

CCCLXVI.—*Melting-point Curves of Optical Isomerides in the Camphor Series.*

By JOHN D. M. ROSS and IAN C. SOMERVILLE.

THE problem as to the existence of racemic compounds, when two optical isomerides are mixed in equal quantities, was not placed on a satisfactory footing until Roozeboom (*Z. physikal. Chem.*, 1899, **28**, 494) studied the question from the point of view of the phase rule. He showed that there were three main types of curve to be expected: (1) the mixed-crystal curve, which would be a continuous curve joining the melting points of the two isomerides and in its simplest form would be a straight line; (2) a curve consisting of two parts giving a minimum of temperature at the point of intersection; and (3) a curve giving two minima (eutectic points) and a maximum point. Group 1 represents the pseudo-racemic mixed crystal, but does not preclude the existence of a racemic compound. Group 2 represents a simple mixture of *d*- and *l*-isomerides, the so-called *d*- and *l*-conglomerate. Group 3 represents the definite formation of a racemic compound.

Whilst the general shape of the melting-point curve of such

isomerides as have been studied has frequently been commented on, an exact mathematical analysis of the curves has not often been attempted. Kremann (*Monatsh.*, 1904, **25**, 1215) has shown how the degree of dissociation of the racemic compound may be calculated, and so a definite statement may be made as to the amount of racemic compound present in the liquid state. The calculations employed are not entirely free from objection, as is pointed out by Kremann himself, but they serve to give a very good indication of the correct result. The method has been applied by Findlay and Hickmans (*J.*, 1907, **91**, 905) to the investigation of the melting-point curve of menthyl mandelate.

Washburn and Read (*Proc. Nat. Acad. Sci.*, 1915, **1**, 191) have suggested a formula which should yield the melting-point curve for so-called "ideal" solutions. As mixtures of optical isomerides fulfil the conditions of such "ideal" solutions more exactly than any other mixtures, it was suggested that the melting-point curves might be investigated from this point of view. A comparison of the results obtained by the Washburn and Read formula, by the van 't Hoff formula, and by the Raoult freezing-point law will be discussed in the course of this investigation. It should also be mentioned that van Laar (*Z. physikal. Chem.*, 1908, **63**, 216; 1908, **64**, 257; 1909, **66**, 197) has worked out a mathematical treatment of the possible curves in great detail, starting from the fundamental relationships given by the thermodynamic potential. From the evidence already accumulated, it seemed unlikely that a definite answer could be given to the question as to whether a racemic compound should exist in the liquid state apart from considerations of the molecular nature of the optical isomerides. If, for example, a molecule of *d*-isomeride shows a tendency to unite with another molecule of *d*-isomeride to give an associated molecule represented by $2d$, then it might be expected that a molecule of *d*-isomeride would unite with one of *l*-isomeride to give a racemic compound analogous to the associated $2d$ molecule. If, on the other hand, the *d*-isomeride shows little tendency to associate with itself, then we might expect that the racemic compound, if formed, would be largely dissociated into its components. To test these conclusions, a number of related substances of various types in the camphor series were investigated, *viz.* :

<i>d</i> - and <i>l</i> -Borneol	Alcohol.
<i>d</i> - and <i>l</i> -Camphor	Ketone.
<i>d</i> - and <i>l</i> -Camphoric acid.....	Acid.
<i>d</i> - and <i>l</i> -Camphoric anhydride	Anhydride.
<i>d</i> - and <i>l</i> -ortho-Methyl hydrogen camphorate	Acid ester.
<i>d</i> - and <i>l</i> -Bornyl hydrogen phthalate	Acid ester.
<i>d</i> - and <i>l</i> -Pinene	Hydrocarbon.
<i>d</i> - and <i>l</i> -Camphene	Hydrocarbon.

If substances are arranged in increasing order of associating power, a sequence is obtained somewhat as follows: Hydrocarbons, anhydrides, ketones, alcohols, acid esters, and acids.

Group 1. The mixed-crystal type of curve is by far the commonest, and in this investigation is given by a hydrocarbon (camphene), a ketone (camphor), an alcohol (borneol), an anhydride, and an acid ester (bornyl hydrogen phthalate). In the case of the acid ester here included, the part conferring optical activity is not in the acidic part of the molecule. The hydrocarbon, anhydride, and ketone which fall into this group show no evidence of association of the pure isomerides and, as the temperatures of melting are all comparatively high, the mixed-crystal type of curve might be expected in place of the curve denoting a simple mixture. With borneol there is evidence of a slight amount of association, and so it might be expected that the racemic compound, if formed, would be largely dissociated. This type of curve is shown by substances which have little or no associating power in the pure isomeride.

