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THE INFRARED ABSORPTION OF SOME ORGANIC LIQUIDS UNDER HIGH RESOLUTION

PART II

By R. Bowling Barnes
John Hopkins University, Baltimore, Maryland

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Abstract

The study of the C-H vibrations bands, which occur in organic liquids between 3.0μ and 4.0μ, has been continued and extended. A more powerful spectrometer, with which wave-lengths can be determined as accurately as $\pm 0.001\mu$, has been developed for this work. Values are given here for water-vapor, benzene and toluene.

In a recent paper,[1] we gave an account of an attempt to obtain very accurate values for the C-H absorption bands of various organic liquids. In this discussion we stated the wave-lengths of benzene and eight of its derivatives with an estimated accuracy of $\pm 0.003\mu$. This present paper is intended primarily to outline the developments in the construction of the spectrometer, and the improvements which have been made in the technique and methods. These advances enable us to state wave-lengths now as close as $\pm 0.001\mu$.

By using an echelette grating rather than a rock-salt prism, the resolving power may be increased by a factor of 10 or more. For instance, in this region of the spectrum, a 10 cm prism has a resolving power of only about 170. So, even by using four-prism dispersion, one still has a resolving power somewhat less than 1000, neglecting any loss due to the finite width of the slits. On the other hand, in the grating spectrometer described in our last paper, the theoretical resolving power was over 10,000. In this region, this puts the theoretical limit of resolution for the two types of spectrometers at 30 A'' and 3 A'' respectively, the approximation to these values being determined by the width of the slits and the perfection of the optical systems being used.

In striving to approach these theoretical limits of resolution one uses very narrow slits. When this is done however, another factor becomes of considerable importance in determining the actual limit. In a paper at the April meeting of the American Physical Society[2] we called attention to the effects of various aberrations in this respect.

If one is not fortunate enough to have properly parabolized mirrors, one must resort to the use of spherical mirrors "off the optic axis." As long as the numerical apertures are small, and the slits are comparatively wide, the effects of the aberrations introduced are negligible. But, if we use apertures as large

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[1] R. Bowling Barnes, Phys. Rev. **35**, 1524 (1930).

[2] R. Bowling Barnes and A. H. Pfund, Bulletin Amer. Phys. Soc. **5**, 2 (1930).

as $f \cdot 4$ the effects of coma become very pronounced, and the image of the first slit is broad and is accompanied by a diffuse wing. This entire image cannot go through a narrow second slit, and consequently, if the eye is placed behind S_2, or in the position of the thermocouple, it will receive light from only a very small fraction of the grating, if the latter is illuminated with monochromatic light. Patterns such as those shown in Fig. 1 may be seen, the jaws of the slit having blocked off the light coming from some parts of the grating. However, if we use continuous radiation, such as that from a Nernst lamp, the spectrum falling upon S_2 will necessarily be very impure, and hence the resolving power will be correspondingly low. This diffuseness of the slit image is also a serious handicap in obtaining a very accurate calibration of the spectometer.

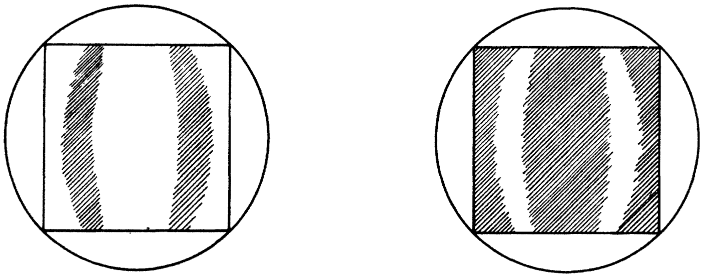
MAIN LINE CUT OFF BY SLIT WING CUT OFF BY SLIT

Fig. 1. Grating viewed through second slit of spectrometer when illuminated with monochromatic light. Spectral line is accompanied by a wing produced by the aberrations of the optical system.

