TABLE 39.—CARBON DIOXIDE.
Heat of Vaporization.

			Internal.		
Temp.	Total.	External.	Observed.	Mills.	Dieterici.
—30°	75.2	9.86	65.34	65.74	66.25
—20	69.0	8.70	60.30	59.60	59.38
0	56.2	7.84	48.36	48.25	48.41
20	35.0	5.22	29.78	31.33*	31.20*
25	26.0	3.93	22.07	24.50*	24.32*
30	11.0	2.15	8.85	13.71*	13.55*
31.35	0	0	0	0	0

TABLE 40.—NITROUS OXIDE.
Heat of Vaporization.

			Internal.		
Temp	Total.	External.	Observed.	Mills.	Dieterici.
—25°	66.90	12.00	54.90	58.62*	54.77
—20	65.04	11.88	53.16	56.88*	53.52
0	58.2	9.68	48.52	47.20*	44.83*
20	40.0	7.09	32.91	34.22*	32.74
30	22.5	5.13	17.37	24.54*	23.55*
38.8	0	0	0	0	0

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ON THE DEPENDENCE OF VALENCE UPON VOLUME IN CERTAIN TRIVALENT ELEMENTS.

By A. LUDWIG.

Received August 16, 1909.

In a paper on the melting point of carbon, published in the year 1902,[1] the cessation of the electrical conductivity during the melting of carbon under a high gas pressure was thought to be an indication of the passage of a less dense form of carbon into the more dense form of diamond. On account of the relatively high inversion temperature, more than 3000°, and the necessarily extreme pressure, a more complete study of this reaction appeared for the moment almost impossible. It seemed much more promising to investigate the volume changes of some other conducting material which would be easier to melt. The element bismuth appeared to me particularly adapted for this purpose, not only on account of its low melting point, 265°, but also on account of its relatively large increase of density (about 3 per cent.) on melting. I was aware that neither Spring[2] nor Kahlbaum[3] succeeded in producing a permanent change in the volume of bismuth, even with very high pressures (over 10,000 atmospheres). But as those scientists applied the pressure at ordinary temperature only, I undertook to heat the metal up to the melting point and to prevent its expansion in passing into the solid state by the application of very high pressures.

The material used for the purpose was 99.6 per cent. pure bismuth, with traces of antimony, lead, copper and iron.

Tammann[4] calculates the lowering of the melting temperature for bismuth through pressure from the formula

$$\Delta t = 0.00386 (p - 1).$$

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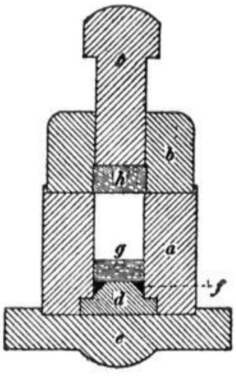
[1] *Z. Elektrochem.*, **8,** 273–281 (1902).

[2] *Ber.*, **16,** 2724 (1883).

[3] *Z. anorg. Chem.*, **46,** 217 (1905).

[4] *Ibid.*, **40,** 54 (1904).

Pressures of 10,000 atmospheres and more here produce a very considerable lowering of the temperature. An expansion of more than 3 per cent. must accordingly be easily noticeable, even in very rough measurements. The problem, therefore, consisted for the moment in introducing a crucible of previously melted bismuth into a pressure bomb and bringing to bear upon the molten metal in a few seconds, before any considerable cooling could take place, a very high even pressure throughout the duration of which all the joints in the apparatus must remain absolutely tight. To accomplish this, a hydraulic accumulator, with adjustable weights, was used in combination with a 300-ton oil press. After a number of unsuccessful trials, an absolutely tight, refractory packing was found. The difficulty was mainly due to changes in the inside diameter of the cylinder with the temperature.



Pressure bomb which held tight at 700° and 17000 atmospheres.