Group 2. Pinene and camphene give different types of melting-point curve. The type for pinene is that of the *dl*-conglomerate, a simple mixture of *d*- and *l*-pinene, with no evidence of a racemic compound. The curve for camphene is that of the mixed-crystal type. Both substances, by cryoscopic determinations in benzene, give normal molecular weights. The only striking difference between the two substances is that of the temperatures at which they melt. In general, a rise of temperature favours the formation of mixed crystals, so it is not surprising that, when such similar substances as optical isomerides are being dealt with, the *d*-form should be able to replace the *l*-form without altering the shape of the crystal or its melting point. The fact that so many mixed-crystal types of curves are found for optical isomerides, and that only one, *viz.*, pinene, yields a simple *dl*-conglomerate, points to the conclusion that in many cases where a simple mixture curve might be expected, a mixed-crystal curve is actually obtained.

Group 3. This type exhibits the definite formation of a racemic compound. It includes the two substances which might be expected to give one, since they belong to groups of substances which generally form associated molecules. By calculation, it is shown that the racemic compound formed is only dissociated to a small extent, and so, at the temperature of melting, the racemic compound is present to a large extent in the liquid state. In both cases the theoretical curves agree well with the experimental curves, especially as regards the percentage of eutectic compound, and the discrepancy in the eutectic temperature may be accounted for by considering the heats of dilution and dissociation, which had not

been taken into account in drawing the curve, as no exact values for them could be obtained. The strongly associating substances, then, show distinct evidence of formation of racemic compounds, and furnish curves in group 3; whilst substances of feebly associating power furnish curves in group 1, where the formation of a racemic compound is possible; and substances which show no associating power may be found in group 2, where no racemic compound is possible, or in group 1, where its absence is very probable. Since both associating power and the percentage dissociation of a racemic compound may vary continuously, the one type of curve might be expected to merge into the other. The larger the percentage dissociation of the racemic compound, the more will the type of group 3 approximate to that of group 1. A general review of the position with regard to racemates and pseudo-racemates was given by Landrieu (*Bull. Soc. chim.*, 1922, **31**, 1234). He advanced the view that if the *d*- and *l*-isomerides could form ions, as in the case of acids and salts, they should also tend to form racemic compounds. If, on the other hand, they were non-dissociable, they should form mixed crystals. This conclusion is in agreement with the results of this investigation. Since polar substances are those which give associated compounds, they are also those which give racemic compounds. The fundamental reasons for the formation of racemic compounds are no better understood than those for the formation of associated substances, and it may be that electrical forces are the main factors in both.

EXPERIMENTAL.

Preparation of Optical Isomerides.—Special care was taken to obtain the *d*- and *l*-forms in as pure a state as possible. A Schmidt and Haensch instrument was used in all polarimetric measurements, and all temperatures were corrected for emergent stem, and comparisons made with a standard thermometer.

l-Borneol was obtained from the British Drug Houses, Ltd. After one recrystallisation from light petroleum, it melted at 207° and had $[\alpha]_D^{25} -36.52^\circ$ in toluene ($c = 11.5$). A second sample gave $[\alpha]_D^{25} -36.81^\circ$. This was not sufficiently pure for our purpose, and so a lengthy purification was carried out. The general method is due to Haller (*Compt. rend.*, 1889, **108**, 456). The final product melted at 207.2° and had $[\alpha]_D^{25} -37.50^\circ$ in toluene ($c = 8$). The second sample gave $[\alpha]_D^{25} -37.65^\circ$. This purified substance was used in the determination of the melting-point curves of *d*- and *l*-borneols and also in the preparation of *l*-camphor, *l*-camphoric acid, *l*-camphoric anhydride, and *ortho*-methyl hydrogen *l*-camphorate.

d-Borneol was obtained from the same firm. After one recrystal-

lisation from light petroleum, it melted at 206° and had $[\alpha]_D^{25} + 29.88^{\circ}$ in toluene ($c = 8$). Haller gives $[\alpha]_D + 37.77^{\circ}$. The correct melting point and the appearance of the crystals seemed to indicate a pure product. The low rotation is due to the fact that commercial *d*-borneol consists of mixed crystals of *d*-borneol and *l*-isoborneol. This was pointed out by McKenzie (J., 1907, **91**, 1225), but the circumstance that Lowry (J., 1925, **127**, 614) employs for accurate polarimetric measurements *d*-borneol of low rotation indicates that this fact is not generally known. After treatment with zinc chloride and further purification as in the case of *l*-borneol, the final product melted at 206.5° and had $[\alpha]_D^{16} + 37.1^{\circ}$ in toluene ($c = 8$).

