to a dark tan color. Determination of the loss of weight on heating this product at 300° for 24 hours indicated that the starting material was $7PbO\cdot PbBr_2\cdot 5H_2O$. If either this hydrate or the original T form was further ground in water and allowed to remain in contact with water for 12 hours or more, a light tan voluminous material was produced. The same product was formed by boiling $7PbO\cdot PbBr_2$ (T form) in water. Determination of the loss of weight on heating this hydrate at 300° for 24 hours indicated that the starting material was $7PbO\cdot PbBr_2\cdot 7H_2O$. The interplanar spacing values of the major reflections for the hydrates are given in Table V.

The two hydrates were heated for 24 hours at various temperatures from 125 to 600°. There were no changes in the pattern for $7PbO\cdot PbBr_2\cdot 5H_2O$ below 250°. At this temperature the material was completely dehydrated and a new phase appeared. The $7PbO\cdot PbBr_2\cdot 7H_2O$ lost two molecules of water on heating at 125° and the remainder at 250°, identical patterns being obtained for both hydrates after heating at this temperature. A second phase change was observed at 350° and a third at 475°. The colors noted for these three phases were light brown, dark brown and reddish-brown, respectively. At 500° the low temperature, T form of $7PbO\cdot PbBr_2$ was produced.

Reaction of $7PbO\cdot PbBr_2$ with SiO_2.—It was observed that molten $7PbO\cdot PbBr_2$ reacts with SiO_2 to form a definite compound. This reaction also occurs to a small degree in the solid state at temperatures as low as 550°. The compound has been prepared by heating a mechanical mixture consisting of equimolar amounts of $7PbO\cdot PbBr_2$ (either T or Q forms) and SiO_2 (α quartz) in a magnesia crucible for 30 minutes at 780°. The same compound has been obtained by heating a mechanical mixture of PbO, $PbBr_2$ and SiO_2 in a 7:1:1 mole ratio at the same temperature. This silicate is not produced by heating a mixture of PbO and SiO_2 in a 7:1 mole ratio. From this preliminary study and chemical analysis the compound is considered to be a basic bromosilicate of the formula, $7PbO\cdot PbBr_2\cdot SiO_2$. Theoretical for the Pb, Br and Si are 83.40, 8.03 and 1.41% respectively. Chemical analyses on two products were: Pb, 83.20, 83.25; Br, 7.95, 7.98; and Si, 1.47 and 1.46%. The silicate is a bright yellow colored compound with a glazed appearance, and is of interest since it has been found to be the chief component on the tips of spark plug insulators under certain conditions of engine operation. The interplanar spacing values for the silicate are given in Table V.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE SIGNAL CORPS ENGINEERING LABORATORIES]

Solid Phases in the System Ag_2HgI_4–Cu_2HgI_4

BY LAWRENCE SUCHOW AND PAUL H. KECK

RECEIVED JUNE 25, 1952

Solid solutions of Ag_2HgI_4 and Cu_2HgI_4 have been prepared by simultaneous precipitation from aqueous solution. X-Ray diffraction studies and measurement of color transition temperatures have led to the construction of a phase diagram with a miscibility gap from 39 to 54 mole % Cu_2HgI_4 at room temperature, and a eutectoid point at 34° and 43 mole % Cu_2HgI_4. All low temperature or β-phases are pseudocubic tetragonal with the c/a ratio equal to unity below 68 mole % Cu_2HgI_4. Outside the heterogeneous range, the β-phases exhibit steady changes in lattice parameters with composition. The high temperature or α_1-phase of a preparation at the eutectoid composition has been found to consist of a single cubic phase with lattice constant intermediate between those previously reported in the literature for the parent compounds. A considerable transition temperature hysteresis has been observed in all materials. Munsell color specifications and spectral reflectance measurements have been made for both high and low temperature phases. The β-phases exhibit colors from yellow to red, and the α_1-phase from red to dark red-purple, as the copper content increases. The energy difference corresponding to the shift of the reflectance edge occurring with the color transition in each case is very nearly constant.

