## Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

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J.J. van Laar, The course of the melting-point-line of alloys, in: KNAW, Proceedings, 6, 1903-1904, Amsterdam, 1904, pp. 21-30

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$\cdots \cdots$ by theory is represented in Fig. 2. The dotted

... ... ... .
lying above and under the middle. The vertical
Fig. 2. medium line of Fig. 1 corresponds to the almost ever present absorption line due to the are light and is thus in no way connected with the phenomenon which occupics as.

The agreement in the region between the two interior components of the quadruplet is undoubtedly of great importance. The whole form of the double curred line may certainly be regarded as a confirmation of theory. How far the darker parts between the exterior components in the middle of Fig. 1 correspond to the U -shaped parts of Fig. 2 is at present not yet to be decided.

Chemistry. - "The course of the melting-point-linu of alloys." (Third commmication). By J. J. van Ilar. (Communicated by Prof. H. W. Bahiuis Roozeboomis).
I. I hare shown in two papers (these proceedings Jan. 31 and March 28, 1903) that the expression (see the second paper):

$$
\begin{equation*}
T=T_{0} \cdot \frac{1+\frac{\alpha x^{2}}{(1+r x)^{2}}}{1-O \log (1-x)}, \tag{1}
\end{equation*}
$$

very accurately represents the solidification temperatures of tinamalgams. This equation may be derived from the general expressions for the molecular thermodynamic potentials of one of the lwo components in solid condition and in the fluid alloy.

I also pointed out (in the first paper), that already the simple formula

$$
\begin{equation*}
T^{\prime}=\frac{T_{0}}{1-\theta \log (1-x)} \tag{2}
\end{equation*}
$$

qualitatively represents the course of the meltug-point-line perfectly. This is simply done by not omitting the logarithmic function $\log (1-x)$. Though it is a matter of course, that - $\log (1-x)$ can only be replaced by $x$, or $x+\frac{1}{2} x^{2}+$ etc. in the case that $a$ is very small, it
seems necessary to continually diaw attention to this circumstance. Already in 1893 in his thesis for a doctor's degree: "De afwijkingen van de wetten voor verdunde oplossingen" Hondius Boldingh used the function - $\log (1-x)$; also, the correction term $\mathrm{c}^{2}$, omitting however the denominator $(1+r x)^{2}$. Lef Chatiaier ${ }^{1}$ ) used the simple equation (2) in a somewhat modified form for the melting-point-curves of alloys. The way however in which he derived this equation is totally wrong ${ }^{2}$ ).
II. Many melting-point-curves show the same type as those of tin-amalgams; it may therefore be important to investigate, whether they also may be represented by formula (1). It must hower er be observed, that this formula is applicable only in the case that the soliel phase cloes not form any mireed crystals. If the formula (1) does not hold good, this may therefore indicate the occurrence of mixed crystals in the solid phase, though it is of course also possible that other influences e. g. dissociating multiple molecules have caused the deviation.

In 1897 Heycock and Nextise 1 a. made experiments on a great many alloys'). They found that the allos sitrep-lead shows the type of themercury very accurately (comp. the figure on p. 59 of their paper). I have subjected the data relating to the point (comp. the tables of p. 37 and 39) to some numerical investigations.

The initial course is again nearly straight - up to about 20 atom procents of lead - and this part yields for 0 the value 0,805 . If we norv use this value for the calculation of the quantities $a$ and $r$ from the observations at lower temperature, we do not find constant values, as in the case of tin-mercury, but considerably different values according as we have calculated these constants at mean temperatures or at low temperatures. If we take the data for $a=0,63$ and $x=0,80$, or $x=0,63$ and $x=0,96$ (the eutectic point) as basis for our calculation, then we find in both cases:

$$
\alpha=0,355 \quad ; \quad r=-0,325 .
$$

The following table may show how bad the agreement is, specially for the mean temperatures:

[^0]SILVER-LEAD. ${ }^{1}$ )

| $x$ | $x^{2}$ |  | $\alpha 2^{2}$ | $\stackrel{\sim}{\text { ¢ }}$ |  |  | - | $\Delta$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0 | 0 | 1.0000 | 0 | 10000 | 1.0000 | 959.1 | 959.1 | 0 |
| 0.0052 | $0.0000^{3}$ | 1.0042 | $00000^{1}$ | 09966 | 100001 | 9540 | 9543 | $-03$ |
| 0.0103 | $0.007{ }^{1}$ | 1.0083 | $00000^{+}$ | 0.9934 | $10000^{4}$ | 9489 | 9490 | $-0.1$ |
| 0.0154 | $00002^{4}$ | 10125 | $00000^{8}$ | 09900 | $10000^{\circ}$ | 9440 | 9'4 0 | 0 |
| 0.0254 | $00006^{5}$ | 1.0207 | $0.0002^{3}$ | 09835 | 10002 | 934.5 | 934.4 | +01 |
| 0.0361 | $0.0013^{\circ}$ | 1.0296 | $00004^{6}$ | 09767 | 10005 | 924.3 | 9244 | -0.1 |
| 0.0504 | $0.002{ }^{4}$ | 1.0416 | $00009^{\circ}$ | 09675 | 1.0009 | 9109 | 910.4 | + 05 |
| 0.0733 | $0.0053^{3}$ | 10613 | 000192 | 0950 | $-10020$ | 890.3 | 8866 | +37 |
| 0.1057 | $0.011^{7}$ | 10900 | $00039^{\text {i }}$ | 09324 | 10043 | 8621 | 8534 | +8.7 |
| 0.1360 | $0.0185^{\text {n }}$ | 11177 | $00065^{\circ}$ | 09136 | 10072 | 837.2 | 8200 | +17.2 |
| 0.1732 | 0.03000 | 1.1531 | $00106^{5}$ | 08906 | 1.0120 | 808.4 | 7827 | + |
| 0.2156 | $0.0464^{8}$ | 11955 | $00165^{\circ}$ | 0.8647 | 10191 | 777.2 | 7416 | $+356$ |
| 02537 | $0.0643^{6}$ | 1.2356 | $00228{ }^{5}$ | 0.8418 | 10271 | 751.1 | 7100 | +-41.1 |
| 0.2949 | 0.08697 | 1.2813 | $00308^{8}$ | 08176 | 1.0378 | 7250 | 6841 | +409 |
| 0.3432 | 0.1478 | 1.3385 | $0.0418^{2}$ | 07894 | 10530 | 6963 | 659.5 | +368 |
| 0.4038 | 0.1631 | 14164 | 0.05792 | 0.7548 | 10767 | 663.4 | 6354 | +28 |
| 0,4542 | 0.2063 | 14876 | $00732^{4}$ | 07260 | 11007 | 638.5 | 0193 | +19.2 |
| 0.4966 | 0.2406 | 1.5527 | $0.0875^{+}$ | 07032 | 1.12 任 | 6191 | 6062 | $+12.9$ |
| 0.5330 | 0.2841 | 16131 | $010 \leq 9$ | 0.6836 | 1.1476 | 603.4 | 5961 | $+7.3$ |
| 0.5851 | 0.3123 | 1.7083 | 0.1215 | 0.6558 | 1.1853 | 581.9 | 580.8 | +1.1 |
| *0.0312 | 03984 | 1.8032 | 01414 | 0.6319 | 1.2238 | 5631 | 5030 | + 0 1* |
| 06790 | 0.4610 | 19149 | 0.1637 | 0.6073 | 1.2696 | 543.9 | 5483 | $-44$ |
| 0.7042 | 0.4959 | 1.9808 | 0.1761 | 05946 | 12962 | 533.2 | 5369 | $-37$ |
| 0.7353 | 0.5407 | 2.0702 | 01920 | 05791 | 1.3316 | 519.5 | 523.6 | $-4.1$ |
| 0.7632 | 0.5917 | 21816 | 0.2101 | 0.4727 | 1.3735 | 503.0 | 5055 | $-2.5$ |
| *0.8064 | 06503 | 23221 | 0.2309 | 0.5625 | 14241 | 482.5 | 481.6 | + 0.9* |
| 0.8333 | 0.6944 | 2.4425 | 0.2465 | 0.5445 | 14635 | 465.1 | 460.6 | +4.5 |
| *0.9615 | 0.9245 | 3.6226 | 0.3282 | 05318 | 16943 | 303.2 | 303.3 | -0.1* |

${ }^{1}$ ) The values of $x$ marked with asterics are those which are used for the calculation of the constants $z$ and $r$.

