

83. *Carbonyl Selenide. Part I. Preparation and Physical Properties.*

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CARBONYL sulphide, first prepared by Than (*Annalen, Suppl.*, 1867, **5**, 236), who obtained it contaminated with much carbon monoxide by passing the latter with sulphur vapour through a heated tube, is a well-characterised compound. By substituting selenium for sulphur, Berthelot (*Ann. Chim. Phys.*, 1901, **22**, 303) detected traces of this element in the outflowing gas. Rathke (*Annalen*, 1869, **152**, 199) heated phosphorus selenide, and von Barta (*Chem. Zeit.*, 1906, **30**, 1044) cadmium selenide, with carbon tetrachloride, and both reported the formation of complex mixtures described as containing carbonyl selenide, but in neither case was the substance separated or characterised. The latter worker also passed carbonyl chloride over cadmium selenide heated to redness, a method successfully applied to the production of the corresponding

sulphide by Nuricsàn (*Ber.*, 1891, **24**, 2967), and obtained a selenium-containing gas, alleged to be carbonyl selenide, which could not, however, be condensed even at -80° .

About two years ago, it was demonstrated in these laboratories that a gaseous selenium compound was undoubtedly produced when the element was heated with carbon monoxide, but attempts to isolate a suspected carbonyl of selenium were abandoned because only a trace of the material was obtained by any of the methods tried, which included the use of a carbon arc in an atmosphere of carbon monoxide and selenium vapour. Furthermore, owing to a spontaneous decomposition which the material underwent at every attempt to concentrate it (herein shown to be due to the presence of moisture) and to the appreciable solubility (now established) of carbon dioxide in the liquid substance, it was never obtained sufficiently pure for characterisation. When the present work was begun, therefore, our knowledge was restricted to the proof of the formation of a gaseous compound when carbon monoxide reacts with heated selenium. We have now demonstrated that this compound is *carbonyl selenide*, and that Berthelot had the gas in concentrations of 3–4% in carbon monoxide. Whether von Bartal's gas was selenium carbonyl has not yet been ascertained, but if so, his observation that it did not liquefy at -80° was in error by more than 55° .

The present communication describes the preparation of carbonyl selenide, its purification, and the determination of its physical properties. Further work dealing with its chemical properties is in progress.

EXPERIMENTAL.

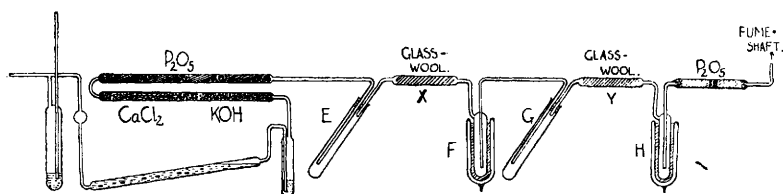
Preparation of Carbonyl Selenide.—Evidence is given of the presence of this compound if carbon monoxide which has been in contact with selenium at about 500° is passed through a glass tube heated with a Bunsen burner, the carbonyl selenide present being dissociated and a deposit of selenium formed on the glass beyond the heated zone. There is some carbon dioxide with the gas and if such a mixture be cooled by passage through a vessel submerged in liquid air, a white solid separates; but, in the earlier experiments mentioned above, when this was allowed to melt, some liberation of selenium took place which has now been shown to be due to the presence of traces of moisture.

In investigating the problem, we first ascertained the approximate proportion of the compound present in the issuing gas when carbon monoxide was passed over a weighed quantity of selenium heated in a vessel provided with a glass-wool filter to prevent the removal of the element in any condition condensable at the atmospheric

temperature. After the passage of a measured volume of gas, the selenium was reweighed, and the loss in weight taken as a measure of the carbonyl selenide formed. With a rate of 4 litres of carbon monoxide per hour, the proportion was about 3.6% by volume.

