ships as this would involve data in regard to the activities which are lacking. According to the general scheme which is roughly outlined in Fig. 1, acids are "strong" only in the solvents which lie above them on the diagram. Thus perchloric acid is strong in all three solvents; sulfuric and hydrochloric acids in ammonia and water and RCOOH only in ammonia. Anhydro bases are neutralized by one equivalent of any acid which is a stronger acid than their "onium ions," provided the action takes place in a solvent which lies below the position of their ions on the scale. Thus an amide ($RCONH_2$) will be neutralized only in acetic acid and only by perchloric or sulfuric acid. We have not yet found a solvent in which triphenylamine can be titrated even with perchloric acid. If such a solvent is found it will lie below acetic acid in the diagram.

We take pleasure in expressing our indebtedness to Mr. N. M. Bigelow for assistance in carrying out the experiments on the inversion of sucrose.

Summary

1. Five arylcarbinols and five unsaturated ketones have been tested for the appearance of halochromic color by introducing them into eleven buffer solutions in glacial acetic acid. The results are all consistent with the determination of the hydrogen-ion activities of the solution by means of the chloranil electrode. The ten substances form a graded series of indicators suitable for use in superacid solutions.

2. The rate of inversion of sucrose in 98% acetic acid solutions of definite acidity has been studied. The rate is approximately proportional to the hydrogen-ion activity as measured by the chloranil electrode or by the use of indicators.

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[CONTRIBUTION FROM THE CHEMICAL WARFARE SERVICE, EDGEWOOD ARSENAL]

APPLICATION OF THE INTERFERENCE REFRACTOMETER TO THE MEASUREMENT OF THE CONCENTRATION OF DILUTE SOLUTIONS[1]

BY RUDOLPH MACY

RECEIVED AUGUST 19, 1927 PUBLISHED DECEMBER 10, 1927

In this Laboratory an extended series of measurements has been made involving accurate determinations of the concentrations in water of various types of organic compounds. A more accurate, more general and more rapid method of determining concentrations in liquid solvents was sought than is afforded by the usual methods of analysis. The instrument selected for this purpose is the interference refractometer designed by Professor F. Haber and made by the Zeiss Company. Although measurements can be made very quickly by means of this instrument, and with a high degree

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[1] Published by permission of Chief, Chemical Warfare Service.

of accuracy, it is also found to be very misleading if some of the precautions to be explained in this paper are not observed. Since it is likely that this type of interferometer is being used by other investigators for analogous purposes, it was thought advisable to publish this account of some anomalies in its behavior. It is hoped that the interpretation given here will be of value to other users. The writer is not aware of any published articles referring to the nature of the calibration lines which are essential in the routine analyses made with the interferometer.[2]

The Instrument

The principle employed in the Zeiss type of interferometer was developed originally by Rayleigh in order to measure the refractive indices of the rare gases. A discussion of the fundamental principle involved can be found in the textbooks by Travers,[3] and by Reilly.[4] Pamphlets describing the instrument can be obtained from the manufacturer;[5] these contain a complete bibliography which includes references to the original articles by Rayleigh and Haber.

The instrument used in the work reported in this article is the portable type in which an easily accessible cell is employed to hold liquids. The interferometer cell consists of two parallel compartments separated by a narrow partition, with plane lenses cemented at each end. It rests in a bath of water at constant temperature. By means of a system of prisms and mirrors two vertical beams of white light from a 4-volt lamp are passed through the cell. Each beam passes *through* one compartment of the cell and also *underneath* the cell through the water in the bath. The two lower halves of the beams interfere and give rise to a series of interference bands which are represented by the lower set in Fig. 1. The interference of the two upper halves of the beams which traverse the cell yields the upper series of bands. These spectra are observed through a microscope arrangement.

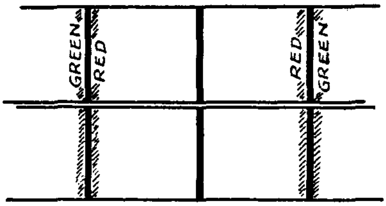

Fig. 1.—Appearance of the colored fringe systems when upper movable spectrum and lower fixed spectrum are matched.

When both compartments of the interferometer cell are filled with water the upper interference spectrum is identical with the lower. There are three distinct transverse bands, the middle one being dense black, with practically no color fringes. The bands to the right and left of the central black reference line, however, are fringed with colors as shown in the accompanying illustration. If now the water in the left compartment

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[2] Since the time this article was written and submitted for approval to the military authorities a recent paper by W. Barth, *Z. wiss. Phot.*, **24**, 145 (1926), has come to the author's attention through *C. A.*, **21**, 1749 (1927). The paper by Barth includes a large number of references which are not cited by Carl Zeiss and which discuss the same phenomena presented in this article. On some important points there are discrepancies between the experimental observations by Barth and by myself.

