It can thus be seen that the lattice energies of rhenium carbides, silicides and germanides decrease regularly with decreasing electronegativity and increasing size of the group IV elements. The irregular trend in the standard heats of formation is caused by the unusually high stability of the graphite lattice. Other transition metal silicides should also have more negative standard heats of formation than the corresponding carbides even though the silicide lattice energies will always be less than those of the corresponding carbides. The transition metal germanides should in general be somewhat less stable than the corresponding silicides.

**Reactivity of $ReGe_2$.**—The reactivity of $ReGe_2$ toward common reagents was tested by adding approximately 10-mg. samples of $ReGe_2$ to 2 ml. of each reagent in a test-tube. The mixtures were observed after 15 minutes and again after 24 hours. At the end of this period the mixtures were heated for about 5 minutes at the boiling point and the results observed. Reagents tested were HCl (both concentrated and dilute), HI (concd.), $H_2SO_4$ (concd. and dil.), $HNO_3$ (concd and dil.), $H_3PO_4$ (85%), $HClO_4$ (68%), $KMnO_4$ (0.1 *N*), $H_2O_2$ (30%. cold only), NaOH (5%), fused NaOH and fused $Na_2CO_3$. Only hot concentrated $H_2SO_4$ and fused NaOH attacked the germanide.

LAFAYETTE, INDIANA

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[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

# Coefficients of Thermal Expansion of Solids at Low Temperatures. I. The Thermal Expansion of Copper from 15 to 300°K.

BY THOR RUBIN, HOWARD W. ALTMAN AND HERRICK L. JOHNSTON

RECEIVED MAY 22, 1954

An apparatus for measuring the thermal expansion of solids over the temperature range 15–300°K. by a differential method making use of a Fizeau interferometer is described. Experimental data for copper are presented and are applied to the Grüneisen relations.

## Introduction

Two general methods are in use for determining the thermal expansion of solids: (a) direct measurement of elongation of a sample by mechanical or optical means; (b) X-ray determination of thermal changes in crystal lattice constants. The two methods are not always in agreement.[1] Disagreements have been attributed to a difference between the lattice expansion, which measures correctly the over-all expansion in single crystals or in separate crystallites, and the over-all expansion of polycrystalline solids, which may involve reorientation of crystallites or other physical changes that affect the spacings between them. Most investigations of thermal expansion have measured total, or integral, expansions over large temperature intervals rather than differential coefficients for small intervals of temperature.

We have designed an improved apparatus that will determine accurate values of differential coefficients of thermal expansion over small temperature intervals in the range from 15 to 80°K., where the coefficients are changing rapidly. This range of temperature has never been explored before by a differential method.

In the present investigation, the expansions of polycrystalline copper (OFHC) and of single crystal copper were measured from 20 to 300°K., by a technique that employs the Fizeau interferometer.[2,3]

The present interferometer consists of two optical plates, whose plane surfaces are held apart by samples of the material to be measured—in this instance, small copper pillars, machined and polished until their lengths are equal within a half wave length of the light used (sodium D radiation).

When the plates are viewed by a telescope located near the light source, a system of concentric rings appears at the focal plane. Uniformity in ring diameter throughout the field of view indicates that the plates are held parallel by samples of equal length. As the temperature of the interferometer is raised, and the samples are correspondingly lengthened for positive expansion, the rings expand. When the increase in separation of the optical planes corresponds to one half-wave length of the monochromatic radiation, an inner ring will have increased in diameter to the previous value of its encircling neighbor. By making a count of the number of rings that pass a fiducial point, such as a cross hair located on a radius of the system of concentric circles, the distention of the sample is accurately measured.

When these data are correlated with the temperature change of the specimen, the coefficient of thermal expansion is calculated for the mean temperature.

**Apparatus and Experimental Technique.**—Figure 1 is a diagram of our apparatus, which is constructed somewhat after the manner of the vacuum calorimeters in use in this Laboratory.[4] A brass cryostat vessel, fitted with leveling screws, encloses a 9.5-in. o.d. Pyrex dewar which contains the refrigerant, liquid nitrogen or liquid hydrogen, whose temperatures may be reduced by evacuation of the cryostat. The main body of the apparatus is suspended from the cryostat lid by a 1-in. o.d. nickel tube (F), which also admits the light beam to the optical plates. This tube and the space within the brass container (E) and the lead-filled copper blocks (B) and (D) are highly evacuated through (J) to provide good thermal insulation to the vacuum-tight copper pipet (C) that encloses the interferometer. The purpose of the blocks (A, B and D) is to shield the pipet

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[1] Wm. Hume-Rothery, *Proc. Phys. Soc.* (*London*), **57**, 209 (1945).

