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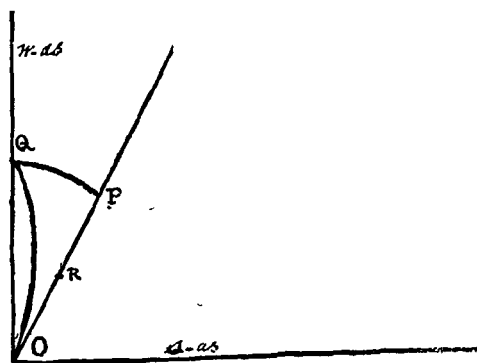


Fig. 3.

11. We conclude with a summary of the cases possible for a floating cube in so far as $\varepsilon > \frac{1}{2}$.

$1 > \varepsilon > 0.788 \dots$	first case in vertical position.
$0.738 \dots > \varepsilon > 0.75$	„ „ „ oblique „
$0.833 \dots > \varepsilon > 0.77 \dots$	fourth case, level plane a pentagon.
$0.833 \dots > \varepsilon > 0.5$	fifth „ „ „ „ hexagon,
	where an interior diagonal is normal to the level of the liquid.

Moreover there are still possible positions belonging to the fifth case, where the interior diagonal is not perpendicular to the level of the liquid. The treatment of this is however attended with great difficulties:

Chemistry. — “*On partial racemism*” By Mr. H. DUTILH. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of October 30, 1909).

A recent article from FINDLAY and HICKMANS¹⁾ induces me to communicate the results of a research on the above subject, on which I have been engaged since August 1908, the publication of which has been delayed, however, through circumstances not under my control.

I have been occupied with the case of partial racemism which occurs in strychnine racemate and I have studied more in particular the behaviour of this substance in presence of its aqueous solution. Although this salt has already been subjected to an extensive

¹⁾ Journ. chem. Soc. Trans. **95**. 1386 (1909).

research under the same conditions by LADENBURG and DOCTOR ¹⁾, I am of opinion that this research, although carried out fully and accurately, is attended with errors and that, therefore, the results do not represent the true state of affairs.

LADENBURG and DOCTOR have determined at different temperatures the solubilities of strychnine racemate and of strychnine *l*-tartrate and strychnine *d*-tartrate together, and they are of opinion that at the temperature at which the solubility of the partially racemic salt became equal to that of the mixture of its two component parts, the transition point of the strychnine racemate was situated, that is to say, that below that temperature the said salt would be stable in presence of its saturated solution but that at a higher temperature it would be resolved under those circumstances, with simultaneous separation of the least soluble of its dissociation products. By this process that temperature was found to be 30°, whereas by the tensimetric method 29°,5 was found. Moreover, the said authors have always endeavoured to determine the content in *d*- and *l*- strychnine tartrate of the solutions saturated with both salts by measuring the angle of rotation of those solutions and calculating the respective proportions from the known specific rotatory power of each of the two salts. Their observations led to the result that at the transition temperature the solution saturated with both components (these will in future be designated by *D* and *L* and their compound by *R*) would contain exactly 50% of both.

Immediately after their publication BAKHUIS ROOZEBOOM ²⁾ pointed out the improbability of their results and in the graphic representation given in his paper the way has been indicated how to set to work when studying the solubility phenomena in cases of partial racemism.

The two components in the system *L*, *D* and water, in which *R* can be formed from $D + L$, have, as we are dealing here with biactive substances whose configurations are partly each other's mirror images, at all temperatures a different solubility, which is shown by an asymmetric form of the solubility isotherms in this ternary system. This is elucidated by fig. 1. Suppose at a certain temperature the solubility of $L = OL$, of $D = OD$. If now *L* is dissolved in water already containing *D*, or *D* in solutions containing *L*, we obtain points situated on LC' or DC' , respectively. C' represents the solution saturated with both *D* and *L*.

At the temperature of the transition point we obtain a similar

¹⁾ Ber. d. d. chem. Ges. 32, 50. (1899).

