INFRA-RED ABSORPTION SPECTRA.

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INTRODUCTION.

MANY investigators have examined the characteristics of absorption spectra, endeavoring to ascertain a possible systematic relation between absorption spectra and chemical constitution. That some relation exists is almost axiomatic in view of the many relations known to exist between chemical structure and other physical properties. With this end in view, all regions of the spectrum have been examined: the visible, the ultra-violet, and the infra-red; but the whole matter is still in a state of great confusion as can readily be seen by examining the summaries given in Kayser[1] and in Winkelmann.[2] This state of confusion, in spite of the excellent and more recent work of Coblentz,[3] indicated the need of a more detailed and if possible more systematic study than had heretofore been made, of some small part of the field. The part chosen for this investigation was the infra-red, and the substances first selected for examination were the liquid alcohols, acids, and esters, for besides permitting a study of homology and isomerism, the most promising lines of attack, these classes of substances also permit a study of the results of certain chemical reactions. Quite naturally these substances were supplemented by others whose desirability was recognized as the work progressed.

APPARATUS.

A general idea of the arrangement of the apparatus is given by Fig. 1. The radiation from a Nernst glower A was focused by the mirror B upon the slit D after passing through the absorption cell C. The cone of rays was made parallel by the mirror E, passed through

[1]Handb. d. Spectr., Vol. 3.
[2]Handb. d. Phys., Vol. 3.
[3]Investigations of Infra-red Spectra, Carnegie Inst., 1905.

the rock salt prism F, reflected from the plane mirror G, and focused by the mirror H upon the bolometer I. The bolometer was connected to a mirror galvanometer J, whose swings were photographed on a plate at K. The spectrometer was turned and the plate dropped by means of gears operated by the chronograph clockwork L. In order that the adjustments might be permanent, all of this

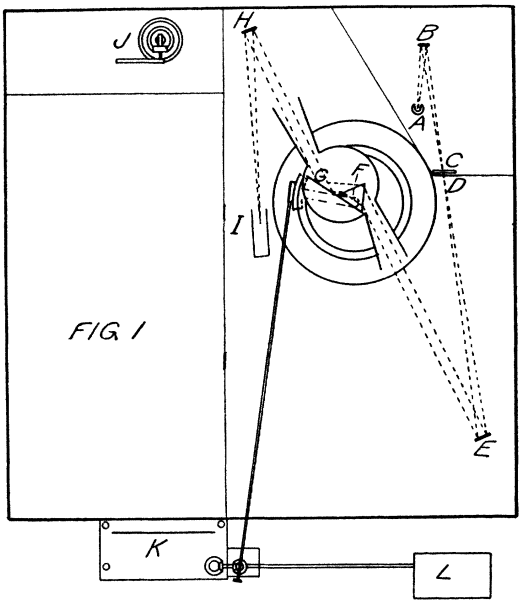


FIG. 1

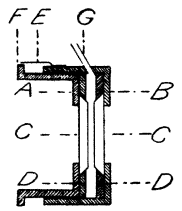


FIG. 2

Figs. 1–2.

apparatus, with the exception of the chronograph, was mounted on a solid brick pier with a large stone top.

A 98-volt, 0.8-ampere, D.C. Nernst glower was used as the source of radiation; for the sake of steadiness it was mounted in a cavity in a piece of fire brick. The current was supplied by storage

batteries and was kept at the rated value except when working beyond 10μ, when it was raised to 0.9 amp.

It was rather difficult to design a suitable absorption cell, as it was necessary to make one that would hold a few drops of some volatile liquid without marked evaporation for an hour and a half or two hours, the time needed for an examination of the liquid. The cell finally made was very satisfactory, inasmuch as a thin film of benzol remained in it for a day before evaporating. It consisted of two brass parts, *A* and *B*, Fig. 2, movable, one within the other, on a carefully cut no. 40 thread; each part carried a rock salt plate *C*, as shown, the plates being held in position by bevelled clamp rings, *D*, and screws. The rock salt plates were polished by hand in the usual manner with rouge on a surface of plant pitch and resin after being turned to size, bevelled to fit the clamp rings, and made plane parallel on a lathe.

The cell was filled by simply pouring a few drops of the liquid into B while in a horizontal position, and then screwing down *A* until the pointer *E* indicated the proper thickness of film on the flange *F*, which was graduated; the excess liquid was forced into a pipe *G* provided for the purpose. Upon opening the cell after an experiment it was found that if the liquid was hygroscopic it would generally attract enough moisture from the air to fog the salt plates while they were drying, while if the liquid was viscous, it would adhere to the plates for several hours in sufficient quantity to give traces of absorption bands. Hence it was made a rule to polish the plates whenever the cell was opened. Contamination of the liquids was carefully guarded against; the only substances with which they came into contact were the brass and the salt of the cell, and possibly a trace of rouge left on the edge of a plate after polishing.

The cell and a pair of salt plates of approximately the same thickness as those in the cell were mounted side by side upon a frame sliding upon horizontal ways so that either the one or the other could be brought before the slit. By getting the absorption due to a full cell and to the clear plates for the same wave-length, all corrections such as those due to absorption by the salt and selective reflection from its surface are done away with; the ratio of the two values found gives the per cent. transmission directly.

When put in the path of the radiation, the cell naturally becomes heated somewhat, but no provision need be made for cooling, as Coblentz[1] has shown that in general a change of as much as 20° C. from room temperature causes no change in the spectra.

The slit was 15 mm. in height and of adjustable width, 0.5 mm. being used in the region from 1 to 10μ, and 1 mm. for the remainder of the spectrum, where the energy was small. This widening of the slit does not, of course, involve a loss of accuracy, as the dispersion of rock salt is far greater for long wave-lengths than for shorter ones.

The spectrometer used was a large one of the fixed arm type specially designed for infra-red work by Professor C. E. Mendenhall. It was provided with a Warner and Swasey twelve-inch circle and an accurate worm and segment of worm wheel; the worm could be turned from the camera by means of a long rod bearing a micrometer head so graduated that the smallest division on it corresponded to a rotation of the prism through ten seconds of arc. The prism table was so constructed that all the adjustments required by the Wadsworth[2] mounting could be accurately made; it was set in hole, slot, and plane plates so that it could be removed entirely for convenience in carrying out the adjustment for minimum deviation, and was provided with a tin hood and several small dishes of sulphuric acid to dry the air surrounding the prism.

The rock salt prism was polished by Brashear and had these dimensions: refracting edge, 7 cm.; width of face, 5 cm.; angle, 60° 5.82′. To translate micrometer head readings into wave-lengths, a curve was plotted connecting angular rotation from the sodium line with wave-lengths, computations for the same being based on the indices of refraction of rock salt for different wave-lengths as given by Langley's[3] composite curve up to 10μ, and by Rubens and Trowbridge[4] beyond that point. For rough work a wave-length scale was made so that the position in the spectrum was indicated by the position of a mark on a string as the latter was wound up on the micrometer head. To check the accuracy of the

[1]Carnegie Institution, p. 106.
[2]Phil. Mag., 38, p. 344.
[3]Ann. Astrophys. Obs., I., p. 261, 1900.
[4]Am. J. Sci., V., p. 41, 1898.

adjustments, the carbon dioxide emission band in a Bunsen burner, and the two sylvite absorption bands were used; all were found accurately in place, the former at 4.4[1] and the latter two at 3.78 and 7.08.[2]

The mirrors *E* and *H* (Fig. 1) had focal lengths of 90 and 60 cm. respectively so that the 15-mm. slit gave a 10 mm. image. The curvature of the image was calculated and found to be negligible.

As required by the size of the mirrors used, the bolometer strips were made 10.5 mm. long from platinum foil 0.5 mm. wide, their resistances when soldered in place and smoked being respectively 5.660 and 5.669 ohms. This strip resistance, by Abbot's[3] method of calculation necessitates balance coils of 9.5 ohms each. These coils were wound non-inductively and in twin to equalize heating effects; they could be balanced by means of a shunt over a small part of one of them consisting of two parallel Ia wires connected by a movable mercury contact. The whole instrument was made as compact as possible, and, exclusive of the water jacket, measured about 20 cm. in length and 6 cm. in diameter. A large opening was left down the axis of the instrument so that a long focus microscope could be used to get the unshielded platinum strip in the focal plane of the mirror *H*.

An attempt was made to attain a high sensibility by enclosing the strips in a vacuum. It was found that the sensibility and steadiness on a given current increased at low pressures, but the high vacuum necessary could not be made to hold permanently. Vacua of one or two millimeters were at times held for a week or ten days, but the slightest jar would start a leak, and as the total volume exhausted was only about two cubic inches, a slight leak would immediately cause great disturbance, for at these low pressures the bolometer is extremely sensitive to pressure changes. The vacuum was finally discarded, but the rock salt window in front of the strips was retained to shut out air pulses.

The 0.5-mm. bolometer strip being placed at the focus of a mirror having a focal length of 60 cm., subtended an angle of a trifle less

[1]Paschen, Ann. d. Phys. (3), 53, p. 337, 1894.
[2]A. Trowbridge, Ann. Phys. u. Chem., 65, p. 612, 1898.
[3]Ann. Astrophys. Obs., I., p. 245, 1900.

than 3′ in the spectrum; this is equivalent to about 0.08μ at 1μ or to 0.5μ at 3.2μ, the region of least dispersion in the rock salt spectrum. The bolometer current was 0.08 amperes as a rule, the current being supplied by three storage cells in parallel.

The galvanometer was of the four-coil astatic type. In order to enable the use of a light system as well as to avoid the use of unwieldy shielding, it was sought to make the instrument as small as possible; consequently the external diameter of the coils was limited to 2 cm. To match the bolometer, a galvanometer resistance of about 5 ohms is best. Using Abbot's[1] formula to determine the sizes and lengths of wire that would give the maximum field strength under these conditions, two coils of respectively 16 and 25 ohms were calculated. In order to give an idea of the effect of varying the different quantities in the formula, all the results are put down in Table I. The coils marked * are of course the best under the limitations set. The 16 ohm coils were wound and all connected in parallel.

The galvanometer shielding consisted of three concentric soft

TABLE I.

Galvanometer coils computed by means of Abbot's formula. R, resistance in ohms; L, length of wire in cms.; H, external radius of coils in cms.; F, force at center of coils; W, size of wire, B & S. gauge. Subscripts—1 refer to inner section of coil, 2 to middle, 3 to outer.

W_1	W_2	W_3	R_1	R_2	R_3	L_1	L_2	L_3	H_1	H_2	H_3	F_1	F_2	F_3	F
40	36	34	12	8	5	369.1	622.3	780.0	.4868	.6099	.7816	824	485	362	1671
40	36	34	10	5	7	307.6	622.3	865.9	.3994	.6026	.7850	743	527	418	1688
40	36	34	7	8	10	215.3	622.3	1237.	.3684	.5923	.8442	607	569	514	1691
40	36	32	7	8	10	215.3	622.3	1967.	.3684	.5923	1.032	607	569	627	1803
40	36	32	11	8	6	338.4	622.3	1180.	.4984	.6059	.9154	785	516	636	1937*
40	34	30	8	5	3	246.1	618.5	938.1	.3795	.6495	.9676	655	475	311	1441*
40	34	30	8	5.5	2.5	246.1	680.4	781.7	.3795	.6649	.9374	655	520	250	1425
36	34	32	8	5	3	622.3	618.5	590.1	.5665	.7273	.8680	826	319	201	1346
36	34	30	8	5	3	622.3	618.5	938.1	.5665	.7273	1.004	826	319	199	1344
40	36	30	8	4.5	3.5	246.1	350.1	1095.	.3795	.5271	.9646	655	356	410	1421

[1]Ann. Astrophys. Obs., I., p. 248.

steel hollow cylinders of dimensions computed by the formulæ of Dubois and Wills[1] to give the maximum shielding; in addition there was within the inner hollow cylinder a solid cylinder of Swedish iron split lengthwise, the galvanometer coils being mounted directly in holes cut into the plane faces of the half cylinders. The inner hollow cylinder was provided with a plate glass top to shut out air draughts.

The astatic system consisted of two sets of tungsten steel magnets, four magnets to a set, mounted on a thin glass rod. The mirror on the system was about 3 mm. in diameter and was obtained by chipping the silvered concave surface of a 0.25 dioptric spectacle lens. To get rid of mechanical tremors, the whole system had to be made quite heavy—5.6 mg. To avoid cutting holes in the shield the system was illuminated from above by means of two small, plane mirrors and a horizontal A.C. Nernst glower, the glower being enclosed in a slotted brass tube. The glower and the photographic plate were of course at conjugate foci of the galvanometer mirror, the distance from the mirror to the plate being 170 cm.

