V. The effect of recrystallization on the purity of samples of the salt.

VI. The relative effect of drying and fusing samples of dichromate.

COLUMBUS, OHIO.

NOTE.

Scandium from a Brazilian Source (Preliminary Announcement).—
While working upon zirconium, the writer observed that certain hy-
droxides from residues from which the most strongly basic elements had
been removed, and which consisted mainly of iron, aluminium and titanium,
dissolved in hydrofluoric acid imperfectly owing to the formation of a
gelatinous substance. Several grams of this were collected and boiled
for some time with concd. sulfuric acid in a platinum dish. The cooled
residue dissolved readily even in hot water. The sulfate solution gave a
precipitate with oxalic acid, and the oxalate upon ignition gave a pale
yellowish oxide. The solution in hydrochloric acid showed no absorption
spectrum. The dilute chloride solution was rapidly precipitated by
boiling with sodium thiosulfate. Oxalic acid gave no precipitate when
heated with the original hydroxides dissolved in hydrochloric acid. These
reactions prove conclusively that the gelatinous precipitate first formed con-
sisted mainly of scandium fluoride.

The above residues were obtained from Brazilian zirconia. At the
present time there may be a little delay before work upon a large number
of varieties of zirconium minerals is undertaken. C. JAMES.

DURHAM, N. H.

THE CONFIGURATIONS OF ORGANIC COMPOUNDS AND THEIR RELATION TO CHEMICAL AND PHYSICAL PROPERTIES. II.

BY ARTHUR MICHAEL.

In this paper the physical and chemical properties of the stereomeric,
unsaturated acids will be coördinated with the configurations given in
the first communication,[1] as far as the experimental observations at
hand permit, with a critical revision of previous views in this field.

Owing to the imperfect and inadequate experimental data, a perfectly
satisfactory treatment of the subject is not possible at present; even in
the few existing systematic investigations, not infrequently the members
of the series most important from the viewpoint of theory were omitted,
as beyond the scope of researches.

[1] THIS JOURNAL, 40, 704 (1918).

The Relations between the Physical Properties and the Configurations of Unsaturated Acids.

Density.—The removal of hydrogen from contiguous carbon atoms proceeds with their greater segmentation,[1] which should augment the increase in gravity already produced by the elimination of the lightest known matter. This change should be in a direct relation to the number of the removed atoms, provided substances with similar configurations and in the same or a strictly comparable, state of molecular aggregation are compared.[2]

That such an increase takes place with unsaturation was shown by Buff,[3] and was confirmed by the later work of Schiff,[4] Lossen,[5] Zander,[6] and Weger,[7] who found that the values of the increments vary considerably in different substances. A reinvestigation of the subject is necessary, however, as the conclusions of these chemists were based largely on the comparison of the compounds with dissimilar stereostructures. That progressive unsaturation, with formation of bodies of comparable configurations, really proceeds with increase in density is shown by the data on the *l*-amyl esters, given in Walden's[8] research on their specific rotary power.

To follow the relations between the position of unsaturation in the aliphatic, monobasic acids and the density increase, it should be borne in mind that the relatively heavy carboxyl group is here the dominating factor in the specific gravity, and that therefore the density values decrease with the increasing *molecular weight* of the hydrocarbon radical. On the other hand, the density should rise in unsaturation with the nearness of the unsaturated hydrocarbon group to the carboxyl, as the segmentation of the axial Δ-carbons is proportional to such a relation. α,β-Unsaturation of a saturated acid augments the density decidedly more than it does in the β,γ-position, and that the difference in the effect due to β,γ-, γ,δ- and δ,ϵ-unsaturation is comparatively slight, is evidently in agreement with theory. The observations at hand do not permit quite sure conclusions on the connection of density with structural and stereostructural chemical changes in unsaturated acids, but it is very probable that the replacement of a nuclear hydrogen in acrylic acid by a primary

[1] THIS JOURNAL, 40, 706 (1918).

[2] Unless otherwise stated, this molecular relation is assumed in the paper.

[3] *Ann. Suppl.*, IV, 158 (1865). In this remarkable paper the relation between the molecular volume of inorganic and organic compounds and state of saturation was first formulated.

[4] *Ber.*, 15, 1270 (1882); *Ann.*, 220, 291 (1883).

[5] *Ann.*, 214, 121 (1882).

[6] *Ibid.*, 214, 138 (1882).

[7] *Ibid.*, 222, 102 (1883).

[8] *Z. physik. Chem.*, 20, 583 (1896).

alkyl group, causes a decrease in the order of cis-, trans- and α-substitu-
tion, and, also, with the molecular weight of the radical. Although the
density relations in stereomeric substances are proportional to the magni-
tude of the compression at the axial carbons, it does not follow from this
connection, that the density relations and those of the heats of combus-
tion, and in the case of acids of the affinity constants, always run parallel
to each other. For the chemical nature of the axial groups may be such,
that the segmentation due to the change of energy at the axial Δ-carbon
atoms may not be proportional to the decrease of bound energy in the
axial groups, or to that of the negative energy relations at the acidic
hydrogen atoms.[1]

As far as is known, however, the fumaroid form shows a greater density,
excepting in the esters of maleic and fumaric acids[2] and those of allocrotonic
and crotonic acids.

Since a reversion in the energy relations of maleic and fumaric acids
occurs in the formation of the sodium salts,[3] there is evidently
a possibility of a corresponding change taking place, but to a less extent,
with esterification. The catalytic transmutation of the maleic into the
fumaric esters[4] shows, however, that this is not the case, although their
physical and chemical properties and their energy relations are much closer
together than those of the acids. The carboxyl group in esterification
evidently looses much of its negative energy, and the esterified carboxyl
groups in furmaric acid, that are cis- to the nuclear hydrogen atoms, become
less capable of neutralizing the positive energy of these atoms, and this re-
sults in a separation of the axial carbon atoms. On the other hand, the
same change in maleic acid, by reducing the negativity of the carboxyl
groups which are in cis-position, increases their attraction, *i. e.*, it causes
an approach of the axial carbon atoms. Moreover, the cis-, much more
than the trans-relation of the carbalkyloxyl groups allows a better intra-
molecular neutralization of the chemical forces in them, through which the
axial segmentation in the maleinoid ester is increased to a greater extent.
Esterification, therefore, causes a relative reversal in the segmentation
relations of the axial carbon atoms, and to an extent sufficient to give
slightly larger densities to the maleic esters.[5]

----

[1] See footnote 7, under Heat of Combustion (p. 1684).

[2] Anschuetz, *Ber.*, **12**, 2280 (1879); Perkin, *J. Chem. Soc.*, **58**, 585 (1890); Walden,
Z. physik. Chem., **20**, 383 and 583 (1896); Walden and Swinne, *Ibid.*, **79**, 738 (1912).

[3] Michael, *Am. Chem. J.*, **39**, 14 (1908).

[4] Anschuetz, *Ber.*, **12**, 2282 (1879).

[5] The densities of the acids do not differ very much, *i. e.*, that of fumaric acid is
1.625 and of maleic acid is 1.590 (Tanatar and Tchelebijeff, *J. Russ. Chem. Soc.*, **22**,
549 (1890)). The value for ethyl fumarate is 1.0496 and for the maleate is 1.0658,
both at 25°. With the increase in the size of the alkyls, in the replacement of nuclear
and also of acidic hydrogen, the differences in the gravities decrease, which is in agree-
ment with theory.

The substitution of a nuclear hydrogen atom in these esters by a methyl group, introduces the different influences of cis-$\overset{5\ 6}{CH_3}$ in a fumaric ester, and trans-$\overset{5\ 6}{CH_3}$ in a maleic ester to the oxygens of one of the carbalkyl-oxyl groups. The positive influence of this methyl group is evidently greater in the fum. derivative, which explains why the densities of the (fum.) mesaconic esters become higher although only very slightly, than those of the (mal.) citra-compounds.

The experimental data on the densities of the ethyl esters of allocrotonic and crotonic acids are less satisfactory, but it is probable that the allo-derivative has a slightly higher value.[1] In allocrotonic acid the β-CH_3 is in the cis-5,6-, and in crotonic acid it is in the trans-5,6-position relative to the oxygens, and esterification may displace their density relations, which are probably not far apart in the acids, in favor of the mal. derivative.

J. Traube[2] has examined the molecular volume of the sodium salts of 6 pairs of stereomeric acids in dilute, aqueous solution. The salts of allocrotonic, dibromocrotonic (94°), cinnamic, furfuracrylic, furmaric and mesaconic acids show a larger volume than those of the stereomeric acids, and classifying the acids according to Wislicenus, Traube concluded that the salts of trans-acids show a larger volume than those of the cis-stereomers. This conclusion is not tenable, since allocrotonic is a cis-acid, and the dibromocrotonic acid melting at 94°, is not, as was assumed, a derivative of crotonic, but of allocrotonic acid.

Traube found further that the molecular volume of allocrotonic acid is somewhat, and that of citraconic acid considerably greater than those of the stereomeric acids, and concluded, as this is also the relation existing between the affinity constants, that the connection is explained by the difference in the "ionization" of the acids. This conclusion cannot be considered proven on account of the meagre experimental data, and no explanation was given why an increase in the "ionization" should cause an increase in the molecular volume.

Solubility.[3]—In the solution of an acid in water a neutralization of its negative energy to a greater or lesser amount by the positive energy of the solvent occurs, and the solubilities of stereomeric acids should stand, therefore, in a direct relation to their affinity constants, that is, the mal. form should show the greater solubility. Further, there should be an approximate proportionality between the differences in the affinity con-

---

[1] The value for the crotonic ester is 0.924 at 20° and for the allocrotonic ester it is 0.927 at 19° (Geuther, Z. Chem., 14, 243 (1871)). The latter value should be somewhat larger, as the allo-acid used contained more than 50% of crotonic acid.

[2] Ann., 290, 69 (1896).

[3] Michael, J. prakt. Chem., [2] 52, 345 (1895).

stants of such, structurally related acids and those of their solubilities. The first conclusion could not have been drawn, *a priori*, and, the latter relation is not valid, in the case of some β-halogen ethylenic acids, in which a reversion of the energy relations in the mother acids took place with the substitution of hydrogen by halogen. For instance, with the conversion of (fum.) crotonic acid into the (mal.) β-chlorocrotonic acid, the less solubility of the fum. mother acid might possibly have outbalanced the effect of the change in the energy relations.[1] Actually, however, in all known cases the maleinoid shows a greater solubility in water than the fumaroid form.[2] The rule does not necessarily apply to other solvents, even when, like water, they are relatively basic towards acids, *e. g.*, mesaconic acid is more soluble in ether than citraconic acid. Whether a relation exists between the affinity constants and the solubility factors in such solvents cannot be determined at present, owing to inadequate experimental data. Generally speaking, however, the maleinoid stereomer in all classes of ethylenic derivatives shows in solvents a greater solubility than the fumaroid body.

Melting Point.—Carnelly[3] connected the higher value in isomeric compounds with the more symmetrical structure, to which the rule of the writer[4] for stereomers conformed, that is, the fumaroid, spacially more symmetrical, form shows the higher melting point. This rule still holds for the stereomeric mono α- and β-derivatives of acrylic acid. With stereomeric, disubstituted β-products, it is impossible to decide which of two forms has the more symmetrical structure, and with β-halogen derivatives of stereomers, whose melting points differ considerably, the maleinoid modification may have, as has been explained before,[1] the higher value.

