CXLVIII.—*The Existence of Liquid Racemates.*

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MUCH discussion has centred for many years upon the existence of racemates, as true chemical compounds, in the liquid state and in solution, although the completeness of the dissociation in the gaseous state is well attested by vapour-density determinations. All such work as the present must be undertaken with inactive substances which are known to be true racemates in the solid state, and moreover, it must be known whether the liquid racemates investigated are approaching or receding from their transition points at the temperatures of investigation. It has been shown by Adriani, from freezing-point curves (*Z. physikal. Chem.*, 1900, **33**, 467), and by Findlay and Campbell, from solubility curves (J., 1928, 1770), that solid methyl tartrate is a stable racemate at room temperature, and that its transition point is approached by lowering the temperature. It has also been shown by Findlay and Campbell (*loc. cit.*) that to bring the transition point of a tartaric ester up to the neighbourhood of room temperature it is necessary to introduce some acid group, such as acetyl, propionyl, or benzoyl, in place of the hydroxyl groups. It is therefore probable *a priori* that the liquid esters of racemic acid would be stable racemates, but this does not, of course, preclude the possibility of complete dissociation into the *d*- and *l*-forms on fusion, as is suggested by some authors in the case of other series.

The view, often stated in text-books, that fusion or dissolution of a true racemate is immediately followed by complete dissociation is by no means generally held; indeed, it is obvious on theoretical grounds that the left-hand side of the equilibrium $r \rightleftharpoons d + l$ must be represented by a certain concentration, however small. The statement that in solution the concentration of racemate is negligible rests chiefly upon cryoscopic measurements, but the evidence is not unexceptionable and there are discrepancies. There is one experiment by Byk (*Z. physikal. Chem.*, 1904, **49**, 682; 1908, **61**, 67) which points to the undoubted existence of at least a trace of racemic acid in aqueous solution, and this experiment has been repeated and confirmed by the author.

The state of affairs in a pure liquid racemate is different: there is no medium to exert a dissociating action. It is said that an examination of the physical constants of corresponding active and racemic compounds does not show any marked difference, but this view is not justified, for the results of all investigators do show a difference, although often only very slight.

It is significant that all investigators hitherto have deliberately avoided the use of liquids which were known to be associated. Judging by the experimental data contained in this paper, however, it would seem that in avoiding the associated liquids, they missed the most fruitful field of investigation, for it is just in those cases where the active forms are associated that a most interesting state of affairs exists. Contrary to expectation, the racemic forms are usually less, not more, associated than the active forms. The effect of raising the temperature will be to increase the dissociation of both forms, and hence it would be expected that the physical properties of the two forms should approach one another with rising temperature: this has been found to be the case. Since, however, the rate of increase of dissociation may not be the same in both cases, it may occasionally happen that the order of the properties may alter, owing to a lag in the dissociation of one form : one such case has been observed.

The literature shows the very conflicting nature of the evidence and of opinions. One fact emerges, however, *viz.*, that the differences in the physical constants are only slight and might be, as is claimed by some, negligible, were it not for the case of ethyl tartrate, investigated by Thole, where the difference between the viscosities of the active and of the racemic form exceeds the experimental error. For the present investigation a series of associated esters of tartaric acid was chosen, *viz.*, ethyl, *n*-propyl, *iso*propyl, *n*-butyl, *iso*butyl, and amyl tartrates and racemates; ethyl diacetyltartrate and methyl dipropionyltartrate were also investigated.

EXPERIMENTAL.

1. *Preparation of the Esters.*—All the active esters, but few of the racemates, had been previously prepared. For the preparation of the latter, the following method was finally adopted. The racemic acid [$(C_4H_6O_6)_2,2H_2O$] (1 mol.) was dehydrated by 6 hours' heating at 110°, finely powdered, and weighed, and the requisite alcohol (4 mols.) was added. The mixture was heated on the water-bath, and saturated with dry hydrogen chloride. (Only by partly esterifying the racemic acid can a large fraction be made to dissolve.) The product was cooled in ice, again saturated, kept over-night, and then distilled under reduced pressure up to 150°. The residue was returned to the esterification flask, and the whole process repeated. Water, alcohol, and hydrogen chloride were removed as before, and the ester was distilled at its appropriate boiling point. The new racemates thus prepared are : n-*Propyl racemate*, m. p. 25° (Found : C, 52·2; H, 7·9. $C_{10}H_{18}O_6$ requires C, 51·5; H, 7·7%); iso*propyl racemate*, m. p. 34° (Found : C, 52·5; H, 7·85%); n-*butyl racemate*, b. p. 185°/12 mm., 320°/765 mm. (Found : C, 55·7; H, 8·65. $C_{12}H_{22}O_6$ requires C, 55·0; H, 8·4%); iso*butyl racemate*, m. p. 58° (Found : C, 55·6; H, 8·5%).