The sensibility of the galvanometer on a complete period of 4 sec. was 5×10^{-10}, but frequently a 6-sec. period was used. With a period of 4 sec. or more the galvanometer was practically dead-beat. The deflections could be cut down by a combination of series and parallel resistances, the entire circuit being made of copper to eliminate thermal electromotive forces. The sensibility of the entire bolometer-galvanometer system when the galvanometer had a period of 4 sec. and the bolometer carried the usual current of 0.04 ampere per strip, was such that if there had been no series or parallel resistance in circuit with the galvanometer, a candle at a distance of a meter from the bolometer would have given a deflection of 30 cm. on a scale one meter from the galvanometer.

The camera consisted of a wooden box about three feet high built up around four standards, the galvanometer light being admitted through a horizontal slit 1 mm. wide. The plate carrier, holding a plate 11.5×14 inches, was guided by two of the standards, one of which was provided with a thread of 12 mm. pitch; a nut on the carrier engaged this thread and allowed the carrier to drop uniformly as the threaded standard was turned.

[1]Ann. d. Phys., II., p. 78, 1900.

This standard and the worm on the spectrometer were geared together so that vertical positions on the plate could be interpreted as angular displacements of the spectrometer and hence as wave-lengths. For the region from 3–4μ, the most condensed interval in the rock salt spectrum, the vertical displacement was 1 cm. The plate was lowered at the rate of 0.5 cm. per min., the speed of the whole system being regulated by the clockwork of a chronograph.

Method of Observation.

The following method of procedure was found to be the most rapid means of getting good consistent results. To make sure that no adjustment of the prism system had been disturbed, the sodium line was thrown on the bolometer both before and after the examination of each substance. After this preliminary test both of the Nernst glowers were started and three spot records made on the photographic plate: one a zero spot obtained by cutting off all radiations by means of a screen in front of the slit; another a clear plate transmission spot obtained by pulling the clear plate in front of the slit; lastly a transmission spot through the cell. The motor was then started and allowed to run for a few minutes, a trace of the transmission through the cell being obtained during this time; the motor was then stopped and zero and clear plate transmission spots again taken. This process was continued throughout the entire spectrum, the sensibility of the galvanometer being changed at some of the stops to obtain suitable deflections. Four curves were usually taken on each plate, two starting near one end of the plate and two near the other. Two curves were taken of each substance, sometimes on the same day, sometimes on different days.

After a plate was developed, all the zero points of any one set and all the clear plate points were connected by ink lines. For any one wave-length, the ratio of the distances zero line to cell line, and zero line to clear plate line, gave the per cent. transmission. For convenience in reading a plate it was laid on a frame at an angle of 45° with the horizontal, light being reflected through it from a sheet of white paper. Along the left hand edge of the frame slid a counterbalanced T square whose arm was graduated

so that each division corresponded to a vertical drop of the plate of 0.1 μ. A celluloid triangle with a millimeter scale graduated on a bevelled edge slid along the T square and served to measure the ratio distances, the actual ratios being read off on a slide rule. Curves were then plotted using per cent. transmission as ordinates and wave-lengths in μ's as abscissas.

To avoid confusion only one curve has been reproduced for each substance (Plates I, II, and III, p. 420). But to give an idea of how closely the curves check one another, both curves are given for isoamyl butyrate (no. 31) and isoamyl propionate (no. 30). The first of these is a fair sample of the way in which two curves checked when the thickness of the film was the same in the two cases, and the second illustrates the difference in appearance of the curves due to a difference in film thickness; some of the bands run together into a deep band, but the individual minima can be distinguished if the film is not too thick. The thickness of the film used in each case is given in Table II.

To give an idea of the actual appearance of the photographic plate, a small part of one is reproduced without reduction in Fig. 3 (Plate I, p. 420).

SOURCES OF ERROR.

In interpreting the curves, use has been made of the relative depths of the absorption bands as well as of their positions, so that errors affecting either the depth or the position of a band must be considered. As the chief sources of error may be mentioned: Variation in brilliancy of the Nernst glower, bolometer drift and unsteadiness, inaccuracy in the drawing of the clear plate transmission curve, impurity of spectrum due to finite widths of slit and bolometer.

Variation in brilliancy of the Nernst glower will affect the transmission curves of both the clear plate and the cell in the same ratio, so that no error would be caused by such a variation if it were possible to get simultaneous traces of the transmission through the clear plate and through the cell. In the trace on the photographic plate, however, the clear plate transmission is represented only by dots taken at intervals. A sudden change in brilliancy between two dots might therefore affect both the depth and the position of a

TABLE II.

Curve No.	Substance.	Sample. b.p. °C.	Sample. Pres. mm.	Thickness of film, mm.	Formula.
1	Methyl alcohol	63.7	726.5	0.01	CH_3OH
2	Ethyl alcohol	77.0	728.8	0.01	CH_3CH_2OH
3	Primary propyl alc.	95.9	726.2	0.01	$CH_3CH_2CH_2OH$
4	Primary butyl alc.	115.9	743.1	0.01	$CH_3(CH_2)_2CH_2OH$
5	Primary amyl alc.	136.8	743.9	0.01	$CH_3(CH_2)_3CH_2OH$
6	Sodium alcoholate			0.005	CH_3CH_2ONa
7	Isobutyl alcohol	105.5	740.3	0.01	$(CH_3)_2CHCH_2OH$
8	Isoamyl alcohol	130.0	732.6	0.01	$(CH_3)_2CHCH_2CH_2OH$
9	Allyl alcohol	95.5–95.6	747.0	0.01	CH_2CHCH_2OH
10	Capryl alcohol	174.0–176.0	729.0	0.01 0.01	$CH_3(CH_2)_5CHOHCH_3$
11	Secondary propyl alc.	81.6	739.9	0.01	$CH_3CHOHCH_3$
12	Secondary butyl alc.	98.9	740.3	0.01	$CH_3CH_2CHOHCH_3$
13	Tertiary amyl alc.	101.0–102.0	738.7	0.01	$CH_3CH_2COH(CH_3)_2$
14	Butyric acid	161.5	743.0	0.03	$CH_3CH_2CH_2COOH$
15	Methyl acetate	57.1	733.0	0.02	CH_3COOCH_3
16	Methyl propionate	77.0–79.0	737.5	0.02	$CH_3CH_2COOCH_3$
17	Methyl butyrate	102.0–102.5	742.0	0.02	$CH_3CH_2CH_2COOCH_3$
18	Methyl isovalerianate	116.7	742.0	0.02	$(CH_3)_2CHCH_2COOCH_3$
19	Isobutyric acid	152.7–153.0	743.0	0.03	$(CH_3)_2CHCOOH$
20	Ethyl acetate	75.0	744.4	0.02	$CH_3COOCH_2CH_3$
21	Ethyl propionate	98.0	737.5	0.01	$CH_3CH_2COOCH_2CH_3$
22	Ethyl butyrate	119.5–119.9	742.0	0.02	$CH_3CH_2CH_2COOCH_2CH_3$
23	Methyl isobutyrate	92.0–93.0	742.0	0.01	$(CH_3)_2CHCOOCH_3$
24	Methyl hexyl carbinol acetic ester	193.0	746.5	0.01	$CH_3COOCHCH_3(CH_2)_5CH_3$
25	Isobutyl acetate	115.8–116.3	744.5	0.03	$CH_3COOCH_2CH(CH_3)_2$
26	Butyl butyrate	164.0–165.0	741.0	0.01	$CH_3CH_2CH_2COOCH_2(CH_2)_2CH_3$
27	Isoamyl isobutyrate	168.0–168.5	742.5	0.01	$(CH_3)_2COOCH_2CH_2CH(CH_3)_2$
28	Isoamyl formate	123.0	746.0	0.02	$HCOOCH_2CH_2CH(CH_3)_2$
29	Isoamyl acetate	138.5–138.7	744.5	0.02	$CH_3COOCH_2CH_2CH(CH_3)_2$
30	Isoamyl propionate	160.0	743.0	0.01	$CH_3CH_2COOCH_2CH_2CH(CH_3)_2$
31	Isoamyl butyrate	177.0	745.4	0.01	$CH_3CH_2CH_2COOCH_2CH_2CH(CH_2)_3$

TABLE II.—*Continued.*

Curve No.	Substance.	Sample. b.p. °C.	Sample. Pres. mm.	Thickness of film, mm.	Formula.
32	Isoamyl isovalerianate	190.0	741.0	0.03	$(CH_3)_2CHCH_2COOCH_2CH_2CH(CH_3)_2$
33	Ethylene glycol	190.0	734.5	0.01	$(CH_2OH)_2$
34	Propylene glycol	181.0–182.0	738.0	0.01	$CH_2OHCHOHCH_3$
35	Glycerin	(m.p.) 17–18		0.01	$CH_2OHCHOHCH_2OH$
36	Acetaldehyde	21.5–22.0	742.0	0.005	CH_3CHO
37	Ethyl oxalate	116.5	120.0	0.01	$COOHCOOCH_2CH_3$
38	Ethyl malonate	193.0–195.0	738.0	0.01	$COOHCH_2COOCH_2CH_3$
39	Ethyl succinate	215.0	736.1	0.02	$CH_2COOHCH_2COOCH_2CH_3$
40	Diethyl oxalate	181.9	741.0	0.01	$COOCH_2CH_3COOCH_2CH_3$
41	Diethyl succinate	213.0	736.1	0.02	$CH_2COOCH_2CH_3CH_2COOCH_2CH_3$

band. Any great error due to this cause is excluded by the fact that two records were always taken for each substance; in case of disagreement the doubtful portion was gone over a third time.

Bolometer drift, through present, was at all times small; it was kept track of by means of the zero spots taken from time to time. As all measurements were made from a smooth curve joining these spots, the effect of drift is practically eliminated.

An error may have been, and probably was made, in joining the points giving the transmission through the clear plate, but the variations of the curve as drawn from the true curve could not have been great in any case as the points on the curve were taken close together, and as, in addition, the form of the true curve was known quite well from direct traces of it made occasionally.

The correction for finite width of slit and bolometer,[1] though appreciable, has not been applied to the curves as plotted since it would affect all similar curves to approximately the same extent at the same points in the spectrum; the comparison of the origina curves leads to the same results as would the comparison of the corrected curves.

[1]Summarized in Preston's Heat, last edition, p. 606.

The Materials Used.

All the substances used were either synthesized or taken from stock and distilled shortly before they were examined. If several days elapsed between the time of preparation and the time of examination, the liquids were kept in glass stoppered bottles in the dark. The thermometer used was compared with one having a Reichsanstalt certificate. The boiling points of the various substances and the corresponding pressures are given in Table II.

The Alcohols were all taken from stock bottles, dried for several days over anhydrous copper sulphate, and distilled over sodium. The solution of sodium alcholate in alcohol was obtained by dissolving sodium in absolute alcohol until the whole mass was just ready to become solid; the sample was tested immediately after it was made.

The Glycols.—Ethylene glycol was taken from stock (Schuchardt), dried over anhydrous calcium chloride, and distilled. Propylene glycol was made by Morley's[1] method, which consists in dissolving lye in glycerin, heating and distilling; this was the only substance examined that was not colorless; it had a pale yellow tinge.

Glycerin.—The purest glycerin obtainable was frozen and the crystals filtered off, the process being repeated twice; melting point 17–18°.

The Acids were taken from stock (Schuchardt), dried over anhydrous calcium chloride and distilled.

The Esters.—All the monobasic esters except two were made from the pure acids and alcohols by the hydrochloric acid method. A mixture of the proper acid and alcohol, containing a large excess of the one that happened to be the more plentiful, was saturated at 0° C. with dry hydrochloric acid; the action was completed by boiling for about fifteen minutes with a reflux condenser; the ester was separated by shaking the mixture with a saturated solution of calcium chloride or with granular calcium chloride, and was then dried and fractionated.

The two isovalerianates were taken from stock (Schuchardt), dried over calcium chloride and distilled.

Of the more complex esters, diethyl oxalate, ethyl malonate and

[1]Chem. Soc. Journ., 47, p. 132.

ethyl succinate were taken from stock, dried and distilled. Ethyl oxalate was made by heating anhydrous oxalic acid and absolute alcohol slowly under diminished pressure. The mixture was cooled and later fractionated in a partial vacuum. Diethyl succinate was made by the hydrochloric acid method from the pure acid and alcohol.

Acetaldehyde.—Some of Kahlbaum's product was distilled with dilute sulphuric acid, dried over anhydrous sodium sulphate and distilled. As acetaldehyde rapidly polymerizes in part to paraldehyde at room temperature, it was examined immediately after being distilled.

DISCUSSION.