This relation may also appear in derivatives of such stereomeric acids, where the carboxyl group has been modified chemically. Thus the chloride of the mal. β-chlorocrotonic acid is a solid (94°) and the fum. derivative is a liquid, and the melting points of the naphthyl esters conform relatively to those of the acids. If the hydroxyl groups of these acids are replaced by NH_2, that is by a radical which in this position is decidedly positive to hydroxyl,[5] the maleinoid melts lower (100°) than the fumaroid derivative (110°), and it is not impossible that the energy rela-

¹ This Journal, **40**, 710 (1918).

² The two α-methyl-β-chlorocrotonic acids (Otto and Holst, *J. prakt. Chem.*, [2] **41**, 475 (1890); *Ber.*, **27**, 948, 1351 (1894)), if they are stereomeric, stand in the same relation to tiglic and angelic acids as the β-chlorocrotonic do to crotonic and allocrotonic acids. That is, the higher melting acid (73°) is a derivative of the fumaroid tiglic acid, but is maleinoid, because the halogen in it is cis- to the carboxyl group and it is, therefore, more soluble in water.

³ *Phil. Mag.*, [5] **13**, 116 (1882).

⁴ *J. prakt. Chem.*, [2] **52**, 345 (1894).

⁵ Michael. *Ibid.*, [2] **60**, 430 (1899); **68**, 496 (1903).

tions have been reversed in these compounds. On the other hand, the anilide (124°), naphthyl amide (169°), and phenylhydrazide (130°), of the mal. chloro-acid, in which NH_2 is replaced by less positive radicals, melt higher than those of the fum. derivative (105°, 155°, 114°).[1]

The former rule, that the fumaroid form always shows the higher melting point, is, therefore, too general and requires modification in the above sense. The explanation of the relation between melting point and structural, or stereostructural symmetry, should be based on the relative free energy contents of the compounds. According to the "thermochemical law of structure"[2] the symmetry of positive radicals in isomeric substances towards a common negative nucleus is connected with an increase in the heat of formation, i. e., with diminution of free energy, and this is also true in stereomeric bodies. As the change in the state of aggregation consists in overcoming the intermolecular attraction to a certain degree, it seems in accordance with the less free energy in the more symmetrical isomer and stereomer, that a greater heat increment is necessary to bring them into the liquid state.[3]

Boiling Point.—Boiling may be considered a continuation of the melting process; and the same reason why the fumaroid should melt higher than the maleinoid form exists in regard to their boiling-point relations. The former rule[4] that the fumaroid stereomer shows the higher boiling point is still valid, with the exceptions that occur in the relations between the esters of several dibasic ethylenic acids, where the maleinoid products show somewhat higher values.[5] When one of the acidic hydrogen atoms in maleic acid is replaced by sodium, the free positive energy still residing in the metal is further converted into bound energy and heat by the

[1] Autenrieth, Ber., 29, 1665 (1896); Autenrieth and Spiess, Ibid., 34, 189 (1901).

[2] Michael, THIS JOURNAL, 32, 1004 (1910)

[3] Werner (Lehrb. d. Stereochemie, 211–212) appears to have overlooked the work of Carnelly, Franchimont (Rec. trav. chim., 16, 142 (1897)) and the writer, and whatever original information he has added to the subject is not tenable. His suggestion that para and fumaroid derivatives have similar configurations is unwarranted, as stereostructural relations in such aromatic compounds are not known, and the assumption would imply the existence of stereomeric para derivatives. It is, also, arbitrary to assume symmetry in the structure of para in contrast to that of ortho compounds, as is evident by placing the groups in the first class of substances on the apexes of the hexagon, and not, as Werner has done, on the opposite sides. The connection between the melting points of aromatic isomers and structure is the same as that of fatty isomeric and stereomeric substances; that is, generally speaking, the body with smaller energy content shows the higher figure. Some of the exceptions to the rule may be explained as has been shown in the first paper, e. g., the reversed order in p-chloro-o-toluic and o-chloro-p-toluic acids which stand in the fum. and mal. relation, analogously to the reasons given for that in β-chloroallocrotonic and β-chlorocrotonic acids (THIS JOURNAL, 40, 710 (1918)).

[4] Michael, J. prakt. Chem., [2] 52, 345 (1895).

[5] Anschütz, Ber., 11, 1644 (1879); 12, 2280 (1880).

oxygens of the remaining carboxyl group. This final conversion is possible only to a much lesser degree in the corresponding acid fumarate, owing to the greater distance in space between the metal and the respective oxygens.[1] Corresponding changes occur again in the formation of the neutral salts, and the energy relations in them are close together, but the reverse of those in the acids, that is, there is an excess of positive energy in the fumarate, and probably, also, in the maleate, but certainly more free energy in the first than the latter salt. This mutation in the energy relations is plainly manifest in the gradual change in the properties of these and analogous derivatives It shows itself, for instance, in the much greater values of the secondary affinity constants of fumaric and mesaconic than those of the maleic and citraconic acids; in the greater value of K for the acid sodium fumarate than for the maleate;[2] in the alteration of the titration curves for fumaric and maleic acids, which are about the same afer half neutralization but are very different before,[3] and in the oxidation of potassium fumarate to the salt of the more acidic racemic acid,[4] while the decomposition of fumaric acid dibromide, by boiling, gives the weaker mesotartaric acid.[5]

A similar change in energy values occurs in the conversion of maleic and fumaric acids into their acid and neutral esters, since in the esterification process a neutralization of acidic energy takes place. In the acid esters the difference in the energy contents must be much less than in the acids, and that in the neutral esters should either approximate each other, or the relations might even be reversed.

The latter contingency is barred by the catalytic convertibility of maleic and citraconic esters into fumaric and mesaconic esters, and we should therefore expect from the energy relations, that the boiling points of these products should lie close together, but that the first-named esters should show somewhat lower values. Evidently, an unusual factor of importance enters into the property in this class of derivatives, which may possibly be that the maleinoid esters have a smaller specific heat than the fumaroid derivatives, and which could well cause the anomalous relationship in the boiling points.

For reasons explained above, the difference in the energy relation of maleic and fumaric acids and their homologs decreases with the replace-

---

[1] Michael, *Am. Chem. J.*, **39**, 14 (1910); Michael and Cobb, *Ann.*, **363**, 68 (1908), where the similar influence of ortho-hydroxyl group is discussed.

[2] Ostwald, *Z. physik. Chem.*, **9**, 559 (1892); Chandler, THIS JOURNAL, **30**, 694 (1908).

[3] Thiel and Roemer, *Z. physik. Chem.*, **63**, 725 (1908).

[4] Kekulé and Anschütz, *Ber.*, **13**, 2150; **14**, 713 (1880); Michael, *Am. Chem. J.*, **39**, 14 (1908).

[5] Lossen and Riebensahm, *Ann.*, **292**, 295 (1897); **300**, 5 (1899).

ment of nuclear or acidic hydrogen by primary alkyl groups,[1] and as it should, in a direct proportion to the size of the radical. The boiling points of such derivatives are in agreement with theory; thus, the difference, which between the methyl esters of the maleic and fumaric esters is $15°$, falls to $7.5°$ in the ethyl esters; and that between the methyl esters of citraconic and mesaconic acids is only $5°$, which decreases in the ethyl esters to $2.3°$.[2]

Viscosity.—According to Reyher[3] the viscosity constants of the sodium salts of aliphatic acids increase, generally speaking, with the decrease of the affinity constants of the corresponding acids; later, Lauenenstein[4] showed that irregularities occur, which are particularly noticeable in the salts of the aromatic acids. As sodium is a strongly positive metal, there is an excess of positive energy in such salts of most monobasic organic acids, and the viscosity relationship appears to stand in a direct relation to the free, positive energy in the salt.

In accordance with such a relation, the viscosities decrease with unsaturation; thus, in passing from (cis) sodium succinate to the comparable sodium maleate, the viscosity falls from 1.3914 to 1.2390, to increase with sodium fumarate to 1.3371. Although, in the next homologous series the values of the salts of the unsaturated acids are less than that of the saturated derivative, and in accord with the K_1 relations are larger than those of the maleate and the fumarate, the relations in the salts of the two saturated acids and in those of the ethylenic acids in this series are displaced.[5] Viscosity is a developed constitutive property, and the relation existing between it and the energy content would doubtlessly appear more marked, if compounds existing in solution in a strictly comparable molecular condition were used as the basis of comparison.

Capillarity.—Walden and Swinne[6] have recently determined the surface tensions and the temperature coefficients of the esters of a number of stereomeric acids. Hydrocinnamic and cinnamic esters have analogous

---

[1] The relation doubtless prevails, too, with secondary and tertrary radicals; the differences in this particular, and in some other physical properties, should decrease in the order of primary, secondary, and tertiary group.

[2] Evidently, the difference between the energy contents of ethyl citraconate and mesaconate is inconsiderable; in esters with so positive a radical as the tertiary butyl (Michael, *J. prakt. Chem.*, [2] **60**, 423, footnote 4, and 432 (1899)) the relations may be slightly reversed. That such changes in the energy relations are induced not only by aqueous solution, and by partial neutralization of the acids in question, but also by esterification, is ample evidence of the insufficiency and untenability of the explanation based on the ionization hypothesis (Ostwald, *Z. physik. Chem.*, **9**, 558 (1892)).

[3] *Z. physik. Chem.*, **2**, 744 (1888).

[4] *Ibid.*, **9**, 417 (1892).

[5] This subject will be considered in a later paper. See THIS JOURNAL, **40**, 119, footnote 2 (1918).

[6] *Z. physik. Chem.*, **79**, 726–746 (1912).

configurations, and along with unsaturation goes an increase in the first and a decrease in the latter values. This relationship is also shown with further unsaturation, and would probably appear between the stereo-structurally analogous allocinnamic and phenylpropiolic esters.

These chemists[1] use the capillary values of succinic and maleic *l*-amyl esters to exemplify the influence of double linkage; while the temperature coefficients likewise decrease with unsaturation, the surface tension values are practically identical. Stereomerically, the comparison is not justified as the fumaric ester is the real stereo analog.[2] The surface tension of maleic is somewhat greater than that of furmaric ethyl ester, and in the above instance, too, a decrease in the constant is undoubtedly caused by unsaturation. On the other hand, the values of chloromaleic and citraconic *l*-amyl esters are less than those of the stereomeric esters, and the interesting relationship exists that the surface tensions and the densities of these compounds stand in direct relation. This connection probably occurs in all other groups of derivatives formed in progressive unsaturation, provided they exist in a like conditions of molecular association, and the two first members of the series have similar stereostructures. For example, it is shown by the *l*-amyl esters of hydrocinnamic, cinnamic and phenylpropiolic acids.

Optical Activity.—In his researches with derivatives of *l*-amyl alcohol, Walden[3] showed that ethylenic α,β-unsaturation in esters causes an increase in the molecular rotation and in the dispersion, but that the values fall in the corresponding acetylenic derivatives. although they are still larger than those of the saturated bodies.

Walden[4] concluded from these relations that the transition from double to triple linkage is accompanied by a change in the nature of the unsaturation. and Werner[5] thinks that it indicates the magnitude of saturation to be greater in acetylenic than in the related ethylenic bodies.

As Walden[6] found that the fum. esters in the dibasic, ethylenic series have larger values than the stereomers, the same line of reasoning lead

---

[1] *Loc. cit.*, p. 746.

