

Citation:

Leeuw, H.L. de & A. Smits, Confirmation of the theory of the phenomenon allotropy. II, in:
KNAW, Proceedings, 14 II, 1911-1912, Amsterdam, 1912, pp. 1199-1217

Chemistry. — “Confirmations of the theory of the phenomenon allotropy.” II. By Prof. A. SMITS and Dr. H. L. DE LEEUW. (Communicated by Prof. A. F. HOLLERMAN).

(Communicated in the meeting of March 30, 1912).

The investigation set on foot more than a year ago to test the above-mentioned theory by different substances, the results of which have already been communicated as far as the substances *mercury iodide*, *phosphorus*, and *sulphur* are concerned, has now already advanced so far also with regard to some other substances, that some results may be published.

As the investigation chiefly concerns the curves of heating and cooling, we will first give some preliminary general considerations about these curves. If we think the temperature (T)-axis to be the vertical one, and the time (S) axis the horizontal one, we find as temperature-time-curve a continuous line, which in the most favourable case has a horizontal middle part.

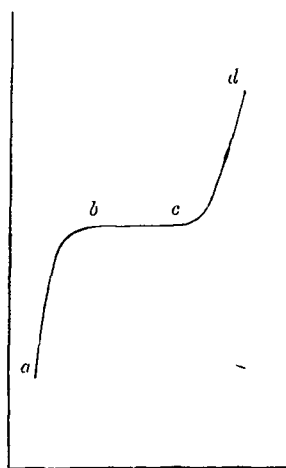


Fig. 1.

before the mass in the immediate neighbourhood of the thermometer, which is thought quite surrounded by the solid substance, has reached the temperature of melting, by which at the same time the supply of heat to the inner layers is greatly diminished.

This rounding, which takes place before the point b , where the horizontal part begins, has been reached, will therefore become the greater as the conductivity of heat of the solid substance is smaller, the specific heat smaller, and the supply of heat greater.

If once a liquid layer has been formed, we must allow for the phenomenon of *super-heating*. Without any doubt the liquid which

If we consider the curve of heating $a b c d$, and begin at a , we commence with the curve of heating of the solid substance, and $\frac{dT}{ds}$ will depend first of all on the quantity of heat that is supplied per sec., and secondly on the specific heat of the solid substance.

Before the point b is reached, $\frac{dT}{ds}$ decreases continuously to the value 0, and the cause of this is that the conductivity of heat of the solid substance is not infinitely great, in consequence of which melting sets already in in the outer layers,

surrounds the solid substance in the experiment discussed here, will always assume a higher temperature than corresponds with the melting-point of the solid substance and now with a certain supply of heat it will depend on the rapidity with which the heterogeneous equilibrium sets in in the border layer, and also on the value of the melting heat, whether the solid substance which surrounds the thermometer will possess a constant temperature for some time.

If the heterogeneous equilibrium in the border layer was established with infinite rapidity, a horizontal part of the curve of heating would have to occur even for the *smallest* melting-heat, and the *greatest* supply of heat, if namely, as has been supposed from the outset, the system behaved in a perfectly unary way.

It follows from this at the same time, that when as is most likely the case, the heterogeneous equilibrium in the border layer is *not* established with infinite rapidity, a substance with small melting-heat will be much sooner super-heated than a substance with a great melting-heat, and if this phenomenon occurs a line will be found for which $\frac{dT}{ds}$ has a positive value in all points instead of the horizontal portion.

Now, however, it has been supposed here that the substance behaves in a perfectly unary way, and *for this case* we have arrived at the conclusion that when a horizontal part is wanting in the curve of heating, this must point to super-heating of the solid substance in consequence of the retarded heterogeneous equilibrium. In most cases, however, we are still entirely ignorant about whether a substance behaves as a unary one or not under definite circumstances, and as the horizontal part will also be wanting for the case that the substance *does not* behave in a unary way in the heating-experiment, but the heterogeneous equilibrium *does* set in rapidly enough, because then superheating occurs in consequence of the retarded homogeneous equilibrium, the curves of heating can teach us anything about the behaviour of the substance only when the circumstances are made as much as possible the same for different heating experiments, while the previous history of the substance is greatly varied.

Before passing on to another subject it is still necessary to point out about the curve of heating that though a horizontal part has appeared, there yet occurs a curvature at *c* where $\frac{dT}{ds}$ increases continuously till all the solid substance has disappeared.

This rounding is owing to this that the liquid, which is certainly superheated and will be the more superheated as the surface of the solid substance decreases, comes more and more into contact with

the sensible part of the thermometer (mercury vessel or windings of the resistance thermometer).

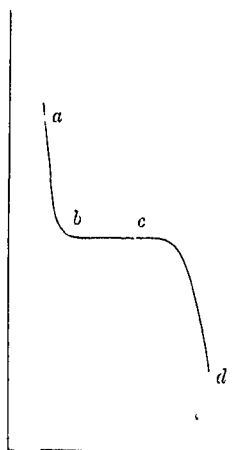


Fig. 2.

Both roundings *b* and *c* will be diminished by slow heating, and augmented by greater supply of heat. Moreover the rounding *c* may be greatly reduced by stirring, which circumstance is, however, expressly excluded here.

Let us now consider the curve of cooling *abcd*. This curve indicates the temperature-time curve which we get when a substance behaves entirely as a unary substance, and the heterogeneous equilibrium between the solid substance and the border layer sets in rapidly enough for the loss of heat to be compensated by the heat of crystallisation.

Starting from *a* we first get the curve of cooling of the liquid. Before the horizontal part is reached, the value of $\frac{dT}{ds}$ becomes here continuously smaller negative over a certain range of temperature, because of the appearance of solidification in the outer layers already before the liquid in the immediate neighbourhood of the thermometer has assumed the temperature of solidification. So this phenomenon is due to the insufficient conductivity of heat of the liquid.