As stated in the introduction, the investigation was begun with a study of the effects of homology and isomerism. Of these two, homology is somewhat the simpler. In any study of the relation between chemical composition and physical properties it is customary to assume that similarities in chemical constitution cause similarities in physical properties. All homologous compounds are similar in constitution, for by definition, two successive members of a homologous series must be similar in their properties, and must differ by CH_2, a hydrogen atom in one having been replaced by a methyl group in the other. Hence regularities in the spectra of the members of such a series may be expected.

Among isomers, however, the case is somewhat different. Isomeric compounds are defined as compounds that have the same percentage composition and the same molecular weight, but different properties. Since isomers are essentially different in structure, differences in the spectra are to be expected; but some isomers differ radically in structure while others differ only slightly, and on the basis of the original assumption a corresponding relative difference in the spectra is to be expected. From a study of those isomers that are somewhat closely related in structure it seemed probable that a definite correlation might be obtained between certain groups or linkages and certain bands. Such correlations, it seemed likely, might afterwards be corroborated and extended by following up the results of a chemical reaction, and by studying related compounds. This is, in outline, the scheme that has been followed in the selection of the substances and in their comparison.

The alcohols were the first substances selected for investigation. Those with a single atom of oxygen fall into three classes having the general formulæ $C_nH_{2n+1}OH$, $C_nH_{2n-1}OH$, and $C_nH_{2n-3}OH$. The members of the first class, which includes most of the specimens examined, are further distinguished as primary, secondary, or tertiary, according as the hydroxyl group is attached to a CH_2, to a CH, or to a C.

A general idea of the relations of the various alcohols of the first class to each other is given by the accompanying table.

Methyl CH_3OH				
Ethyl CH_3CH_2OH				
Normal or primary propyl $CH_3.CH_2.CH_2OH$			Secondary propyl $CH_3CH_3>CH.OH$	
Normal butyl $CH_3(CH_2)_2CH_2OH$	Isobutyl $CH_3CH_3>CH.CH_2OH$		Secondary butyl $CH_3CH_2CH_3>CHOH$	Tertiary butyl $CH_3CH_3CH_3>COH$
Normal amyl $CH_3(CH_2)_3CH_2OH$	(Active amyl) $CH_3CH_2CH_3>CH.CH_2OH$	Isoamyl $CH_3CH_3>CH.CH_2.CH_2OH$	(Secondary amyl) $CH_3(CH_2)_2CH_3>CHOH$	Tertiary amyl $CH_3CH_3CH_2CH_3>COH$

Columns in this table represent homologous series and any alcohogives rise to the next succeeding one in the same column if a hydrol gen atom be taken from a methyl (CH_3) group and replaced by another methyl group. Rows in the table represent isomers, but the change in structure is different for different pairs of consecutive members. Isomers from the first and second columns, for example, differ only slightly from one another chemically; the difference in structure exists entirely in the hydrocarbon part of the compounds, the linking of the characteristic hydroxyl group remaining unchanged. The same is true of isomers of the first and third columns but those from the first and fourth or first and fifth differ more materially since in these the linking of the hydroxyl is changed.

The table is complete as far as it goes except that three of the amyl alcohols, which were not used, have been omitted to save

space. Capryl alcohol, one of the higher secondary alcohols, belonging two rows below secondary amyl, was examined in addition to those put down in the table. Those alcohols that are included in parentheses were not available.

The saturated monobasic acids, $C_nH_{2n+1}COOH$, are divided, just as the alcohols are, into primary, secondary, and tertiary compounds, an acid being primary if the carboxyl group, COOH, is attached to CH_2, secondary if attached to a CH, and tertiary if attached to a C. The primary acids form the series:

$HCOOH$ formic,
CH_3COOH acetic,
CH_3CH_2COOH propionic,
$CH_3CH_2CH_2COOH$ butyric,
$CH_3(CH_2)_2CH_2COOH$ valeric,
$CH_2(CH_2)_3CH_2COOH$ caproic.

Of these Coblentz[1] has examined acetic, valeric, and caproic, and in the present investigation, butyric has been added.

Analogous series of iso, secondary and tertiary acids also exist, of course, but of these only one specimen could be obtained, the so-called isobutyric, which is really a secondary acid as shown by its formula (Table II.).

The esters are salt-like derivatives of the various acids and alcohols, and hence a great many different ones exist, offering a correspondingly large number of homologous series and isomers. The esters examined were for the most part those obtained by the interaction of primary or iso alcohols with primary acids. The esters formed by the interaction of the primary alcohols and the primary acids may be arranged for convenience in tabular form as shown on page 403.

The members of any column, representing the combinations of some one alcohol with a series of acids, evidently form a homologous series. So also do the members of a row, for each row shows the results of combining some one acid with a series of alcohols. Those esters lying on lines that might be drawn in the diagram slanting from the right on the top to the left below, as, *e. g.*, ethyl formate and methyl acetate, or propyl formate, ethyl acetate and methy propionate, illustrate a particular kind of isomerism, the isomer-

[1]Carn. Inst., pp. 209–215.

ism being due to the successive transfer of a methyl group from the basic to the acid part of the compounds.

Methyl formate $HCOOCH_3$	Ethyl formate $HCOOCH_2CH_3$	Propyl formate $HCOO(CH_2)_2CH_3$	Butyl formate $HCOO(CH_2)_3CH_3$	Amyl formate $HCOO(CH_2)_4CH_3$
Methyl acetate CH_3COOCH_3	Ethyl acetate $CH_3COOCH_2CH_3$	Propyl acetate $CH_3COO(CH_2)_2CH_3$	Butyl acetate $CH_3COO(CH_2)_3CH_3$	Amyl acetate $CH_3COO(CH_2)_4CH_3$
Methyl proprionate $CH_3CH_2COOCH_3$	Ethyl proprionate $CH_3CH_2COOCH_2CH_3$	Propyl proprionate $CH_3CH_2COO(CH_2)_2CH_3$	Butyl proprionate $CH_3CH_2COO(CH_2)_3CH_3$	Amyl proprionate $CH_3CH_2COO(CH_2)_4CH_3$
Methyl butyrate $CH_3(CH_2)_2COOCH_3$	Ethyl butyrate $CH_3(CH_2)_2COOCH_2CH_3$	Propyl butyrate $CH_3(CH_2)_2COO(CH_2)_2CH_3$	Butyl butyrate $CH_3(CH_2)_2COO(CH_2)_3CH_3$	Amyl butyrate $CH_3(CH_2)_2COO(CH_2)_4CH_3$
Methyl valerianate $CH_3(CH_2)_3COOCH_3$	Ethyl valerianate $CH_3(CH_2)_3COOCH_2CH_3$	Propyl valerianate $CH_3(CH_2)_3COO(CH_2)_2CH_3$	Butyl valerianate $CH_3(CH_2)_3COO(CH_2)_3CH_3$	Amyl valerianate $CH_3(CH_2)_3COO(CH_2)_4CH_3$

A similar square array of esters can be made by combining the iso acids with the primary alcohols; another by combining the iso alcohols with the primary acids; another by combining the secondary acids with the primary alcohols, etc. Each such array would give rise to the two kinds of homologous series and to the kind of isomerism mentioned above. In addition, the substances occupying the same position in the different square arrays might be compared, all such substances being isomers of the primary—iso, primary—secondary, etc., types mentioned in connection with the alcohols. The preparation and study of all of these compounds is, however, unnecessary, as will be seen when the spectra of a few of them are compared.

To facilitate the comparison of the curves, related substances have been plotted as nearly as possible in the same order as the formulas tabulated above. In the esters the scheme of the square array has been followed except that the normal compounds have in some instances been replaced by the corresponding iso compounds. If, to economize space, any substance has been plotted out of its regular order, the fact is indicated by a heavy border. To aid in finding the curves, they have all been numbered in the order in which they appear on the sheets.

EFFECT OF ISOMERISM.

Primary-iso isomerism in the alcohols; this includes alcohols that differ in the hydrocarbon part but not in the linking of the hydroxyl. Two pairs of these isomers have been examined: butyl (no. 4) and ¡sobutyl (no. 7), and amyl (no. 5) and isoamyl (no. 8). The three absorption regions from about 3.0–3.5, 6.5–7.5 and 9–10μ look very much alike in each primary and its isomer. In butyl and isobutyl the first absorption region has two bands, the first occurring at 3μ in both, and the second at 3.5 in the primary and 3.4 in the iso; the second region also has two bands, 6.9 and 7.2, alike in both; the third region has one band at 9.6 in both. There is also a band at 10.5 in the normal and 10.4 in the iso. The region between the second and third absorption regions has two minor bands in the primary and only one in the iso. Beyond 11μ the spectra are dissimilar.

In amyl and isoamyl the location of bands in the first region is identical to that in the butyls; the second region has two bands, 6.9 and 7.3, alike in both; the third region has two bands, 9.6 and 9.9 in amyl, and 9.5 and 9.9 in isoamyl. There is also a band at 10.3 in both. The region between the second and third main regions has three minor bands in the normal and two in the iso. Beyond 11μ the spectra are dissimilar.

The change from primary to iso therefore leaves the three main regions unchanged except for the shift of the 3.5 band to 3.4. In the region between the second and third absorption regions the iso alcohol has fewer minor bands than the primary. The regions beyond 11μ differ.

Primary-secondary isomerism in the alcohols; in these isomers the linking of the hydroxyl group is changed from CH_2OH to CHOH. Two pairs of these alcohols have been examined: Primary and secondary propyl (nos. 3 and 8), and primary and secondary butyl (nos. 4 and 9). The three absorption regions that were noted in the primaries before 10μ change their appearance somewhat in the secondaries. The first region is situated between 3 and 3.5μ in both the primaries and the secondaries, and shows two bands in each; the second region lies between 6.5 and 7.5μ in both, but has two bands in the primaries and three in the secondaries; the third region occurs between 9 and 10 in the primaries and between 8.5 and 9.5 in the secondaries. Several deep bands also appear in the secondaries beyond 10μ. In detail, the bands at 3.0 and 6.9 are again unchanged, and 3.5 again goes to 3.4. In place of a minor band at 6.1 in the primaries there is in both cases a much deeper one at 5.9 in the secondaries. The 7.2 band does not shift in the propyls but goes to 7.3 in secondary butyl. A new deep band exists at 7.7 in secondary propyl and at 7.6 in secondary butyl. The 8.2 band in primary propyl still exists in secondary propyl, but the 8.0 band in primary butyl has disappeared in secondary butyl. If the two absorption regions from 9–10 in the primaries and from 8.5 to 9.5 in the secondaries can be correlated, it means that the band near 9.6 in the primaries corresponds to that near 9.1 in the secondaries; in other words the band near 9.6 in the primaries has shifted by 0.5μ toward the shorter wave-lengths in the secondaries.

Another new band exists near 9.8 in the secondaries, being much deeper in the more complex compound. The band at 13.0 is not shifted in the propyls, but goes from 13.1 to 13.0 in the butyls. The change from primary to secondary, therefore, shifts more bands in the compounds richer in CH_2; more characteristic still is the appearance of the two new bands near 7.6 and 9.8 and the shift of the 9.6 band by 0.5μ toward the shorter wave-lengths in both secondary propyl and butyl.

Primary-tertiary isomerism in the alcohols; in these alcohols the linking of the hydroxyl is changed from CH_2OH to COH. Only one pair of these alcohols could be obtained: primary and tertiary amyl (nos. 5 and 13). The absorption regions between 3 and 4μ are again similar; the second region, near 7μ, has three bands in the tertiary in place of two, the three bands being separated somewhat farther from each other than in the secondaries where they also occur; the third region occurs between 9 and 10μ in the primaries and between 8 and 9 in the tertiary; beyond this region, the spectrum of the tertiary is more cut up than in the primaries or secondaries. In detail the bands at 3.0, 6.9, 7.3, 13.0, are unchanged; a weak band at 6.1 is found in the tertiary where there is none in the primary; a band appears at 7.9 and another disappears at 8.3, which may possibly indicate a shift. If the third absorption regions in the primary and the tertiary can be correlated, the 9.6 bands must be regarded as having shifted to 8.6; the fact that this shift from primary to tertiary is just double the shift of the same band from the primaries to the secondaries, strengthens the belief that the regions compared are really analogous. There is, to be sure, a band at 9.6 in tertiary amyl which may be due to a weakening of the deep band found at the same place in the primaries, but judging by the general similarity of the spectra, it seems best to correlate the 8.6 band in the tertiary with the 9.6 band in the primaries as indicated above. With this interpretation, the most noticeable changes in these isomers are the appearance of the new band at 7.9 and the shift of the 9.6 band by 1.0μ toward the shorter wave-lengths.