Introduction

The compounds silver(I) iodomercurate(II), Ag_2HgI_4, and copper(I) iodomercurate(II), Cu_2HgI_4, are thermochromic, each having low and high temperature phases (called β and α, respectively). Ketelaar[1,2] in reporting the crystal structures of the two phases of both compounds, states that they are isomorphous with each other in both phases. The low temperature forms are both of pseudocubic tetragonal symmetry, although in the case of Ag_2HgI_4 the unit cell is actually isometric. The high temperature forms of both compounds are cubic. Ketelaar has also given an explanation of the mechanism of the phase transition based on ionic mobility and an order–disorder rearrangement and has confirmed it by specific heat and conductivity measurements.[3,4]

Because of the close proximity of the lattice constants of the two compounds, and the apparently similar transition mechanism in each case, it seemed quite likely that solid solutions of Ag_2HgI_4 and Cu_2HgI_4 could be formed which would show similar transitions. The objectives of the work to be reported below were, therefore, to study the possibility of preparation of solid solutions in this system and to determine the relations of structure, transition point, and color with composition.

Preparation and Chemical Analysis.—The preparations were made by simultaneous precipitation from solutions

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(1) J. A. A. Ketelaar, *Z. Krist.*, **80**, 190 (1931).

(2) J. A. A. Ketelaar, *ibid.*, **87**, 436 (1934).

(3) J. A. A. Ketelaar, *Z. physik. Chem.*, **B26**, 327 (1934); **B30**, 53 (1935).

(4) J. A. A. Ketelaar, *Trans. Faraday Soc.*, **34**, 874 (1938).

containing stoichiometric amounts of reactants. This method yielded more satisfactory results than solid state reaction. Aqueous solutions containing mixtures of cupric and silver nitrates with total metal concentration about 0.4 *M* were added to boiling solutions of approximately 0.1 *M* K_2HgI_4 (prepared from mercuric nitrate and potassium iodide) and sufficient potassium iodide to reduce the cupric ion to the cuprous state. The resulting mixture was boiled almost to dryness in order to remove the iodine formed[5] and to decrease the loss of material remaining in solution. If this was not done, results were found to be poor wherever copper was involved, the product consisting largely of CuI rather than Cu_2HgI_4. No such difficulties were encountered with Ag_2HgI_4, but the treatment required for the Cu_2HgI_4 preparation did not affect the preparation of Ag_2HgI_4. If large excesses of K_2HgI_4 were employed (without change in volume of solution), the colors of the resulting materials were considerably darker than otherwise and the transition points slightly higher. For instance, Ag_2HgI_4 prepared in this way was orange instead of yellow and had a transition one degree higher than otherwise, although the X-ray diffraction powder patterns of the two were identical. However, the yield when using excess reagent was slightly above the quantitative amount and the silver analysis was low, indicating perhaps that K_2HgI_4 was trapped in the lattice. Precipitation from solutions containing stoichiometric quantities of reactants followed by boiling almost to dryness was therefore adopted as the standard method for synthesis. The preparation was completed by filtration, thorough washing, and drying at 70°. It is possible that materials thus prepared still contain small amounts of impurities. However, since the preparation procedure was standardized, any trapped impurities would be expected to result in rather uniform shifts in colors and transition temperatures without affecting the over-all picture.

The compositions of the products were checked by chemical analysis as follows: Cu_2HgI_4 was analyzed for copper by solution in boiling aqua regia followed by evaporation to dryness, redissolving of the residue in dilute sulfuric acid, neutralization with ammonia, addition of glacial acetic acid and of a large excess of potassium iodide, and finally titration of the resulting iodine with standard sodium thiosulfate solution, using starch as indicator.

All preparations containing silver were analyzed by treatment with boiling aqua regia, followed by filtration, washing, and weighing of the resulting AgCl. The percentage of Ag_2HgI_4 could then be calculated and the percentage Cu_2HgI_4 determined by difference.

