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$$e_1 = - \frac{m\phi k I_2 R^2}{8 W_1 c^2}$$

is circulated in the first conductor. The electromotive force in that conductor amounts to $E_1 = I_1 \cdot W_1$. In consequence of the circulation of the quantity of electricity e_1 , the generator of the current yields, besides the JOULE heat, the quantity of energy $-E_1 e_1$, which amounts to:

$$-E_1 e_1 = \frac{m\phi k I_1 I_2 R^2}{8 c^2}.$$

We find in the same way that after subtraction of the JOULE heat, an equal amount of energy is yielded by the second generator of current. Together the total quantity of energy yielded by the generator of current, amounts therefore to:

$$\frac{1}{4c^2} m\phi k I_1 I_2 R^2,$$

which corresponds with the value $A + \Delta T$, required for the work of the ponderomotive forces and the increase of the magnetic energy.

Chemistry. — “*Molecular-Allotropy and Phase-Allotropy in Organic Chemistry.*” By Prof. A. SMITS. (Communicated by Prof. J. D. VAN DER WAAALS).

1. *Survey of organic pseudo-systems.*

I have indicated the appearance of a substance in two or more similar phases by the name *phase-allotropy*, and the occurrence of different kinds of molecules of the same substance by the name of *molecular-allotropy*. It may be assumed as known that one of the conclusions to which the theory of allotropy leads, is this that phase-allotropy is based on molecular-allotropy.

The region in which the existence of molecular allotropy is easiest to demonstrate is the region of organic chemistry, and I think that I have to attribute this fact to this that the velocity of conversion between the different kinds of molecules which present the phenomenon of isomery or polymery, is on the whole much smaller in organic chemistry than in anorganic chemistry; in organic substances it seems even not perceptible in many cases. The substances, for which this is, however, the case, and which were formerly called

tautomers, are comparatively few as yet, but undoubtedly their number will increase as the experiment is made more refined.

It is obvious that a test of the just mentioned conclusion from the theory of allotropy will be most easily carried out in the region of organic chemistry, but on the other hand a test in the region of anorganic chemistry will be, especially for elements, of greater scientific interest.

Accordingly the research is continued both in anorganic and organic domain, and the purpose of this communication is to draw attention to the gigantic field of research which is opened up for us in organic region for a study in this direction.

BANCROFT ¹⁾ was the first to take into account the influence of the time in the study of systems of organic substances which can occur in two different forms. In this consideration he came to *three* cases.

1. The time element vanishes in consequence of the practically immediate setting in of the (internal) equilibrium.

2. The setting in of the (internal) equilibrium takes place so slowly that so-called "false equilibria" occur, for which case BAKHUIS ROOZEBOOM ²⁾ derived different *T*, *X*-figures.

3. The (internal) equilibrium sets in with such a velocity that the system behaves as a binary one in case of rapid working, as a unary one in case of slow working.

The substances belonging to the latter group, and their number is undoubtedly enormously great especially in the domain of organic chemistry, yield very satisfactory material of research.

BANCROFT was the first who discovered a pseudo binary system in *dichlorostilbene* examined by ZINCKE ³⁾ and explained its behaviour. ZINCKE had discovered that when the form with the highest melting point was kept in molten condition for a long time (200°), there took place a lowering of the point of solidification from 192° to 160°, which was to be attributed, as BANCROFT stated, to this that the substance had assumed (internal) equilibrium at 200°, in which the molecules of one form had been partially converted to those of the other form.

Among the organic substances which can occur in different isomer forms, variations of the melting point are met with in very many cases according to the literature, which variations must be attributed to a conversion in the direction of the internal equilibrium or to a retardation of the setting in of the internal equilibrium.

¹⁾ Journ. phys. Chem. **2**. 143 (1898).

²⁾ Z. f. phys. Chem. **28**. 289 (1899).

³⁾ Lieb. Ann. **198**. 115 (1879).

Specially the group of the *oximes* furnishes several examples. In this respect we may mention in the first place *acetaldoxim* studied by DUNSTAN and DYMOND¹⁾, and later more closely examined by CARVETH²⁾.

Further may be mentioned *benzaldoxim*, for which the first data have been given by BECKMANN³⁾, the discoverer of the isomeric conversions of these substances. This substance was more closely investigated by CAMERON⁴⁾, whose results were later tested and improved by SCHOEVERS's study⁵⁾. CARVETH⁶⁾ investigated also another *oxim*, viz. *anisoldoxim*, of which BECKMANN⁷⁾ had also found two isomers.

A very interesting substance is the *benzilorthocarbonic acid*, of which GRAEBE and JUILLARD⁸⁾ found two distinctly different crystallized products, one white, the other yellow.

While enantiotropy is a very frequently occurring phenomenon in inorganic chemistry, we find this phenomenon only exceedingly rarely mentioned in the organic literature. We should undoubtedly be mistaken if we supposed that it must be inferred from this that the phenomenon of enantiotropy in organic region is met with only by great exception. In the first place this circumstance is much sooner to be ascribed to this that on account of the slight velocity of conversion between the different kinds of molecules of organic substances, the phenomenon of enantiotropy manifests itself much less easily, and in the second place to the absolute absence of an accurate systematic investigation in this direction.

