triple point, added anthraquinone in solid condition will not pass into the vapour state. Then $x_s = 1$ and $x_d = 0$. We get:

$$T\frac{dp}{dT} = \frac{r - x_l\,(r + \lambda)}{v_d - v_l - x_l(v_d - v_s)}$$

The quantity λ is now the latent heat of liquefaction of anthraquinone.

For vanishing value of x_l we find increase of p with T, as is found in case of equilibrium between liquid and vapour. In neither of these cases the numerator can become equal to zero when a small quantity of the second substance is added to the principal substance.

But I shall not enter into more particulars, nor discuss the treatment of special circumstances. If they are brought to light by the experiment, they can necessarily be derived from the above formulae. Nor shall I discuss the v, x, T curves, which would lead to greater digressions. For this discussion we should have to make use of two equations, of which that for the coexistence of liquid and vapour occurs in Cont. II, p. 104. For the v,x projection of the three-phase-equilibrium we get for anthraquinone and ether two separate branches, lying outside the limits of the maximum and the minimum value of x mentioned above. When these two values of x coincide, these branches meet, intersecting at an acute angle; at further modification the two v,x curves, viz. those for liquid and vapour, will yield a highest and a lowest value for the volume; at any case the v,x curve for the vapour phase. As appeared in an oral communication, Dr. SMITS had already arrived at this result.

I shall conclude with pointing out, that cases of *retrograde solidification* must repeatedly occur, both when the temperature is kept constant with change of pressure and when the pressure is kept constant with change of temperature.

Chemistry. — *"The possible forms of the meltingpoint-curve for binary mixtures of isomorphous substances."* By J. J. VAN LAAR. (2nd communication). (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

1. My investigations concerning the possible forms of the meltingpoint-curve for binary mixtures of isomorphous substances, communicated in the Proceedings of the meeting of the 27th of June 1903, have, apart from the different theoretical considerations, led to the following practical results.

a. When the latent heat of mixing in the *solid* phase $\alpha' = q_1 \beta'$ is *great*, the *solid* phase contains but very little of the second component. The portion of the meltingpoint-curve which may be realized, has a course as in fig. 1 (see the plate). The curves $T = f(x')$, viz. *Aa* and *Bb* show *maxima* at *m* and *n*, which maxima descend gradually for smaller values of β' till they are below *a* and *b*, the maximum at *n* sooner than that at *m*. (fig. 2). [We leave for the moment out of consideration what happens below the horizontal line through the point *C*, the *eutectic* point: for this see my preceding communication].

b. For smaller values of β' we get the case of fig. 3, where the branch *BC* shows a *minimum*, no longer below the temperature of *C*, but exactly *at C*. Immediately after (i. e. when β' is still somewhat smaller), the meltingpoint-curve assumes a shape as in fig. 4. *C* remains the eutectic point, where the two branches of the meltingpoint-curve meet with a *break*. As appears from the figure, we have now got parts of the meltingpoint-curve, which may be *realized*, also *below* the point *C* (see also fig. 14 and 14*a* of the communication referred to).

It is however very well possible, that in the meantime the minimum at *D* has *already disappeared*, and then we get a course as is represented in fig. 5 (observed i. a. by HISSINK for mixtures of $AgNO_3$ and $NaNO_3$. (see also fig. 14*b* l.c.).

c. For still smaller values of β' the curve $T = f(x')$ becomes *continuously realizable*. The points *b* and *a* coincide in a point of inflection *b, a* with *horizontal* tangent (fig. 6), which point of inflection soon passes into one with an *oblique* tangent *L* (fig. 7), while in most cases it disappears afterwards altogether for still smaller values of β'. (fig. 8).

The break at *C* has disappeared in the case of fig. 6 and from this moment there is no longer question of a eutectic point, and the meltingpoint-curve assumes the perfectly continuous shape of fig. 7 and 8.

d. As has already been observed in *b*, also the minimum at *D* will sooner or later disappear. For very small values of β' we get then *always* a course as in fig. 9.

Observation. As has been elaborately demonstrated in the preceding paper, a maximum at *A* for *normal* components can *never* occur with *positive* values of the different absorbed latent heats of liquefaction and mixing (see p. 156 l. c.). When such a maximum is observed, as was done e. g. by F. M. JAEGER[1]) for two isomeric

[1]) Akademisch Proefschrift (1903), p. 173—174.

tribroomtoluols, this always points to difference in size of the molecules in the liquid and solid phase [1]). In fact JAEGER, found that his isomers are very likely *bi-molecular* in the *solid* phase [2]).

2. We may now put the question: When will the minimum at D, which will disappear in any case for values of β' *smaller* than those for which fig. 3 holds, disappear *before* the case of fig. 6, so that a course as in fig. 5 becomes possible; and when will it disappear *after* the case of fig. 6, as has been assumed in our figures 6 to 8.

To answer this question, we shall first state for what values of β' the case of fig. 6 occurs.

The point b,a lying then on the top of the curve $\frac{\partial^2\zeta'}{\partial x'^2}=0$ at $x'=1/_2$ [3]), we have, besides the equations (2) for $x'=1/_2$ (see p. 153 l. c.), also the relation $\frac{\partial^2\zeta'}{\partial x'^2}=0$ or $\frac{RT}{x'(1-x')}-2\,\alpha'=0$, i. e. with $R=2$ the relation $T=\alpha'x'(1-x')$.

The condition sought is accordingly:

$$T=\frac{T_1\left(1-\frac{1}{4}\beta'\right)}{1+\frac{RT_1}{q_1}\log\frac{0,5}{1-x}}=\frac{T_2\left(1-\frac{1}{4}\frac{q_1}{q_2}\beta'\right)}{1+\frac{RT_2}{q_2}\log\frac{0,5}{x}}=\frac{1}{4}\,q_1\,\beta',$$

for which with regard to the fundamental equations, some simplifying hypotheses permissible for our purpose have been made, which may be found on page 152 of the paper mentioned.

