over a wide range of temperature. The specific heat and heat of fusion of crystalline ethyl alcohol have also been measured.

From an examination of the data, it appears probable that the entropy of the equimolal mixture is not zero at the absolute zero.

With the assumption of the applicability of the third law to the process C_2H_5OH (super-cooled) $\longrightarrow$ C_2H_5OH (crystalline), $\Delta S_{156.2}$ has been calculated in two ways. The difference (per gram atom) between the results obtained is 0.12 cal. per degree, or 20 calories at 156.2° K.

By means of the third law of thermodynamics the free energy of pure ethyl alcohol has been calculated. $F_{298}° = -43{,}000$ cal.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY.]

THE MELTING POINTS AND THERMOELECTRIC BEHAVIOR OF LEAD ISOTOPES.

BY THEODORE W. RICHARDS AND NORRIS F. HALL.

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Among the properties of the isotopes of lead, the melting points stand out as of especial interest. Since the molecular volumes of these substances are essentially equal,[1] the question as to whether or not the melting points are likewise equal, compels attention.

Thermocouples were used for this measurement, not only because they could be used with small amounts of material but also because they are essentially suited to "differential" estimation. W. P. White's papers[2] on this topic afforded many useful suggestions.

The thermo elements employed were 4 in number, 3 single elements and one of 4 junctions. The difficulty with work at high temperatures is the breaking down or the increasing conductivity of most insulating materials even below the melting point of lead. Through the kindness of Professor Harvey N. Davis and Dr. F. Wheeler Loomis, asbestos-insulated copper and nickel wire were available for the construction of the elements. This combination has thermoelectric advantages. The thermoelectric effect (about 23 microvolts per degree at 327°) is much higher than that of noble-metal elements, although not so high as copper-constantan; moreover, both sorts of wire are generally very free from the inhomogeneity often met with in alloys, and both metals are sufficiently resistant to oxidation under ordinary conditions.

The use of copper here as well as for connections to the rest of the measuring apparatus diminishes the danger of parasitic effects to a minimum.

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[1] See T. W. Richards and Charles Wadsworth, 3rd, THIS JOURNAL, 38, 221, 1658 (1916).

[2] W. P. White, *ibid.*, 36, 1856–1885, 2011–2020 (1914).

The asbestos insulation, which had an inflammable binder, was removed from a few millimeters at the ends of the wires, and the ends were twisted together. They were then soldered with a minimum amount of silver solder, using borax as a flux.

The junctions were insulated from each other by a thin glaze of lead borate prepared from litharge and boric anhydride in a nickel crucible in the proportion represented by $Pb_2B_2O_5$. For convenience in introducing into the glass tube the several separately insulated elements were twisted together and the whole glazed so as to form a single bead. The single element used to measure the bath temperature was simply enclosed in a glass tube. All the "cold ends" were contained in a single glass tube under paraffin. The free ends were, after several windings, soldered firmly to thin copper strips which made contacts through strong clamps.[1]

The furnace consisted of 2 tall glass beakers of which the smaller was wound with a commercial resistance wire wrapped in asbestos and placed in the larger beaker. The beakers thus nested were set in the center of a fiber pail, of which the bottom had been covered with magnesia and asbestos, the whole being packed in this mixture. Around the top of the beakers a smooth covering was made of plaster of Paris. The heavy tempering oil placed in the inner beaker and used for the bath needed renewal from time to time; it carbonized and evaporated but never burned, and its odor while unpleasant was not unbearable. The viscous oil was rapidly stirred with a brass stirrer and the bath was covered with a block of asbestos nearly 3 cm. thick. After the stirrer, the melting point apparatus, the thermo-couples and a mercury thermometer had all been inserted through the cover all the holes were luted with a paste made of magnesia, asbestos threads and oil. The whole furnace was thickly surrounded and covered with wool felt. The rapidity of stirring was such that no difficulty whatever was found in keeping the temperature of the 2 samples of lead the same within 0.1° while the furnace was rising in temperature at the rate of 10° per minute, or in keeping the furnace temperature constant within 0.05° for hours at a time with proper regulation of heating current. The alternating 110-volt lighting circuit was used as a source of heat, but on account of fluctuating voltage needed frequent regulation if constant temperature was desired. The heat insulation was satisfactory; cooling curves could be taken with the heating current broken completely. Nevertheless, in order that greater accuracy might be obtained a small current was usually passed through the heating coil to delay the cooling.