If when the liquid round the thermometer has reached the temperature of solidification, the said compensation takes place, the curve of cooling will present a horizontal part. Before the mass has, however, become entirely solid, a change sets in, because the thermometer comes more and more in contact with the solid substance, which for so far as it is not in direct contact with the liquid will possess a lower temperature than the liquid, which will render $\frac{dT}{ds}$ again continuously stronger negative, till the last trace of liquid has vanished.

If the heterogeneous equilibrium is not established with infinite rapidity, the loss of heat can no longer be compensated by the heat of crystallisation, in consequence of which the liquid in contact with the solid substance is undercooled. In this case a more or less descending line will be found instead of the horizontal part.

To simplify the case it has been supposed here that the substance behaves as a unary one, which in reality is very doubtful, and therefore we may not conclude when we find a curve of cooling

without a horizontal middle part, that the *heterogeneous* equilibrium has not set in rapidly enough, for it is also possible that the *undercooling* is partly or wholly to be attributed to the fact that the *homogeneous* equilibrium does not set in, or in other words that the substance does not behave as a unary one.

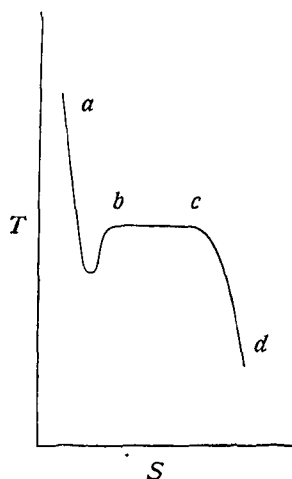


Fig. 3.

Accordingly to decide by means of curves of cooling whether or no a substance behaves in a unary way, we follow the course indicated just now in the discussion of the curves of heating; during the solidification the circumstances are made as equal as possible, whereas the previous history of the substance is made very different.

If it is in any way possible, the substance is then made to undercool a little in the determination of the curves of cooling, and then it is seeded in some way or other, because the maximum to which the temperature then rises in the subsequent solidification, can give very valuable indications.

The practically ideal curve has then a form as is indicated in fig. 3.

MERCURY.

In the first place we will communicate what results the investigation of the element *mercury* has yielded, because this substance is distinguished from other substances examined up to now by the great chance it offers for an ideal behaviour when heated.

For mercury we meet namely with the case that even on a considerable supply of heat a temperature-time curve is found with a horizontal middle part, from which follows that the substance behaves in a *unary* way under these, in general disturbing, circumstances, and the heterogeneous equilibrium sets in with great rapidity in case of *heating*.

So in a case like this we need not apply the method mentioned just now, for if a substance continues to behave in a unary way when not only the previous history, but also the circumstances during the melting are chosen different, this will certainly be the case when a modification is applied only to the previous history.

Fig. 4 refers to an experiment, in which a wide test-tube, partially filled with mercury, is heated from -80° by being exposed to the air. In the mercury a resistance thermomefer had been placed which

(1203)

was inserted in one of the branches of a WHEATSTONE bridge. The observation of the image of a NERNST-lamp cast by the mirror of

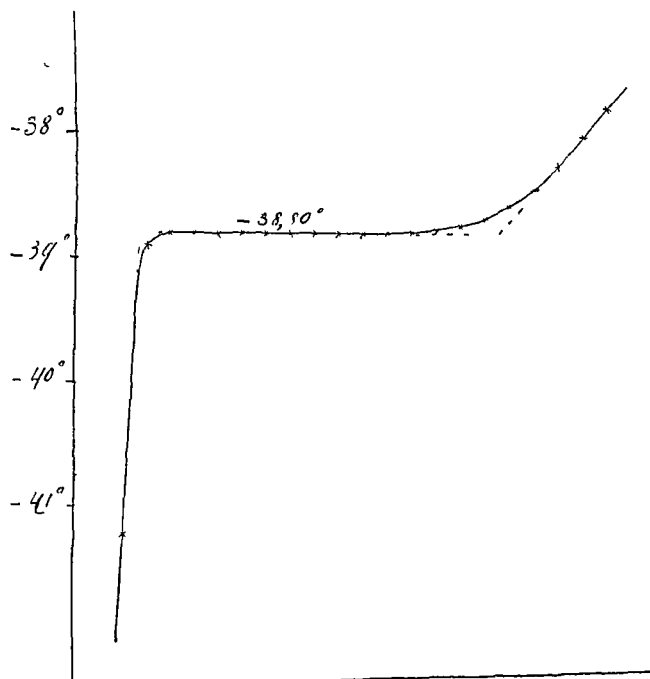


Fig. 4.

the galvanometer on a scale, enabled us to follow the change of the temperature. From the readings, which were made every 10 seconds it appeared that the resistance thermometer, and so also the mercury in the immediate neighbourhood, maintained the same temperature for 95 seconds, which temperature is exactly the same as that which is found, when solid mercury is melted in a bath of low temperature, and for which $-38^{\circ}.80$ was found with the gas-thermometer. So in spite of the great difference in temperature between the mercury and the surroundings no superheating of the solid mercury took place.

The following fig. 5 shows the result that we obtained when we rapidly heated mercury from -80° in an air-jacket placed in boiling water. It appears from the observations, which were recorded here every 5 seconds, that the temperature now remained perfectly constant for 45 seconds. The melting proceeded, indeed, more rapidly now, in consequence of the great supply of heat, but in spite of this the ideal course was observed, which points to a unary behaviour and perfectly heterogeneous equilibrium.