Between $\imath=0,10$ and $\imath=0,53$ the agreement is decidedly bad; at lower temperatures slightly better. It is striking that the value we find for $\alpha$ is much too large, namely 0,355 ; for tin-mercury we found for $a$ only the value 0,0453 .

We will further investigate whether the value of $\theta$ which is calculated from the initial straight part of the melting-point-line, namely $0=0,805$, is in agreement with the latent heat of solidification of pure silver.

As

$$
\theta=\frac{R T_{0}}{q_{\mathrm{o}}}
$$

and as Person has found $q_{0}=107,94 \times 21,07=227 \pm$ Gr. kal., we shonld have for 0 :

$$
0=\frac{2 \times 1232}{2274}=1,084 .
$$

We have, however, found the much smaller value 0,805 . This indicates the occurrence of mixed crystals already in the initial part of the molting-point curve, unless we assume, either that the value of Plerson is about 1,35 times too small, or that the association of the lead, contained in the silver, is 1,35 .
III. Let us discuss in the second place the melting-point curve of silver-tin. We conclude at once from the figure of Heycock and Nevilus, that complications, mixed crystals for instance, must occur. For though the melting-point curve from 30 atom-procents tin upwards shows the normal typical course, the initial part, instead of being nearly straight, is strongly concave towards the side of silver, so that two inflection points occur, quite contrary to the course indicated by formula (1) or (2).

It is accordingly impossible to determine the value of $\theta$ from the initial part of the curve. If we calculate $\theta, a$ and $r$ from three observations, for instance $a=0,43, x=0,61$ and $x=0,86$, then we get with:

$$
\left.T_{0}=961,5^{1}\right)+273,2=1234,7
$$

the following values (comp. the table of Hercock and Nevimsu, p. 40 and 41):

$$
0=1,491 \quad ; \quad a=0,718 \quad ; \quad r=-0,277
$$

1) The value $959^{\circ} .2$ given by Heycock and Nevilue has been augmented to $961^{\circ} .5$ on account of the accurate observations of Holborn and $D_{A Y}$ (quoted in Z. f. Ph. Ch. 35, p. 490-491), from which appeared that pure silver, the air being excluded, so that no oxygen can be absorbed, has a higher melting point $\left(961^{\circ} .5\right)$ than silver containing oxygen ( $955^{\circ}$ ).

We see that the value calculated for 0 is cousiderably higher than the normal value 1,08 and that $a$ is also again excessively high. In order to get a survey of the degree of the deviation from the theoretical course we will perform here the calculation of equation (1) with these values of $0, a$ and $r$. (see table p. 26).

This bad agreement does not improve considerably if we determine $n$, " and $r$ from other values of $x$, for instance from $x=0,30, x=0,61$ and $x=0,93$. For these values of $x$ we find:

$$
\theta=1,326 \quad ; \quad \alpha=0,47 \dot{4} \quad ; \quad r=-0,38,
$$

so 0 has come somewhat nearer to 1,08 and $a$ is also somewhat lower. It is true that the agreement for values of $a$ below $x=0,30$ has somewhat though not noticeably improved ( $\triangle=-70,3$ for $x=0,13$ becomes now $\Delta=-55,7$ ) but the agreement for values of $x$ higher than $t=0,30$ is in general still worse. So we find for instance for $w=0,47$ for $\Delta$ the value $\Delta=+8,5$, whilst in the above table we found $\Delta=+2,6$, etc.
IV. For completeness' sake we shall draw attention to the two very short melting-point curves of lead-silver and tin-silver. We may easily calcuiate the quantities 0 from the data of the two eutectic points. As namely these lines may be considered to be straight, we find $\theta$ immediately from

$$
\theta=\frac{T_{0}-T}{T_{a}}
$$

We have for lead-siluer:
$T_{0}=327,6+273,2=600,8 ; ~ T=303,3+273,2=576,5 ; x=0,0385 \pm$, therefore

$$
0=\frac{24,3}{576,5 \times 0,0385}=1,095,
$$

hence

$$
q_{0}=\frac{R T_{0}}{\theta}=\frac{2 \times 600,8}{1,095}=1097 \mathrm{Gr} . \mathrm{cal} .
$$

Person found $q_{0}=5,369 \times 206,9=1111$ Gr. cal. The agreement appears to be nearly perfect. From this follows that silver, solved in lead, occurs in it as atom, at least for small concentrations.