The analytical results show the compositions to be very close to those expected from molar ratios employed in the preparation. The analyses do not, of course, provide any information concerning possible small impurities.

X-Ray Diffraction Investigations.—The structures of the low and high temperature forms of the preparations were studied by the X-ray diffraction powder method. For the investigation at elevated temperature, a stream of hot air was directed at a glass capillary holding the sample.

The X-ray patterns were measured, and calculations then made with the use of the Straumanis method for film radius determination. Precision lattice constants of both β- and α-phases were obtained by Bradley–Jay extrapolation using lines occurring in the back reflection region, principally those where $h^2 + k^2 + l^2 = 51$, 56 and 59. The values for the low temperature forms are plotted against composition in Fig. 1. The lattice constants of the β-phases were calculated disregarding a number of observed weak lines not reported by Ketelaar and not fitting his unit cell dimensions. The weak lines observed in the Ag_2HgI_4 pattern correspond quite well to those reported by Frevel and North[6] who believe they indicate a doubled lattice constant.

The results indicate formation of solid solutions with a miscibility gap between 39 and 54 mole % Cu_2HgI_4 at room temperature. These limits of the heterogeneous range, indicated by vertical marks in Fig. 1, were found by the following variation of the "disappearing phase" method. Throughout the heterogeneous range, where there exist two isomorphous, isometric, pseudocubic tetragonal phases with lattice constants in close proximity (as will be discussed further below), each plane is represented by a doublet formed from one line from each phase. However, the lines due to the 111 planes, being of a low Bragg angle, are not resolved and actually appear on the film as a single line. Because there are only slight variations in composition over the heterogeneous range, this line was taken as an internal intensity standard for each pattern, since it alone represents the sum of both phases. The relative intensities of the lines due to the 111 plane as well as those due to six other prominent planes in both phases were determined by comparison with spots of known intensity on X-ray film of the same type. Following this, plots were made of composition *vs.* the ratio of relative intensity of the plane to that of the 111 plane on the same film. One plot was made for each of the six planes in each phase, and by extrapolating the resulting curves to zero intensity ratio, the limits of the heterogeneous range were located. Those reported here are averages of results obtained with data from all six planes in each case.

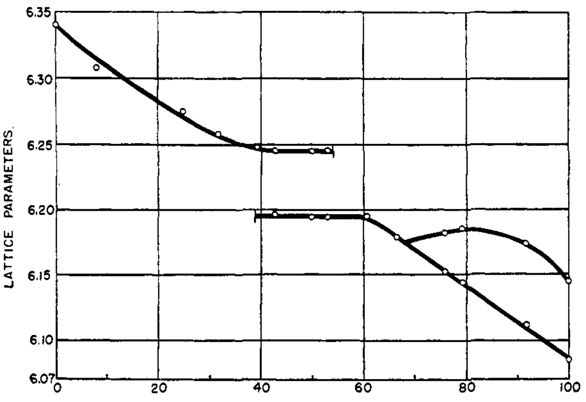

Fig. 1.—Lattice parameters *vs.* composition.

The X-ray diffraction powder diagram of a preparation with composition near the eutectoid point maintained above its transition temperature indicated one single cubic phase with lattice constant, $a = 6.250$ Å., a value intermediate between those reported by Ketelaar[2] for the parent compounds ($a = 6.383$ Å. for Ag_2HgI_4 and 6.103 Å. for Cu_2HgI_4).

