will take place also when we bring these tissues into such a large quantity of liquid i. that the composition of this liquid will practically change only a little.

We may imagine also that the wall of a space partly loses its elasticity through some influence or other; then this wall will put a smaller pressure on the liquid at the same volume; we may imagine also that at the same time the change in the permeability of the membrane discussed above, occurs as well. A closer consideration of these cases is left to the reader.

(To be continued).

Leiden, Lab. of Inorg. Chemistry.

Chemistry. — The Exact Measurement of Specific Heats at Higher Temperatures. XI. On the Variability of the Specific Heats of Fused and Solidified Silver under different Circumstances. By F. M. JAEGGER, E. ROSENBOHM and W. A. Veenstra.

(Communicated at the meeting of March 25, 1933).

§ 1. In the course of our previous work on the specific heats of stabilized and preliminarily worked metals, some unexplained peculiarities in the behaviour of fused and solidified silver 1) were observed, which made it desirable again to study this metal at higher temperatures more in detail. On repeating our measurements of the mean specific heats $c_p$ with a lump of silver B fused and solidified in air 2), but being afterwards preserved at room-temperature during five or six months, — the remarkable fact was stated that all values of $c_p$, measured by means of the same instrument as formerly used, proved to be appreciably diminished. The deviations from the values previously found were in all cases much greater than could be accounted for by the possible experimental errors (see curve $B'$ in Fig. 1). Originally we thought that the stabilized lump of silver, by its long preservation at room-temperature had, in some way or other, returned to a less stable condition, — such as, for instance, was met with in the case of cold-plated and laminated silver (curve P in Fig. 1). Soon,

1) F. M. JAEGGER, E. ROSENBOHM and J. A. BOTTEMA, Proceed. R. Acad. Sciences Amsterdam, 35. (1932), 768; Recueil d. Trav. d. Chim. Pays-Bas, 52, (1933), 74; conf. Note 13) at the bottom of page 77, loco cit., on the more rapid increase of $c_p$ above $600^\circ - 700^\circ$ C.

2) On page 74, loco cit., it was erroneously mentioned, that the lump of silver used was fused and solidified "in a vacuum": really it occurred in air.
however, it became clear to us, that here the situation was quite another one, as may be concluded from the following series of experiments.

Two lumps of silver, fused and solidified in air, yielded values of $c_p$, which, — within the limits of experimental error, — proved to be identical with those formerly observed in the case of the original mass (conf. curve C in Fig. 1). But if these lumps were remelted and solidified in a perfect vacuum, the values of $c_p$ at each temperature now proved, — also within the limits of experimental error, — to be the same as those obtained in the case of the lump of silver $B'$, which had been preserved during six months (conf. the curve $C'$ in Fig. 1). On the other hand, if this last mentioned lump of silver was, in its turn, heated in air at $940^\circ$ C. for 5 or 10 hours, it again yielded values of $c_p$, which were the higher, the longer its heating in air was continued (see curves $aa'$ and $bb'$ in Fig. 1). The limits of experimental error in all these experiments never surpassed 0.1—0.2 % of

