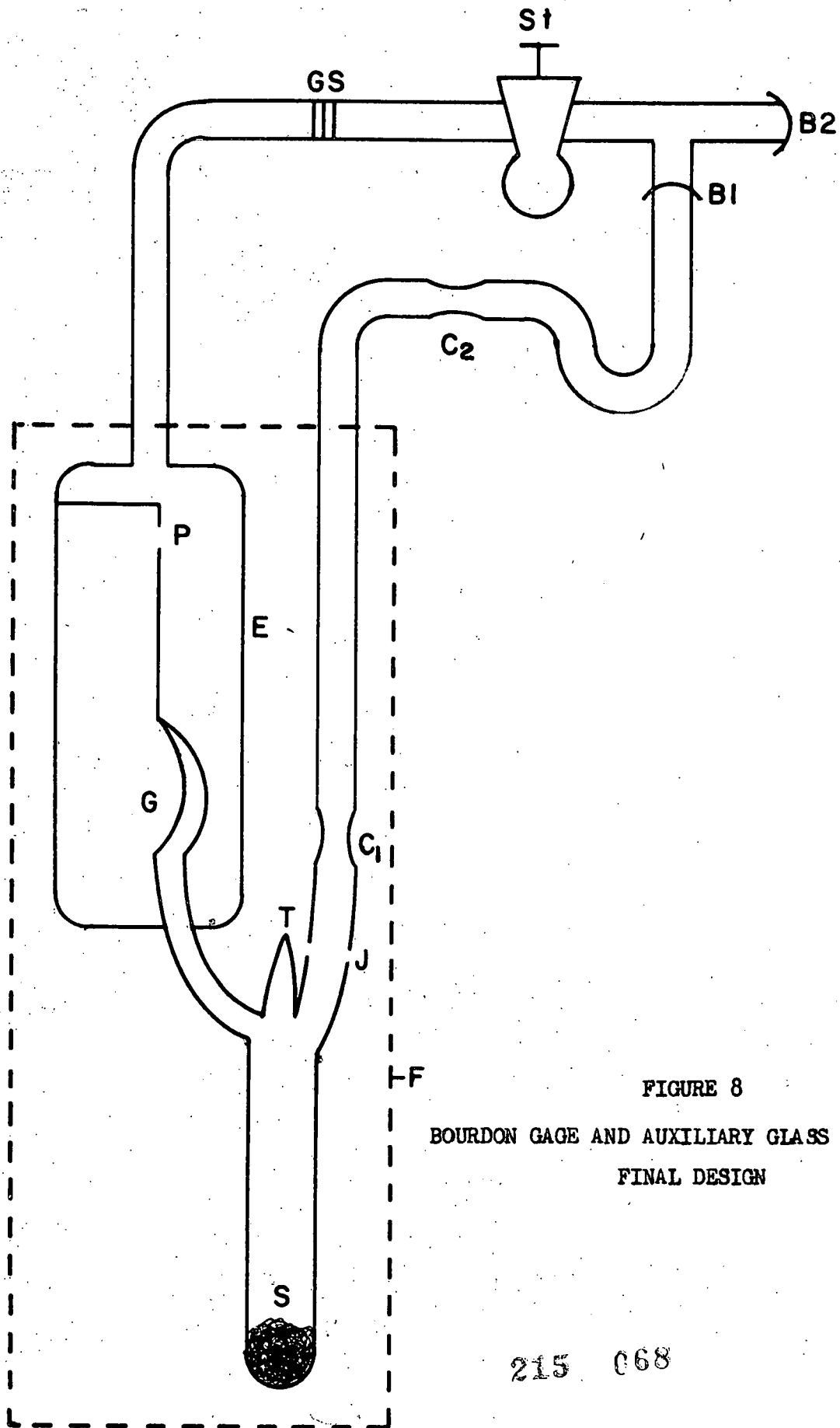


FIGURE 8  
BOURDON GAGE AND AUXILIARY GLASS APPARATUS--  
FINAL DESIGN

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on and brought up to 800° and then the lower furnace was heated to 800°. As the temperature of the lower furnace was raised, tellurium distilled up and condensed in the connecting tube where it projected from the furnace. This tube could be cooled by an air blast, but since the tellurium apparently could not get around the corner, it was maintained at a temperature estimated at 200° in the hopes that volatile impurities, if present, would distil around the corner and out of the system. After about 24 hours the stopcock was closed (since the degree of vacuum in the envelope was not of interest), the temperature dropped to 780°, and the vacuum tested. If the outgassing was adequate, the constriction (C<sub>2</sub>) was thoroughly softened with an oxy-hydrogen flame to outgas it, then sealed off, taking care not to subject the silica-to-pyrex graded seal (GS) to thermal shock. The furnace was now cooled down, the apparatus removed from the furnace, and the tellurium distilled down past construction (C<sub>1</sub>). This tellurium had been refluxing continuously in a small region of the tubing, and for the final measurement on pure tellurium, only the lower portion of it was distilled down, since volatile contaminants, if any\*, would be presumed to be at the top. In the case of the nickel tellurides, however, it was necessary to distil down all of the tellurium to maintain the stoichiometry. In either case, the distilling was done as quickly and at as low a temperature as possible, to avoid driving down contaminants less volatile than tellurium and driving gas out of the silica. The constriction was then sealed off.

\* Throughout most of this research the author was under the mistaken belief, supported by several sources, that the vapor pressure of TeO<sub>2</sub> is higher than that of Te. Recent measurements have shown that it is considerably lower<sup>33</sup>.



The two pieces of the silica connecting tube were now returned to the glassblower to be prepared for the next run, the ball joint ( $B_1$ ) was plugged, and the apparatus placed in the furnace and connected to the manometer through ball joint ( $B_2$ ). Null readings are now taken, first with the entire apparatus at room temperature, then with the upper furnace hot but the sample at room temperature, and finally with the upper furnace hot and the lower furnace warm ( $420^\circ\text{C}$ , at which temperature tellurium has a vapor pressure of 0.07 mm). These null corrections are compared with those taken after the run, to determine whether change in null correction is due to gas or to aging of the silica membrane (Sec. 3.E.3.).

The sample must now be heated to a high temperature so that diffusion of the tellurium back into the center of every crystallite may take place to equilibrium, and the measurements are then made in any desired order. Usually they were made from  $700^\circ$  down on the first day, and from  $780^\circ$  down to  $700^\circ$  on the second day, with null readings being made on the mornings of the first, second, and third days. The sample was always cooled down until its pressure was about 2 mm before the stopcock was closed for the night. From the time of the first null reading in the morning until this closure at night, a matter usually of 14 or 15 hours, the stopcock was always open, and the gage was under continuous surveillance so that it was never subjected to appreciable differential pressure. During such a day pressure readings were taken at 10 to 15 temperatures, with two to five readings at a single temperature (enough to ensure constancy of temperature and agreement between independent pressure readings).

When the measurements are completed, the furnace is cooled, the apparatus removed, and a glass tube connected to ball joint ( $B_1$ ) as shown in Fig. 9. Over the end of this tube is slipped a rubber tube (R), the other end of which is slipped over the crack-off tip (T), which is also shown in Fig. 8. This tip, which is not as fragile as those ordinarily used for cracking in vacuo, is scratched immediately before the rubber tube is slipped over it. The rubber tube has the thinnest wall which will not collapse when evacuated. (A transparent plastic tube supported against collapse by an internal wire helix has also been suggested). The apparatus is now connected through ( $B_2$ ) to the low-vacuum system and pumped down to 1 mm or less. Stopcock (St) is now opened, the crack-off tip is firmly grasped through the tubing and broken, and inert gas is slowly admitted to both sides of the gage. With the rubber tubing still in place, the apparatus is disconnected at ( $B_2$ ) and a blowing tube inserted there, so that the silica may be opened with a torch where it has been sealed at ( $C_1$ ). When this has been prepared for the butt joint (J), the apparatus is ready for the next sample. Note that silica cannot be cracked with heat as Pyrex can; nor can it be sawed, because this might damage the delicate gage or pointers, and might introduce impurities into the sample space; hence all work must be done with the oxyhydrogen torch.

It is difficult if not impossible to remove the old sample completely from the sample space without introducing impurities. Hence it is desirable, when possible, to go from one sample to the next merely by addition. For example, the second set of measurements on  $NiTe_{2.0}$  was made on a sample of weight 4.350 grams. At the conclusion of the measurements the gage was opened and 0.345 grams of  $NiTe_{1.1}$

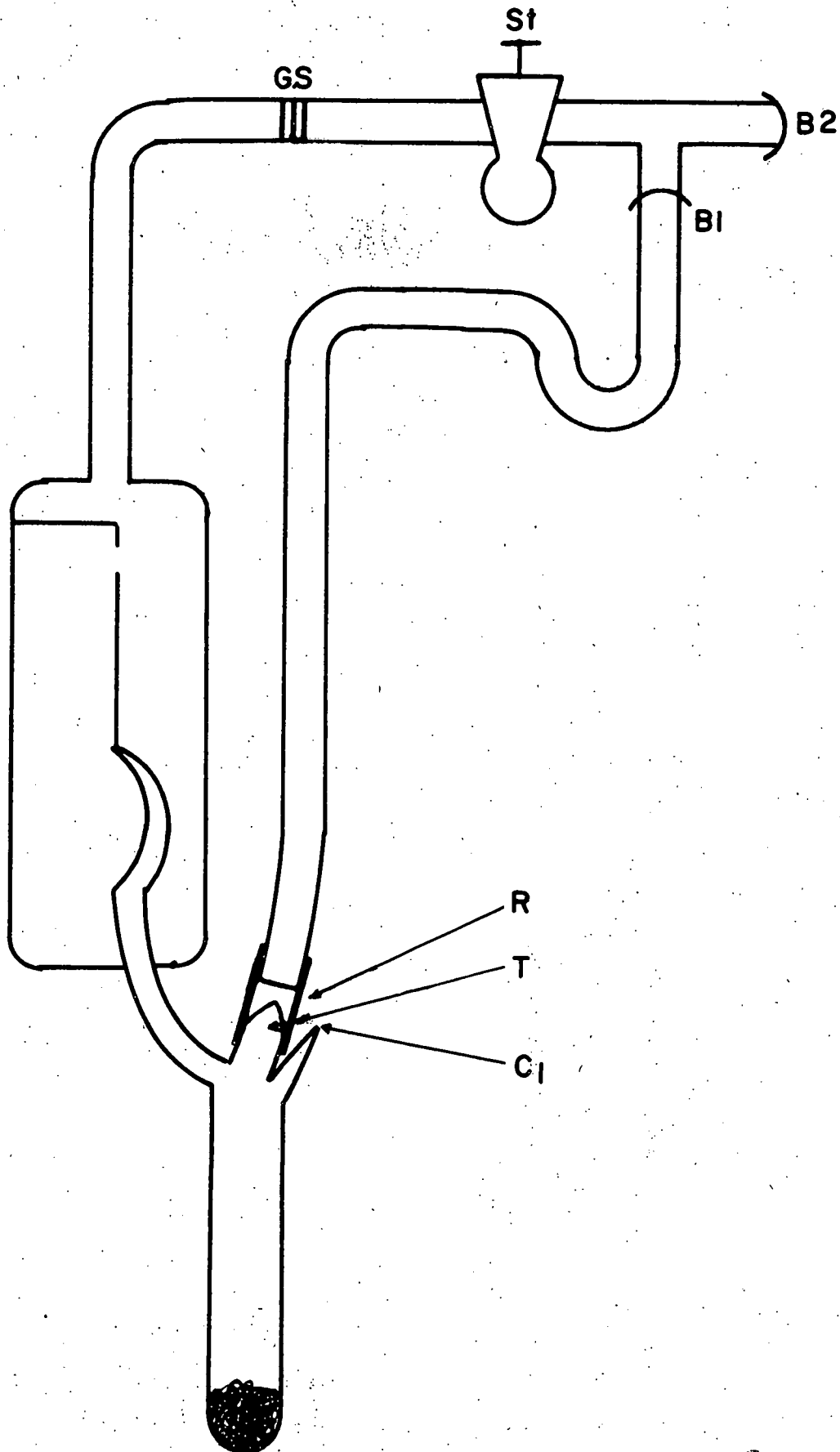


FIGURE 9  
METHOD OF OPENING THE GAGE

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were added, bringing the stoichiometry to  $\text{NiTe}_{1.900}$ . At the conclusion of the measurements on  $\text{NiTe}_{1.9}$ , the sample was recovered and found to be uniform and grossly crystalline in appearance, quite different from the  $\text{NiTe}_{2.0}$ , and to weigh 4.691 grams. The loss of 0.004 grams is presumed due to incomplete transfer (i.e., some of the  $\text{NiTe}_{1.9}$  remained stuck to the silica) but in any case would have had an insignificant effect on the stoichiometry.  $\text{NiTe}_{1.1}$  was used instead of pure nickel because the latter reacted much more slowly (Sec. 4.E.). When a completely new sample was to be used, the sample tube was removed and a new one put on. When this occurred, it was necessary to replace the entire sample tube (rather than splice on a piece) because the sample tube fit very snugly in the isothermal block (clearances were nowhere greater than 0.1 mm when the furnace was cold, and often much less, as indicated by the fact that the furnace sometimes had to be heated to several hundred degrees in order to free the silica apparatus; the reason for such small clearances was partly to obtain good heat transfer, and partly to position the pointers precisely and immutably in the proper position for viewing).

Instead of opening the gage each time to change the stoichiometry, it is possible to distil out a small amount of the volatile constituent and then seal off by means of a plug of this constituent in a capillary. This has been done in a series of measurements on sulfides<sup>39</sup>; with phosphorus it works less well, and with arsenic not at all<sup>71</sup>. Whether or not it would work with tellurium is not certain, but even its discoverer admits that from the point of view of accuracy it is not desirable as the method of opening the gage. If

such a "sulfur valve" were to be used, a by-pass would have to be provided for outgassing.

The volume of the space available to the vapor, including the gage, the sample tube, the connection to the constriction ( $C_1$ ), and the crack-off tip, was estimated to be 45 cc. This amounted to 2 millimoles at STP, or about  $2/3$  micromole per millimeter of pressure being measured at  $800^\circ\text{C}$ . Since the volume estimate was probably accurate within 10%, a correction could have been made for this amount of vapor, but it turned out to be unnecessary. In every case where the pressure was greater than about 20 mm the pressure was either independent of composition ( $\text{NiTe}_{2.0}$  and  $\text{NiTe}_{1.9}$  were both in the two-phase region, and pure tellurium is of course not affected) or was only very slightly affected by composition ( $\text{NiTe}_0$  was a dilute solution of nickel in liquid tellurium, whose pressure is little affected by changes in concentration--see Fig. 12 and compare the slope of the pressure vs. composition curve in the liquid-solution range around  $\text{NiTe}_0$  with the slope in the solid-solution range around  $\text{NiTe}_{1.7}$ ).

3.E.3. The Pointers and Reading Corrections The pointers and their visibility in the furnace caused more difficulty and wastage of time than any other single factor in this research, although the final solution was simple.

It is necessary to be able to see the pointers clearly at all temperatures, and to be able to line them up with a precision of 0.1 mm Hg or better. It is important to note that the criterion for null (that is, for lining up the pointers) need not be exactly 0 mm of pressure; neither need it be absolute (that is, it is permissible, though not desirable, to have it highly subjective); it is only required that it be

completely reproducible, independent of temperature, total pressure, or fortuitous circumstances.