Determination of the Color Transition Temperatures.—Preliminary measurements of the color transition temperatures were made by immersing glass capillaries filled with the samples in a water- or glycerol-bath, the temperature of which was slowly raised. This method gave fair results for the color transition temperatures. However, more accurate values can be obtained if the color range corresponding to an adjusted temperature interval is displayed rather than the entire sample being held at constant temperature. The location of a more or less abrupt change in color and its corresponding temperature can then be determined with good precision. For this reason a temperature gradient bench was built. It consists of a chromium plated brass block, 3 by 3 by 10 inches, with a highly polished plane top surface. Both ends of the block contain chambers through which thermostated liquids can be circulated or in which electric heaters can be mounted. Thus, predetermined temperature gradients over various ranges can be produced along the block. The temperatures are measured by eleven built in iron–constantan thermocouples which are located at 1-cm. intervals and connected to a potentiometer by means of a serial switch. Two parallel, engraved millimeter scales along the edges of the top surface enable position determination. Thin uniform coatings of the thermochromic materials were prepared on glass plates, using Dow-Corning Silicone Lacquer DC 804 as a binder. After adjusting the bench to a desired temperature gradient a strip of the sample under test was laid face down onto the top surface. Equilibrium was reached after a few minutes and the locations of more or less sharp color changes were then measured on the millimeter scale, which was in turn calibrated in terms of temperature by the thermocouples. The measurements were carried out for two initial conditions; that is, the samples were kept either at 10 or at 70° for a half-hour before measurement, in order to observe changes with both rising and falling temperature.

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[5] M. Meyer, *J. Chem. Ed.*, **20**, 145 (1943).

[6] L. K. Frevel and P. P. North, *J. Applied Phys.*, **21**, 1038 (1950).

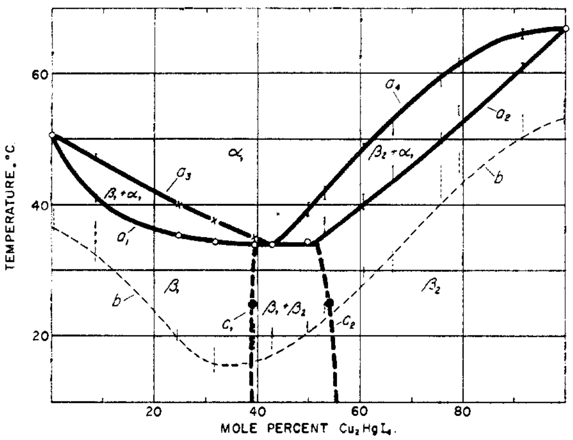

Fig. 2.—Phase diagram for the system Ag_2HgI_4–Cu_2HgI_4: O, sharp color transition observed upon increasing temperature; I, range of gradual color transition observed upon increasing temperature; ×, color transition observed only upon cooling; |, range of gradual color transition observed upon cooling; ●, limit of heterogeneous range as determined by X-ray diffraction; α_1, solid solution of α-Cu_2HgI_4 and α-Ag_2HgI_4; β_1, solid solution of β-Cu_2HgI_4 in β-Ag_2HgI_4; β_2, solid solution of β-Ag_2HgI_4 in β-Cu_2HgI_4.

On heating, some preparations display sharp, contrasting color changes, and others show two definite, but more or less gradual, ranges of color changes. On cooling, all samples exhibit a rather gradual change in color. The results of the measurements are plotted in Fig. 2. The branches a_1 through a_4 refer to the color transitions observed with rising temperature and curve b to those measured with decreasing temperature. On heating, Ag_2HgI_4 and Cu_2HgI_4 exhibit sharp changes from yellow to orange and from red to dark red-purple, respectively. The materials containing 25 to 50 mole % Cu_2HgI_4 also display very abrupt color changes. In these cases the transitions take place from orange to red at temperatures much lower than those of the transitions of the parent compounds. With the three samples containing 24.8, 31.6 and 39.4 mole % Cu_2HgI_4 only one sharp color change appears on the hot-bench, but upon removing the sample and allowing it to cool to room temperature a fairly sharp second step is clearly observed at a location which has been heated to a temperature above that of the first transition. This second dividing line may be observed because the color in the area between the two positions gradually fades. The temperatures of these second positions are indicated by crosses on the curve a_3. The sample containing 42.7 mole % Cu_2HgI_4 gives evidence for only one sharp color change. In the remaining ranges of composition, two definite, though more or less gradual, color transitions are observed directly and simultaneously on the temperature gradient bench.