As to the melting-point curve tin-silver we have for it:
$T_{0}=232,1+273,2=505,3 ; T=221,7+273,2=494,9 ; x=0,0385 \pm$.
We find therefore:

$$
\theta=\frac{10,4}{494.9 \times 0,0385}=0,546,
$$

and

## SILVER-TIN.

| $x$ | $x^{2}$ |  | $\mu r^{2}$ | $\frac{9}{\frac{9}{8}}$ |  |  | - | $\triangle$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0 | 0 | 1.0000 | 0 | 1.0000 | 1.0000 | 961.5 | 959.2 | $+2.3$ |
| 0.00459 | $0.0000^{2}$ | 1.0068 | $0.0000^{2}$ | 0.9975 | $1.0000^{2}$ | 953.2 | . 956.1 | $-2.9$ |
| 0.01299 | $0.0001^{7}$ | 1.0195 | $0.0001^{2}$ | 0.9928 | 1.0001 | 938.0 | 950.0 | $-12.0$ |
| 0.03058 | $0.600{ }^{4}$ | 1.0463 | $0.0006^{7}$ | 0.9831 | 10007 | 907.9 | 936.3 | -28.4 |
| 0.04842 | $00023^{4}$ | 1.0739 | $0.0016^{8}$ | 0.9734 | 1.0017 | 878.4 | 921.8 | $-43.4$ |
| 0.08114 | $0.0065^{\text {s }}$ | 1.1260 | $0.0047^{3}$ | 0.9555 | 1.0049 | 828.7 | 891.0 | $-62.3$ |
| 0.1324 | $0.0175^{3}$ | 1.2144 | $0.0125^{9}$ | 0.9279 | 1.0136 | 759.9 | 830.2 | $-70.3$ |
| 0.1813 | $0.0323^{7}$ | 1.2978 | $0.0236^{\circ}$ | 0.9021 | 1.0262 | 703.2 | 755.9 | $-52.7$ |
| 02253 | $0.0507^{6}$ | 1.3801 | $0.0364^{5}$ | 0.8791 | 1.0415 | 658.5 | 691.7 | $-33.2$ |
| 0.2633 | 0.06933 | 1.4549 | $0.0497{ }^{8}$ | 08595 | 1.0579 | 624.6 | 648.2 | $-23.6$ |
| 0.3095 | $0.0957^{\text {² }}$ | 1.5514 | $0.0687^{8}$ | 0.8359 | 1.0823 | 588.1 | 603.1 | -15.0 |
| 0.3516 | 0.1236 | 1.6450 | 0.0887 ${ }^{4}$ | 0.8147 | 1.1089 | 559.0 | 567.5 | $-8.5$ |
| 03917 | 0.1534 | 1.7400 | 0.1101 | 0.7948 | 1.1385 | 534.8 | 538.7 | $-3.9$ |
| *0.4371 | 0.1911 | 1.8555 | 0.1372 | 0.7725 | 1.1776 | 510.4 | 510.2 | + 0.2 * |
| 0.4764 | 0.2270 | 1.9633 | 01630 | 0.7534 | 1.2164 | 49:.8 | 489.2 | +2.6 |
| 05107 | 0.2608 | 2.0641 | 0.1873 | 0.7370 | 1.2541 | 476.9 | 474.0 | +2.9 |
| 0.5426 | 0.2944 | 2.1643 | 02114 | 0.7220 | 1.2928 | 464.3 | 463.6 | $+0.7$ |
| 0.5731 | 0.3284 | 2.2672 | 0.2358 | 0.7076 | 1.3332 | 452.8 | 453.3 | - 0.5 |
| *0.6148 | 0.3780 | 2.4203 | 0.2714 | 0.6884 | 1.3943 | 438.2 | 437.9 | + 0.3 * |
| 0.6510 | 0.4287 | 2.5670 | 0.3042 | 0.6719 | 1.4527 | 4256 | 424.9 | $+0.7$ |
| 0.6812 | 0.4640 | 2.7019 | 0.3332 | 0.6582 | 1.5062 | 415.1 | 413.0 | +2.1 |
| 0.7173 | 0.5145 | 2.8808 | 0.3694 | 0.6421 | 1.5753 | 402.0 | 399.2 | +2.8 |
| 0.7547 | 0.5696 | 3.0921 | 0.4090 | 0.6255 | 1.6539 | 387.2 | 381. 4 | +5.8 |
| 0.7687 | 0.5909 | 3.1796 | 0.4243 | 0.6195 | 1.6849 | 381.0 | 380.8 | $+0.2$ |
| 0.8192, | 0.6711 | 3.5463 | 0.4819 | 0.5977 | 1.8063 | 355.7 | 355.2 | + 0.5 |
| *0.8692 | 0.7555 | 4.0283 | 0.5425 | 0.5764 | 1.9412 | 321.8 | 322.6 | $-0.8{ }^{*}$ |
| 0.9006 | 0.8111 | 4.4369 | 0.5824 | 0.5633 | 2.0339 | 292.8 | 296.9 | $-4.1$ |
| 0.9344 | 0.8731 | 5.0557 | 0.6269 | 0.5494 | 2.1411 | 229.9 | 259.5 | -29.6 |
| 0.9615 | 0.9245 | 5.8490 | 0.6638 | 0.5383 | 2.2332 | 198.2 | 221.7 | -23.5 |
|  |  |  |  |  |  |  |  |  |