Now we can solve ($R=2$):

$$\log\frac{0,5}{1-x}=\frac{2\left(1-\frac{1}{4}\beta'-\frac{1}{4}\frac{q_1}{T_1}\beta'\right)}{\beta'};\quad \log\frac{0,5}{x}=\frac{2\left(1-\frac{1}{4}\frac{q_1}{q_2}\beta'-\frac{1}{4}\frac{q_2}{T_2}\frac{q_1}{q_2}\beta'\right)}{\frac{q_1}{q_2}\beta'},$$

hence, as $(1-x)+x=1$:

$$e^{-2\left[\frac{1}{\beta'}-\frac{1}{4}\left(1+\frac{q_1}{T_1}\beta'\right)\right]}+e^{-2\left[\frac{1}{q_1/q_2\,\beta'}-\frac{1}{4}\left(1+\frac{q_2}{T_2}\right)\right]}=2,\quad(1)$$

[1]) See p. 208 and 209 of the "Proefschrift", where JAEGER gives the proof of this thesis, which I had communicated to him in a letter.

[2]) See p. 208 and 194 of the "Proefschrift".

[3]) Only if we assume $x'_1=x'_2$ (so $b_1=b_2$), this parabolic curve will be *symmetric* and its top will be exactly at $x'=1/_2$.

and this is the equation, from which β' can be solved. Unfortunately however β' cannot be solved from this in an *explicit* form.

Now the minimum disappears, when (see p. 168, l. c.):

$$\beta' = \frac{T_1 - T_2}{T_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

That this takes place exactly at the *same moment* as that at which the case of fig. 6 occurs, is expressed by the relation:

$$e^{-2\left[\frac{T_1}{T_1-T_2} - \frac{1}{4}\left(1+\frac{q_1}{T_1}\right)\right]} + e^{-2\left[\frac{q_2}{q_1}\frac{T_1}{T_1-T_2} - \frac{1}{4}\left(1+\frac{q_2}{T_2}\right)\right]} = 2. \quad (3).$$

If we write for shortness:

$$\frac{q_1}{T_1} = \varphi_1 \quad ; \quad \frac{q_2}{T_2} = \varphi_2 \quad ; \quad \frac{T_2}{T_1} = \lambda \left(\text{so } \frac{q_2}{q_1} = \frac{\varphi_2}{\varphi_1} \lambda \right),$$

the equation (3) becomes:

$$e^{-2\left[\frac{1}{1-\lambda} - \frac{1}{4}(1+\varphi_1)\right]} + e^{-2\left[\frac{\varphi_2}{\varphi_1}\frac{\lambda}{1-\lambda} - \frac{1}{4}(1+\varphi_2)\right]} = 2, \quad (3a)$$

where λ will always be < 1 (T_2 is assumed $< T_1$).

It is now easy to see that there are always corresponding values of λ, φ_1 and φ_2 to be found, which satisfy (3), so that the minimum may just as well disappear before as after the case of fig. 6. In order to define the limits of T_1, T_2, q_1 and q_2, in which either the one or the other will occur, we shall express e. g. φ_2 in function of φ_1 and λ. We get then successively:

$$e^{\frac{1}{2}(1+\varphi_1) - \frac{2}{1-\lambda}} + e^{\frac{1}{2}(1+\varphi_2) - 2\frac{\varphi_2}{\varphi_1}\frac{\lambda}{1-\lambda}} = 2\,,$$

$$e^{\frac{1}{2}\varphi_1 - \frac{2}{1-\lambda}} + e^{\frac{1}{2}\varphi_2 - 2\frac{\varphi_2}{\varphi_1}\frac{\lambda}{1-\lambda}} = 2\,e^{-{}^1/_2}\,,$$

$$\frac{1}{2}\varphi_2 - 2\frac{\varphi_2}{\varphi_1}\frac{\lambda}{1-\lambda} = \log\left(2\,e^{-{}^1/_2} - e^{{}^1/_2\,\varphi_1 - \frac{2}{1-\lambda}}\right),$$

so finally:

$$\varphi_2 = \frac{\log\left(2\,e^{-{}^1/_2} - e^{{}^1/_2\,\varphi_1 - \frac{2}{1-\lambda}}\right)}{\frac{1}{2} - \frac{2}{\varphi_1}\frac{\lambda}{1-\lambda}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This will be equal to 0 (first limiting-value, as $\frac{q_2}{T_2}$ cannot become <0), when

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$$2e^{-\frac{1}{2}} - e^{\frac{1}{2}\varphi_1 - \frac{2}{1-\lambda}} = 1\,,$$

or

$$\frac{1}{2}\varphi_1 - \frac{2}{1-\lambda} = log\,(2\,e^{-\frac{1}{2}} - 1) = -\,1{,}546\,,$$

so when

$$\varphi_1 = \frac{4}{1-\lambda} - 3{,}092$$

or

$$\varphi_1 = \frac{4\lambda}{1-\lambda} + 0{,}908 \quad (\varphi_2 = 0)\,. \quad . \quad . \quad . \quad (5)$$

The quantity φ_2 will be ∞ (second limiting-value, as $\frac{q_2}{T_2}$ may have all values up to ∞), when

$$\frac{1}{2} - \frac{2}{\varphi_1}\frac{\lambda}{1-\lambda} = 0\,,$$

i. e. when

$$\varphi_1 = \frac{4\lambda}{1-\lambda} \quad (\varphi_2 = \infty)\,. \quad . \quad . \quad . \quad (5a)$$

It is evident that the difference between the two limits of φ_1 is exactly 0,91.

We have now the following survey for different values of λ.

	$\lambda = 0$	$\lambda = \frac{1}{4}$	$\lambda = \frac{1}{2}$	$\lambda = \frac{3}{4}$	$\lambda = 1$
$\varphi_2 = 0$	$\varphi_1 = 0{,}91$	$\varphi_1 = 2{,}24$	$\varphi_1 = 4{,}91$	$\varphi_1 = 12{,}91$	$\varphi_1 = \infty$
$\varphi_2 = \infty$	$\varphi_1 = 0$	$\varphi_1 = 1{,}33$	$\varphi_1 = 4$	$\varphi_1 = 12$	$\varphi_1 = \infty$

From this we see, that $\varphi_2 = \frac{q_2}{T_2}$ may have all values from 0 to ∞, but that the values of $\varphi_1 = \frac{q_1}{T_1}$ are limited to an *interval,* which varies with the value of $\lambda = \frac{T_2}{T_1}$. The greater λ becomes, i. e the more T_2 approches to T_1, the smaller this interval comparatively becomes; so the value of q_1 required must then become larger and larger.

