

**Chemistry.** — *The Exact Measurement of the Specific Heats of Solid Substances at High Temperatures. XI. On the Remarkable Behaviour of Beryllium after preliminary Heating above 420° C.* By F. M. JAEGER and E. ROSENBOHM.

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§ 1. In the course of our precision-measurements of the specific heats of metals executed in this laboratory<sup>1)</sup>, we were confronted by serious difficulties in the case of *beryllium*, as soon as the metal was heated at temperatures above 420° C. Two very pure samples of the metal were at our disposal: one obtained from SIEMENS and HALSKE in Berlin, the other from the *American Beryllium Company*, — which both possessed about the same degree of purity. Analysis proved, that the metals used contained 99.55 % *Be*, about 0.4 % *Fe* and almost undeterminable traces of aluminium and carbon. Both samples showed *exactly the same* behaviour; there cannot be any doubt whatsoever about the fact, that the phenomena here described are truly characteristic for the *pure* element.

Although several determinations of the specific heat of *beryllium* already have been made<sup>2)</sup>, the results obtained by different investigators appear in general strongly deviating from each other. This divergence of the data obtained is, however, by no means restricted to the specific heats alone: quite a number of other physical properties: the thermoelectric and thermo-ionic behaviour, the electrical resistance, etc. in their dependence on the temperature, — all these properties equally show characteristic irregularities, which mostly were accounted for by assuming some allotropic change in the metal, occurring at various and not quite determinable temperatures<sup>3)</sup>. As we soon will see, however, the phenomena manifested by this metal are of a very particular kind; so that up till now it does not seem allowed to explain them exclusively in the way just mentioned, although it is certain, that they are accompanied by such an allotropic change. It must be emphasised, that the discovery of the very curious behaviour of the previously heated metal has only been possible, because of the high

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<sup>1)</sup> F. M. JAEGER, and E. ROSENBOHM, *Recueil des Trav. chim. Pays-Bas*, **47**, (1928), 513; **51**, (1932), 1—46; F. M. JAEGER, E. ROSENBOHM and J. A. BOTTEMA, *Proceed. R. Acad. Sciences Amsterdam*, **35**, (1932) 347, 763, 772; E. ROSENBOHM, *ibid.*, **35**, (1932) 876; F. M. JAEGER and J. A. BOTTEMA, *ibid.*, **35**, (1932), 352, 916, 929.

<sup>2)</sup> J. EMERSON REYNOLDS, *Phil. Mag.*, (5), **3**, (1877), 38; T. S. HUMPHIDGE, *Proc. R. Soc. London*, **38**, (1885), 188; E. J. LEWIS, *Phys. Rev.* **34**, (1929) 1577; P. VERNOTTE and A. JEUFROY, *Compt. rend. Paris*, **192**, (1931), 612; A. MAGNUS and H. HOLZMANN, *Ann. der Phys.*, (5), **3**, (1929) 600; etc.

<sup>3)</sup> *Conf. e.g.*; E. J. LEWIS, *Phys. Rev.*, **34**, (1929), 1577, 1584, 1585.

perfection of our calorimetrical device now in use, which allows the reproduction of the data obtained within 0.1 % of their values and because of the extreme sensitiveness and reliability of the much improved method of measurement; it is not astonishing therefore, that hitherto the said phenomena evidently have escaped observation.

§ 2. *Beryllium* melts at  $1278^{\circ} \pm 5^{\circ} \text{C}$ . Especially at higher temperatures its investigation is much hampered because of its specific chemical and physical properties: its enormous affinity to oxygen compels the investigator to study it at higher temperatures in a *complete vacuum*, avoiding any contact with reducible substances; the metal is brittle and extremely hard, so that it cannot, or only with great difficulty, be worked with tools; it cannot be brought into the shape of sufficiently thin wires, hardly into that of thin plates; etc. For these reasons the X-ray-analysis of this metal at higher temperatures is extremely difficult and the data hitherto obtained are still so contradictory, that we need postpone their publication, till a more complete evidence about their significance will have been obtained. In this preliminary communication we, therefore, will only deal with the *thermal* data and simply will communicate the facts observed, without trying to give a final explanation of them.