Now it was to be expected, however, that the equilibrium of the

substance mercury, which continued to behave in an ideal way under greatly disturbing circumstances, might nevertheless be upset, when

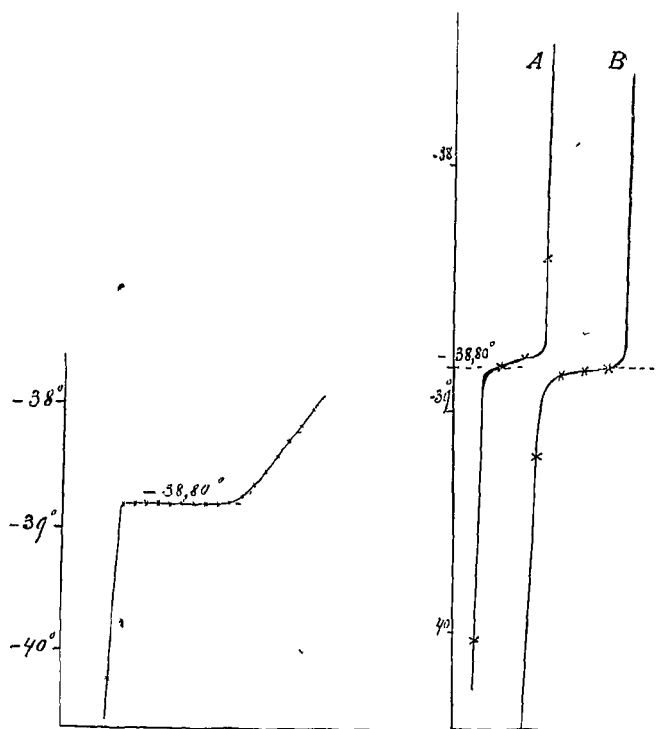


Fig. 5.

Fig. 5a.

the disturbing influences are only made strong enough. To ascertain this the experiment was repeated under much intenser circumstances: a quartz tube with solid mercury of -80° was suddenly placed in water of 80° resp. in water of 100° *without* an air-jacket. We then found the lines *B* and *A* fig. 6, the crosses indicating the readings every 5 seconds. It follows from these lines that this experiment was too much even for mercury, which was in no way astonishing. As it now appeared that the previous history had absolutely no influence on the shape and the situation of the curve, we thought we were justified in concluding from this that the mercury had been superheated here in consequence of a retardation of the heterogeneous equilibrium.

In connection with what precedes it is exceedingly interesting to see what was found in the determination of the curve of cooling. Whereas it is exceedingly difficult to make the mercury behave in a non-ideal way when it is heated, this is much easier to reach in case of cooling, and this is very remarkable, for the foregoing has

perfectly convinced us of the unary behaviour of mercury, unless in cases of very excessive treatment, so that the fact that a horizontal middle part in the curve of cooling fails to appear under *not* extraordinarily disturbing circumstances, must undoubtedly be attributed to the too slow setting in of the heterogeneous equilibrium.

If mercury is cooled down in an air-jacket which is placed in a bath of -80° , we may succeed when the jacket is wide enough, and the cooling in consequence of this takes place very slowly, to obtain a curve of cooling with horizontal middle part, as Fig. 6 (readings every 40 seconds) shows, but as soon as the cooling takes

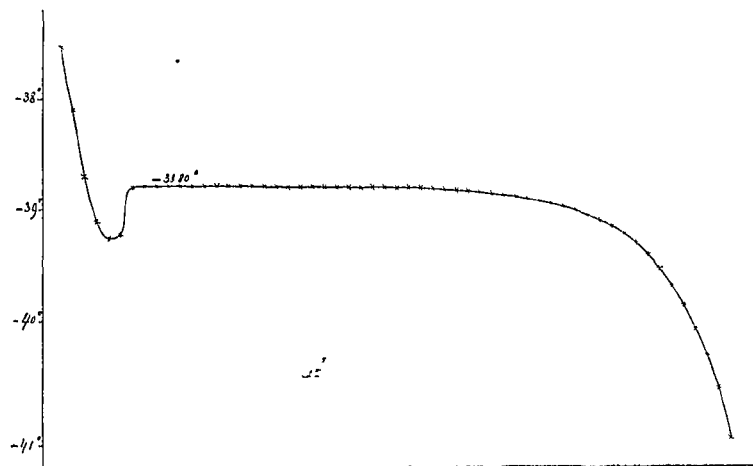


Fig. 6.

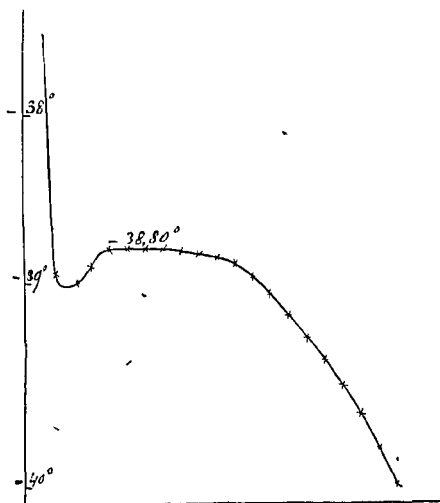


Fig. 7.

in exceedingly rapidly in case of heating, but slowly in case of cooling. It follows from this that superheating of the solid substance

place somewhat more rapidly, e.g. by the use of a somewhat less wide air-jacket, the mercury does *not* behave ideally, as fig. 7 shows. The top, indeed lies at $-38^{\circ},80$ here, but a purely horizontal part is wanting, in spite of the comparatively slow process of the solidification. With a still narrower air-jacket, the curve was much steeper. So we arrive at the surprising result that the *heterogeneous equilibrium between solid mercury and the border layer sets*

is not ascertained or only under very particular circumstances, whereas undercooling of the liquid in contact with solid substance seems to appear very easily.

T I N.

In the second place tin was investigated, because the existence of points of transition led us to expect here that the experiment might be able to reveal the complexity of the system.

We expected this the more confidently, as phenomena have been observed in the technique that point to this that the temperature of the liquid tin at the moment of casting has an influence on the properties of the solidified mass.