It is, however, known of *benzilorthocarbonic acid* that it is enantiotropic. SOCH⁹⁾ has namely demonstrated this with certainty, and considerably extended GRAEBE's¹⁰⁾ investigation.

We have further a very important group of allotropic substances with distinct transformation in the *keto-* and *enol compounds*.

WOLF¹¹⁾ devoted an investigation to *formylphenyl acetic ester*, of

¹⁾ Journ. chem. Soc. **61**, 470 (1892); **65**, 206 (1894).

²⁾ Journ. phys. chem. **2**, 159 (1898).

³⁾ Ber. **20**, 2768 (1887); **37**, 3042 (1902).

⁴⁾ Journ. phys. chem. **2**, 409 (1898).

⁵⁾ Dissertatie 43.

⁶⁾ Journ. phys. chem. **3**, 437 (1899).

⁷⁾ Ber. **23**, 2103 (1890).

⁸⁾ Ber. **21**, 2003 (1888).

⁹⁾ Journ. phys. chem. **2**, 364 (1898).

¹⁰⁾ Ber. **23**, 1344 (1890).

¹¹⁾ Journ. phys. chem. **4**, 123 (1900).

which WISLICEŃUS¹⁾ had discovered two modifications a few years before, viz. the solid *keto* and the liquid *enol* compound.

Of late a number of investigations on other substances with intermolecular transformation have been published by DIMROTH²⁾. These very interesting publications treat molecular conversions in derivatives of triazol, in different solvents.

One of the isomers is always an acid which can be determined titrimetrically, which may be called a very favourable circumstance for the study of the phenomena of conversion.

Another substance whose peculiar behaviour has already induced many investigators to occupy themselves with it, is the *hydrazone of acetaldehyde*, of which FISCHER³⁾ discovered two modifications.

BAMBERGER and PEMSEL⁴⁾ undertook a further investigation, a few years later also LOCKEMANN and LIESCHE⁵⁾, and six years later LAWS and SIDGWICK⁶⁾, but none of these investigators has succeeded in unravelling the behaviour of this peculiar substance.

P. nitrobenzal-phenyl-methyl-hydrazone, investigated by BACKER⁷⁾ is another hydrazone which shows great resemblance with the former. Also this substance possesses two modifications, a red and a yellow one, but it is not known as yet, in what relation these forms are to each other.

The system *ureum-ammoniumcyanate*, further examined by WALKER and HAMBLY⁸⁾, just as the system *sulpho-ureum-ammoniumsulphocyanate* studied by VOLHARD⁹⁾ WADDELL¹⁰⁾, REYNOLDS and WERNER¹¹⁾, FINDLAY¹²⁾, and finally by SMITS and KETTNER¹³⁾, likewise belong to the organic pseudo-systems, just as *cyanogen-paracyanogen* investigated by TERWEN¹⁴⁾ and *cyanogenichydrogenic acid*, *cyaniric acid* and *cyamelide* investigated by TROOST and HAUTEFEUILLE¹⁵⁾.

¹⁾ Ber. **20**, 2933 (1887); **28**, 767 (1895).

²⁾ Ber. **35**, 4041 (1902); Lieb. Ann. **335**, 1 (1904); **338**, 143 (1905), **364**, 183 (1909); **373**, 336 (1910), **377**, 127 (1910).

³⁾ Ber. **29**, 795 (1896).

⁴⁾ Ber. **36**, 85 (1903)

⁵⁾ Lieb. Ann. **342**, 14 (1905).

⁶⁾ Journ. Chem. Soc. **99**, 2085 (1911).

⁷⁾ Dissertation, Leiden 1911.

⁸⁾ Journ. chem. Soc. **67**, 746 (1895).

⁹⁾ Ber. **7**, 92 (1874).

¹⁰⁾ Journ. phys. chem. **2**, 525 (1898).

¹¹⁾ Journ. chem. Soc. **83**, 1 (1903).

¹²⁾ Journ. chem. Soc. **85**, 403 (1904).

¹³⁾ These Proc. Vol. **15**, p. 683 (1912).

¹⁴⁾ Dissertation Amsterdam 1913.

¹⁵⁾ Compt. rend **66**, 795; **67**, 1345.

Among the organic nitro compounds there are some that belong to the group of the pseudo acids, as was found by HANTSCH¹⁾ and HOLLMAN²⁾ in the investigation of *brominephenylnitromethane* and of *phenylnitromethane*, these substances too are to be counted among the pseudo systems.

The same thing may be remarked about the *dimethylketol*, examined by PECHMANN and DAHL³⁾, the *benzolazocyanogen acetic ester* studied by F. KRÜCKEBERG⁴⁾, KIPPING's *benzylidenehydrindon*⁵⁾, and *tolane-dibromide*⁶⁾ of LIMPRICHT and SCHWANERT.