The original difficulties were concerned with seeing the pointers. The pointers were thin pieces of silica, which had to be viewed through a silica envelope and glass window by means of a telescope, at a temperature when all of the silica, and also the much more emissive background, were incandescent. Light was thrown into the furnace and onto the pointers by means of a small light bulb, a system of lenses, and a half-silvered mirror arrangement through the same hole in the furnace which was used for viewing the pointers; a piece of clear (unsilvered) optically flat glass served the function of the half-silvered mirror. Although the inside of the telescope was lined with black velvet and the inside of the Alundum tube painted black, the amount of background was so great that the pointers could be seen only with difficulty and occasionally not at all. The various components of the system move about considerably as the temperature changes from 20° to 800° (the silica expands not at all, the Alundum furnace core a great deal, and the iron can, which supports the outer end of the viewing tube, very little, because it remains comparatively cool), and the pointers would move either out of the field of view, or else out of the light beam. The furnace was finally partly disassembled and another tube inserted (Sec. 3.A.) so that the light might be thrown in directly rather than by the half-silvered mirror arrangement. This system was better, but still marginal. Furthermore, it meant that the pointers had to be in exactly the right position not only up-and-down and left-and-right in order to be visible, but also back-and-front in order to be in the light beam. (Actually the 40-mm envelope with the pointers on its

axis was not coaxial with the sample tube and isothermal block; instead it was about half an inch further back, to permit room for the connecting tube (Fig. 8) during the outgassing). This not only placed extra restrictions on the fabrication, but allowed a new degree of freedom for difficulties due to thermal expansion.

What was needed for good visibility of the silica pointers through the silica envelope was not high-intensity illumination but high-contrast illumination. Toward this end, the light source was replaced with a "grain-of-wheat" bulb of extremely small filament size, and the lenses with very high-quality multiple lenses. These threw a small, sharply focused spot of light directly onto the pointers.

The next difficulty was with finding a consistent null. If the pointers were less than about 1 mm in diameter, they vibrated excessively, tended to curl from radiant heat when sealed in the envelope, and were exceedingly difficult to see. But with such thick pointers (40 times as thick as the motion corresponding to 0.1 mm of pressure) it was difficult to locate a reference spot on the pointer. At constant temperature, and particularly at low temperature, streaks of light could be lined up; but at higher temperatures such streaks changed or disappeared.

After numerous attempts with small points on thick pointers, pointers made of capillaries, and the like, the problem was finally solved by sealing 6-mil tungsten wires into the silica. The wires were first finely pointed by the exothermic reaction with sodium nitrite, although it latter turned out that square-ended wires were easier to read. These wires worked well for part of one series of measurements, and then started to corrode; on the second series (pure tellurium) the temperature was raised to more than 800°, and the wires

corroded so badly that the null correction was indeterminate by more than 1 mm Hg. Investigation in the literature then showed that tungsten does indeed react with carbon dioxide (which was being used as the inert gas) at these temperatures. The tungsten wires could not be replaced with platinum, since this melts at a temperature lower than that of silica. Rhodium wires (0.008 diameter, the only size available) were therefore tried, and proved quite satisfactory, although it was necessary to anchor them very firmly in the silica, which was difficult not only because of the different coefficients of expansion, but also because rhodium melts only slightly higher than silica.

There was still some difficulty in seeing the metal pointers, until it was realized that high intensity rather than high contrast of illumination was now required. To supply this, a 1/2" silica rod was sealed in to the top of the furnace to act as a light-pipe, whenever the apparatus was in the furnace, and the top of this rod was heavily illuminated with a 75-watt light and reflector. Thereafter visibility of the pointers was always excellent.

The third difficulty with the pointers was vibration. The source of the vibration was never located, but was assumed to be the general 60-cycle vibration of the entire building. Vibration was somewhat damped by a few tenths millimeter of pressure outside the gage, and this amount of gas was always admitted as soon as possible after the outgassing. The tendency to vibration was apparently largely a function of the individual gage, though it could not be correlated with any obvious shape factors. It could be greatly reduced, however, by eliminating thin spots in the silica pointer



(between the gage and the rhodium) and, as indicated above, by rounding the sharp edges of the gage. It could also be reduced by supporting the silica apparatus rigidly at both ends. This apparatus is normally supported rigidly at the lower end, the upper end being connected to the manometer through flexible glass tubing. To support the upper end, the top of the furnace is closed with a piece of Silocel brick which has two holes (one for the silica tubing and one for the light pipe), which is split for assembly, and which is cemented to the top of the furnace. The space around the silica tube is then packed with asbestos fibres, and the whole covered with Santocel insulation. This is all cemented in place and then removed each time the apparatus is inserted in and removed from the furnace.

For ease in lining up the pointers, they should be as close together as possible, but of course they must not hit one another, since this would bend them and change the null calibration. It turned out that for reproducibility of null, the best arrangement was overlapping wires. The overlap was 0.01 to 0.02, and the wires were separated, in the direction of viewing, by about 0.02, large enough to preclude physical contact, but small enough to make possible having both pointers in focus at the same time. With this arrangement, there was no difficulty in reproducing null readings to 0.1 mm every time; furthermore, the null criterion had the advantage of being objective, so that it was unlikely to be subject to slow fluctuation.

The first sets of pointers were originally lined up exactly opposite one another. This meant that to check the null reading the system had to be pumped down below 0.1 mm, which took an excessive length of time. Furthermore, the null reading often changed, and if it happened to change in the wrong direction, a null reading could not

be taken. In the later work, the wires were offset when the gage was fabricated in such a direction and to such an extent that 0.5 to 1.0 mm of pressure in the envelope was required to line them up. This made null readings easy, but also introduced a new possibility of error, since a change in the Young's modulus of the silica would now affect the null correction. However, the null reading and the actual measurements were always made with the gage at the same temperature. There was conflicting evidence as to whether this null correction was, in fact, affected by changes in gage temperature of several hundred degrees. However, such change certainly amounted to less than 0.1 mm for a change in gage temperature of 100°.

In making successive readings at the same temperature, the pressure was always changed by at least 0.5 mm before readjusting to a null. During the adjustment, the needle valve was controlled by feel, while only the pointers were being watched, so that the successive adjustments were independent. The manometer was not read until after a satisfactory null had been reached.

The largest source of error in pressure measurement, and therefore the largest single source of error at low temperatures (below about 50 mm pressure), was due to the shift in the null correction. Brooks<sup>26</sup> reported shifts of 0.8 mm per day when the gage was kept at 750° and a shift of 4.0 mm on the day when the gage was kept at 850°. He corrected for this on the assumption that the change was linear with time, but this was still the major source of error in his measurements. No shifts of this magnitude were encountered in the present work, but after a day of measurements the pressure required so bring the pointers back to null had invariably increased, by a minimum of 0.1 mm and a maximum of 0.4 mm.

It was originally assumed that Brooks' shifts were due to leakage of nitrogen or air (the gases which he used) through the silica membrane, and therefore carbon dioxide was used as the inert gas in all the experiments except the final run on tellurium. There is considerable disagreement in the literature<sup>34, 35</sup> concerning the leakage of gases through silica. It is known that hydrogen, and to a lesser extent helium, diffuse through silica readily at high temperatures. It is probable that nitrogen, argon, and oxygen also diffuse through, to a lesser extent, at very high temperatures, and probable<sup>35</sup> that the ability of a gas to diffuse through silica can be correlated not with the size of its molecules but with its boiling point or sublimation energy. On any of these grounds, silica should be quite impermeable to carbon dioxide. On the other hand, carbon dioxide decomposes at high temperatures into carbon monoxide and oxygen ( $\log K_p$  is 10.19 at 1000°K, 8.86 at 1100°, and 7.74 at 1200° homogeneously<sup>36</sup>), and these gases may diffuse.

Whatever the mechanism of diffusion, xenon should be exceedingly unlikely to diffuse through silica, and the final run on tellurium was made with xenon as the inert gas. The shift in null correction was 0.15 mm the first day and 0.25 mm the second day. The shift on the second day is sufficiently high that it is certainly not imaginary, but the experiment is unfortunately not conclusive. The xenon was slightly contaminated with, among other things, water vapor. Furthermore, the gage was heated to a higher temperature than ever before (880°), and some outgassing may have taken place. Finally, some gases which may have diffused into the silica on the previous run (with carbon dioxide) may have diffused out again during this run.

At the conclusion of the xenon run, the gage was heated to 825°C, and the sample heated to create a tellurium pressure of about 90 mm, and

these conditions were maintained for four hours with nitrogen on the outside of the gage. The null shift was 0.1 mm. Thus there were no significant differences among nitrogen, xenon, and carbon dioxide.

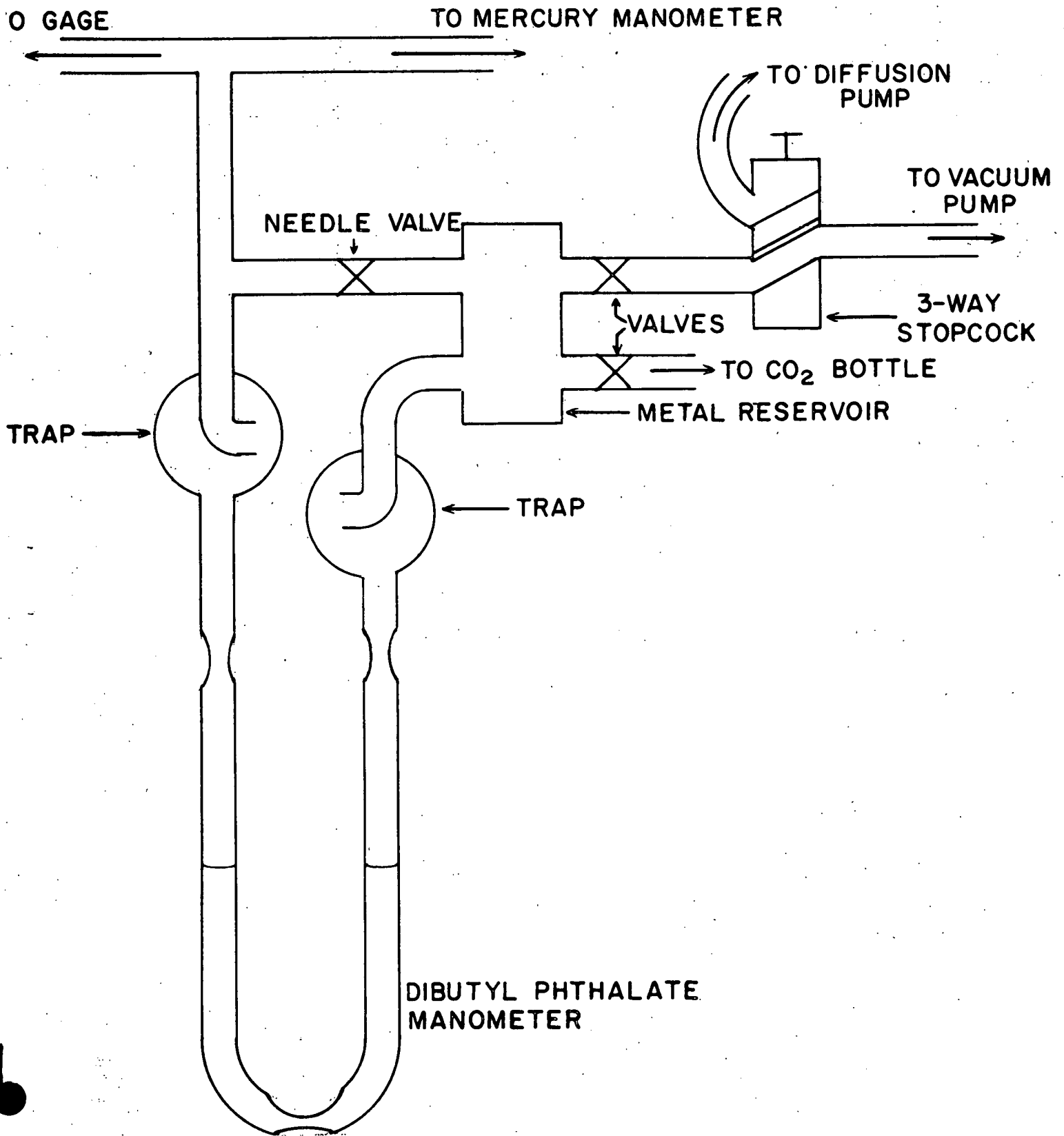
The null shifts could not have come from outgassing of the sample, particularly in the case of tellurium which was completely volatilized, and not subsequently exposed to possible contamination by gas. They might have come from continued outgassing of the silica, but if so the rate of evolution of gas must have increased for some reason from the  $10^{-5}$  mm per 5 minutes which was observed at the end of the outgassing period. They might have been due to some mechanical change (crystallization, annealing, "aging") of the silica membrane, but in the first place when the gage was opened, a new sample added, and the outgassing repeated, the null correction appeared to go back to its original value, and in the second place, such aging should have been accompanied by decreases in sensitivity of the gage, which did not occur. Furthermore, there was always gas in the gage at the end of the run, as indicated by a Tesla coil. The amount of this gas was hard to judge, but it was not incompatible with the null shifts. The shifts might have been due to some artifact in the observation (say a shift in lighting, or position of the telescope), but this would not account for the consistent increase. The shifts might have been due to some chemical reaction, as between tellurium and silica, but it is hard to conceive of any reaction products which would be volatile at 420°C. It seems, therefore, that in all likelihood gas was leaking through the silica membrane. No such leakage occurred when one gage was allowed to stand under vacuum for six weeks at room temperature, and it seems impossible that it was due to identical pinholes in the many gages used. The gage is, of course,

exceedingly thin and of considerable area (perhaps 30 sq. cm.). The cause of these null shifts is an interesting problem not only from a theoretical viewpoint but also because, if it could be removed, the pointer and manometry problems could probably be solved to yield an additional order of magnitude in the precision of the general method.

### 3.F. THE CONNECTIONS

The connecting piping and valving are shown in Fig. 10A. The mechanical pump was used both as the fore pump of the high-vacuum system and for pumping the inert gas out of the gage. By opening one of the two valves, either inert gas or vacuum could be admitted to the metal reservoir, its amount being measured by the dibutyl phthalate manometer. This valve being closed, the needle valve was slowly opened while the pointers were observed, and some of the gas (or vacuum) was thus admitted to the system. Because the volume of the system (including the mercury manometer, the envelope around the silica gage, and the connecting piping) was larger than the volume of the metal reservoir plus the volume of the trap above the dibutyl phthalate, a change of pressure of 0.1 mm Hg at the pointers amounted to about 0.4 mm Hg, or 5 mm dibutyl phthalate, on the dibutyl phthalate manometer. Thus, delicate adjustments could be made with ease. The needle valve was very good in this respect, but its resistance made pumping very slow. The needle valve and the other two valves were of metal, with kovar used for some glass-to-metal seals and Apiezon W (black wax) for others.

This system worked adequately, but never really well. It always leaked, the leaks amounting to perhaps 0.3 mm per day, and probably being due to outgassing or impurities rather than true leaks. Constrictions



DIBUTYL PHTHALATE  
MANOMETER

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FIGURE 10a  
CONNECTIONS FOR CARBON DIOXIDE

were placed in the top and bottom of the dibutyl phthalate manometer as shown to slow down the motion of the liquid in case of a sudden pressure change, but these could not have slowed it enough in case of a break or the wrong valve being turned, and as soon as the dibutyl phthalate had moved to the bottom of the manometer, this would supply a by-pass from the metal reservoir to the system. It would probably have been better to use mercury in this manometer, accepting the reduction in sensitivity in exchange for safety of the gage. Furthermore, a needle valve or by-pass which opened more widely should have been used, and all of the valving system should have been susceptible to outgassing and to checking for leaks.

