

of reaction should be proportional to the 4th power of the CO-concentration whereas it appears to be proportional to the 1st power of the CO-concentration. Rejecting this hypothesis two further suppositions remain.

Firstly:

- I. $\text{CO} = \text{C} + \text{O}$ (with measurable velocity)
- II. $\text{CO} + \text{O} = \text{CO}_2$ (with unmeasurable velocity).

Secondly:

- I. $\text{CO} + \text{Ni} = \text{C} + \text{Ni O}$
- II. $\text{CO} + \text{Ni O} = \text{CO}_2 + \text{Ni}$.

In the last case it need not be assumed that one of these reactions takes place with unmeasurable velocity, but only that the second one proceeds more rapidly than the first.

As regards the nature of the catalyzer we think we may conclude from the result of several experiments, that it is not the carbon but the finely divided nickel which possesses the catalytic action.

Amsterdam, Chem. Lab. University. Dec. 1902.

Chemistry. — Professor BAKHUIS RÖDZEBOM presents a communication from Dr. J. J. VAN LAAR on: “*The course of the melting-point-lines of solid alloys or amalgams.*” (First Communication). (Communicated in the meeting of December 27, 1902).

1. In the researches of VAN HETEREN¹⁾ on Tinamalgams a meltingpoint-line occurs²⁾ of a kind, which has not as yet been studied over such an extended course (from 0 to nearly 100 atom % of mercury). This is chiefly due to the fact, that the temperatures of fusion of the two metals are so very different; tin 231°, mercury —38.6°. In consequence the meltingpoint-line of the tin meets that of the mercury

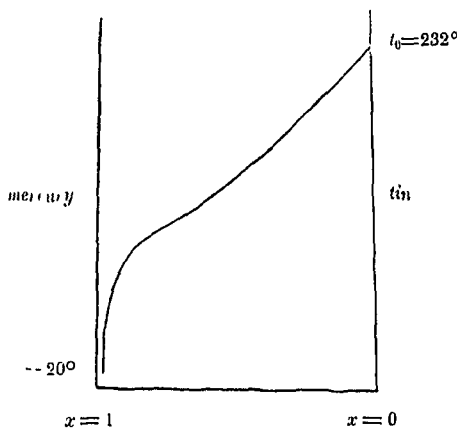


Fig. 1.

practically at 100 atom % mercury, so that the meltingpoint-line of the mercury has not even been observed. We therefore see for the first time a meltingpoint-line in its full course, and the question arises whether the course, found by VAN HETEREN, may be predicted theoretically.

The answer to this is in the affirmative. Let us, to start with, take the most simple view as regards the molecular poten-

¹⁾ Dissertation 1902. (also Report Meeting 20 Nov. 1902).

²⁾ l. c. pg. 18.

tials μ of the tin as solid substance and μ_1 of the tin in the liquid amalgam, namely that

$$\left. \begin{aligned} \mu &= e - c T \\ \mu_1 &= e_1 - c_1 T + RT \log(1-x) \end{aligned} \right\} \dots \dots \dots (1)$$

In this it has been assumed, firstly that the tin, crystallised from the amalgam, does not consist of mixed crystals, but of pure tin — a supposition, which has been proved by experiment to be nearly correct — and secondly, that the energy-quantity e is no function of x . Later on we will drop this last simplified supposition, and demonstrate, that a more accurate calculation of the function μ_1 affects the course of the meltingpoint-lines *quantitatively*, but not *qualitatively*. Then it is our object to demonstrate at once, that the entire qualitative course, as represented in the figure, follows from the equations (1) in connection with the *course of the logarithmic function of* $1-x$. By putting the two potentials equal to each other, we obtain:

$$(e_1 - e) - (c_1 - c) T = - RT \log(1-x),$$

or calling $e_1 - e = q$ (the heat of fusion of the solid tin, when passing into the amalgam), and the quantity $c_1 - c = \gamma$:

$$q - \gamma T = - RT \log(1-x),$$

from which follows:

$$T = \frac{q}{\gamma - R \log(1-x)} \dots \dots \dots (2)$$

This is then the most simple form of the meltingpoint-line.

On introducing the temperature of fusion of pure tin T_0 , x becomes 0, and we obtain:

$$T_0 = \frac{q}{\gamma},$$

so that we may also write:

$$T = \frac{T_0}{1 - \frac{RT_0}{q} \log(1-x)} = \frac{T_0}{1 - \theta \log(1-x)}, \dots \dots \dots (3)$$

if we abbreviate $\frac{RT_0}{q}$ to θ .