In DAMMER's "Handbuch der chemischen Technologie" this has been expressed as follows. "Glanz und Festigkeit des Zinns hangen von der Temperatur beim Giessen ab. Es darf weder so sehr erhitzt sein, dass seine Oberfläche in Regenbogenfarben spielt, noch so kalt, dass sie matt ist. In beiden Fallen, zu heiss oder zu kalt gegossen, büsst das Zinn an seinem Glanze und an seiner Festigkeit ein: im ersteren Fall wird es roth, im letzteren kaltbrüchig".

The apparatus used by us in the investigation of tin, has been represented in fig. 8. The resistance thermometer has been ground at *c* into the melting-vessel *A*, which consisted of not very readily fusible glass. This ground joint is surrounded by a jacket, which

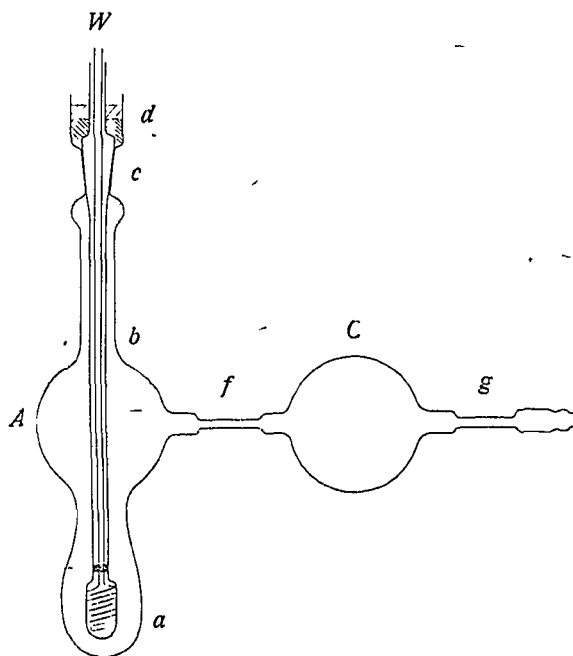


Fig. 8.

was filled with mercury, and was then closed by a layer of paraffin

The melting-vessel had been blown out to a diameter of 5 c.m. at the bottom, there where the windings of the resistance thermometer are found, so that this part could contain 250 gr. of tin. Above this the vessel had been blown out to a still wider bulb *b*¹⁾, which could be fused to a second bulb *C* by means of a capillary, which was supplied on the opposite side with a second capillary.

Before it was fused to bulb *b*, bulb *C* had been filled with pieces of very pure tin, excellently prepared by KAHLBAUM. The only impurity it contained was lead, and only 0,04 %.

Then first of all the capillary *g* was connected with the Gaedepomp by means of an air-pump rubber tube, and so far exhausted that a Geissler tube, which was permanently in connection with the P_2O_5 -vessel of the Gaedepump, no longer showed phenomena of discharge.

Then the capillary *g* was melted off, and the bulb *C* was heated to melt the tin that is in it. At the same time also the bulb *b* of the melting-vessel *A* was heated, and the whole apparatus was held horizontal. The melted tin was now covered with a coat of oxide, and the capillary *f* served to remove this before the tin arrived in the melting-vessel *A*. If, viz., now the apparatus was made to rotate a little round the resistance thermometer as horizontal axis, the tin flowed from the bulb *C* through the capillary *f* into the bulb *b*, the coat of oxide remaining behind in *C*. The melting-vessel remained in a horizontal position, till all the tin had solidified in the bulb *b*, after which the capillary *f* was melted off.

The tin filtered in this way was so perfectly free from the coat of tin-oxide, that in its melted condition it looked quite like mercury, and in solid condition it consisted of fine glittering crystals.

Of course we cannot guarantee that our tin was *perfectly* pure, for though the solid tin-oxide had been removed, the tin will have contained some tin-oxide in a dissolved condition. As this quantity was, however, very small, and as it was at all events the same in the different experiments, this circumstance did not afford an insuperable difficulty for our purpose.

Now the apparatus was ready for the experiment, and was carefully immersed in a bath of melted potassium-sodium nitrate in order to melt the tin, and make it flow into the widened part *a*. The quantity of tin had been chosen so that the melting-vessel was

¹⁾ After the experiment the liquid tin was conducted to this bulb to solidify here. This was done in order to prevent damage of the resistance thermometer in the solid mass.

filled up to the constriction between a and b in a vertical position.

Now in order to find the point of solidification of tin for an it possible unary behaviour, the melting vessel, which had only been heated a few degrees above the melting-point of tin, was suddenly conveyed to an air-jacket, which was found in another larger potassium-sodium nitrate bath of a constant temperature $\pm 220^\circ$.

The connection of the thermometer with the WHEATSTONE bridge had already been effected before, and the image of a NERNST lamp, cast on the graduated scale by the mirror of the galvanometer showed, that the liquid undercooled on cooling. If the liquid was lightly shaken, crystallisation set in, and the image rose to a maximum, where it remained immovable for more than 2,5 minutes;

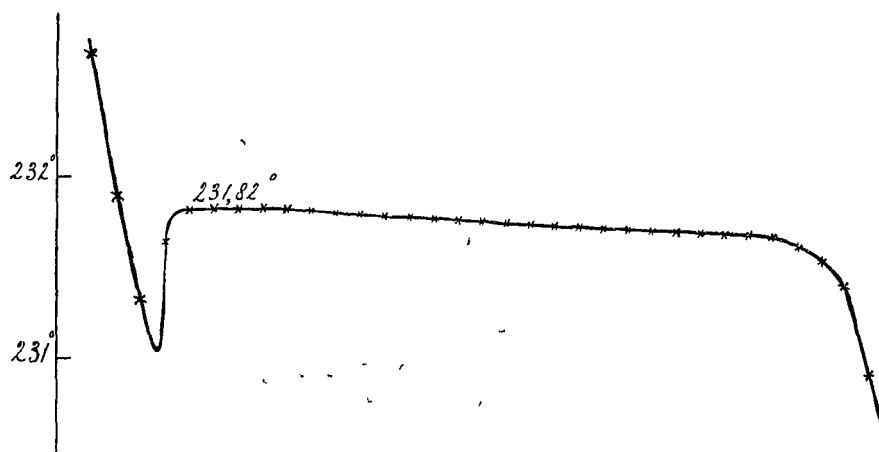


Fig. 9.

then it descended very slowly for a long time, after which it pretty suddenly began to descend rapidly. The temperature-time curve that follows from these experiments, which were repeated every 10 seconds, has been drawn in figure 9, in which only the observations every 40 seconds are indicated to restrict the number of crosses.