[2] Bruni, *Atti Accad. Lincei*, [5] **13**, I, 626 (1904). In accepting Bruni's results on the configurations of ethylenic derivatives, and disregarding those that lead to the classification of the acetylenic acids as fumaroid, it should be emphasized that only in this way is it possible to develop a consistent theoretical treatment of the physical and chemical properties of unsaturated compounds in their relation to configurations. Moreover, the acceptance of fumaroid stereostructures for the acetylenic derivatives implies an enormous repellent force between radicals like phenyl and carboxyl, which does not exist, and leads also into a maze of contradictions between properties and configurations (See *Am. Chem. J.*, **39**, 12 (1908); *Ann.*, **390**, 40 (1912)).

[3] *Z. physik. Chem.*, **20**, 569 (1896).

[4] *Loc. cit.*, p. 580.

[5] *Lehrb. d. Stereochemie*, 135 (1904).

[6] *Z. physik. Chem.*, **15**, 651 (1894).

to the conclusion that the extent of their unsaturation exceeds that in the mal. esters. Obviously, this conclusion is opposed to the other physical and to the chemical properties shown in these groups of substances. These apparent contradictions are due to the comparison of substances with dissimilar configurations. Hydrocinnamic and cinnamic, or succinic and fumaric, esters are stereomerically alike; the effect of further unsaturation should not be deduced from differences between the unlike cinnamic and phenylpropiolic esters, or fumaric and acetylenic dicarboxylic esters, but between those of the acetylenic derivatives and the similarly constructed allocinnamic and maleic esters, whose values are undoubtedly considerably smaller.[1] Further, there is no way of ascertaining directly the effect of acetylenic unsaturation on the relations of these properties, as stereostructurally similar, saturated bodies are not known.

Magnetic Rotation.—In no other physical property does the effect of ethylenic unsaturation vary to such a marked extent with the chemical nature of the compounds, and Sir W. H. Perkin[2] found that it always causes an increase in the values, and also, although from an examination of only a limited number of stereomeric bodies, that a fumaroid shows a higher value than the maleinoid form.

To determine the effect of unsaturation in the stereomeric ethyl esters, Perkin subtracted the values of the crotonate, oleate, maleate and citraconate from those of the butyrate, stearate, succinate and pyrotartrate, and found the rotations of the unsaturated derivatives to be $1.1-1.2$ units greater, which he considered the normal value for ethylenic, α,β-unsaturation. Since the difference between the values of crotonic and butyric esters is about the same as that between the dibasic esters, it has been concluded that the configuration of crotonic acid "is like that of maleic acid, which is confirmed by the chemical relations,"[3] i. e., $(H_3C)HC = CH(COOH)$.[4] Perkins' conclusions were written before Bruni[5] proved that crotonic and butyric, elaidic and stearic, and fumaric and succinic esters have analogous, fumaroid configurations, but the quotation given above was written years subsequently. Since the values for fum. and mal. stereomers vary considerably, it is evident that the normal value of ethylenic unsaturation can be obtained' only from stereomers with similar stereostructures, and, that therefore, the above

[1] These remarks apply also to the connections between configurations and the absorption spectra (Stewart, *J. Chem. Soc.*, **91**, 208 (1907)) where the relations appear to be similar.

[2] *J. Chem. Soc.*, **45**, 561 (1884); **49**, 205 (1886); **53**, 597 (1888); **67**, 261 (1895).

[3] "Smiles, *Relations between Chem. Constitution, Etc.*, 510 (1910); Smiles-Herzog, *Ibid.*, 615 (1914).

[4] Wislicenus, *Ann.*, **248**, 281 (1888).

[5] *Feste Lösungen*, 47 (Ahren's Sammlung, **1901**).

conclusion attaching a cis-configuration to crotonic acid is quite as untenable from the rotation data as that of Wislicenus from the chemical was shown to be years ago.[1]

The difference between the rotations of the similar (fum.) fumaric and succinic, and mesaconic and pyrotartaric, esters is 1.7–1.8, which is also that between β-ethoxy-crotonic and β-ethoxy-butyric esters; therefore the configuration of the first ester "is fumaroid"[2]: *i. e.*, $CH_3(EO)C = CH(COOE)$."

The correctness of this conclusion depends whether ethylenic unsaturation in all classes of fum. esters is represented by the above figure, which is doubtful, as the difference between the fum. crotonic and butyric esters is 1.1. Evidently, no importance can be attached to conclusions based on such imperfect data, and, under any circumstance, the configuration of the fum. β-ethoxycrotonic ester is not the above, but (CH_3)-$EOC = CH(COOE)$.[3]

Perkin[4] applied magnetic rotation to the study of keto- and enol-tautomerization, basing his calculations on the assumption that aliphatic, ethylenic unsaturation is represented by the difference between the values for crotonic and butyric esters (1.1) and using additive values in the substitution of different atoms, or in the increment of radicals. These assumptions can only be approximately correct, which in compounds of different chemical nature, *e. g.*, the mono- and di-ketones, may decidedly effect the conclusions regarding the quantitative proportions between the enol and keto forms. But, the method may only serve to show with some degree of certainty, whether a substance is the keto derivative or exists largely in that form, as no experimental data is known that gives the rotation difference between fum. and mal. fatty, α,β,Δ-esters. Further, it is not known, whether in the enolization of complicated keto derivatives, like acetylacetone, the mal. or fum. enol, or a mixture of both these is formed.[5]

Heat of Combustion.[6]—Louguinine[7] in 1888 found that the heats of combustions of maleic and citraconic acids are greater than those of fumaric and mesaconic acids, and Stohmann[8] concluded, from results on quite a number of related stereomeric acids, that this relationship may be gener-

[1] Michael, *J. prakt. Chem.*, [2] **52**, 349–365 (1895).

[2] Smiles and Smiles-Herzog, *Loc. cit.*

[3] Michael, THIS JOURNAL, **40**, 712 (1918).

[4] *J. Chem. Soc.*, **61**, 800 (1892); **65**, 815 (1894).

[5] A discussion of "magneto-optic exaltation" will be given in a later paper, in connection with that of the Thiele hypothesis.

[6] Michael, *Am. Chem. J.*, **39**, 1 (1908).

[7] *Compt. rend.*, **106**, 1290 (1888); *Ann. Chem. phys.*, [6] **23**, 186 (1890).

[8] *J. prakt. Chem.*, [2] **40**, 202 and 357 (1890); **42**, 373 (1891); **45**, 530 (1892).

alized; that is, the unstable modification of such stereomers have the greater heats of combustion, and that they lose energy in passing over into the stable forms. Evidently, if the transmutation of a maleinoid into the fumaroid stereoform is accompanied by the conversion of free into bound energy at the axial carbon atoms, and also spacially between the atoms grouped about them, the latter substances must have smaller heats of combustion, since in the change some of the atomic energy in the maleinoid derivatives is dissipated as heat.

Stohmann[1] also stated that in stereomeric esters the unstable modifications show the larger heats of combustion, and lose energy in passing over into the stable forms. However, no experimental data to confirm the statement were published in his papers, and the only observations bearing on such stereomeric bodies are on maleic and fumaric, and ethyl-cumaric and ethyl-cumarinic, methyl esters. The greater heat of combustion of a maleinoid over that of a fumaroid acid is due to a less complete intramolecular, atomic neutralization, and the heat of conversion value should be larger for a pair of acids than for their esters, since the carboxyl group has lost considerable negative energy in the act of esterification. This is the relation found for the above-mentioned liquid aromatic esters.[2]

On the other hand, Ossipoff[3] found the difference between maleic and fumaric methyl esters to be 6.8 Kg-Cals., while for the acids 6.2 (Stohmann), 6.5 (Roth) and 8.2 Kg-Cals. (Louguinine) are the ascertained values. Roth and Stormer call attention that the last value (8.2) is greater than that (6.8) for the esters, but there is no doubt that Louguinine's figure is too high and that 6.2–6.5 represents the correct value, which is less than that between the esters.

This apparent exception to the conclusion stated above has a physical and chemical cause. First, fumaric methyl ester is a solid (102°), while the maleic ester is a liquid, and the real heat of conversion is 6.8 Kg-Cals. less that of the heat of conversion of solid into liquid furmaric methyl ester. This value has not been determined, but Stohmann[4] found that it is considerable (4.9 Kg-Cals.) with the much lower melting (78°) methyl succinate. Second, the cis-relation of the carbmethoxy groups in maleic ester permits a proportionately greater conversion of the free energy

[1] J. prakt. Chem., 45, 531 (1892).

[2] Roth and Stormer (Ber., 46, 278 (1912)). These chemists (Ibid., p. 261)) in stating that Stohmann proved the rule for isomeric acids, and also for maleic and fumaric acids, and that it has been accepted for stereomeric acids on inadequate experimental data, appear to have overlooked that Stohmann (J. prakt. Chem., [2] 45, 531 (1895)) showed its validity for the principal stereomeric acids.

[3] Ossipoff, Compt. rend., 109, 310 (1889); Ann. chim. phys., [6] 23, 186 (1890).

[4] J. prakt. Chem., 40, 349 (1890).

of the alkyl groups into bound energy and heat than the trans-relation does in the fumaric derivative.[1]

It is evident that the heat of conversion of liquid maleic into liquid fumaric methyl ester must be considerably smaller than that of the corresponding acids, and that the values of the heats of combustion of the liquid esters must lie close together. That the maleic esters still represent the maleinoid forms, is apparent from their convertibility into fumaric esters by catalysis, even then when both of the derivatives are liquids.[2]

The Relations between the Chemical Properties and the Configurations of Unsaturated Acids.

Addition.—In unsaturated acids the additive relationships to structure and stereostructure are identical. Velocity of addition depends on the quantity of the free energy that is manifest at the unsaturated carbon atoms or at the carbonyl group, and on its quality in respect to that of the components of the addenda; reactive capacity on the sum total of the free and bound energy and chemical affinities that there come into play, which constitute the chemical factors entering into the entropy increase.[3]

The affinity values of the unsaturated carbons should vary with the chemical nature of the other elements in the molecule,[4] and the magnitude of this influence should accord with their spacial positions to them and should be indicated in the "scale of combined influence."[5] Further-

[1] Roth and Oestling (*Ber.*, **46**, 37 (1912)) show that "Stohmann's rule" is not valid for the isomeric pinonic and tanacetone keto-carboxylic acids. Stohmann (*J. prakt. Chem.*, [2] **40**, 357 (1890)) intended the rule only for simple (*"stellingsisomeren"*) not for complicated acids of unlike structures, especially when the branched groups are unsaturated and in different positions to the carboxyl groups. It was theoretically improbable that the total free energy in such derivatives, which finds an expression in the heats of combustion, should always be proportional to the free energy manifest at the acidic hydrogens. They state, however, that the rule holds for trimethylene carboxylic, crotonic, allocrotonic and vinylacetic acids, in which the heat of combustion and affinity constants increase in the above order. The allocrotonic acid used in the Stohmann determinations contained at least 50% of crotonic acid (Michael, *Ber.*, **42**, 322, footnote 4) and its real affinity constant must certainly be decidedly greater than that of vinylacetic acid. Roth and Oestling state further, that the "stability" of these acids decrease in the order mentioned above. "Stability" as a general chemical term is quite as indefinite as "decomposibility" and "reactivity" (see Michael, *J. prakt. Chem.*, [2] **68**, 496 (1903)), and conveys no precise meaning, unless it is coördinated in a particular physical or chemical system. No better illustration could be adduced than Roth and Oestling's contention that vinylacetic acid is less "stable" than allocrotonic acid, for the statement is as ambiguous and meaningless as it is inexact.

[2] Anschuetz, *Ber.*, **12**, 2282 (1879).

