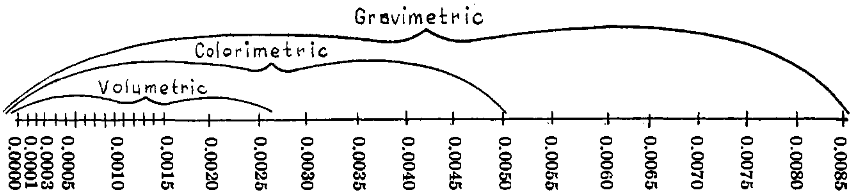
Summary

1. Quick determinations of magnesium can be made by precipitating it as the salt of 8-hydroxyquinoline and estimating the magnesium content of the salt either gravimetrically, volumetrically or colorimetrically. In many cases where the saving of time is an important factor and extreme accuracy is secondary, one of these methods may prove useful.

2. The most advantageous method to use depends on the amount of magnesium in the sample. (a) For amounts ranging from 0.0010 g. up to the highest concentrations, the gravimetric method is most accurate. (b) For amounts ranging from a minute trace up to 0.0025 g. the volumetric method is most accurate, and is very quick in comparison with many methods commonly used. (c) For amounts ranging from 0.0005 g. up to high concentrations (if proper aliquots are taken), the colorimetric method is very accurate and is the quickest of the three methods.

3. The following scale will illustrate at a glance the advantageous range of the three methods.



4. None of the other metals commonly found in natural waters will react with 8-hydroxyquinoline, except calcium.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE EMISSION SPECTRA OF SOME SIMPLE BENZENE DERIVATIVES

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The main features of the spectra obtained from the vapor of benzene and its simple derivatives under the excitation of the Tesla discharge have been described by McVicker, Marsh and Stewart,[3] who designated them as Tesla luminescence spectra to distinguish them from the fluorescence and absorption spectra. The present investigation was undertaken as an extension of this work; it was hoped on the purely chemical side to develop the suggestion made by them that a means of ascer-

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[1] From a dissertation presented by J. B. Austin to the Graduate School of Yale University, June, 1928, in candidacy for the degree of Doctor of Philosophy.

[2] Commonwealth Fellow 1926–1928.

[3] McVicker, Marsh and Stewart, *J. Chem. Soc.*, **123**, 642, 2147 (1923).

taining the purity of an organic solvent, and the nature of any impurities present, could be elaborated. In this respect it has been shown that such a method is unwieldy in practice, except perhaps for routine work in which a large number of samples are to be tested. Its application to a qualitive analysis would be relatively simple since a mere comparison of the unknown spectrum with a series of spectra of suspected impurities would suffice, but unfortunately the number of substances which yield satisfactory spectra under this means of excitation is rather limited. For a quantitative estimation of the amounts of impurities present it is necessary to compare the intensities of the bands, a procedure which is rendered difficult by the presence of a continuous background in many of the spectra.

On the other hand, it was thought that more comprehensive data on such spectra could be obtained which, with an increased accuracy, might enable the regularities observed in the bands to be given some theoretical interpretation. In this object some success has been achieved. A great many new band heads have been recorded with an accuracy believed to be ±0.5 Å. or better, except in the case of the faintest and most diffuse bands.

The spectrum of benzene appears to be unique among the substances thus far investigated in that it possesses an unusual completeness, its bands are very sharp and there is little if any continuous background. Because of these features it has been given special attention and has been discussed in a previous paper.[4] The present paper describes the spectra of toluene, ethylbenzene and the xylenes.

It was our original intention to extend this work to some of the aliphatic compounds but all the substances investigated, including pentane, 2,2,4-trimethylpentane and acetylene gave unsatisfactory results. The molecules broke down into fragments yielding spectra similar to those obtained with the electrodeless discharge. These have been described elsewhere.[5]

Experimental

Each hydrocarbon was shaken with concd. sulfuric acid until no color was imparted to fresh acid; it was then washed successively with concd. sodium hydroxide, dilute sodium hydroxide and distilled water until the final wash water was neutral to litmus. The resulting product was dried over sodium and distilled. The several boiling points were as follows:

Toluene	110–111° at 758 mm.
o-Xylene	142–142.5° at 750 mm.
m-Xylene	137–138° at 750 mm.
p-Xylene	136–137° at 750 mm.
Ethylbenzene	136–137° at 770 mm.

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[4] Austin and Black, *Phys. Rev.*, **35,** 452 (1930).

[5] Austin, THIS JOURNAL, **52,** 3026 (1930).

The materials as finally used appeared to be quite pure and were at least free from each other, since in no case did the spectrum of any one contain the spectrum of any other.