Also in the domain of structure isomery, tautomery or internal transformation has been observed. POLAK⁷⁾ found a fine example of this in the *para-* and *metabenzoldisulphonic acid* and SMITS and VIXSEBOXSE⁸⁾ in *methylnhodanide* and *methylnmustard oil*. In connection with this TERWEN⁹⁾ advanced the supposition that the structure isomers should be tautomers that very slowly pass into each other.

2. Discussion of the binary pseudoternary systems consisting of an allotropic substance and a solvent.

The survey of organic substances given here, of which it is certain that they are pseudo systems, can by no means lay claim to completeness, nor did we try to reach it. Our purpose was only to demonstrate by a mere enumeration of some facts, how enormously large is the territory in organic region, on which the theory of allotropy might be tested.

Here and there an attempt has been made to find a connection between the pseudo binary and the unary melting-point diagram, but this study has never been exhaustive.

BANCROFT and his pupils have proceeded furthest in this direction, but the theory of allotropy requires more at present.

Nor has a systematical investigation of tautomeric substances with a solvent, so that we get a pseudo ternary system to study, in which the situation of the isotherm for the internal equilibrium in

1) Ber. **29**, 699, 2251 and 2253 (1896).

2) Kon. Akad. van Wetensch Vol. XIV (1906).

3) Ber. **23**, 2421 (1890).

4) J. f. prakt. Chem. [2] **46**, 579 (1892).

" " " " " **47**, 591 (1893).

5) Journ. chem. Soc. **65**, 499 (1894).

6) Lieb. Ann. **145**, 348 (1868).

7) Thesis for the Doctorate, Amsterdam.

8) These Proc. Vol. **16**, p. 33.

9) Thesis for the Doctorate Amsterdam

the liquid phase leads to the knowledge which solid phase at a definite temperature is the stable one, which the metastable, been sufficiently carried out as yet.

As we shall show presently, DIMROTH has indeed, made very important investigations in this directions, but an investigation carried through systematically at different constant temperatures only can bring us further here.

To show this it is necessary to subject DIMROTH's important work, which is of great interest for us here, to a closer examination.

DIMROTH¹⁾ has made use here of VAN 'T HOFF's formula²⁾ about the change of the equilibrium through the solvent, but in a somewhat modified convenient form, viz. in this shape:

$$\frac{C_A}{C_B} = \frac{L_A}{L_B} \cdot G \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which C_A and C_B indicate the concentrations of the substances A and B in the state of (internal) equilibrium at a definite temperature.

L_A and L_B are the concentrations of saturation of A and B in the *pure* solvent at the same temperature, G being a constant independent of the solvent.

DIMROTH, now, points out that important conclusions can be drawn from this relation, which are of great importance for the preparation of isomers transforming themselves into each other.

He says: suppose that for a certain temperature $G = 1$, it follows from this that when at this temperature we have saturated an arbitrary solvent with the two isomers A and B , and solid A and B lie on the bottom, the whole system remains unchanged in equilibrium. It might have been stated here that the temperature at which this takes place, would be the point of transition between A and B , the temperature, therefore, at which the two solid phases A and B are in equilibrium.

If $G < 1$, then $\frac{C_A}{C_B} < \frac{L_A}{L_B}$. In this case the solution saturate with respect to two solid isomers A and B will contain more A than corresponds to the state of equilibrium. A consequence of this is that A is converted to B in the liquid, B crystallizing out, and solid A going into solution, till the solid A has entirely disappeared. The reverse will take place when $G > 1$. In connection with these considerations he says: "Bringt man also zwei wechselseitig mit

¹⁾ Lieb. Ann. **377**, 133 (1910).

²⁾ Vorlesungen über theor. u phys. Chemie, 219.

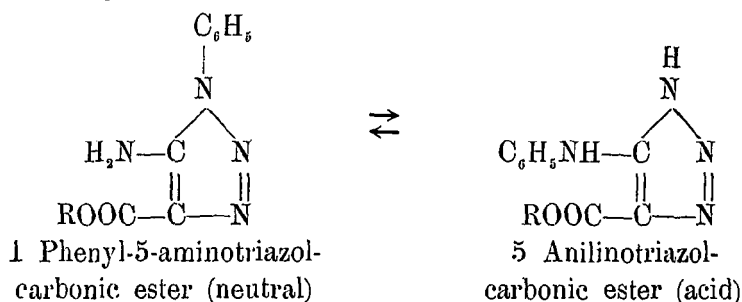
ausreichender Geschwindigkeit umwandelbare Isomere mit einer zur Lösung unzureichenden Menge eines Lösungsmittels zusammen, so muss, wenn der Satz von VAN 'T HOFF zu Recht besteht, die Richtung des sich abspielenden Isomerisationsvorganges ausschliesslich von der Konstanten G abhängen, also gänzlich unabhängig sein von der Natur des Lösungsmittels".

Experience, says DIMROTH, is however in conflict with this, for it often occurs that it is possible to convert isomers into each other by treatment with different solvents.