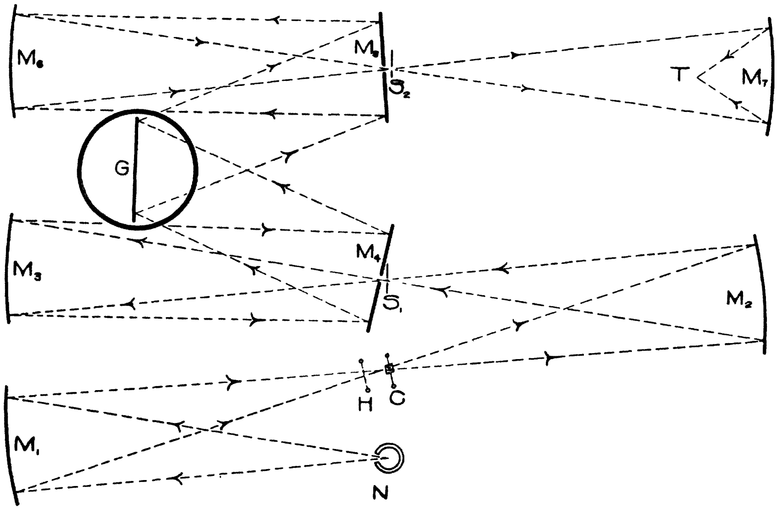

Fig. 2. Plan of spectrometer. Designed to minimize the effect of aberrations.

The apparatus which we are using at present is a grating spectrometer, the plan of which is given in Fig. 2. It makes use of about 3.5 inches of a 3600 line per inch echelette grating, which gives it a theoretical resolving power of over 12,000. By a method analogous to that described by Pfund,[3] we have been able to use $f\cdot 4$ spherical mirrors along the axis and so minimize all of these aberrations mentioned above. The radiation diverging from S_1 passes through a slot in M_4, is collimated and returned along the axis by M_3 to the plane mirror M_4 which directs it to the grating. Similarly, the diffracted beam is reflected by M_5 to M_6, the second spherical mirror, and this focusses upon S_2 which lies on the axis just behind M_5, an image of S_1 that is sharp and free from aberrations. With this optical system, we have satisfied the condition that the thermocouple shall receive radiation which comes from the entire grating, when monochromatic light is used and the slits are very narrow.

CALIBRATION

A calibration more accurate than ±5 A'', was obtained by observing the settings of the grating which would direct the various orders of the spectrum from a mercury lamp, on to the second slit. By interposing a plane mirror at 45° just behind S_2, the transmitted light could be reflected into a microscope which was a permanent part of the apparatus. This microscope was focussed upon S_2, the crosshairs set upon the center of the slit, and then the latter was opened very wide. As the grating was rotated, the spectral lines passed in turn by the cross-hairs, and an observer could thus tell accurately when the grating was set so as to send known wave-lengths through S_2. A second observer noted the grating positions by reading on a scale 3 m distant, the image of a lamp filament that had been twice reflected by a mirror which rotated rigidly with the grating. This was accomplished in the manner shown in Fig. 3. Light from an incandescent lamp after passing through a lens was reflected by M_0 to a fixed mirror M_1, which returned it to M_0. After a second

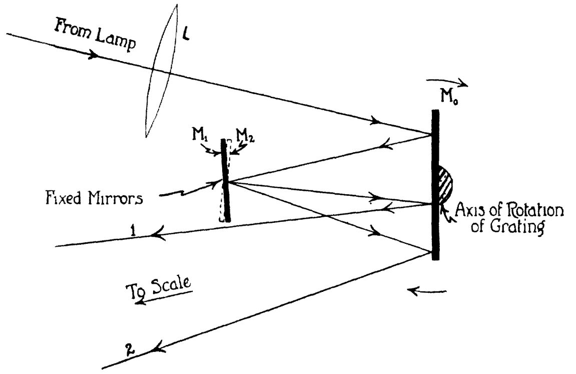

Fig. 3. Calibration mirror system.