The initial materials in all these preparations were British Drug Houses A.R. racemic acid and A.R. alcohols, with the exception of amyl alcohol, which, being a commercial mixture, gave rise to esters of corresponding isomerides.

2. *Melting Points.*—Although ethyl, *n*-butyl, and amyl racemates were cooled in a freezing mixture to − 16°, and vigorously scratched with glass rods, they could not be induced to crystallise. In the case of *n*-butyl racemate, this is consistent with its physical constants, which indicate that it is very highly dissociated even at room temperature (see below). Thus the eutectic corresponding to the racemate will be far below the freezing point of the active form.

In several cases, notably those of *n*- and *iso*-propyl tartrates, the active ester is liquid at room temperature, whereas the racemic ester is solid. It was thought, in view of this fact and of the high viscosity, that possibly the active esters were merely supercooled liquids. Accordingly, *n*- and *iso*-propyl and amyl tartrates were also cooled to − 16°. Both the propyl tartrates became very viscous but did not solidify. The amyl tartrate crystallised only partly, doubtless owing to its heterogeneous composition (see p. 1113). Table I gives the melting points, when known, of the active and the inactive esters. The reference (C) denotes that the value is due to the present author.

TABLE I.

Tartrate.	Dextro.	Racemate.	Reference.
Ethyl	17°	Liquid	Franchimont; see Beilstein, Vol. III, p. 513, 1921 edtn.
n-Propyl	Liquid	25° (C)	
*iso*Propyl	Liquid	34 (C)	
n-Butyl	22—22·5	Liquid	Freundler, *Ann. Chim.*, 1894, **3**, 447.
*iso*Butyl	68 (P) 70 (C)	58 (C)	Pictet, *Ber.*, 1881, **14**, 2790.
Amyl	Liquid	Liquid	
Methyl dipropionyl-	27·5	34·2	Freundler, *Bull. Soc. chim.*, 1894, **11**, 310.
Ethyl diacetyl-	67—68	50·5	McCrae and Patterson, J., 1900, **77**, 1098; Perkin, J., 1887, **51**, 368.

Where the melting point of the inactive form is higher than that of the active, there can be no doubt that the inactive form is, in the solid state, a true racemate. It does not seem reasonable to suppose that, where the racemate has a melting point very much higher than that of the active form, its melting is immediately attended by complete dissociation, but for a more exact knowledge of this it is necessary to investigate fully the form of the freezing-point curve.

3. *Boiling Points.*—The boiling points under reduced pressure and under atmospheric pressure, determined in the usual way, are given in Table II. A short-range Anschütz thermometer was used to minimise the error due to the exposed stem. It is seen that, although in some cases the boiling point of the racemate is lower than that of the active form, it is rarely higher.

4. *Densities and Coefficients of Expansion.*—The densities of all the inactive esters were determined at a number of temperatures. A Sprengel pyknometer holding about 5 c.c. was used in an electrically controlled thermostat, the temperature of which did not vary by more than ± 0·05°. For temperatures of 100° and over, a sulphuric acid bath was used, and here the temperature control was not so good. The coefficients of cubical expansion, α, were also

TABLE II.