[2] H. L. Fizeau, *Ann. chim. phys.*, [4] **2**, 143 (1864); *ibid.*, **7**, 335 (1866).

[3] R. M. Buffington and W. M. Latimer, THIS JOURNAL, **48**, 2305 (1926).

[4] H. L. Johnston and E. C. Kerr, *ibid.*, **72**, 4783 (1950).

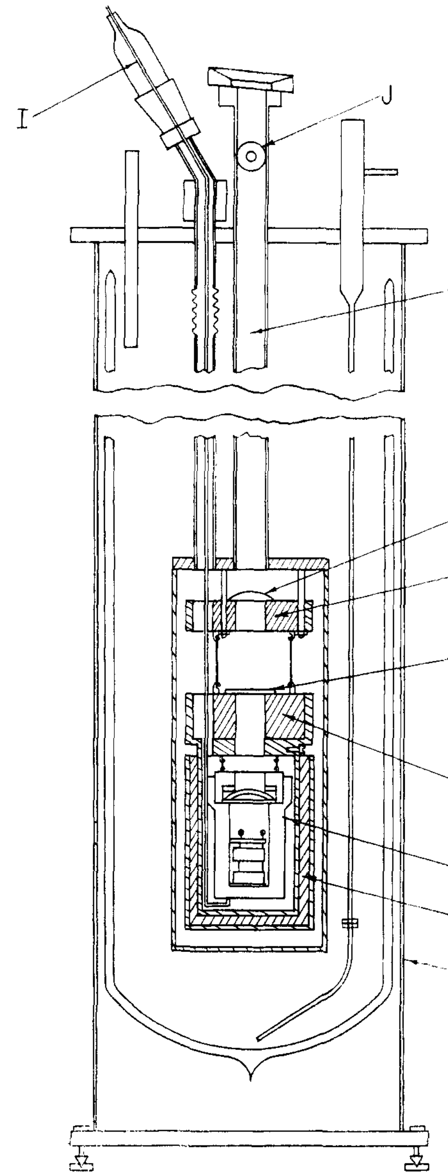

Fig. 1.—Apparatus for measuring thermal expansion of solids.

from both thermal radiation from the container walls and heat leak down the electrical leads and the helium filling tube (I). A heat filter (K) made from Corning glass No. 4084 is placed in thermal contact with block B to minimize heat radiation flowing down the tube F. These blocks possess sufficient heat capacity to hold the temperature of the pipet constant for several hours, and are provided with copper constantan thermocouples and with insulated No. 30 B. and S. gage manganin wire heaters for regulation and control of temperature. The pipet is also provided with a thermocouple and is wrapped with double nylon-covered No. 40 B. and S. gage gold wire (containing 0.15% silver), which serves as a combination resistance thermometer and heater. Good thermal contact between the gold wire and the pipet wall is provided by application of G.E. 7031 adhesive, air-dried.

The upper end of the pipet (C) is closed by a vacuum-tight window that admits sodium light to the pipet. This window, which follows the design of Collins[5] for a window that will withstand high pressures, is illustrated in Fig. 2. A stainless steel band, C, supports the full load of an oval spring, G, that is compressed by the nut, H. This band, wider than either recess, pushes into V-shaped recesses cut into both of the circular Teflon gaskets, B and E. When the spring is tightened, gasket B presses tightly against the periphery of the window A, while gasket E expands into a recess cut into the body of the copper pipet. D is a recessed ring which distributes the force exerted by the spring on the gasket assembly, and F is part of the wall section of the pipet.

