Summary

1. The specific heats of *tert.*-butyl alcohol, mannitol, erythritol and *n*-butyric acid have been measured over a wide range of temperatures. The heats of fusion of *tert.*-butyl alcohol and *n*-butyric acid have also been determined.

2. The entropies and free energies of the four compounds have been calculated by means of these heat-capacity data. The experimental results thus obtained are in good agreement with the entropy and free-energy values predicted for these substances upon the basis of previously observed regularities.

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[CONTRIBUTION FROM THE LABORATORIES OF PHYSICS AND CHEMISTRY OF OHIO STATE UNIVERSITY]

INFRA-RED ABSORPTION IN ETHERS, ESTERS AND RELATED SUBSTANCES

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By a study of the absorption spectra of a number of hydrogen-carbon compounds in the region between 0.9 μ and 2.4 μ Ellis[1] has been able to show that in such compounds there appears to be a harmonic relationship between the absorption bands. He attributes this series of bands to the hydrogen-carbon linkage in the molecule. Except for the observations of Dreisch[2] on benzene and chloroform and those of Coblentz[3] on lard oil, there are few detailed data on the absorption of hydrogen-carbon compounds in this region of the spectrum. The more comprehensive work of Coblentz[4] and that of Weniger[5] covered the spectral region as far as about 15 μ but they did not study the near infra-red with sufficient detail to locate many of the bands which Ellis arranges in a harmonic series. It seemed of interest, therefore, to make some observations on other hydrogen-carbon compounds to see in how far this series of bands remains unchanged with the introduction of various groups into the molecular structure.

Apparatus

Spectrometer.—The spectrometer (Fig. 1), which was a standard Hilger instrument for the infra-red region of the spectrum, was provided

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[1] Ellis, *Phys. Rev.*, [2] **23**, 48 (1924); *J. Optical Soc. Am.*, **8**, 1 (1924).

[2] Dreisch, *Z. Physik*, **30**, 200 (1924).

[3] Coblentz, *Bur. Standards, Sci. Papers*, No. 148, **1921.**

[4] Coblentz, "Infra-red Absorption Spectra," Part I, *Carnegie Inst. Pub.*, No. **35,** (1905).

[5] Weniger, *Phys. Rev.*, **31,** 388 (1910).

with a calibrated wave-length drum from which the wave lengths were read directly.

The source of radiation L was a large, single filament tungsten lamp supplied with a current of 16 amperes from a transformer T. The radiation from this source was focused on the slit S of the spectrometer by means of the concave mirror M whose aperture was 6 in. The radiation from the slit S, made parallel by the second concave mirror M_3 passed through the rock salt prism P. After reflection by the plane mirror M_2, it was focused by means of a third concave mirror M_1 on the slit S_1 in front of the thermopile. A Coblentz linear thermopile with ten bismuth-silver junctions was used. This thermopile was connected in series with a Leeds and Northrup high sensitivity galvanometer, having a resistance of 11.4 ohms and a figure of merit of 3.30×10^{-9} amperes per mm. for a scale distance of 1 meter. The scale was used at a distance of 2 meters and the deflection could be estimated with certainty to 0.1 mm. The whole of the spectrometer was enclosed in a black wooden box to exclude extraneous radiations. Each slit of the spectrometer was 0.127 mm. (0.005 in.) in width.

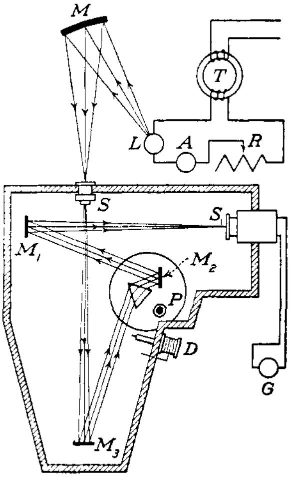

Fig. 1.