Tartrate.			
Ethyl	*d*	157°/11 mm. (A)	280°/760 mm. (A)
	r	157°/11·5 mm. (A)	281°/765 mm. (C)
n-Propyl	*d*	171—172°/17 mm. (P)	303°/760 mm. (A)
	d	174°/12 mm. (C)	297°/765 mm. (C)
	r	167°/11 mm. (C)	286°/765 mm. (C)
*iso*Propyl	*d*	154°/13 mm. (C)	275°/760 mm. (Pi)
	d		275°/765 mm. (C)
	r	154°/12 mm. (C)	275°/765 mm. (C)
n-Butyl	*d*	200—203°/18 mm. (F)	320°/765 mm. (C)
	d	186°/14 mm. (C)	
	r	185°/12 mm. (C)	320°/765 mm. (C)
*iso*Butyl	*d*	197°/23 mm. (Pi)	323—325°/760 mm. (Pi)
	d	195°/13 mm. (C)	311°/768·5 mm. (C)
	r	195°/13 mm. (C)	311°/768·5 mm. (C)
Ethyl diacetyl-	*d*	193°/30 mm. (C)	291—292°/760 mm. (Pi)
	d		296°/764 mm. (C)
	r	180°/22 mm. (C)	297°/764 mm. (C)

(A) Anschütz, *Ber.*, 1885, **18**, 1399.
(C) Present author.
(Pi) Pictet, *Jahresber.*, 1882, 856.
(F) Freundler, *Ann. Chim.*, 1894, **3**, 447.
(P) Patterson, J., 1904, **85**, 767.

calculated, as it was thought that these might be less affected by an erroneous determination. The results are in Table III—the figures for the active forms are mostly those of other workers.

An examination of the figures on p. 1116 confirms the statement of Ranken and Taylor (*Proc. Roy. Soc. Edin.*, 1907, **27**, 172) that the racemic form is on the average less dense than the active form : the difference is slight, but persistent. The coefficients of cubical expansion of the active form are almost always higher than those of the racemic form, the mean values of $\alpha \times 10^5$ being :

Ester.	Dextro.	Rac.	Ester.	Dextro.	Rac.
Ethyl	87·5	75	*n*-Butyl	63·5	67
n-Propyl	86	68	*iso*Butyl	17	18
*iso*Propyl	88	79·5	Ethyl diacetyl- ...	128	177

The greater densities and coefficients of expansion in the case of active ethyl, *n*-propyl, and *iso*propyl tartrates point to a greater association of the active forms. In all cases the coefficient of expansion of the active form increases with rise of temperature, indicating progressive dissociation of the associated molecules.

5. *Viscosities.*—The viscosities of both active and racemic forms were determined at 18°, 40°, and 80°. An ordinary Ostwald viscometer, standardised with water, was used in an electrically controlled thermostat. No special precautions were taken to ensure accuracy in the stop-watch used, beyond comparing it with another in the department; although a slight error might thus affect the absolute value of all these measurements, the relative values for active and

TABLE III.