[3] If a solvent is used, and it enters into the composition of the "polymolecule," it may radically influence both factors, but especially the velocity (Michael and Hibbert, *Ber.*, **41**, 1091 (1908)).

[4] THIS JOURNAL, **32**, 995 (1910).

[5] *Ibid.*, **32**, 999 (1910); **34**, 849 (1912); **40**, 708 (1918).

more, the nature of their effect should be to change the affinities of the Δ-carbon atoms in the direction of their own values to the addenda, and owing to the "chemical plasticity" of carbon, its free energy must be extremely susceptible to such influence.[1] Substituting a hydrogen in ethylene by an acid radical containing oxygen, changes the affinities of the Δ-carbon atoms in the direction of those of the latter element, $i.\ e.$, it reduces the values for halogen, although it increases their free energy. The resultant of such a structural change is to diminish the addition velocity and the addition capacity for halogen in proportion to the affinity constant of the acid whose radical is introduced, and to the number of such groups. This influence is greater in unsymmetrical than in symmetrical substitution, as the change in affinity values of a single Δ-carbon must be the dominating factor in determining the velocity and capacity of halogen addition.

The accumulation of such acid radicals, or even a single one when it is so negative as NO_2, at a Δ-carbon atom, may reduce its affinity value for halogen to practically nil, and addition will not take place. Corresponding replacement by alkyl increases the affinity of the Δ-carbon atoms for halogen, but decreases their free energy; both of the changes are in proportion to the positivity[2] and number of the groups introduced. Substitution, in this case, results in an increased velocity of reaction, but a number of very positive radicals, like the tertiary alkyl groups,[3] through the reduction of the free energy in the Δ-carbons atom, may result in practically no change or even a falling off in the velocity.

The shifting of the unsaturation from the α,β- to the β,γ-position removes the Δ-carbons from the 3,4 to the 4,5 place from the oxygens, and, since 3 is much more important than 5 in the "scale," the velocity of halogen addition in monobasic acids with similar configurations is greatly increased.[4] Methyl introduced into acrylic acid in the β-posi-
  5 6
tion, $i.\ e.$, CH_3 to the oxygens, reduces the negativity of that element more when it is in the cis- than in the trans-position, and in accord with this relation is the greater addition velocity of allocrotonic over crotonic acid.
  5 6

This accelerating influence of cis-, over trans-CH_3 is again shown in the larger values of angelic acid (19×10^{-5}) over tiglic acid (9.9×10^{-5}); β-dimethylacrylic acid (700×10^{-5}) shows a very large increase, owing to both the methyl groups influencing the same Δ-carbon atom, and a further great augmentation occurs in trimethylacrylic acid (2200×10^{-5}),
  4 5
which is due to the strong positive influence of the CH_3 on the oxygens.

[1] THIS JOURNAL., **32**, 995 (1910).

[2] Michael, $J.\ prakt.\ Chem.$, [2] **60**, 432 (1899).

[3] $Loc.\ cit.$, 423, footnote 4; **64**, 107 (1901); $Ber.$, **39**, 2790 (1906).

[4] Sudborough and Thomas, $J.\ Chem.\ Soc.$, **97**, 714 and 2450 (1910).

As would be expected, the extent of the influence of the methyl group is modified with larger, primary alkyl groups, but not the relative relations in the homologous, stereomeric derivatives; thus, the mal. oleic and erucic acids add bromine with greater velocity than the respective fum. derivatives.[1]

The influence of bromine and methyl on the additive capacity for bromine in acids of the type $R_2C = CR(COOH)$, has been treated by Bauer,[2] who gives the rule that addition occurs until R is entirely replaced by Br, or by Br with ("neben") methyl.[3] Perbromoethane decomposes on heating into perbromoethylene and bromine,[4] and, since replacing a Br in the latter body by carboxyl greatly diminishes the affinity of the Δ-carbon atoms for halogen, the inertia of tribromoacrylic acid accords with theory. Replacing a halogen in this acid by methyl should facilitate addition, and that substitution and not addition products have been obtained from the stereodibromocrotonic acids,[5] is probably due to the replacement of the methyl hydrogen atoms by halogen proceeding easier, *under the conditions of the experiments*, than halogen addition.

The addition velocities of such bromo-acids have not been investigated. In acids of the same group, a mono-α-Br derivative should unite less readily than either of the stereo-β-products, as in it the retarding influences are both exercised on the same Δ-carbon atom; and in the latter compounds, the trans- easier than the cis-form. Further, the affect of replacing hydrogen in these acids by alkyl should be to accelerate the velocity in the order of trans-, cis- and α-substitution.

The affinity of nitrogen for bromine is also extremely small, but that CN reduces the additive capacity more than $COOC_nH_{2n+1}$, in the same position to the Δ-carbon atoms,[6] is the result of the partial neutralization of the negative energy in the oxygen atoms by the positive alkyl group. This effect shows itself, too, in the easier additivity of the esters under comparable conditions over the corresponding Δ-acids, which should increase with the relative positivity of the alkyl group.

In several addition reactions, with compounds whose Δ-carbon atoms show but slight additive capacity for bromine, a balanced reaction has been observed,[7] which is due to the affinity of the solvent employed for the halogen. Indeed, the preliminary formation of a "polymolecule" of halogen

[1] Sudborough and Thomas, *Loc. cit.*

[2] *Ber.*, **37**, 3318 (1904).

[3] The latter statement is too vague and broad; it may be correct if changed to read by Br and one β-methyl. Perbromomethacrylic acid should add bromine.

[4] Merz and Weith, *Ber.*, **11**, 2239 (1878).

[5] Pinner, *Ibid.*, **28**, 1877 (1895).

[6] Bauer and Moser, *Ibid.*, **40**, 919 (1907); *J. prakt. Chem.*, [2] **72**, 201 (1905).

[7] Bauer and Moser, *Loc. cit.*

and solvent undoubtedly precedes the addition in some cases, which explains the sometimes observed dependence of the velocity on the solvent, notwithstanding that the compound and the addition product are both in solution.

It is generally accepted, that the fum. modification of the dibasic, α,β,Δ-acids shows a smaller addition velocity for halogen than the mal. form, but, since the insolubility of a Δ-acid as well as that of the product of addition are large deterring factors,[1] and they are usually greater in the fum. product, no sure conclusion is furnished by the available experimental data. According to Anschuetz[2] the esters of maleic and fumaric acids, whose energy relations[3] and physical properties are much closer together than those in the acids, add bromine approximately with like readiness, even with the methyl esters where the fum. form is a solid and the mal. derivative is a liquid.

A comparable though smaller approach in the energy contents and in the physical properties takes place in the dibasic acids with the replacement of a nuclear hydrogen atom by an alkyl group, and accordingly, the additive velocities of such derivatives lie closer together than those of the mother substances.

Since citraconic anhydride and mesaconic acid unite readily in sunlight with bromine, an increase in the addition capacity with nuclear methylation is indicated theoretically. In reality, dimethyl-maleic anhydride and dimethyl-fumaric acid do not unite at all with bromine.[4] The spontaneous anhydrization of dimethyl-maleic acid has been explained as resulting from the spacial approach of the axial Δ-carbons, which must also occur in dimethyl-fumaric acid, and it is possible that this slight spacial distance may be a deterring factor.[5]

Although the anhydride does not add bromine, the methyl ester of the corresponding acid does so readily,[6] and the anhydride itself unites with chlorine.[7] These facts do not necessarily conflict with the above view. On the one hand, the chemical nature of the ester gives its axial Δ-carbons greater additive power than those in the anhydride and their segmentation is less, and, on the other hand, chlorine has not only more free energy and a greater affinity for carbon than bromine, but a smaller atomic volume.

Alkylene iodides decompose readily with loss of the halogen. The re-

[1] Michael, *J. prakt. Chem.*, [2] **52,** 291 (1895).

[2] *Ber.*, **12,** 2282 (1879). Unfortunately no quantitative data on this interesting subject are known.

[3] See above, under Density.

[4] Fittig, *Ann.*, **304,** 117 (1898).

[5] Bischoff, *Jahrb. Chem.*, **1,** 176 (1890).

[6] Baeyer, *Ann.*, **258,** 162 (1890).

[7] Michael and Tissot, *J. prakt. Chem.*, [2] **46,** 382 (1892); **52,** 340 (1895).

placement of a hydrogen by carboxyl adds to this instability, and in a direct relation to the spacial distances of the oxygen atoms from the carbon atoms joined directly to the iodine. This reduction of the affinity value is so great with the α,β,Δ-carbons in ethylenic acids, as to render such addition products unstable under ordinary conditions, $i.\ e.$, these acids do not unite with the halogen.[1]

It may seem anomalous, therefore, that the α,β-acetylenic acids are able to add iodine,[2] although very much less readily than chlorine and bromine. There are several reasons for this exceptional behavior. First, iodine shows a greater affinity than chlorine for oxygen, and a further decrease is shown by bromine;[3] the carboxyl must, therefore, relatively decrease the affinity values of the completely Δ-carbon atoms for the halogens, inversely in the order named, since there is no hydrogen joined directly to them to offset these affinity relations. Second, the affinity of carbon for halogen increases with unsaturation,[4] which is undoubtedly connected with the accompanying increment in the free energy.[5]

Elimination.—The writer[6] showed experimentally that the relative ease of addition of halogens and halhydric acids to unsaturated derivatives, and the elimination of the addenda from the addition products, stand in a direct relation, even when stereomeric compounds are involved in the reactions. A theoretical foundation of these relations is possible in the dibasic acid series, but it is less evident for monobasic derivatives, and the question will not be considered in this paper.

Werner[7] believes that the relation could have been foreseen from Ostwald's[8] "law of reaction stages," according to which the least stable

---

[1] It is probable that the monobasic ethylene β,γ- and γ,δ-acids are capable of adding iodine. If so, the first derivatives should unite somewhat more readily, and their addition compounds should show less instability towards heat, than the isomeric products from the latter acids.

[2] Liebermann and Sachse, *Ber.*, **24**, 412 and 2588 (1891); Bruck, *Ibid.*, p. 4118; **26**, 845 (1893).

[3] For this reason, and because of its greater free energy and larger affinity value for carbon and hydrogen, chlorine should require more carboxyl or nitrile groups than bromine to prevent addition. The difference in the behavior of such relatively quite negative carbon towards these halogens is characteristically shown by CO. Probably all or at least most of the unsaturated compounds that are inert towards bromine should be capable of uniting with chlorine.

[4] *J. prakt. Chem.*, [2] **61**, 448, rule II (1900).

[5] The relations in the addition of halhydric acids to Δ-acids will be treated in a separate paper, in connection with the influence of solvents on the course of the reactions, which has been reinvestigated experimentally.

[6] *J. prakt. Chem.*, [2] **52**, 289 (1895); *Ber.*, **34**, 4221 (1901).

[7] *Lehrb. d. Stereochemie*, **1904**, p. 210.

[8] *Grundlinien d. anorg. Chem.*, **1900**, p. 215. The statement of facts in the form of a rule is not an explanation, as Ostwald supposes (*Ibid.*), and the reactions advanced in its support, *e. g.*, the preliminary formation of hypochlorites (p. 216) and the products

of the possible reaction compounds is always primarily formed. The direct formation of fumaroid addition products from acetylene derivatives and halhydric acids 'or bromine, not to mention other facts, renders such a conclusion untenable, as they also do Ostwald's supposed law.