$$
q_{0}=\frac{2 \times 505,3}{0,546}=1851 \mathrm{Gr} . \text { cal. }
$$

Person found for the latent heat of solidification for tin

$$
14,252 \times 118,5=1689 \text { Gr. cal. }
$$

The difference is so small, that we may assume also here that the silver is present as atom also in tin. This conclusion is the more justified as Heycock and Nevilue give for $x$ : "somewhat smaller than 0,0385 ", from which follows that $\theta$ will be somewhat greater and $q_{0}$ somewhat smaller, so that $q_{0}$ approaches still more to 1690.

I draw attention to the fact, that the good agreement of the value for tin found by Prrson justifies the conclusion that this value is really rather accurate, so that we must assume that the mercury (see my previous communication), solved in tin, is present in partially associated condition, the association amounting to about 1,5 . It appeared namely that - when mercury did not occur in the solid phase, which consisted therefore exclusively of tin - the value of $O$ was such, that it yielded $q_{0}=2550$. In order to make this value $1 \frac{1}{2}$ times smaller, $U$ must be augmented, i. e. $x$ must be diminished, and this can only be done by assuming association to the same amount.
V. Let is now return to the question of the point of inflection on the melting-point curve. From:

$$
T=T_{0} \frac{1+\frac{\alpha \alpha^{2}}{(1+r x)^{2}}}{1-U \log (1-x)}
$$

follows

$$
\frac{d T}{d x}=-\frac{T_{0}}{N^{2}} \frac{0}{1-v}\left(1+\frac{\alpha v^{2}}{(1+r v)^{2}}\right)+\frac{T_{0}}{N} \cdot \frac{2 \alpha x}{(1+r \cdot x)^{3}},
$$

therefore

$$
\begin{aligned}
& \frac{d^{2} T}{d x^{2}}=\frac{T_{0}}{N^{2}} \frac{\theta}{(1-x)^{2}}\left(\frac{2 O}{N}-1\right)\left(1+\frac{\alpha x^{2}}{(1+r x)^{2}}\right)- \\
& -2 \frac{T_{0}}{N^{2}} \frac{0}{1-x} \frac{2 \alpha v}{(1+r x)^{3}}+\frac{T_{0}}{N} \frac{2 \alpha(1-2 r x)}{(1+r x)^{4}},
\end{aligned}
$$

or

$$
\begin{align*}
& \frac{d^{2} T}{d x^{2}}=\frac{T_{0}}{N^{2}}\left[\frac{\theta}{(1-x)^{2}}\left\{\left(\frac{2 \vartheta}{N}-1\right)\left(1+\frac{\alpha x x^{2}}{1+r v)^{2}}\right)-\frac{4 \alpha v(1-v)}{(1+r x)^{3}}\right\}+\right. \\
& \left.+\frac{2 \alpha N(1-2 p x)}{(1+r x)^{4}}\right] \cdot . \cdot . . . . \cdot . \cdot . \cdot . \cdot . . \tag{3}
\end{align*}
$$