The Electrical Measuring System and Connections.

A 20,000 ohms resistance Wolff potentiometer was employed, instead of an apparatus of lower resistance, because it was somewhat more

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[1] W. P. White, *loc. cit.*, p. 1861.

convenient (especially in that it simplified the standard cell connections) and because even with it, the galvanometer gave all the sensitiveness desirable. The floated battery arrangement described by White[1] was used to keep the battery voltage constant, and with about 19,800 ohms in series with the 2 cells, gave variations so small that it was seldom necessary to change the resistance by as much as 0.1 ohm, in making a balance against the standard of which the voltage was assumed to be $1.0183 + 0.00004\ (t^\circ - 20^\circ)$. Three single-knife switches connected the 3 single elements with the potentiometer galvanometer circuit, which was provided with an eliminating switch and a switch for making direct connection with the standard cell. The whole battery circuit was shielded and the shield carried into the eliminating switch. Another switch made connection with the differential element, and at the same time cut out the potentiometer. A suitable protective resistance for the galvanometer was an integral part of the potentiometer.

The galvanometer was a Leeds and Northrup wall type with a mirror. The lamp signal, focussed sharply on a translucent scale, was easily read to tenths of a millimeter. The deflection was nearly 2 mm. per microvolt, so that it was easy to read hundredths of a degree with the single elements and thousandths of a degree with the multiple element. All the measuring apparatus was on a single shielded table, under which, but separate from it, was a box with the switches of the lighting and heating circuits and the slide resistors for the latter.

The entire measuring system was shielded by a complete equipotential shield, as advocated by White. After the hope that the insulation of oil and glass would prevent leakage from the heating current had proved illusory, the shield was extended into the furnace itself by the device of silver-plating the several parts of the entire melting apparatus, winding their tops with tin-foil and then continuing the winding with thin copper foil. This was wound spirally around the sheaf of connecting wires, forming a continuous flexible protective sheath, and connected into the shield, which quite eliminated trouble from electrical leakage unless the heating current switches were handled simultaneously with some part of the measuring system.

Parasitics were detected and allowed for by means of a suitable eliminating switch. Early in the day's work they were large and often quite variable, but always seemed to become fairly constant and of rather small value about noon when the room and furnace temperatures had reached approximate equilibrium. In the final measurements, they were always tested immediately before and after the experimental crisis and all trials in which they varied enough to cause appreciable error were rejected.

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[1] W. P. White, "Constant Battery," *Phys. Rev.*, **23**, 447 (1906).

The two sorts of lead were contained in identical sealed cylinders of Pyrex glass from which the air was exhausted before melting the lead. Each vessel was provided with a smaller co-axial cylindrical glass sheath for the thermo-elements, which thus extended into the center of the cylindrical mass of lead.

The 2 kinds of lead were prepared as follows. Ordinary lead, in the form of acetate, was dissolved, filtered, and precipitated as nitrate from concentrated solution, and then recrystallized (with centrifuging) 6 times as nitrate from concentrated solution. The purified crystals were then dissolved in warm water in a quartz dish, about 10% of pure nitric acid was added, and the lead was precipitated electrolytically as dioxide in order to eliminate possible traces of silver. The lead dioxide was washed repeatedly, dried on the steam bath, and heated to redness in order to reduce it, at least partially, to litharge and expel any included nitrogen compounds. The orange-red mixture of oxides was then cautiously heated in an unglazed porcelain crucible with potassium cyanide of high purity, until it was reduced to metallic lead, which was next melted in small "alundum" crucibles and poured into a carefully cleaned steel die kindly loaned by Professor P. W. Bridgman. This die, containing the lead, was heated to about 250°, the melting point of soft solder, in a blast flame, and then transferred to a press, where the lead was extruded in the form of wire about 1 mm. in diameter, of which the first 3 meters were rejected. The remainder of the wire, cut into pieces about 5 mm. long with a clean knife on a glass plate, was introduced into one of the cylindrical lead containers.

