

Citation:

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Chemistry. — “*The metastability of the metals in consequence of allotropy and its significance for Chemistry, Physics, and Technics*”. II. By Prof. ERNST COHEN.

The specific heat of the metals 1.

1. In my first paper ¹⁾ on this subject I called attention to the fact that the physical constants of the metals hitherto known, are to be considered as entirely fortuitous values which depend on the previous thermal history of the material used.

In that paper I wrote with regard to the specific heat of the metals: Considering, for instance, the important part which the specific heats of the metals have played in chemistry and physics during the last few years, it is evident that a revision of these constants is wanted.

2. Reviewing the earlier literature dealing with this constant, I found that it contains already a number of data which prove unequivocally that the specific heat of the metals does indeed depend on their previous thermal history.

LE VERRIER published in the year 1892 a paper ²⁾ “sur la chaleur spécifique des métaux”, in which he describes his measurements with copper, zinc, lead, aluminium, and silver. The calorimetric determinations were carried out between 0° and 1000° by the method of mixtures. The temperature of the metal at the moment at which it was brought into the calorimeter was determined by means of a LE CHATELIER pyrometer.

3. LE VERRIER stated that the mean specific heat remains as a rule constant till 200–300°, after which it changes abruptly, as PIONCHON ³⁾ also found in the case of iron, nickel and cobalt.

The variation of the total heat (i. e. the quantity of heat required to raise the temperature of 1 gr. of the substance from 0° to t° C.) with the temperature is consequently to be represented by a curve with breaks and not by a continuous one.

In the neighbourhood of these breaks the condition of the metals is not only a function of the temperature, but also of their previous thermal history.

¹⁾ These Proc. **16**, 632 (1913).

²⁾ C. R. **114**, 907 (1892).

³⁾ C. R. **102**, 675, 1454 (1886); **103**, 1122 (1886). In full: Ann. de Chim. et de Phys. (6) **11**, 33 (1887).

As a consequence of the retardations in the structural change (changements d'état) of the metal, a different value of the total heat is found on cooling from that on heating.

If a certain piece of metal is cooled or heated repeatedly, different values for the total heat are found. If we start from a lower temperature and return to it after having overpassed the break in the curve of total heat, a closed and not a single curve is obtained.

4. This result is in complete harmony with the dilatometric and electromotive force measurements carried out by myself in collaboration with messrs. HELDERMAN and MOESVELD, on copper, cadmium, zinc and bismuth, measurements which led to the conclusion mentioned above.

5. LE VERRIER'S paper contains some interesting data which we shall now consider in connection with our dilatometric and electromotive force measurements.

The curve representing the variation of the total heat of copper as a function of the temperature, consists of four parts. At 350° an absorption of 2 Cal. occurs; at 550° an absorption of 2 Cal.; while at 750°, 3.5 Cal. are absorbed.

Thus, while our dilatometric measurements proved that there exist more than two modifications of copper, the same fact was noted a long time before by LE VERRIER, using a different method.

The measurements of LE VERRIER which are summarized in table I, have, however, been quite overlooked hitherto.

It may be pointed out here that the transition temperatures which can be deduced from LE VERRIER'S determinations will generally be too high. This is a consequence of the retardation of the molecular changes, which were also observed by him. Fresh experiments with the pure modifications of the different metals will throw light upon this point.

6. From the determinations of LE VERRIER there follows also, that there exists a transition point for lead which has so far been unknown. Experiments in this direction are in progress in my laboratory.

7. The same may be said with regard to silver.

8. Aluminium shows, according to LE VERRIER, an absorption of 10 Cal. at 535°. It may be pointed out that DITTENBERGER (Phys. Techn. Reichsanstalt at Charlottenburg—Berlin) proved ten years

TABLE I

Temperature.	Mean spec. heat.	Total heat.
Pb.		
0—230°	0.038	$0.038 \times t$
220—250	Almost nil.	Almost constant.
250—300	0.0465	$8.15 + 0.0465(t-250)$
Zn.		
0—110°	0.096	$0.096 \times t$
100—140 very variable	absorption of 0.8 Cal. in the neighbourhood of 110°	
110—300	0.105	$11.36 + 0.105(t-110)$
300—400	0.122	$31.4 + 0.122(t-300)$ increases rapidly above 400° and amounts to 46 Cal. in the neighbourhood of 410° immediately before melting.
Al.		
0—300°	0.22	$0.22 t$
300—530	0.30	$65 + 0.30(t-300)$
530—560	The crystallization of the silicium occurs at $\pm 500^\circ$ and the break lies with Al which contains Si in the neighbourhood of this temperature	Absorption of 10 Cal. in the neighbourhood of 535°
540—600		$139 + 0.46(t-530)$ 170 Cal. at $\pm 600^\circ$; increases rapidly and exceeds 200 before melting (620°).
Ag.		
0—260°	0.0565	$0.0565 t$
260—660	0.075	$14.7 + 0.075(t-260)$
660—900	0.066	$44.7 + 0.066(t-660)$ 62 Cal. at ± 930 , immediately below the melting point.
Cu.		
0—360°	0.104	$0.104 t$
320—380	0.104	Absorption of 2 Cal. at $\pm 350^\circ$
360—580	0.125	$37.2 + 0.125(t-360)$
560—600	0.125	Absorption of 2 Cal. at $\pm 580^\circ$
580—780	0.09	$37 + 0.09(t-580)$
740—800	0.09	Absorption of 3.5 Cal. at $\pm 780^\circ$
780—1000	0.118	$92 + 0.118(t-800)$ 117 Cal. at $\pm 1020^\circ$.

after LE VERRIER that this metal is capable of existing in more than one allotropic modification and he found a transition temperature between 500 and 600°. I hope shortly to report on this point, in connexion also with a question which is important from a technical standpoint i.e. the disintegration of aluminium objects at room temperature, a disease which is the cause of a good many complaints in industrial circles as well as in daily life.

9. That others had never observed the phenomena described by LE VERRIER may be explained by the fact that they had not heated their preparations *repeatedly* to high temperatures, as he did. We have also observed during our dilatometric researches that such a transition point can be overpassed several hundreds of degrees without any effect. If on the contrary the metal is repeatedly cooled and heated the transition is "set going". As the means of overcoming these retardations are now known we are able to avoid them. A systematic research in this direction is now possible and I hope to report shortly on it.

Utrecht, June 1914.

VAN 'T HOFF-Laboratory.

Physics. — "*Measurements of isotherms of hydrogen at 20° C. and 15°.5 C.*" By Prof. PH. KOHNSTAMM and Dr. K. W. WALSTRA. VAN DER WAALS fund researches N°. 7. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of April 24, 1914).

§ 1. *Choice of the substance and the temperature.*

With the apparatus described in N°. 5 and 6 of this series we have made measurements of hydrogen isotherms at 20° C. and 15°.5 C. This choice was led by the following considerations. As we already set forth in the beginning of Communication N°. 5, one of the motives of our research was the desire to be able to make an accurate comparison with the results obtained by AMAGAT. Our first intention was to determine anew AMAGAT's air isotherms; then we were, however, checked by peculiar difficulties. Every time, namely, when a measuring tube was filled with air in the way described in the previous Communication, and was then left for