l-Camphor was obtained from *l*-borneol, prepared as above, by oxidising it with concentrated nitric acid (Aschan, *Acta Sci. Fennica*, 1895, **21**, No. 5) and recrystallising the product from benzene. It melted at 177.7° and had $[\alpha]_D^{16} - 43.61^{\circ}$ in absolute alcohol ($c = 16.51$). Beckmann (*Annalen*, 1889, **250**, 253) gives $[\alpha]_D^{16} - 44.22^{\circ}$.

d-Camphor was obtained from the commercial product Camphor Ang. After recrystallisation from alcohol, it melted at 178.6° and had $[\alpha]_D^{16} + 44.20^{\circ}$ in absolute alcohol ($c = 16.51$). Beckmann gives $[\alpha]_D^{16} + 44.22^{\circ}$. This sample was employed in all the experiments without further purification.

l-Camphoric acid was prepared from *l*-borneol by heating it with concentrated nitric acid. After extensive purification, the final product melted at 187.5° and gave $[\alpha]_D^{16} - 48.12^{\circ}$ in absolute alcohol ($c = 8.24$).

d-Camphoric acid was obtained from the British Drug Houses, Ltd. After one recrystallisation from aqueous alcohol, it melted at $177-178^{\circ}$ and gave $[\alpha]_D^{16} + 47.15^{\circ}$ in absolute alcohol ($c = 8.24$). After purification, it had m. p. 187.6° and $[\alpha]_D^{17} + 47.6^{\circ}$. From camphoric anhydride, a *d*-acid was obtained of m. p. 188.2° and $[\alpha]_D^{17} + 47.75^{\circ}$.

ortho-Methyl hydrogen *l*-camphorate was prepared (a) by acting on *l*-camphoric anhydride with sodium methoxide (Walker, J., 1892, **61**, 1088), (b) by passing dry hydrogen chloride into a solution of *l*-camphoric acid in methyl alcohol. The oil thus obtained crystallised after some months and thereafter crystallisation could be easily induced by "seeding." After several recrystallisations from light petroleum, the ester melted at 73.5° and gave $[\alpha]_D^{16} - 52.95^{\circ}$ in absolute alcohol ($c = 10$) (1 g. required 12.40 c.c. of 0.0371*N*-baryta. Calc.: 12.58 c.c.).

ortho-Methyl hydrogen *d*-camphorate was prepared similarly. It had m. p. 76° and $[\alpha]_D^{16} + 51.95^{\circ}$ in absolute alcohol ($c = 10$). Haller (*Compt. rend.*, 1892, **114**, 1516) gives m. p. $75-76^{\circ}$ and $[\alpha]_D + 51.52^{\circ}$. Titration with baryta showed that the oil and the

crystals had the same composition, and coincided with the theoretical value.

The *l*- and *d*-forms of bornyl hydrogen phthalate were prepared in the course of purification of *l*- and *d*-borneols, and were utilised after one recrystallisation from their respective solvents, benzene and glacial acetic acid.

Pinene gives an optical rotation which seems to depend on its source. It was purified by repeated distillation in steam (a little carbonate being added to the pinene before starting), followed by drying and careful fractionation. The sample of *l*-pinene used was obtained from the British Drug Houses, Ltd.; it had $[\alpha]_D - 35.23^\circ$ and *d* 0.8682. After purification, the main fraction boiled at 160° , had $[\alpha]_D - 37.58^\circ$ and *d* 0.8674, and melted sharply at -63° . *d*-Pinene was obtained from Kahlbaum: $[\alpha]_D + 45.38^\circ$, *d* 0.8665. After purification, the main portion had b. p. 156° , $[\alpha]_D + 46.80^\circ$, and *d* 0.8590, and melted sharply at -64° .

l-Camphene was obtained from purified *l*-pinene by converting it into pinene hydrochloride and heating this with potassium phenoxide. After fractionation, pure *l*-camphene was obtained, b. p. 160.5° , m. p. 44° , $[\alpha]_D^{25} - 77.15^\circ$ in absolute alcohol ($c = 10$).

d-Camphene was prepared from purified *d*-pinene in a similar way. It had b. p. 160° , m. p. 46° , and $[\alpha]_D^{25} + 72.8^\circ$ in absolute alcohol ($c = 11.7$).

As in the case of the pinenes, the rotation seems to depend on the source of the material.

Determination of Curves.