²⁾ Zeitschr. f. physikal. Chem 28, 494 (1899).

which are not saturated with respect to R , but to $L + R$) and this goes on when we increase the temperature, until above t_3 the R can absolutely exist no longer in the presence of any solute whatever (retardation phenomena excluded). The temperature region $t_2 - t_3$ is called the transition interval.

In my research I have endeavoured to construct experimentally a similar diagram for the system strychnine *l*-tartrate, strychnine *d*-tartrate and water. For this purpose complete isotherms were determined successively by observing the change in the solubility of D , or L , if L or D was previously dissolved in water. In this manner I determined in this system the isotherm of 40° which being situated above the transition point found by LADENBURG and DOCTOR, had a form which agrees very well with that of the lines LC' and DC' . Isotherms at a lower temperature were then determined in a similar manner. First of all, I determined the D - and L -solubility curves at 25° , 16° and 7.5° , which notwithstanding the fact that these are interrupted by the solubility curve of R , could be followed up to their intersecting point. The solubility as to $L + R$ and $D + R$ was then measured at the same temperatures (also that of $D + L$, and this always agreed very well with the intersecting point of the D - and L -solubility curves found finally, by extrapolation).

When the solubility of these two salt couples was known, I placed them on the L - and the D -axis, connected these points with a straight line and looked, in the case of $L + R$ solutions, for the intersecting point with the L solubility curve; on the other hand in the case of $D + R$ solutions the intersecting point with the D curve was determined. In this manner, points on the lines PA and PB were determined successively in an indirect way and it was my intention to endeavour to trace the intersection of PA with OR , as the terminating point of the transition interval would then be known and the analogy between partial racemates and the inorganic double salts investigated by VAN 'T HOFF and his scholars be completely demonstrated. I succeeded in showing that at 7.5° the solubility of the racemate must be put down in the point where the L curve of the isotherm of that temperature intersects the line OR , and also that R and $R + L$ became equal as regards solubility. This gave the end of the transition interval and this temperature region, which in LADENBURG and DOCTOR's research was supposed not to exist at all, was shown to extend over about 20° . Saturated solutions of the partial racemate are therefore stable below 7.5° only: the solubility of the salt may

however, also be determined at higher temperatures (by retardation in the decomposition) and points like R^I , R^{II} etc. may be thus established.

Similarly, the possibility of determining points like C^II , C^{III} etc. is due to the retardation in the formation of R from $D + L$ and the non-crystallisation of this salt from the solution.

The end of the transition interval is characterised by the fact that the saturated solutions of R and of $R + L$ are in equilibrium with each other; their vapour tensions are the same and, consequently, this point ought to be controllable by the tensimetric method (with the aid of BREMER-FROWIN's tensimeter). The solubilities of R , D , and L at 7.5° have, however, become so small that the vapour tensions of these solutions do not practically differ from that of pure water at that temperature; consequently their mutual difference at a somewhat lower, or somewhat higher temperature and their equality at that temperature itself, is difficult to demonstrate. As a matter of fact I have not succeeded in verifying the result in this manner.

In the method followed by me I have carefully avoided analysing the liquids saturated with $R + D$, $R + L$ or $D + L$, by means of the polarimeter, as to their contents in L and D . For from the commencement of my research I was of opinion that such a method of analysis gives a wrong idea as to the inner composition of the solutions saturated with two salts.

A saturated ($R + D$), ($R + L$) or ($D + L$) solution contains not only R and D , R and L , or D and L , but in those solutions it must be assumed that R - as well as D - and L -molecules will occur. Such solutions conform, being homogeneous phases, to the law of the mass-action and therefore an equilibrium is formed between D -, L - and R - molecules, which is determined not only by the temperature of the solutions, but also by their concentrations. This equilibrium may be expressed by $R \rightleftharpoons D + L$.

