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

## Citation:

Bakhuis Roozeboom, H.W., On solubility and meltingpoint as criteria for distinguishing racemic combinations, pseudoracemic mixed crystals and inactive conglomerates, in:
KNAW, Proceedings, 1, 1898-1899, Amsterdam, 1899, pp. 310-313

This PDF was made on 24 September 2010, from the 'Digital Library' of the Dutch History of Science Web Center (www.dwc.knaw.nl)
> 'Digital Library > Proceedings of the Royal Netherlands Academy of Arts and Sciences (KNAW), http://www.digitallibrary.nl'
8. Finally we consider a tangential net.

Two right lines through $P$ which intersect at right angles are touched by one conic of the net. If the right angle included by these lines turns about the vertex $P$ the pairs of tangents drawn through $Q$ to the variable conic form an involution. For every ray $s$, drawn through $Q$, determines a tangential pencil belonging to the net, having the pairs of an involution $\left(r, r^{\prime}\right)$ in common with the point $P$. The conic touched by the orthogonal pair ( $r, r^{\prime}$ ) has a second tangent $s^{\prime}$ through $Q$, forming with $s$ a pair of the involution indicated above. The orthogonal pair $\left(s, s^{\prime}\right)$ determining a conic for which $r$ and $r^{\prime}$ are at right angles to each other, we can draw but one orthoptical circle through the points $P$ and $Q$.

According to the circles ( $\omega$ ) possessing an orthogonal circle or intersecting a fixed circle in two diametrically opposite points or passing through a fixed point, the obtained net of circles is represented by an orthogonal hyperboloid of revolution with one or two sheets or by an orthogonal right cone.

Chemistry. - "On solubility and meltingpoint as criteria for distinguishing racemic combinations, pseudoracemic mixed crystals and inactive conglomerates." By Prof. Bakiois Roozeboom.
Though several times attention has been drawn to the phenomena of solubility and melting in order to distinguish between the types mentioned above, no certainty has been attained as yet.

1. Solubility. We only get a clear insight in the phenomena of solubility by drawing attention to the number of solubility curves obtainable at a given temperature.


Fig. 1.

If $O a$ is the proportion of the saturated solution of the dextrosubstance $D$, and $O b$ the same for the laevosubstance $L$, these two are equal at the same temperature.

By adding $L$ to the $D$-solution and vice-versa we now get, if no racemic combination appears at the temperature used, nothing else than two solubilitycurves, starting from the points $a$ and $b$ and meeting in c. Their precise direction depends on the manifold actions that can take place in the solution. From the perfect equivalence of $L$ and $D$ it results however necessarily that $c$ must always lie on the line $O B$, which halves the angle of
the axes, so that the solution which is equally saturated with $L$ and with $D$ is inactive, no matter how great the excess of $L$ or $D$ with which it is in contact.
If at another temperature a racemic combination is possible, we get three solubility-curves de, efg and gh. The second regards the solutions of the combination; here $f$ represents the pure solution, $e$ and $g$ those which are acquired in presence of an excess of $D$ or $I$.
At the transition temperature the curse in the middle disappears (point A). Here too the solution is always inactive. If therefore an inactive substance is a conglomerate (by which I mean a solid mixture in which the components lie side by side separately) of $L$ and $D$, we shall never get as a saturated solution anything else than point $c$; if the substance is a combination we can get three solutions, as we dissolve it alone or with an excess of $L$ or $D$.
Phenomena observed at evaporation. On this subject experiments have latels been made by Kipping and Pope. From the figure of the solubility-curves it is easy to deduct, in the graphic manner first instituted by Schreinemarers, that in case of the evaporation of a solution containing an excess of $D$ or $L$, the solution arrives at last in point $c$ - that is to say becomes inactive - in case no racemic combination exists at the temperature used. If on the other hand this combination does exist - we arrive with an excess of $D$ to a final point in $e$, with an excess of $L$ in $g$.
In this manner it would be equally possible to make out what is deposited: conglomerate or combination - if in these evaporation experiments care were always taken that the necessary crystallisationnuclei were present - a circumstance to which $K$. and P. have paid no attention.
Partially racemic combinations. These have lately been discovered by Ladenburg and been studied with a view to the solubility in $D$ - and $L$ strychninetartrate.
The symmetry of fig. 1 disappears in that case owing to the unequal solubility of the two components. Consequently puint $A$ will generally lie no longer on $O B$. It results therefrom that the combination, even before its transition-temperature is reached, already possesses a temperature-interval of partial decomposition. So Mr. Ladenborg is wrong in the opinion that this combination in its transitiontemperature must furnish a solution, contaning an equal amount of $D$ - and $L$-tartrate.
At temperatures situated in the decomposition interval, we now only get two kinds of solutions in case the combination is dissolved aloue and with an excess of $D$ or $L$.