The final apparatus used is illustrated in Fig. 1; it consists of a safety valve, whence the carbon monoxide, prepared by the action of sulphuric acid on sodium formate, passed through the inclined tube and bubbler charged with a saturated solution of caustic potash, through the drying train containing successively potash pellets, fused calcium chloride, and phosphoric oxide, and then by way of a porcelain delivery tube into the porcelain test-tube E (25 cm. long, 3 cm. diameter) to the first condensing vessel F. After being relieved of its trace of carbonyl selenide, the carbon monoxide passed into a second porcelain test-tube G, and thence to the second condenser H and through a phosphoric oxide guard-tube to the fume-shaft. Each porcelain tube contained 10 g. of selenium,

FIG. 1.



previously freed from moisture by melting in a vacuum, and was heated to dull redness at its lower extremity by means of a blast Bunsen burner. The condensing vessels were submerged deeply in liquid air contained in Dewar flasks. That the separation was well-nigh complete was shown by the mere trace of deposit on the central limbs of the condensing tubes. The only difficulty experienced, through the choking of the glass-wool filters mounted at X and Y by a sublimate of selenium, was overcome by using a sufficiently large filtering area. The precautions to be observed in the experiment are dryness of all apparatus and reactants and a sufficiently rapid stream of carbon monoxide (at least 4 litres per hour).

A normal run lasted for 4 hours, and the collected solid yielded on melting about 1 c.c. of a colourless, mobile liquid. This was immediately distilled into a separate vessel by connecting receivers F and H in series with such a vessel cooled in liquid air, and allowing the material to evaporate in a slow stream of carbon monoxide. By this procedure certain possible less volatile impurities were eliminated, the presence of which in the original collecting vessels F and H was

shown by one or two minute droplets of a yellow, oily liquid which did not evaporate at the room temperature.

The distillate constituted the source of crude material for the determinations described below.

Gaseous Density.—A vessel of approximately 100-c.c. capacity (Fig. 2) was filled with the gas by displacement of dry carbon monoxide, and sealed off at x and x^1 under atmospheric pressure, the temperature being controlled by surrounding the vessel with pure ice. The following data were obtained :

Temp.	Corrected weight, g.	Corrected vol. at N.T.P., c.c.	Density at N. T. P., g./c.c.	M.
0°	0.2905	64.85	0.004479	100.3
99	0.3830	83.28	0.004599	103.0

The values for the molecular weight are only in approximate agreement with that required for carbonyl selenide, COSe, *viz.*, 107.2. The discrepancy may be due to the presence of either carbon monoxide or carbon dioxide, which are appreciably soluble in the liquid. Owing to the limited quantities of material at our disposal, never more than 4 c.c. at any one time, the Hofmann method was used as requiring only a small quantity as a definite fraction from a distillation. The fractionation was conducted in a vacuum, and the material was collected in bulbs (Fig. 3) designed to enable the tip to be broken off under mercury whilst it was itself held below the receiving tube with the material still in the solid state above the level of the mercury. The results, given below, show that the more volatile fractions are contaminated with a substance of lower density and b. p.

Sample.	Wt., g.	Corrected vol. at N.T.P., c.c.	Density at N.T.P., g./c.c.	M.
Extreme head fraction	0.1554	54.70	0.002841	63.62
Main head fraction	0.0253	5.78	0.004377	98.04
Middle fraction	0.0600	12.59	0.004766	106.80

Analysis.—The method of preparation and the gaseous density make it evident that the gas is *carbonyl selenide*, but this was finally proved by decomposing it by means of an electric discharge. In these circumstances, the compound dissociates quantitatively into carbon monoxide and selenium without change in gaseous volume, indicating that 1 mol. of the oxyselenide contains 1 mol. of carbon monoxide. About 0.025 g. of the liquid was sealed up in a small glass tube, the tip of which, after the contents had been frozen, was broken under mercury in such a way that the released gas was entrapped in a eudiometer over dry mercury, where it gave approximately 25 c.c. under the temperature and pressure conditions prevailing. This gas was decomposed by means of an electric spark,

and gave rise to a copious deposit of selenium both as a finely divided powder and as a film adhering to the walls, but sparking was continued until further dissociation was not evident, whereupon it was found that the volume had decreased by less than 1.6%. This slight reduction probably arose through adsorption on the very finely divided selenium produced in the decomposition.