LADENBURG and DOCTOR have determined the ($D + L$) solubilities by pipetting off quantities of the saturated solution; these were then weighed and evaporated. After having ascertained in this manner the total concentration, the residue was dissolved up to a definite volume. After determining the angle of rotation α , the content in D and in L was calculated by means of the equation $\alpha = \alpha_d + \alpha_l$

$$\alpha = \frac{[\alpha_d]_D \cdot p_d \cdot S.l}{100} + \frac{[\alpha_l]_D \cdot p_l \cdot S.l}{100}; \quad \frac{100\alpha}{L.S} = [\alpha_d]_D \cdot p_d + [\alpha_l]_D \cdot (p - p_d)$$

in which $[\alpha_d]_D$ and $[\alpha_l]_D$ represent the specific rotatory power of D

and L , p the total concentration, p_d the content in D , p_l the content in L , S the sp. gr. of the solution and l the length of the tube.

This manner of calculation, however, is not admissible; for at a total concentration p and a content p_d for D , we have a content p_l for L and $p - p_d - p_l$ for R and the equation thus becomes:

$$\frac{100a}{l \cdot S} = [\alpha_d]_D \cdot p_d + [\alpha_l]_D \cdot p_l + [\alpha_r]_D \cdot (p - p_d - p_l).$$

In this are known a , $[\alpha_d]_D$, $[\alpha_l]_D$, $[\alpha_r]_D$, p , l and S .

The equation contains two unknown quantities and therefore we cannot get an insight into the inner composition of the solutions saturated with $(R + D)$, $(R + L)$ or $(D + L)$ by means of a polarimetric determination, even when assuming that the three compounds which occur in the solvent do not affect each other's rotations (which has not been ascertained).

To this it may be attributed that LADENBURG and DOCTOR found the point P , that is the transition point, on the line OR , whereas I have reasons to conclude that the isotherm of the temperature of the transition point, like all others, retains its asymmetric form.

This untrustworthy method of analysis has been applied by FINDLAY and HICKMANS in their investigation of the partial racemism of the l -menthyl- r -mandelic ester, which must be considered as the binary compound of the l -menthyl- d -mandelic ester with the l -menthyl- l -mandelic ester, a fact which has been clearly shown by the authors ¹⁾ from the form of the melting point curve of those two esters. The partially racemic ester the binary system formed by possesses in this system a melting point curve of its own with a flat top and has, therefore, been partly resolved in the fused mass into the two components.

In their second publication ²⁾ the solubility isotherms are given at 35°, 25° and 10°. Of each isotherm only five points have been determined, namely, the solubilities of D , L , R , $R + D$ and $R + L$, whilst the solutions $(R + D)$ and $(R + L)$ have been analysed according to the above mentioned method.

It now appears to me that their graphic representation, which I reproduce, shows at once the deceiving conclusions drawn from the polarimetric method. If we look at fig. 2 we observe that the solubility of the d -acid ester decreases on addition of the l -acid ester to the solution at 10°, whilst it increases at 25° and 35°.

¹⁾ FINDLAY & HICKMANS Journ. chem. Soc. Trans. 91, 905, (1907).

²⁾ Ibid. 95, 1386 (1909).

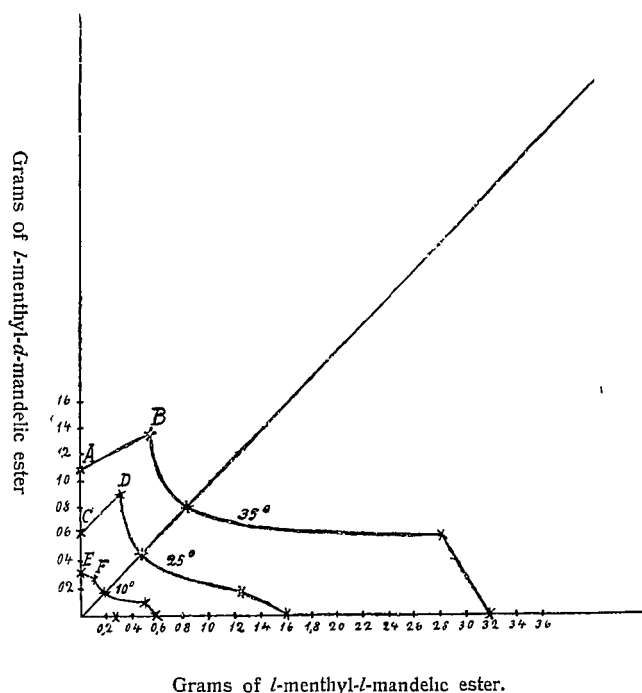


Fig. 2.