The apparatus used in obtaining and measuring these spectra is described in detail in our paper on benzene. In each instance the pressure of the vapor was of the same order of magnitude as that used in the benzene study, being about 0.05 mm. Various vacuum waxes and cements were used in sealing the window on the discharge tube but no difference in the spectrum was observed. A Hilger size C quartz spectrograph, giving a photograph 200 mm. in length for the range 2100 to 7000 Å. was used throughout, with exposures ranging from three to twelve hours. Since the resolution of this instrument was not very great the lines in the bands were not resolved, therefore most of the bands appeared as band heads shading off toward the red. The measurements given in Tables I to V were made on the heads of these bands.

Results

The first column in Tables I to V gives the wave lengths of the band heads in Ångström units as measured by us, the second column those of McVicker, Marsh and Stewart and the third column our values expressed as wave numbers in cm.$^{-1}$ ($\nu = 1/\lambda$). Our values are in general in agreement with those of McVicker, Marsh and Stewart, in most cases the differences being within their limit of error.

TABLE I

TESLA LUMINESCENCE BANDS OF TOLUENE

λ in Å., Austin and Black	λ in Å., McVicker, Marsh and Stewart	ν in cm.$^{-1}$ ($\nu = 1/\lambda$) Austin and Black
2667.5	2667	37477
2672.0	2671	37414
2680.2	2680	37300
2684.3		37243
2687.7	2688	37196
2692.5	2693	37129
2705.0	2705	36958
2713.0	2713	36849
2717.8	2718	36784
2724.9	2725	36688
2733.6	2733	36571
2741.1	2742	36471
2756.9	2755	36262
2771.2	2771	36075
2802.3	2804	35674
2818.6	2820	35468
2834.4	2834	35270
2884.3		34660
2896.3		34517

TABLE II

TESLA LUMINESCENCE BANDS OF *o*-XYLENE

λ in Å., Austin and Black	λ in Å., McVicker Marsh and Stewart	ν in cm.$^{-1}$ ($\nu = 1/\lambda$), Austin and Black
2679.1	2681	37315
2684.2	2686	37244
2688.5	2691	37184
2693.4		37117
2700.3		37022
2733.1	2736	36578
2738.3	2740	36508
2742.5		36452
2747.3		36389
2758.8		36237
2764.0		36169
2769.0		36103
2773.3		36048
2775.7		36016
2783.0		35922

Table I gives the data for the bands in the toluene spectrum, which contains, beside the bands, a continuous background starting sharply at λ2667 and gradually shading out at about λ3100. The bands seem to be related in much the same way as are those of benzene but do not show the division into groups which is so evident in the latter.

The data for *o*-xylene are found in Table II. In this case the heavy background is the most prominent feature of the spectrum. It neither starts nor ends sharply but extends from about λ2700 to λ3300. No band groupings are apparent as with the other substances.

m-Xylene (Table III) also has a strong continuous spectrum superimposed on the band system. It begins sharply at λ2700 and disappears at λ3300.

The *p*-xylene bands (Table IV) are quite strong and are easily visible against the continuous background which starts sharply at λ2750 and extends to λ3300.

TABLE III

TESLA LUMINESCENCE BANDS OF *m*-XYLENE

λ in Å., Austin and Black	λ in Å., McVicker, Marsh and Stewart	ν in cm.$^{-1}$ $(\nu = 1/\lambda)$ Austin and Black
	2673	
2703.6	2705	36977
2709.0		36903
2712.4	2712	36857
2721.4	2719	36735
2727.9	2730	36647
2735.0		36552
2742.6	2744	36451
	2750	
2758.0	2761	36247
2771.2	2765	36075
2784.0	2781	35909
2792.6		35798
2799.1	2802	35715
2813.7	2817	35530
2820.4		35446
2850.6		35070
2861.6		34935
2881.4		34695
2885.3		34648

TABLE IV

TESLA LUMINESCENCE BANDS OF *p*-XYLENE

λ in Å., Austin and Black	λ in Å., McVicker, Marsh and Stewart	ν in cm.$^{-1}$ $(\nu = 1/\lambda)$, Austin and Black
2704.3		36967
2709.3		36899
2715.4		36816
2721.3	2724	36736
2728.0		36646
2732.5	2732	36586
2736.1		36538
2742.5		36452
2745.0	2746	36419
2761.1		36207
2770.4		36085
2772.3	2774	36061
2784.7		35900
2786.1	2787	35882
2791.2		35816
2794.8	2794	35770
2799.8	2803	35706
2810.1	2812	35575
2814.5	2817	35520
2823.5	2824	35406
2830.0		35325
2850.5	2853	35071
2865.0	2869	34894
2881.2	2883	34698
2925.5	2922	34172
2951.3	2954	33874
2976.6		33586

The spectrum of ethylbenzene (Table V) has like all the rest a continuous background extending from a sharp lower limit at λ2667 to a very diffuse one at about λ3200; the bands are rather poorly defined.