We notice at once, that on the development of the logarithmic function, the formula, for very small values of x , passes into

$$T = \frac{T_0}{1 + \frac{RT_0}{q} x},$$

that is to say into
$$T_0 - T = \frac{RT_0}{q} x,$$

the ordinary formula of VAN 'T HOFF for extremely dilute solutions. If, however, the solutions are no longer extremely dilute, we can no longer be satisfied with one or two terms in the development of $\log(1-x)$, but $\log(1-x)$ must remain.

I will now show, that the approximative relation

$$T = \frac{T_0}{1 - \theta \log(1-x)}$$

gives indeed the observed course qualitatively. For $\frac{dT}{dx}$ we find:

$$\frac{dT}{dx} = - \frac{T_0}{(1 - \theta \log(1-x))^2} \cdot \frac{\theta}{1-x}.$$

Whilst T itself, for $x=0$, passes into T_0 , and for $x=1$ into $T=0$, which already agrees with the steadily declining course — it appears from $\frac{dT}{dx}$, that this quantity, for $x=0$, becomes:

$$\left(\frac{dT}{dx}\right)_0 = - T_0 \theta = - \frac{RT_0^2}{q},$$

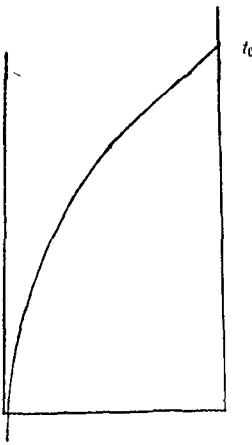


Fig. 2.

the limiting value of VAN 'T HOFF, whilst for $x=1$ it passes into $-\infty$. It may now still be asked, whether there will be a point of inflection or not. In the case, examined by VAN HETEREN, a point of inflection plainly occurred at about $x=0.8$, but it may also be possible, that the course was like the one in the following figure, without point of inflection. Let us therefore determine

$$\frac{d^2T}{dx^2}.$$

$$\frac{d^2T}{dx^2} = \frac{2 T_0}{(1 - \theta \log(1-x))^3} \cdot \frac{\theta^2}{(1-x)^2} - \frac{T_0}{N^2} \frac{\theta}{(1-x)^2} = \frac{T_0}{N^2} \frac{\theta}{(1-x)^2} \left[\frac{2\theta}{N} - 1 \right].$$

Evidently $\frac{d^2T}{dx^2} = 0$, when $2\theta = N$, that is to say, when

$$\begin{aligned} 1 - \theta \log(1-x) &= 2\theta \\ - \log(1-x) &= 2 - \frac{1}{\theta}. \end{aligned}$$

As $\theta = \frac{RT_0}{q}$ will be positive, we see, that the point of inflection can

only occur if θ is situated between $1/2$ and ∞ . For $\theta = 1/2, x = 0$; for $\theta = \infty$ we find on the other hand $x = 0.865$. A point of inflection further than $x = 0.865$ can only occur with negative values for θ ($\theta = -\infty$ till $\theta = 0$, when $x = 0.865$ till $x = 1$). But there is no point of inflection if $\theta < 1/2$, that is to say, if

$$q > 2 R T_0,$$

or in gram-cals.

$$q > 4 T_0.$$

In our case therefore, where $T_0 = 505$ — when $q > 2000$ gram-cals.

This last conclusion will however be modified, when we apply the necessary correction to the approximate formula (3). *But the fact of the possible occurrence of a point of inflection* may already be completely explained by the simple formula (3), and this by the course of the function $\log (1-x)$.

II. We now proceed to write down a more stringent relation than (3).

Assuming an equation of condition of the VAN DER WAALS's kind, the value of μ_1 (the molecular potential of the component n_1) becomes as follows:

$$\begin{aligned} \mu_1 = & -k_1 T (\log T - 1) - RT (\log (V-b) - 1) + \left((e_1)_0 - T (\eta_1)_0 \right) + \\ & + \frac{\sum n_i \cdot RT}{V-b} b_i - \frac{2}{V} (n_1 a_{11} + n_2 a_{12} + \dots) + RT \log n_1 \dots \dots \dots (4) \end{aligned}$$

For b has been written:

$$b = n_1 b_1 + n_2 b_2 + \dots,$$

whilst for a the quadratic relation

$$a = n_1^2 a_{11} + 2 n_1 n_2 a_{12} + \dots$$

has been taken.