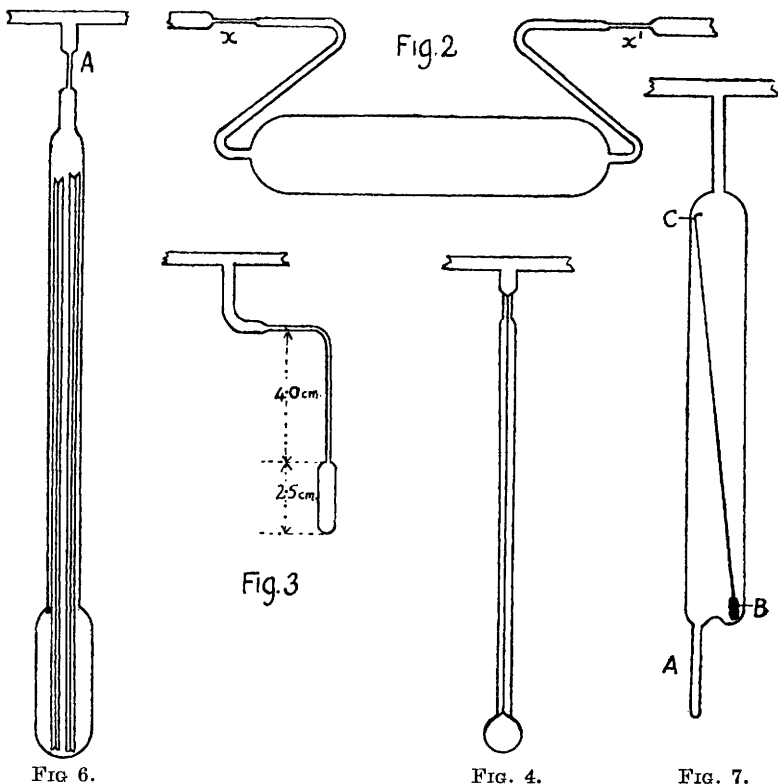


FIG. 6.

FIG. 4.

FIG. 7.

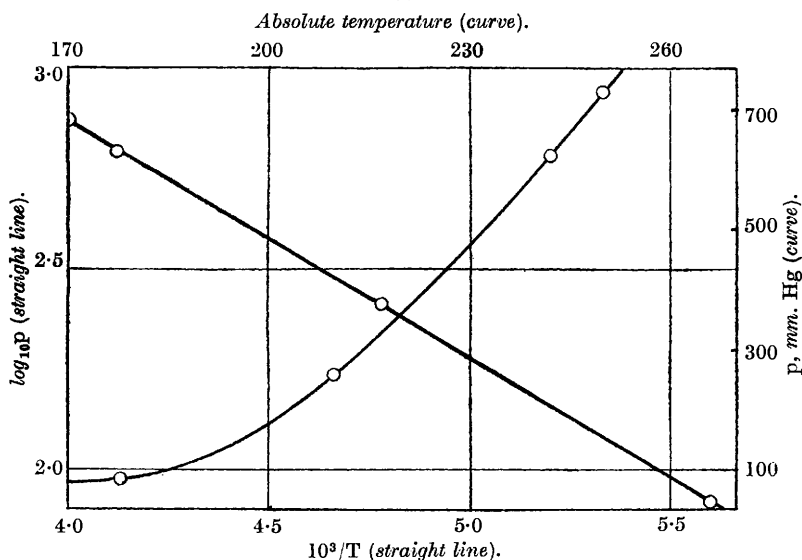
Liquid Density.—A vessel (Fig. 4) consisting of a stout-walled bulb connected to a capillary tube was attached to an evacuated system containing solid carbonyl selenide, and was partially filled with liquid by the usual procedure. The heights of the liquid, at a series of known temperatures, relative to a datum mark on the stem were measured by means of a cathetometer reading to 0.02 mm. Subsequently, the volume of the bulb and stem was ascertained by filling with water and weighing. The data (Table I) indicate a density of 1.812 g./c.c. at 4.1°, under the pressure of its own vapour and a coefficient of expansion of 0.001756 between 4.1° and 21.1°.