All this applies to the case that the minimum disappears at the same moment as in the case of fig. 6. It is easy to see that when the minimum disappears *before* the case of fig. 6 the value of φ_1 will have to be *larger* than that which is determined by (4) for given values of φ_2 and λ. The opposite case, i. e. that the minimum disappears *after* the case of fig. 6, will take place when φ_1 is *smaller* than that value.

For, when the minimum *has already disappeared*, the value of β' in fig. (6) will be *smaller* than $\frac{T_1 - T_2}{T_1}$. We must accordingly substitute a smaller value of β' in (1), or what comes to the same thing, give a higher value to T_2, i. e. increase the value of λ. But it is obvious from the above table that when λ increases, a *higher* value of φ_1 will correspond to the *same* value of φ_2.

Let us take as first example $T_1 = 1000$, $T_2 = 500$, $q_1 = 4500$ Gr. cal., $q_2 = 250$ Gr. cal. λ is therefore $= {}^1/_2$, $\varphi_1 = 4{,}5$ and $\varphi_2 = 0{,}5$. The value of φ_1 ranges therefore within the interval 4 to 4,91, which holds for $\lambda = {}^1/_2$, so that it is *possible*, that the minimum disappears *in the neighbourhood* of (or exactly in) the case of fig. 6. The condition for its disappearance *for* the value of β' corresponding to that case, would be that there corresponded to $\lambda = {}^1/_2$, $\varphi_1 = 4{,}5$, according to (4), a value of φ_2, given by:

$$\varphi_2 = \frac{\log\left(1{,}2131 - e^{-1{,}75}\right)}{0{,}5 - {}^4/_9} = \frac{\log 1{,}0322}{{}^1/_{18}} = 0{,}571.$$

So to $\varphi_2 = 0{,}50$ corresponds a greater value of φ_1 than the one given, viz. 4,5. This value is therefore *too low*, and the minimum will disappear *after* the case of fig. 6.

Second example. Let T_1 be again 1000, T_2 be 500, but now $q_1 = 3000$, $q_2 = 1000$.

We shall not have to execute any calculation now, as this value falls *beyond* the interval 4 to 4,91, φ_1 being 3 with $\lambda = {}^1/_2$; φ_1 is much *too low* to be *able* to correspond with any value of φ_2 whatever, and again the minimum will have to disappear when the case of fig. 6 occurs.

If on the other hand T_1 had been 1000, $T_2 = 500$, $q_1 = 5000$, $q_2 = 2000$, then it would be clear without any calculation, that now the minimum *has already disappeared* when the case of fig. 6 occurs, $\varphi_2 = 5$ now lying *beyond* the interval on the *high* side. A course as in fig. 5 therefore becomes now possible, when the value of β' lies between that of fig. 3 and fig. 6.

The case of fig. 5, observed among others by HISSINK in mixtures of $AgNO_3$ and $NaNO_3$, belongs therefore to the *possibilities*, and can occur for given T_1, T_2 and q_2, as soon as q_1 has a sufficiently *high* value, or what comes to the same thing, as soon as for given T_1, T_2 and q_1 the quantity q_2 has a sufficiently *low* value. The value of $\frac{q_2}{T_2}$ or φ_2 must then be *smaller* than that calculated from (4). If we then find a negative value for φ_2, the case of fig. 5 is entirely excluded for the given values of T_1, T_2 and q_1. In the equation (4) we have therefore at any rate a *criterion* to determine whether or no the case of fig. 5 can occur, when the value of β' lies between those to which the figures 3 and 6 apply.

3. Another important question will be, when the point of inflection L with oblique tangent (fig. 7) will disappear, and whether it can still be present e. g. with $\beta'=0$.

Let us for this purpose determine the values $\frac{dT}{dx'}$ and $\frac{d^2T}{dx'^2}$.

We found before (l.c. p. 155).

$$\frac{dT}{dx}=-T\frac{(x-x')\frac{\partial^2\zeta}{\partial x^2}}{(1-x')w_1+x'w_2} \quad ; \quad \frac{dT}{dx'}=-T\frac{(x-x')\frac{\partial^2\zeta'}{\partial x'^2}}{(1-x)w_1+xw_2},$$

where

$$\frac{\partial^2\zeta}{\partial x^2}=\frac{RT}{x(1-x)}-2\alpha \quad ; \quad \frac{\partial^2\zeta'}{\partial x'^2}=\frac{RT}{x'(1-x')}-2\alpha',$$

$$w_1=q_1+\alpha x^2-\alpha' x'^2 \quad ; \quad w_2=q_2+\alpha(1-x)^2-\alpha'(1-x')^2.$$

Hence we get:

$$\frac{dT}{dx}=-T\frac{(x-x')\left[\frac{RT}{x(1-x)}-2\alpha\right]}{(1-x')w_1+x'w_2}; \quad \frac{dT}{dx'}=-T\frac{(x-x')\left[\frac{RT}{x'(1-x')}-2\alpha'\right]}{(1-x)w_1+xw_2}, \quad (6)$$

from which we see i. a., that when e.g. $\frac{dT}{dx}$ has been calculated, $\frac{dT}{dx'}$ can be found by substituting x' for x, $-T$ for T, $-\alpha'$ for α' and $-\alpha$ for α' and by then reversing the sign of the second member. The same holds for $\frac{d^2T}{dx'^2}$, when $\frac{d^2T}{dx^2}$ is determined. From (6) follows for the point A, where $T=T_1$, $x=x'=0$, $w_1=q_1$:

$$\left(\frac{dT}{dx}\right)_0=-\frac{RT_1^2}{q_1}\left(1-\left(\frac{x'}{x}\right)_0\right); \quad \left(\frac{dT}{dx'}\right)_0=-\frac{RT_1^2}{q_1}\left(\left(\frac{x}{x'}\right)_0-1\right). \quad (7)$$

The initial direction depends therefore on the limit of the value of $\frac{x'}{x}$. We found for this expression (l.c. p. 156):

$$log\left(\frac{x'}{x}\right)_0=\frac{1}{R}\left(\frac{q_2+\alpha-\alpha'}{T_1}-\frac{q_2}{T_2}\right), \quad \ldots \ldots \quad (8)$$

from which appears, i. a. that for $\alpha' = \infty$, $\frac{x'}{x}$ approaches to $e^{-\infty}$, hence it approaches rapidly to 0.