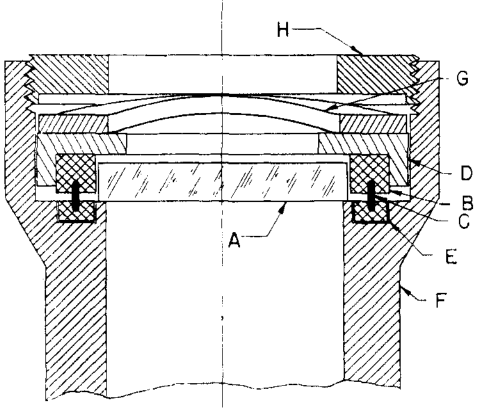

Fig. 2.—Gasket assembly of interferometer pipet.

Helium, introduced to a few millimeters of pressure through the thin-walled inconel tube (1 of Fig. 1), serves to establish thermal contact between the interferometer and the copper walls of the pipet.

The absolute temperature of the pipet wall was measured by means of a standard copper–constantan thermocouple calibrated to the Temperature Scale of the Ohio State Cryogenic Laboratory,[6] and accurate in an absolute sense to within 0.03° at all temperatures between 20 and 300°K. Temperature differences that are significant in determining the differential coefficients of thermal expansion were determined from the readings of the gold resistance thermometer and are precise to within 0.005°.

**Samples and Experimental Procedure.**—The polycrystalline copper samples were cut from a large bar of oxygen-free, high-conductivity (OFHC) copper, obtained from the American Brass Company. The single-crystal copper samples were cut from a small rod of single-crystal copper obtained from the General Electric Company. Light etching of the single-crystal samples after their use in the apparatus gave no evidence of a polycrystalline phase.[7]

The diameters of the inner three rings are determined as a function of time while the interferometer cell is held at a known temperature, constant to within 0.005°, for one hour at a time. When at least three successive sets of ring-diameter measurements agree, the interferometer pipet is assumed to be at temperature equilibrium. Electrical energy is then added to the pipet, by use of the resistance thermometer winding and block heaters, until the pipet and block temperatures rise several degrees. The temperature increments are made about 10% of the absolute temperature of the pipet. The pipet is again brought to constant temperature by slight readjustment of the block temperatures, and the first three ring diameters are again measured.

The number of fringes that pass a fiducial mark in going from the lower to the higher temperature is noted. Each of these corresponds to distension of the sample by a half-wave length of the light employed. In addition, the diameter of the ring nearest the fiducial mark at the higher temperature is carefully determined and is compared with the diameter of the ring nearest this point at the lower temperature. This permits interpolation to a fractional fringe and hence to the fractional part of the half-wave length. This interpolation is based on the fundamental equation of interferometry

$$2dN \cos \theta = n\lambda \tag{1}$$

in which $d$ is the separation of the optical plates; $N$, the refractive index of the gas between the plates, which may be

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(5) G. R. Collins, *Phys. Rev.*, **39**, 305 (1930).

(6) T. Rubin, H. W. Altman and H. L. Johnston, This Journal, **73**, 3401 (1951).

(7) J. O. Lord, private communication.

taken as unity for very low pressures of helium; $\theta$ is the angle of incidence; a constant, $\lambda$, the wave length of incident light—5896 × $10^{-8}$ cm. for the sodium D lines, and $n$, the order number of the interference ring.

From this equation, one can derive the relationship

$$r^2_{j+1} - r^2_j = D \qquad (2)$$

where $r_j$ is the radius of the jth interference ring, numbered from the inside, and $D$ is the optic constant that depends on the distance between the plates, the distance between the interferometer and the telescope, and the wave length of incident light. Our data (Tables I and II) indicate that values of $D$ were reproducible to within 1% for a fixed alignment of the apparatus.

One can likewise derive the analogous equation

$$(r^2_f - r^2_i)/D = \Delta \qquad (3)$$

in which $r_f$ is the radius of the ring nearest to the fiducial mark at the higher temperature, $r_i$ is the radius of the nearest ring on the same side of the fiducial mark at the lower temperature, and $\Delta$ is the fractional part of a half-wave length through which the plates must be moved to expand or contract an interference ring from the radial value $r_i$ to $r_f$.

We were able to evaluate $\Delta$ with sufficient accuracy, by this interpolation method, to determine the "number of fringes" to within 0.01 fringe per degree.