Absorption Cells.—Two cylindrical cells (Fig. 2) about 2.5 cm. in diameter and 1.5 mm. thick were mounted on a plate of brass.

They were provided with mica windows which were about 0.002 cm. in thickness. These windows were held in position by placing a rubber gasket on the top of each of them and then pressing them against brass shoulders by means of a screw cap which transmitted its pressure to the gasket through a brass bushing. The windows were so matched that when both cells were empty, they produced the same amount of absorption. The upper cell was connected by means of a hole about 0.5 mm. in diameter to the well W by means of which this cell was filled. This well was closed with a screw which was forced against a rubber gasket. A mounting with suitable stops was fastened to the box surrounding the spectrometer so that the cells could be brought in turn before the slit of the spectrometer and thus the positions of the empty and the filled cells could be interchanged. Between the cells and the slit of the spectrometer there was a sliding shutter which could be raised or lowered to allow the radiation to fall on the slit of the spectrometer when observations were actually being made through the empty or the filled cell. Except when observations were being made through the cell containing the liquid, this cell was drawn up behind an opaque shield of cardboard to prevent, as far as possible, changes in the temperature of the liquid.

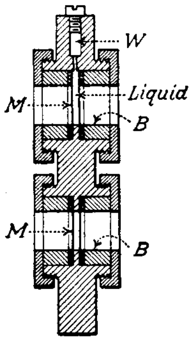

Fig. 2.

Method of Observation

The prism was put in adjustment by setting it so that the D lines of sodium fell on the slit of the thermopile when the calibrated drum read 0.589 μ. This setting was checked by making a similar observation on the red line of lithium, having a wave length of 0.7608 μ.

The zero reading of the galvanometer was noted. The shutter was raised and the reading through the cell containing the liquid was determined. The empty cell was then brought before the slit of the spectrometer and the reading corresponding to this position of the cells was determined. With the shutter closed the zero reading of the galvanometer was again taken. The percentage transmission was then found by dividing the deflection when the cell containing the liquid was in front of the slit by the corresponding deflection when the empty cell was in front of it. Observations at intervals of 0.02 μ were made over nearly all the spectral region covered in this investigation. In a few parts of the spectral region, removed from the heads of the absorption bands, intervals of 0.04 μ were used. All the observations were made at room temperature which varied from 22° to 25°.

In order to have a test of accuracy of the method of observation, chloroform was studied. Data on the wave lengths of the absorption bands of this liquid in the near infra-red region of the spectrum are available from the work of two observers. Table I gives a comparison of the values previously obtained with those found in this investigation. It will be noted that the agreement is satisfactory.

TABLE I

ABSORPTION BANDS IN CHLOROFORM

Observer	Absorption maxima, μ					
Ellis	1.145	1.385	1.66	1.835	2.105	2.425
Dreisch	1.19	1.44	1.72	1.885	2.10	2.388
Mean	1.168	1.412	1.69	1.860	2.102	2.406
Authors	1.151	1.411	1.687	1.870	2.09	2.356

Sources and Purities of Compounds

The compounds listed in Table II were obtained from the several sources as indicated opposite their names and had the boiling-point ranges shown in Col. 2. The ethers and other compounds marked E. K. were the best grade from the Eastman Kodak Company. The other ethers in this list were, without exception, prepared by Mr. Arthur J. Yaney by the Williamson method and are identical with those used by him in an unpublished research involving a spectrographic study of the ultraviolet absorption of the aliphatic ethers.[6] The esters were, with the exception of amyl acetate, obtained from the Special Chemicals Corporation, Pfanstiehl best grade. The ethyl alcohol, ethyl ether, methyl diethyl carbinol and chlorinated hydrocarbons were laboratory and commercial products and were purified especially for this work.