The apparatus, the essential features of which are described below, fulfilled all the requirements made upon it. A heavy nickel-steel cylinder, *a*, open at both ends, is provided with a guide tube, *b*, above, in which moves a hardened steel piston, *c*, ground to fit very perfectly. The lower opening of the cylinder is closed by a readily removable plug, *d*, which, together with the cylinder itself, rests upon a plate, *e*. Before the charge is introduced, a copper ring, *f*, together with a stout magnesia or asbestos plug, *g*, covering the ring is pressed down upon *d* with a hydraulic press and suitable piston. The cylinder is then ready to receive the molten charge or the charge can be introduced cold and melted in position. The copper or soapstone plug, *h*, with which the working chamber is closed at the top, is made about 2 mm. larger in diameter than the internal diameter of the bomb itself. When the apparatus is assembled in this way, an operation requiring but a few seconds after a little practice, the closing plug, *h*, is pressed into place in the cylinder, while the latter is cooling and contracting. In order that the apparatus shall perform with absolute certainty and quickly, it has been found necessary to provide the piston, as well as the pressure cylinder, with a centering arrangement, the operation of which will be immediately obvious from the rounded end surfaces of the apparatus which seat in appropriate plates attached to the press platens. It is hardly possible for a man, however skilful he may be, to adjust the apparatus so as to provide an absolutely uniform surface pressure and accurate piston travel without the centering device and guide tube. The first trials were made without guiding arrangements and resulted in each case in a deformation of the cylinder or of the piston. The centering device used is the same which is described in the paper on the melting of carbon, and which yielded uniformly successful results in those experiments. Difficulties of this kind were encountered by Threlfall,[1] and more recently by Masing,[2] in all their experimentation at extreme pressures. The latter regarded it as impossible to use pressures higher than 5,000 atmospheres in the apparatus which he described. Notwithstanding this, in all of the numerous tests which I conducted upon construction materials, not a single cylinder or piston was damaged by pressures up to 17,000 atmospheres. The cylinder comes to its proper position at once and remains sensitive to the slightest inequality in the application of pressure.

With this apparatus, pressures up to 17,000 atmospheres were held without appreciable loss.

Bismuth.—Even in the earliest trials, up to a pressure of 8,000 atmospheres, no yielding of the piston was observed on cooling the melt, and yet the bismuth, after cooling, did not differ in density from the common form. An increase in the pressure to above 17,000 atmospheres made no difference in this particular. The crystalline structure, although obviously in the same system, differed much in appearance from that of ordinary bismuth. Its texture resembled fine-grained iron which had been exposed to heavy shocks or magnetization and becomes very finely crystalline. Upon reducing the pressure to 3,000 atmospheres, the piston sprang back with an audible shock, showing that the bismuth had suddenly expanded again. This phenomenon has also been recognized in many other metals, particularly in its near relative, the so-called explosive antimony. The rapidity of the reaction in passing over from one form into the other appears to decrease as the melting point and electrical resistance become higher. This recalls the analogy between yellow arsenic and yellow antimony. The former, as is well known, is obtained by the sudden cooling of arsenic vapor from which the light is excluded.[3] Yellow antimony is much more difficult to prepare because of the more metallic character of the element and consequently greater rapidity of its reactions. It is obtained by passing air and oxygen over stibine at a temperature of —90° and is therefore a separation in the nascent state. Even at this temperature it goes over into the black modification,[4] while yellow arsenic is much more stable. In the parallel case the more dense bismuth must be far less stable than the explosive antimony. Very low temperatures must accordingly be applied in order to obtain this modification, but its successful preparation does not appear to me impossible.

At the very beginning it looked to be much easier to reduce the speed of the reaction through combination with negative elements. The sup-

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[1] *J. Chem. Soc.*, **93**, 1333 (1908).

[2] *Z. anorg. Chem.*, **62**, 265 (1909).

[3] Erdmann and v. Unruh, *Z. anorg. Chem.*, **32**, 437 (1902)

[4] Stock and Guttmann, *Ber.*, **37**, 899 (1904).