All determinations of the color transitions upon heating were repeated several times, and the temperature values were found to be reproducible within ± 1°.

With decreasing temperature the color changes were usually so gradual that it was difficult to determine their location accurately. Curve b is an indication of the lowest temperature levels at which the color changes were noticeable after leaving samples on the temperature gradient bench for 15 minutes. A remarkable temperature lag for the transition of the α-form into the β- is indicated.

Munsell Color Specification.—Color notations of the low and high temperature forms were made in terms of the Munsell system. The measurements were carried out with the coatings prepared on glass plates as described above. The color specifications of the β-phases were obtained with the samples cooled to a temperature of 10°, whereas the readings of the α-form were taken at 70°. The results are included in Table I.

TABLE I

MUNSELL COLOR SPECIFICATION

Mole % Cu_2HgI_4	α-Form at 70°	β-Form at 10°	Cooled from 70 to 25°	Heated from 10 to 25°
0.0	10.0 R 5/10	5.0 Y 8/12	2.5 Y 8/10	2.5 Y 8/10
8.0	7.5 R 5/8	1.0 Y 6/8	9.0 YR 6/8	10.0 YR 6/8
24.8	5.0 R 4/10	6.0 YR 6/12	7.5 R 5/12	4.0 YR 6/10
31.6	4.0 R 4/12	4.0 YR 6/12	5.0 R 4/12	2.5 YR 6/12
39.4	4.0 R 4/12	2.5 YR 6/12	5.0 R 4/12	1.0 YR 6/12
42.7	2.5 R 3/10	10.0 R 6/12	5.5 R 4/12	9.0 R 5/12
49.9	2.5 R 3/10	10.0 R 6/12	6.0 R 4/12	8.0 R 5/12
53.0	2.5 R 3/10	9.0 R 5/12	7.0 R 5/12	7.5 R 5/12
60.6	2.5 R 3/8	8.0 R 5/12	7.0 R 5/12	7.5 R 5/12
66.4	2.5 R 3/4	7.5 R 5/12	7.0 R 5/12	7.0 R 5/12
75.9	2.5 R 3/4	6.0 R 5/12	6.0 R 5/12	6.0 R 5/12
79.3	2.5 R 2/6	6.0 R 5/12	5.5 R 4/12	6.0 R 5/12
91.8	2.5 R 2/4	5.0 R 5/12	5.0 R 4/12	5.0 R 4/12
100.0	1.5 R 2/4	5.0 R 4/12	5.0 R 4/12	5.0 R 4/10

In terms of the Munsell system the first group of figures and the letters R, YR or Y denote the *hue* of the sample. The numerator of the fraction following indicates the *value* or brightness, and the denominator expresses the *chroma* of the sample. The hue values of the α- and β-forms are plotted *versus* composition in Fig. 3 as curves 1 and 2. In specifying the colors of the materials at room temperature (25°) it is important to distinguish between two cases: (a) samples previously cooled, and (b) samples previously heated above the color transition points. In the former case the samples are always in the β-form, but a small, gradual, reversible change in color with temperature takes place within that phase. Cooling causes a shift toward shorter wave lengths and a temperature increase shifts the color toward red (see curve 4 of Fig. 3, and also Table I). In case (b) the samples with Cu_2HgI_4 content of less than 10 and more than 60 mole % change into the β-form readily upon cooling and therefore assume the same color as in case (a). The preparations containing between 10 and 60 mole % Cu_2HgI_4 behave differently in that the α-form is frozen in at room temperature (see curve 3 of Fig. 3, and also Table I). The shape of curve 3 depends to a certain extent upon cooling rate and time during which the sample is kept at 25° after having been heated to 70°. The data plotted in curve 3 were obtained with the samples allowed to cool from 70 to 25° within about 10 minutes and left at this temperature for approximately 5 hours. In the

