[COMMUNICATION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANITOBA]

The Density of Selenium

BY A. N. CAMPBELL AND S. EPSTEIN

The only figures in existence for the density of liquid selenium are those of Dobinski and Wesolowski,[1] who carried their measurements up to 350° and reported a straight-line relationship between density and temperature. They made their determinations by a plummet method and, in view of the high viscosity of liquid selenium, we thought it desirable to repeat their measurements by an independent, pycnometric method. We extended our measurements to certain of the solid forms also.

Experimental

The selenium was of two kinds: (a) pure, from British Drug Houses, (b) crude. The crude material was purified by the method of Hugot,[2] followed by sublimation of the red amorphous selenium under reduced pressure: vitreous selenium was thus obtained. The results obtained with both samples were practically identical.

The method was to melt the selenium under an inert liquid in a calibrated pycnometer which was constructed of combustion tubing, since it was found that anything frailer than this cracked under the expansion of the solidified selenium. The inert liquid was Russian mineral oil (Paraffinol). The density of this oil was determined between 20 and 300° and was found to be represented by the equation

$$D = 0.8823 - 0.000622(t - 20.5)$$

but, of course, the density will vary somewhat for different samples.

Enough selenium (about 80 g.) was introduced to fill about three quarters of the pycnometer, when the selenium was molten. The oil was then added and the pycnometer kept in a bath at 250° until the selenium had melted. While the selenium was liquid, air bubbles were expelled by tapping and suction.

Before using the Paraffinol, experiments were carried out to determine its suitability. Its boiling point was found to be in the neighborhood of 310°. The solubility of selenium in the boiling oil was found to be 0.0013 g. per cc. of oil. The selenium did not react chemically with the oil for, on cooling the hot saturated oil, red selenium precipitated.

Density determinations for liquid selenium were made at temperatures ranging from 227 to 277°. Determinations at higher temperature were unsatisfactory because bubbles of vapor were evolved after prolonged heating. In all determinations the selenium was kept at one temperature for two hours to ensure attainment of a possible internal equilibrium. All determinations were repeated, with very good agreement.

(1) Dobinski and Wesolowski. Bull. intern. akad. polon. sci., Classe sci. math. nat., No. 8–9A. 446 (1936).
(2) Cf. Hittorf. Pogg. Ann.. 84, 214 (1851).

The Paraffinol proved to be too viscous for determining the density of solid (metallic) selenium. Benzyl benzoate gave satisfactory results. The density of benzyl benzoate at various temperatures is given in Table I.

TABLE I

Temperature in °C.	d^t_4
21.8	1.12000
175.0	0.99359
193.0	0.97723
203.0	0.96834

These results can be expressed by the equation

$$D = 1.12001 - 0.000834(t - 22)$$

After the powdered selenium had been introduced into the pycnometer, weighed and covered with benzyl benzoate, it was heated for several hours at 150° to ensure conversion of all the selenium into the metallic state. The results for metallic and for liquid selenium are contained in Table II.

TABLE II

in °C.	Exptl.	d^t_4 Calcd.	Δd	Dobinski and Wesolowski[1]
		Metallic Selenium		
20.4	4.7924	4.7966	+0.0040	4.80 (at 17°,
90.0	4.7641	4.7560	− .0081	"Int. Crit.
159.5	4.7152	4.7165	+ .0013	Tables")[a]
188.5	4.6954	4.6989	+ .0035	
197.5	4.6940	4.6937	− .0003	
205.5	4.6919	4.6891	− .0028	
		Liquid Selenium		
225	3.9705	3.9727	+ .0022	3.976
241	3.9540	3.9479	− .0061	3.955
244.5	3.9394	3.9424	+ .0030	3.947
257	3.9276	3.9236	− .0040	3.929
277	3.8904	3.8925	+ .0024	3.891

[a] The figures of Kruyt [Z. anorg. Chem., 64, 310 (1909)] for the density of metallic selenium cannot refer to stable states; he gives densities ranging from 4.49 to 4.63. These figures are interpreted along the lines of Smits' theory of pseudo-components. The most recent treatment along these lines is that of Briegleb [Z. physik. Chem., 144, 321 (1929)].