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[3] A. H. Pfund, J.O.S.A. **14**, 377 (1927).

reflection by M_0 it was sent along path 1 to the scale upon which an image of the lamp filament was formed. This double reflection causes the beam of light to swing through an arc four (4) times that through which the grating is rotated. The linear displacement of the image of the filament thus becomes large. To avoid the necessity of having a very long scale, a second fixed mirror, M_2, was mounted as is shown. The angle between M_1 and M_2 was adjusted so that as the grating and M_0 were rotated image 2 came onto the scale just as image 1 was going off the opposite end. If the grating must be rotated through a large angle, a third mirror M_3 could be mounted in a similar manner causing a third image to follow image 2. A linear motion of the filament image of 1 mm at 3 m scale distance, represents a rotation of the grating of about 17 sec. of arc. If the beam of light is allowed to be reflected by M_0 three times, a displacement of 1mm would represent a rotation of only 8.5 seconds. If necessary, more than three reflections can easily be used, and also the image of the filament can safely be read to 0.1 mm. This gives us a method of handling with ease rotations of the order of 1 second of arc. In all of this work the image was moved in steps of 1 mm, this indicating a change in the wave-length falling upon the thermocouple slightly less than 10 A″. The calibration was carefully checked from time to time, and was always known closer than ±5 A″.

PROCEDURE

At best, the point by point method which is usually employed in making infrared measurements is a rather long and tedious process. Every step taken to improve the instruments used, in regard to sensitivity and resolving power, requires that more readings per μ be taken. Obviously, with very high resolution the problem of making such measurements becomes painfully taxing. However, we have so improved our methods that at present we can measure the absorption at over 500 different grating settings within an hour, whereas last year 50 readings constituted a full hour's work. The most fundamental step in making this possible resulted from the recent work of Dr. Pfund on controllable filters for the infrared. Since a grating superposes orders, the effect of the second order of the 1.5μ region and the third order of the 1.0μ region must be eliminated, or to say the least, must be taken into account. For this purpose, one of the MgO filters described by Dr. Pfund[4] is admirably suited. Also, a filter of a glass designed for use in solar observations was found, which was over 60 percent transparent at 3.5μ, and only 5 percent at 1.75μ and below. These filters, it is true, did not entirely eliminate the effect of the higher orders, but did succeed in reducing it sufficiently for our purposes. For instance, the one we used, though it had a transmission of only 5 percent at 1.75μ, due to the intense emission of the Nernst filament in that region transmitted enough higher order radiation to cause a contamination of the 3.5μ energy of 30 percent. It was shown separately, however, by using 100 percent 1.75μ energy, that in such small thicknesses the

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[4] A. H. Pfund, Phys. Rev. July 15, 1930.

absorption of these higher orders was negligible. So, by using either of these filters, the desired results were obtained.

Further, it was found that by proper shielding the zero drift of the galvanometer could be held to a very small amount and so, instead of reading the zero between each spectrometer setting as is customary, we used the method employed in instruments which record the galvanometer deflections automatically. The zero was read before and after each series of measurements, and the results corrected for the sloping base line caused by the zero drift. Some slight discrepancies in the relative intensities of the various bands may be introduced, because of the fact that we must assume that this zero drift was linear with time. Such errors however will be small, for evidence indicates that this drift is linear. One observer changed the spectrometer setting in intervals of 10 A″, while the other read and recorded the respective galvanometer deflections. By plotting the results thus obtained we got directly a curve showing the energy transmitted (galvanometer deflections) for the various wave-lengths. The minima of these curves gave us the wave-lengths of the absorption bands.

It must be remembered that in using such a method the total energy transmitted at any wave-length is affected by many factors, namely: the emission of the source, the absorption of the atmosphere, the absorption of the empty cell, the absorption of the filter, and finally the absorption of the sample which is being studied. Separate experiments proved that the empty cell and the filter were not selective in their absorptions, but only reduced the values throughout the entire range by a constant factor. By making a series of measurements, with the absorption cell removed entirely, the combined results of the first two effects was obtained. In Fig. 4 (a) and (b) we have drawn two such curves. They are drawn from different base lines so they may be easily compared. Here we see some 65 or more weak bands, which are evidently due chiefly to the water vapor in the air. The trustworthiness and accuracy of the instrument and methods used, are shown by the manner in which the weak minima of these two curves check each other.

RESULTS

Last year[5] readings were taken at intervals of 0.007μ on an instrument whose calibration was accurate to $\pm 0.0015\mu$ and the wave-lengths then stated were thought to be accurate to $\pm 0.003\mu$. This year readings were taken every 0.001μ, using an instrument calibrated to $\pm 0.0005\mu$, and therefore we believe that we can now state our wave-lengths to $\pm 0.001\mu$.