For the final run with xenon, the connecting glassware was modified as shown in Fig. 10B. Because of its expense, the xenon was never pumped away; instead a trap cooled in liquid nitrogen was used as a pump (and operated rapidly and effectively to produce a vacuum of less than 1 mm). The source of xenon was a one-liter bulb (at about one seventh atmospheric pressure) which was connected, as shown, with another trap which could be cooled to pump the xenon back. Measurements up to 700° were made on the first day. On the second day measurements were made above 700°, and because the pressure error in this region was small compared to the temperature error, only one measurement was made at each temperature. Thus xenon was admitted into the system and never pumped out. In spite of this, the xenon became exhausted at 205 mm pressure, and caused the experiment to stop at 855°C.

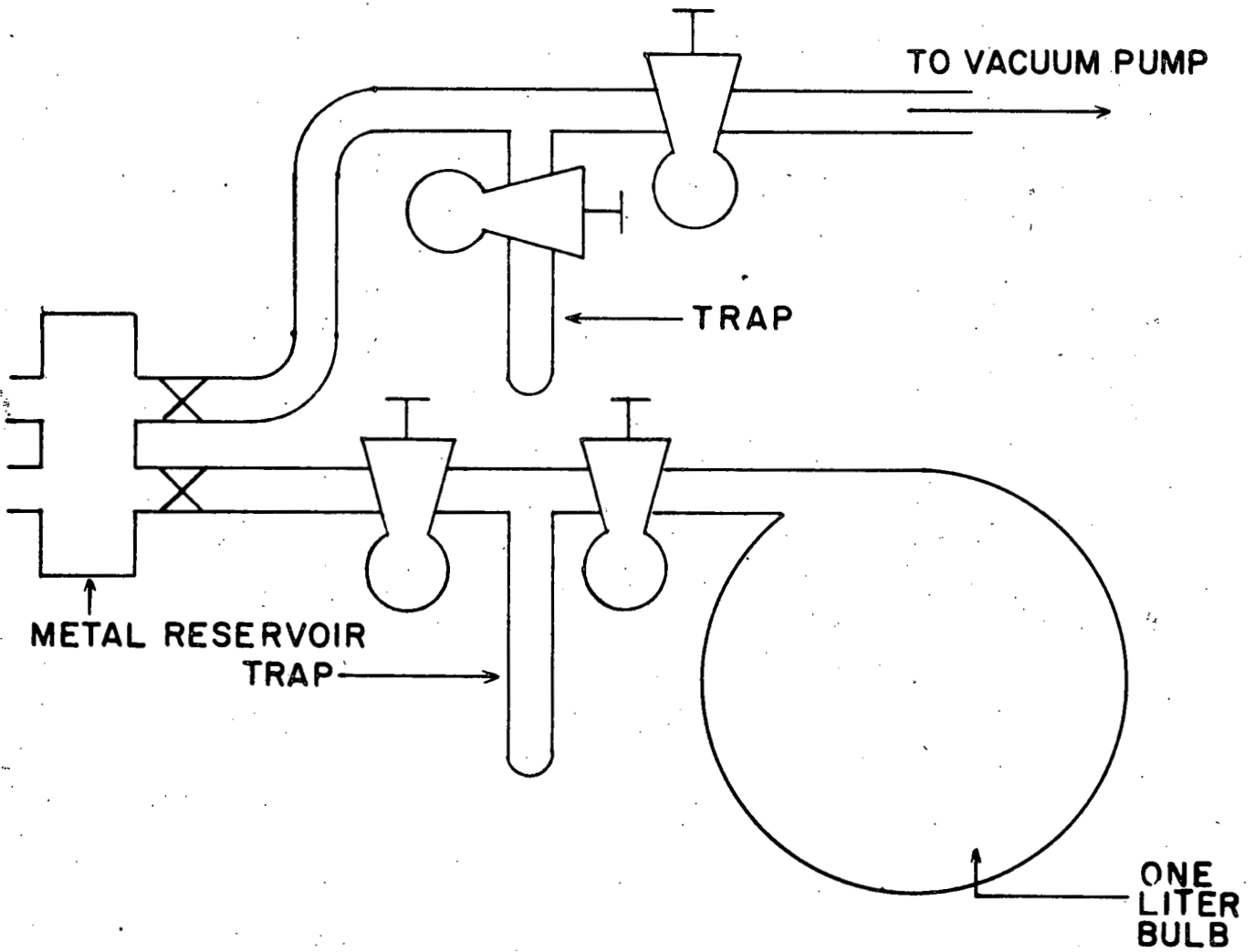


FIGURE 10b

CONNECTIONS FOR XENON

215 085



### 3.G. ERRORS AND LIMITATIONS OF THE METHOD

In reducing the data, there were usually two to six points at approximately the same, but not exactly the same, temperature. A single temperature was then picked, and all points converted to this temperature by adding to each the product of  $dP/dT$  and  $\Delta T$ . The  $dP/dT$  was determined by a rough plot of the raw data. The mean of the group of observations was then taken, and the null correction subtracted from it. At least one temperature was always read both on the way up and on the way down; this provided a check, and also aided in assigning values to the null correction as a function of time if the null shift had been unusually high (say 0.4 mm during the day). The resulting pressures were corrected for the density of the mercury in the manometer. All computations were carried to 0.01 mm, although the last digit is comparatively meaningless.

There were several internal checks on the consistency of the data. The vapor pressure of tellurium was measured twice, over an interval of several months, using samples from different origins, with different methods of purification, using different gages and different thermocouples. The results are in complete agreement. It was intended to check the vapor pressure of  $NiTe_{1.9}$  formed from  $NiTe_{2.0}$  and  $NiTe_{1.1}$ , by making  $NiTe_{1.9}$  from  $NiTe_{1.5}$  and Te, the tellurium coming from a different source. However, it turned out that above  $712.5^\circ$  the pressures of  $NiTe_{2.0}$  and  $NiTe_{1.9}$  were identical. Furthermore, the pressures of  $NiTe_{2.0}$  and  $NiTe_9$  were identical below  $682^\circ$ , and the tellurium in these cases did come from entirely separate sources. The reason for this identity is that the material is in a two-phase region and the pressure is independent of composition; however, it was entirely unexpected.

Further confirmation of internal consistency is given by the smoothness of the curves. The data are more self-consistent than can be indicated on any plot which can be shown here. Almost every point could be brought onto the appropriate smooth curve by adding or subtracting not more than  $0.1^\circ$  (in the high-temperature region), 0.1 mm (in the low-temperature region) or both.

This says nothing about the systematic errors. Here one can only rely on the general agreement in the tellurium data with Brooks<sup>26</sup> and on faith in the nature of the experimental details.

Although the pressure changes very rapidly with the composition in the solid-solution region, it is believed that the composition was known at all times with almost the ultimate precision permitted by knowledge of the atomic weights, and that this did not contribute to the error. Temperature errors, then, are the principal sources of error at high temperatures and pressure errors at low temperatures. Temperature measurement was certainly accurate to  $0.1$  to  $0.2^\circ$  on a relative basis and probably to  $0.2$  to  $0.3^\circ$  on an absolute basis. Pressure measurement is believed accurate to about 0.1 mm on a relative basis, with systematic errors being no greater.

One possible source of systematic error which was avoided was thermal transpiration. If the temperatures at two ends of a tube are different, and the tube is filled with gas at low pressure, the pressures at the ends will in general be different. If the tube is long compared with its diameter, the magnitude of this effect is roughly proportional to the temperature difference and inversely proportional to the square of the total pressure and to the square of the tube diameter. For example, for a temperature head of  $100^\circ$ , a tube diameter

of 0.5 mm, and a total pressure of 0.5 mm, the pressure difference at the two ends is about 5%. To eliminate error from this source, the silica tube projecting through the top of the furnace had an i.d., of 12 mm, and the tube connecting the gage with the sample tube an i.d., not less than 5 mm, both of which were more than ample.

The fundamental difficulties in reducing errors pertain only to the measurement (not to the control) of temperature--which indicates an ultimate limitation on the method of close to 0.1°C--and to the shifts in the null position of the pointers. The latter is not well understood, but it is believed that the problem could be greatly reduced.

There is no lower pressure limit to the present method except that imposed by the increasing percentage errors at lower pressure caused by the constant absolute pressure error. It is thus desirable to supplement this method by some other for the low-pressure measurements. In the absence of such supplement, however, the low-pressure data are of considerable use in plotting the trend of the data, since they occupy so large an area on a log p vs 1/T plot. The upper pressure limit could probably be raised to two or three atmospheres if one wished to build a tall enough manometer and catheter; it seems probable that with little modification any glass apparatus which will hold a vacuum will also hold one atmosphere of pressure in excess of atmospheric.

There is no low-temperature limit, just as there is no low-pressure limit, although if the furnace designed for high temperatures is to be used for low-temperature work, some means must be found to cool it rapidly. The high-temperature limit depends on

whether the substance being measured vaporizes with or without decomposition. In the former case (e.g., tellurium), the weak link in the chain is the gage, its limit being set either by annealing, crystallization, or permeability to the inert gas. The normal anneal point for silica is about 1050°C, but this exceedingly thin membrane, which is under considerable stress even when evacuated inside and out, might anneal at a lower temperature--perhaps as low as 1000°. Whether crystallization might set in at a lower temperature would be hard to say, and would probably depend upon the purity of the sample of silica, the length of exposure to high temperature, and other factors.

These limitations apply only to the vapor temperature. In dissociating substances such as nickel-rich nickel tellurides, the gage may be kept considerably cooler than the sample, and now the temperature limit is set only by the chemical and mechanical resistance of the silica of the sample tube. In fact, the dissociation pressure of uranium oxide has been measured<sup>37</sup> by a method similar to that used here, with the gage cold and with the sample at temperatures up to 1250°C. For such temperatures, of course, the isothermal block must be built of suitable metals, such as nickel.

### 3.H. RESULTING DATA

3.H.1 Pressure Data The vapor-pressure data are given in Table III. The first sample of tellurium was the sample described in Sec. 4.B. The third was kindly supplied by Dr. Gwynn Suits, who had purified spectroscopically pure tellurium by zone refining and sublimation to a purity in excess of 99.999999%. The  $\text{NiTe}_{1.5}$  and  $\text{NiTe}_{2.0}$  samples were those described in Sec. 2.A.3. The  $\text{NiTe}_{1.9}$  and  $\text{NiTe}_9$  were made by mixing  $\text{NiTe}_{2.0}$  with  $\text{NiTe}_{1.1}$  and tellurium (99.999%) respectively

TABLE III

VAPOR PRESSURE

P(mm), obs.	T, °C	P(mm), calc	dP/dT, mm/°C
NiTe <sub>2.00</sub> - Feb. 22, 1957			
45.28	781.9	45.44	.27
38.21	755.0	37.90	.29
30.25	728.6	30.27	.29
22.59	700.2	22.44	.26
15.23	667.9	14.84	.20
9.06	632.7	8.96	.14
4.93	597.4	5.05	.09
2.64	562.3	2.64	.05
Te - March 20, 1957			
0.52	483.8	.43	.01
2.18	553.1	2.20	.04
17.68	666.1	17.57	.28
41.39	723.5	41.24	.58
88.25	782.1	88.67	1.09
88.53	782.1	88.67	1.09
41.59	723.5	41.24	.58
17.76	666.1	17.57	.28
2.27	553.1	2.20	.05
Te - April 3, 1957			
52.99	742.3	53.28	.71
48.67	735.7	48.75	.66
41.32	723.5	41.24	.58
37.64	716.8	37.54	.53
32.58	706.8	32.55	.47
28.97	698.8	28.97	.43
25.60	690.4	25.57	.38
22.97	683.3	22.97	.35
22.85	683.3	22.97	.35
19.47	673.2	19.65	.31
Te - April 5, 1957			
19.56	673.2	19.65	.31
19.55	673.2	19.65	.31
19.79	673.2	19.65	.31
16.09	660.2	16.00	.26
13.57	649.9	13.52	.22
11.41	639.9	11.44	.19
7.51	615.9	7.52	.14

P(mm), obs.	T, °C	P(mm), calc	dP/dT, mm/°C
Te - April 5, 1957 (continued)			
5.98	604.4	6.10	.11
5.99	604.4	6.10	.11
4.26	587.3	4.41	.09
2.10	553.1	2.20	.04
NiTe <sub>2.00</sub> - May 6, 1957			
22.13	699.6	22.21	.27
19.62	689.6	19.66	.24
17.38	679.6	17.32	.22
14.84	667.2	14.71	.20
12.55	655.6	12.54	.18
10.55	643.5	10.54	.15
8.37	630.4	8.65	.13
6.80	615.9	6.88	.11
5.10	599.0	5.19	.09
2.74	564.5	2.76	.05
NiTe <sub>2.00</sub> - May 7, 1957			
44.32	777.4	44.22	.27
41.38	766.0	41.05	.28
38.39	755.6	38.07	.29
35.12	744.5	34.86	.29
35.10	744.5	34.86	.29
31.21	731.9		
27.56	719.4	27.66	.28
24.17	707.1	24.27	.27
22.28	699.6	22.28	.26
8.16	627.0	8.21	.13
3.37	574.7	3.35	.06
1.68	538.4	1.62	.03
NiTe <sub>1.90</sub> - May 17, 1957			
8.11	666.6	8.08	.23
11.03	678.1	11.10	.30
14.21	687.7	14.26	.37
18.17	697.2	18.05	.44
5.42	653.0	5.42	.17
3.54	638.6	3.44	.11
2.29	623.1	2.03	.07
1.07	599.5	.84	.03
NiTe <sub>1.90</sub> - May 18, 1957			
1.12	599.5	.84	.03
5.40	653.0	5.42	.17
18.13	697.2	18.05	.44
46.09	783.7	45.92	.27

P(mm), obs.	T, °C	P(mm), calc	dP/dT, mm/°C
NiTe <sub>1.90</sub> - May 18, 1957 (continued)			
43.64	773.8	43.23	.28
40.26	761.6	39.80	.29
36.87	749.6	36.34	.29
32.50	735.5	32.26	.29
28.43	721.9	28.36	.28
24.62	710.5	24.62	.56
17.97	697.2	18.05	.44
5.50	653.0	5.42	.17
1.22	599.5	.84	.03
NiTe <sub>1.50</sub> - June 11, 1957			
0.70 or 0.75	688.0		
5.00	781.0		
NiTe <sub>1.70</sub> - August 6, 1957			
1.32	672.9	1.05	.03
0.73	652.1	.55	.02
0.43	623.0	.21	.01
0.23	592.1	.07	.00
NiTe <sub>1.70</sub> - August 7, 1957			
0.39	623.0	.21	.01
2.46	701.1	2.38	.07
18.00	781.4	17.93	.41
12.46	765.2	12.33	.29
7.97	747.0	7.95	.20
5.46	732.0	5.45	.14
3.46	712.4	3.25	.09
2.25	695.8	2.05	.06
0.44	623.0	.21	.01
NiTe <sub>9</sub> - September 1, 1957			
1.73	544.0		
7.29	620.1	7.37	.12
22.78	698.2	22.90	.35
19.00	686.0	19.00	.30
15.39	670.6	15.39	.21
12.44	655.1	12.45	.18
9.78	638.7	9.81	.15
7.34	620.1	7.37	.12
5.73	604.2	5.67	.10
4.23	587.4		
2.94	565.9		
1.85	544.0		
1.27	525.6		
0.92	511.3		
0.62	489.8		

P(mm), obs.	T, °C	P(mm), calc	dP/dT, mm/°C
NiTe <sub>9</sub> - September 2, 1957			
1.94	548.8		
7.29	620.1	7.37	.12
23.11	698.2	22.90	.35
70.42	783.3		
61.53	771.4		
51.56	757.3	51.53	.65
43.12	743.3	43.09	.56
34.81	727.7	34.97	.48
28.96	714.3	28.99	.42
22.92	698.2	22.90	.35
Te - September 11, 1957			
0.68	506.7	.76	.02
1.93	548.8	2.01	.04
4.28	587.2	4.40	.09
9.46	629.1	9.50	.17
18.16	667.6	18.00	.29
32.00	705.6	31.99	.47
24.79	688.1	24.70	.37
13.52	649.7	13.47	.22
6.77	609.9	6.75	.12
3.34	569.9	3.12	.06
Te - September 12, 1957			
27.16	694.7	27.26	.41
39.02	719.6	39.05	.55
58.21	748.9	58.15	.77
84.45	778.4	84.72	1.05
117.09	805.7	117.67	1.39
157.78	831.2	157.46	1.76
204.21	855.0	204.09	2.18
Te - Theory			
—	449.7	0.167	0.0049
—	993.6	760.00	6.47



in the correct proportions; the NiTe<sub>1.7</sub> was similarly made from NiTe<sub>1.5</sub> and tellurium. The data are plotted in Fig. 11, as log<sub>10</sub>P (mm Hg) vs 1/T (°K). All of the data are tabulated and plotted (i.e., no gross errors have been removed) except for the last points on one tellurium run, when the pointers were corroding very badly, and the first two points on NiTe<sub>1.7</sub> and NiTe<sub>1.9</sub>, when equilibrium had not yet been established within the crystallites. The first point is retained on NiTe<sub>1.5</sub>, however, because while it is known to be high, only one other point was obtained before the gage broke, and that point was not measured accurately.

