[Contribution from the Department of Chemistry, Yale University]

THE FREEZING POINT–SOLUBILITY RELATIONS OF GEOMETRICAL ISOMERS. I. THE β-CHLOROCROTONIC ACIDS[1]

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If the freezing point–solubility data of any component of an ideal solution are plotted $1/T$ against log N, the slope of the line at any point is proportional to the molal heat of fusion of the component.[2] Alternately, we may take as our criterion that the activity, a, or N calculated by means of this equation from a calorimetrically determined value of ΔH, should be equal to the actual value of N. With these criteria of ideality, a number of cases have been cited in which two substances are substantially mutually ideal and these seem to show that ideality is realizable when, and only when, the substances are quite similar in chemical constitution,[3] but not similar enough, especially in crystallography, to form mixed crystals to a pronounced extent.[4] For example, certain isomeric *ortho, meta* and *para* disubstituted benzenes form practically ideal binary and ternary systems.[5]

It seemed reasonable to suppose that isomers of the *cis-trans* or the *syn-anti* type might form ideal solutions of the simple eutectic type, since there appears to be a marked resemblance in structure between the *cis* and *ortho* on the one hand and the *trans* and *para* on the other.[6] Further, it appears from the rather meager data which are available that geometrical isomers show substantially the same percentage differences between their heats of combustion as are shown by *ortho, meta* and *para* isomers. At their melting points the molal heat capacities of the geometrical isomers studied in this paper do not show a greater difference than the differences

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[1] From a dissertation submitted by Evald L. Skau to the Graduate School of Yale University, June, 1925, in candidacy for the Degree of Doctor of Philosophy.

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[2] From the equation $(d \log N_A)/[d(1/T)] = -\Delta H_A/4.575$, where log N_A is the common logarithm of the mole fraction of A, the component crystallizing at temperature T, and ΔH_A is its molal heat of fusion at that temperature. For a bibliography and discussion of this equation see Johnston, *J. Phys. Chem.*, **29**, 882 (1925).

[3] For a more detailed discussion see Hildebrand, "Solubility," The Chemical Catalog Co., New York, **1924**, p. 59 ff.

[4] In such a case the equation must be modified. For example, see Van Laar, *Z. physik. Chem.*, **55**, 435 (1906); **63**, 216 (1908); **64**, 257 (1908). In some cases where limited solid solutions are formed nearly straight lines are obtained by plotting log N against $1/T$, but this alone is not a criterion of ideality in the liquid phase.

[5] Narbutt, *Z. physik. Chem.*, **53**, 697 (1905); Holleman, Hartogs and van der Linden, *Ber.*, **44**, 704 (1911); Andrews, *J. Phys. Chem.*, **29**, 1041 (1925); Kohman, *ibid.*, 1048.

[6] See Werner, "Lehrbuch der Stereochemie," Gustav Fischer, Jena, **1904**, p. 211.

calculated for the *ortho*, *meta* and *para* isomers investigated by Andrews, Lynn and Johnston.[7] Indeed, Andrews[8] found practically no differences in the molal heat capacities of the solid isomers of the type C_6H_4XY from 30° below the lowest melting isomer to 110°K. Hence he concluded that they would give substantially the same free energy change of formation. Probably this can also be said for geometrical isomers. Furthermore, it was hoped that a study of such systems might aid in the solution of the nature of this type of isomerism, which, following Wislicenus, has been called geometrical isomerism. If it could be shown that the *cis-trans* isomers of a substance form systems of the simple eutectic type, whereas the *cis-cis* or the *trans-trans* forms of two closely related substances form solid solutions,[9] the structure of such isomers might be referred to fumaric and maleic acids, whose structures are conceded to be reasonably well established.