position that such an unstable modification would yield comparatively few stable combinations has subsequently been completely confirmed. First the attempt was made to form the oxide at the melting temperature of bismuth through the decomposition of water. The experiment was undertaken in this way: The bismuth was melted and raised to a temperature of 280° in the nickel-steel cylinder, after which it was lightly covered with a magnesia plug moistened with water. A few seconds sufficed to close the bomb, and then, with the help of the accumulator, a pressure of 10,000 atmospheres or more was suddenly brought down upon it. Gas was rapidly generated with a noise like a shot, but the bomb held tight. The cylinder was brought rapidly down to the temperature of the room, the pressure released and the still enclosed gas allowed to escape. When the solid charge was removed from the crucible, the greater portion of the bismuth appeared to have gone over into a brownish black mass. Portions of this, when reheated in a Bunsen flame, retained their original form even beyond the melting point, but gradually took on the greenish, and finally the yellow color characteristic of bismuth trioxide, with a separation of tiny drops of bismuth. If the heat was applied rapidly, fragments crushed in the forceps yielded a black powder which rapidly assumed the yellow color. The assumption that this black powder was nothing other than the bismuth monoxide, BiO, which has been obtained and described in various other ways, was established by analysis as follows: The product was carefully freed from the magnesia, shaken up with mercury, and the resulting dark powder dried and heated in a stream of hydrogen behind a layer of asbestos which had been saturated with gold solution and then heated to redness. Thus the powder was completely reduced to the metal and the water was collected in the weighed calcium chloride tube. Subtracting the mercury, 0.64 gram of the substance yielded 0.0564 gram of water, as compared with 0.0514 gram of water required by theory for BiO. The quantity of water is slightly overweight, due probably to the unavoidable passage of a trace of mercury into the calcium chloride tube. It is probable that a perfect analysis can only be obtained by this method when all the bismuth is converted into the oxide, BiO. This could not be accomplished just then, and further trials were postponed to some future time. Meanwhile, it appeared to be fully proved that the true monoxide of bismuth had been obtained.

The methods of preparing bismuth oxide which have succeeded heretofore primarily depend on the reduction of trivalent bismuth compounds in aqueous solution with chloride of tin. In this category belong the papers of O. Vogel[1] and H. Schiff.[2] Schneider[3] accomplishes the reduc-

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[1] *Vide* Gmelin-Kraut, *Handbuch anorg. Chem.*, 7th Ed., III (Pt. 2), 951 (1908).

[2] *Ibid.*

[3] *Pogg. Ann.*, **88**, 45, 1853.

tion through the action of $SnCl_2$ on a neutral or weakly alkaline solution of bismuth nitrate according to the following equation:

$$Bi_2O_3 + 4SnO = SnO_2 + BiO.$$

The weakness of these methods lies in the fact that it is difficult, if not impossible, to separate completely the bismuth oxide from the tin salt. Furthermore, it is difficult to avoid a partial reduction to metallic bismuth.

Another method of preparing it is due to S. Tanatar,[1] who asserts that basic bismuth oxalate heated in a vacuum tube goes over completely into bismuth monoxide and carbon dioxide, according to the equation

$$(BiO)_2C_2O_4 = 2BiO + 2CO_2.$$

The reaction begins at 15 mm. pressure and 180°, and ends between 245° and 250°. At higher temperatures a mixture of Bi and Bi_2O_3 results (Herz and Guttmann).[2] There is also a method of obtaining BiO by reduction of Bi_2O_3 in a stream of hydrogen at 265°.[3]

It is worth noting in passing that these separations occur at temperatures where the lighter form passes over into the specifically heavier form. The assumption of Berzelius that in the oxidation of the molten bismuth, BiO forms first, in direct analogy to the formation of oxide of lead, appears to be completely justified, especially in view of the decomposition of the molten bismuth by water.

Antimony.—The question then immediately suggested itself, How does the closely related trivalent antimony behave in melting? The melting point of antimony is high, and special arrangements require to be made for the protection of the bomb in order to repeat the bismuth experiments with it. About 100 grams of antimony were melted in a magnesia crucible and quickly placed in the steel cylinder which had been carefully lined in advance with magnesia. The opening was then closed with a magnesia plug moistened with water as before, and a pressure of about 6,000 atmospheres applied. Gas was generated at once, exactly as in the case of bismuth. The grayish black product, consisting for the most part of metal, was carefully freed from adhering magnesia powder and shaken up with mercury. The amalgamating required several days and was much more difficult than with bismuth. Here also the product obtained was a black powder which went over into the characteristic tetroxide of antimony at about red heat. The mean value of the water content obtained from two analyses is also slightly higher than the calculated value for SbO, and probably for the same reasons as with the bismuth. Found, 13.66; calculated for SbO, 13.24 per cent. This value, which is the mean of two analyses, also points plainly to the

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[1] *Z. anorg. Chem.*, **27**, 437 (1901).

[2] *Ibid.*, **53**, 63 (1907).

[3] P. Muir, *J. Chem. Soc.*, **39**, 21 (1881).

formation of monoxide with the decomposition of the water when antimony is melted under high pressure.