Let us now differentiate the expression (6) for $\frac{dT}{dx}$ with respect to x. We find then, logarithmically differentiated:

$$\frac{\frac{d^2T}{dx^2}}{\frac{dT}{dx}} = \frac{\frac{dT}{dx}}{T} + \frac{RT\frac{x(1-x)\left(1-\frac{dx'}{dx}\right)-(x-x')(1-2x)}{x^2(1-x)^2} + \frac{R(x-x')}{x(1-x)}\frac{dT}{dx} - 2\alpha\left(1-\frac{dx'}{dx}\right)}{(x-x')\left(\frac{RT}{x(1-x)} - 2\alpha\right)} -$$

$$- \frac{(w_2-w_1)\frac{dx'}{dx} + (1-x')\frac{dw_1}{dx} + x'\frac{dw_2}{dx}}{(1-x')w_1 + x'w_2}.$$

We find therefore for $T = T_1, x = x' = 0$, where therefore $\frac{RT}{x(1-x)} - 2\alpha$ may be replaced by $\frac{RT}{x(1-x)}$, and where $\frac{dw_1}{dx}$ is evidently 0:

$$\left(\frac{d^2T}{dx^2}\right)_0 = \left(\frac{dT}{dx}\right)_0 \left[\frac{1}{T_1}\left(\frac{dT}{dx}\right)_0 + \frac{x(1-x)\left(1-\frac{dx'}{dx}\right) - (x-x')(1-2x)}{x(x-x')} + \right.$$

$$\left. + \frac{1}{T_1}\left(\frac{dT}{dx}\right)_0 - \frac{2\alpha x\left(1-\frac{dx'}{dx}\right)}{(x-x')RT_1} - \frac{(w_2-w_1)\frac{dx'}{dx}}{w_1}\right].$$

Now we must calculate the value of $\left(\frac{dx'}{dx}\right)_0$.

From (6) follows immediately:

$$\frac{dx'}{dx} = \frac{\frac{RT}{x(1-x)} - 2\alpha}{\frac{RT}{x'(1-x')} - 2\alpha'} \cdot \frac{w_1 + x(w_2-w_1)}{w_1 + x'(w_2-w_1)} \quad . \quad . \quad . \quad . \quad . \quad (a)$$

or

$$\frac{dx'}{dx} = \frac{x'(1-x')}{x(1-x)} \frac{1 - \frac{2\alpha x(1-x)}{RT}}{1 - \frac{2\alpha' x'(1-x')}{RT}} \cdot \frac{1 + x\frac{w_2-w_1}{w_1}}{1 + x'\frac{w_2-w_1}{w_1}},$$

hence for $T = T_1$:

$$\left(\frac{dx'}{dx}\right)_0 = \frac{x'}{x}\Big(1 + (x-x')\Big)\left(1 + \frac{2\alpha' x' - 2\alpha x}{RT_1}\right)\left(1 + (x-x')\frac{w_2-w_1}{w_1}\right),$$

or ($R = 2$)·

$$\left(\frac{dx'}{dx}\right)_0 = \frac{x'}{x}\left[1 + \frac{a'x'-ax}{T_1} + (x-x')\frac{w_2}{w_1}\right].$$

So this approaches to $\frac{x'}{x}$, but as will appear presently, for the determination of the term

$$x(1-x)\left(1-\frac{dx'}{dx}\right) - (x-x')(1-2x)$$

we must also retain the terms of lower order, as those of higher order disappear. We have further:

$$x\left(1-\frac{dx'}{dx}\right) = (x-x') - x'\left[\frac{a'x'-ax}{T_1} + (x-x')\frac{w_2}{w_1}\right] =$$

$$= (x-x')\left[1 - x'\left\{\frac{a'x'-ax}{(x-x')T_1} + \frac{w_2}{w_1}\right\}\right] = (x-x')(1-\Delta).$$

The term mentioned becomes therefore:

$$(x-x')\Big((1-x)(1-\Delta) - (1-2x)\Big) = (x-x')(x-\Delta).$$

Hence we get:

$$\left(\frac{d^2T}{dx^2}\right)_0 = \left(\frac{dT}{dx}\right)_0\left[\frac{2}{T_1}\left(\frac{dT}{dx}\right)_0 + \frac{x-\Delta}{x} - \frac{ax\left(1-\frac{x'}{x}\right)}{(x-x)T_1} - \frac{x'}{x}\frac{w_2-w_1}{w_1}\right],$$

or introducing the value of Δ, and of $\left(\frac{dT}{dx}\right)_0 = -\frac{2T_1^{\,2}}{q_1}\left(1-\frac{x'}{x}\right)$:

$$\left(\frac{d^2T}{dx^2}\right)_0 = \left(\frac{dT}{dx}\right)_0\left[-\frac{4T_1}{q_1}\left(1-\frac{x'}{x}\right) + 1 - \frac{x'}{x}\left[\frac{a'x'-ax}{(x-x')T_1} + \frac{w_2}{w_1}\right] - \frac{a}{T_1} - \frac{x'}{x}\frac{w_2-w_1}{w_1}\right] =$$

$$= \left(\frac{dT}{dx}\right)_0\left[-\frac{4T_1}{q_1}\left(1-\frac{x'}{x}\right) - 2\frac{x'}{x}\frac{w_2}{w_1} + \frac{x'}{x} - \frac{x'}{x}\frac{a'x'-ax}{(x-x')T_1} + 1 - \frac{a}{T_1}\right] =$$

$$= \left(\frac{dT}{dx}\right)_0\left[\left(1 - \frac{a}{T_1} - \frac{4T_1}{q_1}\right) + \frac{x'}{x}\left\{1 + \frac{4T_1}{q_1} - 2\frac{w_2}{w_1} - \frac{a'x'-ax}{(x-x')T_1}\right\}\right].$$

Now $(w_2)_0 = q_2 + a - a'$, $(w_1)_0 = q_1$, so that we finally get:

$$\left(\frac{d^2T}{dx^2}\right)_0 = \frac{1}{q_1}\left(\frac{dT}{dx}\right)_0\left[q_1\left(1-\frac{a}{T_1}\right) - 4T_1 + \left(\frac{x'}{x}\right)_0\left\{q_1 + 4T_1 - 2(q_2 + a - a') - \right.\right.$$

$$\left.\left. - \frac{q_1}{T_1}\,\frac{a'\left(\frac{x'}{x}\right)_0 - a}{1-\left(\frac{x'}{x}\right)_0}\right\}\right] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

where $\left(\frac{x'}{x}\right)_0$ has the value given in (8).