He refers in particular to the investigation of E. BAMBERGER ¹⁾ on the isomers of *nitroformaldehydrazons*, the α -form of which is converted by water or alcohol into the β -form, the β -modification being reversely transformed into the α -modification by benzene, chloroform, or ligroine.

In this connection he states explicitly: "Es kann kein Zweifel sein, dass diese mit Erfolg geübte Laboratoriumspraxis mit dem VAN 'T HOFF'schen Satze in Widerspruch steht."

This statement may seem somewhat strange, as in a test by means of the *aminoderivatives* of *triazol carbonic ester*, which show the following conversion,



DIMROTH himself found a very fine confirmation, so that doubt of the true interpretation of the said laboratory experience was sooner to be expected.

DIMROTH determined the concentration of the two isomers C_A and C_B in different solvents, in which the isomers had assumed equilibrium at $\pm 60^\circ$ under influence of the catalytic action of a trace of acid.

Further the solubility of each of the isomers, so L_A and L_B , was determined at the same temperature in the same solvent, and then the quantity G calculated by means of equation (1).

The investigation of the isomers of the *ethyl* resp. *methyl ester* yielded the following interesting result:

¹⁾ Ber. **34**. 2001 (1901).

Ethyl ester.

Solvent	$\frac{C_S}{C_n}$	$\frac{L_S}{L_n}$	G
Ether	20.7	8.4	2.4
Ethylalcohol	4.56	2.1	2.3
Toluol	1.53	0.74	2.1
Benzene	1.2	0.6	2.4
Nitrobenzene	0.85	0.33	2.6
Chloroform	0.32	0.19	1.7

Methyl ester.

Ether	21.7	53.0	0.4
Methylalcohol	2.3	7.0	0.33
Toluol	1.8	4.3	0.33
Benzene	1.02	3.2	0.32
Nitrobenzene	0.8	2.2	0.36
Chloroform	0.32	1.1	0.32

On the whole G yields a good constant value. As the value of G happens to be larger than 1 for the *ethyl ester*, and smaller than 1 for the *methyl ester*, it was to be foreseen that when the two isomers of the ethyl ester at 60° are left in contact with the saturate solution, the neutral form vanishes entirely, whereas the reverse must take place with the methyl ester. Experiment was in perfect harmony with this, so that the investigation of these isomers yielded a fine qualitative confirmation.

3. *A relation of general validity, by means of which both for isomers and for polymers it can be decided in an exceedingly simple way which modification is the stable one.*

The substances discussed here present the phenomenon of molecular allotropy, because they are built up of two kinds of molecules. Besides they present the phenomenon of phase allotropy, because the substance appears in two solid phases.

Hence the substance without solvent belongs to the pseudo binary systems, and only when the different kinds of molecules in the

homogeneous phase(s) are in internal equilibrium, the system behaves as a *unary* substance, i.e. as a substance of one component.

When we consider the behaviour of the two modifications with a solvent, we have a pseudo ternary system, which becomes binary when the different kinds of molecules assume internal equilibrium in the homogeneous phases.

To set forth the cases discussed by DIMROTH in the most easily comprehensible way, I will follow the method which I discussed already before in the publication: "Das Gesetz der Umwandlungsstufen OSTWALDS im Lichte der Theorie der Allotropie"¹⁾.