According to J. Wislicenus the addition of halogen to ethylenic, stereomeric compounds, and subsequent elimination of halhydric acid from the addition products, with the acceptance of cis-processes leads to an inversion in the stereomeric types. Notwithstanding that such cis-processes, generally speaking, have long since been experimentally disproven, and also that attention was called to the fact that the intraconversion of the mal. into the fum. derivative, and *vice versa*, was not dependent on the above theoretical explanation,[1] such stereomeric reactions are still frequently quoted as evidence in favor of Wislicenus' views.[2] As far as has been investigated, all such additions to stereomeric ethylenic compounds are trans-processes, as also are the eliminations of halhydric acids from the addition products.[3] These relations were clearly indicated in the behavior of the acetylenic compounds, where the additions are largely or completely trans-processes, and where trans-eliminations proceed more readily than cis-processes, since the intramolecular shifting of atoms or groups, which is involved, experiences greater hindrance in them than in the less unsaturated ethylenic derivatives.

Substitution.—With unsaturation of contiguous carbon atoms, one of which is directly joined to a non-metallic atom, part of the bound energy thus liberated passes over into bound energy between the Δ-carbon and the negative atom, which causes a large increase in the hindrance to its direct replacement, and at the same time, a great increment of free energy appears at the Δ-carbons. For these reasons a chemical change involving the non-metal in such substances, possibly with a few exceptions, passes over from a substitution process to that of a preliminary elimination or an addition.[4]

The further behavior of the primary reaction product depends on the chemical nature of the above-mentioned negative component, on the

of progressive oxidation, leads one to believe that he not only overlooked Dalton's atomic theory, but that each salt is formed alone under given experimental conditions. The "rule" is illustrated graphically by steps leading to the highest product of oxidation, and the statement is made that "a further step ('Stufe') between chlorate and oxygen is realized when $KClO_3$, or another chlorate, is carefully heated." This reminds one of S. C. H. Windler's (*Ann.*, **33**, 308 (1840)) famous conversion of $Mn(C_2H_3O_2)_2$ into $Cl_{24}.H_2O$, and Ostwald was unaware that most chlorates do not yield perchlorates.

[1] Michael, *J. prakt. Chem.*, [2] **52**, 362 (1895).

[2] For instance, in Stewart, *Stereochemistry*, **1907**, p. 182; Meyer-Jacobson, *Lehrb. org. Chem.*, **1**, 487, 488, 527 (1910); also, in numerous papers in chemical literature.

[3] Michael, *Loc. cit.*, footnote 1; THIS JOURNAL, **40**, 714 (1918).

[4] Michael, *J. prakt. Chem.*, [2] **37**, 473 (1888); **60**, 435 (1899); **61**, 448, rule II (1900).

hindrance to the separation of hydrogen from an adjacent carbon, and on the additive capacity of possibly reformed Δ-carbons for the reagent used.

Although stereostructural and structural chemical changes are closely allied in this field, a comprehensive discussion of these complicated relations will be reserved for a later paper,[1] and the application of the underlying principles will be shown by analyzing several reactions involving stereomeric changes.

It should be premised that stereostructural like structural chemical reactions tend to form new systems involving the maximum possible entropy change, $i. e.$, the greatest possible conversion of the free energy into bound chemical energy and heat, and that chemical like mechanical force starts in the direction of the least hindrance to the change.[2]

Tanatar[3] found that $CH_2 = CBrCOOH$, heated with alcoholic KNC and subsequent saponification, yields the maleate, a statement which has been doubted,[4] as the current, superficial views on this subject indicate the formation of a salt of $CH_2 = C(COOH)_2$.

The first phase in this reaction is the formation of a bromoacrylate with liberation of HCN, and, as this substance shows a great additive power in a nascent state, it and not the cyanide unites with the Δ-carbon atoms. In this addition the negative CN radical must go to the β-carbon, not only for its free energy is relatively positive to that in the α-carbon, but in so doing, after the addition, a more complete, intramolecular neutralization of the atomic energy is realized. Furthermore, this course of the reaction is favored more by the behavior of NC—CH$_2$—CHBr—COOK towards the somewhat basic KNC than by that of the other possible compound, $i. e.$, CH$_3$—CBr(CN)—COOK. In the first product, the affinity of H to C in CH_2 is greatly decreased by the negative CN, and the elimination of HBr proceeds with a slight expenditure of chemical energy;[5] in the other compound, such a course of the reaction would proceed with such difficulty, that the further change would consist in the direct replacement of Br by CN. The first product, as a saturated derivative,[6] should assume the configuration representing the maximum capacity to neutralize the alkali, which is when CN is in the cis-position to —COOK, $i. e.$, (NC)—CH$_2$—CHBr—(COOK), and which, through loss of HBr and saponification, should give the maleate.

The affinity of iodine for carbon and hydrogen is far less than that of

[1] In connection with considerable experimental material; see $Ibid.$, **60**, 414 (1899); $Ber.$, **28**, 2512 (1895); **29**, 1792 (1896).

[2] $J. prakt. Chem.$, [2] **60**, 293 (1899); THIS JOURNAL, **32**, 990 (1910).

[3] $Ber.$, **13**, 159 (1880).

[4] Meyer-Jacobson, $Lehrb. org. Chem.$, **1**, 412 (1910).

[5] $J. prakt. Chem.$, [2] **60**, 292, rule VIII; and 361–369 (1899).

[6] THIS JOURNAL, **40**, 707 (1918).

bromine, and the value is so small in the alkylene iodides that they decompose easily with liberation of the halogen.   With a compound like acetylene iodide there is a possibility of direct halogen replacement; indeed, the solid modification by heating with alcoholic KNC and saponifying the product thus formed has been converted into a fumarate.[1]

It would be a mistake to conclude definitely from this synthesis that the change proceeds by direct substitution.   The primary action of the somewhat basic KNC may consist first in splitting off HI, and the next in the union of the iodo-acetylene thus formed with the nascent HCN; a repetition of these processes would lead, with trans-eliminations and trans-additions, to fumaric nitrile: $(H)IC = CH(I) \longrightarrow HC \equiv CI \xrightarrow{HCN}$ $(NC)HC = CH(I) \longrightarrow NC - C \equiv CH \xrightarrow{HCN} (NC)HC = C(H)CN$. According to this interpretation, the maleinoid acetylene iodide would likewise pass over primarily into iodo-acetylene, and in that case it would also yield the fumaroid nitrile.

That certain stereomeric halogen derivatives give, apparently by substitution, the same reaction product may be explained in an analogous manner.[2]   For   instance, the stereomeric sodium β-chlorocrotonates heated with alcoholic sodium ethylate give the fum. ethoxy-derivative. Each of these chloro-salts lose HCl readily under the conditions of the experiments and form the tetrolate, which should pass over, as such acetylenic derivatives add alcohol easily in the presence of ethylate, by trans-addition into the fum. β-ethoxycrotonate.

We can now explain why these β-chlorocrotonates with alcoholic sodium ethylmercaptide give stereomeric thio-derivatives.[3]   Ethylmercaptane is decidedly more acidic than ethyl alcohol, and the mercaptide for this reason is much less basic, and therefore, less capable of splitting off HCl from the salts; further, the additive capacity of the mercaptide to Δ-carbon atoms is much greater than that of the ethylate.   On account of these properties, the primary action of the mercaptide is to unite with the Δ-carbons, and then, whether the replacement of halogen in the saturated derivatives thus formed proceeds by substitution or by elimination and subsequent addition, stereomeric β-thioethoxy compounds must be formed.

Evidently, the use of such synthetic reactions to establish the configuration of unsaturated compounds is of doubtful value, when the structures of the simpler compounds are such that the hindrance to reaction by elimination and addition is less than to direct substitution, and the results should only be used in confirmation of stereostructures, which are ascertained by more certain methods.
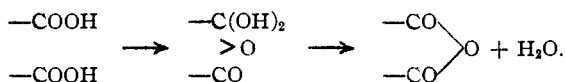
[1] Keiser, *Am. Chem. J.*, **12**, 99 (1890).

[2] Friedrich, *Ann.*, **219**, 322 (1883).

[3] Autenrieth, *Ibid.*, **254**, 222 (1889).

Anhydride Formation.—Van't Hoff explained the facile anhydriza-tion of the maleinoid, ethylenic dibasic acids by the spacial nearness of their carboxyl groups, in comparison with those in the fumaroid forms. A closer analysis leads to the conclusion that the main contributory cause is the slight hindrance to the formation of five-membered rings from groups in the cis-position, owing to the proximity in space of certain atoms in positions one and five. In every respect, the anhydride corresponds to the lactone formation,[1] and provided a less resistance to the course of a decomposition in another direction does not exist, the effect of heat on all such hydroxy and dibasic acids should lead, more or less readily, to the formation of lactones or anhydrides. That the fumaroid acids do not yield anhydrides by physical or chemical means is not because of the im-possibility of a fumaroid anhydride, but because the resistance to a trans-mutation into the corresponding maleinoid configuration of the acid, with subsequent dehydration, is less, and therefore the energy required is less than in the direct anhydride formation. Indeed, such fumaroid an-hydrides would be bodies of slight stability, and owing to the great strain existing in the fumaroid rings, they would pass over, more or less readily, into the maleinoid forms.

The phases in the lactone formation from γ- and δ-hydroxy acids, are the addition of hydroxyl to carbonyl, and then the loss of water; that is in this case an intramolecular esterification;[2] and the formation of an acid anhydride, irrespective of the basicity of the acid, proceeds in a similar manner.

$$\begin{array}{ccc} \text{—COOH} & \text{—C(OH)}_2 & \text{—CO} \\ & \searrow\text{O} & \diagdown\text{O} + H_2O. \\ \text{—COOH} & \text{—CO} & \text{—CO}\diagup \end{array}$$

Here, too, the carbonyl oxygen and the acidic hydrogen are the atoms with the greatest free energy content that may be involved in the change, and which have the requisite affinity relations.

The chemical factors that increase the facility of this ring formation are (1) constitutive changes causing spacial approach of the involved carboxyls, and (2) those which reduce the affinity of the hydrogen to the oxygen of the hydroxyl, and the additive capacity of the respective car-bonyl for that group, since with each change the intramolecular addition process is facilitated. Replacing a nuclear hydrogen in maleic acid by a methyl group increases the bound energy of the remaining nuclear cis-hydrogen and of the carboxyls, causing increased segmentation of the axial carbons, and with it ease of anhydride formation;[3] repeti-

---

[1] Michael, *J. prakt. Chem.*, [2] **60**, 338 (1899).

[2] Michael, *Ibid.; Ber.*, **42**, 312 (1909).

[3] Krafft, *Ibid.*, **28**, 2588 (1895); **42**, 214 (1904); Fittig, *Ann.*, **304**, 124 and 145 (1899). Since the accumulation of alkyls near hydroxyl and carboxyl groups favor ring formation, possibly fumaroid lactones and anhydrides may be obtained from poly-

tion of the chemical change gives in pyrocinchonic acid a substance that decomposes spontaneously into anhydride and water. The successive replacement of the nuclear hydrogens by halogens also favors anhydrization, because the free energy in halogen and hydrogen or that in two halogens,[1] which are here in cis-relations, tend to neutralize each other spacially; and particularly, because halogen greatly increases the additive capacity of carbonyl for water.[2]

Stereomutation.[3]—Even after the radical difference presupposed by van't Hoff between the spacial relations in the axial carbons of saturated and unsaturated derivatives had been experimentally disproven,[4] various attempts were made to explain stereomeric introconversions in the latter group on that basis, as well as upon such hypotheses as the intermediate formation of α-lactones,[5] which are unknown and could not possibly show the properties assumed for them; or that of intermediate tetramethylene derivatives,[6] which are known but show properties incompatible with the suggestion.