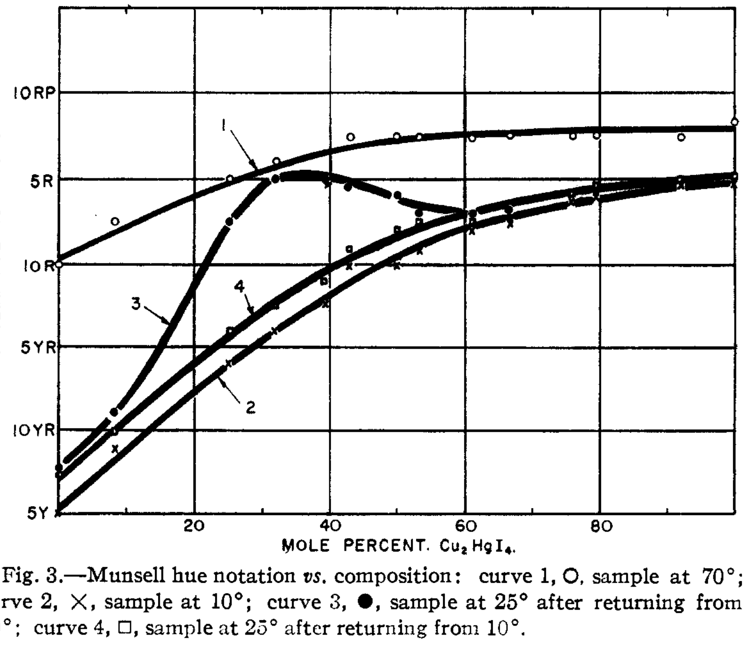

Fig. 3.—Munsell hue notation *vs.* composition: curve 1, O, sample at 70°; curve 2, ×, sample at 10°; curve 3, ●, sample at 25° after returning from 70°; curve 4, □, sample at 25° after returning from 10°.

case of faster quenching and samples kept at 25° for less than 1 hour, curve 3 shifts toward curve 1, whereas for much longer times the shift occurs toward curve 4. The maximum of curve 3, however, was found to be very stable at room temperature even after a period as long as 6 months. This characteristic makes the preparations containing between 25 and 45 mole % copper compound capable of producing lasting records of the respective transition temperatures having been surpassed.

Measurements of Spectral Reflectance.—The spectral reflectance curves of the samples were measured with the Hardy recording spectrophotometer. Each sample was measured at approximately 10 and 70°. All reflectance curves are very similar and exhibit a fairly steep edge rising from a constant toe value of approximately 5% reflectance on the short wave length side to a constant value of about 55% on the long wave length side. The characteristic wave length values corresponding to half the heights of the steps in the reflectance curves are plotted in Fig. 4. It will be noted that a gradual change of the reflectance edge occurs from 510 to 610 mμ in the β-phase and from 560 to 680 mμ in the α-phase, as the copper content of the preparations increases. This is consistent with the previously described color notations. The wave length difference between the low and high temperature reflectance edges of each compound indicates a steady increase with the Cu_2HgI_4 content. Expressed in energy this difference turns out to be fairly constant for all the samples and has an approximate value of 0.21 electron volt. Since this energy difference has been determined from the measurements at 10 and 70°, respectively, the value for the abrupt transition alone is somewhat smaller. With the compound containing 31.6 mole % Cu_2HgI_4, in which either the high or low temperature form can be independently obtained at room temperature, the optical energy difference between the two phases at 25° was found to be approximately 0.18 electron volt. The 0.03-electron volt difference therefore corresponds to the gradual part of the color change between 10 and 70°.

Discussion

The X-ray diffraction work has shown that there is a very definite relation between composition and structure. Two ranges of solid solutions exist at room temperature, with a miscibility gap between 39 and 54 mole % Cu_2HgI_4.