![Mean Specific Heats of Silver in Different Circumstances.](image-url)
<table>
<thead>
<tr>
<th>Temperature $t$ in °C</th>
<th>Original Lump of Silver $B$</th>
<th>The same Lump $B'$, after having been preserved at room-temperature during several months</th>
<th>Lump of Silver C melted and solidified in Air</th>
<th>The same Lump C after being remelted and diluted in a Vacuum</th>
<th>The Lump of Silver $B'$ after being heated at 940° C. in Air</th>
<th>Cold plated and laminated Silver $P$ heated in Vacuum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_h$ in Calor. pro Gr.</td>
<td>$\bar{c}_p$</td>
<td>$Q_h$ in Calor. pro Gr.</td>
<td>$\bar{c}_p$</td>
<td>$Q_h$ in Calor. pro Gr.</td>
<td>$\bar{c}_p$</td>
</tr>
<tr>
<td>500.0</td>
<td>5.608 0.05621</td>
<td>-</td>
<td>5.625 0.05631</td>
<td>-</td>
<td>5.628 0.05626</td>
<td>-</td>
</tr>
<tr>
<td>500.7</td>
<td>5.634 0.05611</td>
<td>-</td>
<td>5.639 0.05620</td>
<td>-</td>
<td>5.635 0.05625</td>
<td>-</td>
</tr>
<tr>
<td>524.1</td>
<td>5.694 0.05640</td>
<td>-</td>
<td>5.695 0.05641</td>
<td>-</td>
<td>5.695 0.05641</td>
<td>-</td>
</tr>
<tr>
<td>549.9</td>
<td>5.705 0.05652</td>
<td>-</td>
<td>5.706 0.05653</td>
<td>-</td>
<td>5.707 0.05654</td>
<td>-</td>
</tr>
<tr>
<td>576.0</td>
<td>5.716 0.05662</td>
<td>-</td>
<td>5.717 0.05663</td>
<td>-</td>
<td>5.717 0.05663</td>
<td>-</td>
</tr>
<tr>
<td>600.0</td>
<td>5.727 0.05672</td>
<td>-</td>
<td>5.728 0.05673</td>
<td>-</td>
<td>5.728 0.05673</td>
<td>-</td>
</tr>
<tr>
<td>624.1</td>
<td>5.738 0.05682</td>
<td>-</td>
<td>5.739 0.05683</td>
<td>-</td>
<td>5.739 0.05683</td>
<td>-</td>
</tr>
<tr>
<td>649.9</td>
<td>5.749 0.05692</td>
<td>-</td>
<td>5.750 0.05693</td>
<td>-</td>
<td>5.750 0.05693</td>
<td>-</td>
</tr>
<tr>
<td>676.0</td>
<td>5.760 0.05703</td>
<td>-</td>
<td>5.761 0.05704</td>
<td>-</td>
<td>5.761 0.05704</td>
<td>-</td>
</tr>
<tr>
<td>700.0</td>
<td>5.771 0.05713</td>
<td>-</td>
<td>5.772 0.05714</td>
<td>-</td>
<td>5.772 0.05714</td>
<td>-</td>
</tr>
<tr>
<td>724.1</td>
<td>5.782 0.05723</td>
<td>-</td>
<td>5.783 0.05724</td>
<td>-</td>
<td>5.783 0.05724</td>
<td>-</td>
</tr>
<tr>
<td>749.9</td>
<td>5.793 0.05733</td>
<td>-</td>
<td>5.794 0.05734</td>
<td>-</td>
<td>5.794 0.05734</td>
<td>-</td>
</tr>
<tr>
<td>776.0</td>
<td>5.804 0.05743</td>
<td>-</td>
<td>5.805 0.05744</td>
<td>-</td>
<td>5.805 0.05744</td>
<td>-</td>
</tr>
<tr>
<td>800.0</td>
<td>5.815 0.05753</td>
<td>-</td>
<td>5.816 0.05754</td>
<td>-</td>
<td>5.816 0.05754</td>
<td>-</td>
</tr>
<tr>
<td>824.1</td>
<td>5.826 0.05763</td>
<td>-</td>
<td>5.827 0.05764</td>
<td>-</td>
<td>5.827 0.05764</td>
<td>-</td>
</tr>
<tr>
<td>849.9</td>
<td>5.837 0.05773</td>
<td>-</td>
<td>5.838 0.05774</td>
<td>-</td>
<td>5.838 0.05774</td>
<td>-</td>
</tr>
<tr>
<td>876.0</td>
<td>5.848 0.05783</td>
<td>-</td>
<td>5.849 0.05784</td>
<td>-</td>
<td>5.849 0.05784</td>
<td>-</td>
</tr>
<tr>
<td>900.0</td>
<td>5.859 0.05793</td>
<td>-</td>
<td>5.860 0.05794</td>
<td>-</td>
<td>5.860 0.05794</td>
<td>-</td>
</tr>
<tr>
<td>924.1</td>
<td>5.870 0.05803</td>
<td>-</td>
<td>5.871 0.05804</td>
<td>-</td>
<td>5.871 0.05804</td>
<td>-</td>
</tr>
<tr>
<td>949.9</td>
<td>5.881 0.05813</td>
<td>-</td>
<td>5.882 0.05814</td>
<td>-</td>
<td>5.882 0.05814</td>
<td>-</td>
</tr>
<tr>
<td>976.0</td>
<td>5.892 0.05823</td>
<td>-</td>
<td>5.893 0.05824</td>
<td>-</td>
<td>5.893 0.05824</td>
<td>-</td>
</tr>
<tr>
<td>1000.0</td>
<td>5.903 0.05833</td>
<td>-</td>
<td>5.904 0.05834</td>
<td>-</td>
<td>5.904 0.05834</td>
<td>-</td>
</tr>
</tbody>
</table>
the values measured; all data obtained are collected in the following table I and graphically represented in Fig. 1.