3.H.2. Derived Results As indicated in Fig. 11, the plot of log P vs. 1/T is almost, but not quite, linear. The reasons for this are most easily seen by rederiving a Clausius-Clapeyron-like equation in a manner similar to that of Brown<sup>70</sup>.

One starts with the thermodynamic relation

$$dP/dT = \Delta H/T\Delta V \quad (10)$$

which is rigorously valid for liquid-vapor equilibrium, and makes the substitution

$$\Delta V = V_g - V_l \quad (11)$$

where  $V_g$  is the molar volume of the gas and  $V_l$  the molar volume of the liquid. The next substitution is

$$V_g = \frac{RT}{P} + B \quad (12)$$

where B is the second virial coefficient. This yields

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_g - V_l)} = \frac{\Delta H}{T V_g \left(1 - \frac{V_l}{V_g}\right)} = \frac{\Delta H}{T \left(1 - \frac{V_l}{V_g}\right) (RT/P + B)}$$

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Multiplying by  $-T^2/P$  yields

$$\frac{dP/P}{dT/T^2} = \frac{d \ln p}{d(1/T)} = - \frac{\Delta H}{(1-V_1/V_g)(R+BP/T)}$$

Making the further substitution  $P/T = R/V_g$ , which contributes negligible error since it is only in a small correction term, yields

$$\begin{aligned} \frac{d \ln p}{d(1/T)} &= - \frac{\Delta H}{(1-V_1/V_g)(R+BR/V_g)} \\ &= - \frac{1}{R} \cdot \Delta H \cdot \frac{1}{1 - \frac{V_1}{V_g}} \cdot \frac{1}{1 + \frac{B}{V_g}} \end{aligned} \quad (13)$$

This formula is to all intents and purposes rigorous (since for our purpose B need not be defined as a constant). Alternatively the derivation can proceed from the Van der Waals' instead of the virial form of the equation of state; this yields the same expression, with  $b = a/RT$  substituted for the second virial coefficient, B.

Equation (13) indicates that the slope of the  $\log p$  vs.  $1/T$  curve will be constant if all four of the factors on the right-hand side of the equation are independent of P and T. Integration of (13) will then lead to an equation of the form

$$\log P = -A/T + B$$

However, we know that the second factor will not be constant, but will instead decrease with temperature. In fact, it can be shown by sophisticated reasoning<sup>74</sup> that

$$d \Delta H/dT = \Delta C_p \quad (14)$$

where  $\Delta C_p$  is the difference between the heat capacities at constant

pressure of the liquid and gas; the error in this equation is of the same order as the last two factors in (13), as discussed below. Estimates of  $C_p$  for both liquid and gaseous tellurium in this temperature range are available<sup>32</sup>; they amount to 18.00 cal/mole deg for the liquid, and 8.92 cal/mole deg for the gas (two gram-atoms per mole in each case). Hence,  $d \Delta H/dT = -9.08$  cal/mole deg (probably accurate to  $\pm 0.2$  cal/mole) and we expect the heat of vaporization of tellurium to vary by over 2000 calories per mole over a temperature range of  $250^\circ$ . In spite of this, one previous investigator<sup>26</sup> has fitted an analytic expression to his vapor pressure data by least squares techniques and computed a heat of vaporization, over this temperature range, to which he assigns a probable error of 70 calories!

If the heat of vaporization varies with temperature at a constant rate over the temperature range of interest, and if the last two factors of (13) are constant, integration of (13) give an equation of the form

$$\log P = -A/T + B - C \log T \quad (15)$$

We may estimate the magnitude of the third and fourth factors in (13).  $V_l$  is approximately 50 cc, while  $V_g$  is approximately 16 Amagat units, or approximately 400,000 cc, at the highest temperature measured (where  $T$  is about four times  $273^\circ\text{K}$  and  $P$  is about one fourth atmospheric). Thus, the third factor varies from 1.0000 to about 1.0001. The second virial coefficient is certainly negative, since the Boyle point of all known substances is, as it should be on theoretical grounds, well above the critical temperature<sup>18f</sup>, and these measurements are certainly well below; hence the fourth factor, like the third, is greater than one, and we may guess that, if tellurium vapor behaves like other gases whose

virial coefficients (or Van der Waals' constants) are known, this factor is not much greater than 1.0001 at 855°C. As the temperature increases, however,  $V_g$  will fall very rapidly, and these factors will rise more and more rapidly, eventually more than compensating for the decrease in the second factor. Thus, the curve of  $\log P$  vs.  $1/T$  may be expected to be concave downward at low temperatures, and to have gradually decreasing curvature until eventually it inflects.

This behavior has, indeed, been found where vapor pressure data of sufficient accuracy have been available over a sufficiently great range, the inflection point occurring<sup>75</sup> at 0.80 to 0.85 times the critical temperature. We do not, of course, know the critical temperature of tellurium, but in the absence of better information we may use Guldberg's rule<sup>18e</sup> and estimate that it is 1.5 times the boiling point, or about 1900°K. In any case, we expect the curvature to decrease with increasing temperature and, at some temperature well above the boiling point, to become zero. To account for this, an additional term must be added to (15), and a convenient one is a linear term in  $T$ , yielding

$$\log P = -A/T + B - C \log T + DT \quad (16)$$

An analytical expression of the form of (16) has been fitted to the vapor pressure data. This expression is

$$\log P = -10,663.14/T + 64,73140 - 18.61687 \log T + 0.00341783 T \quad (17)$$

where  $P$  is in mm Hg,  $T$  is in degrees Kelvin, and all logarithms are to the base 10. The agreement of this function with the data is excellent, as indicated in Table III, where it is shown that, if an allowance of 0.1° is made, most of the pressures computed from (17) agree with the observed pressures within 0.1 mm, and none disagrees by

so much as  $0.3^\circ$  and  $0.3$  mm.\* Equation (17) also indicates a pressure of  $0.17$  mm at the triple point, which is compatible with extrapolated results of measurements on the vapor pressure of solid tellurium (see Appendix 2).

It is clear from Fig. 11 that the plot of  $\log p$  vs.  $1/T$  is concave downward at low temperatures and almost linear at temperatures from about  $750$  to  $850^\circ\text{C}$ . The exact curvature and slope at low temperatures cannot be determined, because of the large percentage error at low temperatures occasioned by the constant  $0.1$  mm error, and the uncertainty of the triple-point pressure. Nevertheless, it is clear that the curvature is of approximately the right magnitude. From analytical differentiation of (17),  $-d\Delta H/dT$  varies from slightly more than  $12$  cal/mole deg at the triple point, to  $9.08$  at slightly over  $600^\circ$  and to zero at about  $910^\circ\text{C}$ . The increase in curvature at low temperature is undoubtedly an artifact due to the simple (linear) term introduced in (16) and (17) to correct for derivatives higher than the second. Had a more complex equation been used, the data could undoubtedly have been fitted equally well with an expression which indicated curvature approximately constant at about  $9$  cal/mole deg at the lower temperatures. However, the decrease in curvature at higher temperatures is in no sense an artifact, although the curvature at  $800$ - $850^\circ$  may be slightly greater than indicated by (17). Equation (13) is thermodynamically rigorous except for terms of very high order; equation (14) is also rigorous except for factors similar

\* This largest disagreement is due to inadequacy of the analytical expression, since the data never deviate from a smooth curve by so great an amount.

to the last two in (13). Since the effect of the finite volume of the liquid can be proven negligible, the decrease in curvature can only be due to one of the following causes: the vapor-pressure data are wrong; the specific heat of the liquid has changed by a factor of two in a temperature range of some  $250^{\circ}$ ; or the gas is behaving in a non-ideal fashion.

The first cause is rejected on two grounds in addition to faith in the accuracy of the data: the excellent agreement with the data of Brooks and the fair agreement with the data of Giorgi (see Appendix 2); and the fact that Brooks' data are sufficiently precise to show that the curvature is, in fact, too small, quite independently of the present work\*. The second cause is almost inconceivable, although some small increase might be explained by the breaking of the chains which exist<sup>38</sup> in liquid tellurium near the melting point. We are left with the conclusion that the deviations of tellurium vapor from ideality in the temperature range  $750^{\circ}$  to  $850^{\circ}$  are greater by an order of magnitude than we would have anticipated. It seems very unlikely, as discussed earlier, that these deviations involve dissociation. Their nature is not clear, but they can be summed up by saying that the Van der Waals' constants (or second and higher virial coefficients) are very much larger than we would have expected.

In view of the above, tabulations of heat of vaporization and

\* An experimental error which caused the observed vapor pressures to be too large by an increasing amount at high temperatures would explain the apparent decrease in curvature. Such an experimental error might arise from the presence of a common volatile contaminant in the tellurium in both Brooks' and the present research. However, the only imaginable contaminant,  $\text{TeO}_2$ , has too low a volatility<sup>33</sup> (0.10 mm at  $733^{\circ}\text{C}$ , the triple point; 0.33 mm at  $780^{\circ}$ ; 1.70 mm at  $855^{\circ}$ ).



extrapolation to the boiling point are both dangerous. Extrapolation of (17) to 760 mm yields a boiling point of 993.6°C. Although this extrapolation goes through an inflection point, the curvature in this region is so small that linear extrapolation of the experimental data from 725° to 855° yields a boiling point only 1.5° lower. Nevertheless, it seems advisable to assign a probable error of several degrees to this boiling point. As for the heat of vaporization, this is commonly computed from (13) by ignoring the last two factors--i.e.,  $\Delta H = -R d \ln p/d (1/T)$ --but it is clear that this will give values of  $\Delta H$  which are too high at high temperatures if  $d \ln p/d (1/T)$  is computed from (17). It therefore seems safest to state that  $\Delta H$  is computed from (17) to be 28,384 cal/mole at 875°K, that  $d \Delta H/dT$  is about -9 cal/mole deg, and then assign a probable error of several hundred cal/mole to the resulting values.

By cross plotting, pressure may be plotted against composition for various temperatures, as in Fig. 12. The extrapolation to low temperatures is made from the plot of  $\log P$ , which is almost linear. Although the curves in the liquid-solution region (high Te concentrations) are drawn through a very small number of points, they are believed to be reliable, as discussed in Sec. 4.E., in connection with Fig. 16. The dotted line in Fig. 12a is a Raoult's law line for NiTe<sub>2</sub> dissolved in Te, for 760°C. Each of the other curves falls below the corresponding Raoult's law curve by about the same percentage. The conclusion is that these solutions deviate negatively from Raoult's law--or to state the same thing differently, each nickel atom is solvated by slightly more than two tellurium atoms of which two (or slightly less) are closely bound.

The partial molal free energy, as computed from Equation (6), is tabulated in Table IV and plotted in Fig. 13 as a function of temperature. The slopes of these curves may be read from this graph, and are also tabulated in Table IV; they are the partial molal entropies. The data in this table and graph apply in each case to two gram-atoms of tellurium passing from liquid tellurium to nickel telluride (or a solution of nickel in tellurium) at the same temperature.

Equations of the form of (15) have been fitted to the data for the dissociation pressures of the nickel tellurides, for convenience in interpolation. The appropriate constants are:

Composition	Temperature, °C	A	B	C
NiTe <sub>1.7</sub>	600-780	18,044.8	65.28115	15.51935
NiTe <sub>1.9</sub>	712.5	41,584.3	268.7524	75.20797
NiTe <sub>1.9</sub>	713-780	27,487.55	190.08879	53.70914
NiTe <sub>2.0</sub>	675-780			
NiTe <sub>2.0</sub>	600-700	12,168.46	65.01199	17.12047
NiTe <sub>9</sub>	600-682			
NiTe <sub>9</sub>	682	12,541.2	59.48815	15.13609

The two-phase region has been fitted by two equations, neither of which has particular theoretical significance, for convenience.

The slopes of all the above equations are equal to the heats of vaporization or dissociation ( $\Delta H = 4.580A - 1.987CT$ ), or, if one prefers, to the partial molal enthalpy of tellurium in the appropriate nickel telluride. However, this partial molal quantity refers to gaseous tellurium, and is therefore not strictly comparable to the partial molal entropies and free energies tabulated above.