TABLE I

COEFFICIENTS OF THERMAL EXPANSION OF OFHC POLYCRYSTALLINE COPPER; $l_0$ = 0.4948 ± 0.0005 cm.

| Run no. | $\Delta T$, deg. | $T_{av.}$, °K. | Optic constant $D$ | $r_i^2$ | $r_f^2$ | Interpolated no. of fringes | $\alpha$ × $10^5$ |
|---|---|---|---|---|---|---|---|
| 14 | 8.592 | 25.25 | 21.4 | 27.563 | 29.376 | 0.085 | 0.055 |
| 15 | 9.968 | 34.53 | 21.4 | 29.367 | 34.928 | .260 | .158 |
| 16 | 7.972 | 43.49 | 21.4 | 34.928 | 42.902 | .373 | .278 |
| 17 | 8.131 | 51.55 | 21.4 | 42.902 | 33.524 | .562 | .412 |
| 18 | 9.542 | 60.38 | 21.3 | 33.524 | 31.360 | .894 | .558 |
| 19 | 8.655 | 69.48 | 21.3 | 31.360 | 31.472 | 1.005 | .692 |
| 20 | 11.674 | 79.65 | 21.3 | 31.472 | 44.890 | 1.630 | .832 |
| 1 | 8.015 | 85.67 | 21.3 | 32.376 | 37.210 | 1.227 | .912 |
| 21 | 9.035 | 90.00 | 21.4 | 44.890 | 32.604 | 1.426 | .940 |
| 2 | 10.158 | 94.75 | 21.3 | 37.210 | 30.914 | 1.705 | 1.000 |
| 3 | 11.201 | 105.43 | 21.3 | 30.914 | 32.149 | 2.058 | 1.095 |
| 4 | 11.590 | 116.82 | 21.3 | 32.149 | 38.812 | 2.310 | 1.187 |
| 5 | 13.400 | 129.32 | 21.3 | 38.812 | 35.046 | 2.817 | 1.253 |
| 6 | 12.129 | 142.08 | 21.3 | 35.046 | 28.944 | 2.714 | 1.333 |
| 7 | 14.191 | 153.70 | 21.4 | 21.068 | 27.457 | 3.298 | 1.385 |
| 8 | 17.194 | 169.40 | 21.4 | 27.457 | 30.580 | 4.146 | 1.437 |
| 9 | 18.253 | 187.12 | 21.4 | 30.580 | 42.510 | 4.557 | 1.488 |
| 10 | 21.732 | 207.11 | 21.4 | 42.510 | 34.105 | 5.607 | 1.537 |
| 11 | 23.662 | 229.81 | 21.4 | 34.105 | 39.313 | 6.243 | 1.572 |
| 12 | 28.003 | 255.64 | 21.4 | 39.313 | 30.692 | 7.597 | 1.616 |
| 13 | 32.003 | 285.64 | 21.4 | 30.692 | 28.944 | 8.918 | 1.660 |

TABLE II

COEFFICIENTS OF THERMAL EXPANSION OF SINGLE-CRYSTAL COPPER; $l_0$ = 0.4953 ± 0.0005 cm.

| Run no. | $\Delta T$, deg. | $T_{av.}$, °K. | Optic constant $D$ | $r_i^2$ | $r_f^2$ | Interpolated no. of fringes | $\alpha$ × $10^5$ |
|---|---|---|---|---|---|---|---|
| 2 | 7.181 | 24.25 | 18.45 | 47.265 | 48.581 | 0.071 | 0.059 |
| 3 | 8.651 | 32.16 | 18.45 | 48.581 | 51.840 | .177 | .122 |
| 4 | 9.437 | 41.21 | 18.45 | 51.840 | 40.768 | .400 | .252 |
| 5 | 10.119 | 51.03 | 18.45 | 40.768 | 53.363 | .683 | .402 |
| 6 | 11.656 | 61.95 | 18.30 | 35.046 | 37.761 | 1.148 | .586 |
| 7 | 11.027 | 73.29 | 18.47 | 37.761 | 44.890 | 1.381 | .745 |
| 1 | 7.433 | 81.35 | 19.00 | 42.575 | 43.560 | 1.052 | .842 |
| 8 | 17.243 | 89.49 | 17.7 | 48.233 | 43.494 | 2.732 | .943 |
| 9 | 11.699 | 103.96 | 17.7 | 43.494 | 45.900 | 2.136 | 1.087 |
| 10 | 19.558 | 119.59 | 17.6 | 45.900 | 44.488 | 3.920 | 1.193 |
| 11 | 25.143 | 141.94 | 17.6 | 44.488 | 37.515 | 5.604 | 1.326 |
| 13 | 24.041 | 166.55 | 17.6 | 37.515 | 50.339 | 5.729 | 1.418 |
| 12 | 29.345 | 169.18 | 17.6 | 37.515 | 38.875 | 7.077 | 1.435 |
| 14 | 21.601 | 189.39 | 17.7 | 50.339 | 40.259 | 5.431 | 1.496 |
| 15 | 19.665 | 210.02 | 17.7 | 40.259 | 41.860 | 5.095 | 1.542 |
| 16 | 19.968 | 229.86 | 17.7 | 41.860 | 47.265 | 5.305 | 1.581 |
| 17 | 29.678 | 254.66 | 17.7 | 47.265 | 48.442 | 8.066 | 1.618 |
| 18 | 29.678 | 284.34 | 17.7 | 48.442 | 53.802 | 8.303 | 1.665 |