All low temperature phases are of pseudocubic tetragonal symmetry. However, the unit cell of the phase with Ag_2HgI_4 as solvent is isometric throughout, as is that of the phase with Cu_2HgI_4 as solvent at compositions below approximately 68 mole % Cu_2HgI_4. Above this composition, there is a transition to the ordinary tetragonal symmetry where $c > a$, but no sharp change in properties has been observed to occur at this point. From Pauling's values for the effective ionic radii of Cu^+ and Ag^+ (0.96 and 1.26 Å., respectively), the average effective univalent radius at the critical point is found to be 1.05 Å. An average radius below this value results in the c/a ratio rising above unity. Since there might be some possibility of reduced temperature causing a decrease in the effective radius of the univalent ion without having as great an effect upon the remainder of the lattice, especially the iodide ions, it would be interesting to determine the c/a ratio at low temperatures of solid solutions with less than 68 mole % Cu_2HgI_4.

From the color transition data along branches a_1 through a_4 in Fig. 2, the existence of a phase diagram with a eutectoid point at about 43 mole % Cu_2HgI_4 is indicated. With the additional information derived from the X-ray diffraction studies, the phase diagram may be completed by drawing branches c_1 and c_2 to define the heterogeneous range. These have been drawn as broken lines because their exact slopes have not been determined.

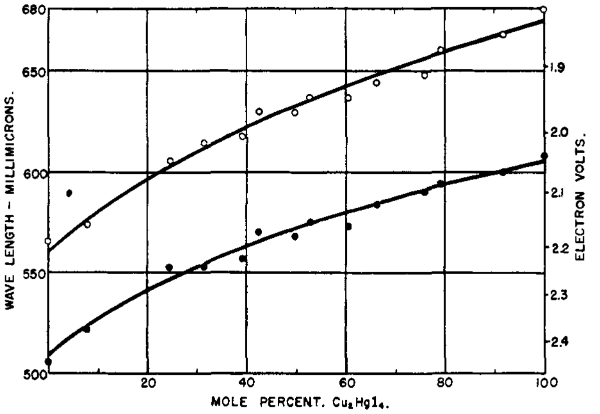

Fig. 4.—Wave length and energy of reflectance edge *vs.* composition: ○, sample at 70°; ●, sample at 10°.

The high temperature X-ray diagram of the preparation near the eutectoid point has shown the existence of a single cubic phase. Comparison of its lattice constant with those of the parent compounds indicates that Vegard's law is followed approximately. A continuous range of solid solutions in the α-phase is indicated, but more high temperature X-ray data would be required to establish this definitely.

The phases existing in all areas are indicated directly on the phase diagram (Fig. 2). For this purpose, curve b should be disregarded because the phase diagram has been determined for rising temperatures.

Comparison of branches a_1 through a_4 with curve b of Fig. 2 indicates a considerable lag in transition temperature upon cooling. This is observed over the entire composition range. At temperatures between branch a_3 and curve b, and a_4 and b, both α- and β-modifications can therefore be obtained, the relative amounts depending upon the previous history of the sample with regard to temperature and length of treatment. The color specification results plotted in Fig. 3 are consistent with this explanation.

Nucleation appears to be an important factor in explaining the results obtained upon cooling from temperatures above the transition points. Materials heated to temperatures within the $\beta + \alpha$ equilibrium areas, already having considerable amounts of the β-phases present, show less temperature lag. It was this behavior which made it possible to observe the upper transition step of the preparations containing Cu_2HgI_4 in the range of 24.8 to 39.4 mole %.

The results obtained indicate that at all compositions, copper, silver and mercuric ions become disordered simultaneously. Of course, the relative amounts of copper and silver entering the disordered state at any one instant vary over the $\beta + \alpha$ equilibrium regions, but at the eutectoid composition, the metal ions all go suddenly from an ordered to a disordered state with no variation in chemical composition.

From conductivity measurements on Ag_2HgI_4, Ketelaar[4] calculated the average increase in potential energy of the crystal when a metal ion is moved from an ordered into a disordered position. He found 5660 cal./g. at. wt. at the transition temperature. This value corresponds to 0.245 electron volt and can be compared with the energy difference of 0.18 electron volt derived from the reflectance measurements. Since only part of the energy involved in the order–disorder transition would be expected to express itself in the absorption or reflectance characteristics in the visible range, the optical values are consistent with the results of Ketelaar's conductivity measurements on Ag_2HgI_4.