A search of the literature reveals only one system of geometrical isomers for which the temperature–composition diagram has been constructed with sufficient accuracy for use in testing ideality by these methods. This is the system crotonic acid–isocrotonic acid as given by Morrell and Hansen.[10] These investigators undoubtedly used pure acids but their experimental method is open to criticism. They made their solutions of different compositions by starting with a known amount of each pure component and adding, successively, small amounts of the other form. The freezing points were determined in the usual way without correcting for the amount of solid separating. Thus the error in composition was accumulative and the freezing points were all lower than the true values. In the course of one series of determinations "it was necessary to substitute a mercury thermometer for the alcohol thermometer." Although correction was made for the solid removed by the thermometer, a considerable error must have been introduced since there is a break in the solubility curve between the points in question. Using their data, we have plotted $(1 + \log N)$ against $1000/T$. On the crotonic acid branch of the plot, the points lie both above and below a nearly straight line drawn from $1000/T_f$ (T is the freezing point of pure crotonic acid) with an initial slope calculated

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[7] Andrews, Lynn and Johnston, THIS JOURNAL, **48**, 1274 (1926).

[8] Andrews, *ibid.*, **48**, 1287 (1926).

[9] This does not seem improbable since, judging from a survey of the literature and from results obtained in this Laboratory by E. P. Jones [Johnston and Jones, *J. Phys. Chem.*, **32**, 593 (1928)] and by Myer Solomon (unpublished), the disubstituted derivatives of benzene seem to form solid solutions only in the *meta-meta*, *ortho-ortho* or *para-para* systems. Further, Bruni [Bruni and Gorni, *Atti. accad. Lincei* (5) **8**, 454, 570 (1899); Bruni, *Gazz. chim. ital.*, I, **30**, 64 (1900)] claims to have shown that the *trans* form of two geometrical isomers forms a solid solution with the corresponding saturated compound, whereas the *cis* form gives a freezing point–solubility diagram of the ordinary eutectic type.

[10] Morrell and Hansen, *J. Chem. Soc.*, **85**, 1520 (1904).

from the molal heat of fusion.[11] Though the experimental points show considerable divergence from this line, the fact that the deviation is not in one direction indicates that experimental error rather than non-ideality is the cause. The points on the isocrotonic acid branch fall remarkably close to a straight line corresponding to a calculated heat of fusion of 3100 cal. per mole. Although this heat has not been determined calorimetrically, we may conclude that the two forms of crotonic acid probably form a nearly ideal solution.

The temperature–composition diagram of another system, *syn-* and *anti*-benzaldoxime, has been constructed by Cameron,[12] but due to the partial transformation on heating above the melting point, the freezing points could be determined only roughly by means of the capillary tube method. On plotting the values of $(1 + \log N)$ against $1000/T$ for this system, decidedly curved lines, concave upwards, are obtained for both branches, which would ordinarily point toward non-ideality.[13] Due to the inaccuracy of the data, however, and since the true heats of fusion are unknown, it would be unsafe to draw any conclusions from this evidence.

In order to secure some definite evidence concerning the ideality of *cis-trans* systems, it was decided to construct accurately the freezing point–solubility diagram for the system β-chlorocrotonic acid-β-chloro-isocrotonic acid and to determine their heats of fusion. These compounds can be synthesized with relative ease; furthermore, proof of the ideality of this system would strengthen the indications as to the ideality of the crotonic acid–isocrotonic acid system, since they are structurally quite similar to the latter.

Experimental Part

Method of Synthesis

Preparation of *cis* and *trans* Forms.—A mixture of the two forms of β-chlorocrotonic acid was prepared from acetoacetic ester by Geuther's method as modified by

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[11] Determined in this Laboratory by Lynn (*Dissertation*, **1925**) using the method described by Andrews, Lynn and Johnston (ref. 7). In the neighborhood of the melting point this can be expressed by the empirical equation $\Delta H = 3695 - 13.56\,t + 0.0736\,t^2$. At the melting temperature, 71.4°, this becomes 3100, or 924 cal. higher than the value obtained by Bruner [*Ber.*, **27**, 2102 (1894)], who probably used impure acid since he gave the melting point as 67.4°. The new value for the heat of fusion corresponds to an entropy of fusion of 9.0 cal. per degree at the melting point instead of 6.4 from Bruner's data. Crotonic acid can no longer be cited as the organic compound with the lowest entropy of fusion (Roozeboom, "Die Heterogenen Gleichgewichte," II, 1, 279). As far as the present authors are aware this position should now be assigned to cyclohexane with a value of 1.75 cal. per degree.