TABLE V

TESLA LUMINESCENCE BANDS OF ETHYLBENZENE

λ in Å., Austin and Black	ν in cm.$^{-1}$ ($\nu = 1/\lambda$), Austin and Black	λ in Å., Austin and Black	λ in A., McVicker, Marsh and Stewart	ν in cm.$^{-1}$ ($\nu = 1/\lambda$), Austin and Black
2660.9	37570	2711.9	2711	36864
2664.5	37519	2716.1		36807
2666.6	37490	2718.3	2725	36747
2670.0	37442	2733.0		36579
2672.0	37414		2740	
2676.7	37348	2752.2		36324
2681.1	37287	2777.5		35993
2689.3	37173	2802.4	2802	35673
2705.5	36951	2812.2	2817	35549
2709.4	36898			

Discussion

It became evident early in the work that an analytical method based on the equipment described would be quite unwieldy. The apparatus is costly and rather troublesome to assemble and the time required to make a good exposure, at least three hours, is rather long; moreover, the decomposition of the vapors makes it necessary to use a new discharge tube for each exposure. However, to gain some idea of the possible utility of the method one trial analytical run was made on the contents of a bottle marked "xylene" which had been standing around the laboratory for some time. On comparing the spectrogram of this unknown with those of the three pure xylenes it was found that the unknown contained all three isomers. The continuous background rendered the task of estimating the amount of each hopeless.

Thus far our attempts to apply the formulas of modern band spectroscopy to these data have not met with success. The problem is very difficult, much more so than in the case of benzene, because comprehensive data of the required accuracy are not available. Even were these at hand the complexity of the emitting molecule would make their interpretation far from simple. However, it is interesting to consider our results in the light of some of the older and less precise generalizations. The first of these was set forth by Staudinger.[6] All chemical substitution which displaces the bands toward the red diminishes the state of saturation of the molecule. The second was made by Henri.[7] Organic bodies which react most easily, that is, are most labile, possess the strongest ultraviolet bands.

[6] Staudinger, "Les Cetenes," Stuttgart, **1912**, p. 98.

[7] Henri, *Compt. rend.*, **156**, 1979 (1913).

Let us now apply the first law to our measurements. We may be sure that the extreme ultraviolet ends of the spectra are lacking because of the absorption by the unexcited vapor and therefore the terminations of the various spectra are not to be taken alone as criteria for displacement. We may, however, arrive at a more reliable standard for obtaining the shifts due to changes in composition by comparing certain sharp band heads which seem to correspond in each spectrum. On making such a comparison on our plates it appeared that the toluene bands are displaced to the red as compared to those of benzene, *o*-xylene showed an increased shift toward the red, while the *p*- and *m*-isomers were still further displaced. Ethylbenzene, however, gave a spectrum in the same general region as toluene.

These shifts are confirmed by the spectra of these compounds in the solid at liquid-air temperatures.[8] Under these conditions these band systems actually show terminal bands whose positions are easily compared. The shifts observed in these spectra are in agreement with the above results. The most significant difference is that the *p*-xylene is slightly, though definitely, shifted toward the red as compared to the *m*-compound.

Interpreted on the basis of Staudinger's law these shifts mean that benzene is the most saturated of the substances studied; toluene is less saturated; *o*-xylene is still less so, while the *p*- and *m*-isomers are the least saturated of all, which conclusions are borne out by the well-known chemical behavior of these compounds; this would indicate that the band spectra data are in complete accord with Staudinger's law.

When attention is directed to the law of Henri, an apparent difficulty arises at once, for the bands of benzene are easily the strongest and most complete, yet there can be no doubt as to the pronounced stability of benzene. This leads us to the conclusion that considerable care must be exercised in applying this "law" to organic compounds. One explanation of this apparent exception is that the intensity of the ultraviolet bands is dependent on the number of excited electrons, which, in general, is related to the relative ease of excitation. The chemical activity on the other hand depends on the ease with which electrons may be removed or shared, which is quite a different thing. Thus it may be possible to have an electronic structure capable of being easily excited by the proper radiation and yet resistant to actual change of configuration, *i. e.*, chemical reaction.

Another explanation of the unique character of the benzene bands may be sought in a study of the source of the emitted radiation. If it is assumed that each C and H atom can vibrate independently, there is at once an explanation of the greater intensity of the benzene bands.