## Experimental Results

Our experimental results for OFHC polycrystalline copper and for single-crystal copper are presented in Tables I and II, respectively. The columns give in order: run number; temperature interval (from the sensitive resistance thermometer); average run temperature (from the standard thermocouple); optic constant $D$; diameters, in arbitrary units that match those used to compute $D$, of rings nearest the fiducial mark at initial and final temperatures (used to interpolate to the fractional part of a fringe); the interpolated number of fringes; and the computed values of the linear differential coefficient of thermal expansion (actually, mean values for corresponding $\Delta T$ intervals). The interpolated number of fringes was obtained by adding to the number that crossed the fiducial mark the algebraic difference $(r_f^2 - r_i^2)/D$, in accordance with equation 3.

Abrupt changes in the optic constant between runs 1 and 2 (Table II) and runs 7 and 8 (Table II) were owing to alterations in the apparatus. The apparatus was not altered during the series of runs with OFHC polycrystalline copper (Table I).

The values of $\alpha$ given in Tables I and II are shown graphically in Fig. 3.

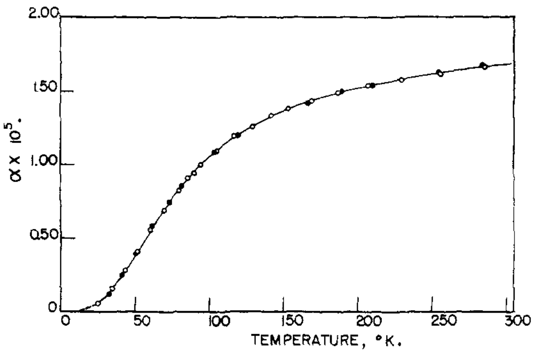

Fig. 3.—Coefficient of thermal expansion of copper: ●, single crystal copper, this research; ○, OFHC polycrystalline copper, this research.

**Experimental Accuracy.**—As is evident from the tables, computed values of $D$ are constant so that deviations are only 0.005 of a fringe order (equivalent to 1.5 × $10^{-7}$ cm. in the length of the specimen) and express the precision with which we were able to measure changes in the length. Temperature increments are accurate to within 0.005°, although the absolute temperature values of the mean temperatures may be in error 0.03°.

Errors in $\alpha$ range, therefore, from about 7% at 25°K. through about 1% at 50°K. and 0.5% at 100°K. to about 0.3% above 200°K. The accuracy is limited at all temperatures by ability to measure differences in fringe diameters rather than by limitations of temperature scale.