It appears from this line that the solidifying mass round the thermometer maintained the same temperature of 231.82° for more than 2.5 minutes, and that it then slowly decreased to about 231.63° , after which the temperature pretty suddenly decreased rapidly. As it always appeared that the mass had already solidified for the greater part at the moment that the slow decrease first commenced, we thought that we had to conclude from the above very peculiar line that the system really behaved in a unary way here on solidification, and that the slow decrease, which preceded the rapid

decrease was not owing to the trace of tin-oxide, but had to be ascribed to an exothermic process, which took place in the solid mass after the solidification, which supposition was corroborated by the subsequent experiments.

HOLBORN and HENNIG¹⁾, who determined the point of solidification of tin in an open vessel found 231.83° , when they used 1.5 K.G., a value which only differs 0.01° from ours.

If we use an open vessel, tin gets covered with a layer of oxide, and strictly speaking, we do not determine the point of solidification of pure tin, but the temperature of the eutectic point of tin oxide — tin. Accordingly we might conclude from the exceedingly small difference between HOLBORN and HENNIG's result and ours that tin-oxide dissolves exceedingly little in tin, and that it is not necessary for the determination of the point of solidification to work in vacuum.

Yet for our purpose the determination of the influence of the previous history of tin on its point of solidification, the vacuum, and the absence of solid tin-oxide appeared an indispensable requirement, as with rapid cooling of liquid tin which had been heated to a high degree exposed to the air, perfectly unreliable and widely divergent results were obtained, whereas they were always the same in vacuum and in absence of solid tin-oxide.

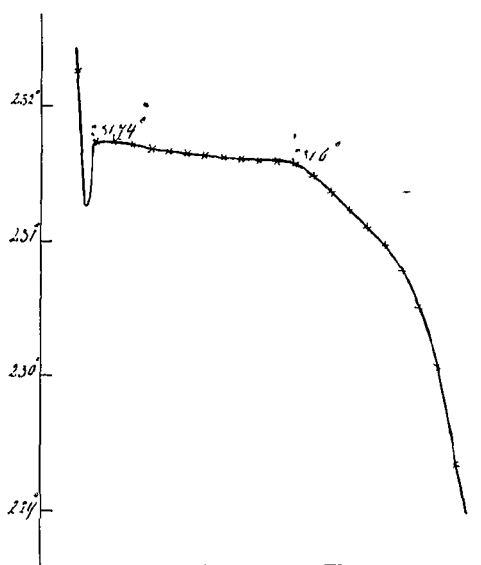


Fig. 10.

have been indicated. So the temperature remained constant for about 40 seconds, but the unary point of solidification could not be reached

As in order to ascertain the influence of the previous history it is necessary to work rapidly, and so also to make the solidification take place rapidly, first the curve of cooling was determined of tin that was heated only just above the melting-point, and was cooled simply by exposure of the apparatus to the air without jacket.

This experiment yielded the curve as seen in fig. 10. Of the observations, which were made every 10 seconds, only those of every 40 seconds

¹⁾ Ann. der Phys. 35, 761 (1911).

in consequence of the more rapid cooling, though there was without doubt a tendency to the setting in of internal equilibrium. The maximum temperature here amounted to 231.74° , and so was 0.08° under the unary point of solidification. Then the temperature first decreased slowly to 231.6° , after which it decreased pretty suddenly with continually accelerated rapidity, just as was observed in the preceding experiment¹⁾.

After having obtained this result, we could proceed to the investigation about the influence of the previous history. The melting-vessel was then heated to a temperature of $\pm 300^{\circ}$ and then cooled as rapidly as possible to about 3° above the point of solidification by a current of air produced by means of a foot-bellows. The further cooling then took place without this means.

Fig. 11, which gives the result of this experiment, shows that

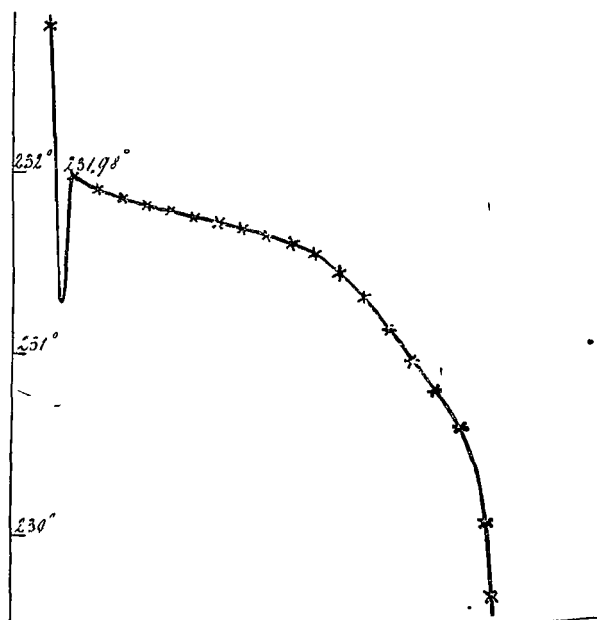


Fig. 11.

after the solidification of the undercooled liquid had set in by means of shaking, the temperature quickly rose to 231.98° , so 0.24° above the temperature maximum of the preceding experiment, and even 0.16° above the unary point of solidification, but the fall of the temperature was now very much quicker than in the former expe-

¹⁾ Thermo-currents were seldom noticeable with our resistance thermometers, and when this was the case, the connection was made so that the effect to be expected was diminished by the thermo-current.

riment, and so the curve deviates very much more from the ideal curve of cooling than any of the other lines (the crosses mark the observations every 40 seconds¹). Now it had been proved that the system tin, as had been expected, presents the same peculiarities as phosphorus, though in a much less degree, which is not surprising, because the point of solidification of tin lies so much higher, and the transformations at that higher temperature will probably take place pretty rapidly.