This expression for $\left(\frac{d^2T}{dx^2}\right)_0$ is still very complicated, even after the great simplifications, which attend the introduction of $x = x' = 0$.

Besides by a direct calculation, the corresponding value for $\left(\frac{d^2T}{dx'^2}\right)_0$ may also be found by changing letters and signs as mentioned above, and the latter method is even the easier. Then we get:

$$\left(\frac{d^2T}{dx'^2}\right)_0 = \frac{1}{q_1}\left(\frac{dT}{dx'}\right)_0\left[q_1\left(1-\frac{\alpha'}{T_1}\right)+4T_1+\left(\frac{x}{x'}\right)_0\left\{q_1-4T_1-2(q_2+\alpha-\alpha')-\right.\right.$$

$$\left.\left.-\frac{q_1}{T_1}\,\frac{\alpha'-\alpha\left(\frac{x}{x'}\right)_0}{\left(\frac{x}{x'}\right)_0-1}\right\}\right] \quad \ldots\ldots\ldots\ldots\ldots \quad (9a)$$

In the discussion of the two quantities $\left(\frac{d^2T}{dx^2}\right)_0$ and $\left(\frac{d^2T}{dx'^2}\right)_0$, two limiting cases are chiefly worthy of consideration, viz. $\alpha' = \infty$ and $\alpha' = 0$. Let us further always put α (latent heat required for the mixing of the liquid phase) $= 0$.

a. For $\underline{\alpha' = \infty}$ $\frac{x'}{x}$ becomes exponentially $= 0$, hence

Lim. $\left(\alpha'\frac{x'}{x}\right)_0$ will be 0. The two expressions are then transformed into:

$$\left.\begin{aligned}\left(\frac{d^2T}{dx^2}\right)_0 &= \frac{1}{q_1}\left(\frac{dT}{dx}\right)_0\left[q_1-4T_1+\left(\frac{x'}{x}\right)_0\alpha'\left\{2-\frac{q_1}{T_1}\left(\frac{x'}{x}\right)_0\right\}\right]\\ \left(\frac{d^2T}{dx'^2}\right)_0 &= \frac{1}{q_1}\left(\frac{dT}{dx'}\right)_0\left[-\frac{q_1}{T_1}\alpha'+\left(\frac{x}{x'}\right)_0\alpha'\left\{2-\frac{q_1}{T_1}\left(\frac{x'}{x}\right)_0\right\}\right]\end{aligned}\right\},$$

i. e. into:

$$\left.\begin{aligned}\left(\frac{d^2T}{dx^2}\right)_0 &= \frac{1}{q_1}\left(\frac{dT}{dx}\right)_0(q_1-4T_1)\\ \left(\frac{d^2T}{dx'^2}\right)_0 &= \frac{1}{q_1}\left(\frac{dT}{dx'}\right)_0\times 2\alpha'\left(\frac{x}{x'}\right)_0 = -\infty\end{aligned}\right\}(\alpha' = \infty) \quad \ldots \quad (10)$$

These expressions teach us, that in case the solid phase contains very little or nothing of the second component, $\left(\frac{d^2T}{dx^2}\right)_0$ becomes 0, when $q_1 = 4\,T_1$. In this case therefore the point of inflection appears in the curve $T_2 f(x)$ exactly at $x = 0$.

$\left(\frac{dT}{dx}\right)_0$ being negative, $\left(\frac{d^2T}{dx^2}\right)_0$ will also be *negative* if $q_1 > 4T$. The meltingpoint curve will then turn its *concave* side to the x-axis at A, and *no* point of inflection will occur. This is in perfect agreement with what we found in our former paper. [1])

As to $\left(\frac{d^2T}{dx'^2}\right)_0$, we see that this expression, just as $\left(\frac{dT}{dx'}\right)_0$ will always be *negatively large*. For great α' the concave side of the curve $T = f(x')$, running almost vertically downward, is turned towards the x-axis, but the curve $T = f(x')$ finally touching the ordinate $x = 0$ asymptotically at $T = 0$, a point of inflection must at any rate be present *beyond* the maximum of the curve $T = f(x')$ (see fig. 1; at L).

This point of inflection L will occur immediately after the maximum at m for large values of α', and these two points gradually approach the point A, where $T = T_1$, $x' = 0$.

As to the maximum m, this is of course represented by

$(1-x)w_1 + xw_2 = 0$ (see (6)) or $x = \frac{w_1}{w_1 - w_2}$. Now $w_1 = q_1 - \alpha' x^2 = q_1$, and $w_2 = q_2 - \alpha'(1-x')^2 = -\alpha'$, when α' is large and x' very small, hence the maximum occurs at

$$x_m = \frac{q_1}{q_1 + \alpha'} = \frac{q_1}{\alpha'} = \frac{1}{\beta'}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

If therefore β' approaches to ∞, then x_m (so also x'_m) approaches to 0.

As to the point of inflection at L, the following remarks hold good for it.

From the expression for $\frac{dx'}{dx}$ (see (a)) follows, when $\alpha = 0$ and α' is large:

$$\frac{dT}{dx'} = \frac{dT}{dx} \cdot \frac{x(1-x)}{x'(1-x')} \frac{w_1}{w_1 + x(w_2 - w_1)} = \frac{dT}{dx} \cdot \frac{x(1-x)}{x'} \frac{q_1}{q_1 - x\alpha'} = \frac{dT}{dx} \frac{x(1-x)}{x'} \frac{1}{1-\beta' x} \cdot (b)$$

At small x' we get:

$$T = \frac{T_1}{1 - \frac{RT_1}{q_1} \log(1-x)},$$

hence:

$$\frac{dT}{dx} = -\frac{T_1}{N^2} \frac{RT_1}{q_1} \frac{1}{1-x} = -\frac{RT_1^2}{q_1} \frac{1}{(1-x)(1 + 2\theta x)},$$

as $N^2 = (1 - \theta \log(1-x))^2 = (1 + \theta x + ..)^2 = (1 + 2\theta x)$.