TABLE II

ABSORPTION BANDS IN ETHERS, ESTERS AND RELATED COMPOUNDS

Compounds	B. p., °C.	Absorption maxima, μ				
Ethyl ether..................	35	1.02	1.20	1.38	1.71	2.34
Methyl *n*-propyl ether........	39	1.03	1.19	1.39	1.73	2.34
Methyl *iso*propyl ether........	32–33	1.02	1.19	1.40	1.72	2.35

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[6] Ph.D. *Dissertation*, Ohio State University, **1925**.

TABLE II (*Concluded*)

Compounds	B. p., °C.	Absorption maxima, μ				
Methyl *n*-butyl ether	70	1.05	1.19	1.42	1.74	2.35
Methyl *iso*butyl ether	59	1.03	1.20	1.39	1.74	2.35
Methyl *sec.*-butyl ether	61–63	1.02	1.19	1.40	1.73	2.35
Methyl *tert.*-butyl ether	59–62	1.02	1.18	1.38	1.72	2.34
Methyl *n*-amyl ether	97–101	1.02	1.19	1.40	1.73	2.35
Methyl *iso*-amyl ether	90–91	1.02	1.19	1.40	1.74	2.35
Methyl *tert.*-amyl ether	84–86	1.03	1.18	1.40	1.73	2.35
Methyl-diethylcarbinyl ether	88–91	1.03	1.19	1.40	1.73	2.36
Amyl formate (P)	120	1.02	1.19	1.39	1.73	2.34
Methyl acetate (P)	55.5	1.02	1.17	1.39	1.71	2.34
n-Propyl acetate (P)	100.5	1.06	1.19	1.39	1.73	2.35
Amyl acetate (Kahl.)	136–140	1.02	1.19	1.40	1.73	2.35
Ethyl propionate (P)	94–98	1.03	1.18	1.39	1.71	2.34
Ethyl butyrate (P)	116–121	1.03	1.18	1.40	1.72	2.34
Diethyl carbonate (P)	124–125.5	1.02	1.17	1.39	1.71	2.32
Ethyl lactate (P)	148–155	1.03	1.16	1.44	1.71	2.35
Methyl benzoate (P)	198–199.5	1.00	1.15	1.38	1.68	2.31
Diethyl phthalate (P)	291–292	1.02	1.16	1.38	1.68	2.31
Ethyl salicylate (P)	231–233	1.03	1.14	1.38	1.67	2.28
Ethyl alcohol	78	1.02	1.18	1.40	1.72	2.34
n-Butyl alcohol (E. K.)	116–118	1.02	1.19	1.42	1.72	2.33
Methyl-diethyl carbinol	122	1.04	1.18	1.42	1.71	2.34
Ethylene chloride (E. K.)	82.5	1.02	1.17	1.39	1.71	2.30
Tetrachloro-ethane	142–145	..	1.17	1.42	1.72	2.36
Trichloro-ethylene	85–87	..	..	1.38	1.65	2.32
Dichloro-ethylene	54–56	1.0	1.12	1.38	1.66	2.32