The behavior of stereomers, and that of other classes of substances, towards heat energy are essentially alike. For instance, barium oxide and carbon dioxide are inert at a very low temperature; under ordinary conditions they unite with loss of free chemical energy and heat, and at a

alkylated derivatives. Although dimethylfumaric acid and acetyl chloride at 100° give pyrocinchonic anhydride, perhaps a fum. derivative may be obtained from the silver salt and the reagent at a lower temperature; or, from di-alkyl fumaric acids where the alkyls are sec. or tert. radicals.

[1] Michael, *Ann.*, **390**, 40 (1912).

[2] Michael, *Ibid.*, **363**, 32, footnote 25 (1908). Owing to the affinity of such very negative carbonyl for water, the anhydrides of these dihalogen acids very likely pass back in aqueous solution, to a more or less extent, into the dihydroxy lactones through which they are formed in the anhydrization of the free acids. Wegscheider (*Ber.*, **36**, 1543 (1903)) considers it probable that pyrocinchonic anhydride goes partly over in solution to such a compound, which also is not unlikely, as the accumulation of alkyl groups about a carbon likewise favors its affinity for hydroxyl (Michael, *J. prakt. Chem.*, [2] **60**, 423, footnote 4 (1899); **64**, 108 (1902)).

[3] This word is suggested in place of stereotransmutation.

[4] Michael, *J. prakt. Chem.*, [2] **46**, 209, 425 (1892). In his *Lehrb. d. Stereochemie*, 1904, p. 222, Werner makes the historically inaccurate statement that Anschuetz (*Ann.*, **254**, 174 (1889)) and Fittig (*Ibid.*, **259**, 30 (1890)) first, then Skraup (*Monatsh.*, **12**, 107 (1891)) called attention to the impossibility of the Wislicenus transmutation explanation, which was based on the instability of addition products that in reality are stable, and then Michael (*J. prakt. Chem.*, [2] **46**, 209 (1892)) proved it experimentally in numerous cases. This inverted order of priority, which is frequently met in the literature, is due to the oversight of the above-mentioned chemists that in the writer's first criticism (*Ibid.*, **38**, 21 (1888)) of the Wislicenus hypothesis, practically all the reasons advanced later by them against that chemist's interpretation are clearly stated, and given in proof of its untenability.

[5] Liebermann, *Ber.*, **23**, 2513 (1890); **28**, 1444 (1895).

[6] Stewart, *Stereochemistry*, **1907**, p. 189.

certain higher temperature the barium carbonate thus formed must either volatilize or decompose into barium oxide and carbon dioxide, with absorption of heat and increase of free energy. Likewise, heat energy enables maleic acid to overcome the hindrance and pass over, with loss of free chemical energy and heat into fumaric acid, which at a sufficiently high temperature must either, with increase of free energy, volatilize, decompose or be transmuted into maleic acid.[1] In one case the change is inter-, in the other intra-molecular, which is characteristic of stereomeric changes, as is also the fact that largely in consequence, generally speaking, they take place within a comparatively small range of temperature.

Evidently, any structural modification in a mal. derivative which decreases the bound energy between the atoms in the axial groups, i. e., decreases the segmentation of the axial carbons, and at the same time, increases the free energy, must facilitate stereomutation. For instance, replacing the hydroxyls of maleic acid by chlorine, enhances the free energy, while it decreases the bound energy that existed between the carboxyls; and in striking contrast to maleic acid, its chloride passes over slowly at ordinary temperature into fumaryl chloride.[2] Or, allo-β-chlorocrotonic acid ($94°$) is only partially stereomerized at $164°$,[3] but at a much lower temperature its chloride in one distillation is completely stereomuted.[4]

Delisle[5] has shown that heating aqueous sodium citraconate, even up to $190°$, gives only traces of the mesaconate; but an excess of caustic soda causes the conversion at $100°$, and with a velocity increasing with the concentration of the alkali; further, that the transmutation is reversible. It was explained above, why the considerable difference in the free-energy relations of the corresponding acids disappears with their conversion into salts, which is evidently connected with the pronounced stability of the citraconate. To effect a change more readily, chemical energy must be added to the system, which is done by the excess of alkali uniting to form either basic salts or "polymolecules," whose stability in solution should increase with the excess of the base. Further, it is evident that the energy relations in the salts favor a balanced reaction.

A further discussion of stereomutation is beyond the scope of the paper; it may be mentioned, however, that as great confusion exists here as in any other field in stereochemistry. This is due, in part, to the frequent use of untenable theoretical conceptions, and to the fact that it is the dump-

[1] Anschuetz and Wirtz, *Ber.*, **18**, 194 (1885).

[2] See Michael, *Am. Chem. J.*, **39**, 5 (1908) for explanations of the effects of physical influences.

[3] Michael and Schulthess, *J. prakt. Chem.*, [2] **46**, 265 (1892).

[4] Autenrieth, *Ber.*, **29**, 1665 (1896).

[5] *Ann.*, **269**, 74 (1892).

ing ground for any pair of easily introconvertible compounds, no matter how improbable it is that they are stereomeric in the usually accepted sense.

Catalysis.—This phenomenon depends on the formation of a "polymolecule" of the organic substance and the catalyte,[1] when the added free energy in the system enables the increase of entropy, accompanying the transmutation of a maleinoid into a fumaroid derivative, to take the place at a lower temperature, or when it is already proceeding, with acceleration of velocity. This hypothesis, which offers the only known explanation of the relations between the quantity of the catalytic reagent and the course of the reaction,[2] and, also, the effect of energy in *status nacens*,[3] has been already applied to explain a number of stereomeric reactions.[4]

In this paper another problem, the catalytic behavior of bromine in stereomeric rearrangements, will be considered, as in this field untenable conclusions have been drawn from apparently paradoxical facts. Van't Hoff's[5] observation, that maleic acid in concentrated aqueous solution gives at once in sunlight and with a trace of bromine a precipitate of fumaric acid, was continued by J. Wislicenus,[6] who was able in this way to stereomute up to 93.5%, and who extended the method to allocrotonic and angelic acids. Wislicenus also found that tiglic dibromide is partially converted into angelic dibromide, and this fact, with the observed limination in the conversion of maleic acid, led him to conclude that the reactions are reversible, *i. e.*, that the fumaroid acids are partially, catalytically convertible into the maleinoid stereomers.

Fittig[7] showed that citraconic acid in solution and in the dark is not stereomerized but adds bromine slowly, while in the sunlight up to 68% of mesaconic acid is formed, and also concluded that the catalytic reaction is reversible. He apparently supported the view by proving that dimethyl furmaric acid is transformed in chloroform solution by traces of the halogen to the extent of about 90% into the maleinoid acid, which then decomposes into anhydride and water.

Wislicenus assumed cis-addition to angelic and tiglic acids, and accordingly grouped the dibromides with the mother substances, but we

[1] Michael, *Am. Chem. J.*, **39**, 3 (1908); *Ann.*, **390**, 43 (1912).

[2] Michael, *Am. Chem. J.*, **39**, 4 (1908).

[3] *Ibid.*, 5. Here chemical explanations of Skraup's (*Monatsh.*, **12**, 133–141 (1891)) observations are given. There is no theoretical or experimental foundation for this chemists view that catalysis is directly contingent on secondary chemical processes; on the contrary, facts are known that disprove it; nor does his "chemical resonance" hypothesis throw any light on the subject. It is merely an improbable suggestion.

[4] *Loc. cit.*, pp. 4–14.

[5] *Dix Années dans l'histoire d'une théorie*, **1887**, p. 90.

[6] *Verh. saech. Gesell. zu Leipzig*, **1895**, p. 489.   Wislicenus overlooked van't Hoff's earlier observations.

[7] *Ann.*, **304**, 117 (1898).

now know that trans-addition takes place, and a comparison of the con-figurations of the dibromides shows that a reversion in the energy rela-tions has occurred.[1] The conversion of the maleinoid tiglic dibromide into the fumaroid angelic derivative is, therefore, not anomalous.

With the symmetrical introduction of two methyl groups into maleic (K_1, 1170×10^{-5}) and fumaric (K_1, 90×10^{-5}) acids, changes in the rela-tive energy relations occur which bring those of the new acids much nearer together than they are even in citraconic (K_1, 340×10^{-5}) and mesa-conic (K_1, 70×10^{-5}) acids.[2] This means that the stereomutation of dimethyl fumaric acid requires much less energy than that of fumaric acid; but, the final product in the conversion is dimethyl maleic anhy-dride, which is formed spontaneously from the acid, $i.\ e.$, with loss of free energy, and which may be the factor which determines that the change, dimethyl fumaric acid $\longrightarrow$ dimethyl maleic anhydride plus water, proceeds with a decrease of free energy. Evidently, this reaction can-not be considered an illustration of a catalytic transformation proceeding with an increase of free energy in the newly formed substance.

That the subject of catalysis, and of balanced reactions, in organic chemistry is in such confusion is largely due to the improbable theoretical conceptions with which it has been burdened by the physical chemist. It begins with the definition that catalysis is due to the presence of cer-tain substances which accelerate the velocity of reactions already pro-ceeding in their absence.[3] The free energy in any mechanical or chemical system must be able to overcome the hindrance to a change, which is otherwise not conceivable. To assume, as is done in the often-quoted, typical illustration, because hydrogen and oxygen may be united catal-ytically, or at a high temperature, the union is proceeding at all tempera-tures above absolute zero, is certainly not scientific.

Again is is stated that a catalyte cannot influence the "affinity of a proc-ess," an unfortunate phrase, as a process does not show an affinity; and that its "action does not extend to the motive force of a reaction, but to overcome the hindrance to the progress." The latter, indefinite assumption is contrary to the function of catalytes acting chemically, which depends on the formation of "polymolecules," whose motive forces thereby become greater. Such a relation, however, does not contradict the second law of thermodynamics, since in the final phase of the reaction the catalyte is present without any change in its energy content.

Furthermore, the statement that a "catalyte does not take part in the reaction" is open to criticism as being ambiguous, and the further state-

[1] THIS JOURNAL, 40, 715 (1918).

[2] Loc. cit., p. 719.

[3] Nernst, Theoretische Chemie, 1907, p. 574. The following definitions are taken from this book, as it is usually considered authoritative on physical-chemical subjects.

ment that a catalyte must "invariably change the velocity of the reaction in a reverse direction," is by no means beyond doubt. The latter assumption is closely connected with the physico-chemical explanation of the cause of balanced reactions, but in the only organic reaction that has been thoroughly examined experimentally, $i.\ e.$, iso-$C_4H_9Br \rightleftarrows$ tert.-C_4H_9Br, this explanation has been proven to be untenable.[1]

This brings us back to the assumptions of Wislicenus and Fittig, that bromine does not catalytically convert the maleinoid, ethylenic acids into the fumaroid forms completely, because the reactions are reversible. A chemical reaction is always feasible under ordinary conditions, if there is a possibility of an increase of entropy, which itself depends on physical as well as on chemical changes; in fact, on the sum-total of all the involved energy changes.[2] To convert furmaric acid into maleic acid would require a considerable expenditure of energy, which in the above case could have only been obtained from the solvent, but, as maleic acid is much more soluble in water, such an endothermic reaction is extremely improbable. From any point of view furmaric acid should be formed in theoretical amount barring the small quantity of dibromide that is formed at the same time,[3] if it were completely insoluble in the surrounding media; and the insolubility factor undoubtedly dominates in the extent of this stereomutation. Indeed, it may be the means of transforming a fumaroid into a maleinoid derivative catalytically, $e.\ g.$, mesaconic acid is much more soluble in ether than citraconic acid, and if its "polymolecule" with bromine should have sufficient energy to overcome the hindrance to stereomerization, the maleinoid acid would be formed to an extent depending on the insolubility factor.[4]

Esterification.[5]—The direct process in the crotonic acid series was examined by Michael and Oechslin,[6] and no general relationship could be traced between the velocity and the affinity constants; butyric acid showed a much greater velocity than either of the stronger crotonic acids. Later, Thomas and Sudborough[7] proved that this relation holds between other saturated and ethylenic α,β-unsaturated acids, and deduced the following

[1] Michael and collaborators, $Ann.$, **379,** 286 (1910); **392,** 92 (1912); THIS JOURNAL, **38,** 654 (1916). Compare Brunel, $Ann.$, **384,** 245 (1911); THIS JOURNAL, **39,** 1978 (1917). The writer believes that the relations disclosed in his investigations on this subject are not uncommon in reversible organic reactions.