[12] Cameron, *J. Phys. Chem.*, **2**, 413 (1898).

[13] The change in slope of such a curve is determined by $d\,\Delta H/dT$; hence this evidence alone does not exclude ideality.

Michael, Wislicenus, Jr., and Scheibler.[14] The ester, in benzene solution, was treated with phosphorus pentachloride and the reaction mixture was added to water. The acids were removed from the benzene layer as their sodium salts by extracting with sodium carbonate solution and were then precipitated by acid and extracted with ether. In removing the ether it was found advisable to use a fractionating column to hold back the volatile β-chloro-isocrotonic acid; the last portions are best removed by evaporation at room temperature from a shallow crystallizing dish. The yield was 36.5%. The two acids were then separated as well as possible by fractional steam distillation.

Purification

β-Chlorocrotonic Acid.—The crude residue from the steam distillation was decolorized with Norite and was then recrystallized once from water and fractionally crystallized from carbon disulfide. It was finally sublimed[15] at 105° at atmospheric pressure. The melting point was at first followed by means of the ordinary capillary tube method and later by means of cooling curves. The final product froze at 93.6°.

β-Chloro-isocrotonic Acid.—The crude product was first fractionally steam distilled. Subsequent sublimation[15] at 105° and atmospheric pressure gave a pure product which gave a "flat" on a cooling curve at 60.5°.

The Freezing Points

The freezing point determinations were made by means of the apparatus described by Andrews, Kohman and Johnston,[16] with some further refinements developed in this laboratory since the publication of their work. The apparatus is sketched in Fig. 1. A cylindrical copper tube or shield (14 cm. long, 5cm. outside diameter, 2.5cm. inside diameter) closed at one end is set on a cushion of asbestos in the silvered pint Dewar flask A. K is a heating coil consisting of a 25-ohm nichrome resistance wound tightly around the metal cylinder and insulated from it by means of a thin layer of mica. A thin-walled freezing point tube G (65 mm. long, 8 mm. diameter) containing the sample, H, fits quite snugly over the end of a thin glass tube. The latter extends up through the cork stopper from which the small unsilvered Dewar tube C[17] is suspended by means of a wire not shown in the diagram. I is an inlet for a stream of hot air,[18] used in melting the sample *in situ*, and E an outlet. The temperature of the shield B is measured by means of the copper–constantan thermoelement J set in hard solder in a hole drilled for the purpose. A plug of cotton wool prevents too rapid radiation from the top of the shield. The thermoelement D, in the melt, is constructed of No. 46 (B. and S. gage) copper and No. 40 constantan wire, the copper being wound around the insulated constantan for a distance of about 4 cm. above the junction in order to minimize the heat conductivity. It is of course an advantage to have the thermoelement directly in the melt but in some cases this is impossible due to the solvent action of the liquid. However, the element responds to a change in temperature with no appreciable lag when

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[14] Geuther, *Z. Chem.*, **14**, 237 (1871); Michael and Schulthess, *J. prakt. Chem.*, [2] **46**, 236 (1892); Wislicenus, Jr., *Dissertation*, Leipzig, **1892**, *Chem. Zentr.*, I, 413 (1893); Scheibler, *Ber.*, **53**, 381 (1920).

[15] Rejecting and resubliming all but the long needle-like crystals that projected from the sides of the sublimation tube.

[16] Andrews, Kohman and Johnston, *J. Phys. Chem.*, **29**, 914 (1925).

[17] Later work showed this tube to be superfluous.

[18] Produced by passing air through a small iron pipe loosely filled with copper turnings and wound with a heating element. The sample may also be melted by using a small resistance heater fitting loosely around tube G.

protected by a thin-walled capillary tube containing vaseline or some high-boiling liquid (for example, benzophenone). We have therefore used this method exclusively since it has the added advantage that the glass around the thermoelement is much more easily cleaned than the bare thermoelement.