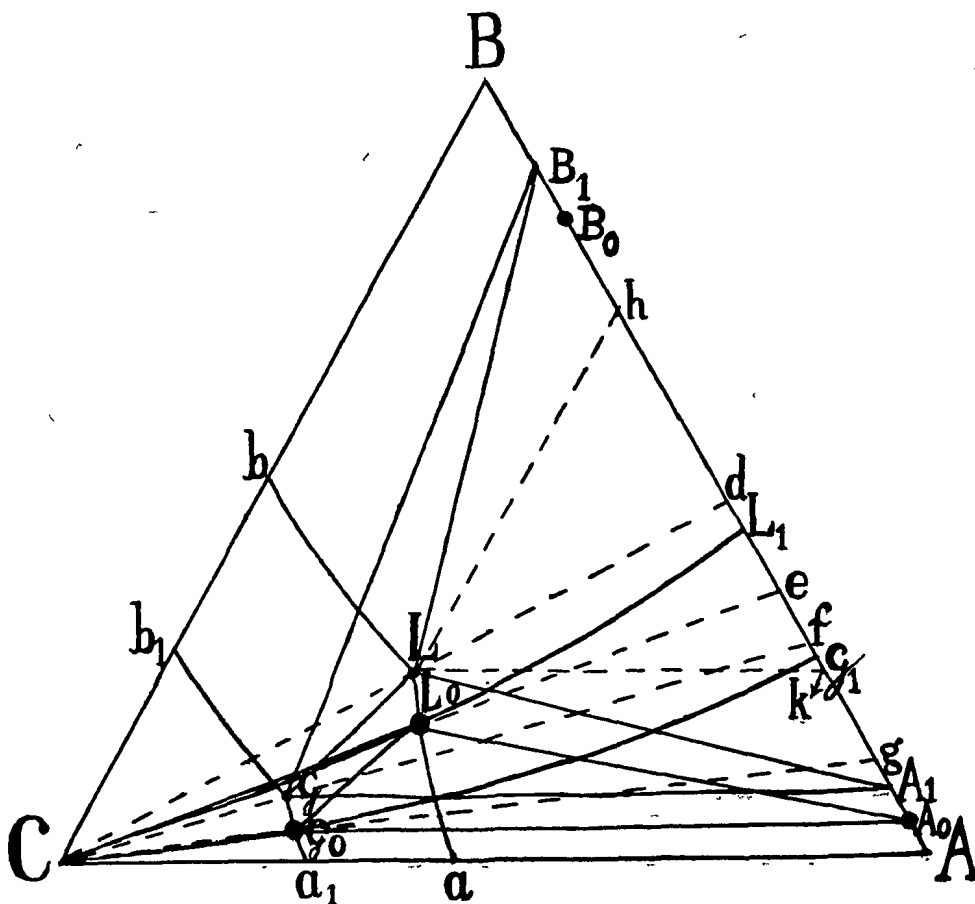


Fig. 1.

At the angles of the equilateral triangle Fig. 1 the letters A , B , and C are placed, of which A and B represent the pseudo-components, which are miscible in the solid state to a limited degree, C denoting the solvent.

In this triangle have been given among others the solubility isotherm of the mixed crystal series AA_1 , represented by the curve

¹⁾ Z. f. phys. Chem. 84, 385 (1913).

aL , and that of the mixed crystal series BB_1 , represented by the curve bL , for a definite temperature, so that the point of intersection L indicates the saturate solution coexisting with the mixed crystal phases A_1 and B_1 .

We imagine the solutions here also in equilibrium with their vapour, in consequence of which the pressure is therefore not constant.

The vapour isotherm belonging to the solubility isotherm aL is the line a_1G , that which belongs to the solubility isotherm bL is denoted by b_1G , so that G represents the vapour phase coexisting with the saturate liquid L and the two solid phases A_1 and B_1 at the four phase equilibrium.

If now CL_0L_1 represents the isotherm of the internal equilibrium in the liquid phase, i. e. the line that indicates how the internal equilibrium between A and B in the liquid phase shifts through change of the concentration of the solvent C , we see immediately that as this line cuts the solubility isotherm of the mixed crystal series AA_1 (point L_0), in case of internal equilibrium between A and B of all the saturated solutions only the saturate solution L_0 is stable, which then of course will coexist with a mixed crystal phase which is likewise in internal equilibrium, and is denoted here by A_0 .

Besides these also the isotherm of the internal equilibrium in the vapour CG_0G_1 is indicated. This line cuts the vapour isotherm a_1G in G_0 , so that it immediately follows from this that in case of internal equilibrium of all the saturated vapours only the vapour G_0 is stable, so that the phases A_0 , L_0 , and G_0 coexist in the stable three phase equilibrium solid-liquid-vapour.

It is known that the concentration of an arbitrary phase can immediately be given. Thus the concentration of the liquid phase L_0 is found by a line being drawn in this point parallel to the side CB , and another parallel to the side CA , as this has been done in fig. 1. One line meets the side AB in h , and the other in k . The number of gr. mol. A to 1 gr. mol. total or x is now given by Bh , the number of gr. mol. B or y by Ak , and the number of gr. mol. solvent C or $1-x-y$ by hk .

I may further assume as known that if our end in view is only the ratio of the concentrations A and B , e.g. in the same point L , this is also directly found when a straight line is drawn through the points C and L . This line meets the side AB in the point d . The ratio of the concentrations of A and B is the same in every point of the line Cd , hence it is in d also the same as in L . In d this ratio is:

$$\frac{Bd}{Ad} = \frac{Bh}{Ak} = \frac{x}{y}$$

Now it is perfectly clear that when the isotherm for the internal liquid equilibrium passes exactly through the point L , or the point of intersection of the two liquid isotherms, this implies that at the considered temperature the solution saturate with respect to the mixed crystal phases A_1 and B_1 is exactly in internal equilibrium. Accordingly it follows immediately from this, that also the coexisting solid phases will be in internal equilibrium in this case, and besides that also the vapour coexisting with L will be in internal equilibrium. The vapour G lying in the point of intersection of the two vapour isotherms will, therefore, in this case have to lie on the equilibrium isotherm for the vapour.

In this case, which presents itself at the transition temperature of the two modifications, we get a coincidence of the points L_0 and L , G_0 and G , A_0 and A_1 , B_0 and B_1 . Then coincide also the points e and d , g and f , which indicate the concentrations, the liquid phases, and the vapour phases as far as the substances A and B are concerned.

To simplify the discussion we shall now denote the concentration by small letters when the system is in internal equilibrium, capitals being used when the system is not in internal equilibrium.

The ratio of the concentration between A and B will therefore be indicated by $\frac{X_L}{Y_L}$ in the liquid L , and by $\frac{x_L}{y_L}$ in the liquid L_0 .