If $\alpha=0$, this equation may be written:

$$
\frac{d^{2} T}{d v^{2}}=\frac{T_{0}}{N^{2}} \frac{0}{(1-i)^{2}}\left(\frac{20}{N}-1\right)
$$

as we have also found before (see p. 481 of my first communication). Whereas for $a=0$ a point of inflection at $x=0(N=1)$ was cletermined with the aid of the simple equation $20=1$, or $0=1 / 2$, this condition becomes, in the case we are treating now, somewhat more intricate. If we equate namely the second number of equation (3) to zero, and further put $a=0, N=1$, then we find:

$$
0(2 \theta-1)+2 \alpha=0,
$$

so

$$
\theta^{2}-\frac{1}{2} \theta+a=0
$$

We find therefore that a point of inflection occurs beyond $x=0$, always when

$$
\begin{equation*}
0^{2}-\frac{1}{2} \theta+a>0 \tag{4}
\end{equation*}
$$

In the case of tin-mercury (see the second communication) we had $0=0,396$, and $\alpha=0,0453$; therefore:

$$
0,1568-0,1980+0,0453=0,0041
$$

This value being positive, a point of inflection was to be expected between $x=0$ and $x=1$. In fact a point of inflection was found at $x=0,75$.

The equation (4) may also be derived in the following way without making use of equation (3). If we resolve equation (1) into a series according to $a$, we get for small values of $a$ :

$$
T=T_{0}\left(1-\theta x+\left(\theta^{2}-\frac{1}{2} O+\alpha\right) x^{2} \ldots\right)
$$

The melting-point curve turns therefore at $x=0$ the concave side towards the ordinate $x=0$ in the case that $\theta^{2}-\frac{1}{2} \theta+\alpha<0$; and as the curve approaches the ordinate $a=1$ asymptotically, a point of inflection cannot occur. If on the other hand $\theta^{2}-\frac{1}{2} \theta+a>0$, then the conver side is turned towards the ordinate $x=0$ and therefore a point of inflection must necessarily occur between $x=0$ and $x=1$.

As $\theta$ can be $+\infty$ at the utmost, there must exist a value, which the abscissa of the point of inflection cannot exceed. This maximum value is found by equating the second member of equation (3) to zero, and 0 to $\infty$ [ $\lambda^{\top}$ being equal to $\left.-\theta \log (1-x)\right]$, so we find:

$$
\begin{aligned}
& \quad \frac{1}{(1-x)^{2}}\left\{\left(\frac{2}{-\log (1-x)}-1\right)\left(1+\frac{\alpha v^{2}}{(1+r x)^{2}}\right)-\frac{4 \alpha x(1-x)}{(1+r x)^{3}}\right\}+ \\
& +\frac{-2 \alpha \log (1-x)(1-2 r x)}{(1+r x)^{4}}=0 .
\end{aligned}
$$

Only if $\alpha=0$, this may simply be written:

$$
\begin{equation*}
\frac{2}{-\log (1-x)}-1=0, \text { or } \quad-\log (1-i x)=2 \tag{29}
\end{equation*}
$$

from which we find: $x=0,865$. If however $a$ is not zero, then the equation $-\log (1-x)=2$ transforms the above equation into the following one:

$$
\frac{1}{(1-x)^{2}}\left\{-\frac{4 \alpha v(1-x)}{(1+r v)^{3}}\right\}+\frac{4 \alpha(1-2 v v)}{(1+r v)^{4}}=0,
$$

. 0 r

$$
1-2 r_{i}=\frac{x}{1-w}\left(1+p_{i}\right),
$$

which is only true, if

$$
r=\frac{\frac{1}{x}-2}{2-a}=\frac{1,156-2}{2-0,865}=-0,744
$$

We happened to find exactly $r=-0,74$ for tin-mercury, so if 0 had been equal to $\infty$ - the point of inflection wonld have been found at $x=0,865$.