Temperatures were determined by means of thermo-couples, since they allowed of equally accurate determinations over the whole of the range (-125° to $+230^\circ$) and required the use of only small quantities of material. The two wires of the thermo-couple (copper-constantan) were sealed through two side-tubes attached to a wider tube ($\frac{1}{2}$ in. diam.), on one end of which a bulb had been blown, and were arranged so that the junction occupied the foot of the bulb. A glass stopper was ground into the other end of the wider tube, so that the determinations could be carried out without loss, some of the substances having a high vapour pressure. In dealing with substances which were volatile at their melting point, stirring was accomplished by an electro-magnetic arrangement (type *a*), and in other cases a glass rod was used as stirrer and worked by hand (type *b*). A sensitive mirror galvanometer was employed, giving an accuracy of 1×10^{-5} volt. The relationship between the *E.M.F.* of the thermo-couple and the difference of temperature between the two junctions is not linear, but for small ranges of temperature the

error in regarding it as such is negligible. In general, therefore, for each curve two substances were chosen which melted at steady temperatures, one at each end of the range, and their melting points were found with each thermo-couple and with an accurate thermometer. The following table gives details of the various experiments.

Substances.	Substances used for calibration.	Table and fig.	Remarks.
<i>d</i> - and <i>l</i> -Borneol.	Borneol (m. p. 206.5°). Camphor (m. p. 178.6°).	I, 1.	Setting point. Each mixture weighed out separately.
<i>d</i> - and <i>l</i> -Camphor.	Same as above.	II, 1.	Same as above.
<i>d</i> -Borneol and <i>d</i> -camphor.	" "	III, 2.	Curve already determined by Vanstone (J., 1909, 95, 597) with impure <i>d</i> -borneol.
<i>d</i> - and <i>l</i> -Camphoric acid.	" "	IV, 3.	Melting point. The melted acid readily decomposed.
<i>d</i> - and <i>r</i> -Camphoric acid.	" "	V, 4.	Melting point. The <i>r</i> -acid was prepared by recrystallising equal quantities of the <i>d</i> - and <i>l</i> -acids from aqueous alcohol.
<i>d</i> - and <i>l</i> -Camphoric anhydride.	Camphoric acid (m. p. 223.8°). Borneol (m. p. 206.5°).	VI, 1.	Setting point. No decomposition of melted anhydride.
<i>d</i> - and <i>l</i> -ortho-Methyl hydrogen camphorate.	<i>m</i> -Dinitrobenzene (m. p. 90.5°). Diphenyl (m. p. 68.7°).	VII, 5.	Melting point. Substance tended to form an oil. Successive quantities of one isomeride added to the mixture in the tube.
<i>d</i> - and <i>r</i> -ortho-Methyl hydrogen camphorate.	Same as above.	VIII, 4.	Same as above.
<i>d</i> - and <i>l</i> -Bornyl hydrogen phthalate.	Bornyl hydrogen phthalate (m. p. 161.4°). Camphor (m. p. 178.6°).	IX, 1.	Melting point. The melted substance decomposed readily.
<i>d</i> - and <i>l</i> -Pinene.	Diethylaniline (m. p. -38.1°). Chloroform (m. p. -63.3°). Toluene (m. p. -94.5°). Ethyl alcohol (m. p. -114.2°).	X, 6.	Melting point.
<i>d</i> - and <i>l</i> -Camphene.	Urethane (m. p. 47.8°). Salol (m. p. 41.6°).	XI, 1.	Setting point. No decomposition of melted substance.

Stirrers of type *a* were used in all cases except Nos. VII, VIII, and X, in which type *b* was used.

A glycerol bath was used in all cases except Nos. VII, X, and XI, in which water, liquid air, and water, respectively, were used.

