TABLE V. Heat of evaporation of argon.

θ	$\varrho_{r\,vap.}$	$\varrho_{r\,liq.}$	$\lambda_{liq.\,vap.}$ in cal.
— 125.49	0.28727	0.78303	12.916
— 129.83	0.21451	0.88342	17.821
— 134.72	0.16621	0.96258	21.014
— 140.80	0.12115	1.04134	24.105
— 150.57	0.06854	1.13680	29.672
— 161.23	0 03723	1.22414	33.005
— 183.06	0.00814	1.37338	35.001

In conclusion I offer my hearty thanks to Prof. KAMERLINGH ONNES for the interest which he has taken in my work.

Chemistry. — "*The Allotropy of Cadmium.*" I. By Prof. ERNST COHEN and W. D. HELDERMAN.

1. In a paper which will be published in the Zeitschrift fur physik. Chemie one of us (C.) proved in collaboration with Mr. A. L. TH. MOESVELD, that bismuth is capable of existing in more than one allotropic modification and that there is a transition temperature at 75° of the enantiotropic transformation

$$\text{Bismuth } \alpha \overset{75^\circ}{\rightleftarrows} \text{Bismuth } \beta.$$

In that paper we mention that we had found in a publication of MATTHIESSEN and VON BOSE[1]) (on the electric conductivity of metals, published in 1862) certain indications which justified the presumption that other metals which till now are only known in one modification would show the same behaviour as bismuth (and tin). The following clauses may be quoted from MATTHIESSEN and VON BOSE's paper as referring specially to the metal cadmium:

"Die nach mehrtagigem Erhitzen auf 100° erhaltenen Veränderungen in der Leitungsfähigkeit der Drahte, sind unglücklicher Weise verloren gegangen. Es mag bemerkt werden, dass die Veränderungen sehr gering waren und dass eine Abnahme in der

[1]) POGGENDORFF's Ann. **115**, 353 (1862).

Leitungsfähigkeit stattfand", and "Wenn reines Kadmium über 80°C. erhitzt wird, so wird es äusserst spröde, ja, es kann sogar in einem heissen Mörser mit der grössten Leichtigkeit gepulvert werden. Wir würden die Bestimmungen der Drähte nicht haben ausführen können, wenn sie nicht überfirnisst gewesen wären, da sie sonst durch das Bewegen des Oeles beim Umrühren in Stücke zerfallen wären. Es ist bemerkenswert, dass diese Aenderung in der molekularen Beschaffenheit der Drähte nicht irgend erheblich in der Leitungsfähigkeit sichtbar wird."

These remarks formed the starting point of the following research.

2. The experiments on tin and bismuth had proved that metals may show very great retardation in undergoing molecular changes, at temperatures either above or below their transitionpoints. This reluctance to undergo change is doubtless one of the reasons why the allotropy of the metals mentioned above, which play an important role in industry, remained undiscovered until so late a period.

Anticipating our results with cadmium, we state that the same may be said about this metal. Cadmium gives at 65° C. an allotropic (enantiotropic) modification; the very strongly marked retardations have concealed the allotropic change from the numerous investigators who studied this metal in different directions.

3. Until the present we have used two methods of investigation.

a. Experiments with the Pycnometer.

The details of these determinations will be described in our paper in the Zeitschrift für physikalische Chemie.

We used a form of pycnometer which has already been described (volume about 25 cc.). The thermometers which could be read with an error not exceeding 0°.01 had been compared with a standard of the Phys. Techn. Reichsanstalt at Charlottenburg—Berlin. Generally we used water as a liquid in the pycnometer, but as a control we sometimes substituted paraffineoil for it.

All determinations we carried out in duplicate (using 16—30 grams of the metal). The difference between two of these never exceeded three units in the third decimal place. The metal (Cadmium-"Kahlbaum") was purchased from KAHLBAUM—Berlin. We were not able to detect any impurity in 100 grams of the material. We received it in two consignments (flat rods) which we shall distinguish by the letters K_1 and K_2.

The density of K_1 we found to be:

$$d\frac{25^\circ}{4^\circ}\ 8.635;\ 8.632;\ 8.633;\ 8.633\ \text{mean}\ \mathbf{8.633}$$

in independent determinations, taking fresh quantities each time. For K_2 we found:

$$d\frac{25^\circ}{4^\circ}\ 8.641;\ 8.644;\ 8.642,\ \text{mean}\ \mathbf{8.643}$$

4. After heating K_1 at a temperature of 150° during 95 hours in a current of dry carbon-dioxyde which was freed from oxygen, we found:

$$d\frac{25^\circ}{4^\circ}\ 8.630\ \text{and}\ 8.633.$$

These figures show that the density of the metal had not been changed by the heating.