Neyative values of $\theta$ (or $q_{0}$ ) are required in order to find a point of inflection between that value of $x$, for which we find the point of inflection with $\theta=\infty$, and $x=1$. These negative values will occur very seldom, if at all. The principle result of the above investigation is therefore that the melting-point curve - the case of mixed crystals being excluded - will show a point of inflection if

$$
\theta^{2}-\frac{1}{2} 0+a>0,
$$

or, $\theta$ being equal to $\frac{R T_{0}}{q_{0}}$ and $a$ to $\frac{\alpha_{1}}{q_{0}}$, if

$$
\frac{R^{2} T_{0}{ }^{2}}{q_{0}}-\frac{1}{2} R T_{0}+\alpha_{1}>0
$$

i. e. if

$$
q_{0}<\frac{2 R T_{0}}{1-\frac{2 G_{1}}{R T_{0}}}
$$

As $R$, expressed in Gr. Cal., amounts to 2 , the condition may finally be written:

$$
\begin{equation*}
q_{0}<\frac{4 T_{0}}{1-\frac{\alpha_{1}}{T_{0}}} \tag{5}
\end{equation*}
$$

where $q_{0}$ represents the latent heat (in Gr. Cal.) of the metal, which is deposited in solid condition, $T_{0}$ the absolute melting temperature and $\alpha_{1}=« q_{0}=\frac{a_{1} b_{2}{ }^{2}-2 a_{12} b_{1} b_{2}+a_{2} b_{1}{ }^{2}}{b_{1}{ }^{3}}$, also expressed in Gr. Cal,

As the quantity $\frac{\alpha_{1} v^{2}}{\left(1+r_{x}\right)^{2}}$ represents in general the heat, which is given out pro molecule when an infinitely small quantity of the pure molten metal is mixed with the fluid metal mixture, the quantity $\alpha_{1} x^{2}$ will represent that same quantity of heat for $x=0$.

We must here notice that the accurate values of $\theta$ and $q_{0}$ must be used, as well in equation (4) as in (5). So in the case of tinmercury for instance $\theta=0,396$ is accurate only if the mercury is solved into the tin as atom. If this is not the case - and in the example mentioned we have every reasou to suppose that the mercury is associated to an amonnt of 1,5 - then $\theta$ must undergo a proportional increase. $\theta$ was namely calculated from $\theta=\frac{\Delta T}{T_{w}}$. If we apply the condition in the form (5), then we must substitute the experimentally determined value of the latent heat for $q_{0}$.

So in the case of tin-mercury $\theta$ will not be equal to 0,4 bat in reality to 0,6 , and therefore $\theta^{2}-\frac{1}{2} 0+\alpha=0,36-0,30+0,04=0,10$, from which the existence of a point of inflection appears still clearer than in the supposition $\theta=0,4$.

If we apply condition (5), $\alpha_{1}$ being equal to $0,0453 \times 1690=77$ Gr. Cal., we have certainly

$$
1700<\frac{4 \times 505}{1-\frac{77}{505}}
$$

If $a_{1}$ is positive, as is the general case, then the simple condition

$$
\underline{q_{0}<4 T_{0}}
$$

will include condition (5). This latter form therefore will provide us in nearly all cases with a reliable criterion whether or not a point of inflection occurs in the melting-point curve.

Physiology. - "On the epithelium of the surface of the stomach." By Dr. M. C. Dekhuyzen and Mr. P. Vhrmat. Veterinary surgeon. (Communicated by Prof. C. A. Pekelharing).

We are accustomed to regard the stomach in the very first place as an organ for the diyestion of food, for the preparation of the gastric juice. About its power of resorption its not so much is known. Glucose, peptones, strychnin, alcohol, dissolved in or diluted with water, are resorbed by the gastric mucous membrane. The rapidity of resorption is different in various kinds of animals. The structure of the cells which


[^0]:    ${ }^{1}$ ) See i.a. "Rapport etc." (Paris, Gauthiers-Villars) : La constitution des alliages métalliques par S. W. Roberts-Austen et A. Stanstield. (1900), p. 24.
    ${ }^{2}$ ) On different occasions I have pleaded already before for not omitting the function $\log (1-x)$. (comp i.a. Zeitschr. fur Phys. Ch. 15, p. 457 sequ. 1894).
    ${ }^{3}$ ) Complete Freezing-Point Curves of Binary Alloys, containing Silver or Copper together with another metal (Phil. Trans. of the R. S. of Londen, Series $\Lambda$, Vol. 189 (1897), p. 25-69).