	Density.				$a \times 10^5$.		
Ester.		Dextro.		Racemate.	Range.	Dext.	Rac.
Ethyl tartrate	d^{14°	1·2097 (A & Pi)					
	$d^{15^\circ}_{15^\circ}$	1·2097 (P)	$d^{15^\circ}_{15^\circ}$	1·2059 (C)			
	$d^{18^\circ}_{4^\circ}$	1·2112 (C)	$d^{18^\circ}_{4^\circ}$	1·2058 (C)			
	$d^{20^\circ}_{4^\circ}$	1·2036 (W)	$d^{20^\circ}_{4^\circ}$	1·2036 (C)			
	$d^{25^\circ}_{25^\circ}$	1·2019 (P)	$d^{25^\circ}_{25^\circ}$	1·2071 (C)			
	$d^{25^\circ}_{25^\circ}$	1·2151 (C)					
	$d^{40^\circ}_{4^\circ}$	1·1840 (W)	$d^{40^\circ}_{4^\circ}$	1·1876 1·1873 } (C)	20— 40°	83	67·5
	$d^{40^\circ}_{4^\circ}$	1·19135 (C)					
	$d^{60^\circ}_{4^\circ}$	1·1642 (W)	$d^{60^\circ}_{4^\circ}$	1·1737 (C)	20— 60	84	64
	$d^{60^\circ}_{4^\circ}$	1·1729 (C)					
	$d^{80^\circ}_{4^\circ}$	1·1445 (W)	$d^{80^\circ}_{4^\circ}$	1·1585 (C)	20— 80	86·5	65
	$d^{80^\circ}_{4^\circ}$	1·1569 (C)					
	d^{100°	1·1279 (Pi)	$d^{100^\circ}_{0^\circ}$	1·1369 (C)	20—100	84	72·5
	$d^{100^\circ}_{0^\circ}$	1·1274 (C)					
	$d^{131\cdot2^\circ}$	1·0919 (Pa)					
	$d^{131\cdot2^\circ}$	1·0919 (Pa)	$d^{131\cdot2^\circ}$	1·1040	20—131·2	92	90
	$d^{131\cdot2^\circ}_{0^\circ}$	1·0991 (C)					
	$d^{173\cdot8^\circ}_{0^\circ}$	1·0507 (Pa)	$d^{173\cdot8^\circ}_{0^\circ}$	1·0553	20—173·8	95·5	92
	$d^{173\cdot8^\circ}_{0^\circ}$	1·0553 (C)					
n-Propyl tartrate	d^{17°	1·1392 (A & Pi)					
	$d^{18^\circ}_{4^\circ}$	1·1361 (C)	$d^{18^\circ}_{4^\circ}$	1·1360 (C)			
	$d^{20^\circ}_{4^\circ}$	1·1390 (W)	$d^{20^\circ}_{4^\circ}$	1·1256 (C)			
	$d^{40^\circ}_{4^\circ}$	1·1204 (W)	$d^{40^\circ}_{4^\circ}$	1·1159 (C)	20— 40	74	41·5
	$d^{40^\circ}_{4^\circ}$	1·1207 (C)					
	$d^{60^\circ}_{4^\circ}$	1·1013 (W)	$d^{60^\circ}_{4^\circ}$	1·0904 (C)	20— 60	86	80
	$d^{77\cdot96^\circ}$	1·0819 (Pa)					
	$d^{80^\circ}_{4^\circ}$	1·0819 (C)	$d^{80^\circ}_{4^\circ}$	1·0791	20— 80	90	72·5
	d^{100°	1·0590 (Pi)	d^{100°	1·0580	20—100	94	79
*iso*Propyl tartrate	$d^{18^\circ}_{4^\circ}$	1·1274 (C)	$d^{18^\circ}_{4^\circ}$	1·1214 (C)			
	d^{20°	1·1300 (Pi)	$d^{20^\circ}_{4^\circ}$	1·1166 (C)			
	$d^{40^\circ}_{4^\circ}$	1·1057 (C)	$d^{40^\circ}_{4^\circ}$	1·1022 (C)	18— 40	89	80
	$d^{80^\circ}_{4^\circ}$	1·0724 (C)	$d^{80^\circ}_{4^\circ}$	1·0743 (C)	18— 80	83	71·5
	d^{100°	1·0537 (Pi)	d^{100°	1·0467 (C)	20—100	91	87
n-Butyl tartrate	d^{15°	1·098 (F)	$d^{15^\circ}_{4^\circ}$	1·0890 (C)			
	$d^{18^\circ}_{4^\circ}$	1·0886 (C)	$d^{18^\circ}_{4^\circ}$	1·0879 (C)			
	$d^{40^\circ}_{4^\circ}$	1·0765 (C)	$d^{40^\circ}_{4^\circ}$	1·0741 (C)	18— 40	51	57·5
	$d^{80^\circ}_{4^\circ}$	1·0392 (C)	$d^{80^\circ}_{4^\circ}$	1·0382 (C)	18— 80	76	77
*iso*Butyl tartrate	$d^{80^\circ}_{4^\circ}$	1·0213 (C)	$d^{80^\circ}_{4^\circ}$	1·0160 (C)	80—100	17	17·8
	$d^{100^\circ}_{4^\circ}$	1·0178 (C)	$d^{100^\circ}_{4^\circ}$	1·0124 (C)			
	d^{100°	1·0145 (Pi)					
Ethyl diacetyl-tartrate	$d^{80^\circ}_{4^\circ}$	1·1065 (C)	$d^{80^\circ}_{4^\circ}$	1·1012 (C)			
	$d^{98\cdot5^\circ}_{4^\circ}$	1·0810 (McC)	$d^{98\cdot5^\circ}_{4^\circ}$	1·0661 (C)	80— 98·5	128	177

(A & Pi) Anschütz and Pictet, *Ber.*, 1880, **13**, 1176.
(P) Perkin, J., 1887, **51**, 363. (W) Winther, *Z. physikal. Chem.*, 1902, **41**, 174.
(Pi) Pictet, *Jahr.*, 1882, 856. (Pa) Patterson, J., 1908, **93**, 1852.
(F) Freundler, *Ann. Chim.*, 1894, **3**, 447.
McC) McCrae and Patterson, J., 1900, **77**, 1098. (C) Present author.

racemic compounds are not affected. The results are in Table IV. Thole (J., 1910, **97**, 1249) found 1·457 for ethyl tartrate and 1·360 for the racemate at 25°.