TABLE I.		TABLE II.		TABLE III.		TABLE IV.	
% <i>d</i> -Borneol.	S. p.*	% <i>d</i> -Camphor.	S. p.	% <i>d</i> -Borneol.	S. p.	% <i>d</i> -Acid.	M. p.
100.0	206.5°	100.0	178.6°	100.0	206.5°	100.0	187.6°
81.3	206.4	86.2	178.8	90.4	201.7	95.4	185.9
72.0	206.6	81.0	178.6	75.7	198.5	93.5	185.4
49.5	206.4	70.8	179.1	57.3	196.2	92.7	185.9
40.8	206.0	57.9	178.7	49.0	192.7	92.1	185.0
35.4	206.2	48.7	178.6	37.8	188.9	87.3	186.5
24.1	206.2	30.1	178.3	21.3	185.3	74.4	191.3
12.4	206.1	19.1	177.8	8.4	181.4	56.9	197.2
10.5	206.8	11.3	178.5	0.0	178.6	49.8	199.5
0.0	207.2	0.0	177.7			47.9	199.6
						40.7	196.9
						34.4	193.4
						28.1	193.3
						13.4	187.3
						8.9	186.7
						5.5	186.8
						0.0	187.5
TABLE V.		TABLE VI.		TABLE VII.		TABLE VIII.	
% <i>d</i> -Acid.	M. p.	% <i>d</i> -Anhydride.	S. p.	% <i>d</i> -Ester.	M. p.	% <i>d</i> -Ester.	M. p.
100.0	188.2°	100.0	223.8°	100.0	74.3°	100.0	74.4°
93.5	187.3	88.8	223.5	95.6	70.8	90.3	70.5
85.4	186.4	71.6	222.8	89.7	66.5	85.1	68.7
81.7	187.2	50.2	222.9	88.0	65.9	73.1	65.6
69.4	189.3	41.4	222.2	87.4	66.2	60.2	67.6
49.2	193.1	25.0	221.6	82.2	66.9	41.3	74.8
36.4	197.1	22.1	221.9	69.5	70.3	26.0	82.2
23.6	198.1	9.4	221.7	53.9	83.6	9.9	85.5
16.0	200.5	0.0	222.9	49.9	84.6	0.0	85.9
0.0	202.6			45.7	83.4		
				38.4	79.1		
				30.7	70.4		
				25.8	66.5		
				17.0	65.0		
				13.4	64.7		
				12.0	64.6		
				9.4	65.0		
				4.8	67.1		
				0.0	73.5		
TABLE IX.		TABLE X.		TABLE XI.			
% <i>d</i> -Phthalate.	M. p.	% <i>d</i> -Pinene.	M. p.	% <i>d</i> -Camphene.	S. p.		
100.0	161.4°	100.0	— 64.1°	100.0	46.5°		
91.6	160.8	84.5	— 72.5	77.2	46.0		
78.9	160.5	75.8	— 77.7	60.6	45.4		
60.0	160.9	63.6	— 98.1	52.9	45.0		
49.7	161.1	56.6	— 113.8	48.0	44.8		
48.1	162.5	54.0	— 115.1	41.6	44.6		
38.6	162.5	50.7	— 120.2	29.8	44.2		
27.0	162.1	48.5	— 115.4	20.7	43.9		
9.7	161.7	42.3	— 109.5	0.0	43.7		
5.3	162.3	28.9	— 79.6				
0.0	162.8	20.1	— 76.7				
		16.9	— 72.2				
		9.4	— 68.0				
		0.0	— 63.1				

* S. p. indicates setting point.

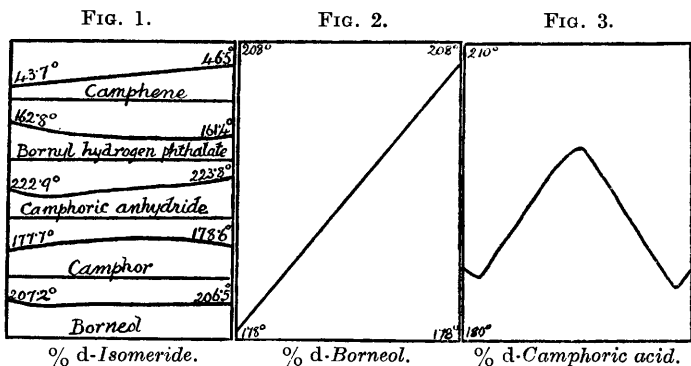
Analysis of Experimental Curves.

The curves obtained fall into the three classes described by Roozeboom (p. 2770).

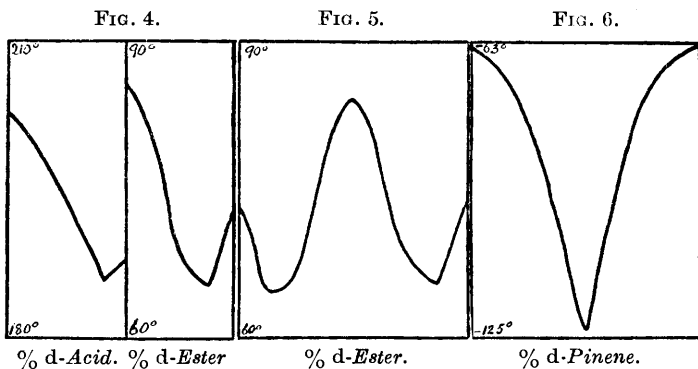
In class (1) are most of the substances investigated, *viz.*, borneol, camphor, camphoric anhydride, bornyl hydrogen phthalate, and camphene. In class (2) is the curve for *d*- and *l*-pinene, and it is

the only curve of this kind that has yet been obtained for two optical isomerides. In class (3) are camphoric acid and *ortho*-methyl hydrogen camphorate.