Primary-secondary isomerism in the acids. Data have been obtained on one pair of these acids, butyric and isobutyric (nos. 14

and 19), and Coblentz[1] has examined another pair, caproic and isocaproic, which may be compared somewhat more closely than he has done. Isobutyric acid is really a secondary acid, as mentioned before, and as shown by its formula in Table II. These acids show the following minima:

Butyric,	3.6	5.9	7.1	7.9		9.3	10.6	12.9
Isobutyric,	3.6	5.9	7.1	8.0	8.5	9.2	10.8	12.3

The most conspicuous change evidently is the appearance of two lines at 8.0 and 8.5 to take the place of the one at 7.9. Coblentz's curves for caproic acid, $CH_3(CH_2)_3CH_2COOH$, and isocaproic acid, which is really a secondary acid, $(CH_3)_2CH.CH(CH_3)COOH$, show a very similar behavior, as can be seen from their minima:

Caproic,	3.5	5.9	7.0	8.0		9.1	10.3	11.6	12.5
Isocaproic,	3.5	5.9	7.0	7.8	8.3	9.1	10.7		12.2

These acids therefore indicate that up to 12μ their spectra are very similar except in the region near 8μ where one band occurs when the carboxyl is linked to a CH_2 and two when linked to a CH.

Primary-secondary isomerism in the esters. Two pairs of these isomers are found in methyl butyrate and methyl isobutyrate (nos. 17 and 23), and isoamyl butyrate and isoamyl isobutyrate (nos. 31 and 27). In the methyl isomers, passing from normal to iso, the band at 4.4 goes to 4.2, that at 5.0 to 4.9, and that at 9.2 to 9.3; the normal compound has a single band in the 8μ region (8.4), while the iso compound has two (8.4 and 8.7). In the isoamyl isomers, similarly, the band at 4.3 goes to 4.2, that at 4.8 to 4.6, that at 9.2 to 9.3, and that at 8.5 into two at 8.4 and 8.6. It will be remembered that the change from primary to secondary acid also caused two bands to appear in place of one in the 8μ region; this splitting persists in the corresponding esters.

Isomerism in the esters due to shifting a CH_2 group from the basic to the acid part of the compound. Of this there are four illustrations:

1. Ethyl acetate (no. 20) and methyl propionate (no. 16).
2. Ethyl propionate (no. 21) and methyl butyrate (no. 17).
3. Isoamyl formate (no. 28), isobutyl acetate (no. 25), ethyl butyrate (no. 22), and methyl isovalerianate (no. 18).

[1]Carn. Inst., pp. 211, 212, 101.

4. Isoamyl propionate (no. 30) and butyl butyrate (no. 26).

On comparing these spectra in detail it appears that the shifting of the CH_2 can be correlated with no definite shift of any line or series of lines. This may mean that in this case the lines present depend on the groups present and not on their linking, or it may mean that the change made is too small to be noticed in so complex a molecule. Since compounds far apart, isoamyl formate and methyl isovalerianate, have been examined, four groups having been shifted from one side to the other in these compounds, it seems that the former view must be accepted.

To sum up: All the alcohols have bands at 3.0 and 6.9; the change from primary to iso causes a number of small shifts, the number being larger in compounds poor in CH_2; the secondary alcohols have a new band near 7.6 and the tertiaries have a corresponding one at 7.9; the change from primary to secondary causes a weakening of the bands in the 8μ region, and the change to tertiary causes a further weakening; a deep band appears at 9.6 in the primaries, is shifted to 9.1 in the secondaries, and to 8.6 in the tertiaries. The isomeric acids show great similarity in their spectra, the main point of difference being the fact that in the primaries there is a single line in the 8μ region, while in the secondaries there are two. The isomeric esters, for the same difference in structure, show the same difference in bands as the acids, indicating that some bands in the esters depend on the structure; on the other hand the fact that no marked change is caused by shifting CH_2 groups from the acid to the basic parts of the compound, indicates that certain other bands depend merely on the presence of certain groups; still, the change in chemical properties caused by this shift is relatively slight, so that comparisons of the different spectra show that the greater the difference in structure between isomers, the greater the difference in their spectra. This substantiates the conclusions of Julius[1] and of Coblentz, who found that a change in structure causes a change in the spectra.

EFFECT OF HOMOLOGY.

Homology in the primary alcohols. Five primary alcohols (nos. 1 to 5) were examined. In all the alcohols there are three deep

[1]Verh. Konikl. Akad., Amsterdam, Vol. 1, No. 1, 1892.

absorption regions before 10μ as was mentioned when discussing isomers. In the primary alcohols the first of these regions is occupied by one band in the lower members of the series and by two in the upper; the same is true of the second region. The space between the second and third regions is occupied by several minor bands whose number and depth increase in the higher members of the series. Beyond 10μ there is no more marked similarity. In detail, the 3μ band is constant in all, and the 3.5μ band is constant in the higher members, being absent in methyl and ethyl. There is a minor band at 4.9 in methyl, 5.2 in ethyl, 5.5 in propyl, 5.6 in butyl, and not observable in amyl; it is strongest in methyl and gets weaker as it shifts to the longer wave-lengths Another minor band behaves very much like this one: it occurs at 5.9 in methyl, 6.0 in ethyl, 6.1 in propyl, 6.1 in butyl, and disappears in amyl. The 6.9 band is practically constant, as is also the 7.2 band after it appears. The deepest band in the third absorption region is at 9.9 in methyl and at about 9.6 in the rest, showing a shift in the lower members of the series. A small band appears at 10.6 in ethyl, 10.4 in propyl and butyl, and 10.3 in amyl. Beyond this there is a band at about 13μ in all except methyl, where there is one at 13.3; but it is doubtful whether these can be correlated, as the general configuration of the spectra is not at all alike in this region. From the preceding it is seen that the bands that shift move towards the 9μ region from each side as the series is ascended, the shift being greater between the lower members.

Before leaving the primary alcohols attention must be called to the difference that exists between Coblentz's[1] curve for ethyl alcohol and mine (no. 2). The minima given in his curve fall at about 3.4, 7.3, 9.6, 11.4, 12.6, whereas mine fall at 3.0, 7.0, 7.2, 9.3, 9.6, 11.3, 12.5, 13.0. His curve shows no band at 3.0 at all, while in the present investigation this band was found in all the alcohols without exception. He mentions that one of his samples was treated with sodium; thinking that this might be the cause of the difference, a solution of sodium alcoholate in alcohol was prepared and examined (no. 6). This gives the bands found by Coblentz with the addition of one at 5.9 due probably either to the fact that more sodium was present or to the fact that a thinner film was examined (0.005

[1]Carn. Inst., p. 192.

mm. as compared to 0.01 and 0.18 mm.). Hence the specimen examined by Coblentz was probably a solution of sodium alcholate and not pure alcohol.

Homology in the Secondary Alcohols.—Curves have been obtained for three members of the secondary series: propyl (no. 11), butyl (no. 12) and capryl (no. 10); these are respectively the first, second and sixth members of the series. All have a characteristic band at about 7.7 which is not found in the primaries. The main bands noted in the primaries occur here, in the order propyl, butyl, capryl, as follows: 7.2, 7.3, 7.3; 9.0, 9.1, 9.1; 9.9, 9.8, 9.4. This again shows a shift toward the 9μ region as the series is ascended, the shift being less in the upper than in the lower members.

In this connection it is interesting to note that myricil alcohol, $C_{30}H_{61}OH$,[1] shows the characteristic bands of the primary alcohols: 3.0, 3.4, 6.9, 7.3, 9.4.

Homology in the Primary Acids.—I have added but one to the list of primary acids studied by Coblentz,[2] but while the data for this group of substances is largely from Coblentz, the point of view is somewhat different from his. Of the primary acids he has examined acetic CH_3COOH, valeric $CH_3(CH_2)_2CH_2COOH$, caproic $CH_3(CH_2)_5CH_2COOH$, stearic $C_{17}H_{35}COOH$, and cerotic $C_{26}H_{53}COOH$. In the present investigation butyric, $CH_3CH_2CH_2COOH$, has been added, so that there are at hand data on six members of the series, showing the following minima:

Acetic,	3.5	5.9	7.2	8.9	9.9	10.6	11.0	13.9
Butyric,	2.6	5.9	7.1	7.9	9.3	10.6	12.9	
Valeric,	3.6	5.9	7.1	7.9	9.1	10.7	12.2	13.3
Caproic,	3.5	5.9	7.0	8.0	9.1	10.8	11.6	12.5
Stearic,	3.5	5.9	7.0	7.8	9.2	10.6	12.2	13.3
Cerotic,	3.5	5.9	6.9	7.7		10.6	10.9	12.9

The first two bands are constant throughout the series, and the fourth and sixth show no particular shift, though the last one grows more prominent as the series is ascended. The third and fifth, however, shift towards the shorter wave-lengths as the series is ascended, the shift being larger in the lower members; the fifth grows weaker in the higher members, being absent entirely in cerotic acid. Beyond the sixth band there is no more regularity. The

[1] Coblentz, Carn. Inst., p. 186.

[2] Carn. Inst., pp. 209–215.

spectra of the homologous acids, therefore, are very similar but wherever there is a shift, it is towards the shorter wave-lengths, and larger between the lower and simpler members of the series.

Homology in the Secondary Acids.—The transmission minima of the two secondary acids, isobutyric and isocaproic, have already been given (pp. 406–7). The characteristic bands of the secondary acids, as noted before, are the two near 8μ that take the place of the single one in the primaries. Both of these are shifted by 0.2μ to the shorter wave-lengths in the higher compound. Two other bands are also shifted: 7.1 to 7.0 and 9.2 to 9.1, so that whenever a shift occurs, it is toward the shorter wave-lengths as the compound becomes more complex.

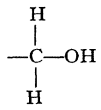
Homology in the Esters.—The complete series of esters as shown in the square array on page 403 could not be obtained on account of the cost of some of the necessary primary alcohols; isoalcohols, being cheaper, were in some cases used in place of the corresponding primary alcohols in the preparation of the esters, the result of course being an ester which differed from the normal ester in the same way that the iso alcohol differed from the normal alcohol. The comparison of primary and iso compounds has shown that their spectra are very similar, and a comparison of esters has shown that the spectra are very little affected even if CH_2 groups be shifted from the acid to the basic parts of the compound. Since the esters formed from the primary and iso alcohols differ only in the arrangement of the C and H in the basic part of the compound, it is probably safe to compare some of the primary and some of the iso esters as though they were all strictly homologous. Comparing the members of each column in the square array mentioned, the band in the 3.4 region shows a slight tendency to shift to longer wave-lengths as CH_2 is added to the compound. A small band lying between 4.8 and 5.0 is present in all the esters except in the column of ethyl compounds. On comparing the members of each row it is seen that a band is present at 6.9 or 7.0 in all the compounds except the acetates. The 4.3, 5.9 and 7.4 bands show no particular shift when comparing members of either rows or columns. That these same peculiarities exist far up the series is shown by methyl hexyl carbinol acetic ester (no. 24), which is, as its name indicates a

complex acetate. The 4.3, 5.9 and 7.4 bands are all in place and the region near 6.9 is still without any definite band.

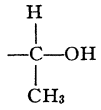
Successive members of a homologous series, therefore, show only slight changes in their spectra. In both the primary and secondary alcohols, in ascending the series, several bands are found to shift towards the 9μ region; in the primary and secondary acids a few bands are shifted toward shorter wave-lengths; in the esters the effect of homology is extremely slight, there being only a small shift of a single band near 3.4μ toward longer wave-lengths as the acid part of the compound is made more complex, and no shift at all as the basic part of the compound is made more complex

EFFECT OF CERTAIN GROUPS AND THEIR MODE OF LINKING.

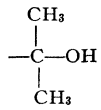
It is probable that the character of the groups present, the number of each kind, and their mode of linking all influence the absorption spectra. In discussing isomers several bands have been noticed to shift in such a way that it is most natural to attribute the shift to the change in the linking of the groups that compose the compound. For example the deepest band in the third absorption region of the alcohols was found to occur at 9.6 in all the primaries, at 9.1 in all the secondaries and at 8.6 in the one tertiary examined. These compounds differ in structure in that the hydroxyl group is linked to a carbon with successively one less hydrogen; that is, the primaries contain the group



the secondaries



and the tertiaries



It is evident that the above shift cannot be attributed to the mere presence of a CH_2 group in one case, of a CH in another and of a C

in the third, for these also occur in the iso alcohols where there is no such shift. Neither is the shift due to linking successively more CH_3 groups to the same C, for this also occurs in the iso alcohols. In these iso compounds, however, the C to which the additional CH_2 groups are linked does not carry the hydroxyl, while in the secondaries and tertiaries it does. Hence the shift must be attributed to the entire change in linking existing between the primary, secondary and tertiary compounds.