[3] Travers, "Study of Gases," Macmillan and Co., New York City, **1901**.

[4] Reilly, "Physico-Chemical Methods," D. Van Nostrand Co., New York City, **1926**, p. 521.

[5] "Industrial Interferometers," and "Interferometers for Gases and Water." Carl Zeiss, New York.

be removed and replaced by a very dilute solution the upper system of bands will be displaced to the left. By means of a compensating lens, operated by a graduated micrometer screw which reads from 0 to 3000 units, the bands are brought back into the field of vision and the spectra are matched up once more. By varying the concentration of the solution and noting the micrometer reading after the bands are matched, a straight calibration line can be constructed as indicated in Fig. 2 by the segment OC of the curve OD.

From this calibration line the concentration of an unknown solution can be read off when its interferometer reading has been determined. Instead of plotting a line as in Fig. 2 it is convenient simply to find the slope of the line, thus

$$\text{factor, or value of 1 scale unit} = \frac{y \text{ mg. per liter}}{x \text{ units}}$$

The slope of the line, or factor, can be found by reading one solution of known concentration, which involves just one or two weighings. The concentration of any solution of the same substance can then be determined simply by multiplying this factor into its interferometer reading.

Observations on the Instrument

I. Additive Properties.—A number of determinations have shown that the interferometer reading for two substances in the same solution is very nearly, although not exactly, the sum of the readings of each taken separately. This phenomenon had an important bearing on some of the work done in this Laboratory.

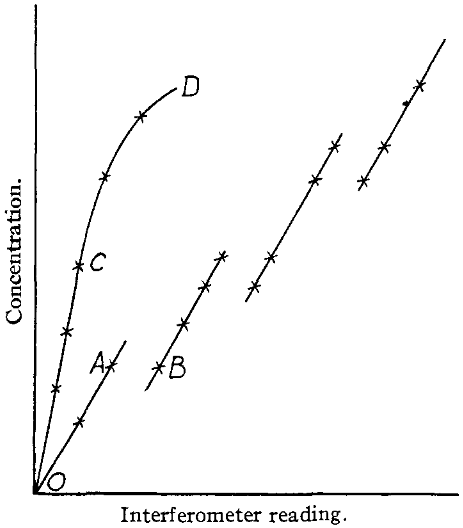

Fig. 2.—Typical calibration curves (schematic).

II. Relation between Sensitivity of the Instrument and Molecular Structure.—A number of organic compounds have been studied in the course of other work and several generalizations can be drawn from the data already at hand. In the following table, instead of expressing the concentrations in milligrams per liter, they are given in millimoles per liter in order to present figures which are theoretically more comparable. These figures indicate that for the simpler aliphatic and aromatic compounds it requires a smaller concentration of an aromatic compound to change the scale reading one unit or, in general, the interferometer is more sensitive to aromatic compounds. For both types of compounds there is a general increase in sensitivity with increase in molecular complexity.

TABLE I

FACTOR, OR VALUE OF 1 SCALE UNIT IN MILLIMOLES PER LITER

(Length of cell = 4 cm.)

Aliphatic compounds		Aromatic compounds	
Acetone	0.115	Phenol	0.025
Urethan	.059	Phenylurethan	.018
Chloro-acetone	.058	Chloro-acetophenone	.018
Sulfonal	.019	Piperonal	.017
Sucrose	.011	Coumarin	.00685

III. Anomalies in the Calibration Lines.—When a solution is placed in one compartment of the interferometer cell, with pure water in the other, and the spectra are matched up by turning the micrometer screw, it is found that the central black band of the upper spectrum is usually no longer pure black but is tinged with green. However, even though this reference band suffers a slight change in its appearance it is easily followed and is readily matched. This is proved by the fact that the calibration line of such a compound as urethan is a straight line up to the appreciably high concentration of 3 g. per liter. (See the straight segment OC of the curve OD in Fig. 2.)

When urethan is studied at higher concentrations than 3 g. per liter it is found that the calibration line OD deviates slightly from a straight line function and becomes a smooth continuous curve which has been followed up to a concentration of 10 g. per liter. The phenomenon of curvature has been proved for a large number of compounds which have comparatively high solubilities in water. The deviation from a straight line at high concentrations may be due to a closer packing of the solute molecules and may therefore be considered simply another abnormal behavior of concentrated solutions.

A large number of compounds have been studied whose solubilities in water are less than 1 g. per liter. In these cases, moreover, since it was necessary to determine concentrations to at least 5 mg. per liter, the calibration curves had to be constructed with great care. Most of these slightly soluble compounds were benzene derivatives, and all these aromatic compounds yielded calibration curves illustrated in Fig. 2 by the series of broken lines beginning with OA. These lines for any one compound are all of the same slope and overlap slightly; and the horizontal distance between two adjacent lines is 13 interferometer scale units for all compounds.