[2] THIS JOURNAL, **38,** 654, footnote 4 (1910).

[3] Wislicenus, $Verh.\ saech.\ Gesell.\ zu.\ Leipzig,$ **1895,** p. 489.

[4] An investigation of this subject, with the use of different solvents and also with the products kept in solution, would be of great theoretical interest.

[5] Many of the conclusions given by Werner in his $Lehrbuch\ der\ Stereochemie$ (pp. 377–400) on this subject are untenable, as the different relations to structure shown in direct and catalytic esterification were not taken into consideration.

[6] $Ber.$, **42,** 322 (1910).

[7] $J.\ Chem.\ Soc.,$ **101,** 317 (1912).

rules from their experimental results: (I) Where the difference in the strength of the acids is not very marked, the unsaturated α,β-acid is esterified less readily, although it is "slightly stronger;" and (II) unsaturated β,γ-acids are esterified more readily than the corresponding saturated acids. Rule (I) is based in part on a comparison of the affinity constants of acids with dissimilar configurations; thus, the value of (trans) cinnamic acid (3.5×10^{-5}) is compared with that of (cis) hydrocinnamic acid (2.3×10^{-7}), and the true analog, allocinnamic acid (14.2×10^{-5}), is decidedly stronger. Indeed, it is more than doubtful if a general connection exists between the affinity constants and the esterification velocities of these acids, although in respect to the latter values, the following rule appears to be valid: the cis- and trans-forms of ethylenic α,β-acids, and their α- and β-monochloro-derivatives, are esterified less readily than the corresponding saturated acids. Rule (II) was deduced from the behavior of trans-β,γ-acids, and as no data for the corresponding cis-derivatives is at hand, it should be restricted to trans-compounds.

The rules show conclusively that in direct esterification the determining factor cannot be, as supposed by Stewart,[1] the "*strength* of the acid," as the stronger,[2] unsaturated trans-α,β-acids under (I) show much smaller velocities, while the likewise stronger trans-β,γ-acids under (II) show larger values than the corresponding saturated derivatives. Thomas and Sudborough's results also prove that in isomeric trans-acids, unsaturation in the α,β-position has a much greater retarding effect than in the β,γ-place, which is opposite to their influence on the affinity constants.

In direct esterification, the writer[3] assumed the primary formation of a "polymolecule" of acid and alcohol; then, in accordance with Henry,[4] that of the addition product $R-C(OR)(OH)_2$, which decomposes into ester and water. According to this view, the velocity depends primarily on the relative quantity of the free energy in the carbonyl of the acidic group, and on the affinity relations of its carbon and oxygen to the alcohol addendum. If the effect of a chemical change is to increase all these factors, then an acceleration necessarily follows; otherwise, the change depends on a resultant which cannot be foreseen with certainty.

The transition from propionic to acrylic acid removes $\overset{3}{H} + \overset{4}{H}$ and $\overset{4}{H} + \overset{5}{H}$ from the C and O of the carbonyl, which increases the free energy in that group, and, also, the affinity of the oxygen to the alcoholic hydrogen of the addendum, but decreases that of the carbon to the $C_nH_{2n+1}O-$ group to a greater extent, as the influence of $\overset{3}{H}$ is greater than $\overset{5}{H}$, and car-

[1] *Stereochemistry*, p. 321.

[2] In the hexyl series the relations are reversed, THIS JOURNAL, **40**, 719 (1918).

[3] *Ber.*, **42**, 312 (1908).

[4] *Ibid.*, **10**, 2041 (1877).

bon is chemically the more "plastic" element.[1] Since the resultant of these forces is decidedly negative, we should expect the same relation between other pairs of similar saturated and unsaturated acids (Rule (I)).

The change from acrylic to crotonic acid introduces $\overset{4\ 5}{CH_3}$ and $\overset{5\ 6}{CH_3}$ as positive groups in the trans-positions to the $\underset{1}{C}$ and $\underset{1}{O}$, which cause a decrease in its free energy, and a proportionately greater decrease in the affinity of the carbon than increase of that of the oxygen to the addendum. These are the same affinity relations as before, and the velocity should decrease.

A further fall in the velocity takes place with the substitution of the cis-H in crotonic acid (1.4%) by CH_3, i. e., dimethylacrylic acid (0.6%), because it introduces the positive $\overset{4\ 5}{CH_3}$ to the carbon and $\overset{5\ 6}{CH_3}$ to the oxygen of the carbonyl; and for the same reason the value for trans-α,β-pentenic acid (0.8%) is less than that of crotonic acid. The shifting of double linkage from the $\overset{2\ 3}{\alpha,\beta}$- to the $\overset{3\ 4}{\beta,\gamma}$-position brings the positively acting $\underset{1}{CH_2} + \underset{1}{CH_2}$ to the CO, in place of the negative influence $\overset{2\ 3}{CH} + \overset{3\ 4}{CH}$, and is accompanied by a large velocity increase (Rule (II)). Thomas and Sudborough[2] also found that the values of the saturated, normal valeric acid (13%) and β-phenylpropionic acid (18.2%) are less than those of the β,γ-unsaturated, ethylidene propionic (22.6%) and benzylidene propionic (39.4%) acids; and they give the rule, that β,γ-unsaturation increases the velocity. This conclusion is too broad and should be restricted to trans-β,γ-acids. In this change, $\overset{4}{H} + \overset{5}{H}$ to the carbon and $\overset{5}{H} + \overset{6}{H}$ to the oxygen of the carbonyl are eliminated, and theoretically the velocity should decrease, but to a much smaller extent than with α,β-unsaturation.

According to these chemists, if the α,β,Δ-acids are very much more acidic than the corresponding saturated derivatives the velocity relations are reversed, and the first acids are easier esterified. This conclusion appears to have been based solely on a comparison of the acid methyl maleate (21.8%) and the acid methyl succinate (11.3%), but the true stereo analog is the acid methyl fumarate,[3] whose affinity constant should be less than that of the acid maleate, and whose esterification velocity may not be as great as that of the acid succinate. The great increase in the reaction velocity of the maleate is due to a carbon and the oxygens of the carbmethoxyl group being in the important 5 and 6 cis-

[1] Michael, THIS JOURNAL, **32**, 995 (1910).

[2] Thomas and Sudborough, J. Chem. Soc., **101**, 317 (1912).

[3] Bruni, Atti accad. Lincei, [5] **13**, I, 626 (1904).

positions to the carbonyl of the carboxyl, which greatly increases its free energy and additive capacity for the alcohol.

In catalytic esterification a primary product of mineral acid catalyst and alcohol[1] has been assumed, which unites with organic acid to form a still larger "polymolecule;" and the next phase may be similar to that in the direct process. Owing to the strong negative character, which the

[1] See Friedel, *Bull. soc. chim.*, [2] **24,** 166, 241 (1877); Archibald and McIntosh, *J. Chem. Soc.*, **85,** 919 (1904); Goldschmidt, *Ber.*, **39,** 711 (1906); Michael, *Ibid.*, **42,** 311 (1909). Base and acid are relative terms, and the oxygen in organic compounds derived from water usually possesses its property of uniting with acids to form more or less stable, salt-like addition products. The compound from

HCl and $(CH_3)_2O$ may be represented by $(CH_3)_2O{\displaystyle <}{\begin{array}{c}H\\ \\Cl\end{array}}$, but it is a mistake to

suppose that the bound energy, which in hydrochloric acid holds the elements together (see THIS JOURNAL, **32,** 991, 1004 (1910)) is involved in its formation to any extent; or, that its existence is not partly due to the interchange between the free energy in the carbons and the hydrogens of the ether and the components of the acid. Indeed the complicated compositions of many of these addition products are probably due to the formation of "polymolecules" mainly by the neutralization of free energy of the constituent molecules. The question of when localized addition occurs has been solved in only a few cases; and there is no doubt that Baeyer's "oxonium theory" is responsible for many formulas that appeal more to the sense of humor than to that of reason. Kendall and Boorge (THIS JOURNAL, **38,** 1735 (1916)) believe that there is no apparent justification for favoring the localized addition of the mineral acid to the hydroxyl oxygen of the organic acid rather than to the carbonyl oxygen; but it is obvious that the first oxygen is relatively less negative, and if such an addition really takes place, it should be at that point.

In his interesting papers on such addition compounds, Kendall has drawn certain theoretical conclusions, which the facts presented do not seem to warrant. Thus (THIS JOURNAL, **36,** 251 (1914)), the slow sulfonation of aniline, which proceeds only at a high temperature, in comparison to the "instantaneous" formation of the double compound of *p*-cresol and sulfuric acid at a low temperature, is in the latter case "in agreement with theory that the reaction is an oxonium salt formation and ionic in its nature." This does not appear to be a correct assumption, for it is not aniline but an acid aniline sulfate that is sulfonated, which is important because it now contains a negative group, which protects the nucleus from direct substitution. Numerous organic reactions demonstrate the untenability of the supposed relation between the time element and the "ionic nature" or, "oxonium salt formation." For instance, the union of alkyl iodides with alkyl sulfides proceeds from explosive violence at ordinary or instantaneous at a lower temperature, to slow union or inactivity at ordinary temperature, according to the nature of the alkyl radical.

Further, the medium may have an enormous influence on the velocity of an organic reaction, and it has been proven that no relation exists between this capacity and its power of ionization or its unsaturated nature (Menschutkin, Kahlenberg, Michael and Hibbert, *et al.*). Indeed, in some reactions the velocity is in inverse ratio to the ionization of the addenda (Michael and Brunel, *Am. Chem. J.*, **41,** 118 (1909); **48,** 267 (1912)).

Generally speaking, it is undoubtedly true that products formed chiefly in the interchange of free energy show a greater velocity formation than those involving proportionately little free and much bound energy. In most cases the energy changes

mineral acid catalyst gives the "polymolecule," it seemed more in line with chemical analogy to assume that, like the "polymolecule" of hydrochloric acid and an alcohol, it decomposes, with the substitution of the alcoholic hydroxyl by the acyl radical, into catalyst, ester and water.[1]

Thomas and Sudborough[2] have objected to the above interpretations, and state "our own view is that the direct and catalytic esterification are essentially the same, the only difference being that in the former case the organic acid is its own catalyst." This old and widely accepted but indefinite view is not proven, nor does it offer an explanation of the mechanism of the process. In the direct method, the organic acid is its own catalyst, if more than one of its molecules and the alcohol unite to form a "polymolecule," which should then change chemically according to the above-mentioned Henry hypothesis. The purpose of such a gathering of acid molecules would be to overcome the hindrance in the addendum to the addition, i. e., to aid the separation of the hydroxyl hydrogen of the alcohol by the resulting accumulation of the free energy in the system. In the esterization of acetic acid, which even in a vapor state consists largely of "polymolecules," this may occur, but this view cannot in a general sense be considered probable, although in some other cases direct esterification may proceed in such a manner.