Aluminium.—It now appeared to be of the greatest interest to learn whether monoxide of aluminium, AlO, could also be obtained at high pressures. About 50 grams of aluminium were melted in a magnesia crucible as before and quickly placed in the magnesia-lined steel cylinder, which was closed with a magnesia cover moistened with water as before, and subjected to a sudden pressure of 6,000 atmospheres. The gas formation reappeared as before, but after cooling the cylinder and separating the product from the magnesia, the aluminium appeared little changed. As soon as the mercury was brought into contact with the metal, fine feathery white threads appeared on its surface, which were not unlike flowers of zinc in appearance. It was, however, impossible to produce an amalgamation in this way. The somewhat brittle aluminium was then broken up with a hammer, whereupon a peculiar and impressive phenomenon appeared. The little particles of aluminium were immediately covered with a slender white feathery growth, which proceeded quite slowly and sometimes reached a centimeter in length. This phenomenon reappeared whenever the breaking exposed a fresh surface, but grew gradually feebler, and finally, after a few moments, ceased altogether. Unfortunately, the substance produced in this peculiar fashion was quite insufficient for an analysis, and no practicable method for the separation of the metal from the supposed oxide could be found. For the moment, therefore, no completely clear explanation of the nature of the substance can be offered, but further trials will be undertaken at the earliest opportunity. This peculiar feathery substance is isotropic and possesses a very low index of refraction, about 1.542, is easily soluble in acetic acid, becomes a grayish white in color upon heating, with loss of aluminium, and goes over into the insoluble trioxide Al_2O_3 when ignited. If a conclusion may be drawn by analogy with the previous results with bismuth and antimony, aluminium is probably also bivalent under a pressure of 6,000 atmospheres, and forms the oxide AlO. It is also probable, by reason of the very much higher melting point, that the product does not go back at once into the less dense form, but returns slowly, like iron, and only after vigorous shaking or pounding. It is perhaps the pressure developed by this change which presses out the enclosed monoxide in fine threads.

Extremely interesting as the behavior of these trivalent elements proved to be, I was unable to extend the investigation to uni-, bi- and quadrivalent metals until apparatus could be devised which would remain absolutely tight for the highest pressures and temperatures. The continuation of the study of these problems must accordingly be postponed. Unfortunately, there are no insulators which can at the same time serve for the transmission of pressure at the temperature of the electric arc except the gases. There is, therefore, a second serious reason for discontinuing such investigations within a permanent building, due to the unavoidable danger, not only to the building but to the experimenter, which accompanies experiments under high gas pressures and which makes it preferable to conduct such experiments in the open. After long and painstaking trials, however, I feel great confidence in the possibility of mantaining constant gas pressures of more than 10,000 atmospheres in the presence of the strongest electric currents, and hope to undertake such investigations with an apparatus constructed especially for this purpose in the immediate future. It is hardly worth while at this time and with the limited experimental material now at hand, to enter upon a discussion of the important consequences for the atomic theory if these preliminary conclusions are consistently borne out. To this subject I therefore plan to return at a more appropriate time.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEP'T OF AGRICULTURE.]

A NEW METHOD FOR MEASURING THE ELECTROLYTIC DISSOCIATION OF WATER.

BY C. S. HUDSON.

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In a recent article[1] it was shown that the measurements of the velocity coefficient of the mutarotation of glucose in acid, alkaline or neutral solutions are accurately expressed over the whole range by the formula

$$k = A + B(H^{\cdot}) + C(OH'),$$

where k is the velocity coefficient, A, B, and C are constants, and $H^{\cdot}$ and OH' are the concentrations of hydrogen- and hydroxyl-ions, respectively, in the solutions. For neutral solutions or pure water let the velocity coefficient be written k_w, and the hydrogen-ion concentration, which is equal for this case to that of the hydroxyl ion be written $H^{\cdot}_w$; the above formula then takes the form, for pure water or neutral solutions

$$k_w = A + (B + C)H^{\cdot}_w.$$

Solving this expression gives

$$H^{\cdot}_w = (k_w - A)/(B + C).$$

This relation gives a new method for measuring the hydrogen-ion concentration, or, in other words, the electrolytic dissociation of water, for the four quantities on the right-hand side of the equation can be determined experimentally by measuring the rate of mutarotation of glucose in ordinary distilled water and in acid and alkaline solutions. The first formula above is based on measurements of the rate of mutarotation of

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[1] THIS JOURNAL, **29**, 1571 (1907).