The absorption of benzene has been measured some 30 odd times this year, under many different conditions. We have used various cells, slit widths and thicknesses of solution. Fig. 4 (c) shows a sample curve for benzene, made with slits 0.1 mm wide (11 A″ 'slit width') and a thickness of 0.05 mm. In comparing this with a curve from last year, we find the same three strong bands located this year at 3.236μ, 3.257μ and 3.296μ. A careful study was made of the weaker indications of absorption lying on each side of the strong

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[5] R. Bowling Barnes, reference 1

group of bands. It was noticed in the work last year, that while the 3 strong bands always checked in the different curves, these weaker ones rarely ever agreed exactly. By comparing the benzene curve with those for the atmosphere, we can see the reason for this. Since we have the absorption of water vapor superposed upon that of benzene, we must expect the locations of the benzene bands to be somewhat affected by the presence of the water bands. This effect will be rather slight in the case of very strong benzene bands. However, in regions where the bands of the two compounds are of approximately the same intensity, a change in the partial pressure of the water vapor present in the room, may produce very noticeable changes in the absorption bands. In the previous work, since readings were taken only every 0.007μ, we always had the combined effect of benzene and water vapor, for neighboring bands could not be separated.

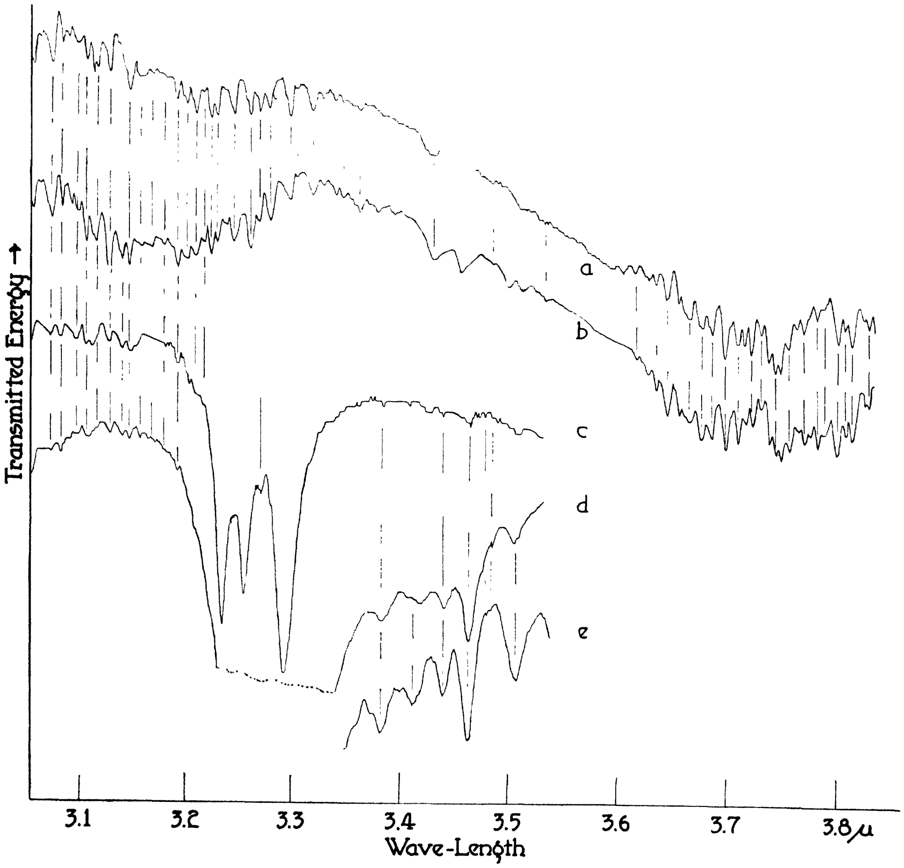

Fig. 4. Absorption curves. (a) and (b) atmospheric absorption. (c) benzene, $t=0.05$ mm. (d) benzene, $t=0.1$ mm. (e) benzene, $t=0.5$ mm.