TABLE IV.

	18°.		40°.		80°.	
Ester.	*d.*	*r.*	*d.*	*r.*	*d.*	*r.*
Ethyl	3·7996	2·5196	0·4479	0·3499	0·0571	0·0536
n-Propyl	2·0760	1·4861	0·3587	0·2965	0·0524	0·0461
*iso*Propyl	7·6161	5·8243	0·5716	0·6150	0·0643	0·0647
n-Butyl	1·0587	0·9455	0·2532	0·2475	0·0455	0·0445
Amyl	1·9851	1·8654	0·4093	0·3326	0·0586	0·0527
Methyl dipropionyl-			0·3411	0·3355		
Ethyl diacetyl-					0·0656	0·0460
*iso*Butyl					0·0640	0·0595

The marked difference in the viscosities is noteworthy; with one exception, that of the active form is, in agreement with Ranken and Taylor (*loc. cit.*), Aguirreche (*Anal. Fís. Quím.*, 1925, **23**, 409), and Thole (*loc. cit.*), higher than that of the racemic form, but *iso*propyl tartrate at 40° showed the reverse behaviour, and this was confirmed with several fresh preparations. As the temperature rises the difference in the viscosities decreases, becoming in some cases almost zero; thus, in the case of *iso*propyl tartrate at 80° we may perhaps conclude that the dissociation of the racemate is complete. The following ratios of $\eta_{\text{tartrate}}/\eta_{\text{racemate}}$ and also the temperature coefficients $(d\eta/dt)/\eta_{18^\circ}$ illustrate these points.

	18°.	40°.			80°.		
			$(d\eta/dt)/\eta_{18^\circ}$.			$(d\eta/dt)/\eta_{18^\circ}$.	
Ester.	Ratio.	Ratio.	*d.*	*r.*	Ratio.	*d.*	*r.*
Ethyl	1·51	1·28	0·0401	0·0393	1·07	0·0159	0·0158
n-Propyl	1·40	1·21	0·0378	0·0363	1·13	0·0157	0·0156
*iso*Propyl	1·30	0·93	0·0420	0·0407	1·00	0·016	0·159
n-Butyl	1·12	1·02	0·0345	0·0336	1·02	0·0153	0·0154
Amyl	1·065	1·23	0·036	0·0374	1·12	0·0157	0·0156
Methyl dipropionyl-		1·01					
Ethyl diacetyl-					1·42		
*iso*Butyl					1·29		

Thole's figures (*loc. cit.*) for ethyl tartrate give ratio = 1·07, and $(d\eta/dt)/\eta_{18^\circ}$ = 0·088 for the tartrate and 0·066 for the racemate.

The temperature coefficients of the active forms are greater than those of the racemic forms, but all approach the value 0·016 at 80°. In view of such striking evidence as the above, it can hardly be denied that there must at least be a great difference in the degrees of association of the two forms. The greater viscosity of the active form points to a greater association of that form.

6. *Refractivities and Dispersions.*—The refractive indices for the hydrogen C and F lines were determined in a Zeiss Pulfrich refractometer, through which water at 18° was circulated. The instrument

was adjusted in the usual manner, and standardised with water. The calculated molecular refraction assumes the presence of two hydroxylic, two ketonic, and two ethereal oxygen atoms. The results, given in Table V, show slight but distinct differences, as elsewhere, the active form having usually the greater refractive index, and the inactive the greater dispersion.

TABLE V.