§ 3. All measurements of the specific heats were made with lumps of the crystalline metal of pea-size, enclosed in evacuated platinum crucibles of the usual type, each containing 3 to 6 grammes *beryllium*.

In our present calorimeter the increase of the temperature of the metallic block commonly reaches its maximum, with ordinary metals, e.g. *copper*, — after 3 minutes. In the case of not previously heated *beryllium* or of the metal being preserved during a long time, — say one year, — this maximum is reached after about 3—7 minutes, as, for instance, may be seen from the curve I in the following figure: the "old" *beryllium* was heated at  $100^{\circ} \text{C}$ . and then dropped into the calorimeter. The metal behaves in this respect quite normally, so that there is no difficulty of determining its mean specific heats, up to  $400^{\circ} \text{C}$ . in the usual way; the corresponding data will be published later-on. Such a sample of the "old" metal, if brought into liquid air, proves, — exactly like each normal metal, — to have assumed the temperature of the surrounding liquified gas in about 3 minutes, — no heat-development then being any more observed. But all this ceases, as soon as the metal has previously been heated at, for instance,  $450^{\circ}$  or  $490^{\circ} \text{C}$ . If such a sample, after previous heating at these temperatures is cooled till room-temperature and afterwards again is heated at  $100^{\circ} \text{C}$ ., — then, if dropped in the calorimeter, its heat-development, as indicated by the time-temperature-curve II of Figure 1, now appears to be *extended over a very long interval of time*, the maximum temperature of the calorimeter only being reached after 35—42 minutes and the normal course of the instrument being not earlier re-established than after many

hours. It is evident, that because of this, *no* reliable measurements of the specific heats can, by means of this method, be any more made, because

*Increase of Temperature  
of the Calorimeter in m.V.*

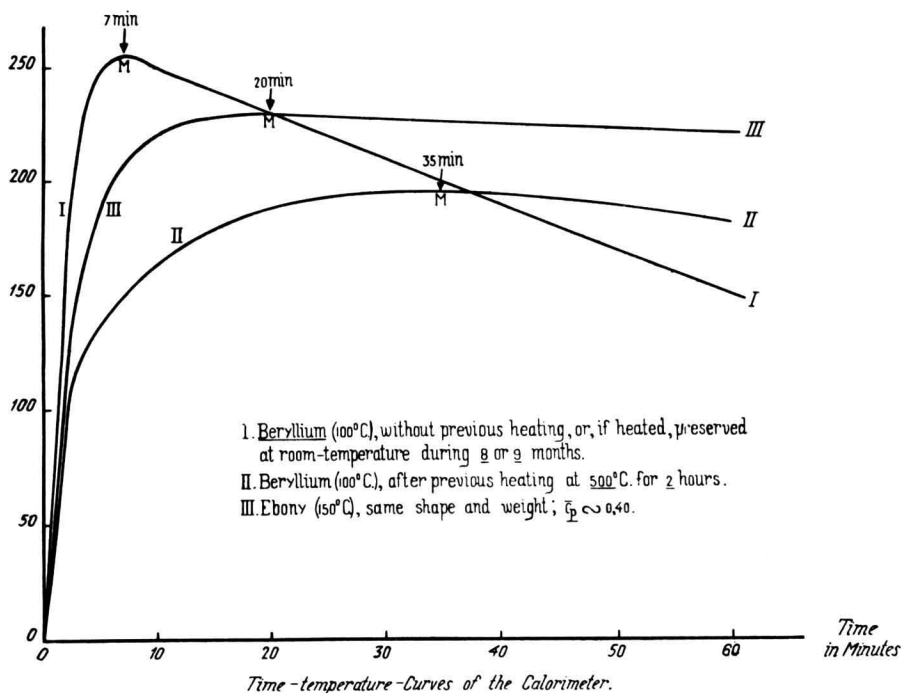


Fig. 1.

it is no longer allowed to determine the necessary cooling correction, with any certainty, by the usual extrapolation to the moment  $\tau_0$ , at which the object was introduced into the calorimeter.