The other specimen of lead—the Australian radioactive sample—was treated in the same way, except that the raw material was not the acetate, but rather in metallic form. This was dissolved in nitric acid, evaporated to dryness, taken up with water, filtered, evaporated, recrystallized 6 times, electrolyzed, and after ignition reduced by cyanide as described above.

Samples of each kind of lead were tested spectrographically before and after extrusion through the die, through the kindness of Professor G. P. Baxter. All the samples showed a trace of silver, and the extruded ordinary lead a very small trace of copper. This sample also showed an intensification of one of the lines which appeared in all the lead samples ($\lambda = 3048$); but such intensification is usually not significant, depending rather upon the vagaries of the arc-spark, than upon differences of material. Evidently neither of the samples was perfectly pure—evidently, too, the ordinary lead was somewhat less pure than the other. The maximum impurity probably amounted to not more than 5 parts in one hundred thousand.

Measurements.

After preliminary trials the method of measurement adopted was as follows. The temperature of the bath was raised rapidly until (with the potentiometer set at the value corresponding approximately to the melting point) the spot of light from the galvanometer was at the extreme low-temperature side of the indicator scale. Resistance was now thrown into the heating circuit until the passage of the spot of light toward the center of the scale was sufficiently slow. Readings of E. M. F. were taken every 15 seconds through the melting interval, the heating being so regulated as to maintain a constant temperature gradient between the bath and the charge to be measured. The cooling curve was taken similarly. Marked super-cooling from one to two degrees was the rule, but after this marked depression the temperature rose again to a constant level which was maintained for a long time. This maximum temperature was taken as the freezing point. The battery voltage was balanced against the standard cell before and after every trial with satisfactory outcome. Corrections for parasitics and galvanometer drift (if any) were made in the immediate neighborhood of the critical portion of the melting and freezing interval. The super-cooling was greater in the radioactive lead than in ordinary lead, probably because of the slightly less purity of the latter.

In the first experiments using single elements, the difference between the melting points of the two isotopes did not greatly exceed the probable error of experiment. In the more sensitive subsequent "differential" experiments, the temperatures of the samples travelled nearly together, differing only ±0.05° during wide variations of the furnace temperature above and below the melting point; but they did not remain together in the immediate neighborhood of the melting point. On heating, a difference in temperature became manifest about 0.5° below the true melting point in the sense that the temperature of the radioactive sample rose more rapidly. Evidently the ordinary lead began to melt at a lower temperature. After reaching the melting point, the difference diminished to less than 0.1°, and afterwards diminished only very slowly until one of the samples melted.

On cooling, as already stated, the ordinary lead crystallized first; but after the radioactive isotope had crystallized, its maximum rose about 0.05° above that of the other. During most of the cooling the radioactive sample showed a temperature about 0.05° above the other. When the heating or cooling was properly regulated and extremely slow it was possible to extend greatly the interval of constancy and to diminish the small unavoidable constant error which tended to increase the apparent difference due to the fact that the ordinary lead was always in a more advanced state either of melting or of freezing than the radioactive.

There seems to be no question then that the radioactive lead showed the higher melting point by about 0.05° or 0.06°—a difference of only one ten-thousandth of the absolute melting temperature of lead. Part of the difference is unquestionably due to slight impurity in the ordinary lead, as shown by the spectroscope and also by a slight obliquity of the melting curve even under the best conditions of heat supply. Possibly all of the difference may be due to this cause. Certainly there is no difference between the melting points at all comparable with the difference between the atomic weights, which was almost 0.5%.