[1]) These proceedings, Febr. 25th 1902, p. 427; June 24th 1903, p. 29—30.

We have therefore:

$$\frac{dT}{dx'} = -\frac{RT_1^2}{q_1}\frac{x}{x'}\frac{1}{(1+2\theta x)(1-\beta' x)} = -\frac{RT_1^2}{q_1}\frac{x}{x'}\frac{1}{1-\beta' x},$$

when β' is great with respect to θ, and hence:

$$\frac{d^2T}{dx'^2} = -\frac{RT_1^2}{q_1}\frac{x'(1-\beta' x)\frac{dx}{dx'} - x\left(1-\beta' x - \beta' x'\frac{dx}{dx'}\right)}{x'^2(1-\beta' x)^2}.$$

Consequently this is 0, when

$$x'(1-\beta' x)\frac{dx}{dx'} = x\left(1-\beta' x - \beta' x'\frac{dx}{dx'}\right).$$

Now we may write for $\frac{dx}{dx'}$ (see (b)):

$$\frac{dx}{dx'} = \frac{x(1-x)}{x'}\frac{1}{1-\beta' x},$$

so that $\frac{d^2T}{dx'^2} = 0$, when

$$x(1-x) = x\left(1-\beta' x - \frac{\beta' x(1-x)}{1-\beta' x}\right),$$

or

$$1-x = 1-\beta' x\left(1+\frac{1-x}{1-\beta' x}\right),$$

or

$$1 = \beta'\left(1+\frac{1-x}{1-\beta' x}\right) = \beta'\left(1+\frac{1}{1-\beta' x}\right).$$

From this we find:

$$1-\beta' x = \frac{\beta'}{1-\beta'} = -1,$$

so finally:

$$x_L = \frac{2}{\beta'}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

being the value of x, at which for large values of β' the point of inflection will be situated after the maximum at $x = \frac{1}{\beta'}$ (see (11)). So this value of x too approaches to 0, when β' approaches to ∞.

It is now evident that according to (10) for large values of β' the quantity $\left(\frac{d^2T}{dx'^2}\right)_0$ approaches to $-\infty$. For already in the *immediate* neighbourhood of A the direction of the curve $T = f(x')$, which was initially *almost* vertical, changes into a *perfectly* vertical direction at the maximum.

b) The other limiting case is $\alpha' = 0$. The expressions (9) and (9*a*) take then the form

$$\left(\frac{d^2T}{dx^2}\right)_0 = \frac{1}{q_1}\left(\frac{dT}{dx}\right)_0\left[q_1 - 4T_1 + \left(\frac{x'}{x}\right)_0\left\{q_1 + 4T_1 - 2q_2\right\}\right],$$

$$\left(\frac{d^2T}{dx'^2}\right)_0 = \frac{1}{q_1}\left(\frac{dT}{dx'}\right)_0\left[q_1 + 4T_1 + \left(\frac{x}{x'}\right)_0\left\{q_1 - 4T_1 - 2q_2\right\}\right]$$

or

$$\left.\begin{aligned}\left(\frac{d^2T}{dx^2}\right)_0 &= \frac{1}{q_1}\left(\frac{dT}{dx}\right)_0\left[(q_1 - 4T_1) - \left(\frac{x'}{x}\right)_0\left\{(q_1 - 4T_1) - 2(q_1 - q_2)\right\}\right]\\ \left(\frac{d^2T}{dx'^2}\right)_0 &= \frac{1}{q_1}\left(\frac{dT}{dx'}\right)_0\left[(q_1 + 4T) - \left(\frac{x}{x'}\right)_0\left\{(q_1 + 4T_1) - 2(q_1 - q_2)\right\}\right]\end{aligned}\right\}(\alpha' = 0), \quad (13)$$

where according to (8) the limit of the proportion $\left(\frac{x'}{x}\right)_0$ is represented by

$$\left(\frac{x'}{x}\right)_0 = e^{-\frac{q_2}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \quad \ldots \ldots \quad (14)$$

We see from these expressions, that even with $\beta' = 0$ a *point of inflection at* $x = 0$ (and so also *before it*) is possible for the *two* curves $T = f(x)$ and $T = f(x')$. For this it is required for the curve $T = f(x)$, that

$$\left(\frac{x'}{x}\right)_0 = \frac{q_1 - 4T_1}{(q_1 - 4T_1) - 2(q_1 - q_2)} = \frac{1}{1 - 2\dfrac{q_1 - q_2}{q_1 - 4T_1}},$$

or

$$\frac{q_2}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = log\left(1 - 2\frac{q_1 - q_2}{q_1 - 4T_1}\right).$$

If $2\dfrac{q_1 - q_2}{q_1 - 4T_1}$ is not large, we may write for it by approximation:

$$\frac{q_2}{2\,T_1T_2}(T_1 - T_2) = 2\,\frac{q_1 - q_2}{4T_1 - q_1}.$$

We see that in any case $\dfrac{q_1 - q_2}{4T_1 - q_1}$ must be *positive.*

The condition may now be written as follows:

$$\frac{q_1 - q_2}{q_2} = \frac{(4T_1 - q_1)(T_1 - T_2)}{4T_1\,T_2} = \left(1 - \frac{q_1}{4T_1}\right)\left(\frac{T_1}{T_2} - 1\right),$$

or

$$\frac{q_1}{q_2} = \frac{T_1}{T_2} - \frac{q_1}{4T_1}\left(\frac{T_1}{T_2} - 1\right),$$

hence

$$\frac{q_1}{4T_1}=\frac{\frac{T_1}{T_2}-\frac{q_1}{q_2}}{\frac{T_1}{T_2}-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

If e.g. $T_1=1100$, $T_2=900$, $q_1=2200$, $q_2=1980$, the first member is $^1/_2$, the second member $\frac{^{11}/_9-^{10}/_9}{^{11}/_9-1}$, so also $^1/_2$. [The term $2\,\frac{q_1-q_2}{q_1-4T_1}$ under the *log*-sign is here $\frac{440}{2200}=\,^1/_5$].