§ 2. From the experience gathered in this way, it must be concluded, that the variability of the values of $c_p$ is immediately connected with a content of oxygen of the melted and solidified metal.

The true values of $c_p$ for really oxygen-free, stabilized silver are the smaller ones, represented by the curves $B'$ and $C'$ in Fig. 1, while the higher ones (curves $B$, $C$ and $aa'$ and $bb'$ in Fig. 1) correspond to a mass of the metal which contains a greater or smaller quantity of oxygen, absorbed during the process of fusion in air and evidently partially retained during its solidification, or absorbed by the solid metal heated at 940° C.

<table>
<thead>
<tr>
<th>Temperature in 0° C.:</th>
<th>Quantity of Heat $Q_0$ in Cal. developed by 1 Gr. silver between $t^0$ and 0° C.:</th>
<th>Mean specific Heat $c_p$ between $t^0$ and 0° C.:</th>
<th>$c_p$ calculated from Formula I:</th>
<th>$c_p$ calculated from Formula II:</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.14</td>
<td>5.639</td>
<td>0.05612</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>300.14</td>
<td>17.275</td>
<td>0.05755</td>
<td>0.05752</td>
<td>0.05770</td>
</tr>
<tr>
<td>397.4</td>
<td>23.120</td>
<td>0.05818</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>516.55</td>
<td>30.416</td>
<td>0.05888</td>
<td>0.05898</td>
<td>0.05893</td>
</tr>
<tr>
<td>628.9</td>
<td>37.558</td>
<td>0.05972</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>701.9</td>
<td>42.271</td>
<td>0.06022</td>
<td>0.06019</td>
<td>—</td>
</tr>
<tr>
<td>749.2</td>
<td>45.396</td>
<td>0.06059</td>
<td>0.06050</td>
<td>0.06054</td>
</tr>
<tr>
<td>801.1</td>
<td>48.791</td>
<td>0.06090</td>
<td>0.06083</td>
<td>—</td>
</tr>
<tr>
<td>849.9</td>
<td>52.052</td>
<td>0.06124</td>
<td>0.06114</td>
<td>0.06129</td>
</tr>
<tr>
<td>895.3</td>
<td>55.298</td>
<td>0.06176</td>
<td>0.06142</td>
<td>—</td>
</tr>
<tr>
<td>(940.3)</td>
<td>(58.553)</td>
<td>(0.06227)</td>
<td>—</td>
<td>(0.06238)</td>
</tr>
</tbody>
</table>

The absorption of oxygen by the metal evidently causes an increase of $c_p$ at each temperature, which is the more considerable, the greater the quantity is of oxygen absorbed by the solid metal. The most accurate values of $c_p$ for oxygen-free, stabilized silver between 0° C. and 900° C. are collected in table II. Without any doubt the more rapid increase of the $c_p-t$-curve above 700° C. and its particular $\sim$-shape, are also connected
with the more accelerated absorption of oxygen by or its diffusion through
the heated metal at higher temperatures: all investigations hitherto made \(^1\)
seem to confirm the fact, that no allotropic changes of the metal, — at least
at higher temperatures, — occur.