Now, $\log (V-b)$ can be supposed to be independent of x , whilst the expression

$$\frac{\sum n_i \cdot R T}{V-b} b_i - \frac{2}{V} (n_1 a_{11} + n_2 a_{12}) = \frac{RT}{V-b} b_i - \frac{2}{V} ((1-x)a_{11} + x a_{12})$$

in regard to x will become not of the order x , but of x^2 . Let us, to prove this, rather start from a more general expression for the total potential ζ (in our case we have only to deal with two single components n_1 and n_2), namely

$$\begin{aligned} \zeta = & n_1 (\mu_1)_0 + n_2 (\mu_2)_0 + \frac{n_1^2 \mu_{11} + 2n_1 n_2 \mu_{12} + n_2^2 \mu_{22}}{n_1 + n_2} + \\ & + RT \left(n_1 \log \frac{n_1}{n_1 + n_2} + n_2 \log \frac{n_2}{n_1 + n_2} \right). \end{aligned}$$

We then find:

$$\mu_1 = \frac{\partial \xi}{\partial n_1} = (\mu_1)_0 - \frac{1}{(n_1 + n_2)^2} (n_1^2 \mu_{11} + 2 n_1 n_2 \mu_{12} + n_2^2 \mu_{22}) + \frac{2}{n_1 + n_2} (n_1 \mu_{11} + n_2 \mu_{12}) + RT \log \frac{n_1}{n_1 + n_2}.$$

With $n_1 + n_2 = 1$, $n_1 = 1-x$, $n_2 = x$ we obtain:

$$\mu_1 = (\mu_1)_0 - [(1-x)^2 \mu_{11} + 2x(1-x)\mu_{12} + x^2 \mu_{22}] + 2[(1-x)\mu_{11} + x\mu_{12}] + RT \log(1-x),$$

or after simplification:

$$\mu_1 = [(\mu_1)_0 + \mu_{11}] - x^2 (\mu_{11} - 2 \mu_{12} + \mu_{22}) + RT \log (1 - x).$$

In analogy with (4) we may therefore write:

$$\mu_1 = e_1 - c_1 T + \alpha_1 x^2 + RT \log (1-x).$$

The terms with $T \log T$ have not been taken into consideration, because they disappear on account of the equality of the quantities k_1 and R in the liquid and in the solid phase.

If, for the sake of a closer approximation, we take up some higher powers of x , we finally get:

$$\left. \begin{array}{l} \text{(solid tin)} \quad \mu = e - cT \\ \text{(tin in liquid amalg.)} \quad \mu_1 = e_1 - c_1 T + (\alpha_1 x^2 + \beta_1 x^3 + \gamma_1 x^4) + RT \log(1-x) \end{array} \right\} \quad (5)$$

Equating, we then find as in § 1:

$$q_0 - \gamma T = - (\alpha_1 x^2 + \beta_1 x^3 + \gamma_1 x^4) - RT \log (1-x),$$

or

$$T = \frac{q_0 + (\alpha_1 x^2 + \beta_1 x^3 + \gamma_1 x^4)}{\gamma - R \log (1-x)} \dots \dots \dots (6)$$

The heat of fusion of the solid tin in the amalgam is now plainly:

$$q = q_0 + (\alpha_1 x^2 + \beta_1 x^3 + \gamma_1 x^4) \dots \dots \dots (7)$$

For $x = 0$, (6) passes into

$$T_0 = \frac{q_0}{\gamma},$$

so we may again write:

$$T = T_0 \frac{1 + \frac{\alpha_1 x^2 + \beta_1 x^3 + \gamma_1 x^4}{q_0}}{1 - \frac{RT_0}{q_0} \log (1-x)},$$

or with $\frac{\alpha_1}{q_0} = \alpha$, $\frac{\beta_1}{q_0} = \beta$, $\frac{\gamma_1}{q_0} = \gamma$:

$$T = T_0 \frac{1 + (\alpha x^2 + \beta x^3 + \gamma x^4)}{1 - \theta \log (1-x)} \dots \dots \dots (8)$$

and this is the more accurate formula, which has taken the place of the simple relation (3).

III. We will now show, that the above formula quantitatively yields the values, found by VAN HETEREN for T , in a satisfactory manner.

As $-\left(\frac{dT}{dx}\right)_0 = T_0 \theta$, θ may be determined with great accuracy from the beginning course of the meltingpoint-line. From the values, found for T (on pg. 16 of the dissertation) for $x = 0$ atom % of mercury (pure tin), $x = 0,1005$, $x = 0,1716$ and $x = 0,2338$, the average value, obtained for $-\frac{dT}{dx}$ is $= 200$. From the determinations of HEYCOCK and NEVILLE between $x = 0$ and $x = 0,1$ it also follows, that $-\frac{dT}{dx} = 200$.

For θ we may therefore take ($T_0 = 505$):

$$\theta = \frac{200}{505} = \underline{0,4}.$$

I calculated the values of α , β and γ as follows:

$$\underline{\alpha = 0,325} \quad ; \quad \underline{\beta = -1,11} \quad ; \quad \underline{\gamma = 1,33}.$$

Formula (8) thus becomes:

$$T = T_0 \frac{1 + (0,325x^2 - 1,11x^3 + 1,33x^4)}{1 - 0,4 \log(1-x)},$$

and so we find the following values for T .