The thermocouples were calibrated at the ice point and at the boiling points of water, naphthalene and benzophenone. Temperatures were read to the nearest microvolt (ca. 0.02°) by means of a Leeds and Northrup type K potentiometer. The freezing points were corrected by using the extrapolation method of Andrews, Kohman and Johnston.[16] The freezing points of the pure substances are correct to within about ±0.05° and, with the solutions, the maximum error, near the eutectic point, is about 0.25°.

The freezing point data for the system are given in Table I, the points marked with an asterisk being values interpolated from the $(1 + \log N)$ *vs.* $1000/T$ plots. In this table are included the ideal values of N, or the activities, a, calculated from the heats of fusion and the changes in heat capacity as measured by us. The ratio a/N, given in the last column for each component, represents the deviation from ideality at the temperature t and mole fraction N.

The system is of the simple eutectic type and on plotting $(1 + \log N)$ against $1000/T$ for the two branches on a large scale it is found that, within the accuracy of our experimental values, straight lines are obtained in both cases. The values of $(\mathrm{d} \log N)/[\mathrm{d}(1000/T)]$ for these lines are 1.1417 for the β-chlorocrotonic acid branch and 0.9009 for the β-chloro-isocrotonic acid branch, from which the calculated heats of solution are 5220 and 4120 cal. per mole, respectively.[19]

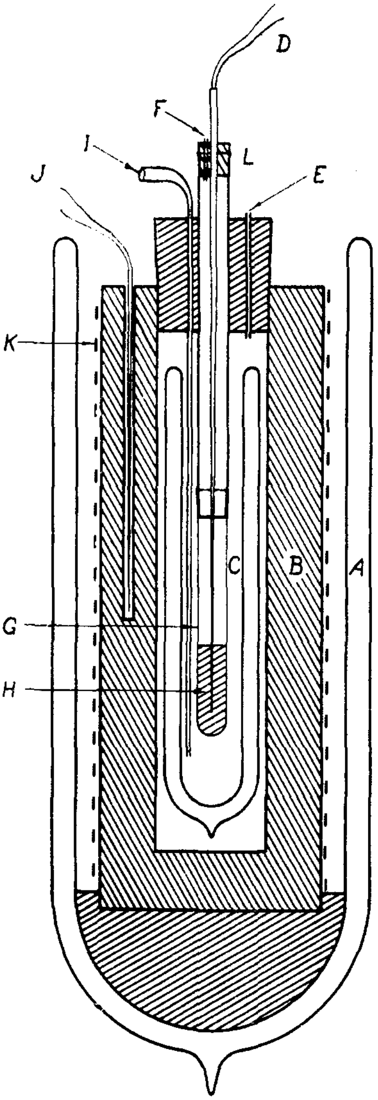

Fig. 1.—Sketch of freezing point apparatus.

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[19] Since $(1 + \log N)$ is plotted against $1000/T$, $s = \dfrac{\mathrm{d} \log N}{1000\ \mathrm{d}(1/T)} = -\Delta H/4575$, from which $\Delta H = -4575\ s$.

TABLE I

FREEZING POINT–SOLUBILITY DATA FOR THE SYSTEM β-CHLOROCROTONIC ACID–β-CHLORO-ISOCROTONIC ACID

	β-Chlorocrotonic acid				β-Chloro-isocrotonic acid		
t	N	a	a/N	t	N	a	a/N
93.6	1.0000	1.000	1.000	60.5	1.0000	1.000	1.000
*88.3	0.9000	0.905	1.006	56.4	0.9250	0.940	1.017
*82.5	.8000	.811	1.013	*53.6	.8800	.902	1.025
75.6	.6848	.708	1.033	49.6	.8167	.848	1.038
*60.3	.5000	.527	1.054	*46.3	.7600	.806	1.061
53.2	.4148	.441	1.062	43.2	.7128	.768	1.077
*46.8	.3500	.381	1.088	41.5	.6920	.747	1.080
41.5	.3080	.335	1.088				

The Heats of Fusion

Direct calorimetric measurements of the differences between the heat contents of each form[20] at several temperatures and that of the solid at 22° were made by the method described by Andrews, Lynn and Johnston.[7]