The secondary and tertiary linkings allow a greater freedom of vibration than the primary, as is shown by the new lines at 7.7 and 7.9 respectively. In the acids the same statement holds, for the change from primary to secondary manifests itself, as mentioned, by the appearance of two lines in place of one in the 8μ region.

It is probably safe to argue that those bands which coincide in the iso alcohols and the secondaries, but not in the primaries, are connected with the

$$\begin{array}{c} -CH- \\ | \\ CH_3 \end{array}$$

grouping. Such a band is that at 3.5 in the primaries and at 3.4 in the isomers. This indicates that the band near 3.5 is probably connected with the CH_3 group. The shifting of the 3.4 band in the homologous esters also indicates the probable connection between CH_3 and a band in this region.

A band such as that at 6.1 in the alcohols which dies out in the higher primaries, being absent entirely in butyl, but which persists longer in the isomers, shows that the same increase in molecular weight does not always have the same effect; the manner of loading the molecule is important.

The lines that are constant throughout an entire series are probably due to something which is constant in all the members; but in any one series several things are usually constant, so that from one series alone bands and groups cannot in general be correlated with certainty. However, by comparing these fixed bands in several series of related compounds, some fairly definite idea may be obtained as to the relation between particular groups and particular bands. With this in view, the alcohols, acids and esters will be compared.

The alcohols all have a strong band at 3μ and all above ethyl also have one at 3.5. This behavior indicates the possibility of a relation between the 3μ band and the OH group since both are present in all the alcohols. The 3.5μ band is most naturally thought of in connection with CH_2 or CH_3, for when there are many of these present, the band is deep and distinct while when there are only a few, as in methyl and ethyl and allyl (no. 9), the band does not appear. These suppositions are strengthened by the fact that the esters and the acids all have the 3.5 but not the 3.0 band. The esters of course have no hydroxyl and are rich in CH_2 so that the above suppositions hold without question, but the acids have an OH as part of the characteristic group acid, COOH, so that the above assumption must be restricted to apply only to an alcohol hydroxyl; this restriction is not arbitrary as the OH when linked to a CO has a different chemical behavior than when linked to a CH_2 or a CH.

The acids and esters have a strong band at about 5.9, a region in which the lower alcohols have a weak one, and the higher ones none at all. Aschkinass[1] ascribes this band in the alcohols to OH, but this is very unlikely in view of the fact that the band disappears in the higher members. By the present method of comparison it is natural to ascribe this band to something common to the acids and esters but not to the alcohols, that is, to the C = O group.

In the alcohols there is a band at 6.9, in the acids at 7.1, and in the esters a less pronounced one at 6.9 or 7.0 which is entirely lacking in the special case of the acetates. This may possibly be explained by assuming the 6.9 band in the alcohols due to OH, and the 7.1 band in the acids due to the COOH or the acid H only; the esters resulting from their combination would in that case not be expected to have a distinct band at that point.

A band appears in the esters at 7.4; since there are more CH_2 groups in the esters than in either the alcohols or the acids, this band is probably due to them. A band does appear at 7.3 in the higher alcohols, strengthening this view.

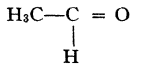
Another deep band at 8.0 in the acids and somewhere between 8.2 and 8.6 in the esters with no corresponding band in the alcohols will again tentatively be ascribed to C = O.

[1]Ann. d. Phys., 55, p. 431. 1895.

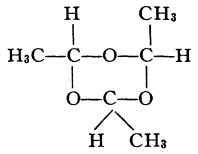
The bands at 9.5 in the alcohols, 9.2 to 9.8 in the esters, and 9.1 in the acids cannot be ascribed to any definite group, for they show no regularity even if each alcohol be compared with each acid and the corresponding ester.

Other facts are available to strengthen the above assumptions. Coblentz[1] gives curves for several hydrocarbons of the series C_nH_{2n+2}, all of which show bands at 3.4, 5.8, 6.9 and 7.3. The 3.4 and 7.3 bands practically coincide with those ascribed to CH_2 above. The 5.8 band is shallow in the hydrocarbons so that the CH_2 groups probably do not play much part in producing the deep bands found in the same place in the esters and acids, as already discussed above. The 6.9 band, however, is very deep, so that at first sight it seems natural to ascribe the deep bands in the alcohols at 6.9 and in the acids at 7.1 to CH_2; but the fact that this band is not characteristic of all the esters, as would be expected on account of the greater number of CH_2 groups, makes the other interpretation offered above seem more probable.

If the 3.0 and 6.9 bands are due to hydroxyl, those bands would not be expected in sodium alcoholate, and upon inspecting the curve (no. 6), they are not found. There is, to be sure, an indication that with greater dispersion a band might be found at 6.9, but this is only to be expected as the spectrum taken was that of a solution of sodium alcoholate in alcohol.



Acetaldehyde.



Paraldehyde.

The bands at about 5.8 and 8.2 in the acids and esters, which were ascribed to C = O occur also in the same place in acetone $CH_3—CO—CH_3$, in methyl carbonate $CH_3—O—CO—O—CH_3$, and in benzaldehyde C_6H_5CHO.[2] In acetaldehyde, CH_3CHO (no. 36), the two bands occur at 6.0 and 8.0, but in paraldehyde[3] the 5.8 band is very weak and the other is absent entirely, as is to be

[1]Carn. Inst., pp. 216–223.

[2]Coblentz, pp. 200, 201, 260.

[3]Coblentz, p. 261.

expected since the C = O group is not present, as shown by the formula. In all compounds, therefore, whose spectra are at hand, and which contain a C = O group, two bands occur near 5.8 and 8.2.

The spectra of acetaldehyde and paraldehyde show incidentally that the relative proportions of each kind of atom plays a secondary rôle as compared with the way in which the atoms are put together; the molecule of paraldehyde consists of three molecules of acetaldehyde, but the arrangement of the atoms is of course changed on polymerization; the spectra differ because the structure does.

To sum up:

OH has bands in the alcohols at 3.0 and 6.9.

CH_2 has bands in the alcohols, acids, and esters near 3.4.

has bands in the esters and higher alcohols near 7.3.

C = O has bands near 5.9 and 8.2.

ADDITIONAL FACTS BEARING ON THE PRECEDING QUESTIONS.

In order to test some of the preceding conclusions, several polyatomic alcohols, *i. e.*, alcohols with more than one OH group, and some dibasic esters, *i. e.*, esters of acids with two COOH groups, were examined. In the diatomic alcohols or glycols (nos. 33 and 34), just as in the monatomic alcohols, there are three general absorption regions before 10μ. In the first region there is a deep band at 3.2 in place of the one formerly found at 3.0. The second region, from 7.0 to 8.5 has only one minimum common to both the glycols examined; it occurs at 7.2. The third region has one band near 9.6. Outside of these regions there is a deep band at 6.0 and a somewhat less pronounced one near 4.2. The triatomic alcohol, glycerin (no. 35), also has three general absorption regions and in addition the new bands at 4.3 and 6.0, the latter being deeper than in the glycols. The minimum in the first region falls at 3.3; the second has two minima at 7.3 and 8.2; the third has a minimum at 9.6. The band in the first region is probably due to OH; if so, the addition of more hydroxyl groups shifts the band to the longer wave-lengths, the first additional OH causing more of a shift than the second. The 6.9 band which was also ascribed to OH in the monatomic alcohols is not distinct here, though the broadness of the band in the second region indicates its presence. The deep

band in the 3.5 region in the higher monatomic alcohols does not show in the polyatomic alcohols, probably because of the small proportion of CH_2 in these compounds as compared to OH. The 7.3 band however does show and is again probably a CH_3 band. The spectra of the polyatomic alcohols therefore have the same general characteristics as the monatomic ones; none of the previous correlations between groups and bands are contradicted. The main features of the spectra are the shift of the band in the first absorption region and the appearance of two new bands at 4.2 and 6.0; the former is due to the addition of more hydroxyl; the latter have not been correlated to any particular group.

The spectra of the acid and normal dibasic esters are almost identical as is shown by ethyl oxalate (no. 37) and diethyl oxalate (no. 40), and by ethyl succinate (no. 39) and diethyl succinate (no. 41). The spectra of the homologs ethyl oxalate, ethyl malonate, and ethyl succinate (nos. 37, 38, 39), and of diethyl oxalate and diethyl succinate (nos. 40, 41), are also very similar, just as the spectra of the monobasic homologs studied above. Up to about 8.6 and beyond 11.6 the absorption lines are practically identical in position, but the two lines between 8.6 and 11.6 show a shift toward shorter wave-lengths as the series is ascended: in ethyl oxalate, malonate and succinate these bands occur respectively at 10.0, 9.8, 9.5 and at 11.0, 10.7, 10.4; in diethyl oxalate and diethyl succinate they are found at 10.0, 9.7 and at 10.9, 9.5; the shift is less in the normal than in the acid esters. Hence the homologous dibasic esters lead to the same general conclusion that has been reached for other homologs: increase in complexity due to homology causes a small shift of several bands.

These esters also substantiate the conclusions regarding the correlation of groups and bands. There is no alcoholic hydroxyl group; neither is there a band at 3μ nor a deep one near 6.9 The two bands near 3.4 and 7.4, which in the monobasic esters were ascribed to CH_2, occur here at 3.5 and 7.5. Two bands, one at 5.9 and the other between 8.2 and 8.6, both of which were ascribed to C = O, occur here at 5.9 and 8.6. The prominent lines found here at about 4.5 and 7.7 are new, but cannot be correlated with any particular group or structure by comparing esters only. The shift

of the two bands between 8.6 and 11.6 can be correlated with the separation of the two carboxyl groups, or rather with the separation of one carboxyl, COOH, and one substituted carboxyl, $COOCH_2CH_3$ for in the lowest member of the series, ethyl oxalate, the two groups are joined directly, while in the next member, ethyl malonate, they are separated by one CH_2 group, in the next member, ethyl succinate, by two CH_2 groups, and so on. In the diethyl esters, where both carboxyls have been changed to $COOCH_2CH_3$, the shift is in the same direction, but smaller, due probably to the fact that more CH_2 is already present. These compounds therefore have spectra similar to the corresponding monatomic compounds: homologs show a similar behavior in the two cases, and the correlations made between particular groups and bands hold in the complex as well as in the simpler substances.

It will be noticed that practically all of the interpretations have been made from the parts of the spectra lying below 10μ. In this region the spectra of chemically similar compounds are similar to that the conclusions reached usually depend on a whole class of substances. In the region beyond 10μ, the spectra differ more materially, as was pointed out by Coblentz; this is the region where the individual characteristics of a substance produce the most pronounced effects, but on account of the nature of the changes produced, no definite conclusion can be drawn, from this investigation at least, as to the relation between particular bands and chemical structure. If it were required to identify a chemical compound by means of its absorption spectrum, the part of the spectrum lyine below 10μ would be useful mainly in determining the class to which the substance belongs, while the part beyond 10μ would determing the individual substance.

SUMMARY.

An apparatus has been built for taking graphic records of infrared absorption spectra.

The substances examined were all freshly prepared or purified, and were so selected as to permit the discussion of the several problems enumerated below. In the discussion of these problems, which all relate to series of compounds, use has been made mainly of the part of the spectra lying below 10μ; the part beyond 10μ gives the individual characteristics of each substance.

1. *Effect of Isomerism.*—Sometimes the spectra of isomers are practically identical, *e. g.*, isomerism in the esters due to transferring CH_2 from the acid to the basic parts of the compound; these compounds are all fairly similar chemically. A greater change in structure causes a greater change in the spectra, *e. g.*, primary-iso isomerism in the alcohols (nos. 4 and 7, 5 and 8). A more pronounced change still, causes more or larger shifts and perhaps the appearance of one or more new bands, *e. g.*, primary-secondary isomerism in the alcohols and acids (nos. 3 and 11, 4 and 12, 14 and 19).

2. *Effect of Homology* —Many different groups of substances were examined for homology: primary alcohols, secondary alcohols, primary acids, secondary acids, monobasic esters, and dibasic esters. In each of these series the spectra are similar; the addition of CH_2 usually causes small shifts of one or more bands, the shifts being larger in the lower members of the series, where the number of CH_2 groups already present is small.

3. *Effect of Certain Groups.*—The following groups and bands have been shown to be related:

OH, 3.0 and 6.9 in the alcohols.

CH_2, 3.4 in the alcohols, acids and esters.

CH_2, 7.3 in the esters and higher alcohols. (The band at 7.1 in the acids may be a CH_2 band also, but is probably a COOH band.)

C = O, 5.9 and 8.2 in all substances for which there are data.