The curves of class (1) do not lend themselves to exact mathematical examination. The equation which they follow has been worked out by van Laar (*Z. physikal. Chem.*, 1908, **64**, 289) and is,

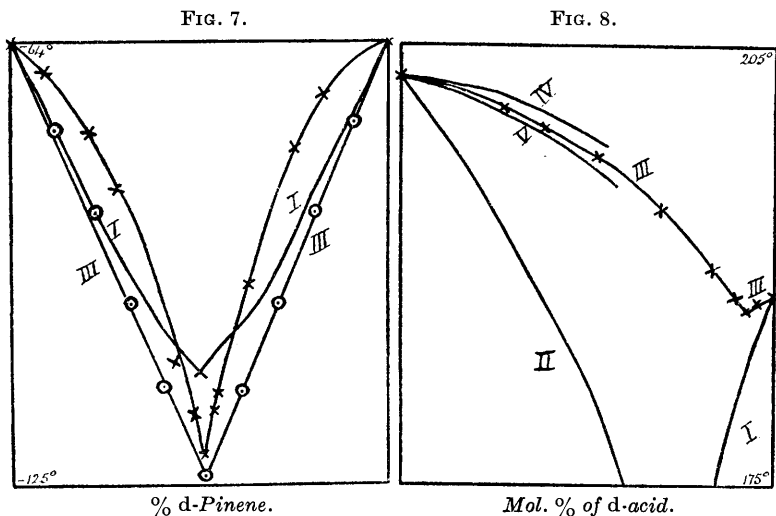


of course, of the simple form $T = T_0 = \text{constant}$, *i.e.*, the curve should be a straight line joining the melting points of the pure *d*- and *l*-isomerides, and should be at right angles to the temperature axis. All the curves found have this general form. Since the *d*- and *l*-isomerides may form mixed crystals with each other, and the



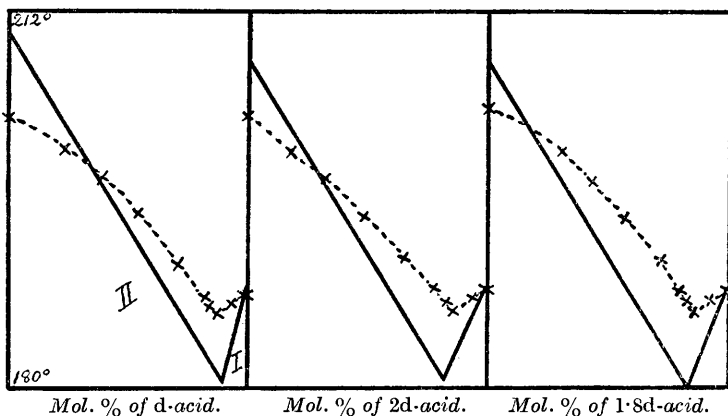
racemate, if formed, may also give mixed crystals with the *d*- and *l*-isomerides, it is evident that this type of melting-point curve does not give a definite answer to the question as to whether a racemic compound is formed or not. Tammann has investigated this question (*Z. physikal. Chem.*, 1914, **87**, 357) and, by calculating the value of the quotient of the latent heat and the absolute tem-

perature of melting, *i.e.*, l_a/T_{0a} for the pure isomerides, and for their 50% mixture, he obtains evidence as to whether he is dealing with a racemate or a pseudo-racemate. The assumption on which



this is based is that the pure *d*- and *l*-isomerides consist of simple molecules. The same criterion, which Tammann takes as evidence of the formation of a racemate, may be applied to the pure *d*- or

FIG. 9.



l-isomerides to determine whether or not they are associated. In the case of the pure isomerides, the formula becomes Trouton's rule, as modified by Walden to apply to melting points. It is evident,

then, that if the *d*-isomeride is associated to the same extent with itself as it is with the *l*-isomeride in the racemic compound, the same value of the ratio l/T should be obtained for the pure

FIG. 10.

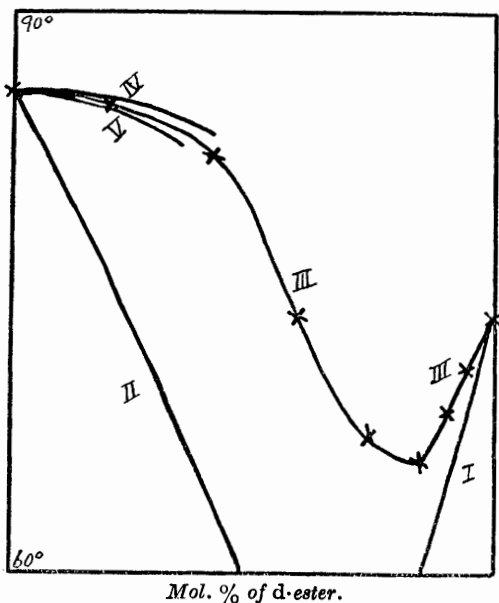
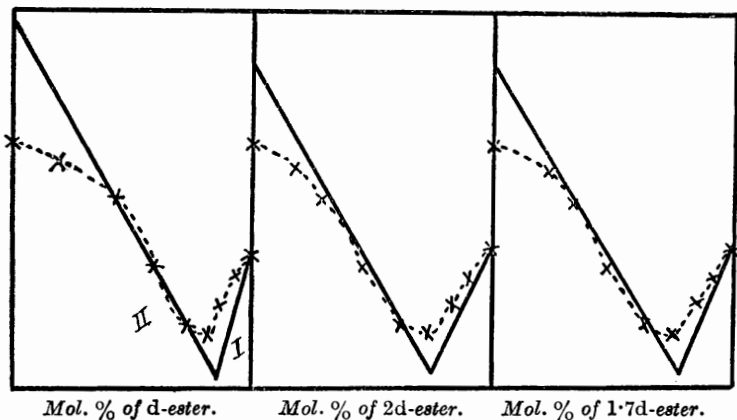