Even with $\beta'=0$ a point of inflection can very well occur somewhere in the curve $T=f(x)$. The corresponding condition for the occurrence of a point of inflection at $x=0$ in the curve $T=f(x')$ becomes:

$$\left(\frac{x}{x'}\right)_0=\frac{q_1+4T_1}{q_1+4T_1-2(q_1-q_2)}=\frac{1}{1-2\,\frac{q_1-q_2}{q_1+4T_1}},$$

or

$$\frac{q_2}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)=-\,log\left(1-2\,\frac{q_1-q_2}{q_1+4T_1}\right),$$

for which we may write for small values of q_1-q_2:

$$\frac{q_2}{2T_1T_2}(T_1-T_2)=2\,\frac{q_1-q_2}{q_1+4T_1}.$$

This is only possible when $q_1>q_2$. Again we may write:

$$\frac{q_1-q_2}{q_2}=\frac{(q_1+4T_1)(T_1-T_2)}{4T_1T_2}=\left(1+\frac{q_1}{4T_1}\right)\left(\frac{T_1}{T_2}-1\right),$$

or

$$\frac{q_1}{q_2}=\frac{T_1}{T_2}+\frac{q_1}{4T_1}\left(\frac{T_1}{T_2}-1\right),$$

i. e.

$$\frac{q_1}{4T_1}=\frac{\frac{q_1}{q_2}-\frac{T_1}{T_2}}{\frac{T_1}{T_2}-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15a)$$

If e.g. $T_1=1100$, $T_2=900$, $q_1=2200$, $q_2=1650$, the first member is again $^1/_2$, and also the second member is $\frac{^4/_3-^{11}/_9}{^{11}/_9-1}=\,^1/_2$.

[The term $2\,\frac{q_1-q_2}{q_1+4T_1}$ is now $\frac{1100}{6600}=\frac{1}{6}$].

Also in the curve $T=f(x')$ a point of inflection may occur even with $\beta'=0$.

And now we have given a complete answer to the question raised in the beginning of § 3. The point of inflection at L (fig. 7) need not have disappeared in either of the two meltingpoint-curves, when β' has reached the extreme value 0.

In a following paper we shall give a fuller discussion of the important limiting case $\beta' = 0$.

4. Finally we wish to discuss more at length an important property of the *eutectic* point C, which was only shortly mentioned in the preceding communication. (l.c., p. 166).

A rule was namely given there of very general application, i. e. .

When $\alpha'_1 = \alpha'_2$ (i. e. latent heat required for the mixing of the first component with $x = 1$ is equal to that of the second component with $x = 0$) *the compositions of the two solid phases will be complementary.*

We shall proceed to give the proof of this thesis.

Evidently the system of equations holds for the eutectic point (the compositions x_1' and x_2' of the solid phase are there in equilibrium with that of the liquid x):

$$T = \frac{T_1(1-\beta' x_1'^2)}{1 + \frac{RT_1}{q_1} \log \frac{1-x_1'}{1-x}} = \frac{T_2\left(1 - \frac{q_1}{q_2}\beta'(1-x_1')^2\right)}{1 + \frac{RT_2}{q_2} \log \frac{x_1'}{x}} = \frac{T_1(1-\beta' x_2'^2)}{1 + \frac{RT_1}{q_1} \log \frac{1-x_2'}{1-x}} =$$

$$= \frac{T_2\left(1 - \frac{q_1}{q_2}\beta'(1-x_2')^2\right)}{1 + \frac{RT_2}{q_2} \log \frac{x_2'}{x}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

If we solve from this $\log(1-x)$ and $\log x$, we get:

$$\left.\begin{aligned}
\log(1-x) &= \log(1-x'_1) + \frac{q_1}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right) + \frac{q_1}{RT}\beta' x_1'^2 \\
\log x &= \log x'_1 + \frac{q_2}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right) + \frac{q_1}{RT}\beta'(1-x'_1)^2 \\
\log(1-x) &= \log(1-x'_2) + \frac{q_1}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right) + \frac{q_1}{RT}\beta' x_2'^2 \\
\log x &= \log x'_2 + \frac{q_2}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right) + \frac{q_1}{RT}\beta'(1-x'_2)^2
\end{aligned}\right\},$$

from which follows by equalization:

$$\log \frac{1-x_1'}{1-x_2'} = \frac{q_1}{RT}\beta'(x_2'^2 - x_1'^2); \ \log \frac{x_1'}{x_2'} = \frac{q_1}{RT}\beta'\left[(1-x_2')^2 - (1-x_1')^2\right],$$

which is evidently satisfied by

$$x_2' = 1 - x_1', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

q. e. d.

J. J. VAN LAAR. **"On possible forms of the meltingpoint-curve for binary mixtures of isomorphous substances." (2nd communication).**

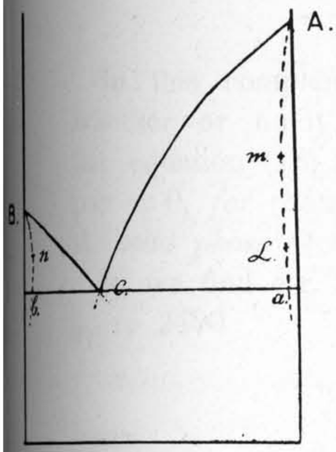

Fig. 1.

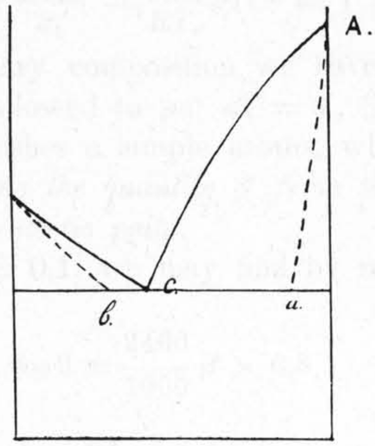

Fig. 2.