4. *Effect of Mode of Linking.*—The 9.6 band in the primary alcohols shifts by 0.5μ to the shorter wave-lengths when the linking of the hydroxyl is changed to secondary, and by 0.5 more when changed to tertiary. (CH_2OH, CHOH, COH.)

The change from the primary to the secondary linking of the carboxyl group (CH_2COOH to CHCOOH), causes the doubling of a band in the 8μ region; this is true for both acids and esters.

The successive introduction of CH_2 groups between the two carboxyl (or methylated carboxyl) groups in the dibasic esters causes two bands lying between 8.6 and 11.6μ to shift toward shorter wave-lengths.

The C = O group is independent of its mode of linking to the

other parts of a molecule, for its bands occur at the same place in all substances for which there are data.

5. *Effect of the Number of One Kind of Group.*—As the number of CH_2 groups is increased, some bands remain unchanged and others shift slightly, as mentioned under effect of homology.

As the number of OH groups is increased in the alcohols, the 3μ band shifts toward longer wave-lengths.

6. *Effect of Polymerism.*—If two polymers differ greatly in structure, their spectra are also greatly different; *e. g.*, acetaldehyde and paraldehyde.

All these results agree with the conclusions of Abney and Festing, and of Coblentz, that the spectra of chemically similar compounds are similar.

The preceding generalizations are based on data covering really only a very small part of the entire chemical field, and are therefore decidedly subject to revision. They are stated in this rather decisive way for the sake of clearness only.

In conclusion, I wish to express my sincere thanks to Professors Kahlenberg and Koelker for their advice on the chemical part of the work, to Professor Snow for placing at my disposal all the necessary apparatus, and especially to Professor Mendenhall who not only suggested the subject but also greatly facilitated the work while in progress by his constant interest and helpful advice.

PHYSICAL LABORATORY,
UNIVERSITY OF WISCONSIN,
August, 1908.

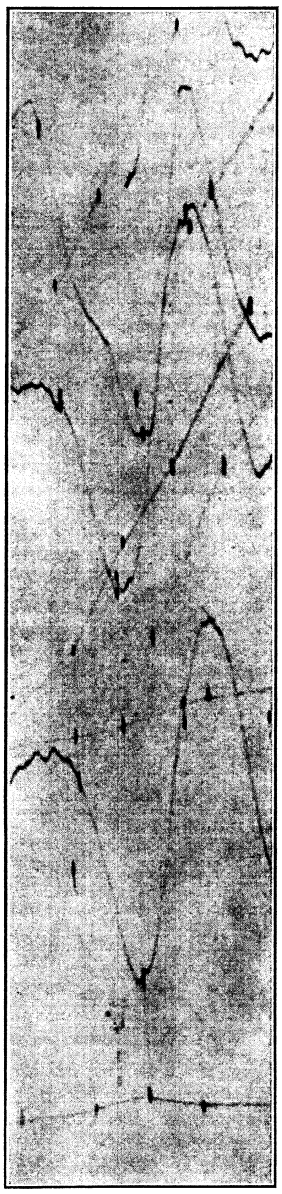
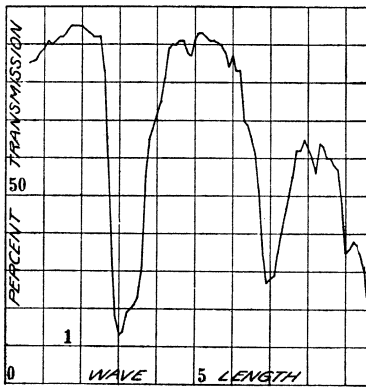
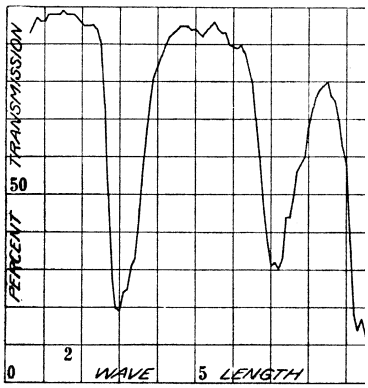


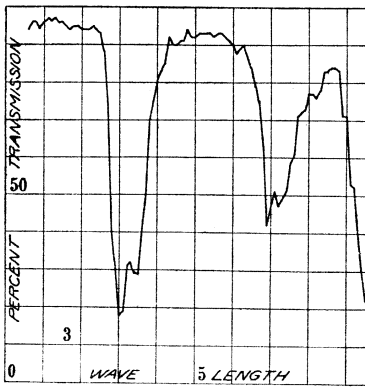
Fig. 3.



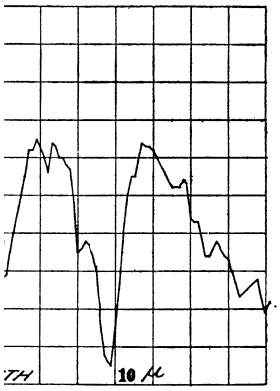
Curve 1. Methyl alcoh



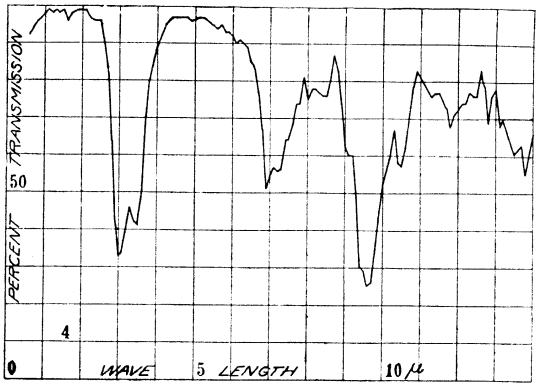
Curve 2. Ethyl alcoh

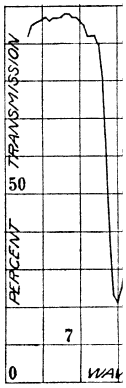


Curve 3. Propyl alcol

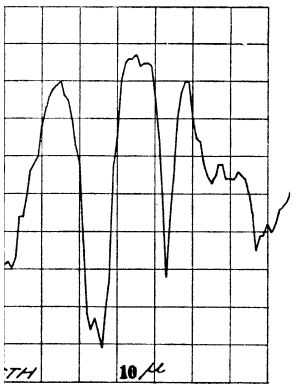


ethyl alcohol.

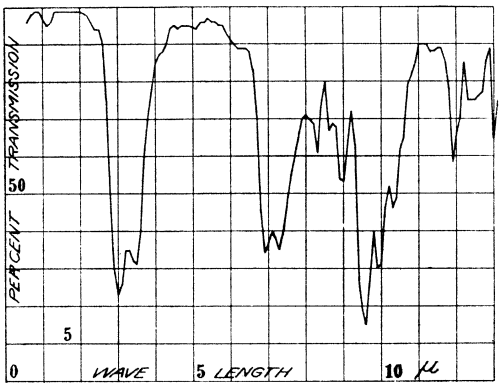


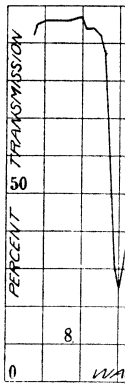


Curve 4. Butyl alcohol.

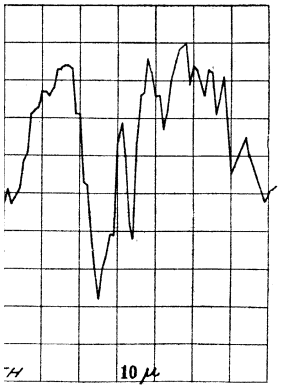


thyl alcohol.

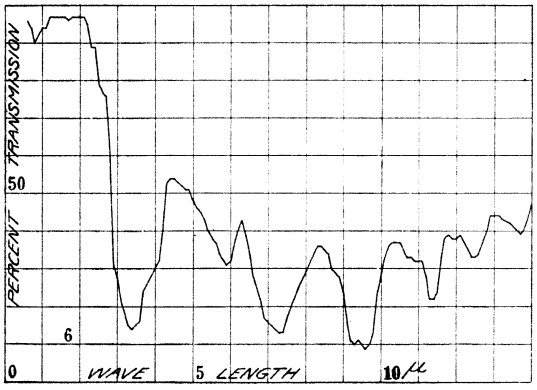


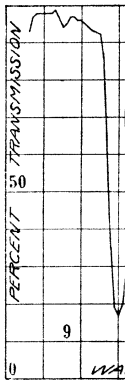


Curve 5. Amyl alcohol.

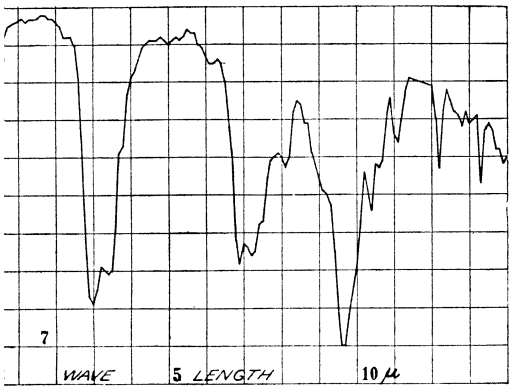


ropyl alcohol.

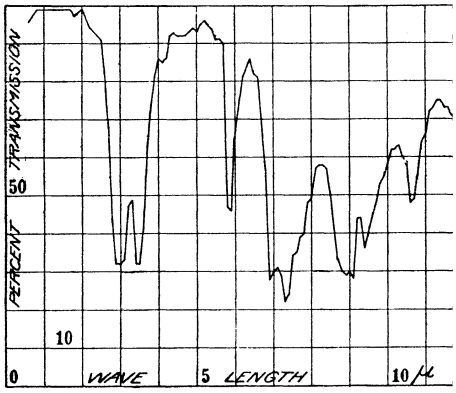




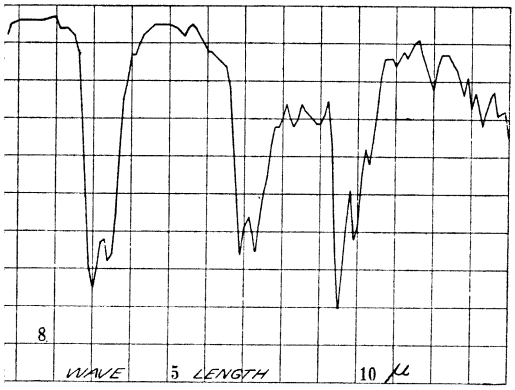
Curve 6. Sodium alcoholate.



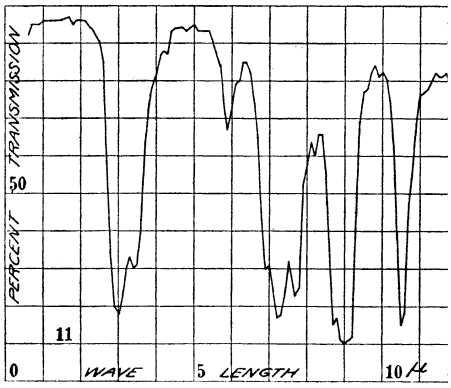
Curve 7. Isobutyl alcohol.



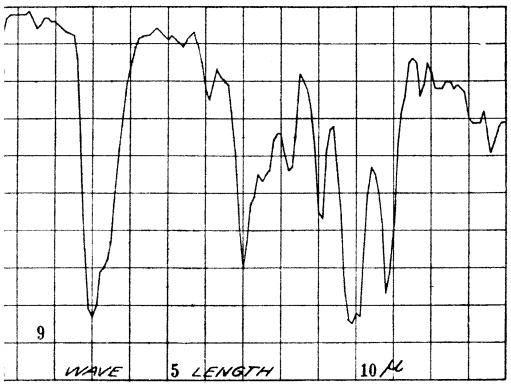
Curve 10. Capril alcohol.



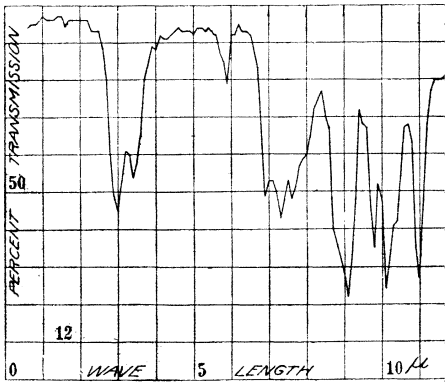
Curve 8. Isoamyl alcohol.



Curve 11. Secondary propyl alcohol.



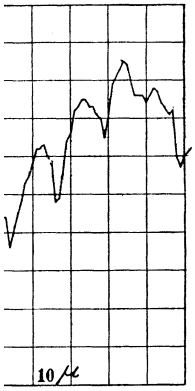
Curve 9. Allyl alcohol.