Results

Curves showing the percentage transmission for different wave lengths between 1 μ and 2.5 μ are given in Figs. 3 to 11, inclusive. An examination of Figs. 3, 4 and 5 shows that the curves for all the ethers have essentially the same characteristics. The positions of the absorption bands do not change with the molecular structure by an amount greater than the error of observation. The percentage of transmission for a particular wave length is very approximately the same for all of these ethers. There are minor variations but no outstanding differences. From Figs. 6, 7 and 8 it is also seen that the absorptions in the esters, ethyl *n*-propionate, ethyl *n*-butyrate, diethyl carbonate, amyl acetate, methyl acetate, *n*-propyl acetate, ethyl salicylate, diethyl phthalate and methyl benzoate are very similar to the absorption in the ethers. A small absorption band in the neighborhood of 1.92 μ is definitely indicated. It is more prominent in methyl acetate than in the other esters of this group. This band is also suggested in some of the ethers, particularly methyl *n*-amyl ether. In ethyl salicylate the absorption band at 1.38 μ has become indistinct due to an increase in the intensity of the absorption band at 1.71 μ and the resulting overlapping of these bands. The band near 2.38 μ has become wider on account of the increase in the absorption in this region. From these curves it is evident that the variations in molecular structure as we pass from one of these compounds to another have only slightly influenced the character of the absorption spectra in this region of the spectrum. The curve for amyl formate (Fig. 9) is not unlike the corresponding curves for the ethers. In the case of ethyl alcohol and *n*-butyl alcohol (Fig. 9) and also in the case of ethyl lactate and methyl diethyl carbinol (Fig. 10) there is a marked increase in absorption in these two parts of the spectrum; there is an overlapping of these absorption bands with the neighboring bands in such a way as to modify the character of the curves showing the percentage transmission of these substances. A shift in the position of the absorption band at 1.38 μ and at 1.94 μ is produced. This shift is probably only apparent and arises from the failure to resolve the bands sufficiently to make their accurate location possible. The substitution of chlorine for the hydrogen in passing from ethylene chloride to tetrachloroethane causes a marked decrease in the absorption for each of the characteristic absorption bands without any evident shift in their positions. Similarly, the absorption bands in dichloro-ethylene are more pronounced than they are in trichloro-ethylene. The decrease in absorption in these cases probably arises out of the decrease in the number of hydrogen-carbon linkages in the molecule.

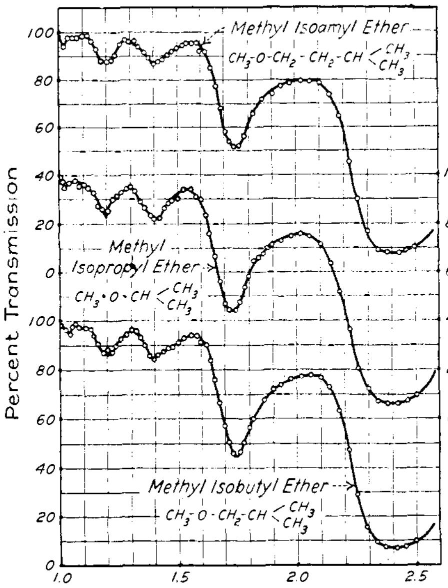

Fig. 3.

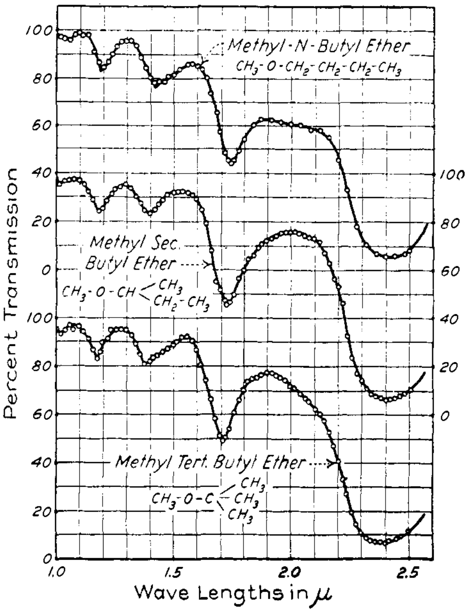

Fig. 4.

In agreement with the conclusion of Ellis the bands recorded in Table

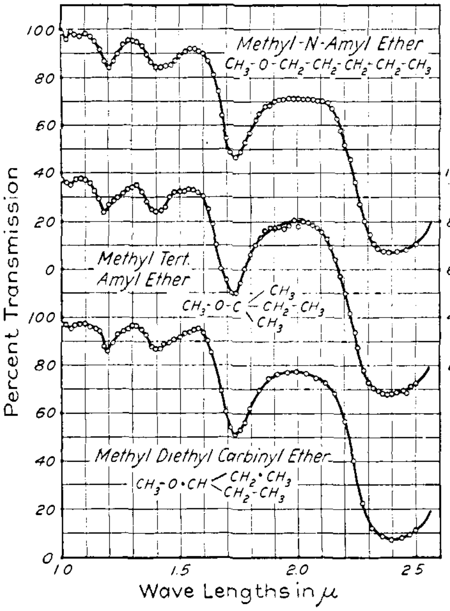

Fig. 5.