TABLE I.

	Temp.	Corrected vol. of liquid, c.c.	Weight of liquid, g.	D^c , g./c.c.
Preliminary detn. on bulk sample	{ 0.0° 16.2	0.1642 0.1699	0.2977 0.2977	1.813 1.752
Final detn. on middle fraction	{ 4.1 21.1	0.1877 0.1933	0.3401 0.3401	1.812 1.759

Vapour Pressure.—About 2 c.c. of material which had been carefully freed from lower-boiling impurities by repeated fractional distillation were sealed in a wide tube connected through a wide side arm to a mercury manometer in the form of a U-tube open at its

FIG. 5.



remote side to the atmosphere. The mercury had been especially dried, and precautions were taken to ensure that no gas was entrapped against the glass. Observations were made with the fluid maintained at definite temperatures by means of partially frozen pure liquids (bromobenzene, -30.6° ; chloroform, -63.5° ; toluene, -94.5°) held in a Dewar vessel, and these are set out in Table II and plotted in Fig. 5.

TABLE II.

Temp., C.	Temp., Abs.	p , mm.	$10^3/T$.	$\log_{10} p$.
-22.9°	250.1°	725.0	3.998	2.8603
-30.6	242.4	620.0	4.126	2.7924
-63.5	209.5	257.2	4.773	2.4102
-94.5	178.5	83.3	5.603	1.9206

Surface Tension.—The method of capillary rise was employed for the determination of the surface tension of the liquid, two tubes (D and F, data given by Mills and Robinson, J., 1927, 1823) being used. These were supported in a vessel (Fig. 6), which after being filled with a suitable quantity of the liquid in a vacuum, was sealed off at A. The difference in level in the capillaries was measured by means of the cathetometer already mentioned, the temperature being controlled in a suitable thermostatic bath. The differences were read many times, and before each set, the level of the liquid in the capillaries was raised so that all measurements were made on a falling meniscus.

The values of the surface tension were calculated from the formula $\gamma = r_1 r_2 g (3h + r_2 - r_1) (D - d) / 6(r_1 - r_2)$. The results obtained, summarised in Table III, give a value of 19.32 dynes per cm. for the surface tension at 4.1°, and a temperature coefficient of 0.156 dyne per cm. per degree between 4.1° and 21.6°.

TABLE III.

	Temp.	D^* , g./c.c.	d , g./c.c.	h , mm.	γ , dynes/cm.	$[P]$.
Preliminary detn. on bulk sample	$\left\{ \begin{array}{l} 3.0^\circ \\ 20.4 \end{array} \right.$	1.813	0.009	3.80	19.64	125.1
Final detn. on middle fraction	$\left\{ \begin{array}{l} 4.1 \\ 21.6 \end{array} \right.$	1.811	0.009	3.74	19.32	124.8
		1.725	0.013	3.36	16.45	126.1

Parachor.—By using the values of γ at 4.1° and 21.6°, the parachors $[P]$ of carbonyl selenide at these temperatures were obtained *viz.*, 124.8 and 126.1 respectively (Calc. : 133.7, from C = 4.8, O = 20.0, Se = 62.5; F = 23.2). The parachor of selenium deduced from the foregoing data is 55.5, which, although several units below the mean value of previous determinations, appears to merit confidence in view of the nature and purity of the material employed, at least in so far as it relates to selenium when in combination with carbon monoxide.

Melting Point.—Owing to the small quantity of material available in the earlier stages of the research, and to the lowness of the m. p. (below -100°), a method was devised whereby melting points at extremely low temperatures may be determined with accuracy.