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[8] Data shortly to appear in the *Bureau of Standards Journal of Research.*

Since each C and H atom is equal to all the others, it follows that the frequency of the light emitted will be independent of the portion of the ring from which it emanates and therefore the light in the frequencies which are emitted will be intense. This leads to a strong spectrum with sharp bands and little if any continuous background, which is just what benzene does give.

In the case of toluene a different state of affairs exists. One of the atoms is definitely marked by having a methyl group attached and the neighboring C atoms are probably slightly affected by the presence of this group; consequently, the various parts of the molecule when excited by the discharge do not all emit the same frequency but instead there appears a series of frequencies which are but slightly different. This leads to a group of strong bands arising from certain favored modes of vibration which are blurred by bands of slightly different frequency arising from other vibrations. An extension of this argument shows that it applies equally well to ethylbenzene and the xylenes. One would expect the bands of these substances to be less sharp than those of toluene, as indeed they are.

It should perhaps be emphasized here that these views are to be regarded as but tentative suggestions. The extreme complexity of the problem and the comparative lack of detail in the spectra of these simple derivatives render it difficult to be more specific in their interpretation.

A study of these spectra also leads one to believe that we should be more careful in keeping the meaning of our chemical symbols constantly in mind. All the existing theories of saturation and stability can be readily reconciled with the ordinary equilateral hexagonal formula for the simple benzene ring; indeed the observations force us to accept such a symbol. Whether the ring is coplanar or not is of small importance in this connection. On the other hand, it should be clearly recognized that the introduction of a group of any kind immediately sets up electrical and magnetic disturbances which are transmitted around the ring, and cannot fail to give a twist to the molecule so that to be accurate in our symbolism we should now write a warped or non-equiangular hexagon. The exact nature of this twist is not at present known but the accumulation of more data will undoubtedly elucidate this point. Meanwhile, we can keep in mind that the substituted benzene ring is not at all the same as the original symmetrical structure.

It is a pleasure to acknowledge our indebtedness to Professor H. S. Uhler for his advice in matters of spectroscopic technique, to Professor John Johnston for his general interest and help and to Mr. L. E. Faulhaber for help in preparing the manuscript. We wish also to thank the Commonwealth Fund for the fellowship held by one of us during the course of this research.

Summary

The emission spectra of toluene, ethylbenzene, *o*-, *m*- and *p*-xylene have been photographed using the Tesla discharge as a means of excitation; they are found to contain a number of bands generally accompanied by a continuous background. The numerical data are in agreement with previous measurements. A comparison of these spectra indicates that substitution produces a profound disturbance in the electrical and magnetic symmetry of the benzene ring. Further, these spectra have a limited application in qualitative analysis but are rendered less suitable for quantitative work because of the continuous background.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, STATE UNIVERSITY OF IOWA]

THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF LITHIUM NITRATE IN CERTAIN BINARY ALCOHOLIC SYSTEMS[1]

BY J. L. WHITMAN AND D. M. HURT

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Investigations of conductivity in mixed solvents were first made by Lenz,[2] and have since been extended from time to time by many other workers. Perhaps the most systematic and extensive results have been obtained by Jones[3] and his co-workers using various solvents such as water, methyl alcohol, ethyl alcohol, propyl alcohol, acetone and glycerin, and a considerable number of solutes.

Data for the conductivity and viscosity of solutions of lithium nitrate in certain aqueous–alcoholic solvents have been reported in a previous paper.[4] As a continuation of these studies data are now given for systems containing various proportions of water, ethyl alcohol, *n*-propyl alcohol and isopropyl alcohol. In some cases density data have also been included.

Materials.—The lithium nitrate, water and ethyl alcohol were prepared and purified by the methods used by Whitman and Spencer. High grade *n*- and isopropyl alcohols from the Eastman Kodak Company were purified by the same method that was used in purifying ethyl alcohol. The specific conductivities of the purified solvents were as follows: water,

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[1] Prepared from a Dissertation presented to the Graduate Faculty of the State University of Iowa by D. M. Hurt, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Lenz, *Mem. l'acad. St. Petersburg*, **7**, 30 (1881); Stephan, *Wied. Ann.*, **17**, 673 (1883); Arrhenius, *Z. physik. Chem.*, **9**, 487 (1892); Wakeman, *ibid.*, **11**, 49 (1893); Zelinsky and Krapiwin, *ibid.*, **21**, 35 (1896); Cohen, *Wied. Ann.*, **25**, 31 (1898).

[3] For a summary and review of this work, see Jones and Kreider, *Am. Chem. J.*, **45**, 282 (1911).

[4] Whitman and Spencer, THIS JOURNAL, **50**, 1840 (1928).