This will be noticed by comparing the lines AB , CD and EF .

Such a behaviour is highly improbable, for it may be expected that at 35° , 25° , and 10° the effect on the solubility of the d -mandelic ester by the presence of the l -mandelic ester in the solution will manifest itself in an equal sense and not cause an increase of solubility at the one temperature and a decrease at the other. In the diagram of FINDLAY and HICKMANS, however, the course of the curves AB , CD , and EF , is, contrary to my investigations, determined exclusively by the situation of the points B , D , and F , whose position is deduced from an observed angle of rotation of the solution of the residues obtained by evaporation. It is not at all improbable that if these points were determined by another method their situation would be quite a different one. In this system the verification would have been a simple one, because the melting point curve of the binary system formed by the two biactive esters is known. The melting point for each content in D , or L in mixtures of $D + L$ is therefore known.

If now, FINDLAY and HICKMANS had only determined the melting point of their residues each time after evaporating their saturated solutions ($R + L$) and ($R + D$), they would have obtained from the situation of this melting point in connection with the melting point

curve of the binary system formed by *D* and *L*, so to speak "thermi analyses of their solutions, which might have been compared with polarimetric ones. It is to be regretted that these investigators have not applied this check as now it cannot, provisionally, be decided whether their isotherms exhibit the true form or not. From my results with the strychnine tartrates, I think I may decide upon the latter view. The truth may, however, be revealed by a determination of the complete isotherms or, perhaps with sufficient accuracy, by melting point determinations of the residues left on evaporation.

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Botany. — "*Contribution to the knowledge of water-secretion in plants*
By Dr. W. BURCK.

(Communicated in the meeting of October 30, 1909.)

II. *Secretion of water in the flower.*

After TREUB¹⁾ showed in 1890 that the flower-buds of *Spathod campanulata* Beauv. are filled with a watery fluid, a similar secretion of water in closed flower-buds has also been observed in a few other tropical plants.

LAGERHEIM²⁾ observed the same phenomenon in a South-American Solanacea, *Jochroma macrocalyx* Benth. GREGOR KRAUS³⁾ soon afterwards described the water-calyces of *Parmentiera cerifera* Seem., and HALLIER⁴⁾ those of *Leea amabilis*. Later a detailed paper was published by KOORDERS⁵⁾ on the flower-buds of the Bignoniaceae: *Parmentiera cerifera* Seem., *Crescentia Cujete* Linn., *Kigelia pinnata* DC., *Heterophragma adenophyllum*, Seem., *Stereospermum hypostictum* Miq.; of the Solanaceae: *Juanulloa parasitica* Ruiz et Pav., *Nicandra physaloides* Gärtn.; of the Verbenaceae: *Clerodendron Minahassae* T. et B. and of a Scrophulariacea *Illysanth* spec. Afterwards there followed important contributions by SHIBATA

¹⁾ TREUB, M. Annales du Jardin botanique de Buitenzorg. Vol. VIII. 1890

²⁾ LAGERHEIM. Zur Biologie der *Jochroma macrocalyx* Benth. Berichte d. deutsch. bot. Gesellsch. Bd. 9, Jahrg. 1891.

³⁾ KRAUS, G. Wasserhaltige Kelche bei *Parmentiera cerifera* Seem. Flora B 81, p. 435—437.

⁴⁾ HALLIER, H. Ueber *Leea amabilis* und ihre Wasserkelche. Annales du Jardin botanique de Buitenzorg. Vol. XIV. 1897.

⁵⁾ KOORDERS, S. H.. Ueber die Blütenknospen—Hydathoden einiger tropischer Pflanzen. Annales du Jardin botanique de Buitenzorg. Vol. XIV 1897.

⁶⁾ SHIBATA, K. Zur Kenntnis der Kelch- und Knospenhydathoden. Bot. Centralblatt 1900. Bd. LXXXIII.