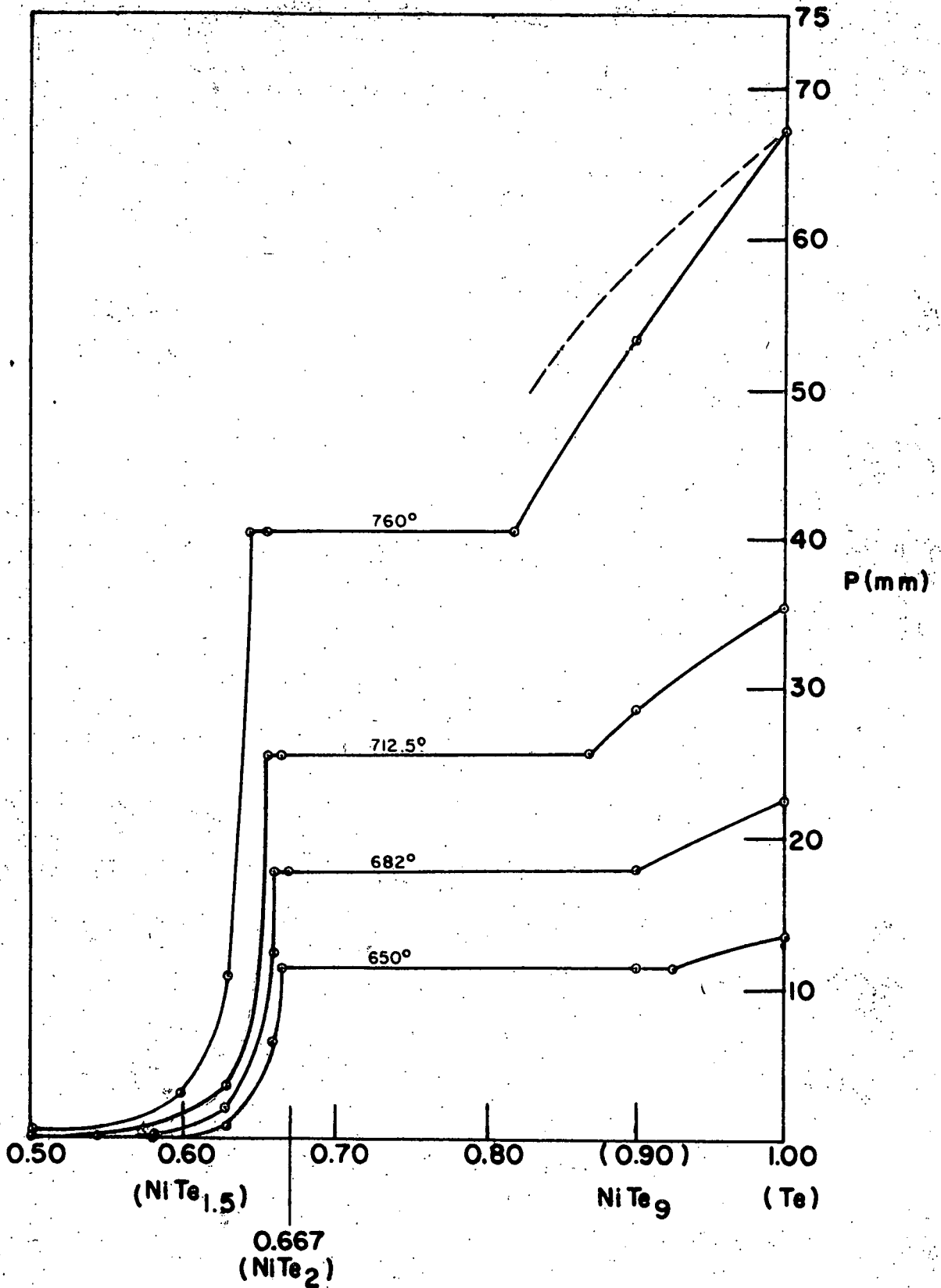


FIGURE 12a

DISSOCIATION PRESSURE OF NICKEL TELLURIDES, AS FUNCTION OF COMPOSITION

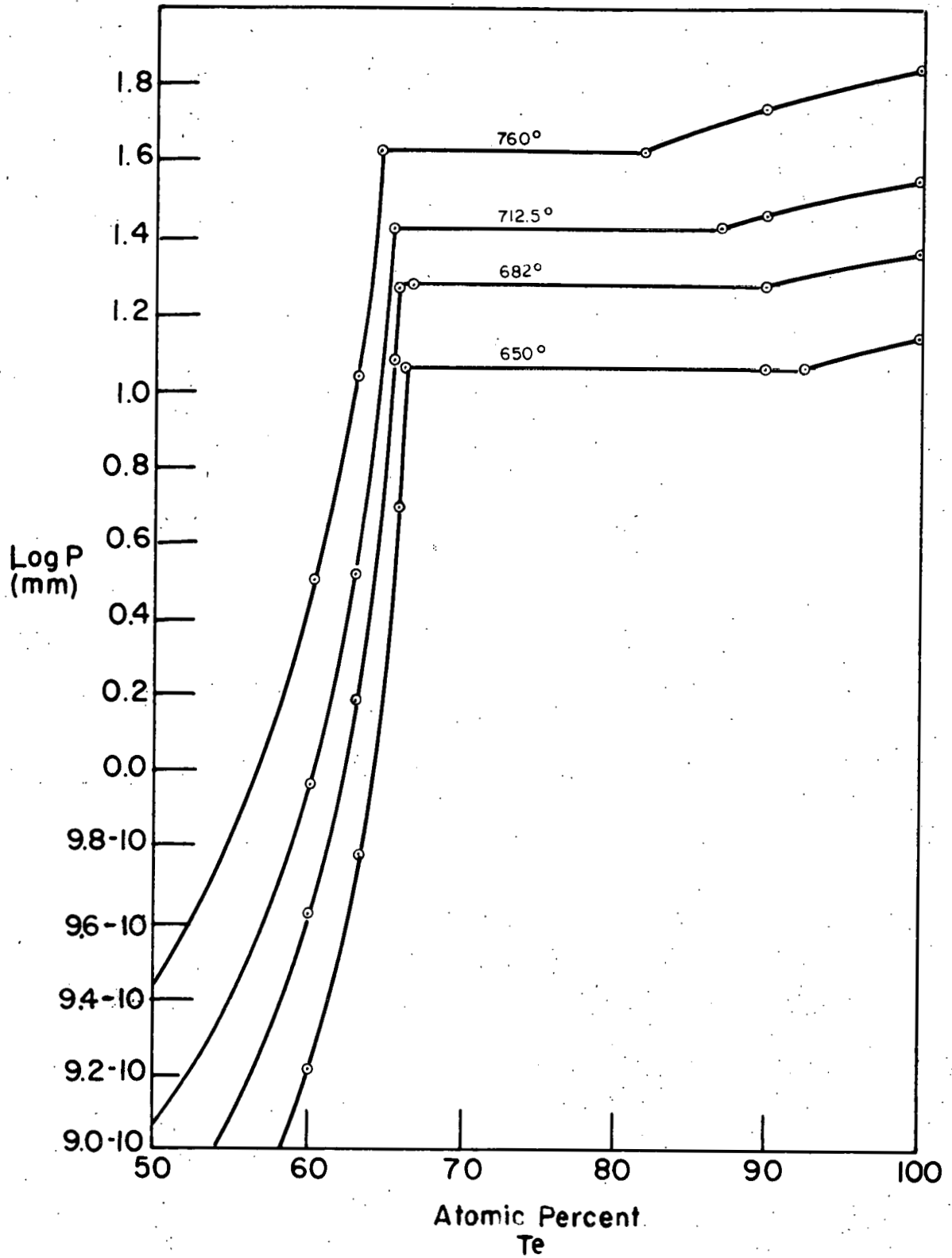


FIGURE 12b 215 103

DISSOCIATION PRESSURE OF NICKEL TELLURIDES, AS FUNCTION OF COMPOSITION

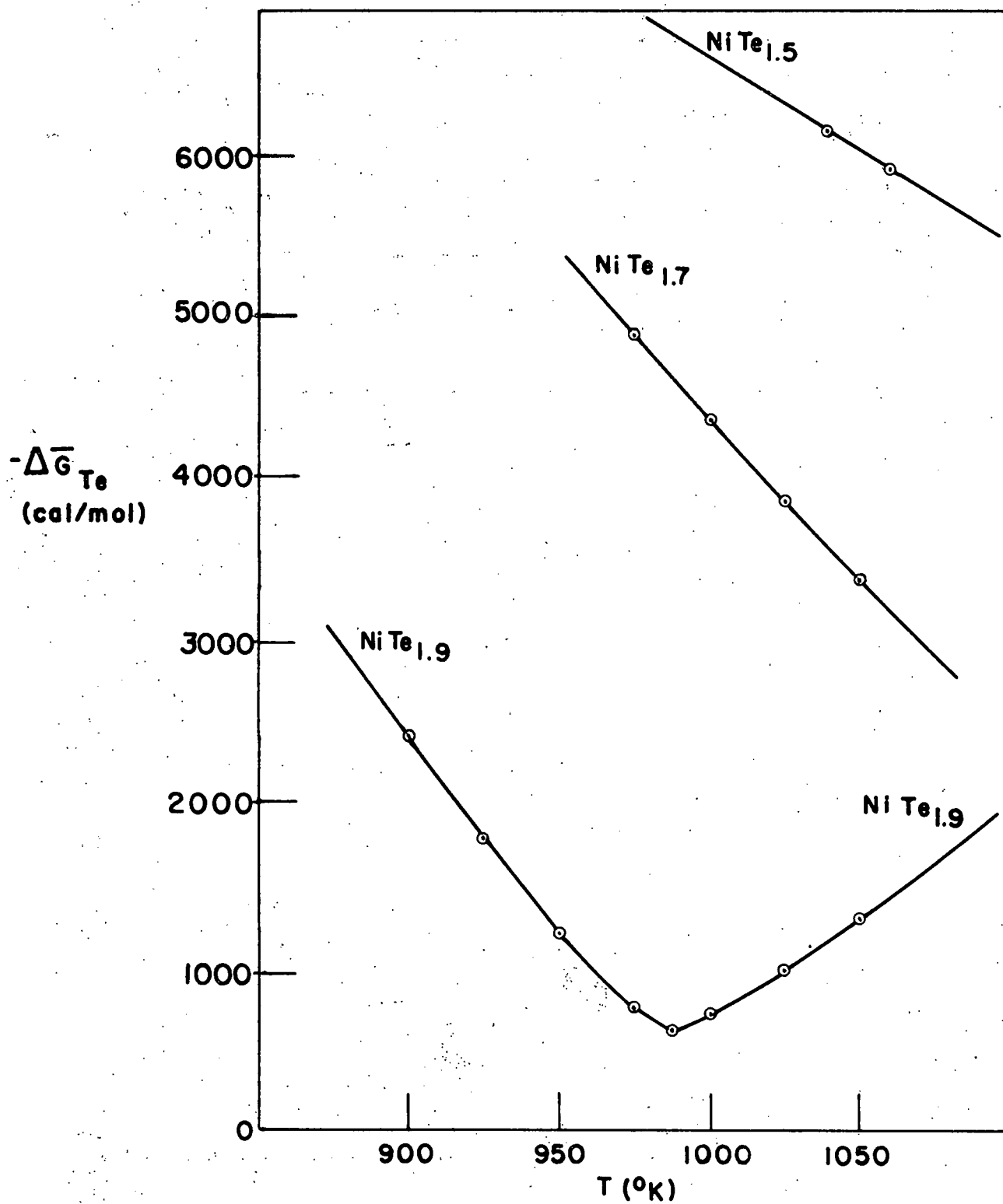


FIGURE 13a

PARTIAL MOLAL FREE ENERGY OF TELLURIUM IN NICKEL TELLURIDES

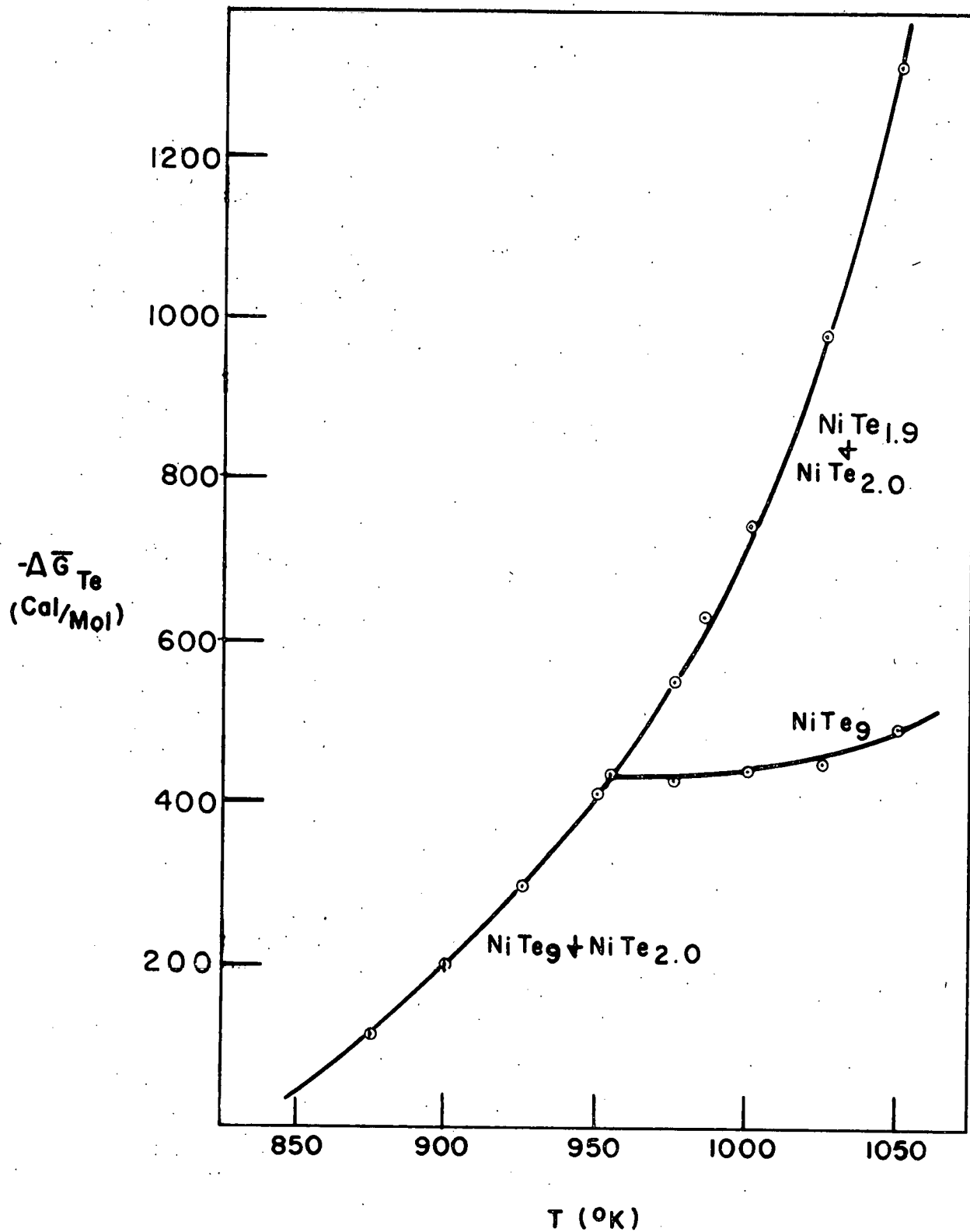


FIGURE 13b

215 105

PARTIAL MOLAL FREE ENERGY OF TELLURIUM IN NICKEL TELLURIDES

Table IV

Partial Molal Entropy and Free Energy of Te in  $\text{NiTe}_x$

COMPOSITION	TEMPERATURE, °K	$\Delta \bar{G}_{\text{Te}}$ , cal/mole <sup>-1</sup>	$\Delta \bar{S}_{\text{Te}}$ , cal/mole <sup>-1</sup> deg <sup>-1</sup>
$\text{NiTe}_{1.5}$	1040	6175	
	1060	5935	
$\text{NiTe}_{1.7}$	975	4898	-20.8
	1000	4378	-20.2
	1025	3874	-19.8
	1050	3400	-18.9
$\text{NiTe}_{1.9}$	900	2375	-24.1
	925	1803	-22.4
	950	1259	-20.7
	975	782.7	-16.9
	985.6	630.7	
	1000	748.3	8.50
	1025	982.4	11.0
	1050	1318	14.7
$\text{NiTe}_{2.0}$	875	115.3	2.85
	900	200.9	3.78
	925	301.2	4.36
	950	415.8	4.94
	955.1	437.7	
	975	553.1	6.30
	985.6	630.7	
	1000	748.3	8.53
	1025	982.7	11.0
	1050	1318	14.7
$\text{NiTe}_9$	875	115.3	2.85
	900	200.9	3.78
	925	301.2	4.36
	950	414.2	4.94
	975	435.2	0.070
	1000	445.5	0.378
	1025	453.4	0.995
	1050	492.3	1.85

#### IV. OTHER EXPERIMENTAL WORK

##### 4.A. HEAT OF FORMATION

The heat of formation of stoichiometric NiTe was measured many years ago<sup>40</sup> by dissolving nickel, tellurium, and nickel telluride in a mixture of bromine and water and measuring the heats of solution. The present research was carried only to the point of showing that the same method would be applicable to the compounds here considered, and some preliminary experimental design.