Between \(0^\circ\) and about \(800^\circ\) C. the values of \(\bar{c}_p\) in table II for pure,
oxygen-free silver can, in function of the temperature, very well be
expressed by the formula:

\[
\bar{c}_p = 0.055401 + 0.7207 \times 10^{-5} \cdot t - 0.54053 \times 10^{-9} \cdot t^2 \quad \cdots (I),
\]
and the corresponding true specific heats, therefore, by:

\[
c_p = 0.055401 + 0.14414 \times 10^{-4} \cdot t - 0.16216 \times 10^{-8} \cdot t^2.
\]

This formula can be applied between \(0^\circ\) and about \(800^\circ\) C.: the
deviations of the values observed and calculated are all situated within the
limits of experimental error. The atomic heats \(C_p\) can, therefore, be cal-
culated, — within the same limits of the temperature, — by means of the
formula:

\[
C_p = 5.9767 + 0.1555 \times 10^{-2} \cdot t - 0.17494 \times 10^{-6} \cdot t^2.
\]

Some values of \(C_p\) thus calculated are the following:

<table>
<thead>
<tr>
<th>Temperature in °C.:</th>
<th>Atomic Heat (C_p):</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>5.977</td>
</tr>
<tr>
<td>100</td>
<td>6.130</td>
</tr>
<tr>
<td>200</td>
<td>6.281</td>
</tr>
<tr>
<td>300</td>
<td>6.427</td>
</tr>
<tr>
<td>400</td>
<td>6.571</td>
</tr>
<tr>
<td>500</td>
<td>6.710</td>
</tr>
<tr>
<td>600</td>
<td>6.847</td>
</tr>
<tr>
<td>700</td>
<td>6.979</td>
</tr>
<tr>
<td>800</td>
<td>(7.109)</td>
</tr>
</tbody>
</table>

This curve I for \(C_p\) is represented in Fig. 2; it may be considered as the
normal curve for the atomic heats in their dependance on the temperature.

and E. Eydmann, Ann. d. Chem., 390, (1912), 340; 398, (1913), 14; G. W. A. Kahlbaum,
K. Roth and P. Siedler, Zeits. f. anorg. Chem., 29, (1902), 177; W. Haidinger,
Bd. Zeits. f. Kryst. (1931), 36–38, 748. The existence of a rhombic modification in
very dubious.
Just as formerly stated, this curve is concave towards the temperature-axis; the values of \( C_p \) are right within about \( \pm 0.5 \% \). If, however, the abnormally steep change of \( \tilde{c}_p \) at higher temperatures shall also be taken into account, \( \tilde{c}_p \) can only be expressed pretty accurately by means of a formula with more than three constants, — for instance, by:

\[
\tilde{c}_p = 0.05355 + 0.37946 \times 10^{-4} \cdot t - 0.15285 \times 10^{-6} \cdot t^2 + 0.3278 \times 10^{-9} \cdot t^3 - 0.32422 \times 10^{-12} \cdot t^4 + 0.1214 \times 10^{-15} \cdot t^5 \quad \text{(II)}.
\]

The true specific heat \( c_p \) is, therefore, expressed by:

\[
c_p = 0.5355 + 0.75892 \times 10^{-4} \cdot t - 0.45855 \times 10^{-6} \cdot t^2 + 0.13112 \times 10^{-8} \cdot t^3 - 0.16211 \times 10^{-11} \cdot t^4 + 0.7284 \times 10^{-15} \cdot t^5,
\]

and the atomic heat \( C_p \) by:

\[
C_p = 5.7770 + 0.81873 \times 10^{-2} \cdot t - 0.49469 \times 10^{-4} \cdot t^2 + 0.14145 \times 10^{-6} \cdot t^3 - 0.17488 \times 10^{-9} \cdot t^4 + 0.7857 \times 10^{-13} \cdot t^5.
\]