The velocity in catalytic esterification appears to depend primarily on the affinity of the "polymolecule" of the mineral acid catalyst and alcohol to the acid, as expressed in the sum total of the free negative energy in the carboxyl group, and should be, owing to the strong negative character of the "polymolecule," inversely proportional to the negative value of that acidic group.[3] That this carboxyl value does not necessarily coincide with the affinity constant of the respective acid, is seen in the relations of the velocity values to the affinity constants in stereomers of the type $RHC = CRCOOH$. Owing to the direct union of CH_2 to $COOH$ in ethylenic β,γ-acids, and the less intimate relation of the acidic group to the Δ-carbons than in α,β-acids, it agrees with the above view that the members of the first group of monobasic acids show greater velocity values

are continuous, that is, the "internal maximum heat" (Wohl., *Ber.*, **40**, 2290 (1907)) from the conversion of free into bound energy favors instability of the primary product, and more or less rapid rearrangement of the bound energy ensues, with partial transformation into heat energy.

Helmholtz's idea, that all reactions are "ionic," transferred by Ostwald into organic chemistry without any discrimination or judgment, has been the source of endless futile and unwarranted speculation, and has without doubt seriously hampered the development of organic chemical theory.

[1] Michael, *Ber.*, **42**, 311 (1909). These views have received further confirmation in the investigation of Baumé and Pamfil (*Compt. rend.*, **115**, 426 (1912)).

[2] *J. Chem. Soc.*, **101**, 318 (1912).

[3] Michael, *Ber.*, **42**, 312 (1909).

than their isomers in the latter class. Anomalous, however, is the more rapid esterification of trans-β,γ-acids than the corresponding saturated derivatives, but this may be due to the comparison of acids with unlike stereostructures.

Sudborough and Roberts[1] found that in substituted acrylic acids the "β-compounds are, as a rule, esterified more readily than the α-isomeride," and later, Sudborough and Davies[2] state that "a comparison of the values for tiglic and dimethyl acrylic acid at once shows that these acids are exceptional." The rule applies, however, in all known cases, if it is restricted to trans-β-compounds.

Tiglic and dimethylacrylic acids do not constitute exceptions to the modified rule, as in them the effect of a cis-alkyl group is compared to that of the group in the α-position. Indeed, the velocity values shown by the di- and tri-methylacrylic acids indicate that allocrotonic acid should show a smaller value than methylacrylic acid, that is, cis-β-methyl probably exerts a greater retarding influence than the radical in the α-place. This strong inhibitory effect of cis-alkyl group manifests itself in Sudborough and Lloyd's[3] rule for stereomers of the type $YHC = CX(COOH)$, in which X and Y are alkyls, as the cis-derivatives are esterified very much slower than the trans-forms.

Further, Sudborough and Roberts[4] believe that the position of β-chloroallocrotonic acid is "remarkable, as there is very little difference between its constant and that of α-chlorocrotonic acid." In comparing the effect of substituents on the constants of stereomeric acids, the derivatives of mother substances with similar configurations should be used; otherwise there are two different factors involved in the problem. We should, therefore, compare α-chlorocrotonic acid (0.163×10^{-5}) with allo-β-crotonic acid (0.438×10^{-5}), where an increase occurs, and the values show that cis-β-Cl inhibits catalytic esterification to a less extent than does α-Cl, which agrees with theory.

The esterification constant (0.905) of allocinnamic acid (14.2×10^{-5}) is only slightly less than that (0.937) of cinnamic acid (3.5×10^{-5}); in α-chlorocinnamic acid (9.7×10^{-5}) and α-chloroallocinnamic acid (107×10^{-5}) the proportionate divergence ($0.028 : 0.101$) increases, because phenyl in the first acid is in the cis-position to the halogen, and in thus neutralizing its negative energy to a larger extent, does not increase the negative energy in the carboxyl to the same degree. It is of interest that the close relationship in the affinity constants of β-chlorocinnamic (28×10^{-5}) and β-chloroallocinnamic (27×10^{-5}) acid, is also shown

[1] *J. Chem. Soc.*, **87**, 1842 (1905).
[2] *Ibid.*, **95**, 977 (1909).
[3] *Ibid.*, **73**, 93 (1898).
[4] *Ibid.*, **87**, 1842 (1905).

in the esterification constants (0.355 and 0.371),[1] that is, the relative influences of the phenyl and chlorine in these positions on the acidic hydrogens also extend to the total negative energy in the carboxyls.

Three decades have just passed since the appearance of van't Hoff's, *"Dix années dans l'histoire d'une théorie,"*[2] and J. Wislicenus's, *"Ueber die räumliche Anordnung u. s. w."* and a backward and forward glimpse at the subject seems in place.

It was unfortunate for the development of stereochemistry that van't Hoff connected it with optical activity, through the tetrahedral form of the carbon atom. Lossen[3] and Auwers[4] have shown that the views connected with this shape conception lead to conclusions incompatible with our ideas on dynamic energy, and the writer,[5] that its application by van't Hoff to explain static and dynamic intramolecular, atomic relations and those due to unsaturation, is opposed by innumerable chemical facts. Further, that optical asymmetry is purely a mechanical phenomenon, resulting from the effect of four unequal chemico-mechanical forces on the atom, and properly belongs to mechano-chemistry.[6]

Using van't Hoff's conceptions as the theoretical basis, Wislicenus, in his remarkably lucidly written monograph, developed them in their application to unsaturated compounds in the only possible logical and consistent manner, indeed, it was generally accepted that the configurations of such bodies were definitely and permanently established by the theoretical and experimental investigations of this chemist, and van't Hoff[7] did not hesitate to make this statement without reserve in the above-mentioned book. In the long theoretical and experimental controversy that followed it was finally conclusively proven[8] that all of the

[1] *J. Chem. Soc.*, **87**, 1843 (1905).

[2] In memory of J. H. van't Hoff, equally great as a man and a profound and original thinker in Science, the following note from him is published, which was written in English and received with a copy of this book: "By the same post, I take the liberty of offering to your kind attention a little work of mine, that treating on isomerism perhaps may attract notice from your side. If it shortens the distance between your conception of 'alloisomerism' and mine, I shall be amply rewarded. In any case, my compliments and my best wishes for the interesting facts on isomerism that your investigations lay clear."

[3] *Ann.*, **204**, 336 (1880); *Ber.*, **20**, 3306 (1887).

[4] *Entwickelung der Stereochemie*, **1890**, p. 22.

[5] *J. prakt. Chem.*, [2] **43**, 587 (1886); **46**, 209, 381 (1889); **52**, 289, 359 (1892).

[6] Michael, *Ber.*, **34**, 3647 (1901); *J. prakt. Chem.*, [2] **75**, 117 (1907). Modifications or further developments of this idea have been advanced by Winther (*Z. physik. Chem.*, **60**, 590, 641, 756 (1907)); Baly (*Z. Electrochem.*, **17**, 211 (1911)); Richards (This JOURNAL, **36**, 2435 (1914)) and Wesson (*Ibid.*, p. 2522). There seems no doubt that optical activity would result if four unequal, purely mechanical forces could be brought to bear on a carbon atom.

[7] *Loc. cit.*, p. 70.

[8] *J. prakt. Chem.*, [2] **52**, 359 (1895).

configurations of Wislicenus had to be changed, as they had been based
on the acceptance of cis-processes, whereas in reality trans-processes
are the rule.   But the new classification showed the inherent weakness
of the fundamental stereomeric conceptions, as such trans-processes
not only find no expression in them, but they are in direct conflict with
the cis-processes that must be assumed to explain ring formation.[1]

As it has been possible to coördinate the chemical and physical proper-
ties of unsaturated stereomers to a very considerable extent with the
stereostructures used in these papers, there must be an intimate correla-
tion between them and the spacial relations of the atoms as they actually
exist in the molecules.   Perhaps the future will solve the difficulties of the
present by configurations based on dynamic, instead as now, on static
conceptions.   It is hoped that these papers will draw attention to the
chaotic condition of much of the available experimental data, that neces-
sarily serve as the basis of theoretical discussion.   The physical proper-
ties of stereomeric compounds, even when they belong to the same car-
bon series, have seldom been determined under comparable conditions,
and their interrelations are often obscured by values obtained from bodies
of apparent impurity or by methods of doubtful accuracy.   In many
cases of great importance, the molecular states of aggregation of the sub-
stances are unknown, which makes their physical constants of little value
for theoretical discussion.

The ideal investigation would start from the simplest derivative from
which stereomers may be formed by substitution. For instance, with acrylic
acid as the mother substance for the monobasic α,β,Δ-acids, and from the
properties of products formed by the replacement of α-, cis-, and trans-β-
hydrogens, the values of atoms and groups in definite positions to the
chemical functions involved in the processes could be ascertained.   Al-
though such values would vary somewhat in different compounds, with
sufficient experimental data allowance could be made for structural
differences, and the relationship between properties and the spacial
relations of the atoms, could then be traced with far greater cer-
tainty than is now possible.   Such studies of the physical and chemical
properties of stereomeric derivatives will give an insight into the
mechanism and nature of chemical change, and the intramolecular
atomic relations and mutual influences, to a far greater degree than is
possible with any other group of compounds.   And, as the properties
of these isomeric substances depend so obviously on the spacial varia-
tions of the atoms, they should help to dispel that curious survival of the
type theory, that a comprehensive organic theory can be based on the
intrarelations of more or less large groups of atoms, instead of on those

[1] *J. prakt. Chem..* [2] **52,** 289 (1895).

of the atoms themselves,[1] whose persistence still not infrequently leads to theoretical conclusions that are incompatible with the facts from which they are drawn.

The law of entropy is valid only in a system that is cooling off, and it is intimately related to the energy transformations connected with changes in the states of aggregation. Hence, all cis- derivatives in the energy sense strive to pass over into trans-compounds; and the transmutations are primarily facilitated by heat, because the assimilated energy assists in overcoming the hindrance to the entropy increase. If a plant were exposed to sufficiently intense, extraneous and chemically readily assimilable, energy, such as ultraviolet light and certain forms of electric energy, it might bring about a reversion in the energetic relations. The free energy might now be increasing, and the dominant law in such a system would no longer be the entropy principle, but one, which may be designated, the law of *extropy*.

Under the present conditions, the law of entropy represents a resultant, in which the conversion of free into bound energy and heat greatly predominates over the inverse relations. Indeed, it is probable that the extropic energy relations in cosmos have not received the consideration that they merit. Is it not possible, for instance that a purpose of some of the less refrangible light waves in the economy of nature is to act as diluents to the ultraviolet rays which are so active chemically, and thus prevent the too rapid accumulation of free chemical energy? Or, is it not conceivable that in other planetary systems extropy may prevail, and that those mysterious disappearances in space may be connected with too great an accumulation of free energy?

It is because it is possible in the group of stereoisomerides systematically to add or take away energy, that this class of compounds is incomparably better fitted than any other for the study of the relations of energy to properties and chemical structure. In the ability of the chemist in the laboratory to reproduce with them changes in the relations of energy to matter, which are similar to those constantly occurring in nature, is an invaluable means to a better insight into nature's chemical secrets.

CAMBRIDGE. MASS.

[1] *J. prakt. Chem.*, [2] **60,** 285 (1899).