Ester.	Ethyl.	*n*-Propyl.	*iso*Propyl.	*n*-Butyl.	Amyl.
d n_C	1·4466	1·4447	1·4385	1·4455	1·4440
d n_F	1·4556	1·4532	1·4467	1·4544	1·4544
r n_C	1·4453	1·4413	1·4374	1·4451	1·4452
r n_F	1·4546	1·4523	1·4461	1·4568	1·4580
d $[R_L]_C$	45·51	54·79	54·41	64·12	72·85
d $[R_L]_F$	46·20	55·69	55·42	65·23	74·33
r $[R_L]_C$	45·48	54·43	54·71	64·12	72·98
r $[R_L]_F$	46·43	55·63	55·65	65·75	74·81
Calc. $[R_L]_C$	45·29	54·49	54·49	63·68	72·87
Calc. $[R_L]_F$	45·97	55·31	55·30	64·74	74·33
d; $[R_L]_F - [R_L]_C$	0·69	0·90	1·01	1·11	1·48
r; $[R_L]_F - [R_L]_C$	0·946	1·205	0·94	1·63	1·83

7. *Surface Tension.*—Following on the work of Mitchell and Smith (J., 1913, **103**, 489), the surface tension, molecular surface energy, and temperature coefficient of the latter were determined. The stalagmometer method was used, the instrument being standardised with water. The high viscosity prevented its use at 18°. For the same reason, the smallest size of Traube stalagmometer, having a drop number of about 21·5 at room temperature, was used. The simple ratio of the drop weights was used, no corrections being applied. The reason for this was principally that only comparative figures were required, and, secondly, that the order of reproducibility of the surface tensions of these viscous esters is not so high as with, *e.g.*, water or benzene. The results are in Table VI.

TABLE VI.

	γ.			$\gamma(Mv)^{\frac{2}{3}}$.		$k = d[\gamma(Mv)^{\frac{2}{3}}]/dt$.	
Ester.	*d.*	*r.*	*t.*	*d.*	*r.*	*d.*	*r.*
Ethyl	31·78	30·71	40°	986	955		
	31·37	30·28	80	993	958	+0·175	+0·075
n-Propyl	28·96	27·32	40	1018	993		
	27·10	25·32	80	977	914	—1·02	—1·98
*iso*Propyl	28·40	26·58	40	1009	946		
	26·27	25·70	80	952	930	—1·425	—0·40
n-Butyl	28·73	28·36	40	1120	1108		
	27·20	26·17	80	1086	1045	—0·85	—1·575
*iso*Butyl	24·17	24·79	80	976	1004		
Amyl	26·90	26·16	40	1143	1120		
	24·90	23·70	80	1085	1035	—1·45	—2·125
Ethyl diacetyl-	27·47	27·57	80	1125	1133		

The most striking observation is that the values of k are, with one exception, greater for the r than for the d form; in other words, the association of the active form is greater than that of the racemic, a surprising result on the basis of the assumption of simple association of oppositely active molecules to single racemate molecules. It is also noteworthy that the only case in which k is smaller for the r than for the d form, and therefore the association of the racemate is greater than that of the active form, is also the only case (at 40°) where the viscosity of the racemate is greater than that of the active form.

8. *Specific Rotations*.—An examination of the preceding physical constants shows that those of the active and of the racemic forms tend to become identical with rising temperature. The most obvious and probable explanation of this is that both forms are dissociating into single molecules. Another explanation is conceivable, however, *viz.*, that with rising temperature a reversible racemisation of the active form takes place. This hypothesis is disposed of by an examination of the specific rotations of the active forms at different temperatures (Table VII). In the case of most of the esters this had already been done by previous workers, but

TABLE VII.

Ester.	Temp.	$[\alpha]_D$.	Ester.	Temp.	$[\alpha]_D$.
Ethyl tartrate	14°	7·07° (S)	*n*-Propyl tartrate	14°	11·7° (C)
	17·8	7·64 (Pa)		17	12·39 (Pa)
	20	7·659 (Pi)		18	12·09 (A & Pi)
	20	7·45 (Wa)		20	12·44 (Pi)
	20	7·48 (Wi)		20	12·00 (Wi)
	35·3	9·39 (Pa)		98·5	17·28 (Pa)
	92·9	13·28 (Pa)		100	17·11 (Pi)
	100	13·29 (Pi)	*iso*Propyl tartrate	14	15·70 (C)
	143	14·75 (Pa)		20	14·886 (Pi)
	175	14·99 (Pa)		100	18·821 (Pi)
*iso*Butyl tartrate	100	19·87 (Pi)	*n*-Butyl tartrate	*14	10·09 (C)
		(homogeneous)		19	10·3 (F)
	14	11·8 (G & F)		80	13·77 (C)
		(c = 1·025 in alcohol)	Ethyl diacetyltartrate	56·8	4·37 (McC & P)
		13·6 (C)		100	6·30
		(c = 37·0 in alcohol)			

* The rotation of *n*-butyl tartrate appears to be affected by a species of mutarotation, for after several months' keeping the rotation had decreased to +8·94°.