**Comparison with Work of Other Investigators.**—Differential coefficients of expansion and integral coefficients of expansion of copper have been measured by several investigators. Table III is a comparison of our own interpolated values of the differential coefficients with those obtained by

Buffington and Latimer,[8] by Dorsey[9] and by Borelius and Johansson.[10]

Table III

Comparative Values for Differential Coefficients of Thermal Expansion of Copper

| Temp., °K. | $\alpha \times 10^5$<br>This research | Buffington and Latimer | Dorsey | Borelius and Johanssen |
|---|---|---|---|---|
| 25 | 0.058 | ... | ... | ... |
| 40 | .232 | ... | ... | ... |
| 60 | .554 | ... | ... | ... |
| 80 | .833 | ... | ... | ... |
| 100 | 1.050 | ... | ... | ... |
| 103 | 1.079 | ... | 1.039 | 1.03 |
| 120 | 1.204 | 1.203 | ... | ... |
| 123 | 1.227 | ... | 1.206 | ... |
| 133 | 1.285 | ... | ... | 1.275 |
| 140 | 1.315 | 1.290 | ... | ... |
| 143 | 1.325 | ... | 1.305 | ... |
| 160 | 1.403 | 1.384 | ... | ... |
| 163 | 1.410 | ... | 1.437 | ... |
| 173 | 1.444 | ... | ... | 1.435 |
| 180 | 1.468 | 1.459 | ... | ... |
| 183 | 1.476 | ... | 1.468 | ... |
| 200 | 1.519 | 1.513 | ... | ... |
| 203 | 1.525 | ... | 1.500 | ... |
| 213 | 1.546 | ... | ... | 1.51 |
| 220 | 1.559 | 1.538 | ... | ... |
| 223 | 1.567 | ... | 1.595 | ... |
| 233 | 1.584 | ... | ... | 1.53 |
| 240 | 1.596 | 1.564 | ... | ... |
| 243 | 1.602 | ... | 1.610 | ... |
| 260 | 1.629 | 1.606 | ... | ... |
| 263 | 1.633 | ... | 1.613 | ... |
| 280 | 1.657 | 1.648 | ... | ... |
| 283 | 1.658 | ... | 1.635 | ... |
| 295 | 1.667 | 1.679 | ... | ... |

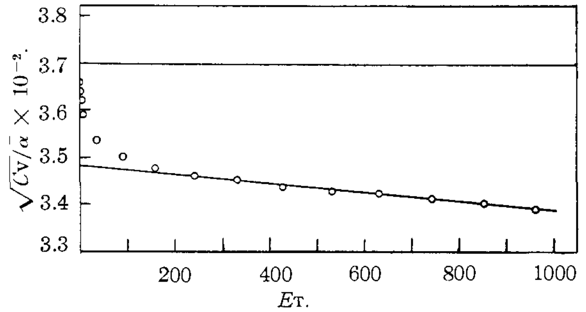

Fig. 4.—Square root of the Grüneisen ratio *vs.* internal energy.

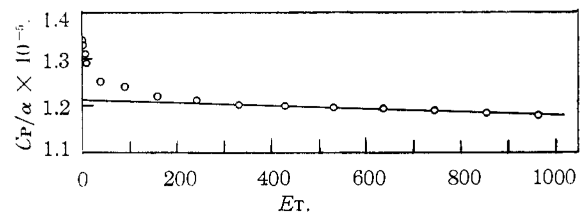

Fig. 5.—Reciprocal of the Grüneisen ratio *vs.* internal energy.

Nix and MacNair[11] measured integral expansions between 0° and various lower temperatures. Their results are given in Table IV and compared with corresponding values computed from our own data by integration of the curve formed by plotting our own differential coefficients against $T$.

Table IV

Comparative Values of $\Delta l/l_0$ for Copper

| Temp., °K. | $-\Delta l_2/l_0 \times 10^4$<br>This research | Nix and MacNair | Temp., °K. | $-\Delta l_2/l_0 \times 10^4$<br>This research | Nix and MacNair |
|---|---|---|---|---|---|
| 20 | 29.301 | .... | 150.2 | 18.838 | 18.761 |
| 40 | 29.076 | .... | 172.7 | 15.672 | 15.677 |
| 60 | 28.296 | .... | 193.0 | 12.677 | 12.644 |
| 80 | .... | .... | 213.0 | 9.627 | 9.535 |
| 87.7 | 26.219 | 25.956 | 233.7 | 6.385 | 6.425 |
| 104.7 | 24.498 | 24.415 | 252.9 | 3.310 | 3.34 |
| 126.2 | 21.977 | 21.840 | 273.2 | 0.000 | 0.00 |

Integral coefficients for special temperature intervals have also been measured by Adenstedt[12] (down to 84°K.), by Keesom, Van Agt and Jansen[13] (down to 23°K.), and by Simon and Bergmann.[14]

We agree with Adenstedt to within 0.3 of 1% but are about 1.5% higher than Keesom, Van Agt and Jansen and several percentage lower than Simon and Bergmann.