The Australian radioactive specimen used in this test had an atomic weight of about 206.4, whereas pure uranium lead probably has an atomic weight very near 206. Accordingly the Australian specimen may be supposed to consist of a solid solution of uranium lead and one or more isotopes of higher atomic weight. Ordinary lead being the most probable admixture, we may assume the specimen to consist of about one part of common lead to three parts of the isotope believed to owe its origin to uranium. But ordinary lead also is probably an isotopic mixture. That two chance mixtures of isotopes in different proportions should assume essentially the same melting point is extremely unlikely, if their melting points were different, or if the addition of one isotope caused any appreciable effect on the melting point of another. Hence from the results just recounted, it is fairly safe to conclude that isotopes must be wholly soluble in one another, in perfectly consolute solid solution, and that all have the same melting point, as indeed one would expect. Separation by freezing is obviously impossible.

Time was lacking for the preparation of yet purer specimens, which would have given a more conclusive verdict.

The Thermoelectric Behavior of Isotopes.

The apparatus being at hand, a test of the thermoelectric behavior of the 2 isotopic forms of lead was worth while. Two precisely similar wires of ordinary lead were connected with the galvanometer terminals, and the other ends were joined by wire made of the radioactive lead—one junction being introduced into an ice bath and the other heated gradually to melting in a flame. No deflection in the galvanometer was observed in any of several repetitions of this test, although one ten-millionth of a volt could have been detected. Evidently, then, there is no difference in thermoelectric power between these two kinds of lead. Presumably this behavior is characteristic of the behavior of isotopes in general.

It was intended also to compare their electrical conductivity, but the time needed to prepare the wires with sufficient care as to exact constancy of cross section was lacking. Later this test was accomplished by Professor P. W. Bridgman upon the same samples with more carefully drawn wire. He has described these experiments in another place.[1] He found no difference (beyond the range of experimental error) in the conductivity of the 2 kinds of lead nor in the effect of pressure or temperature upon their conductivity.

We are glad to acknowledge our indebtedness to the Carnegie Institution of Washington for much of the apparatus used in this research.

Summary.

In this paper experiments are described which show that the difference in the melting points of 2 specimens of lead differing 0.8 in atomic weight is, if appreciable, not over 0.05°. From this outcome, it is fairly safe to assume that the kinds of lead not only have very nearly the same melting point but also (since the sample consisting chiefly of the lighter isotope doubtless contained ordinary lead) they mix (or rather mutually dissolve) without affecting the melting point.

The Seebeck thermoelectric effect produced at a junction of the two kinds of lead is also shown to be nil.

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THE ACTIVITIES OF THE IONS IN AQUEOUS SOLUTIONS OF SOME "STRONG" ELECTROLYTES.

BY FREDERICK H. GETMAN.

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In a recent number of THIS JOURNAL, Noyes and MacInnes[2] gave an interesting summary of a series of investigations which have been carried out under their direction with a view to determining the activity of several electrolytes which are known to be largely ionized in solution.

The appearance of this paper has made it seem worth while to the author to publish a brief account of some studies made by him along similar lines which not only confirm the experimental results of Noyes and MacInnes but also furnish additional evidence in support of the validity of the formula developed by MacInnes[3] for the calculation of the electromotive force developed at a liquid junction.

The term "activity," which was first introduced by Lewis[4] to express the effective concentration of a dissolved substance may be defined as the quantity which must be introduced into the mass action equation to express correctly the effect of concentration in determining the equilibrium.

Apparently the first to derive activity coefficients from measurements

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[1] Bridgman, *Proc. Nat. Acad. Sci.*, **5**, 351-3 (1919).

[2] THIS JOURNAL, **42**, 239 (1920).

[3] *Ibid.*, **37**, 2301 (1915).

[4] *Proc. Am. Acad. Arts Sci.*, **43**, 259 (1907); *Z. physik. Chem.*, **61**, 129 (1908).