FIG. 11.



d-isomeride and for the 50% mixture with the *l*-isomeride. This is the criterion which Tamman uses to establish the absence of a racemic compound.

Before the mathematical analysis of the curves of types (2) and (3) is discussed, the equations which apply to substances at their melting points may be considered generally. The ordinary law for the lowering of the melting point of a pure substance A by the addition of another pure substance B may be written as

$$dT/dx_a = RT^2/L_a \dots \dots \dots (1)$$

where T is the melting point on the absolute scale, R the gas constant, L_a the latent heat of the substance A per g.-mol., and x_a the molar fraction of the substance A.

Washburn and Read (*loc. cit.*) suggest that for the exact analysis of the melting-point curves of the two substances A and B we should use, instead of the formula of van 't Hoff, the expressions

$$dT/dx_a = RT^2/L_a x_a \text{ and } dT/dx_b = RT^2/L_b x_b \dots \dots (2)$$

On integrating equation (1) we get

$$x_b = 1 - x_a = (1/T - 1/T_{0a})L_a/R$$

and from equation (2) we get

$$\log_e x_a = (1/T_{0a} - 1/T)L_a/R.$$

These two equations are the same for small values of x_b .

The values for the latent heats of the substances used were calculated from the values of the molecular depression, k . If $K = 100k$, and M is the molecular weight of the substance, Raoult's freezing-point law gives the third equation

$$dT/dx_a = K/M \dots \dots \dots (3)$$

d- and l-Pinenes.—The values of the melting points were calculated according to the equations (1), (2), and (3). The curves are shown in Fig. 7: curve I is calculated from equation (1); curve III from equation (3); circles \odot represent equation (2); and the experimental points are indicated by crosses. All the curves intersect at the 50% mixture, but the value for the eutectic temperature is slightly lower than the experimental value in the case of the straight-line curve. The value given by the van 't Hoff equation is considerably higher than the experimental value. There is no doubt that in the case of *d-* and *l-*pinenes we are dealing with a simple mixture of two substances, and the curve approximates closely to that given by an "ideal" solution. The value of K was found by determination of the molecular depression to be 16500.

d- and r-Camphoric Acids.—In this case the curves have to be considered in two sections: (1) *d*-acid in presence of *r*-acid, and (2) *l*-acid in presence of *r*-acid. For the *d*-acid, $K = 17500$ and $L = 4835$; and for the *r*-acid, $K = 13000$ and $L = 13840$. The curves corresponding to equation (1) are shown in Fig. 8, I and II.

In the same figure the experimental values are indicated by crosses. It is evident that the course of the curve calculated from equation (1) does not follow the experimental curve.

The shape of the curve near the melting point of the *r*-acid indicates the degree to which the acid is dissociated into its components. Kremann (*loc. cit.*) has shown how the shape of the curve may be found, if definite percentages of dissociation of the compound are assumed (compare Findlay and Hickmans, *loc. cit.*). On the assumption of 10% and 15% dissociation the following values for the melting points corresponding to different fractions of *d*-acid added were obtained.