In accordance with this the ratio between A and B in the vapour G is then indicated by $\frac{X_g}{Y_g}$, and that in the vapour G_0 by $\frac{x_g}{y_g}$.

Thus the ratio of concentration of A and B is denoted by $\frac{X_{s_1}}{Y_{s_1}}$ in the solid phase A_1 , and that in the phase A_0 by $\frac{x_{s_1}}{y_{s_1}}$, that in B_1 being given by $\frac{X_{s_2}}{Y_{s_2}}$, and that in B_0 by $\frac{x_{s_2}}{y_{s_2}}$.

For the temperature of the point of transition the following simple equations hold :

$$\frac{x_L}{y_L} = \frac{X_L}{Y_L} \quad \dots \quad (2) \qquad \frac{x_{s_1}}{y_{s_1}} = \frac{X_{s_1}}{Y_{s_1}} \quad \dots \quad (4)$$

$$\frac{x_g}{y_g} = \frac{X_g}{Y_g} \quad \dots \quad (3) \qquad \frac{x_{s_2}}{y_{s_2}} = \frac{X_{s_2}}{Y_{s_2}} \quad \dots \quad (5)$$

At another temperature, however, we get the following relations:

$$\frac{x_L}{y_L} = f_1 \frac{X_L}{Y_L} \quad \dots \quad (6) \qquad \frac{x_{s_1}}{y_{s_1}} = f_3 \frac{X_{s_1}}{Y_{s_1}} \quad \dots \quad (8)$$

$$\frac{x_g}{y_g} = f_2 \frac{X_g}{Y_g} \quad \dots \quad (7) \qquad \frac{x_{s_2}}{y_{s_2}} = f_4 \frac{X_{s_2}}{Y_{s_2}} \quad \dots \quad (9)$$

About the factors f we will only state here that they are in connection with each other and become at the same time = 1 at the temperature of transition.

These relations (6) and (9) are of *general validity*, and of these relations equation (6) is the most suitable to decide which modification is the stable one at a definite temperature.

Let us suppose that $f_1 > 1$, i.e. that the case presents itself indicated in fig. 1. The internal equilibrium L_0 requires here a greater concentration of A_1 than prevails in the solution L . If therefore at first we have the saturate solution L in coexistence with the two mixed crystal phases A_1 and B_1 , the transformation



will take place in the solution, which renders the solution unsaturate with respect to B -mixed crystals, and supersaturate with respect to A -mixed crystals, with this consequence that B -mixed crystals dissolve, and A -mixed crystals deposit. This process continues till the B -mixed crystals have entirely disappeared, and a solution L_0 is left, in which A and B are in internal equilibrium, which solution coexists with a mixed crystal phase A_0 , which is then also in internal equilibrium.

For the case $f < 1$ we then get the reverse.

It is now perfectly clear that by consideration of the relations (7) or (8) and (9) we come to the same conclusion.

These now are all self-evident relations, which, indeed, only allow of a qualitative test, but which have this advantage, that as has been said, they have *general validity*.

It will repeatedly happen that we do not know which of the two forms of a substance is the stable modification at a definite temperature, and then equation (6), as has been shown, indicates an exceedingly simple way to decide this.

At the said temperature we determine the concentrations of A and B in the solution, which is saturate with respect to the two solid phases A_1 and B_1 (which will be mixed crystals). Thus we find $\frac{X_L}{Y_L}$.

What is particular about this method is this that $\frac{x_L}{y_L}$ does not refer

to an arbitrary solution in which A and B are in internal equilibrium, but very specially to the solution L_0 . We therefore take a part of the saturate solution with some crystals of the two solid phases, and let the internal equilibrium set in at the same temperature, at which one kind of crystals disappears (except at the point of transition). We now determine the concentration of A and B in