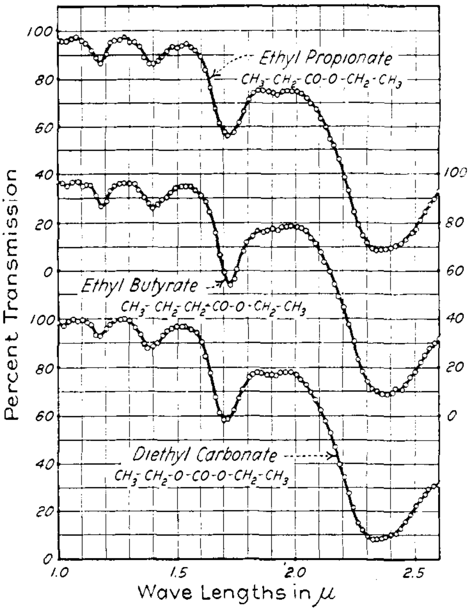

Fig. 6.

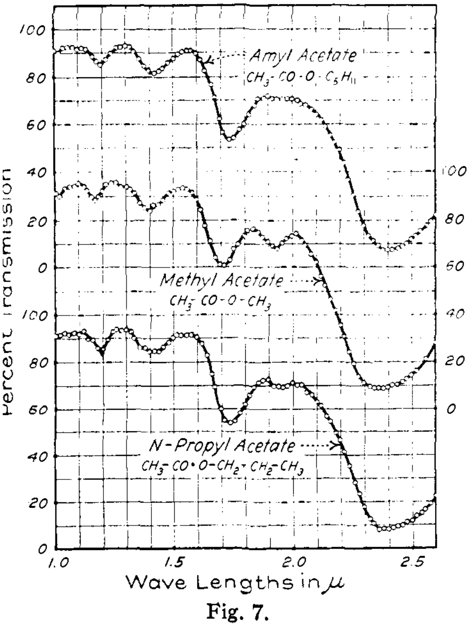

Fig. 7.

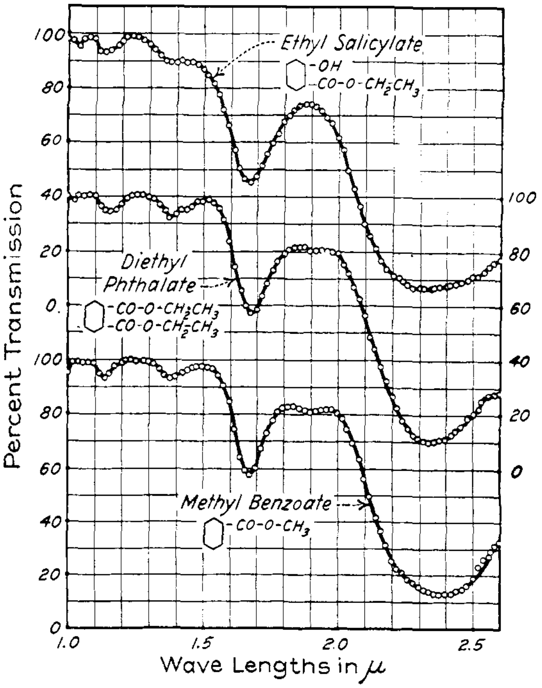

Fig. 8.

II should be ascribed to the presence of the hydrogen-carbon linkage in the molecule. The correctness of this conclusion is also clearly indicated by the fact pointed out by Ellis that such substances as carbon disulfide and carbon tetrachloride, which have carbon without hydrogen, have no absorption bands in this region of the spectrum. The curves also show that the depths of the bands are approximately a direct function of the number of hydrogen-carbon linkages. Although the intensities of the different bands are somewhat altered by variations in the molecular structure, the locations of the bands remain essentially unchanged.