If finely divided and continually shaken, small amounts of nickel tellurides will dissolve completely in dilute HCl saturated with bromine in a few minutes at room temperature. Increasing the temperature did not appear to help, perhaps because of loss of bromine through volatilization. Excess bromine also appeared not to help; the problem may have been one of dissolving the tellurium bromides formed. These problems would probably have been soluble, although the corrosive and volatile nature of bromine would have necessitated care.

The usual method of performing heat of formation experiments is to make separate measurements on the heat of solution of each element and each of the compounds. It would appear to be more accurate, however, to make the measurements on the compound and on the appropriate mixture of elements, so that the final solutions would be identical and no corrections would be required for heats of dilution and the like. This would require some additional measurements if one were to run a series of compounds such as the nickel tellurides.

Unfortunately, the heat of solution<sup>40</sup> is about ten times the heat of reaction, so that one must determine the heat of reaction by the difference between large numbers. The heat of reaction then further



becomes one of two large numbers (the other is the free energy of reaction) whose difference is computed to determine the entropy desired. An unsophisticated error analysis showed that heat of solution would have to be determined to about  $\pm 0.01\%$  accuracy, which seemed forbiddingly difficult, and the work was therefore dropped.

#### 4.B. TRIPLE-POINT TEMPERATURE OF TELLURIUM

Interest was directed to the melting point of tellurium for two reasons: the desire to draw the phase diagram of nickel and tellurium; and the desire to extrapolate the vapor pressure of tellurium to the triple point. Accurate data were available<sup>41</sup> on the vapor pressure of solid tellurium from 320° to 410°C, and it seemed that this data could be confidently extrapolated to 450°, the triple point, to provide a point on the curve of liquid vapor pressure. An examination of the literature (Table V) showed extraordinary disagreement on this value. Furthermore, two recent publications<sup>38,42</sup>, both based on measurements of extremely pure tellurium, gave values which were 7° apart. There seemed to be no reason why this figure could not be tied down once and for all within a few tenths of a degree at most, except for the fact that tellurium tends to supercool and it is therefore very difficult to obtain a freezing point\*.

\* In private communication Prof. Lark-Horovitz asserted that the supercooling made it impossible to obtain an accurate freezing point. His value<sup>38</sup> is based on discontinuities in electrical properties at the melting point.

TABLE V

MELTING POINT OF TELLURIUM

<u>Author</u>	<u>Year</u>	<u>M. P.</u>
Pictet <sup>44</sup>	1879	525
Carnelley and Carleton-Williams <sup>43</sup>	1880	452,455
Töpler <sup>45</sup>	1894	420
Matthey <sup>46</sup>	1901	450
Fay and Gillson <sup>47</sup>	1902	446
Mönkemeyer <sup>48</sup>	1905	428
Pellini and Vio <sup>49</sup>	1906	450
Chikashige <sup>50</sup>	1907	438
Pélabon <sup>51</sup>	1909	452
Biltz and Mecklenburg <sup>52</sup>	1909	455
Kobayashi <sup>53</sup>	1910	437
Jaeger and Menke <sup>54</sup>	1912	452½
Damiens <sup>55</sup>	1922	453
Umino <sup>22</sup>	1926	446
Kraus and Glass <sup>57</sup>	1929	451.1
Simek and Stehlik <sup>58</sup>	1930	452.0
Kracek <sup>59</sup>	1941	449.8±0.2
Weidel <sup>42</sup>	1954	452
Epstein, et al. <sup>38</sup>	1957	445
This Research	-	449.5±0.3

The melting point of tellurium was determined in the same way that the melting point of zinc was determined. A small silica thermocouple well was sealed axially into a 15-mm silica tube, as shown in Fig. 14. Since the pure tellurium which was available (semiconductor grade, 99.9994% pure, from American Smelting and Refining Co.) was in large pieces, and it seemed undesirable to grind it, it was melted into the melting-point tube. For this purpose a 15 mm silica tube more than two feet long was sealed to the top of the melting-point tube, as shown in Fig. 14, and then was connected to a high-vacuum line with Apiezon W black wax. After a good vacuum had been obtained and the silica had been flamed to outgas it, the tellurium was melted and ran down into the melting-point tube. It was then boiled vigorously (to the appearance of the green color of tellurium vapor) to eliminate possible volatile contaminants\*, and sealed off. It was then placed in the furnace.

The melting point was first determined approximately by rapid heating, and then redetermined more slowly. Melting occurred over a period of 30 minutes, and over a temperature range which increased irregularly from 449.4 to 449.7°. The furnace was then cooled to 447° and held there, with occasional shaking, until crystallization commenced, which required a little more than an hour. The sample temperature rose to 449.5° and remained there for 20 minutes, after which it fell again to the furnace temperature.

Most of the discrepancies indicated in Table V can be explained. Many of the measurements were semiquantitative (Carnelley and Carleton-

\* See footnote, page 63

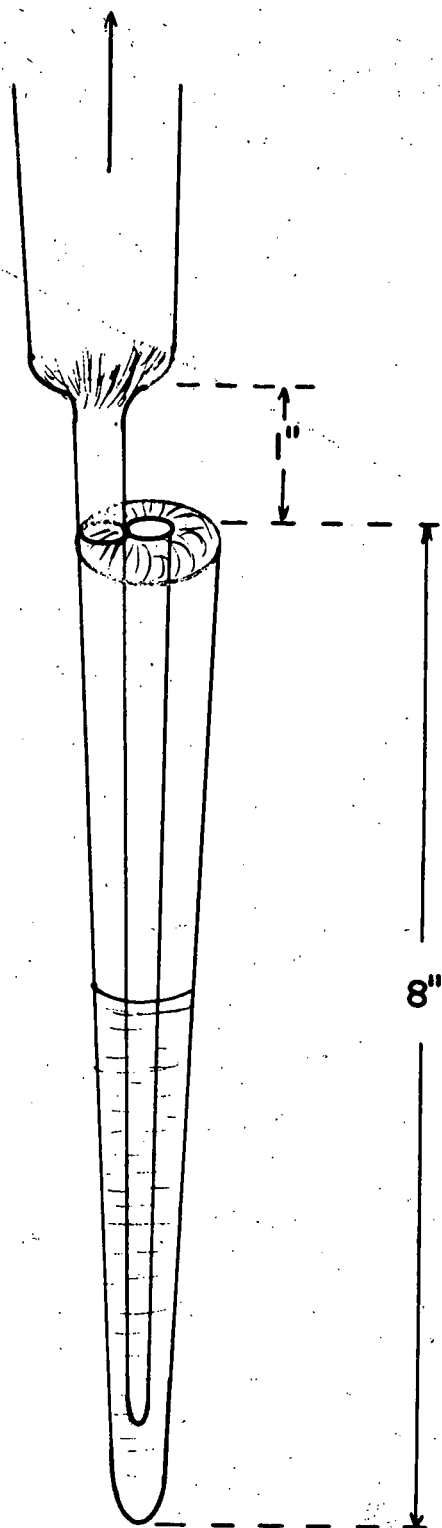


FIGURE 14

TELLURIUM MELTING POINT APPARATUS

Williams<sup>43</sup>, for example, were fortunate to get within 10° of the correct melting point by the method they adopted). Impurities may have played a part in some of the low values, but most of these were probably due to supercooling, and to the fact that the investigators were measuring the melting point of tellurium incidentally to thermal analysis designed to elucidate the phase diagram of binary systems containing tellurium; in fact, several of the references mark the observed value as "start of crystallization". In other cases no indication is given as to how the temperature scale was established; if one uses an unannealed and uncalibrated Pt vs Pt-Rh thermocouple, one can easily be off by several degrees (the thermocouples used in the early part of this research had a correction of almost 4° at 450°). This is probably the explanation of Epstein's error, since it is difficult to believe that 99.999999% tellurium has a melting point 4° lower than 99.999% tellurium, or that a gross discontinuity in electrical properties would appear 4° below the melting point and the properties would then be continuous at the melting point.

Of the remaining entries in Table V, three<sup>46,49,59</sup> agree with this result. One<sup>57</sup> disagrees by 1.6° and cannot be explained. Jaeger and Menke<sup>54</sup> apparently had serious temperature measurement errors which are discussed in detail by a subsequent investigator of the same binary system<sup>55</sup>. The work of Šimek and Stehlik<sup>58</sup> was very careful, and their relative temperatures must be considered accurate. Thus, their conclusion that hydrogen and carbon dioxide lower the melting point 0.15° and 0.20° respectively per atmosphere of pressure should probably be accepted. Fortunately, however, the journal in which they reported allowed them space to describe the thermocouple calibration in detail.

This makes it possible to notice (as Kracek<sup>59</sup> has also remarked) that their operation of their sulfur boiler was almost certainly in error, and when the sulfur-point calibration is ignored and the corrections made only for their calibrations at the zinc and antimony points, their result is in good agreement with the present one.

The work of Kracek<sup>59</sup> appears to be the most accurate of all. Since his result of  $449.8^{\circ}$  is perhaps more reliable than the present result of  $449.5^{\circ}$ , one might accept as the "best" value  $449.7^{\circ}$ .

#### 4.C. TRANSITION IN SOLID TELLURIUM

A transition in solid tellurium at  $350^{\circ}\text{C}$  was reported<sup>22</sup> many years ago, on the basis of apparent discrepancies in drop calorimetry results. This result was not adequately supported in the first place, has not been noted in more recent calorimetry<sup>23</sup>, and its absence was noted in the measurement of the melting point of tellurium<sup>58</sup> and in the vapor pressure of solid tellurium<sup>41</sup>. No evidence of it has appeared in the careful electrical measurements<sup>38</sup> made by a number of recent investigators. It was therefore reasonably certain that this transition did not exist, but it seemed worth while to prove it, using the apparatus described above. For this purpose, the sample was taken from the melting point down to  $300^{\circ}$  and back up to  $400^{\circ}$  very slowly, taking readings on the thermocouples at time intervals corresponding to not more than  $0.3^{\circ}$ . No evidence of any transition or other anomaly was found.

#### 4.D. QUANTITATIVE ANALYSIS

An attempt was made to analyse a sample of nickel telluride for total content of nickel and tellurium, both to check the composition

and to determine oxygen by difference to see if the sample had become oxidized.

Quantitative analysis for nickel within 0.1% is, of course, easy. Tellurium, however, is more difficult. Most of the procedures reported are designed for determination of tellurium in the presence of selenium. Whether a better method could be found for this situation, where selenium is known to be absent, is not known. A routine method<sup>60</sup> was used, in which the tellurium is reduced to the metallic state with sulfur dioxide and weighed as metal. The results were invariably slightly high (oxidation of tellurium during drying?) and inconsistent, and results accurate to better than about 0.5% could not be achieved. One recent investigator<sup>72</sup> was satisfied with  $\pm 3\%$ , although these analyses were an integral part of his results.

#### 4.E. PHASE RELATIONS

At the start of this research, nothing was known about the tellurium-rich region of the nickel/tellurium phase diagram except that the melting point of tellurium was about  $450^\circ$  (see above); that the solid solutions underwent some sort of melting phenomena<sup>3</sup> at about  $900^\circ$ ; and that the boundary between the solid solution region and the two-phase region (solid solution plus solid tellurium, with possibly a little nickel dissolved in the tellurium) lay very close<sup>2</sup> to the stoichiometric composition  $\text{NiTe}_2$  at  $450^\circ$ , and probably at all temperatures below that, since phase changes or recrystallization appeared not to take place<sup>2</sup> in reasonable times at lower temperatures.

It was necessary to know something about the phase diagram in order to choose wisely the compositions on which vapor pressure measurements should be made. Unfortunately it was also necessary to know something

about the phase diagram in order to investigate the phase diagram, and the experiments described here were foredoomed to failure because they were based on false conjectures as to the nature of that diagram.

The first experiments were cooling curves. Some nickel telluride was sealed in vacuo into a silica ampule provided with a reentrant well for a thermocouple. It was then heated to  $900^{\circ}$  in a furnace in a beaker full of insulator, then removed and allowed to cool in air. The initial cooling was very fast, and by the time all the connections were made, the first reading was taken at about  $700^{\circ}$ . It is now known that nothing interesting happens below this temperature except at compositions between  $\text{NiTe}_{1.91}$  and  $\text{NiTe}_{1.99}$ , compositions which were not measured, other than the freezing of the tellurium.

In the first experiment on the vapor pressure of  $\text{NiTe}_{2.0}$ , it was noted that the vapor pressure of this substance was less than that of pure tellurium at all temperatures high enough for the vapor pressure to be measureable; however, when the apparatus was cooled and removed from the furnace, a few minute crystals of tellurium were found adhering to the silica a few millimeters above the sample. These crystals were analysed by x-ray diffraction and found to be pure tellurium. This indicated that at some temperature above about  $400^{\circ}$  (below which the tellurium would distill too slowly) and below about  $500^{\circ}$  (above which the vapor pressure was demonstrably lower than that of pure tellurium),  $\text{NiTe}_{2.0}$  was in the two-phase region. It was falsely assumed that the lowered vapor pressure of  $\text{NiTe}_{2.0}$  as compared with pure tellurium indicated that at higher temperatures



this composition was in the solid-solution region, and that the phase diagram looked like Fig. 15a.