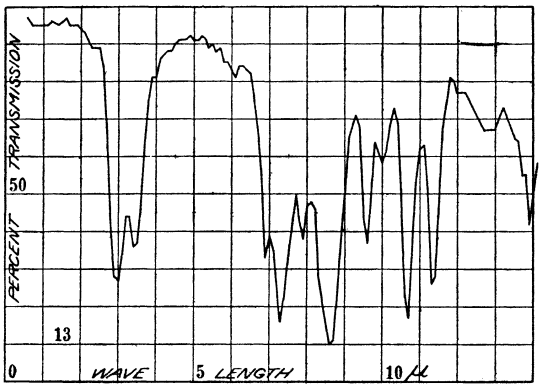
Curve 12. Secondary butyl alcohol.

Absorption Spectra. PLATE I.

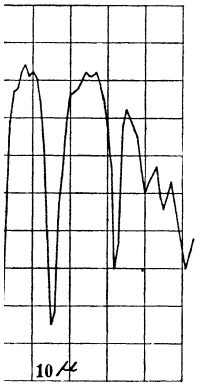
to face page 420



hol.



Curve 13. Tertiary amyl alcohol.



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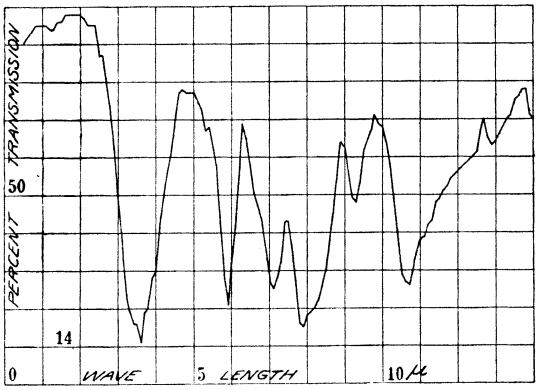
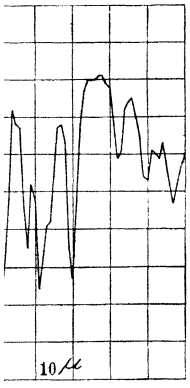
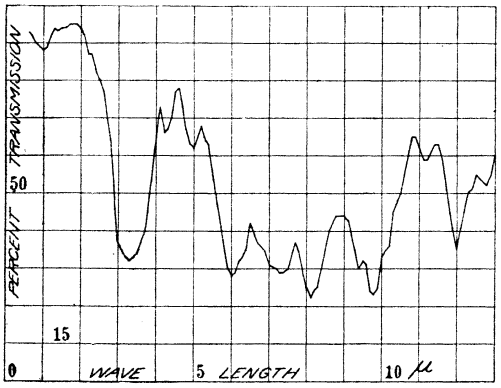


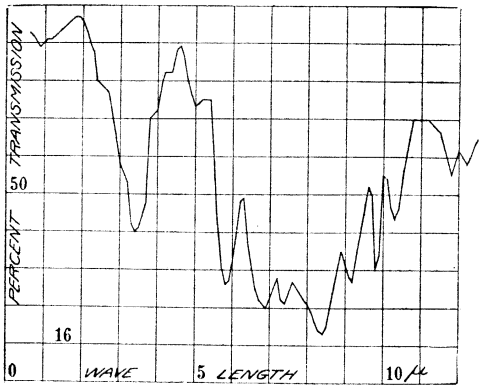
Curve 14. Butyric acid.



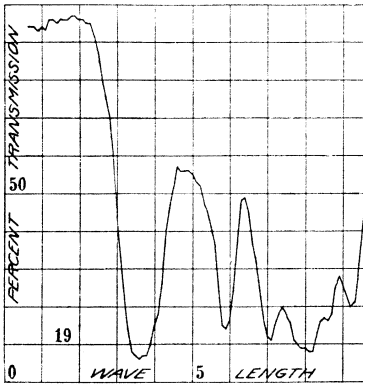
yl alcohol.



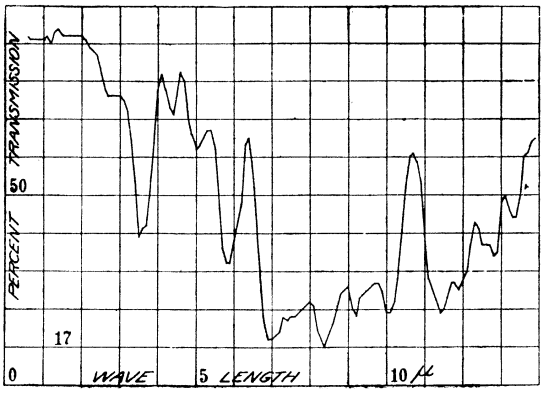
Curve 15. Methyl acetate.



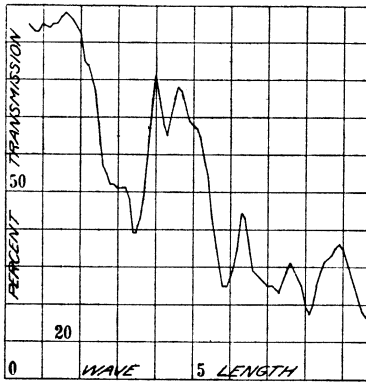
Curve 16. Methyl propionate.



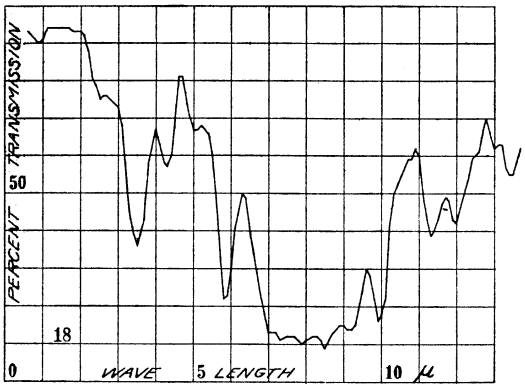
Curve 19. Isobutyric acid.



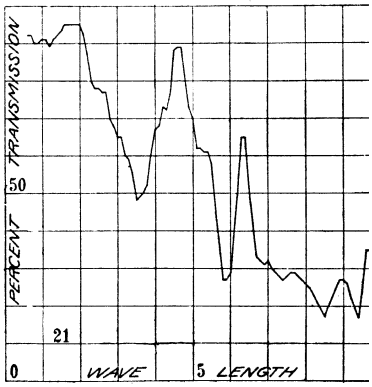
Curve 17. Methyl butyrate.



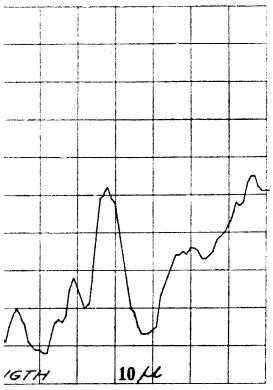
Curve 20. Ethyl acetate.



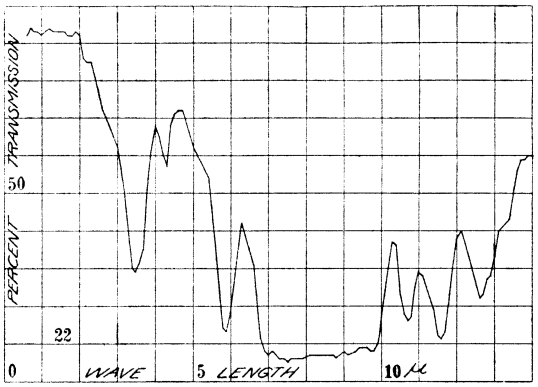
Curve 18. Methyl isovalerianate.



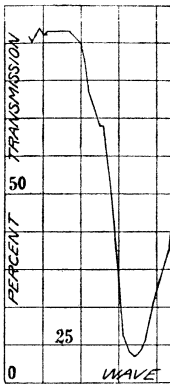
Curve 21. Ethyl propionate.



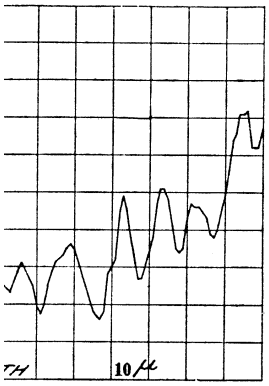
ic acid.



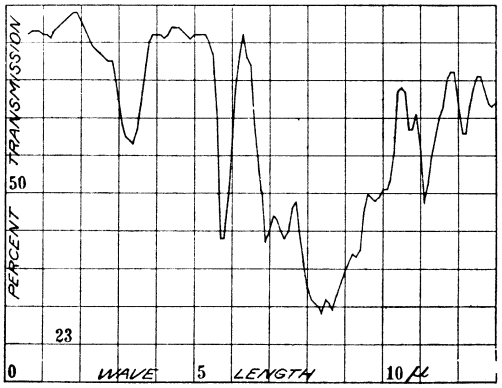
Curve 22. Ethyl butyrate.



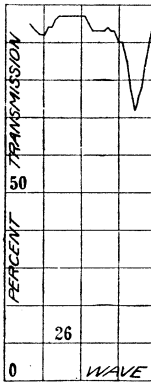
Curve



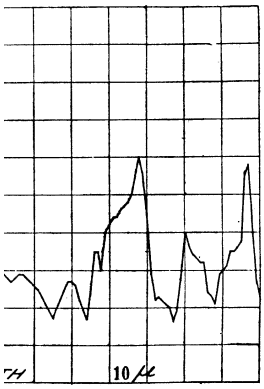
acetate.



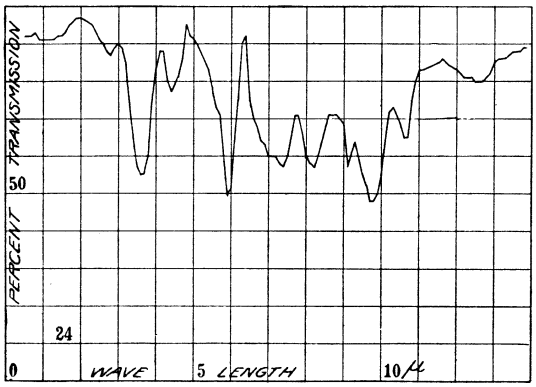
Curve 23. Methyl isobutyrate.



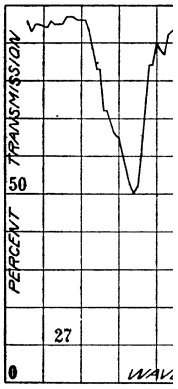
Curv



ionate.



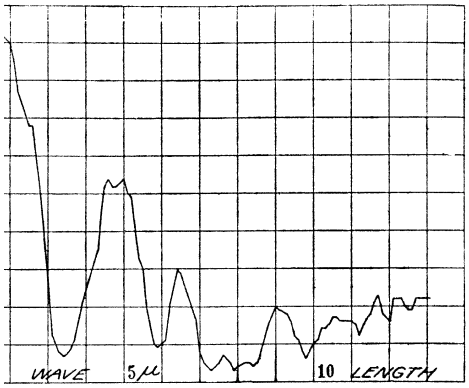
Curve 24. Methyl hexyl carbinol acetic ester.



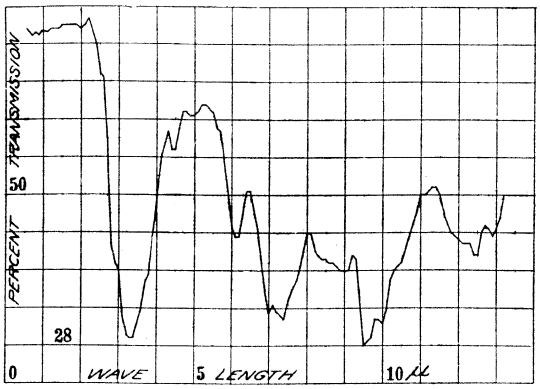
Curve 2

WENIGER: Infra-red Absorption Spectra. PLATE II.

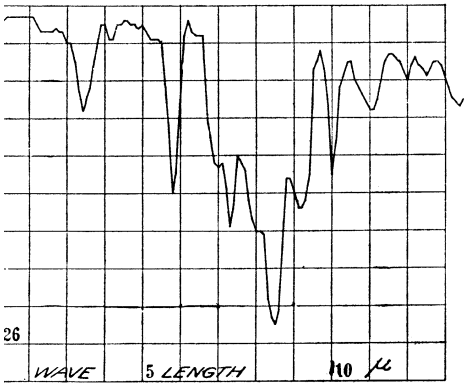
To face page 420,



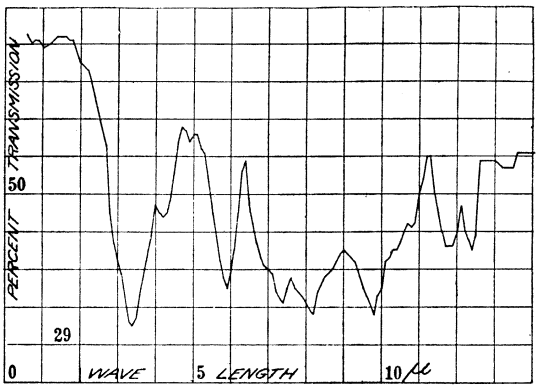
Curve 25. Isobutyl acetate.