In order to identify further the weak benzene bands, we made measurements on benzene in 5 different thicknesses. Fig. 4 (c), (d) and (e) show a comparison of 3 such curves, and it is easily seen that on the short wave-length side of the 3 strong bands, benzene has no absorption. However, toward longer wave-lengths several bands show decided changes as the thickness is increased. The bands which show these changes, do not correspond to any of the air bands, and thus we can say definitely just which of the weaker minima indicate benzene bands, and which, water vapor. With this process we finally arrived at the results given for benzene in Table I. Here we have also listed for reference the wave-lengths of the water-vapor bands.

Obviously, if we could eliminate this atmospheric absorption the results could be interpreted more easily and no doubt would be more exact. This could be done by taking one set of values through the compound and then a set through an empty cell, and subtracting the respective ordinates. This, however, would again require zero readings and would thus make the procedure very much longer and harder. The only course which offers a convenient solution to the problem seems to be to enclose the entire spectrometer in a vacuum, or to say the least, in an enclosure which has been carefully freed from water-vapor and CO_2. The entire instrument from Nernst lamp to thermocouple must be in such an atmosphere. Czerny[6] enclosed his spectrometer in a tin case, which contained trays of P_2O_5 and KOH. Plans are at hand for putting this instrument into just such an enclosure. Until this is accomplished however, we must continue to use our method of locating the atmospheric bands, and then picking them out of the other absorption curves.

TABLE I. *Wave-lengths of observed bands.*

Air	Air (con)	Air (con)	Air (con)	Air (con)	Benzene	Toluene
3.054μ	3.193μ	3.331μ	3.633μ	3.748μ	3.236μ	3.240μ
3.073	3.202	3.342	3.642	3.754	3.257	3.263
3.083	3.210	3.348	3.654	3.762	3.296	3.301
3.093	3.217	3.364	3.659	3.768	3.383	3.386
3.098	3.224	3.379	3.664	3.781	3.412	3.426
3.106	3.230	3.397	3.675	3.787	3.440	3.489
3.115	3.241	3.430	3.685	3.801	3.463	
3.127	3.246	3.455	3.697	3.807	3.508	
3.139	3.267	3.485	3.709	3.813		
3.146	3.270	3.498	3.715	3.825		
3.153	3.281	3.512	3.721	3.830		
3.158	3.305	3.603	3.730			
3.178	3.312	3.614	3.736			
3.180	3.321	3.626	3.743			

In this manner, the bands of toluene were also located. Curve (d) of Fig. 5 shows this absorption clearly. The air bands are easily identified. The remaining bands, whose wave-lengths are given in Table I, agree nicely with those stated in the previous paper. Again we note only a slight shift toward longer wave-lengths in the locations of the three strong bands of the benzene C-H's. These shifts are 0.004μ, 0.006μ and 0.005μ respectively. The minimum at 3.307μ shows up in the other curves for toluene to be due to air. The general intensity distribution throughout this entire region is the same as that shown previously.

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[6] M. Czerny, Zeits. f. Physik **34**, 227 (1925).

Curve (b) of Fig. 5 shows an attempt to measure the absorption of cyclohexane at a thickness of 0.05 mm. As is shown in the curve the intensity of the absorption is extremely great. From 3.35μ to 3.46μ this thickness is opaque, the only energy transmitted being the 30 per cent contamination due to 1.75μ. The results were the same, using a film formed by putting one drop of the liquid between two cover glasses, which were then pressed together. Le Compte[7] gives a curve for it, but does not mention the thickness. He finds for it bands at 3.16μ, 3.26μ, 3.60μ and 3.90μ. We find the strong band somewhere between 3.35μ and 3.46μ. It is interesting to note that the three benzene bands are entirely absent. In this molecule no C atom has only one H atom attached as in benzene, but each has two. Apparently, the H–C–H vibrations are quite different from the C–H vibrations. Cyclohexene, also shows an extremely strong absorption in this region.