A series of values of \( c_p \) and \( C_p \) thus calculated are the following:

<table>
<thead>
<tr>
<th>Temperature in °C</th>
<th>True specific Heats ( c_p )</th>
<th>Atomic Heats ( C_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>0.05966</td>
<td>6.436</td>
</tr>
<tr>
<td>400</td>
<td>0.06041</td>
<td>6.517</td>
</tr>
<tr>
<td>500</td>
<td>0.06220</td>
<td>6.710</td>
</tr>
<tr>
<td>600</td>
<td>0.06377</td>
<td>6.879</td>
</tr>
<tr>
<td>700</td>
<td>0.06491</td>
<td>7.003</td>
</tr>
<tr>
<td>800</td>
<td>0.06678</td>
<td>7.204</td>
</tr>
<tr>
<td>900</td>
<td>0.07276</td>
<td>7.849</td>
</tr>
<tr>
<td>950</td>
<td>0.07916</td>
<td>8.540</td>
</tr>
</tbody>
</table>

From the graph (Fig. 2) it becomes clear that, within the limits of experimental error, there is only above 780° C. a more considerable deviation between the two curves I and II: indeed, taking into account the exactness reached in the measurement of \( \tilde{c}_p \), the uncertainty in \( c_p \) is still about 0.5 %, so that both curves I and II may be considered as practically coinciding up to about 800° C. Curve I evidently represents the true values of \( C_p \) in function of the temperature between 0° and 800° C.; its shape is the same as that previously found for stabilized silver.

The rapid increase of the curve II above about 780° C. is clearly manifested and certainly must be connected with the absorption of oxygen by the heated metal, as it exactly begins at the temperature, at which,
according to TROOST\textsuperscript{1)}, the diffusion of oxygen through solid silver sets in with an observable velocity.

Fig. 2. True Atomic Heats $C_p$ of Oxygenfree Silver.

Above 800° C., therefore, the values of $C_p$ determined, evidently have no longer a real significance, as they depend on the accidental way of executing the experiments.

§ 3. The fact that molten silver absorbs considerable quantities of oxygen has already been known\textsuperscript{2)} since 1819 and also the fact, that, on cooling, the metal gives off the total or the greater part of this oxygen by manifesting the phenomenon of “spitting”. As to the question, whether all the gas absorbed by the liquid metal is really liberated on cooling and solidifying, there has been much controversy. DUMAS\textsuperscript{3)}, TROOST\textsuperscript{4)} and other investigators stated, that the solidified metal, on heating, still gave off considerable quantities of oxygen; but VAN DER PLAATS\textsuperscript{5)}, BRAUNER\textsuperscript{6)}

\textsuperscript{1)} L. TROOST, loco cit.
\textsuperscript{4)} L. TROOST, Comp. rend. Paris, 98, (1884), 1427.
\textsuperscript{6)} B. BRAUNER, Bull. Acad. de Belg., (3), 18, (1889), 81.
and other investigators \(^1\) have contested this. **Heycock and Neville** \(^2\) found that the melting point of silver in an atmosphere of oxygen is lowered by \(10^\circ - 17^\circ\); **CalleNDAR** \(^3\) demonstrated, that molten and solidified silver, — after "spitting", — still showed a depression of its melting point of \(6^\circ 4\). **Le Chatelier** \(^4\) found, that solid silver already at \(300^\circ\) C. takes up oxygen, if the pressure of the gas be greater than 12 atmospheres. According to **Manchot** \(^5\), silver is covered with a very thin film of its oxide, if it be heated in air at \(200^\circ\) C. **Troost** \(^6\) demonstrated, that at \(780^\circ\) C. oxygen *diffuses* through solid silver, while to other gases, like \(CO\), \(N_2\), etc. it is impermeable under the same circumstances. As the concentration of the oxygen absorbed by the molten metal proves to be proportional to the square root of the oxygen-pressure \(^7\), the oxygen in it cannot be present as \(O_2\), but must be present either in the atomic state \(^2\) or as \(Ag_2O\). Between these two alternatives a final decision cannot be made (conf. **Donnan** and **Shaw** \(^8\)).