<i>x</i>	0.0	0.2	0.4
<i>t</i> for 10%	202.6°	201.0°	198.3°
<i>t</i> for 15%	202.6	201.9	199.7

The curves IV and V were drawn in Fig. 8 corresponding to 15% and 10% dissociation, respectively; and the experimental curve was found to lie between them. The degree of dissociation of the *r*-acid being assumed to be 12%, its calculated melting point would be 209.6° if there were no dissociation. Taking this value for the melting point of the pure *r*-acid, we have drawn the straight line with $dT/dx = 32.5$, and that with $dT/dx = 87.5$ for the *d*-acid (Fig. 9, curves I and II). These two straight lines give the percentage of the eutectic mixture fairly accurately, but not the eutectic temperature. The curves were again drawn on the assumption that we were dealing with *r*-acid and 2*d*-acid. The melting point of the pure racemic acid would now be 206.5° if we assume it to be dissociated into 2*d*- and 2*l*-acids to the extent of 12% (Fig. 9). Thirdly, the curve was drawn on the assumption that the *d*-acid was associated to the same extent as it is associated with the *l*-acid in the racemic compound, so that the average size of the *d*-molecule is 1.8*d*. The melting point of the pure racemic acid would be 206.8° if we assume it to be dissociated into 1.8*d*- and 1.8*l*-acids to the extent of 12%. The curves are shown in Fig. 9.

All three curves give the eutectic percentage about equally well, but not the eutectic temperature accurately. It is obvious that no assumption with regard to the molecular complexity of the *d*- and *l*-acid will give two straight lines intersecting both at the eutectic temperature and at the eutectic percentage. The reason for this may be that in calculating the gradient we have taken into account only the latent heat of fusion, and not the possible heat of dilution of *d*- and *r*-acid, or the heat of dissociation of those acids. Van Laar has worked out a formula for α , the degree of dissociation of a compound, in terms of known values. Kremann found that the values given by this formula were about twice as large as those

given by the graphical method. Calculating α for racemic acid, we get

$$\alpha = \frac{RT^2}{L} \cdot \frac{x^2(1+x)}{4(T_0 - T)} = \frac{K}{M} \cdot \frac{x^2(1+x)}{4(T_0 - T)} = \frac{13000}{400} \cdot \frac{0.04 \times 1.2}{4 \times 1.2} = 0.32.$$

The value for the degree of dissociation given by this formula is nearly 2.5 times as great as that given by the graphical method. This value would, of course, be reduced if we took into account the possible heat of dilution and the heat of dissociation. Evidence for the molecular complexity of camphoric acid is somewhat difficult to obtain, since it is not sufficiently soluble for a molecular weight determination to be made in benzene. In alcohol the molecular weight is rather less than normal, but that is not a surprising result, since alcohol generally gives low results even with associated substances. The general behaviour of organic acids would show that as a class they are associated.

d- and r-Methyl Hydrogen Camphorates.—The curves obtained for the esters may be considered in the same way as those for the acids. For the *d*-ester, $K = 23000$ and $L = 2234$, whilst for the *r*-ester, $K = 18800$ and $L = 5838$. The curves corresponding to equation (1) are shown in Fig. 10, I and II, and experimental values are indicated by crosses. Again the curve drawn according to equation (1) does not follow the experimental curve.

By a similar calculation to that employed in the case of camphoric acid, we can draw curves for the various percentages of dissociation of the *r*-compound. Assuming 20% and 15% dissociation, the following values of the melting points corresponding to different fractions of *d*-ester added were obtained.

x	0.0	0.2	0.4
t for 15%	85.9°	84.9°	82.0°
t for 20%	85.9	85.4	83.4

The curves IV and V were drawn in Fig. 10 corresponding to 20% and 15% dissociation, respectively, and the experimental curve was found to lie between them. The degree of dissociation of the *r*-ester was taken as 18%. Taking $dT/dX = 43.9$ for the *r*-ester, and $dT/dx = 107.5$ for the *d*-ester, the curves in Fig. 11 were drawn as in the case of the acid. In the case of the ester the curves for 2*d*- and 1.7*d*-ester give very good agreement for the eutectic percentage, and the eutectic temperature is not so much below the experimental value as in the case of the acid. It is probable, therefore, that the heat of dilution and the heat of dissociation are not so large as in the case of the acid. Calculating α , the degree of dissociation of the *r*-ester, in terms of van Laar's formula we get

$$\alpha = \frac{18800}{428} \times \frac{0.04 \times 1.2}{4 \times 0.75} = 0.70.$$

This is nearly 3.5 times as great as the value given by the graphical method. An ebullioscopic determination in benzene gave M , 325; there is thus a considerable amount of association. The values of the melting points of the ester mixtures are more trustworthy than those found for the acid, because there was no sign of decomposition in the case of the melted ester. The only difficulty was that the ester tended to remain as an oil for a long time so that calorimetric determinations of the heat data were not obtainable.

The authors wish to thank Professor Sir James Walker for his suggestions and advice and for the interest which he has taken in the progress of this research. They also acknowledge their indebtedness to the Carnegie Trust for the grant of a Teaching Fellowship to one of them (J. D. M. R.), and to the Department of Scientific and Industrial Research for a grant to the other (I. C. S.).

UNIVERSITY OF EDINBURGH.

[Received, July 16th, 1926.]