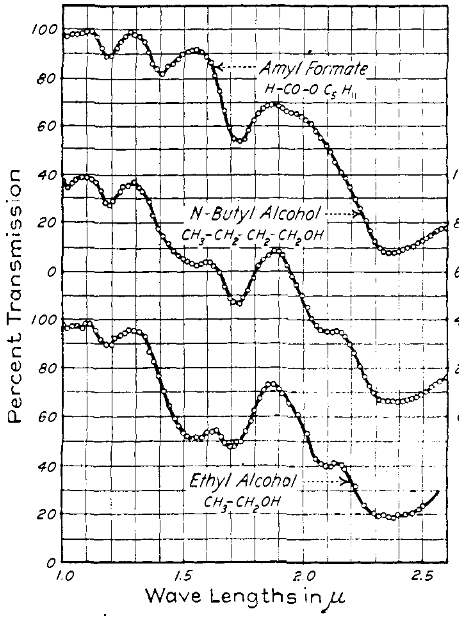

Fig. 9.

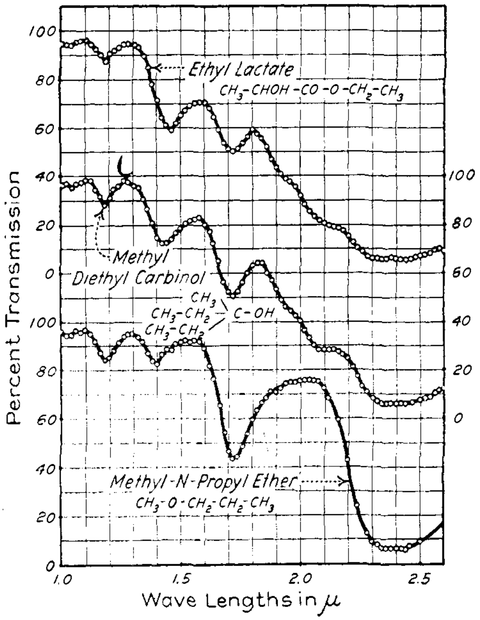

Fig. 10.

Ellis has shown that the members of this series of bands are related to each other through the equation, $\nu_n = n\nu_0(1-nx)$, where ν_0 is the fundamental wave number, ν_n is the wave number of the nth overtone band, n has the values of 2, 3, 4, 5, etc., for the first, second, third, etc., overtone bands, and x is a small correction factor to take account of the fact that the series of the bands is not truly harmonic. According to this equation, there is a progressive deviation of the wave numbers of the higher overtone bands from a simple harmonic relation. By choosing the absorption band at 6.9 μ, which Coblentz found to be characteristic of hydrogen-carbon compounds, as the fundamental wave band of the series, it is possible by means of this equation to express the frequency numbers of these overtone bands with an accuracy which is within the error of observations made in determining the wave lengths. Hence, these observations on ethers and related hydrogen-carbon compounds are in agreement with the conclusions found by Ellis, that this series of absorption bands is characteristic of the hydrogen-carbon linkage and that they are approximately related to each other as fundamental, first, second, etc., overtones. In view of the complexity of the absorption spectra of the hydrogen-carbon compounds and the apparent arbitrariness of choosing 6.9 μ as the fundamental wave length for this series, it seems doubtful whether this method of relating this group of absorption bands is after all very significant. Before a decision on this point can be made there must be a more critical analysis of all the absorption bands which are characteristic of the hydrogen-carbon compounds. This analysis must include not only the bands in the near infra-red region of the spectrum but also those with wave lengths longer than 6.9 μ. Those bands with wave lengths which are greater than 6.9 μ are not included in the harmonic series used by Ellis and these absorption bands must be related in some way to those of the shorter wave length.