5. As there was a possibility that we had passed a transition point, but that cadmium showed similar retardations to those which we had found in the case of bismuth (and tin), we heated a certain amount of K_2 $\left(d\frac{25^\circ}{4^\circ} = 8.643\right)$ during 3 days and nights at 100° in contact with a dilute solution of cadmiumsulphate. After this time the metal was chilled (at 0°) and washed with water, dilute hydrochloric acid (these liquids had been cooled) alcohol and aether. It was then dried at 30°. Two determinations of the density gave:

$$d\frac{25^\circ}{4^\circ} = 8.633\ \text{(and 8.633)}$$

This experiment showed, that by heating at 100° a change had been produced in the metal which lowered its density (measured at 25°.0) by 10 units in the third decimal place; our duplicate determinations prove that this difference exceeds considerably our experimental errors.

6. In order to determine if a change of density takes place at temperatures below 100°, we warmed the metal $\left(d\frac{25^\circ}{4^\circ}\ 8.633\ \text{and}\ 8.633\right)$ again in contact with a solution of cadmiumsulphate during 14 hours at a temperature of 60°—70°. After the manipulation the metal was chilled, washed, and dried in the manner described above. Its density was now:

$$d\frac{25^\circ}{4^\circ}\ 8.620,$$

which proves that there occurs at 60—70° a diminution of the density of 11 units in the third decimal place.

7. We repeated the experiment described in § 6 with the specimen the density of which was now $d\frac{25^\circ}{4^\circ}$ 8.620, keeping it this time

during 24 hours at 40°. We found:

$$d\frac{25^0}{4^0}\text{8.642 and 8.643.}$$

Its density (taken at 25°.0) showed an increase of 22 units in the third decimal place.

8. The experiment of § 6 was repeated again with the metal that had now a density of $d\frac{25^0}{4^0}$ 8.642 (8.643) (Vide § 7). After having kept it during 24 hours at 60—70° in a solution of cadmium-sulphate, we found (after chilling, washing etc.):

$$d\frac{25^0}{4^0}\text{ 8.631 and 8.633.}$$

At 60—70° there has been again a *decrease* of 10 units in the third decimal place.

9. The experiments of § 5—8 prove that there is a transitiontemperature between 40° and 70°.

10. In order to fix this temperature more closely, we carried out the following

b. Experiments with the Dilatometer.

In order to measure as accurately as possible the changes of volume which the metal undergoes within short times, we used 360 grams of our metal K_2.

After having reduced the metal to turnings, we heated it during 24 hours in contact with a solution of cadmiumsulphate. The metal was then chilled and washed and transferred into a dilatometer which was then filled with paraffineoil. This had been heated for some hours at 200° (under reduced pressure) in contact with finely divided cadmium, until there was no more evolution of gasbubbles.

In order to reduce as far as possible the quantity of this oil the expansion of which would have made the measurements more troublesome, a quantity of small glass-beads was put into the bulb.

11. The dilatometer was now kept at different but constant temperatures by means of an electrically heated thermostat which we shall describe in full later. The temperatures at which the readings of the meniscus were made, remained constant within 0.002 degrees. (A Beckmann-thermometer was used in the thermostat). By this device the dilatometer becomes an instrument of precision.

The results are given in the following tables [1]).

[1]) The capillary tube (diameter of bore 1 mm.) was bent into a horizontal position.

TABLE I.

Temperature	Duration of the observations in hours.	Rise of the level of oil in mm.	Rise in mm. per hour
49°60	$10^1/_2$	— 1500	— 140
59.60	5	— 233	— 46
60.45	$3^1/_2$	— 66	— 19
€2.40	$9^1/_2$	— 74	— 8
64.90	4	0	0
66.90	$16^1/_2$	+ 53	+ 3
84.40	6	+ 267	+ 44

With a second dilatometer we got the following results:

TABLE II.

Temperature	Duration of the observations in hours.	Rise of the level of oil in mm.	Rise in mm. per hour
62°.4	$5^1/_2$	— 246	— 44
64.7	9	— 59	— 7
64.8	15	— 57	— 4
65 0	$4^1/_2$	+ 32	+ 7

The transition temperature has thus been fixed at **64°.9** within 0.1 degree.

12. It may be pointed out here that the expansion which accompanies the transition of Cadmium-α into Cadmium-β (at 64°.9) explains the disintegration of cadmium wires observed at 80° by MATTHIESSEN and VON BOSE.

13. We hope to be able to give shortly the details and conclusions of our research, as well as the values of the density for the two pure modifications of cadmium.

Utrecht, October 1913. VAN 'T HOFF-Laboratory.

(November 27, 1913).

ERRATUM.

In the paper *on canonical elements* by Prof. W. DE SITTER in the Proceedings for September:

pages 290—291: From page 290 line 19: "In the same way ...."
to page 291 line 21: "We then have"

should be inserted on page 289 between the lines 19 and 20, after "... already quoted".