Following their usage, we have expressed the heat content of the solid and of the liquid by empirical equations, valid over a short temperature range in the neighborhood of the melting point, of the form $H = a + bt + ct^2$. In these equations H is expressed in gram-calories per mole at $t°$, referred to the heat content of the solid at 22° as zero. The value of H for the liquid minus that for the solid is the heat of fusion, ΔH. For β-chlorocrotonic acid this is $\Delta H = 20{,}300 - 94.15\ T + 0.1426\ T^2$; and for β-chloro-isocrotonic acid it is $\Delta H = 11{,}660 - 61.26\ T + 0.1085\ T^2$. These equations have been used in calculating the activities given in Table I. This involves the assumption that the heat content equations for the liquids are valid down to the eutectic temperatures, but this seems preferable to considering the heats of fusion as constant. The values of ΔH, calculated to the freezing temperatures, are given in Table II.

By differentiating the heat content equation with respect to temperature, C_p can be expressed over a limited temperature range. Since the heat content equations are necessarily empirical, the heat capacity equations derived from them are only approximate. The heat capacities of the solids and liquids have been calculated to the freezing temperatures and are given in Table II. The difference, $C(l) - C(s) = \Delta C_p$, approximately expressing the variation of ΔH with temperature in the neighborhood of the freezing point, is about the same for the two isomers. The

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[20] The sample of β-chlorocrotonic acid was not quite so pure as that used in the freezing point experiments, hence its freezing point was about 0.3° lower. In attempting to carry the curve to higher temperatures, it was found that decomposition of some kind took place, as was shown by the heat content values of the sample when redetermined at lower temperatures. The β-chloro-isocrotonic acid, on the other hand, was of the highest purity and the heating curves run on this sample afterwards proved that there had not been the slightest decomposition.

values are of the same order of magnitude as those found by Andrews, Lynn and Johnston[7] for the organic acids studied by them. The results are summarized in Table II. In addition to the quantities above described we have included Δ_m and Δ_a, expressing the maximum and the average (disregarding sign) differences between the experimental values of H and those calculated from the empirical equations.

TABLE II

HEAT CONTENTS OF THE β-CHLOROCROTONIC ACIDS

No. of obs.		Temp. range, °C.	a	b	c	Δ_m	Δ_a	ΔH_f at t_f	C_p at t_f	ΔC_p
				β-Chlorocrotonic acid						
solid	9	33	−756	36.68	0.0303	62	31	4950	39.4	
liquid	4	121	4470	17.42	.1729	14	9		49.8	10.4
				β-Chloro-isocrotonic acid						
solid	6	33	−712	31.45	0.0416	48	22	3300	36.5	
liquid	9	121	2308	29.44	.1501	71	24		47.6	11.1

It will be noted that the values for the heats of fusion calculated from the freezing point data and those experimentally determined differ by 270 cal. per mole in the case of the β-chlorocrotonic acid and by 820 cal., per mole in the case of the β-chloro-isocrotonic acid, both deviations being in the same direction. That these differences are due to experimental error is out of the question. The freezing points calculated from the experimentally determined heats of fusion are *lower* by 3 and 5°, respectively, near the eutectic composition, than the observed freezing points. This is many times the probable error in the freezing point determinations. The experimental accuracy in the calorimetric determinations is about 50 cal. per mole, so that the error in the heats of fusion so determined would be 100 cal. per mole at the greatest. Inasmuch as the experimental measurement of the heat of fusion involved the sudden cooling of the molten sample to about 22°, it seemed possible that under these conditions the substances may have solidified in some unstable crystalline modification whose heat of fusion was smaller. In order to test this possibility three successive heating curves were run on the same sample of β-chloro-isocrotonic acid and for the data so obtained the relative heats of fusion in the three cases were calculated, by evaluating the appropriate area under the temperature–time curves,[21] with a reproducibility of about 5%. The first and third curves were run on the sample after melting it and chilling it suddenly to room temperature; the second after inoculating it just below the melting point and then allowing it to cool very slowly, thus duplicating the conditions in the freezing point determinations. The results are as follows.

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[21] See Andrews, Kohman and Johnston, who have applied this method to cooling curves (ref. 16).