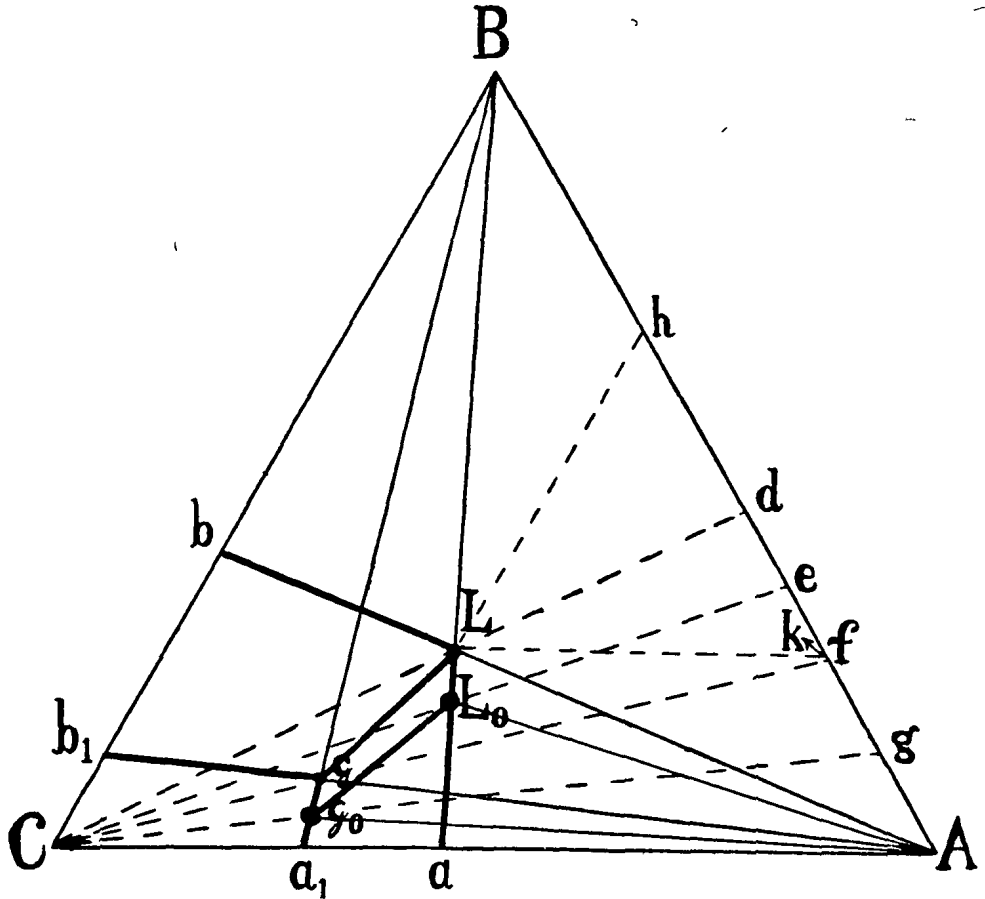


Fig. 2.

this solution, and thus find $\frac{x}{y}$, in which it is perfectly indifferent whether these concentrations are great or small. If we now calculate the quotient:

$$\frac{\frac{x_L}{y_L}}{\frac{X_L}{Y_L}} = f_1$$

we know with perfect certainty that without any exception A will be stable when $f > 1$, and that B will be stable when $f < 1$.

In this method it is quite immaterial whether A and B are isomers or polymers. Whatever molecular weights we may assume for the calculation of the concentration ratios between A and B , whether these are correct or wrong, all this is of no importance whatever, because the factor f_1 is not affected at all by this.

3. DIMROTH'S relation for isomers.

The relation of DIMROTH.

$$\frac{C_A}{C_B} = \frac{L_A}{L_B} \cdot G \quad (1)$$

is not universally valid, and this is already seen by this that here $\frac{L_A}{L_B}$ is written instead of $\frac{X_L}{X_L}$, in which L_A indicates the solubility of A in the pure solvent. $\frac{L_A}{L_B}$ is therefore *not* the ratio of concentration of A and B in the liquid L saturated with respect to A and B in Fig 1, but:

$$L_A = \frac{Ca}{Aa} \quad \text{and} \quad L_B = \frac{Cb}{Bb} .$$

This circumstance is to be explained by this that Dimroth's formula only holds for the ideal case that even to the liquid and the vapour phases saturated with respect to the solid phases the laws for the ideal solutions and gases may be applied, so that also a mutual influencing between A and B is excluded.

Accordingly it need not astonish us that this relation of DIMROTH has a very limited validity, but on the other hand it can also give us further information about these ideal cases.

I shall demonstrate this by the aid of fig. 2, which likewise holds for an ideal ternary system. We see that this fig. differs from fig. 1; first in this that the solubility isotherms, at least for so far as they represent stable states, are straight lines, which join the points a resp. a_1 with the angular point B , and the points b resp. b_1 with the angular point A , which expresses that the substances A and B do not influence each other's solubility. Secondly it is noteworthy that the isotherms for the internal liquid resp. vapour equilibrium are also straight lines, because it is supposed here that A and B are isomers. And in the third place it is assumed that A and B do not form mixed crystals.

For the internal equilibrium in every liquid phase, hence also in L_o , holds:

$$K_{L_0} = \frac{x_L}{y_L} \dots \dots \dots (10)$$

and for that in the coexisting vapour phase G_0

$$K_{G_0} = \frac{x_g}{y_g} \dots \dots \dots (11)$$

If now, as was supposed above, the laws for the ideal solutions and gases may be applied, HENRY's law will also hold both with regard to A and to B for all the coexisting liquid and vapour phases to be considered here, independent whether or no internal equilibrium prevails in these phases

If we now consider that in the application of HENRY's law the concentrations must be indicated per volume unity, we get what follows.

If the liquid possesses x_L gr. mol. A per 1 gr. mol. total, and if this quantity of 1 gr. mol. occupies a volume of v_L ccm., the concentration per liter of solution is $= \frac{1000 x_L}{v_L}$.

If further the concentration of A in the coexisting vapour is x_g gr. mol. per gr. mol. total, and if the volume of this quantity of 1 gr. mol. gas at the considered temperature and the prevailing vapour tension amounts to v_g ccm., the concentration of A in the vapour is per liter of gas mixture $\frac{1000 x_g}{v_g}$.