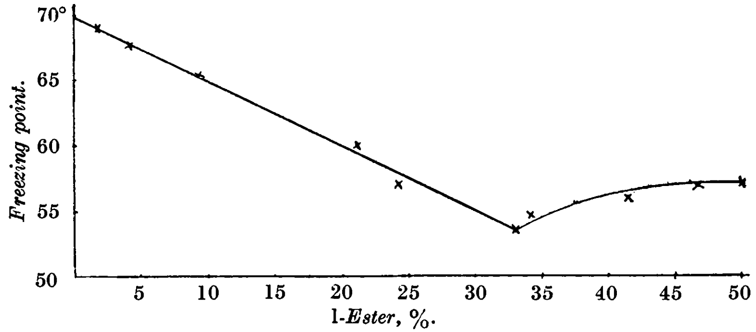
(Pa) Patterson, J., 1908, **93**, 1852; 1904, **85**, 767.
(Pi) Pictet, *Jahresber.*, 1882, 856.
(Wa) Walden, *Ber.*, 1905, **38**, 399.
(Wi) Winther, *Z. physikal. Chem.*, 1907, **60**, 576.
(A & Pi) Anschütz and Pictet, *loc. cit.*
(F) Freundler, *Ann. Chim.*, 1894, **3**, 447.
(G & F) Guye and Fayollet, *Bull. Soc. chim.*, 1895, **13**, 207.
(McC & P) McCrae and Patterson, J., 1900, **77**, 1098.

a few new determinations are added. From these figures it is evident that the rotation always increases with rise of temperature, and therefore the hypothesis of racemisation is untenable.

9. *Freezing-point Curve of* iso*Butyl Tartrate.*—*iso*Butyl tartrate breaks the series of liquid esters, for it is solid up to 70°, and the racemate up to 58°. It was thought, however, that some light might be thrown on the degree of dissociation of the racemate from the form of the freezing-point curve (compare Roozeboom, Adriani, Findlay and Hickmans, Findlay and Campbell, *locc. cit.*). As these tartaric esters all tend markedly to remain superfused, the temperature was allowed to fall slightly below the expected freezing point, and a crystal of the phase separating was then added. In this way the following data were obtained, from which Fig. 1 is plotted.

Fig. 1.

Freezing-point curve of mixtures of iso*butyl* d- *and* l-*tartrates.*



l-Ester, %	0·00	1·57	4·19	9·43	21·26	24·24
F. p.	69·8°	69·0°	67·7°	65·2°	60·0°	57·0°
l-Ester, %	32·8	34·10	41·44	46·52	48·64	50·00
F. p.	53·4° (eutectic)	54·5°	55·9°	56·8°	57·0°	57·2°

From the form of the curve, the range of stability of the racemate appears to be much less than that of the racemate of methyl tartrate investigated by Adriani (*loc. cit.*). The flatness of the intermediate portion of the curve indicates a high degree of dissociation of the racemate in the molten state.

10. *Solubility Curves of* iso*Butyl Tartrate.*—It has been shown by Roozeboom that a study of the solubility of the active, inactive, and mixed active and inactive phases will decide whether the solid inactive form is a true racemate or simply a *dl*-conglomerate. Accordingly, such measurements were carried out on *iso*butyl tartrate. In the case of the mixed solid phase, it was necessary to analyse the solution polarimetrically to determine the relative

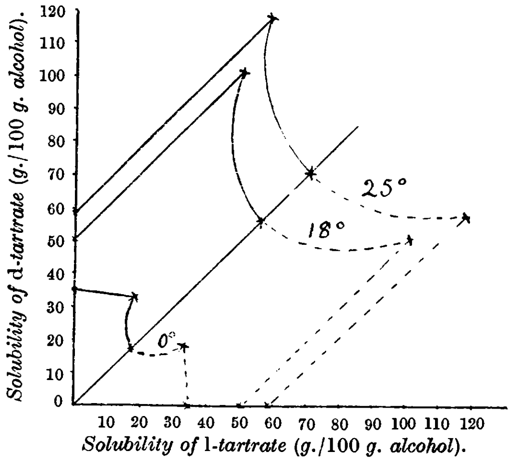
proportions of active and inactive ester. The author's value for the specific rotation of *iso*butyl tartrate in alcoholic solution was used rather than that of Guye and Fayollet (see Table VII) since it is more nearly related to saturated solutions. The following values were obtained, and they are plotted in Fig. 2.