In those cases, where the crucible was heated at higher temperatures than  $500^{\circ}\text{C}$ ., — say at  $800^{\circ}$ ,  $900^{\circ}\text{C}$ ., etc., — it even lasted 60 or 90 minutes, before the maximum temperature of the block was reached; subsequently the normal cooling-rate of the instrument then also appeared diminished during several hours.

This fact, which never was observed with ordinary metals<sup>1)</sup>, clearly indicates, that the metal shows a *strong retardation of the delivery of its heat-content to its surroundings*, after having been brought into its new condition. If such a heated sample of the metal, — say previously heated at  $900^{\circ}\text{C}$ ., — be dropped into solid carbondioxide and then in liquid air, it continually seems to develop heat during 40—90 minutes, before it has obtained the temperature of the surrounding liquid. If the sample thus

<sup>1)</sup> On the contrary: with ordinary metals the maximum temperature of the calorimeter is, in general, reached the sooner, the higher was the temperature of the heated metal itself.

treated be brought at room-temperature, subsequently be heated at  $100^{\circ}\text{C}$ . and then dropped into the calorimeter, it still shows its abnormal behaviour: but the time-interval necessary for reaching the maximum temperature of the block now proves to be somewhat diminished, — for instance, to 25 minutes, while also the cooling-rate of the calorimeter sooner assumes its normal size. A sample of the previously heated metal, after being preserved at room-temperature during several days, still manifests a prolonged heat-development, if brought into liquid air. Even if the sample be preserved during 7 or 8 months, it still shows, when heated at  $100^{\circ}\text{C}$ . and dropped into the calorimeter, a slight abnormality, — the interval of time necessary for reaching the maximum temperature of the block being somewhat greater than in the case of a sample of non-heated *beryllium*; only “old” *beryllium*, i.e. a metal preserved at room-temperature for at least 9 months or one year, proves to behave in a normal way. These facts prove, that the metal surely goes back to its original state, but with an ever more decreasing velocity, so that its *complete* transformation exiges months and months.

§ 4. Now it is a highly remarkable fact, that the total area of the surface bordered by the curves I and II in figure 1, if measured by means of the planimeter, up to the time at which the calorimeter has resumed its normal cooling-rate, — or if it is calculated by means of integration of the heat-effects observed, — proves practically to be *the same* in both cases.

From this evaluation of the areas considered by measuring them or by integral calculation, — the total amount of heat given off can be determined with a fair degree of accuracy: for the heat given off by the *platinum* is exactly known and that corresponding to the cooling of the *beryllium* also, because the mean specific heats of *beryllium* are, up to  $400^{\circ}\text{C}$ ., very well measurable. In this way the heat-effect “in excess”, — which should correspond to the supposed heat of transformation of the metal, — can easily be found. By these calculations the remarkable result is obtained, that practically *there remains no supplementary heat-effect at all*: it is zero or, at least, *unappreciably small*.

This leads to the conclusion, that practically there is *no additional heat-effect* superimposed upon the heat given off by the heated metal, after having been brought into the new state, if compared with the metal in its original state. The whole phenomenon rather makes the impression, as if *beryllium*, — after previously being heated above  $420^{\circ}\text{C}$ ., — is brought into a new state, in which its heat-development to its surroundings, — if a temperature-difference between these and the metal be established, — is *enormously retarded*; it seems, as if a certain phenomenon of “thermal hysteresis” there were present. This might be explained, if it could be supposed that the thermal conductivity of the metal, after its change above  $420^{\circ}\text{C}$ ., were *very considerably* diminished. In Fig. 1 the curve III represents the behaviour of a lump of *ebony*, — which has about the same

