

CXIII.—*Polymorphism of Arsenic.*

By PORPHYRY NICOLAEVITCH LASCHTSCHENKO.

ARSENIC, like phosphorus, is known in three modifications: two crystalline, yellow and metallic arsenic, and one amorphous. The last variety has been least investigated. It is produced from yellow arsenic under the influence of light, by reduction of arsenious oxide, and also by sublimation of metallic arsenic. In the last method of preparation, there appear in order a mirror-like deposit, dark brown specks, and a grey crust, this being most remote from the source of heat.

The majority of authors deny the existence of two modifications of amorphous arsenic. Erdmann and Reppert (*Annalen*, 1908, **361**, 6) regard brown arsenic as the amorphous variety, of density (at 15°) 3.70, and deem the grey one an individual crystalline modification, of density 4.64. Besides difference in form, colour, and density, Erdmann ("Lehrbuch der anorganischen Chemie," 1910, p. 370) attributes to them different molecular compositions— As_8 for the brown, and As_2 for the grey arsenic—and gives 180° as the transition point of the brown and the grey forms.

According to Bettendorf (*Annalen*, 1867, **117**, 110) and Engel (*Compt. rend.*, 1883, **96**, 497, 1314) amorphous arsenic at 360° is transformed irreversibly and with considerable development of heat into the metallic form; Erdmann and Reppert (*loc. cit.*) refer the same point to 303°. Jolibois (*Compt. rend.*, 1911, **152**, 1767) and Gaubeau (*ibid.*, 1914, **158**, 121) determine the point of irreversible transformation both of brown and grey arsenic at 270–280°.

Discrepancies such as these, and the want of definite knowledge of the temperature and the heat of transition of metallic arsenic into the yellow modification, and also of the amorphous into the metallic form, furthermore, the interest attaching to the comparatively little investigated irreversible (monotropic) type of transformation, and the uncertainty of the data concerning the heat of fusion of arsenic, all these led the author to investigate the polymorphism of arsenic. The method adopted, consisting in the determination of the amount of heat evolved during the

cooling of a polymorphous substance, sealed in a quartz-glass tube, from various high temperatures down to that of the calorimeter, was first employed by Le Chatelier (*Compt. rend.*, 1908, **147**, 58) and has been described in detail in the author's previous papers (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1604; 1911, **43**, 793; 1913, **45**, 552; 1914, **46**, 311).

EXPERIMENTAL.

The metallic arsenic used was purified by sublimation in a vacuum. Its density, d_{16}^{15} 5.7301, was in fair agreement with the values recorded in the literature (Moissan, "Traité de chimie minérale," I, 808). The amorphous arsenic was prepared by reduction with tin of arsenious oxide dissolved in concentrated hydrochloric acid, its density, d_{16}^{15} 3.693, was determined pyknometrically in a mixture of spirit and water.

The results of measurements of the heat evolved on cooling are given in Tables I and II; in the first column are given the temperatures to which the arsenic had been heated, and in the second the amounts of heat (Q) evolved during the cooling of 1 gram of arsenic.

TABLE I.

Heat evolved on cooling of metallic arsenic. The highest temperature of the calorimeter = 11—12°.

Temp.	Q (cal.).	Temp.	Q (cal.).	Temp.	Q (cal.).	Temp.	Q (cal.).
173°	17.25	308°	25.27	435°	35.08	682°	57.75
196	18.19	317	26.58	450	35.14	714	62.06
216	19.25	332	27.00	475	37.92	738	62.63
217	19.96	354	27.67	538	44.07	750	72.61
250	21.54	376	28.90	595	50.61	775	74.60
258	21.92	400	30.82	628	53.44	822	76.46
300	25.00	414	34.00	659	57.31	868	136.76
						895	168.05

TABLE II.

Heat evolved on cooling of amorphous arsenic. The highest temperature of the calorimeter = 14—15°.