Enough carbonyl selenide to provide about 0.25 c.c. of liquid was condensed in a vessel (Fig. 7) provided with a small prolongation (0.25 cm. diameter, 4 cm. long) at A, in which the rod B carrying the pointer C fitted easily. By suitable manipulation, the material was all condensed in A, and then frozen solid. The rod B was then shaken into A, and rested on the top of the solid, and a thermocouple was bound close to the outside of A. The vessel was then allowed to warm up slowly in a packing of cotton wool which had

been saturated at first with liquid air and was accommodated in a Dewar vessel. The temperature at which the top of the pointer C began to move was taken as the m. p. Separate observations yielded the values -122.0° , -122.2° , and -122.0° ; mean -122.1° . The chromel-eureka thermocouple was calibrated in the following standards: melting carbon tetrachloride (-22.9°), bromobenzene (-30.5°), chloroform (-63.5°), solid carbon dioxide in acetone (-79.2°), ethyl acetate (-83.6°), toluene (-94.5°), ether (-116.2°), and the eutectic of ether and toluene (-127.2°). In all experiments the cold junction was surrounded by melting ice. The potential measurements involved were made with a thermocouple potentiometer reading to one microvolt with a 500-ohm A. and M. galvanometer which gave a scale deflexion of 11 mm. per 0.01 millivolt.*

The value of the m. p. was subsequently determined by allowing some 4 g. of solid to melt round a thermocouple junction. The temperature recorded, which remained steady for 20 minutes, was -122.2° .

Boiling Point.—The b. p. was determined by allowing about 4 g. of liquid to boil at the atmospheric pressure into an atmosphere of dry nitrogen, a thermocouple junction in a very thin glass sheath being supported in the vapour just above the liquid. The temperature remained constant for 25 minutes at $-22.9^\circ \pm 0.2^\circ/725.0$ mm. This was confirmed by measurements on an independently prepared sample.

Critical Temperature.—For the determination of the critical temperature, a stout-walled tube, 0.75 cm. diameter by 10 cm. long, was one-third filled with liquid carbonyl selenide in a vacuum, and sealed. The tube was bound to a standardised thermometer, and suspended in a well-stirred bath of colourless liquid paraffin, which could be heated or cooled at will. The phenomena were observed on cooling, and the temperature of formation of the meniscus in the cloud in the change of vapour to liquid taken as the critical temperature. Several successive readings gave 121.1° , with a probable error of $\pm 0.2^\circ$.

Discussion and Summary.

Carbonyl selenide, prepared by the action of carbon monoxide on heated selenium, is a colourless evil-smelling gas, condensing to a colourless, mobile liquid, b. p. $-22.9^\circ \pm 0.2^\circ/725$ mm., and

* So far as actual temperature measurements were concerned, an accuracy of $\pm 0.025^\circ$ may be claimed. Consideration of the accuracy of the fixed points used leads to the view that the results may be trusted to $\pm 0.5^\circ$, but that they are probably even more accurate.

freezing to a snow-white, crystalline solid, m. p. $122.1 \pm 0.5^\circ$. Its critical temperature is $121.1^\circ \pm 0.2^\circ$. Its gaseous density agrees with the formula COSe and analysis supports this conclusion. The liquid density is 1.812 g./c.c. at 4.1° , and the molecular volume 59.2 at the same temperature; the coefficient of thermal expansion is 0.001756 between 4.1° and 21.1° . The surface tension is 19.32 ± 0.1 dynes/cm. at 4.1° , with a temperature coefficient of 0.156 dyne/cm. between this temperature and 21.6° . Substitution of the determined surface tension and critical temperature in the Eötvös-Ramsay-Shields equation leads to a value for K of 2.4, which indicates that the liquid is not associated. The observed parachor is 126.2 (Calc. : 133.7).

In Table IV the physical properties of carbonyl selenide are compared with those of its sulphur analogue.

TABLE IV.

	Carbonyl selenide.	Carbonyl sulphide.
M. p.	-122.2°	-138.2°
B. p.	-22.9°	-50.2°
$d_4^{4.1}$	1.811	1.062*
γ at 4.1° , dynes/cm.	19.32	12.71*
Critical temperature	121.1°	105°

* This vol., p. 661.

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