	Solubility (g./100 g. alcohol).		
Solid phase.	0°.	18°.	25°.
d	35·0	50·7	58·4
r	34·9 *	56·5 *	71·5 *
d + *r*	33·75 *d* 18·35 *l*	101·85 *d* 51·15 *l*	117·75 *d* 58·25 *l*

* Total, *d* + *l*.

FIG. 2.

Solubilities of iso*butyl* d- *and* l-*tartrates.*



The total solubility is always increased by addition of the active form to the inactive, *i.e.*, the liquid phase becomes active. At all the above temperatures, therefore, the solid inactive form is a solid racemate. It will be observed that the length of the intermediate portion of the curve is decreasing with falling temperature, and at 0° is comparatively small. Therefore, at temperatures somewhat below 0°, the solid phase will pass from true racemate to *dl*-conglomerate. The point of significance for this work, however, is that at temperatures above 0°, the stable solid phase is always a true racemate, and it might therefore be expected that differences might exist in the physical constants of the two forms. The above state of affairs has also been shown to exist in the case of methyl tartrate (Findlay and Campbell, *loc. cit.*) and therefore, by analogy, in that of all the simple tartaric esters.

11. *Byk's Experiments.*—Although not directly concerned with the matter of this paper, the experiments of Byk (*loc. cit.*) on the existence of racemic molecules in solution were thought of sufficient interest to be repeated. That author prepared two specimens of alkaline Fehling solution, one made up with tartaric acid, and the other with the equivalent amount of racemic acid; the latter was bluer and the former greener, and this difference was still very marked at 100-fold dilution, and still detectable at 250. On repeating this experiment, the present author noticed at first a decided difference, but this seemed rather to consist in a greater opacity of the racemic solution than in a difference of tint. On dilution 50 times, the relative difference in tint became more marked, and the racemic solution was then distinctly bluer.

The absorption spectra of the original solutions were then determined with a Hilger constant-deviation spectrometer. The visible spectrum extended from λ = 7610 Å. to λ = 4255 Å. There was no absorption in the violet. The following table shows the wavelengths of the absorption bands for given layer thicknesses for the two solutions :

Tartrate.		Racemate.	
λ.	Thickness, mm.	λ.	Thickness, mm.
7610—6180	29	7610—5438	40
7610—6640	15	7610—6500	20
7610—7195	8	7610—6800	10
No band	4	7610—7550	5

The λ–log thickness plot gives two closely parallel graphs, the difference being probably due to a slight difference in concentration. There is therefore no evidence here of the existence of racemic molecules. The head of the band lies in the infra-red.

Another interesting observation is that when both the tartrate and racemate Fehling solutions were kept for several weeks, cuprous oxide was deposited from the former solution, but not from the latter. Now, according to Byk (*loc. cit.*), tartrate Fehling is photochemically active : as the racemic molecules cannot be present to any great extent, the effect must be an anticatalytic one.

Conclusion.

From an examination of the physical constants, the conclusion is irresistible that in the case of the liquid esters of tartaric acid there is a marked difference in the chemical nature of the active and inactive forms.

As the series of esters is ascended from the ethyl to the amyl members, the difference in the degree of association decreases, at room temperature, so that amyl tartrate appears to be but little more associated than its racemic form. As the temperature rises, the active form dissociates more than the racemic form, so that *n*-butyl racemate has become identical with its active form. At the same time, it must be supposed that sometimes the racemate (which must also be associated to some extent) dissociates at a different rate from the active form, for, *e.g.*, the order of viscosities of *iso*propyl *d*- and *r*-tartrate is reversed at 40°, whereas the viscosities of the amyl esters, almost identical at 18°, show a considerable difference at 40°. At 80°, the constants are still closer.

UNIVERSITY OF ABERDEEN. [*Received, March* 15*th*, 1929.]