Some lack of agreement may be owing to chemical or physical differences in the samples employed by different investigators—such as differences in oxygen content, crystal orientation or physical strain. Nix and MacNair state that their copper had an oxygen content of 0.02% but the other investigators do not specify purity. In our own work we found no detectable difference between single-crystal copper and polycrystalline copper that was oxygen free.

**Application to the Grüneisen Relationships.**—Grüneisen[15] gives two relationships

$$3\alpha/C_v = 1/Q[1 - (R/Q)E_T]^2 \qquad (4)$$

$$3\alpha/C_p = 1/(Q - 2RE_T) \qquad (5)$$

where $Q$ and $R$ are constants and $E_T$ is equal to the integral

$$\int_0^T C_v \mathrm{d}T$$

By using our data for $\alpha$ and calculated data for copper, we plotted equations 4 and 5 and Figs. 4 and 5. It is apparent from the figures that the Grüneisen relationships hold quite well for copper down to values of $E_T$ equal to about 200 cal., a point which corresponds to about 110°K.

Extrapolation of the straight line portion of our Fig. 5 gives $Q = 1.21 \times 10^5$ and $R = 1.75$, which is in very good agreement with Hume-Rothery[1] values, $Q = 1.17 \times 10^5$ cal./g. atom and $R = 2.63$ as values of the parameters in equation 5.

Nix and MacNair[11] report $Q = 1.2 \times 10^{-5}$ and $R = 2.8$ for the parameters in equation 4, whereas the straight line portion of our Fig. 4 yields $Q = 1.21 \times 10^{-5}$ and $R = 3.38$, and indicates that

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[8] R. M. Buffington and W. M. Latimer, ref. 3.

[9] H. Dorsey, *Phys. Rev.*, **25**, 88 (1907).

[10] G. Borelius and C. H. Johansson, *Ann. Physik*, **75**, 23 (1924).

[11] F. C. Nix and D. MacNair, *Phys. Rev.*, **60**, 597 (1941).

[12] H. Adenstedt, *Ann. Phys.*, **26**, 69 (1936).

[13] W. H. Keesom, F. P. G. A. J. Van Agt and A. F. S. Jansen, *Commun. Phys. Lab. Univ. Leiden*, **182A**, 3 (1926).

[14] F. Simon and R. Bergmann, *Z. physik. Chem.*, **B8**, 255 (1930).

[15] E. Grüneisen, *Ber., physik. Ges.*, 426, 491, 836 (1911).

equations 4 and 5 hold between 110 and 1000°K.

**Acknowledgments.**—It is a pleasure to acknowledge the help of Prof. J. O. Lord, who examined the single-crystal copper sample, and of L. E. Cox, Cryogenic Laboratory Shop Foreman, who made helpful suggestions in the design of the vacuum-tight glass window.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

# The Preparation and Some of the Properties of Diboron Tetrachloride, $B_2Cl_4$[1]

BY GRANT URRY, THOMAS WARTIK,[1] R. E. MOORE[1] AND H. I. SCHLESINGER

RECEIVED APRIL 22, 1954

The latest procedure for preparing diboron tetrachloride, $B_2Cl_4$, is described as are the physical properties and the chemical behavior of the compound. It absorbs hydrogen rapidly at room temperature, forming diborane and boron trichloride. The chlorine atoms of the compound may be replaced by bromine, by alkoxy and dimethylamino groups, but not by methyl radicals. It forms a dietherate stable in excess ether, and a monoetherate which loses ethyl chloride at room temperature. At low temperatures in ether solution it adds one mole of diborane to form an unstable compound the behavior of which is described. With trimethylamine it forms a stable compound having the molecular formula $[B_2Cl_4 \cdot N(CH_3)_3]_4$. Hydrogenation of diboron tetrachloride by treatment with lithium borohydride or with aluminum borohydride results in the formation of diborane and tetraborane together with smaller amounts of pentaborane ($B_5H_9$), and decaborane. The relative amounts of the boranes obtained depend on the temperature and other conditions under which the reaction is carried out.