Pseudo-racemic mixed crystals. As I demonstrated on a former occasion; mixed crystals must be considered as one solid phase. For mixed crystals formed of optical antipodes, if they exist, it will perhaps be possible to appear in every proportion. In such a case we should only get one solubility-curve in fig. 1, connecting the points a and $b$ and being symmetrical again.

If at lower temperatures, a racemic combination should appear, the continued mixing-series would be broken by it. The sketch of the solubility curves would consequently be altered in so far that the lines $E A$ and $C A$ would pass into one continuous curve. The evaporation phenomena would equally be altered.


Fig 2.


Fig 3.


Fig. 4.
II. Melting points. The opinion exists that a higher melting point is a proof of a racemic combination when compared with the melting puint of the antipodes. Uncertainty exists when the melting point of the inactive substance is equally high or lower.

Here too, it is only the study of the melting- and congealingcurves along their entire lengths, that can give us sufficient certainty.

If no combination, nor mixed crystals exist, fig. 2 must give the groundplan for the congelation. The mixing proportions of $L$ and $D$ are indicated on the horizontal axis, the temperature on the vertical. $A$ and $B$ are the melting points of $L$ and $D . A C$ is the congealing-line for liquids depositing $L$, $B C$ for such as deposit $D$. Every mixture congeals at last in $C$ to an inactive conglomerate of $L$ and $D$. If on the other hand there is a racemic combination, two types are possible, represented by fig. 3 and 4. In these $C$ is the melting point of the combination, which is higher or lower than the melting points $A$ and $B$. Independent of this fact, the congelation now leads to three curves, the one in the middle representing the case that the combination is deposited. It has two branches.

If, to end with, there is a continual mixingseries, there will be but one congealing curve. But the latter need not be, in a repre-
sentation as the one used here, a horizontal line connecting $A$ and $B$-as was the opinion of Kipping and Pope, but may quite as well show a maximum or a minimum, which then however lies at 50 pCt. I even suspect such to be the case in camphersulfonic chlorid and carvontribromide.

According to these views, neither a higher nor a lower meltingpoint furnishes a proof on the nature of an inactive substance, but the study of the entire melting-line does.

A single curve serves in case of mixed crystals, two curves in case of an inactive conglomerate, three in case of a combination.

Other remarkable phenomena may still present themselves, in case transformations of the combination, mixture or conglomerate appear after the congelation.

Mathematics. - " $A$ geometrical interpretation of the invariant $I I(a b)^{2}$ of a binary form $a^{2 n}$ of even degree". By Prof. $n+1$
P. H. Schoute.

With regard to the creation of the beautiful theory of the invariants undoubtedly very much is due to Sylvester as well as to Aronhold, Boole, Brioschi, Cayley, Clebsch, Gordan, Mermite and others. As early as 1851, indeed, he developed in his treatise: "On a remarkable discovery in the theory of canonical forms and of hyperdeterminants" (Phil. Mag., Vol. II of Series 4, p. 391-410) the fnundation upon which the theory of the canonical forms is based. The principal contents consist of the proof of two theorems. According to the first the general binary form of the odd degree $2 n-1$ can always be written in a single way as the sum of the $2 n-1^{\text {st }}$ powers of $n$ binary linear forms; according to the second the binary form of the even degree $2 n$ can be written as the sum of the $2 n^{\text {th }}$ powers of $n$ binary linear forms - and in that case in a single way too - only when a certain invariant vanishes. For this invariant with which we shall deal here compare a.0. Gundelfinger's treatise in the "Journ. f. Math.", Vol. 100, p. 413-424, 1883, and Salmon's "Modern higher algebra", $4^{\text {th }}$ ed., p. 156,1885 . So the theory of invariants of a certain form of any kind is ruled by the question about the minimum number of homonymous powers of linear fornss by which it can be represented. (Compare a.o. Reye in the "Journ.f. Math.", Vol. 73 ${ }^{1 \mathrm{~d}}$, p. 114-122). With this the theory of involutions of a higher dimension and order are closely allied. Likewise theorems are deduced from it relating to