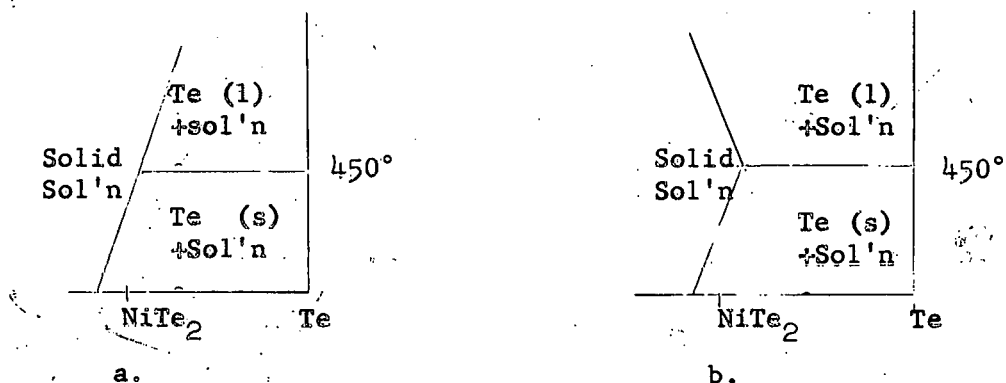


FIGURE 15

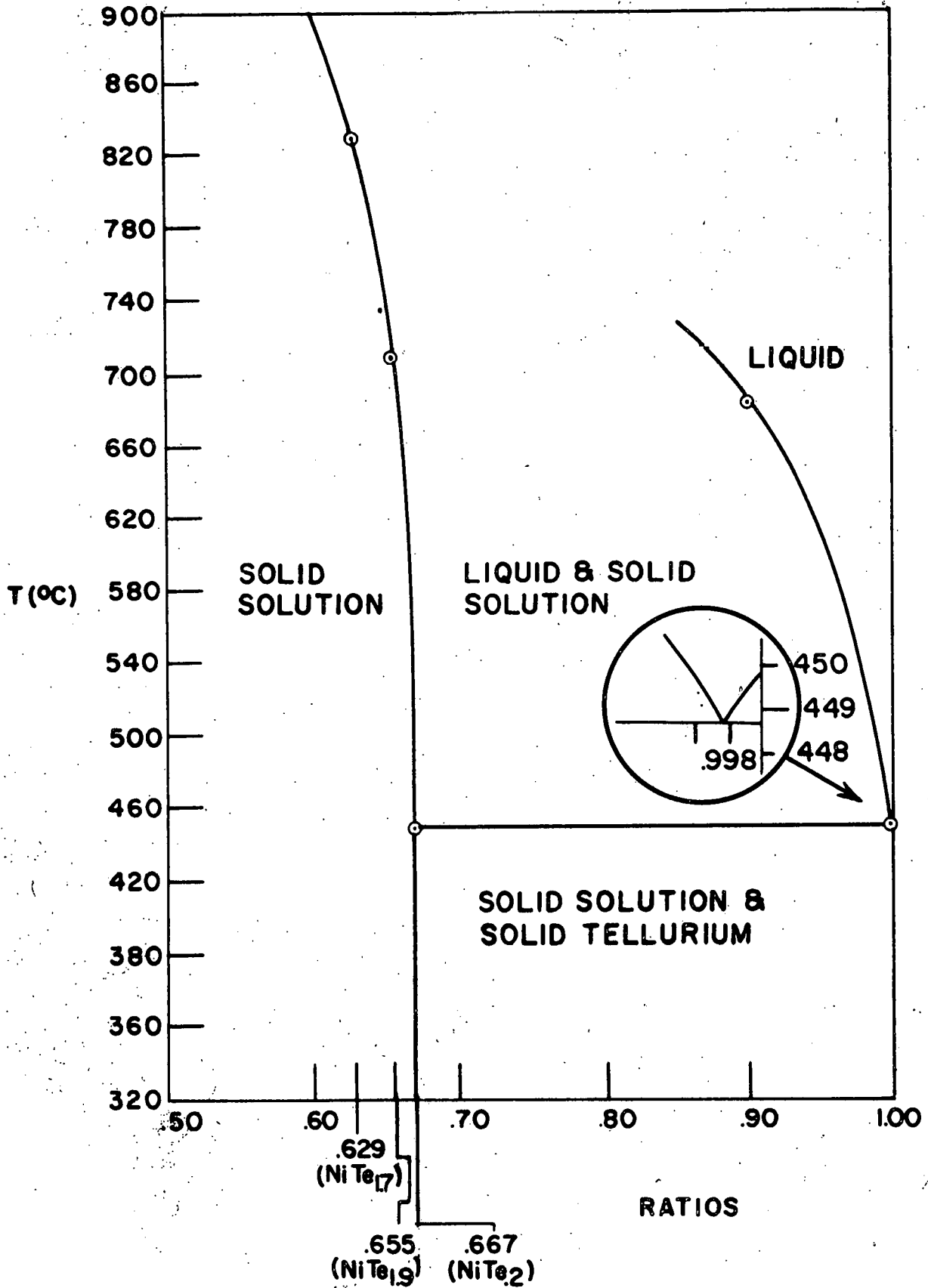
HYPOTHETICAL PHASE DIAGRAMS (EXAGGERATED)

To confirm this, the region from NiTe<sub>2.0</sub> to NiTe<sub>2.3</sub> was investigated by x-ray analysis. Samples were prepared in evacuated silica ampules, heated to 900°C, and quenched in cold water. The samples were recovered, powdered in a mortar and pestle (which is very difficult because of the mica-like crystalline habit of NiTe<sub>2</sub>), and studied.

For this purpose, pure nickel was necessary. It was prepared from C.P. nickel sulfate by precipitation of the oxalate with pure oxalic acid and freshly prepared ammonia water. The oxalate was washed by decantation, then transferred wet to a silica boat and placed in a Vycor tube where it was decomposed in a stream of dry hydrogen at 250 to 350°. The furnace was then heated to 1000° while the hydrogen (which had been passed through a Deoxo unit to free it of oxygen) was continued, in order to reduce the nickel oxide to

nickel. This nickel was mixed with pure tellurium in the correct stoichiometric proportions. Unfortunately the nickel and tellurium did not react completely within a reasonable time at  $900^{\circ}$ , and so the experiment was repeated, using appropriate mixtures of nickel telluride and tellurium, which did react quickly and completely. Pure tellurium and pure  $\text{NiTe}_{2.0}$  were also analysed by x-ray diffraction. The result of these experiments was that lines of both tellurium and nickel telluride appeared in all samples, including a quenched sample of stoichiometry  $\text{NiTe}_{2.0}$  which was used as a check. It was assumed from these results that the phase diagram was as in Fig. 15b. Actually, the phase diagram is as in Fig. 16, and  $\text{NiTe}_{2.0}$  is in the two-phase region at all temperatures where pressure measurements were made; the reduction in vapor pressure is due to the solubility of nickel in liquid tellurium.

It turned out that the vapor pressure measurements themselves were a powerful tool for investigating the phase diagram, and Fig. 16 was drawn from these measurements. Each of the curves of Fig. 16 has been drawn through only two points. Nonetheless, they are considered quite reliable. These curves were drawn in conjunction with those of Fig. 12, and their reliability is interdependent. Thus, the point on the liquidus curve at 90% tellurium and  $682^{\circ}$  is probably accurate to  $\pm 1^{\circ}$ ; no other point is known except the eutectic. But the vapor pressure of compositions along this curve is known (since this is the vapor pressure measured for both  $\text{NiTe}_2$  and  $\text{NiTe}_9$ ), and the ratio of this vapor pressure to that of pure tellurium indicates that the curve must behave as shown, since this ratio shows approximately the same approximation to Raoult's law at all temperatures. Similarly, the



215 118

FIGURE 16  
PHASE DIAGRAM OF NICKEL AND TELLURIUM

point on the solidus curve at 65.5% tellurium and  $712\frac{1}{2}^{\circ}$  is probably accurate to  $\pm 1^{\circ}$ , and the behavior of the solidus curve between this temperature and the eutectic must be as shown, because the ratio of the vapor pressure of  $\text{NiTe}_{1.9}$  to  $\text{NiTe}_{2.0}$  shows approximately this behavior. The solidus curve point at 62.9% is obtained by extrapolating the  $\log P$  vs.  $1/T$  curves for  $\text{NiTe}_{1.7}$  and for the two-phase region until they intersect. This point is uncertain by perhaps  $10^{\circ}$ .

As shown in the main part of Fig. 16, the solubility of nickel in tellurium at the melting point is zero, but as the inset shows, the phase behavior in this region is not quite degenerate. The melting point of a dilute solution of  $\text{NiTe}_2$  in tellurium was determined exactly as described in Sec. 4.B. 200 mg of  $\text{NiTe}_2$  was added to 18 g of tellurium and the mixture vigorously boiled in vacuum to effect solution. The egress of gas was restricted, so that the pressure increased sufficiently to make the green color of tellurium vapor plainly visible. This represents at least 20 mm of pressure, which corresponds to  $682^{\circ}\text{C}$ , at which temperature the solubility of nickel in tellurium is known to be ten atomic percent; hence the solution should certainly have been saturated after cooling to the melting point. The undissolved  $\text{NiTe}_2$  could be presumed to settle to the bottom, since its density<sup>62</sup> is over 7 and that of tellurium is about 6.

Immediately before taking the melting point, the thermocouple was calibrated by taking the melting point of the tellurium sample described in Sec. 4.B. Thus, the melting point difference may be presumed accurately measured. The eutectic temperature thus found was  $1.0^{\circ}$  lower than the triple point of pure tellurium. The cryoscopic constant of tellurium has been determined<sup>51</sup> to be 520 degrees per mole solute per

100 grams tellurium; hence a freezing-point depression of  $1.0^{\circ}$  corresponds to 0.0025 nickel and 0.9975 tellurium as the atomic fractions of the eutectic composition.

The accuracy of this relative temperature measurement is not in doubt, and it seems very unlikely that sufficient impurity could have been present to affect the eutectic temperature. It is possible, however, that the solution was not saturated, and in this case the true eutectic temperature might be a trifle lower and the true eutectic composition slightly richer in nickel.

#### 4.F. A VAPOR-PRESSURE THERMOMETER

The vapor pressure of  $\text{NiTe}_{2.0}$  is plotted in Fig. 17 as a function of temperature. It can be seen that up to about  $650^{\circ}$  this curve has the familiar quasi-exponential form typical of vapor pressure curves, but that at about  $750^{\circ}$  it inflects. This behavior caused a good deal of worry during this research, and various theoretical attempts were made to explain it, including crossing of phase boundaries, extraordinary corrections to the Clausius-Clapeyron equation, etc. The actual explanation is, of course, simple:  $\text{NiTe}_{2.0}$  is in the two-phase region over the entire temperature range of Fig. 17, and the pressure being measured is that of a saturated solution of nickel in liquid tellurium. As the temperature rises, two opposing tendencies operate on the vapor pressure: the normal effect, expressed in the Clausius-Clapeyron equation, of increasing the pressure; and the effect of dissolving more nonvolatile solute, thereby decreasing the pressure. The point of interest here is that from about  $700^{\circ}$  to  $800^{\circ}$ , pressure and temperature are related almost linearly, with  $dP/dT$  varying between

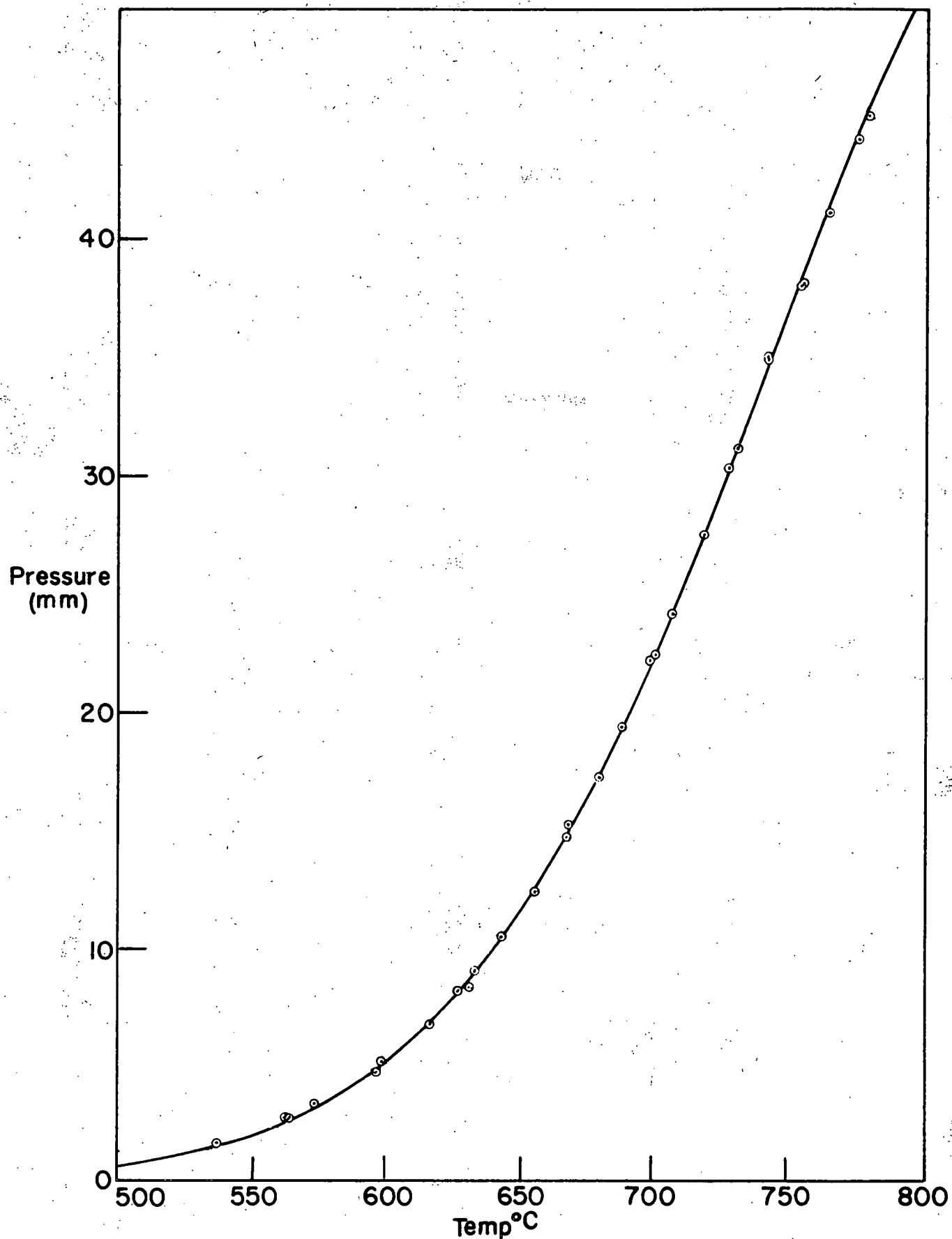


FIGURE 17  
DISSOCIATION PRESSURE OF NICKEL DITELLURIDE

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0.24 mm/degree at the ends of the range and 0.27 in the center.

Vapor pressure has often been used as a property for determining temperature. Several of the fixed points on the international temperature scale are based on the temperature at which the vapor pressure of some pure substance (e.g. oxygen, water, sulfur) reaches 760 mm. This pressure is convenient, but not particularly rational; at this pressure,  $dP/dT$  is high for all substances, but a good deal higher for low-boiling than for high-boiling substances. In fact,  $dP/dT$  is too high for use in a vapor-pressure thermometer, because an increase of a very few degrees takes the pressure beyond the range measurable with the same apparatus. On the other hand, a moderate decrease of temperature makes  $dP/dT$  so small that the vapor pressure is no longer a sensitive measure of temperature. Thus, although vapor-pressure thermometers have been extensively used<sup>18d</sup>, they have been useful only over a very small temperature range.

This situation could be improved by using, instead of a pure substance, a saturated solution with an excess of solute, as represented by  $NiTe_{2.0}$ . The thermometer would consist of an isothermal block, as described herein, with two holes: one for the vapor-pressure apparatus, which would act as the thermometer; and the second for the subject of the experiments. The composition would not have to be accurately known, since vapor pressure is independent of composition in the two-phase region. Such a thermometer would not require calibration in the ordinary sense (since unlike a resistance thermometer or thermocouple, the calibration is not variable from one thermometer to another) although it would of course be desirable to check the thermometer against at least one fixed point.