In spite of numerous efforts to find more efficient procedures for the preparation of diboron tetrachloride[2] ($B_2Cl_4$), *e.g.*, by the reduction of boron trichloride by metals, metal borides and other reducing agents we have not yet found a method more satisfactory than the electrical discharge procedure described by Wartik, Moore and Schlesinger.[1] We have, however, improved that procedure by making it almost automatic, with the result that 5–10 g. of the desired compound may be produced per week with very little attention, as is described in the Experimental part.

Diboron tetrachloride is a colorless liquid which ignites in air,[3] and which, at temperatures of 0° and above, undergoes partial decomposition into the moderately volatile, crystalline, pale yellow tetraboron tetrachloride, $B_4Cl_4$,[3] a much less volatile, viscous red material, and a white, non-volatile solid. The composition of the red material may be represented by the formula $(BCl_{0.9})_x$, whereas that of the white solid corresponds to the formula $(BCl_{0.6})_y$. In spite of the reproducibility of the analytical data obtained from different samples, it is not certain that the red and the white products were homogeneous. The methods of analysis, as well as the analytical data for and physical properties of diboron tetrachloride itself are recorded in the Experimental section.

The chemical properties of diboron tetrachloride are best discussed under the following headings, although the classification is somewhat arbitrary: reaction with hydrogen, replacement of chlorine by other atoms or groups, hydrogenation and addition reactions. In most cases description of experimental details, yields, analyses and physical properties of the compounds involved are deferred to the Experimental part.

**Reaction with Hydrogen.**—Hydrogen is taken up rapidly at room temperature and below by diboron tetrachloride in the absence of catalysts. If the reaction is carried out with the liquid tetrachloride, a variety of products is obtained, among them boron trichloride, diborane and mixtures of solid materials with viscous liquids. Results are difficult to reproduce under these conditions. It was soon recognized that the difficulty is due to secondary reactions of diborane with unchanged diboron tetrachloride, as described in the section devoted to "addition reactions." If hydrogen and diboron tetrachloride vapor are mixed at room temperature, the reaction proceeds about 80–90% according to the equation

$$3B_2Cl_4 + 3H_2 \longrightarrow 4BCl_3 + B_2H_6 \qquad (1)$$

Traces of hydrogen chloride as well as the presence of small quantities of solid material indicate that secondary reactions of diborane with diboron tetrachloride were not completely prevented by the procedure. Some monochlorodiborane was also present, as must be the case in mixtures of diborane and boron trichloride, but a correction for its presence was applied in calculating the yield.

The reaction might have been considered as an addition reaction since the first step is probably that represented by the equation

$$B_2Cl_4 + H_2 \longrightarrow B_2Cl_4H_2 \qquad (2)$$

Since chlorodiboranes disproportionate almost completely into diborane and boron trichloride unless a considerable excess of boron trichloride is present, the postulated intermediate would be almost com-

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(1) In view of the name, tetraboron tetrachloride, which we have assigned to the compound $B_4Cl_4$ (see footnote 3), the name diboron tetrachloride for $B_2Cl_4$ is considered more appropriate than tetrachlorodiborine, as originally suggested by T. Wartik, R. E. Moore and H. I. Schlesinger, THIS JOURNAL, **71**, 3265 (1949). Since a committee is now considering boron nomenclature, the new compounds herein described are referred to only by formula. Some of the subject matter of this paper is taken from the thesis presented to the Department of Chemistry of the University of Chicago in 1950 by R. E. Moore, in part fulfillment of the requirements for the degree of Doctor of Philosophy. Most of the subject matter is taken from reports submitted to the Office of Naval Research on Contract No. N6ori-20, Task Order 10, Project NR 356-255, during the period July 1, 1948, to January 31, 1954.

(2) First prepared by A. Stock, A. Brandt and H. Fischer, *Ber.*, **58**, 855 (1925).

(3) Although the sample used for the reaction with air had been carefully purified, it is nevertheless possible that its inflammability may have been due to the presence of traces of tetraboron tetrachloride, which seems to react more vigorously with air than does the diboron compound (Grant Urry, Thomas Wartik and H. I. Schlesinger, THIS JOURNAL, **74**, 5809 (1952)).