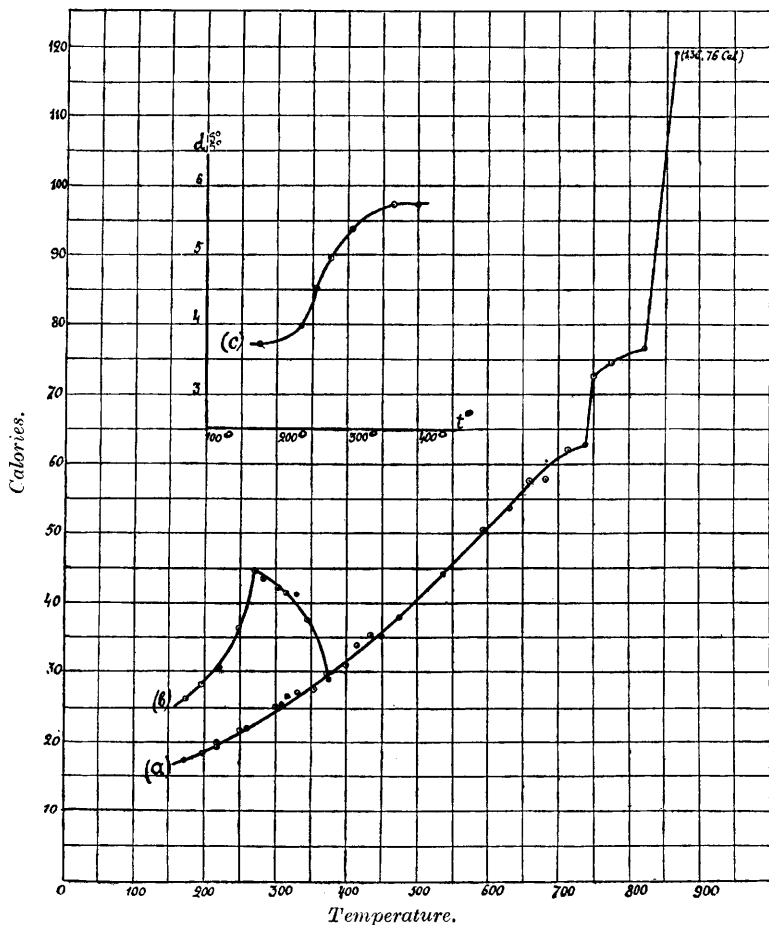
Temp.	Q (cal.).	Temp.	Q (cal.).	Temp.	Q (cal.).
173°	26.30	270°	44.68	330°	41.31
194	28.28	283	43.67	345	37.58
221	30.44	304	42.26	372	30.15
248	36.24	315	41.50		

The curves expressing the relation between the amount of heat evolved and the temperature are represented in Fig. 1.

In the case of metallic arsenic (α) a break in the curve occurs at 738—750°, and between 822—868° a sudden increase in the amount of heat evolved, owing certainly to fusion of arsenic, is to be noted. The first observations of the melting point of arsenic

were made by Landolt (1859) and Mellet (1872), who located this temperature between the melting points of antimony and silver (Moissan, *op. cit.*). In good agreement with this is Jonker's statement (*Z. anorg. Chem.*, 1909, **62**, 91) that arsenic heated in a sealed quartz-glass tube does not show any sign of fusion at 800°. How-

FIG. 1.



ever, Guntz and Broniewski (*Bull. Soc. chim.*, 1907, [iv], **1**, 977) deny the definite fusion point of arsenic. Schemtschuschny (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 1463) found that arsenic melts at about 624°. Other melting points recorded are 480° by Erdmann (*op. cit.*), 850° \pm 10° by Jolibois (*loc. cit.*), and 817° by Gaubeau (*loc. cit.*). The value deduced from measurements of

the heat evolved on cooling (Fig. 1, *a*) is in good agreement with the last two observations.

The latent heat of fusion of arsenic is unknown, and a particular difficulty attends its determination. When sublimed in a sealed tube, arsenic melts when its boiling point does not coincide with the temperature of fusion; in other words, at this temperature we have to deal with a triple point in the system: solid, liquid, and gaseous arsenic. Above this point, we have in a sealed tube a liquefied vapour of arsenic. At temperatures above 868° (Table I) the heat evolved on cooling increased very rapidly and irregularly and the experiments had to be discontinued because the tubes burst when placed in the calorimeter, diffusing a strong smell of garlic. This observation is noteworthy, as this characteristic smell is evidence of the presence of yellow arsenic.

Bettendorf (*loc. cit.*) observed the formation of the yellow modification when metallic arsenic was heated at a temperature near the melting point, but more exact information is wanting; the curve in Fig. 1 locates this point of transition of metallic into yellow arsenic between 738° and 750°, where the heat change amounts to about 7 calories per gram. The heat change at 624° observed by Schemtschuschny (*loc. cit.*), who heated arsenic above 700°, is probably attributable to this transition, for it cannot, as he supposed, be due to heat of fusion.

Turning to the curve for amorphous arsenic (Fig. 1, *b*) it is at once evident that its general form is typical of monotropic transformation. The same type of curve was obtained (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 793) in investigations of the transformation of aragonite into calcite. In this case, the quantities of heat given out by aragonite and calcite on cooling from about 400° are practically identical. At 445°, however, a distinct separation of the curves occurs; the heat evolved on cooling of aragonite increases rapidly until the temperature reaches 460–465°, but at 470° the curve again coincides with that of calcite. The attempt to trace the portion of the curve from the maximum to the points of coincidence failed, but here, on the curve for amorphous arsenic, a series of intermediate points was observed, furnishing evidence of the gradual transformation.

The change was also indicated by determinations of the density of amorphous arsenic which had been heated in sealed quartz-glass tubes and rapidly cooled to 15°. The results are as follows:—

Temp.	15°	175°	235°	255°	275°	305°	365°	400°
d_{15}^{15}	3.693	3.698	3.974	4.493	4.947	5.365	5.731	5.729

The corresponding curve (Fig. 1, *c*) is continuous, becoming horizontal at 360°. At 270–280° the density of amorphous

arsenic is equal to that of the grey modification, and at 360° to that of the metallic form.