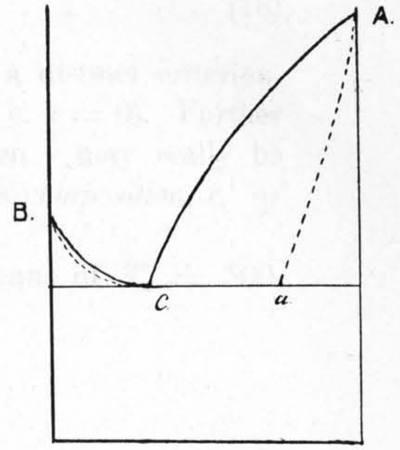

Fig 3.

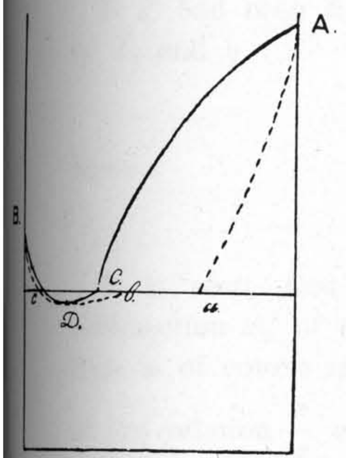

Fig. 4.

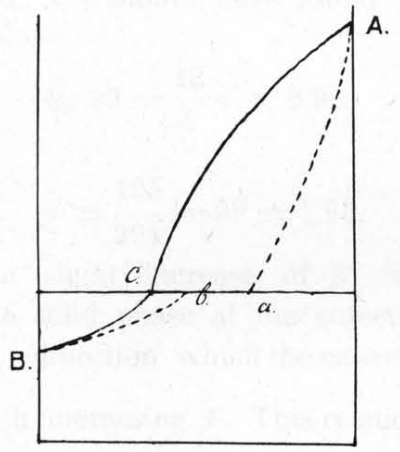

Fig. 5.

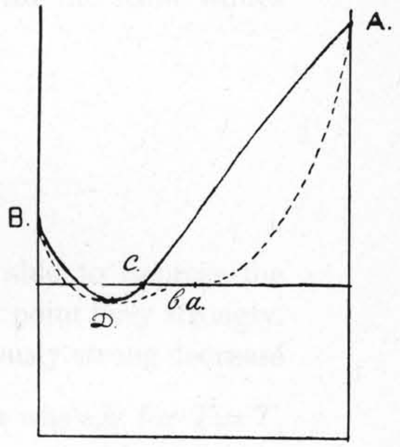

Fig. 6.

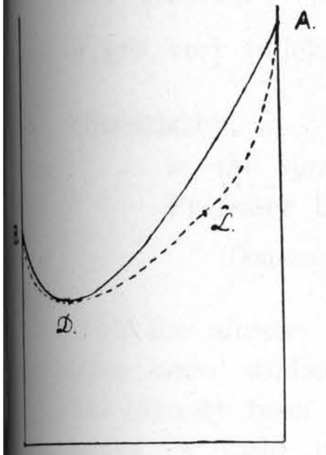

Fig. 7.

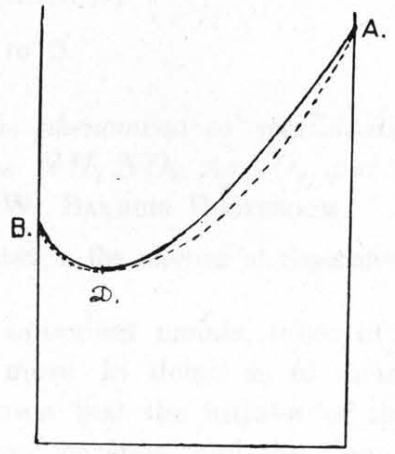

Fig 8.

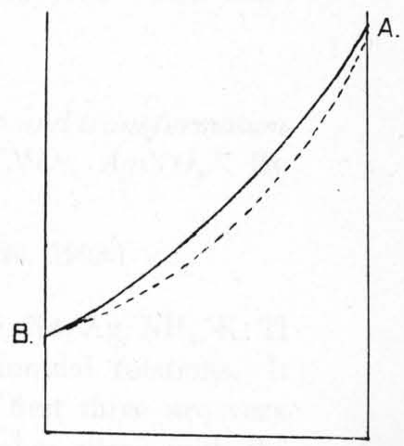

Fig 9.

The two above equations pass now into one:

$$log \frac{1-x_1'}{x_1'} = \frac{q_1}{RT_e} \beta'(1-2x_1') \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

In this complementary composition we have a distinct criterion, whether or no it is allowed to put $\alpha'_1 = \alpha'_2$ (i. e. $r = 0$). Further the equation (18) furnishes a simple means, when r may really be put $= 0$, *for calculating the quantity β' from the composition x_1' of the solid phase at the eutectic point.*

If we find e.g. $x'_1 = 0{,}1$, we may find by means of $T_e = 500$, $q_1 = 2400$.

$$log\, 9 = \frac{2400}{1000} \beta' \times 0{,}8,$$

hence:

$$\beta' = \frac{25}{48} log\, 9 = 1{,}14.$$

If x' had been 0,01, we should have found with the same values of T_e and q_1:

$$log\, 99 = \frac{12}{5} \beta' \times 0{,}98,$$

hence.

$$\beta' = \frac{125}{294} log\, 99 = 1{,}95.$$

It is seen, that a slight increase of β' is able to depress the composition x_1' of the solid phase at the eutectic point very strongly. This is of course in connection which the enormously strong decrease of the relation $\frac{x'}{x}$ with increasing β'. This relation was e.g. for $T = T_1$ and great β' represented by $\left(\frac{x'}{x}\right)_0 = e^{-\frac{\alpha'}{RT_1}}$ (see § 3), which converges very quickly to 0.

Chemistry. — "*The phenomena of solidification and transformation in the systems NH_4NO_3, $AgNO_3$ and KNO_3, $AgNO_3$.*" By Professor H. W. Bakhuis Roozeboom.

(Communicated in the meeting of September 26, 1903.)

Of the nitrates of univalent metals, those of Li, Na, Ag, NH_4, K, Tl have been studied more in detail as to their mutual relations. It has already been shown that the nitrates of the first three are very prone to yield mixed crystals and the same takes place with the last three. $LiNO_3$ and also $NaNO_3$ do not seem to form with the