In Table II, "t" represents the temperature, "d Exptl." the values of density obtained experimentally, and "d Calcd." those obtained from the formulas

$$D = 4.8073 - 0.0005753t \quad \text{(for metallic selenium)}$$

and

$$D = 3.9851 - 0.001551(t - 217) \quad \text{(for liquid selenium)}$$

These formulas were computed from the experimental results by the method of least squares: Δd represents the difference between "d Calcd." and "d Exptl." The figures calculated from Dobinski and Wesolowski's equation are given in the fifth column.

The density of vitreous selenium was also determined. In order to ensure that the sample might consist, as far as possible, entirely of vitreous selenium, liquid selenium was quenched in a steel mold. It was found possible only to determine the density of this form at room temperature because at higher temperatures, e. g., 90°, the velocity of conversion to the stable metallic form was appreciably great. The result obtained was: $d^{21.8}{}_4 = 4.2524$.

Discussion

The formula obtained by Dobinski and Wesolowski for the density of liquid selenium is

$$D = 3.987 - 0.0016(t - 220)$$

The close agreement of Dobinski and Wesolowski's results with ours shows the suitability of the methods employed by both. The conclusion is that the results of Dobinski and Wesolowski are equally reliable throughout their range of measurement, i. e., up to 345°. The linear relationship between density and temperature indicates that as far as density is concerned the behavior

of both solid and liquid selenium is quite regular, i. e., unaccompanied by a shifting internal equilibrium.

From our results, the change in volume on melting results as +0.03737 cc. per gram. Taking the heat of fusion as 13.4 cal. per gram,[3] we obtain for the change in fusion temperature with pressure +0.033° per atmosphere. This seems abnormally large and might make selenium an interesting subject for pressure experiments.

Summary

The densities of selenium (metallic and liquid) have been measured over the range 20–277°. In agreement with the conclusion of Dobinski and Wesolowski[1] these measurements give no indication of a shifting internal equilibrium. The rise of the melting point with pressure has been calculated.

(3) Mondain and Monval, *Bull. soc. chim.*, [4] **39**, 1349 (1926).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANITOBA]

The Systems: LiNO₃–NH₄NO₃ and LiNO₃–NH₄NO₃–H₂O

BY A. N. CAMPBELL

The system $LiNO_3$–NH_4NO_3 is interesting as one of the series of binary systems consisting of NH_4NO_3 and the nitrates of the univalent metals, viz., $TlNO_3$, $AgNO_3$, $LiNO_3$, $NaNO_3$, KNO_3, all which have been studied. In some of these systems, compound formation occurs, in others solid solution, and in others again, the equilibrium diagram is of the simple eutectic form, unaccompanied by solid solution. This appears to be the case with lithium nitrate, according to Perman and Harrison,[1] who investigated the system up to a content of 45% $LiNO_3$.

Certain of the observations of Perman and Harrison are important in the present work and I quote: "On increasing the proportion of lithium salt, the stability was reduced, so that the range of the experiments at higher temperatures was very limited." I have not found this to be the case; on the contrary, measurements were carried as high as 230° (in presence of $LiNO_3$) before decomposition invalidated the results.

"The curve shows the usual two branches, with a eutectic at 97° and 25% $LiNO_3$. There is,

however, a marked break in the left branch at 122° indicating a change (on cooling) from the δ to the γ-form of NH_4NO_3.

"A cooling curve was obtained for $LiNO_3$ (in a separate experiment) between 265° (its melting point) and 80°. It showed no breaks, thus proving that this salt exists in but one crystalline form between these limits of temperature."

I have repeated the work of Perman and Harrison, using a refined technique, and have carried the measurements to a higher content of lithium nitrate. The technique used was that of metallurgical practice, and consisted essentially in the use of a neutral body and two thermocouples in opposition: very small thermal changes in the system are thus rendered evident by large displacements of a sensitive galvanometer: the method is due to Roberts-Austen.[2] In the course of this investigation I frequently detected a point of recalescence which led me to suspect either limited solid solubility or the existence of a compound with incongruent melting point. I there-

(1) Perman and Harrison. *J. Chem. Soc.*, **125**, 1709 (1924).

(2) Fifth Report. Alloys Research Committee. *Proc. Inst. Mech. Engrs.* (London), (1899).