$\text{NiTe}_2$  would not be particularly valuable for such a thermometer because  $dP/dT$  is too small; if pressure-measuring precision were 0.1 mm, the temperature precision would be only  $0.4^\circ\text{C}$ . However, there seems no reason why other similar mixtures could not be found with greater values of  $dP/dT$ . If, for example, the solubility of nickel in selenium (which is not known) were about the same as that in tellurium, the  $dP/dT$  values would be ample to give a temperature precision of about  $0.02^\circ\text{C}$ . Similarly, if some substance were found which dissolved in tellurium as nickel does, but  $200^\circ$  higher, this also would provide the desired type of  $dP/dT$  relationship over a long temperature range. The same idea seems extensible to low-temperature thermometry (where vapor-pressure thermometers have found their principal use in the past) if nonvolatile (or comparatively nonvolatile) substances can be found which dissolve endothermically in liquefied gases.

The construction of such a thermometer has not proceeded beyond the "gedanken" stage.



## V. SUMMARY AND CONCLUSIONS

The original objective of this research was to gather sufficient data to determine the zero-point entropies of the nickel tellurides as a function of composition. This objective is far from having been reached. Low-temperature heat capacities (to about 350°K) have been obtained on all of the compounds from  $\text{NiTe}_{1.1}$  to  $\text{NiTe}_{2.0}$ , and the corresponding heat capacities on the elements are available. High-temperature heat capacities remain to be run. Partial molal free energies and partial molal entropies of tellurium have been obtained for the tellurium-rich compositions at temperatures from 780°C down to about 600°C, with the accuracy becoming poorer at the lower temperatures. To obtain integral free energies or entropies of reaction requires data on the partial molal free energy of nickel at any one composition and at various temperatures. If and when these data are obtained, with equivalent accuracy, the zero-point entropies can be determined.

As a direct by-product of this work, the dissociation pressures of the nickel tellurides have been determined up to 780°C. In the course of this work the vapor pressure of tellurium was determined, originally as a check on the apparatus. However, these measurements are more accurate than previous measurements on liquid tellurium; they have also been extended to higher temperatures (855°C). Thus the boiling point and heat of vaporization of tellurium are now more accurately known than before (although less precision is claimed for the heat of vaporization than by previous investigators).

The triple-point temperature of tellurium has been redetermined experimentally, and the discordant literature on this subject critically examined. The precision of the result is sufficient to justify the distinction between triple-point temperature and "melting point"; it is also sufficient to justify an additional significant digit in the value of this constant reported in reference books.

The thermodynamics, and by inference some of the chemistry, of the nickel tellurides investigated is now well understood, and in particular the phase diagram from 60% to 100% tellurium is now clear. Because of this understanding it is possible, for example, to state that the conclusions drawn<sup>66</sup> from recent measurements on the electrical properties of these compounds are almost certainly wrong (see Appendix).

Finally, an old method for measurement of vapor pressures at high temperatures has been adapted to the present system, but in addition has been improved and generalized so that it is available over a wide variety of conditions and can achieve greater accuracy than ever before. More than a dozen papers a year are being published on vapor pressures and dissociation pressures in this temperature range; of the recent papers examined, none was comparable in accuracy to the present work, and at least one was less accurate by a factor of 1000.

## APPENDIX

### Critical Discussion of Literature

1. Nickel Telluride Nickel telluride was first prepared by Fabre<sup>40</sup> seventy years ago by reacting the elements at high temperature. He reported that he had produced the stoichiometric compound NiTe, but it now seems possible that the stoichiometry may not have been perfect. He measured the heat of solution of the compound in bromine water, and from these results the heat of formation<sup>56</sup> can be calculated.

During the early 20th century, nickel tellurides were prepared twice<sup>61,67</sup> by wet methods (from nickel salts such as sulfate, and sodium or hydrogen telluride). Both authors reported that the product was Ni<sub>2</sub>Te<sub>3</sub> (or in the notation of this document, NiTe<sub>1.5</sub>), and that on heating in vacuo it yielded NiTe, but they may have been expecting stoichiometric compounds. Thus, the mineral mellonite, which consists of nonstoichiometric nickel telluride of apparently variable proportions, has been frequently reported to have one or another precise stoichiometry.

The heat capacity of stoichiometric nickel telluride was measured at several temperatures by drop calorimetry by Tilden<sup>17</sup>, at about the turn of the century. As mentioned at the beginning of Sec. 2, Tilden was apparently a very careful experimenter, and both the stoichiometry and thermal data are probably trustworthy.

The crystal structure of NiTe was elucidated<sup>4</sup> in 1927, but the crystal structure of NiTe<sub>2</sub>, the continuous transition, and the resulting interest of the system was not discovered until 1938<sup>1</sup>. Shortly

thereafter, Klemm<sup>62</sup> made detailed measurements on the entire series of compounds by means of x-ray diffraction, pycnometry, and magnetic susceptibility. In the light of later work<sup>2</sup>, and as also indicated by the irregularities of the data, these results must be considered as having only qualitative value, although Klemm is usually a careful experimenter.

Over the next several years there was only one experimental paper, namely a short series of magnetic measurements<sup>65</sup> on the stoichiometric compound NiTe. There were also some theoretical papers, such as those of Ehrlich<sup>64</sup> and Klemm<sup>63</sup>, in which the transition chalcogenides were examined as a whole, and in which the continuous transition in the nickel tellurides (and to some extent in others of these compounds) was discussed. Insofar as these applied to the nickel tellurides, they were based on Klemm's partly invalid data<sup>62</sup>.

Within the past two years, quantitative measurements extending over wide ranges of stoichiometry have been undertaken by a least five groups of investigators in as many countries, and with the exception of the collaboration of Grönvold with this endeavour, they have been entirely independent.

The Japanese work<sup>3</sup> consists of an extensive series of magnetic measurements over the entire composition range from nickel to tellurium and over the temperature range from -200 to over 900°C. Unfortunately, measurements were made only on certain prechosen compositions, so that the complex phase behavior<sup>2</sup> in the neighborhood of NiTe<sub>0.7</sub> was missed entirely, as was the phase behavior, of more interest to this investigation, in the tellurium-rich region of the diagram. They did observe a phenomenon which they attributed to "melting" at about 900° in the region from NiTe<sub>1.5</sub> to NiTe<sub>2.0</sub>, but it is not possible to locate these

points within  $100^\circ$  from the data they present, and it is not clear whether they are reporting liquidus or solidus lines, or a mixture of the two. The work, which was received a few months after this investigation was started, was particularly useful in indicating the lack of any transitions in the region of this investigation; it is likely that second-order transitions, if present, would be picked up by careful magnetic studies.

The Russian work<sup>66</sup> concerns measurements of thermal and electrical conductivity and thermoelectric potential at room temperature for compositions ranging from below  $\text{NiTe}_{1.0}$  to above  $\text{NiTe}_{2.0}$ . There are also cryptic references to other work, such as a mention of the heat capacity of  $\text{NiTe}_2$ . This work is suspect for a number of reasons. The curves which are drawn do not in fact pass through the points which are supposed to support them. Furthermore, the data show nicely symmetrical peaks at both  $\text{NiTe}$  and  $\text{NiTe}_2$ . Yet from our present understanding of the phase behavior (which was presumably not available to these authors) the phase break on the nickel-rich side is much closer to  $\text{NiTe}_{1.1}$  than  $\text{NiTe}_{1.0}$ , and it should be nonsymmetric, since there is a two-phase region on one side and a one-phase region on the other. Similarly, there is a two-phase region on one side of  $\text{NiTe}_{2.0}$  and a one-phase region on the other, so that the peak should be nonsymmetric. Finally, the evidence from very careful work on other comparable compounds (for example, the bismuth tellurides<sup>69</sup>) supports the fact, which is also indicated on theoretical grounds, that the type of phenomena which they report--that is, extrema in thermoelectric potential and electrical conductivity at stoichiometric composition--should be related to composition changes away from "intrinsic" which

are smaller by several orders of magnitude than those which they have reported. Pending subsequent confirmation, therefore, this paper should probably be considered useful only in giving qualitative indications. Thus, the knowledge that the electrical resistance is approximately  $10^{-4}$  ohm cm for these nickel tellurides is valuable in assessing their nature.

The Austrian work<sup>68</sup> is a careful roentgenographic analysis, over the composition range NiTe to NiTe<sub>2</sub>, and from room temperature to 800°. This work is particularly useful in supplementing the work of Barstad and Grønvoid at higher temperatures.

The Norwegian work<sup>2</sup> is a very precise set of measurements covering the entire composition range from nickel to tellurium at room temperature, with some measurements at other temperatures; careful crystallographic studies have been made by x-ray diffraction, and there are also some magnetic measurements. This work has not yet been published, but most of the results were made available to the author.

2. Vapor Pressure of Tellurium The vapor pressure of liquid tellurium was first measured by Doolan and Partington<sup>24</sup>, and subsequently by Schneider and Schupp<sup>25</sup>, by the transport method; this method involves passing a known quantity of inert gas over the sample, which is held at known and constant temperature, and measuring the quantity of vaporized material which is transported away from the sample. The method is subject to a number of systematic errors, and the pressures of Doolan and Partington are consistently low, while those of Schneider and Schupp are consistently high. Within each the scatter of the data is less than the systematic errors, and each gives a straight line in the plot of log P vs. 1/T.

A very accurate series of measurements was made by Brooks<sup>26</sup> a few years ago, using a method very similar to that used in this research-- in fact, his method was basically copied at the start of this research. The principal source of error in his measurements was due to shifts in the null position of the pointers, which were considerably greater in Brooks' work than in the present work. The scatter of Brooks' data is several times as great as in the present work, and so Brooks did not detect the slight curvature in the  $\log P$  vs.  $1/T$  plot, and fitted his data with a linear analytic expression. Brooks' pressures are slightly higher than those of the present measurements, but this difference is small--certainly within his error and possibly within the error of the present experiments. Thus, his extrapolation to 760 mm pressure gives as the boiling point  $989.8^{\circ}\text{C} \pm 3.8^{\circ}$ , while the present data (extrapolated over a slightly shorter range) give  $992^{\circ} \pm 1^{\circ}$  for linear extrapolation (see Sec. 3.H.2.).

A very recent series of measurements<sup>72</sup> has not yet been published. It measures the vapor density directly, by radioactive tracer methods, and the vapor pressure is computed on the assumptions that the gas is diatomic and perfect. The scatter of the results is somewhat greater than that of Brooks, and the pressures are consistently slightly higher. The author also checked the number of atoms per tellurium molecule. He states that "the values were all slightly higher than 2.00, indicating a possible constant error...probably associated with the analytical determination of the tellurium..." (see Sec. 4.D.).

A very clever, and apparently accurate, series of measurements was made some years ago in Japan<sup>41</sup> on the vapor pressure of solid tellurium from  $320^{\circ}$  to  $410^{\circ}$  by effusion methods. Two distinct methods

were used simultaneously. One measured the loss of weight in the sample boat due to effusion, while the other measured the reactive force (by means of a torsion balance). One of these methods requires knowledge of the molecular weight to effect the calculation, while the other does not; conversely, having computed the vapor pressure from one set of data, the molecular weight can be computed from the other. This was the basic purpose of the experiment--to determine the number of atoms in the tellurium vapor molecule--and the conclusions from this experiment were that the number is  $2.00 \pm 0.05$ . The pressure data are remarkably self-consistent; in fact, they are too consistent, since the pressures are given only to two significant digits, but the linearity of the  $\log P$  vs.  $1/T$  plot is considerably better. For example, at  $330^\circ\text{C}$  the pressure is 0.0014 mm, and at  $399.5^\circ\text{C}$  it is 0.030 mm. All of the temperatures are at, or almost at,  $10^\circ$  intervals, in this fashion. Furthermore, although the experiments check each other, there were some common parameters in the two which could have introduced common systematic errors. However, these results appear to be the best available for obtaining (by extrapolation) the triple-point pressure, which is a useful point since it effectively extends the vapor pressure measurements downward an extra  $100^\circ$  or more. Using the formula  $\log P = -7691.552/T + 9.912$ , and  $T = 722.8^\circ\text{K}$  as the triple-point temperature yields  $p = 0.187$  mm as the triple-point pressure. But the curve should be concave downward (due to decrease in heat of vaporization with increase of temperature--see Sec. 3.H.2), and a curvilinear extrapolation yields about 0.17 mm, the exact extrapolation being somewhat doubtful because of the precise linearity of the data reported.



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THERMODYNAMIC PROPERTIES OF NONSTOICHIOMETRIC NICKEL  
TELLURIDES AND OF TELLURIUM

By Robert E. Machol

ABSTRACT

The system nickel/tellurium is of interest because of the continuous and homogeneous transition between  $\text{NiTe}$  and  $\text{NiTe}_2$ , which have different crystal structures. As part of a thermodynamic study of these compounds, an attempt was made to gather data which would determine zero-point entropies as a function of composition. Part of the necessary data have been gathered, and in addition a number of other pertinent or interesting properties of the nickel tellurides, and of tellurium, have been investigated.

Specific heats from  $4^\circ$  to  $350^\circ$  K have been measured on  $\text{NiTe}_{1.1}$ ,  $\text{NiTe}_{1.5}$ , and  $\text{NiTe}_{2.0}$ , and the thermodynamic functions of these and all intermediate compositions may be considered accurately known over this temperature range. The method employed was conventional precise adiabatic calorimetry in an existing apparatus.

The melting point of tellurium has been redetermined and the highly discordant literature critically reexamined; the triple point may now be stated with some confidence to be  $449.7^\circ \pm 0.2^\circ\text{C}$ .

The dissociation pressures of compositions from  $\text{NiTe}_{1.5}$  to  $\text{NiTe}_{2.0}$  have been accurately measured at temperatures up to  $780^\circ\text{C}$  in order to determine the partial molal free energies and entropies of tellurium in these compounds. These measurements have incidentally

elucidated the phase behaviour in the tellurium-rich region, showing a high solubility of nickel in liquid tellurium at elevated temperatures, and incongruent melting of the solid solutions such that tellurium-rich solid solutions are unstable at elevated temperatures.

To obtain these measurements, an old method of measuring vapor pressures at high temperatures--namely the use of a silica bourdon gage--has been modified and improved, so that it is capable of very high accuracy (0.1 mm Hg and 0.1°C) over a wide range of conditions and up to at least 855°C and probably much higher. Improvements consisted of methods of effectively outgassing the apparatus, of purifying the sample, of making the pointers visible so that accuracy and consistency of pressure measurements were possible, and of ensuring homogeneity and accuracy of measurement of sample temperature.

The vapor pressure of tellurium was measured originally to check out the apparatus. The final results were more accurate than those of previous investigators, and sufficiently precise to require the use of a four-parameter equation. The results are represented by

$$\log P = -10,663.14/T + 64.73140 - 18.61687 \log T + 0.00341783 T$$

where P is in mm Hg and T is in degrees Kelvin. Theoretical study of the data has indicated that deviations from ideality of tellurium vapor appear at a much lower pressure than one would predict from the behavior of more familiar gases. Since this cannot be due to molecular dissociation, it must mean that the van der Waals' constants (or second and higher virial coefficients) are unusually high. By extrapolation, the boiling point of tellurium is computed to be  $993.6 \pm 2^\circ\text{C}$ , and the heat

of vaporization to be 33,850 - 908 t cal/mole (one mole equals two gram-atoms), with an accuracy of plus or minus several hundred calories, from the triple point to  $t = 850^\circ$ , or perhaps  $950^\circ\text{C}$ . This figure may be considered more accurate, though stated with less precision, than those of previous investigators.