The temperatures of transformation of amorphous arsenic into metallic arsenic recorded by Engel (360°) and by Jolibois and Gaubeau (270—280°) (see above) correspond respectively with the maximum point and the point of coincidence on the curve *b* (Fig. 1).

The questions now arise, Which of these points is the transition temperature? What is the nature of amorphous arsenic? What is the way of its irreversible and exothermic transformation into the metallic modification?

The close analogy between the polymorphism of arsenic and phosphorus suggests at once that, as in the case of red phosphorus (Cohen and Olie, *Z. physikal. Chem.*, 1910, **71**, 1), amorphous arsenic is a solid solution of the yellow and metallic forms. This view is supported not only by the change of density of amorphous arsenic with temperature (see above), but also by Engel's experiments (*loc. cit.*) on its sublimation. He found that the sublimation temperature of amorphous arsenic in a vacuum is 260°, whilst that of metallic arsenic is 450° (Conechy) or 616° (Jonker); at 360° sublimation ceases, but transformation of the amorphous into the metallic form may be effected by sufficiently prolonged sublimation at 310°. The deduction from these observations, which are analogous to those of Chapman for red phosphorus (Cohen and Olie, *loc. cit.*, p. 16), is that distillation of the more volatile component of a solid solution occurs and that metallic arsenic, which is non-volatile at this temperature, remains. In favour of this supposition is the fact that the density of brown (3.7) and grey (4.6) arsenic is the mean of the densities of the yellow (2.0; Erdmann) and metallic (5.7) forms.

The transformation of amorphous arsenic into metallic arsenic is, however, quite irreversible and consequently the most important feature of the supposed dynamical allotropy— $\text{As}_{\text{yellow}} \rightleftharpoons \text{As}_{\text{met.}}$ —namely, the reversibility, is absent.

Erdmann's hypothesis, that brown arsenic passes into the metallic form with intermediate production of the grey modification at 180°, the metallic form being ultimately obtained at 303°— $\text{As}_8 \rightarrow \text{As}_2 \rightarrow \text{As}_2$ —is not tenable because first, there is great doubt as to the existence of a critical point at 180° for amorphous arsenic, and, secondly, the hypothesis that such compositions may be assigned to the brown, grey, and metallic modifications of arsenic itself needs proof.

The relation between amorphous and metallic arsenic therefore remains an open question. The solution of the problem

would, however, appear to be closely connected with our conceptions of the amorphous state of matter. The modern colloid chemist denies the existence of an amorphous state of matter. In his view, amorphous substances are constituted of indefinitely crystalline individuals that have not yet attained their full form. Such "cryptocrystalline" structure, which is optically undetectable, has been attributed by some authors (Retgers, Linck, Cohen, Erdmann) both to amorphous arsenic and amorphous (red) phosphorus. However this may be, there is no doubt that the amorphism of brown arsenic, as well as of red phosphorus, is, not its primary, but its secondary state; the first product of the action of light on yellow arsenic or white phosphorus is colloidal. So also, amorphous arsenic is prepared by a method of reduction favourable to sol formation, and in the presence of stannous chloride the coagulation of this sol to dark brown flakes with a red tint can be observed. With regard to the grey variety, it is remarkable that it always appears as the secondary phase in the formation of amorphous arsenic. In this connexion Engel's remark (*loc. cit.*) deserves particular attention: grey arsenic is similar to the brown, but is composed of less dispersed particles. This is the more probable, since brown arsenic is to some extent soluble in carbon disulphide (Erdmann, *loc. cit.*), whereas the grey modification is quite insoluble. Regarded from this point of view, grey arsenic is not an allotropic modification at all, but is merely a stage in the continuous passage of arsenic from the colloidal state to the crystalline, a phenomenon observable in a number of cases and realisable experimentally (Janek, "Text-book of Colloid Chemistry," Petrograd, 1915, pp. 141—150). The production of grey arsenic from the brown form by heating is a step in the process; it occurs, as has been shown, just when the vapour pressure of amorphous arsenic becomes determinable and sublimation begins.

It was mentioned above that Erdmann records 303° as the temperature of transformation of amorphous arsenic, as at this temperature electrical conductivity becomes apparent in the amorphous modification. Repeating these experiments, the author found that this point depends on the conditions of heating and on the form and the distance apart of the electrodes, and is determined by the formation on the inner walls of the electrolytic tube of a very thin, mirror-like deposit by means of which contact is made; the contents of the tube consist of a baked, brittle, dark-grey mass, of density almost equal to that of grey arsenic. Thus, together with sublimation of amorphous arsenic in a sealed tube, there is the appearance of the first minute crystals of the metallic

form. This occurs at $270\text{--}280^\circ$, the maximum point on the curve *b* (Fig. 1). Above this temperature, the transformation proceeds by distillation of the metastable phase of the amorphous arsenic and condensation of the vapour in the form of the stable metallic modification. This continues up to 360° , at which temperature sublimation of the metastable phase ceases and the process of irreversible and exothermic transformation is practically finished.

PHYSICAL CHEMISTRY LABORATORY, POLYTECHNIC INSTITUTE,
NOWOČERKASSK, SOUTH RUSSIA. [Received, February 3rd, 1922.]