If we now apply HENRY's law, we may write:

$$\frac{\frac{1000 x_L}{v_L}}{\frac{1000 x_g}{v_g}} = \frac{\frac{1000 X_L}{V_g}}{\frac{1000 X_g}{V_g}} \dots \dots \dots (12)$$

and

$$\frac{\frac{1000 y_L}{v_L}}{\frac{1000 x_g}{v_g}} = \frac{\frac{1000 Y_L}{V_L}}{\frac{1000 X_g}{V_g}} \dots \dots \dots (13)$$

If now the quotients of the first member of equations (12) and (13) hold for the ratio of concentrations of the substances A and B between the coexisting phases L_0 and G_0 , which are in internal equilibrium, and are also saturate with respect to solid A , we see that these quotients are equal to the corresponding ratios in the coexisting phases L and G , which are not in internal equilibrium and are saturate with respect to solid A and solid B .

From equation (12) (13) now follows the relation :

$$\frac{\frac{x_L}{y_L}}{\frac{x_g}{y_g}} = \frac{\frac{X_L}{Y_L}}{\frac{X_g}{Y_g}} \dots \dots \dots (14)$$

from which it appears that in the ideal case the factors f_1 and f_2 of equations (6) and (7) become equal, so that *the relative distance in concentration, as far as A and B are concerned, has the same value for the coexisting liquid and vapour phase L and G in the four phase equilibrium of the pseudo ternary system as the relative distance between the internal equilibria Lo and Go in the binary system.*

Equation (14), therefore, says with reference to fig. 2 that :

$$\frac{\frac{Be}{Ae}}{\frac{Bg}{Ag}} = \frac{\frac{Bd}{Ad}}{\frac{Bf}{Af}} \dots \dots \dots (15)$$

If we now write equation (14) in the form :

$$\frac{x_L}{y_L} = \frac{X_L}{Y_L} \cdot \frac{x_g}{y_g} : \frac{X_g}{Y_g} \dots \dots \dots (16)$$

we may remark that according to DIMROTH's terminology :

$$\frac{\hat{x}_g}{y_g} : \frac{X_g}{Y_g} = G.$$

If we introduce also this substitution, we get :

$$\frac{x_L}{y_L} = \frac{X_L}{Y_L} \cdot G \dots \dots \dots (17)$$

whereas DIMROTH wrote :

$$\frac{C_A}{C_B} = \frac{L_A}{L_B} \cdot G \dots \dots \dots (18)$$

Now X_L and Y_L indicate the concentrations of A and B in the solution L (see fig. 2), which is saturate with respect to A and B , L_A and L_B representing the saturation concentrations of A resp. B in the pure solvent.

As a rule these are of course *not* the same quantities, but when, as in the ideal case, the substances A and B do not influence each other's solubility, this *is* the case, as also appears from fig. 2, for from this follows immediately :

$$L_A = \frac{Ca}{Aa} = \frac{Bd}{Ad} = \frac{X_L}{Y_L} \dots \dots \dots (19)$$

so that DIMROTH's formula is perfectly correct for the ideal case.

We must finally still point out here that in contradistinction with equation (6) the quotient $\frac{x_L}{y_L}$ in equation (17) and $\frac{C_A}{C_B}$ in equation (18) is the ratio of concentration of *A* and *B* in an arbitrary solution, in which *A* and *B* are in internal equilibrium.

4. The relation for the case of polymery.

Up to now we have supposed that *A* and *B* are isomers, but the same considerations are valid for the case of polymery.

Put the case that *B* is a polymer of *A*, and that the internal equilibrium is represented by:



then the just given derivation may be applied also here. We must only bear in mind that to get a relation that is analogous to equation (16) i. e. in which the expression for the equilibrium constant in the liquid- and gasphase occurs, we must apply HENRY'S law to those concentrations of *A* and *B* which occur in the equation for the equilibrium constant. Hence we consider the concentration x^2 of *A*, and y of *B*.

In this way we then get the relation:

$$\frac{x^2_L}{y_L} = \frac{X^2_L}{Y_L} \cdot \frac{x^2_g}{y_g} \cdot \frac{X^2_g}{Y_g} \dots \dots \dots (20)$$

This equation expresses, indeed, the same thing as equation (16), which holds for isomers, but differs from it in shape. Of course this equation, too, can only be applied to the ideal case, and only then, written in the form:

$$\frac{x^2_L}{y_L} = \frac{X^2_L}{Y_L} \cdot h \dots \dots \dots (21)$$

it can be used to examine which modification is the stable one at a certain temperature. This is however, *only possible when we know the size of the different kinds of molecules*. Now the great advantage of equation 6 is evident, as this can be applied, without the size of the molecules of *A* and *B* being known.

In this communication I have tried to treat the problem in the simplest way possible; in the next the relations considered here will be derived by a thermodynamic way, and there the significance of the phenomena known in practice which seem in conflict with this theory, will also be pointed out.

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