specific heat as *beryllium*, but a much smaller thermal conductivity, — after it was brought into exactly the same shape as the platinum crucibles used, heated at  $150^{\circ}\text{C.}$ , and then dropped into the calorimeter: here the maximum temperature of the calorimeter-block, indeed, was reached only after 20 minutes and the normal cooling-rate of the instrument also appeared only to be re-established after a rather long time. At first sight, however, it must appear highly improbable, that the metal in its new condition, would have a thermal conductivity even poorer than that of a block of *ebony*. Indeed, the experiment soon proved, that this supposition is completely *inadequate* for explaining the behaviour of the metal: direct *comparitive* measurements of the thermal conductivities between  $100^{\circ}$  and  $0^{\circ}\text{C.}$  of *copper*, of *ebony*, and of *beryllium* in its original and in its new state <sup>1)</sup>, lead to the following results:

a. *Copper* and *beryllium* have perfectly comparable thermal conductivities between  $100^{\circ}$  and  $0^{\circ}\text{C.}$

b. The thermal conductivity of *beryllium* previously heated at  $500^{\circ}\text{C.}$  remains, between  $100^{\circ}$  and  $0^{\circ}\text{C.}$ , *the same* as that of "old" *beryllium*.

c. *Ebony* has, in the same interval of temperatures, a thermal conductivity, which is appreciably lower than that of the metals just considered.

There can be no doubt, *that the phenomenon observed cannot be explained by a change of the thermal conductivity of the metal* in its new state; its "thermal hysteresis" can, therefore, neither be caused by this fact, nor by a simple process of transformation, slowly going back, because there is only an apparently *unappreciably* small heat-effect accompanying it.

§ 5. There are, moreover, other particularities which are contradictory to the supposition, that here we would only have to deal with an "ordinary" allotropic change of the metal. Experiments proved, that the prolonged heat-development of the previously heated *beryllium* is *not* appreciably *retarded* by quenching the sample at  $-190^{\circ}\text{C.}$ : evidently it is impossible to "fix" the new state of the metal by such quenching, — for instance after heating at  $900^{\circ}\text{C.}$  and suddenly cooling at  $-190^{\circ}\text{C.}$ , — because the velocity of the inverse transformation is, at  $-190^{\circ}\text{C.}$ , apparently *not appreciably smaller* than at room-temperature. This fact is completely contradictory to the general experience gathered about the transformation-velocity of allotropic or polymorphous modifications in its dependence on the temperature: the whole method of stabilizing "metastable" modifications by quenching, exactly is founded upon the well-known, generally very rapid decrease of the velocity of transformation with diminishing temperatures.

Special experiments taught us, that also the specific gravities of the original and of the heated and quenched material, remained about the

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<sup>1)</sup> The metal was preliminary heated in a vacuum at  $485^{\circ}\text{C.}$  during many hours and then compared with the original sample.

same: although really there are two modifications, their specific volumes evidently can only differ quite unappreciably<sup>1)</sup>. These experiments on the specific weight under different circumstances were made with samples of *beryllium* enclosed in small evacuated platinum crucibles, which, during a long time, were heated at different constant temperatures, ranging from 0° to 800° C.; then suddenly they were quenched and the crucibles were rapidly opened. The determinations of the specific weights were made by means of the pycnometer at 17° C. and several times repeated after a sufficient lapse of time, with the purpose of stating accidentally occurring gradual changes of  $d_{40}$ , as a function of the time elapsed. The experiment after quenching at 800° C. gave:  $d_{40} = 1.903$  at 17° C.; after 2 hours: 1.902; after 3 hours: 1.903; after 14 hours still: 1.903. These values are somewhat greater than those published in the literature; according to FICHTER and JABLEZYNSKI<sup>2)</sup> such deviations might be explained by an admixture of some *BeO*, generated by the contact of the metal with the water of the pycnometer. Using *toluene* in stead of water in the pycnometer, we found, however, the same values; so that the small difference of about 3 % seems to be a real one, — the theoretical value of  $d_{40}$  being: 1.837, as calculated from the spectrographical data.