Finally we proceeded to the determination of the curve of heating of tin which had solidified slowly beforehand, and had not been cooled further than a few degrees below the point of solidification.

With slow heating in a wide air-jacket, which had been placed in a nitrate-bath of $\pm 300^\circ$, the curve represented in fig. 12 was obtained.

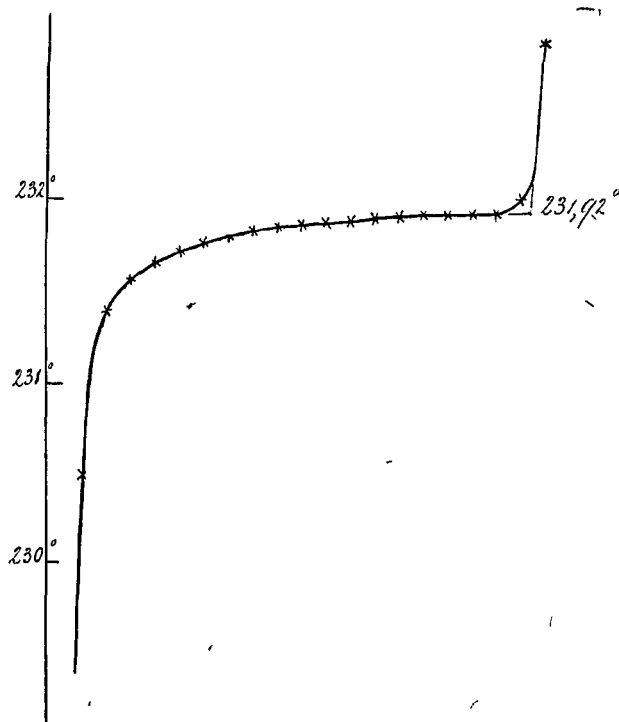


Fig. 12.

Characteristic is the long bend on the left, which for a pure substance with such a great conductivity of heat as the metal tin, points to a conversion in the solid mass, which is accompanied by an absorption of heat.

¹) Here it deserves notice that the damping of the galvanometer was so perfect that the image never passed through the zero position, even though the mirror moved very rapidly at first.

An almost horizontal part was found at $231,92^\circ$, but this point lies $\pm 0,1^\circ$ above the unary point of solidification.

As we have observed, tin can also melt in a unary way at $231,82^\circ$ in case of very slow heating, but we must heat more rapidly, if we wish to get good regular lines, because else the temperature depends too much on accidental disturbances; this is the reason that the nitrate-bath had to be regulated at $\pm 300^\circ$.

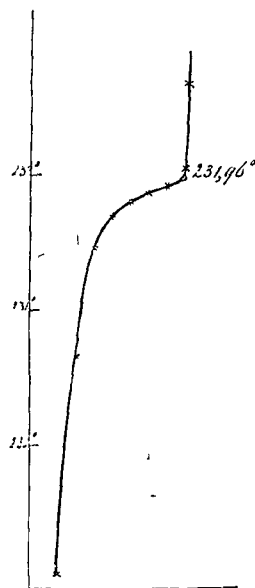


Fig. 13

The more rapid the heating is the more gradually do the two parts of the curve of heating, the righthand one and the lefthand one, merge into each other, and with heating without an air-jacket, so directly in the nitrate-bath of 300° , we obtained the curve as it is drawn in fig. 13. The final melting-point here lies only $0,04^\circ$ higher than in the preceding experiment. So it has appeared from what precedes that when we work rapidly the system tin betrays its complex nature, as the theory of allotropy led us to expect in virtue of the three different solid modification of tin.

In connection with the said supposition that the internal equilibrium in the solid state under the point of solidification is subjected to a pretty considerable displacement, some more experiments were made according to the capillary-method of SOCH. Powdery pure tin was put in very thin-walled capillaries of about 0,5 mm. diameter. These capillaries were heated in a bath of $\text{KNO}_3 - \text{NaNO}_3$ for some time at a certain temperature, and then suddenly conveyed to another bath, the temperature of which was varied till the tin was just going to melt after 10 seconds. The result was the following :

Temperature at which the equilibrium of the tin had set in.	Temperature at which the melting began after 10 seconds.
165°	238°
200°	237.5°
228°	235°
230°	234°

So the lower the temperature at which the tin has assumed its equilibrium, the higher the initial melting point lies with very rapid heating.

That the observed differences cannot be owing to the fact that more heat is to be supplied to tin of 165° than to tin of 230° before it melts, in consequence of the difference of temperature of 65° , is at once seen, as the initial melting-point appeared to have changed only 0.5° , when the initial temperature was brought from 165° to 200° . This result, to which of course, only qualitatively value can be ascribed, shows that really in the solid state, chiefly a little below the point of solidification, a considerable displacement of the internal equilibrium seems to take place¹⁾.