Since the energies corresponding to the shift of the reflectance edge between the β- and α-forms have been found to be very nearly constant for all compositions, conductivity measurements on these materials might be expected to indicate approximately constant energy differences for their order–disorder transformations. It would therefore be interesting to carry out such conductivity measurements. Also interesting would be a determination of specific heat of these materials over the entire composition range as a function of temperature.

It has been noted that the colors and transition temperatures of these materials are dependent to some extent upon the exact method of preparation employed. It therefore appears that very small quantities of impurities may be responsible for such slight variations superimposed upon the primary effect reported herein. Further study along these lines would be of interest.

Acknowledgments.—The authors wish to express their appreciation to Mr. Steven Levinos for his supporting interest, to Mr. Andrew Drukalsky for preparation of most of the room temperature X-ray diffraction powder photographs, and to Messrs. Marvin Fredman and Francis Hone for assistance in measurement of the color transition temperatures.

FORT MONMOUTH, NEW JERSEY

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Heat Capacity Standards for the Range 14 to 1200°K.

BY DEFOE C. GINNINGS AND GEORGE T. FURUKAWA

RECEIVED SEPTEMBER 2, 1952

In an effort to supply accurate heat capacity data on pure materials which will serve as standards in precision calorimetry, there are given the results of new heat capacity measurements at the National Bureau of Standards on *n*-heptane (25° to 523°K.) and on aluminum oxide (corundum), (14 to 1173°K.). These materials together with benzoic acid had been recommended by the Calorimetry Conference (U. S.) as standards for the intercomparison of calorimeters. Diphenyl ether is suggested as an additional standard to supplement the above three substances and water which is universally used as a standard. Tables of smoothed values of heat capacity and enthalpy are given for *n*-heptane, aluminum oxide, benzoic acid (up to 430° K.), diphenyl ether (up to 570°K.) and water (0 to 100°C.).

Since the beginning of calorimetry, water has been used as a standard for heat capacity measurements, partly because it is universally available in high purity. However, as heat measurements were extended below 0°, the large expansion of water on freezing made it impracticable to use in many calorimeters. Above 100°, the increasing vapor pressure of water is a serious drawback, both because of resulting constructional difficulties and also because of the necessity of accounting for the change with temperature of the relative amounts in the two phases. With these considerations, it is apparent that, in addition to water, other heat capacity standards are desirable. In 1949, the Fourth Conference on Calorimetry[1] recommended three substances to be used as standards for the intercomparison of heat capacity calorimeters, and the National Bureau of Standards undertook the task of preparation and distribution of these substances. It was the original purpose that samples of these substances be made available to those laboratories interested in very precise measurements of heat capacity. By having samples of any one substance taken from one source of very high purity, it was hoped to have a means of comparing measurements made in different laboratories under different experimental conditions. The National Bureau of Standards has prepared the samples of benzoic acid, *n*-heptane and aluminum oxide for the Calorimetry Conference Program. These samples are not regarded as part of the Standard Sample series of the Bureau, but are available without charge to a limited number of laboratories. It is the main purpose of this report to give a summary of the results of our new heat capacity measurements on the Calorimetry Conference samples of *n*-heptane and aluminum oxide. In addition, the previously published heat capacity results on the Calorimetry Conference sample of benzoic acid are included, together with earlier results on diphenyl ether and water. All of the results given are derived entirely from measurements at the National Bureau of Standards. Other measurements (unpublished) on the Calorimetry Conference Sample of *n*-heptane have been made at the Bureau of Mines, Bartlesville, Oklahoma. It is hoped that other laboratories (including those outside the United States) will also make heat capacity measurements on these Calorimetry Conference Samples, and that after the comparison of results, agreement may be reached on heat capacity values for the standard materials.

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(1) This conference consisted of an informal group of representatives from various U. S. Laboratories which were interested in precision calorimetric measurements (*Chem. Eng. News*, **27**, 2772 (1949)).