The agreement is as good as can be expected: the difference between the calculated value of T and the observed value generally amounts to fractions of a degree, average $0,8$; as regards to the absolute temperatures the deviation is only average $0,2\%$. Only the two last values are too low (the last 3%), but then the influence of a small inaccuracy in the determination of the coefficients β and γ makes itself strongly felt. If we except these two last values, the calculated meltingpoint-line fully coincides with the observed line in the scale of the figure in the dissertation. And by means of a slight alteration in the value of β and γ we might perhaps cause the two last observations to agree. Let us not forget, that the formula (8) always remains an approximate one. In the last values of x the composition of the separated tin must also make its influence felt. For this is no longer pure tin but contains certainly 1% , or perhaps even 6% of mercury.

As regards the value of q (the heat of fusion of tin, when passing into the amalgam) — when $x = 0$, $q = q_0$, that is to say $= \frac{RT_0}{\theta} = \frac{1010}{0,4} = 2550$ gram-cals. At 25° our formula is no longer available, as

x	x^2	x^3	x^4	$-\log(1-x)$	Numer.	Denom.	$T-273$ calcul.	$T-273$ found	Δ
0,1005	0,0101 ⁰	0,00101 ⁵	0,00010 ²¹	0,1059	1,0023	1,0424	212,4	211,6	0,8
0,1716	0,0294 ⁵	0,0050 ⁵³	0,0008 ⁶⁷³	0,1883	1,0051	1,0753	198,9	198,6	0,3
0,2338	0,0546 ⁹	0,0127 ⁸	0,0029 ⁸⁸	0,2663	1,0076	1,1065	186,7	183,7?	3,0?
0,2969	0,0881 ⁵	0,0261 ⁷	0,0077 ⁷¹	0,3523	1,0099	1,1409	173,8	173,0	0,8
0,3856	0,1487	0,0573 ³	0,0221 ¹	0,4872	1,0141	1,1949	155,4	155,2	0,2
0,5001	0,2501	0,1251	0,0625 ⁵	0,6933	1,0256	1,2773	132,3	133,4	-1,1
0,5973	0,3568	0,2131	0,1273	0,9095	1,0488	1,3638	115,2	115,2	0,0
0,6467	0,4182	0,2705	0,1745	1,0404	1,0682	1,4161	107,7	107,4	0,3
0,6754	0,4562	0,3081	0,2081	1,1252	1,0830	1,4501	104,0	103,4	0,6
0,6813	0,4642	0,3162	0,2155	1,1435	1,0866	1,4574	103,3	102,4	0,9
0,7104	0,5047	0,3585	0,2547	1,2393	1,1047	1,4957	99,8	99,0	0,8
0,7155	0,5119	0,3663	0,2620	1,2570	1,1083	1,5028	99,2	98,8	0,4
0,7477	0,5591	0,4180	0,3126	1,3772	1,1335	1,5509	95,9	95,4	0,5
0,7547	0,5696	0,4299	0,3244	1,4053	1,1393	1,5621	95,1	94,0	1,1
0,7963	0,6341	0,5049	0,4021	1,5912	1,1805	1,6365	91,1	90,0	1,1
0,8189	0,6706	0,5492	0,4497	1,7087	1,2064	1,6835	88,7	88,4	0,3
0,8921	0,7958	0,7100	0,6333	2,2266	1,3128	1,8906	77,5	79,7	-2,2
0,9483	0,8993	0,8528	0,8087	2,9623	1,4212	2,1849	55,3	65,2	-9,9

according to the above table it only yields trustworthy values for T up to about 90° . At 90° $x = 0,8$, and then, according to (7), we have:

$$q = q_0 [1 + (\alpha x^2 + \beta x^3 + \gamma x^4)],$$

or

$$q = q_0 [1 + 0.325 x^2 - 1.11 x^3 + 1.33 x^4],$$

that is to say $q = 1.185 q_0 = 3020$ gram-cals.,

whilst VAN HETEREN (at 25°) found ± 3000 gram calcs, by means of electromotive measurements¹⁾. The concordance is absolute.

We, finally, wish to remark, that according to the determinations of VAN HETEREN and of HEYCOCK and NEVILLE, regarding the lowering of the temperature of fusion of tin on adding small quantities of mercury, q_0 must be = 2550 calcs. We therefore see, that the value, assigned by PERSON, namely $14.25 \times 118.5 = 1690$ gram calcs., is much too small. In a later communication I will show, that the heat of fusion of mercury, given by PERSON, is also many times too small.

Dec. 1902.

¹⁾ Dissertation pg. 49.