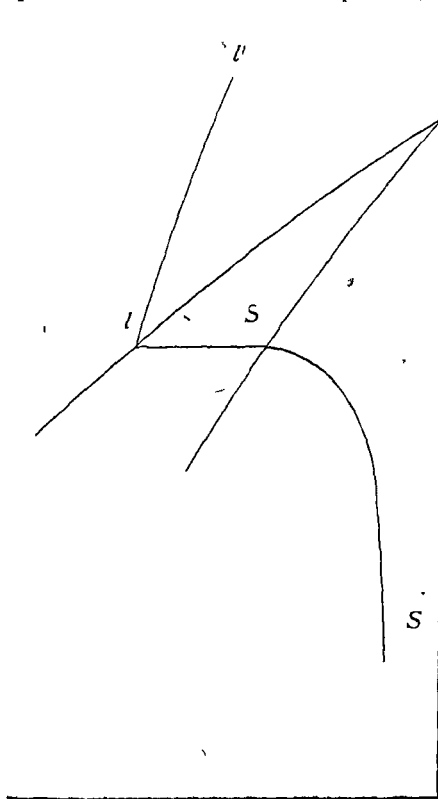


Fig. 14.

There with regard to tin is supported by the investigation communicated here to such an extent that without any doubt the most obvious explanation of the so-called *recrystallisation* is the transformation of a solid state out of equilibrium to one of internal equilibrium, as the theory of allotropy led us to expect. It follows from this theory that the phenomenon of

Though the system tin seems to be so complicated that we scarcely venture to assume anything about the pseudo $T-x$ -figure, we might now say this, that when there were only two kinds of molecules, the lines for the internal equilibria in the liquid phases and in the solid phases might run as indicated in fig. 14. So the quantity $\frac{dT}{dx}$ would differ in sign for the two said lines, which, however, is very well possible.

Before leaving the system tin we refer once more to what one of us communicated in these Proc. March 26, 1910 p. 774 about the metastability of the metals, to which we can now add that the supposition made there with regard to tin is

¹⁾ This phenomenon is also studied dilatometrically.

recrystallisation will be of frequent occurrence, just as those which, not very appropriately, have been compared to diseases by COHEN. These phenomena occur in more or less degree for every polymorphous substance, and so it is absolutely senseless to assign a special place to tin on this account¹⁾.

W A T E R.

The third substance subjected by us to an investigation was the substance water. The experiments were made in open vessels, so that the water contained some air, of which, however, not the slightest disturbing influence was observed.

In the first experiment distilled water was put in a test-tube of 2.5 cm. diameter, in which the resistance-thermometer had been placed. The water was carefully made to solidify. For this purpose the melting-vessel was first placed in a second empty wider tube, and then the whole was immersed in a bath of common salt and ice. On purpose we did not allow the temperature of the ice to descend below -0.3° , and then we conveyed the melting-vessel with air-jacket to a water-bath of 30° .

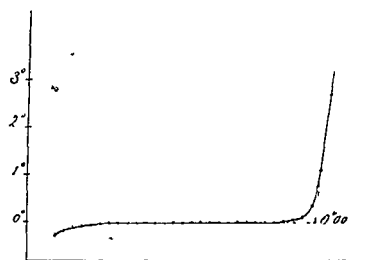


Fig. 15.

In this way we succeeded in making the water melt ideally, which clearly appears from the curve of heating of Fig. 15 (observations every 10 seconds).

This curve has namely a pretty long horizontal piece, which lies exactly at 0° .

That it is absolutely required to cool down the ice only very little below 0° in order to make the ice melt ideally, follows from the figures 16 and 17. The line of Fig. 16 was obtained by keeping the ice at -7° for some time beforehand, and then to convey the melting-vessel with air-jacket into a bath of 30° , just as in the preceding experiment. The result was now that the ice did not melt ideally, but showed a clear melting range from -0.22 to -0.04° and when the ice had been kept for some time beforehand at the temperature of -80° , the deviation from the ideal behaviour was still somewhat greater, as fig. 17 shows, from which a range of

¹⁾ Cf. what WYRUBOW says about this [Bull. Soc. franç. Minéral 33 296-300 Nov. (1910)].

(1215)

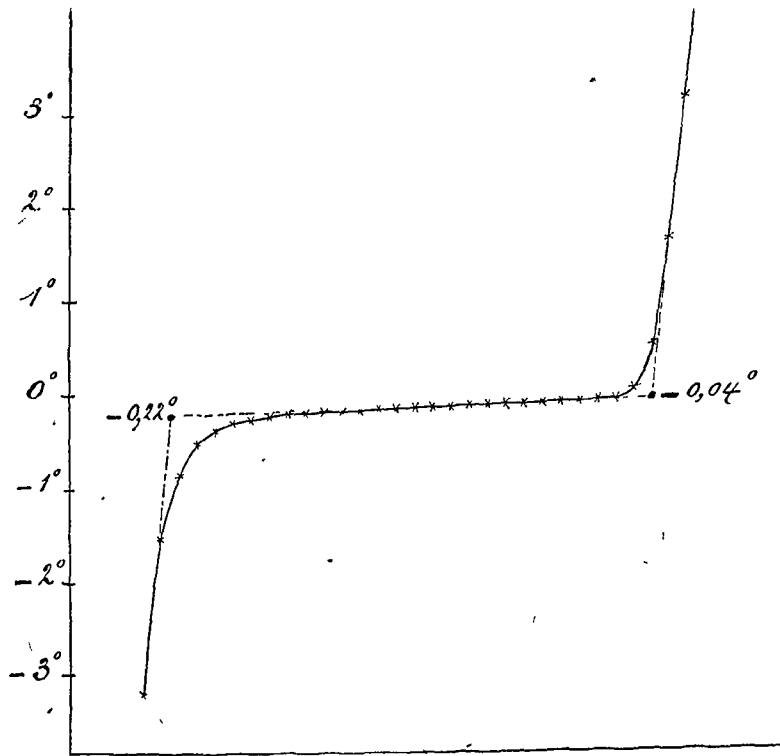


Fig. 16.