Ultimately it should be possible to treat absorption in liquids from the standpoint of the quantum theory which has so successfully described the fine-line structure in the infra-red absorption bands of some inorganic gases.[7,8,9] The fine-line structure found by Cooley[10] in the infra-red absorption bands of methane and its theoretical discussion by Dennison[11] indicate that a similar analysis can finally be made for organic vapors. Since in liquids rotational motions are not free, the rotational energy levels may be blurred in such a way as to destroy the fine-line structure. It is perhaps for this reason that no successful application of the quantum theory to absorption in liquids has yet been made and such an application does not seem possible until more detailed information

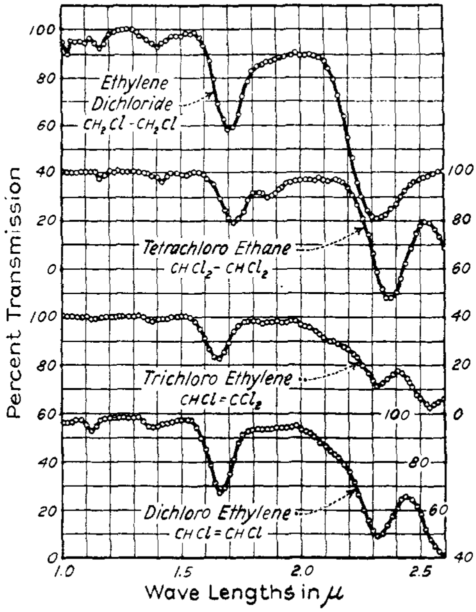

Fig. 11.

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[7] Sleator, *Astrophys. J.*, **48,** 124 (1918).

[8] Imes, *ibid.*, **50,** 251 (1919).

[9] Sommerfeld, "Atombau und Spektrallinien," Friedr. Vieweg und Sohn, **1924,** 4th ed., pp. 701–718.

[10] Cooley, *Astrophys. J.*, **62,** 79 (1925).

[11] Dennison, *ibid.*, **62,** 84 (1925).

on absorption is available. For this reason we are postponing a discussion of the relation of our observations to the quantum theory until the completion of experimental and theoretical work now in progress on the absorption of organic vapors and liquids in the infra-red and ultraviolet regions of the spectrum.

Grateful acknowledgment is made to L. A. Yingling and O. R. Fouts for assistance in making observations.

Summary

1. The absorption spectra between 1 μ and 2.5 μ have been studied for a series of ethers, esters and related compounds.

2. The positions of the absorption bands found in these compounds do not change appreciably with molecular structure.

3. The decrease in the intensity of these absorption bands in such compounds as tetrachloro-ethane and trichloro-ethylene as compared with ethylene chloride and dichloro-ethylene, respectively, is probably due to the decrease in the number of hydrogen-carbon linkages in the molecule.

4. These absorption bands are characteristic of the hydrogen-carbon linkages and can be expressed approximately as a harmonic series.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 94]

THE SPECIFIC HEAT AND ENTROPY OF HYDROGEN CHLORIDE DERIVED FROM INFRA-RED BAND SPECTRA

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I. Introduction

It is the purpose of the following paper to compute the rotational-oscillational specific heat of hydrogen chloride and its rotational-oscillational entropy, using the actual experimental energy levels for the different states of rotation and oscillation, which can be calculated from the interpretation of the absorption spectrum of hydrogen chloride in the near infrared. A number of previous investigators have calculated the specific heat and entropy of rotating or rotating-oscillating dipole molecules, but in general have assumed some simple dumbbell-like model for the molecule and have then theoretically calculated the different energy levels by quantizing the rotation and oscillation of their models. Many of these earlier calculations do not now seem applicable, since the rotation of the molecules was quantized using whole rather than half quantum numbers. Tolman,[1] however, has calculated a rotational specific-heat curve of hydrogen using

[1] Tolman, *Phys. Rev.*, 22, 470 (1923).