In all cases, no striking physical differences between the two states of the metal could be found, with the exception of the calorimetric behaviour just described. It may be remarked that these negative results are in agreement with those obtained by LEWIS<sup>3)</sup>: according to this author, no allotropic change of the metal betrays itself in the temperature-curve of the specific heats between  $-190^{\circ}$  and  $+200^{\circ}$  C., nor in that of the thermal conductivity within the same interval of temperature. In this connection we, moreover, can draw attention to the fact, that between  $-190^{\circ}$  C. and the ordinary temperature, no change of the *X*-ray-spectrogram of *beryllium* could be stated by us: besides the ordinary diffraction-lines, some faint extra-lines are always present, evidently persisting after a preliminary heating of the metal. HIDNERT and SWEENEY<sup>4)</sup> observed no discontinuity in the curve of the linear expansion of the metal, — not even in the vicinity of 420° C. These facts seem to prove, that *a discontinuous and abrupt change in the physical properties of beryllium does not manifest itself*, as would be expected in the case of the occurrence of an enantiotropic,

<sup>1)</sup> F. FICHTER and K. JABLEZYNSKI, Ber. d. d. chem. Ges., **46**, (1913), 1609.

<sup>2)</sup> Recent experiments have definitely shown that an allotropic change really occurs at higher temperatures, which, on cooling, only partially and slowly goes back; both modifications evidently are simultaneously present at a whole series of temperatures, so that the metal at ordinary temperatures represents a not quite definite, complex system. This is proved by the appearance of new diffraction-lines amongst the ordinary ones in the *X*-ray-spectrogram, if the metal is heated in a vacuum at 650° C. for several hours, and by the subsequent fainting of these new lines, if the preliminary heated metal is cooled in acetone and solid carbondioxide or in liquid air.

<sup>3)</sup> E. J. LEWIS, loco cit.

<sup>4)</sup> P. HIDNERT and W. T. SWEENEY, Bull. Bur. of Stand. Washington, **22**, (1927), 533.

completely reversible allotropic transformation. But, especially from LEWIS' experiments it must, however, be concluded, that a continuous heating of the element at  $700^{\circ}\text{C.}$ , undoubtedly causes more or less radical changes in its physical condition. We will return to this question in a later publication, dealing with the spectrographical peculiarities of *beryllium* heated at this temperature for a long time. The most remarkable effect of those changes, manifests itself in the thermal behaviour here described, with its gradual disappearance after a sufficiently long interval of time, which, at ordinary temperatures, can be extended over several months.

§ 6. Although the results of the *X*-ray-analysis, as already mentioned, cannot yet here be considered in detail, finally some general remarks concerning them may, however, be made. In the first place it has become clear during these experiments, that the problem about the true structure of *beryllium* is still *unsettled*. All investigators observed the occurrence of a smaller or greater number of *extra* structure-lines in their spectrograms, even at the ordinary temperature, which hitherto, always were ascribed to the presence of mysterious "impurities" in sufficient quantities. Moreover, neither the relative intensities of these extra lines with respect to each other appear to be quite constant, nor is there a sufficient agreement between the observed and calculated intensities of the *normal* diffraction-lines, — as they follow from the structure of the metal, as indicated by MC KEEHAN <sup>1)</sup> and others. That a certain number of the additional diffraction-lines certainly do *not* correspond to "accidental impurities" or to admixed *beryllium-oxide*, now has become quite clear to us, — although it proved hitherto impossible, completely to determine the special circumstances, under which they are produced. Certainly there exists a second modification of the element, which seems to co-exist with the ordinary form *at all* or, at least, *at a whole series* of temperatures. However, — as already has been said, — even then the curious thermal behaviour of the metal *cannot be explained in this way alone*; but it seems rather to be connected with some other kind of change, — perhaps occurring in the atoms or molecules themselves, — by which the crystalline *beryllium* is built up. For both modifications seem to possess almost the same thermal conductivity; so that even their simultaneous presence in the metal cannot explain its curious thermal behaviour, after being heated at higher temperatures, which more particularly manifests itself in the strange hysteresis of its heat-development. All this, however, must still be thoroughly investigated, before a final decision will be possible. We soon hope to return to these interesting questions in a following publication on this subject.

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Physical Chemistry of the University.*

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<sup>1)</sup> L. W. MC KEEHAN, *Proceed. Nat. Acad. Sciences Washington*, **8**, (1922), 270. An analogous disagreement between the calculated and observed intensities of the diffraction-lines is present in the case of *magnesium*.