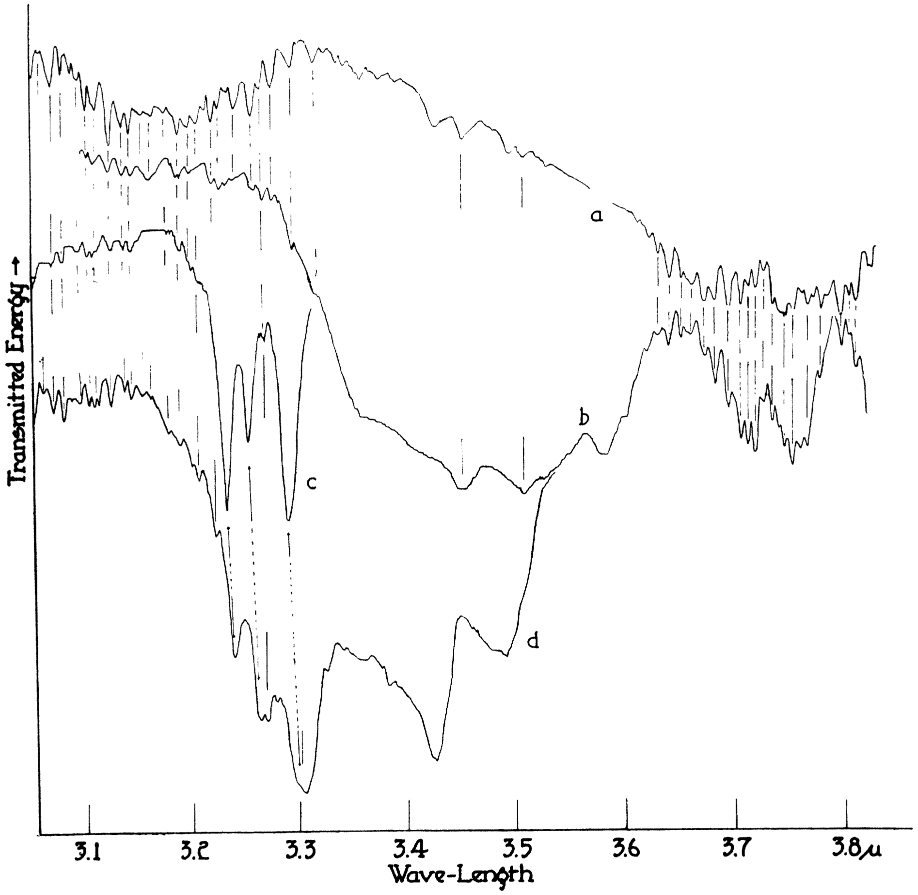

Fig. 5. Absorption curves. (a) atmospheric absorption. (b) cyclohexane, $t=0.05$ mm. (c) benzene, $t=0.05$ mm. (d) toluene, $t=0.05$ mm.

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[7] J. Le Compte, Le Spectra Infrarouge., p. 218.

CONCLUSIONS

Specific heat calculations[8] and Raman photographs[9] each show definitely that the C–H linkage must vibrate with a frequency very close to 3.5μ. In most organic liquids then, we must expect to find very complex absorption bands in this region. Remembering that water also has a strong band close to 3.0μ, we see that almost every liquid will have pronounced absorption between 3.0μ and 4.0μ. The resulting fact, that so many liquids have complex bands around 3.5μ, makes this spectral interval a most interesting and fruitful source of information concerning the structure of the molecules. To obtain all of this information we must develop instruments of still higher sensitivity and resolving power. With the present spectrometers however, we can learn quite a bit.

In our first paper we showed several progressive shifts and changes in the bands, which were apparently connected with the symmetry and structure of the molecule. The curve on cyclohexane shows no trace of the three strong benzene bands. This is the first curve in which they have been entirely absent, and this is the first molecule we have examined which had no simple C–H bonds. Toluene and each of the other derivatives had some C–H linkages, in addition to their respective radicals. In these we found separate absorption due to the C–H, CH_3, C_2H_5 and C_4H_9 groups. Here in cyclohexane the absence of bands for C–H gives us additional evidence, which seems to show a mutual effect between two neighboring C–H bonds. Every shift and intensity change tells something about the molecule, and it is hoped that a theoretical discussion of these will soon appear.

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[8] D. H. Andrews, Chem. Reviews **5,** 4 (1928).

[9] A. Dadieu and K. W. F. Kohlrausch, Berichte der Deutschen Chemischen Gesellschaft **2,** 251 (1930).