TABLE III

EFFECT OF RATE OF COOLING ON HEAT OF FUSION OF β-CHLORO-ISOCROTONIC ACID

No.	Previous treatment	% deviation from mean of I and III
I	Suddenly chilled	+3.8
II	Seeded and slowly cooled	−1.9
III	Suddenly chilled	−3.8

Since the difference to be accounted for is of the order of 20%, this evidence shows that only one modification of β-chloro-isocrotonic acid was involved. Further, inasmuch as no break was detected in the heat content–temperature curve of the solid until the melting point was reached, it seems reasonable to conclude that it undergoes no transition above 22°.

Conclusion

The only plausible conclusion to be drawn from the data, therefore, seems to be that the system is not entirely ideal. That no complexes are formed in appreciable amounts by association or reaction seems to be probable since the $(1 + \log N)$ *vs.* $1000/T$ plots are substantially straight lines throughout the whole range considered for both branches of the freezing point diagram. Neither would mixed crystal formation explain the discrepancies satisfactorily. On the other hand, the non-ideality might be explained by a slight difference in the internal pressures or polarity of the two substances.[22] That is, there may be a slight heat of mixing in the liquid state for the two forms which deviates from constancy at the various compositions in such a way that when it is added to the heat of fusion, which also changes, it gives practically a straight line for the $(1 + \log N)$ *vs.* $1000/T$ plot.

If this explanation is correct, one would predict a slight volume change on mixing the two liquids.

Summary

A modification of the freezing point apparatus as given by Andrews, Kohman and Johnston[16] has been described.

Accurate freezing point measurements for the system β-chlorocrotonic acid–β-chloro-isocrotonic acid have been made and calorimetric data, including heat contents, specific heats and heats of fusion, have been determined for each of these two compounds. The heat of fusion of crotonic acid has been reported. An examination of these data and those existing for the crotonic acid–isocrotonic acid system has been made to test the ideality of these two systems. It was found that in the former system the values for the heats of solution based on freezing point measurements are higher than those determined calorimetrically and the activities calculated from the thermal data are, for each component, greater than the corre-

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[22] See, for example, Hildebrand "Solubility," The Chemical Catalog Co., New York, **1924**, p. 69 ff.

sponding mole fraction to the maximum extent of about 8% at the eutectic point. Judging from our present knowledge of such systems, geometrical isomers seem to show slight deviations from mutual ideality but not such as would indicate complex or mixed crystal formation.

It is possible that similar studies made on less polar isomers of this type may show them to be more nearly ideal than those discussed in this paper.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY OF McGILL UNIVERSITY]

THE SURFACE ENERGY OF SOLID SODIUM CHLORIDE. III. THE HEAT OF SOLUTION OF FINELY GROUND SODIUM CHLORIDE

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In previous papers[1] it was shown that finely divided sodium chloride had a heat of solution different from that of coarsely ground sodium chloride. This difference was attributed to the energy bound up in the surface of the finely divided salt, and from the measurement of the difference in the heat of solution, the actual value of the surface energy of solid sodium chloride was calculated. In these experiments the finely divided salt had been obtained by sublimation.

In the present paper an account is given of similar measurements but here the finely divided salt is obtained by grinding. It has been found in this case also that the finely divided material had a lower (negative) heat of solution than the coarsely ground sodium chloride.

Experimental Procedure

Pure sodium chloride was ground in a mechanically driven agate mortar for fifteen minutes. The ground salt was then placed at the bottom of a vertical glass tube about 1 m. long and 4 cm. in diameter and dry air, at a constant pressure, was blown into the tube through a fine nozzle at the bottom. The air was admitted so as to impinge on the ground salt. The current of air carried up the fine particles of salt which then passed into a series of settling chambers[1b] where they were sorted out according to size. The vertical glass tube was jarred continuously by an automatic tapper to prevent salt from adhering to the walls of the tube. The salt in the tube was recharged every fifteen minutes.

In order to see whether the salt was contaminated by silica rubbed off the agate mortar, samples of the product were analyzed but no weighable amount of silica was found in them.

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[1] (a) Lipsett, Johnson and Maass, THIS JOURNAL, **49**, 925 (1927); (b) **49**, 1940 (1927).