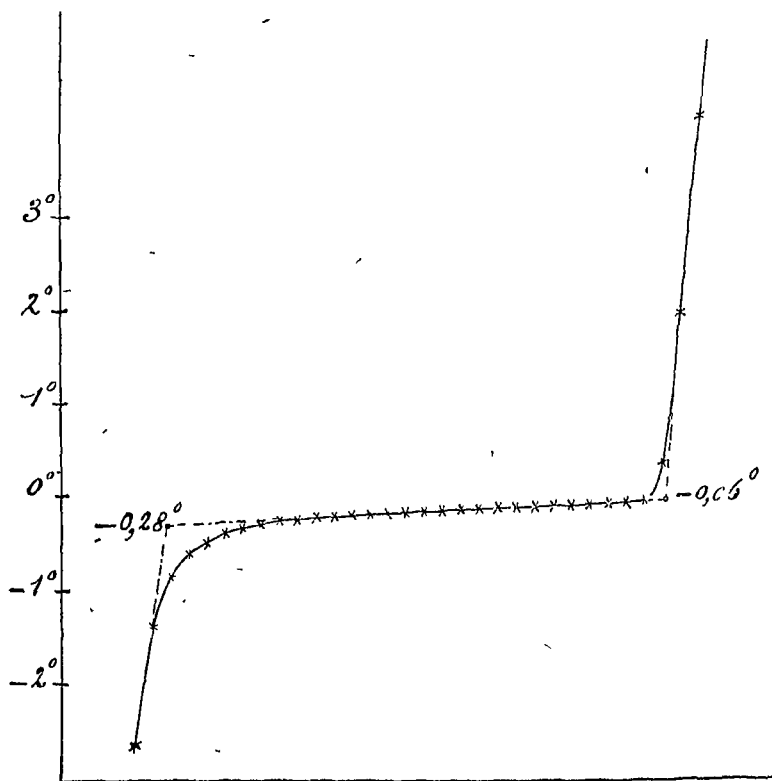


Fig. 17.

melting-temperature follows from -0.28° to -0.06° . So these experiments afforded the proof that the substance water did *not* behave as a unary one under these circumstances.

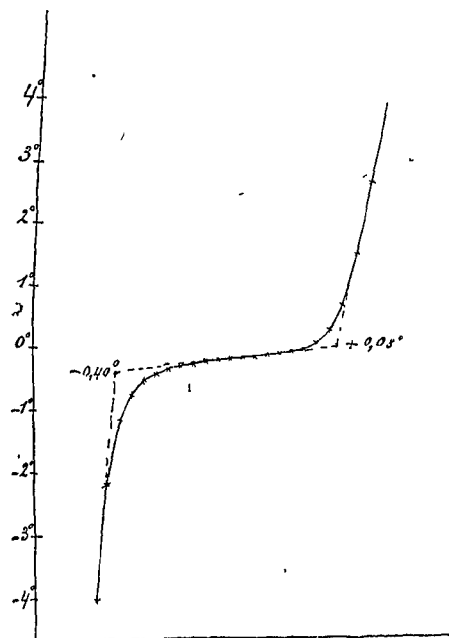


Fig. 18.

Finally the melting-vessel with resistance thermometer was placed in liquid air, and water of higher temperature, varying between 10° and 100° was squirted into the melting-vessel, in which way we tried to bring about a fixation of the internal state in the liquid. If then the curve of heating was determined in the described way the melting-range appeared to be greater than in the former experiments, and the final melting-point always lay above 0° then. Fig. 18 shows one of these curves, but we think that we cannot attach so much value to this curve as to the preceding one,

because in this way of procedure the ice often possesses hollows, which render the result less reliable.

The investigation of ice communicated here, however, shows with the greatest clearness that the substance water is a complicated state, and can easily be treated in such a way that it reveals its complexity ¹⁾.

The investigation of the testing of the theory of allotropy will be continued with different elements, and with both anorganic and organic substances, the results of which will be communicated here in due course.

*Anorganic Chemical Laboratory
of the University.*

Amsterdam, March 29 1912.

¹⁾ The application of the theory of allotropy to the four modifications of ice will be given later on.

Physics. — “Contribution to the theory of binary mixtures” XX.

By Prof. J. D. VAN DER WAALS.

In the preceding Contribution I repeatedly pointed out that not all mathematical possibilities for partial miscibility really occur. Among others the case of only partial miscibility seems to be mathematically possible for all values of n and l , whereas for small value of n this partial miscibility has only been seldom observed. So if we want to find decisive rules for the occurrence of incomplete miscibility, this seems not possible to me without first having found a rule for the determination of the quantity l in the formula $a_{1,2} = la_1 a_2$. And this will no doubt require that we have first succeeded in forming a clear idea of what the cause is of the attraction of the molecules, so also of the cause which determines its value for a simple substance. But though the knowledge of the properties of the different mathematical possibilities, also in connection with the temperature, is not sufficient — and not even the principal factor that should be studied, still this knowledge is indispensable. And therefore I will start with giving some results about this.

In the formula:

$$\frac{(v-b)^2}{x(1-x)} + \left(\frac{db}{dx}\right)^2 = \frac{c}{a} v^2$$

the projection on the v, x -plane has been given of the section of the two curves $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$ at the different temperatures, though on simplified suppositions. Of course there might also be given two such projections of this section on the v, T -plane and on the x, T -plane, which would also be closed curves. But the formulae for them would not be simple, and so we shall not try to give them. In both there would occur a minimum and a maximum of T , the minimum and the maximum value of v or of x being the same which also occur in the v, x -projection. If we imagine the three axes, an x -axis, a v -axis, and a T -axis, there is a closed curve in the space — and then the differential equation of this curve is given by a relation between dv , dx , and dT , which is derived from the simultaneously existing relation between these three differentials for the two functions $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$. These two relations are:

$$\frac{d^3\psi}{dT dv^2} dT + \frac{d^3\psi}{dv^3} dv + \frac{d^3\psi}{dx dv^2} dx = 0$$

and