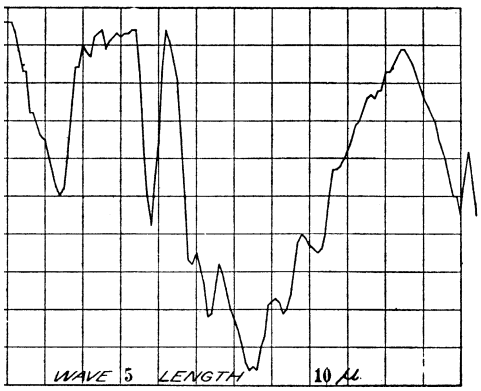
Curve 28. Isoamyl formate.



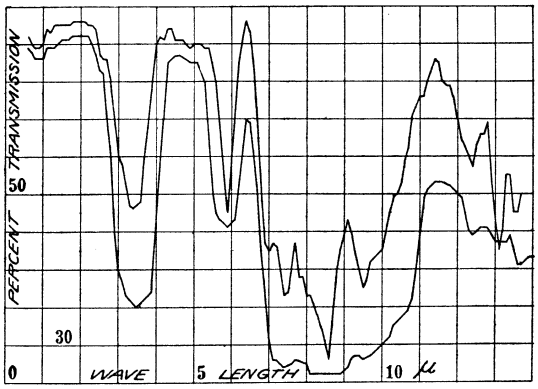
Curve 26. Butyl butyrate.



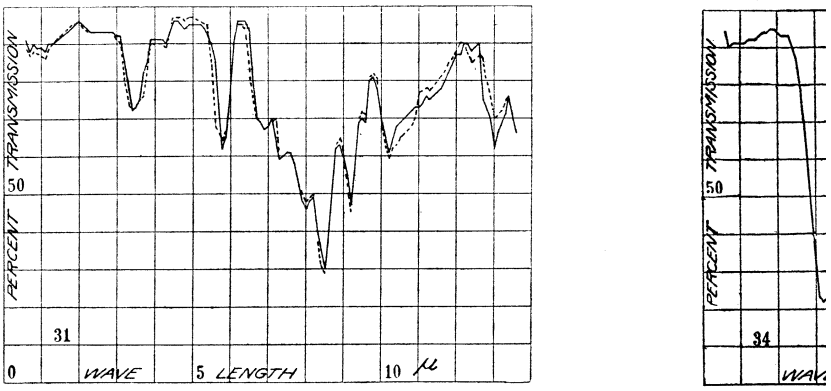
Curve 29. Isoamyl acetate.



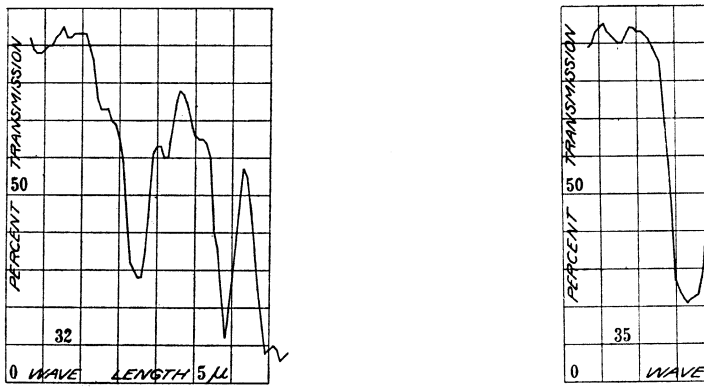
Curve 27. Isoamyl isobutyrate.



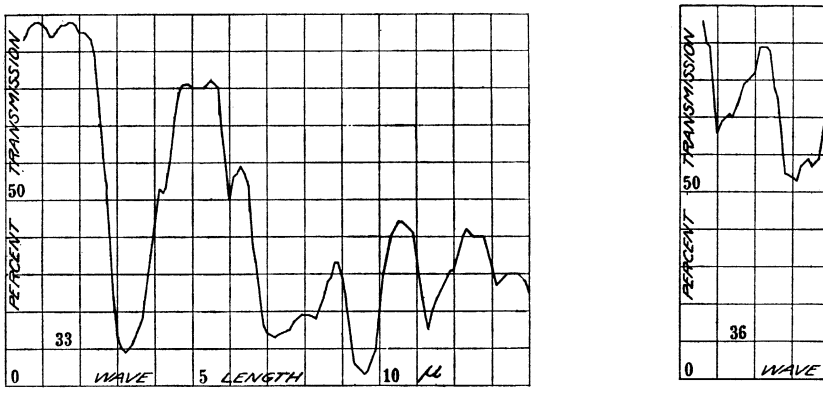
Curve 30. Isoamyl propionate.



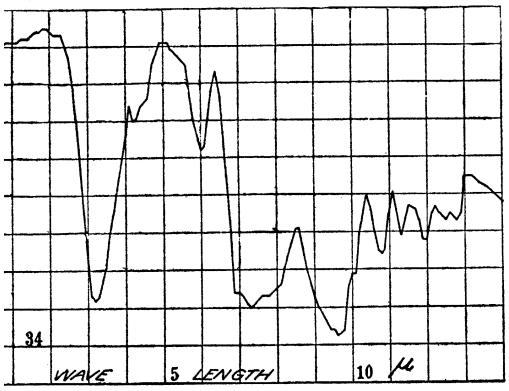
Curve 31. Isoamyl butyrate.



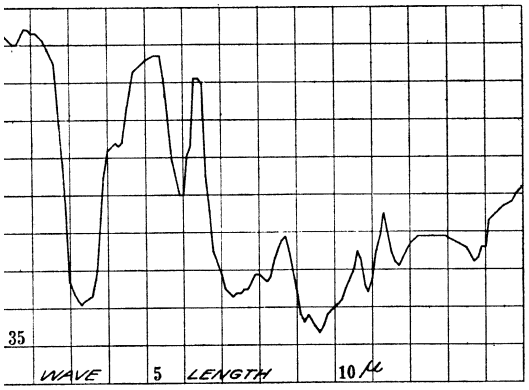
Curve 32. Isoamyl isovalerianate.



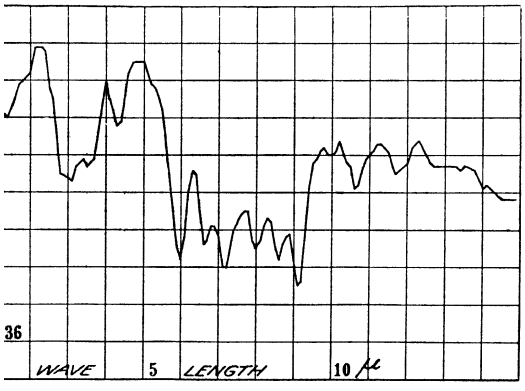
Curve 33. Ethylene glycol,



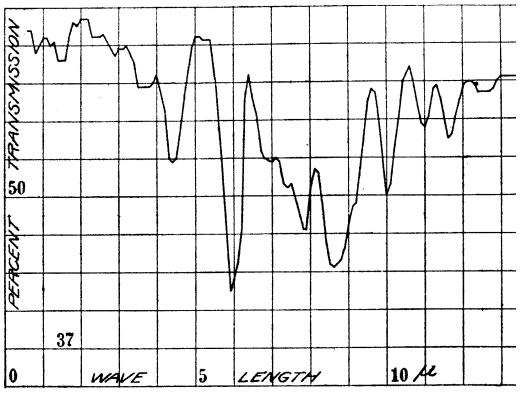
Curve 34. Propylene glycol.



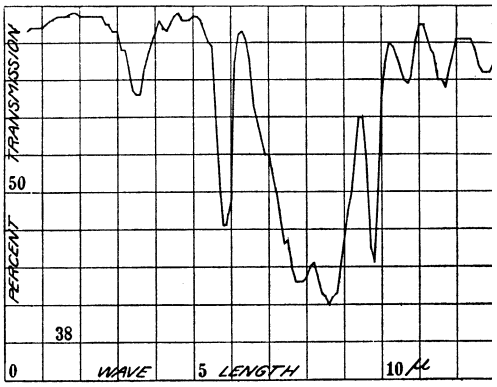
Curve 35. Glycerin.



Curve 36. Acetaldehyde.



Curve 37. Ethyl oxalate.



Curve 38. Ethyl malonate.

WENIGER: Infra-red Absorption Spectra. PLATE III.

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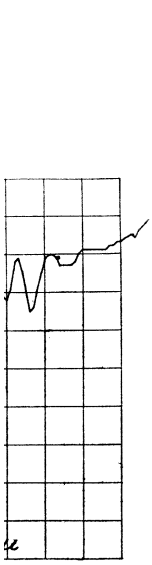
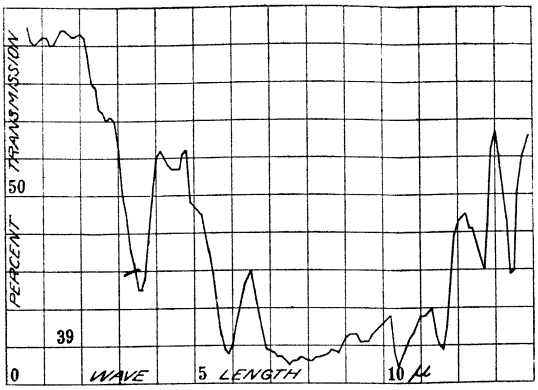
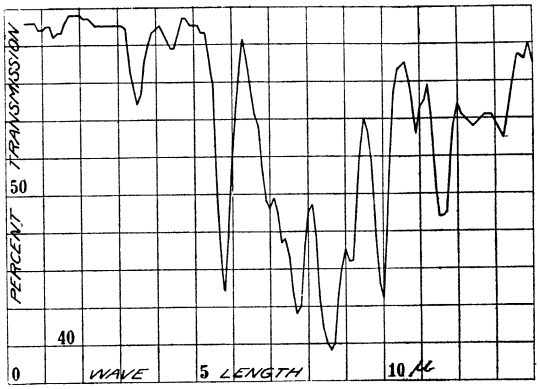
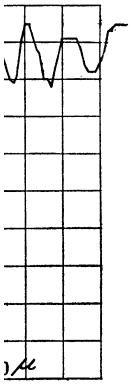


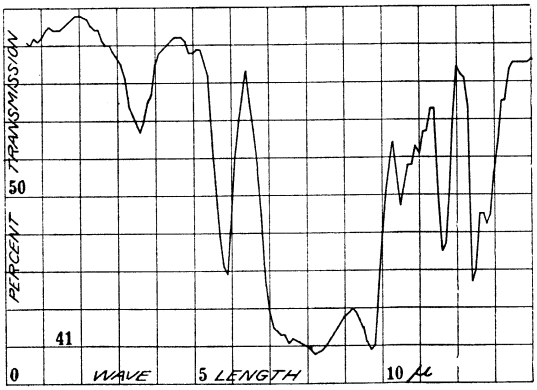


Curve 39. Ethyl succinate.



Curve 40. Diethyl oxalate.





Curve 41. Diethyl succinate.

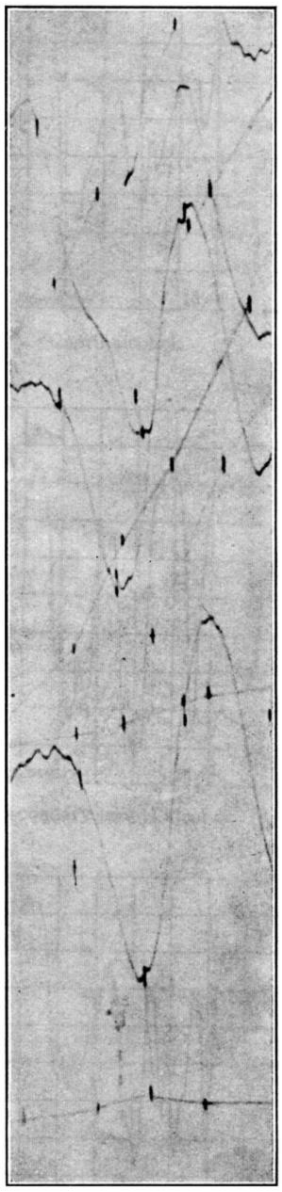


Fig. 3.