Although \(Ag_2O\), once formed, is more or less rapidly decomposed already at \(270^\circ - 300^\circ\) C., all investigations hitherto made seem to indicate, that the affinity of oxygen for silver at higher temperatures is rather considerable \(^9\), but that the oxide formed then is decomposed at lower temperatures.

The experiments here described now clearly demonstrate, that the oxygen absorbed by the liquid metal is, on solidification, certainly *not completely* given off, but is partially occluded in the crystalline mass; moreover, that on preserving such an oxygen-containing lump at room-temperature for a long time, the gas is gradually set free by a very slow process of diffusion and that, reversely, by heating the solid metal in air at temperatures above about \(650^\circ\) C., oxygen is again absorbed. The slowness of its progress is readily explained by the extreme slowness of the diffusion of the gas through the crystalline mass of the metal at these temperatures. The method of measurement of the specific heats, however, appears to be sufficiently sensitive for revealing the absorption and the subsequent escaping of the gas, by the increase or by the diminution respectively of the values for \(C_p\) at each temperature.

\(^3\) H. CalleNDAR, *Phil. Mag.*, (5), 33, (1892), 220.
\(^6\) E. Troost, loco cit.
§ 4. From the data given in the literature concerning the compressibility 1) and the linear expansion 2) of silver, the approximate values of $C_p$ can be calculated by means of the usual thermodynamical equation.

From the measurements, the linear expansion of silver between $0^\circ$ and $875^\circ$ C., can fairly well be expressed by the formula:

$$l_t = l_0 (1 + 0.000018033 \cdot t + 0.000000004833 \cdot t^2).$$

The following values of $c_p$ and $C_p$ thus are found:

| Temperature in °C. | $c_p$ : | $c_p$ : | $C_p$ : | $C_p$ :
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>0.05540</td>
<td>0.05329</td>
<td>5.977</td>
<td>5.748</td>
</tr>
<tr>
<td>100</td>
<td>0.05682</td>
<td>0.05415</td>
<td>6.130</td>
<td>5.841</td>
</tr>
<tr>
<td>200</td>
<td>0.05822</td>
<td>0.05495</td>
<td>6.281</td>
<td>5.928</td>
</tr>
<tr>
<td>300</td>
<td>0.05958</td>
<td>0.05557</td>
<td>6.427</td>
<td>5.995</td>
</tr>
<tr>
<td>400</td>
<td>0.06091</td>
<td>0.05610</td>
<td>6.571</td>
<td>6.052</td>
</tr>
<tr>
<td>500</td>
<td>0.06220</td>
<td>0.05652</td>
<td>6.710</td>
<td>6.098</td>
</tr>
<tr>
<td>600</td>
<td>0.06347</td>
<td>0.05701</td>
<td>6.847</td>
<td>6.150</td>
</tr>
<tr>
<td>700</td>
<td>0.06469</td>
<td>0.05743</td>
<td>6.979</td>
<td>6.195</td>
</tr>
<tr>
<td>800</td>
<td>0.06590</td>
<td>0.05775</td>
<td>7.109</td>
<td>6.230</td>
</tr>
</tbody>
</table>

These values of $C_p$ are also graphically represented in Fig. 2; no indication is manifested of a maximum in this curve, as was found by MAGNUS and HODLER 3).

Groningen, Laboratory for Inorganic and Physical Chemistry of the University.

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1) P. W. BRIDGMAN, Proceed. Amer. Acad. Arts and Sciences, 58, (1923), 165. For $x \cdot 10^6$ at $30^\circ$ C. the value: 0.987, at $75^\circ$ C. the value: 1.004 was used and a linear increase of $x$ with the temperature was assumed.


3) A. MAGNUS and A. HODLER, Zeits. f. phys. Chem., 110, (1924), 188.