The writer's interpretation of this phenomenon of the stepwise breaks in the calibration line is as follows. It has been stated that when a solution is placed in the cell the central black band of the upper interference spectrum becomes tinged with green. In the case of most compounds this green fringe grows wider as the concentration increases; as this reference band grows wider the next band to the left of it grows narrower and the red fringe originally on it becomes less distinct. In a certain range of concentrations it is difficult to distinguish between these two bands since they have practically no red coloration. In such a case it is best to record the readings of both lines; expressed graphically in Fig. 2 the scale readings would be 13 units apart as represented by points A and B. The calibration lines are removed from one another by 13 units on the horizontal axis because of the fact that the distance between two adjacent bands in the interference spectrum is equivalent to that number of divisions on the micrometer screw.[6]

At concentrations slightly higher than that represented by points A and B, the lines become more easily differentiated again and it is a simple matter to match up the two interference spectra. However, the black line which

TABLE II

CALIBRATION DATA

(Length of cell = 4 cm.)

Urethan Mg./liter	Reading
0	0
121	23
242	45
363	66
484	87
605	112
1214	233
2000	375
3000	565
7000	1359
10000	1994

Phenylurethan	
0	0
94	31
187	63
187	76
281	107
375	138
375	151
469	185
562	216
562	229
656	260
750	293
844	327

Sodium nitrate Mg./liter	Reading
0	0
94.8	21
189.6	41
284.4	61
379.2	81
474	101
474	114
663.6	153
758.4	174
948	214

Potassium dichromate	
0	0
25	8
25	21
50	28
100	45
100	58
150	75
200	90
250	105
300	121

Potassium dichromate (continued) Mg./liter	Reading
300	134
335	145
400	166
447	182
447	195
500	211
558	231
600	245
600	258
625	267
670	281
700	290
700	303
782	318
782	331
800	336
800	349
900	382
900	395
1000	428

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[6] According to Barth (ref. 2) the distance between spectral lines varies along the scale, in his instrument the variation being from about 18 to 28 scale units. On this basis Barth builds up an equation by means of which a standard calibration line can be calculated.

is now being used as a reference originally held a red fringe. The process by which the central black band gains a red fringe and the adjacent band to the left loses its red fringe continues with marked regularity for most aromatic compounds. For example, phenylurethan solutions show the phenomenon at every increase in concentration of 180 to 200 mg. per liter. The data in Table II are grouped according to the number of broken lines; when plotted on millimeter cross section paper the lines appear as illustrated in Fig. 2. Dilutions were all made by means of calibrated burets.

That the change in coloration of these spectral lines is due to the difference in dispersion of white light by the solution and by pure solvent has already been noted quite often in the literature.[7] In Table II are given the data for the calibration of the yellow solution of potassium dichromate which was studied in order to observe the effect of color on the calibration lines. Even at the low concentration of 25 mg. per liter in a 4cm. cell this causes a shift of one wave length in the spectrum. The complete calibration of the compound resulted in a stepwise shift of eight bands up to a concentration of one gram per liter, but the phenomenon did not occur at periodical increases in concentration as found for colorless solutions. In the same range of concentrations the colorless solution of sodium nitrate causes only one shift in the black reference line and this occurs just above the concentration of 500 mg. per liter.

It is evident, therefore, that a complete calibration curve over the entire range to be studied is essential in the case of most compounds. The aliphatic compounds do not, as a rule, bring about a break in the calibration curve below one gram per liter. Even a more complex substance such as sucrose has been found to give a straight, unbroken line. In regard to the curvature of the calibration lines of aliphatic compounds at higher concentrations, which has already been noted, it may be stated that there has been no explanation in the literature and none will be offered here.

The abnormal effect of the benzene ring on white light is shown by the results obtained with thymol and menthol. These are very much alike, but differ in that thymol contains the benzene ring in the unreduced state. Over a range of 500 mg. per liter thymol causes a shift of 2 bands in the spectrum, while menthol causes none.

It may be noted that Mitchell[8] reported the use of a Jamin[9] type of interferometer for solubility measurements. This instrument employs monochromatic light and the calibration lines obtained with it by Mitchell are all continuous. The technique in the use of the Jamin instrument is not so simple as for the Zeiss type in that the interference bands of mono-

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[7] Barth and his references (ref. 2) ascribe the breaks in the calibration lines to differences in the refraction between glass lenses, solution and distilled water.

[8] Mitchell, *J. Chem. Soc.*, **129**, 1333 (1926).

[9] Jamin, *Ann. chim. phys.*, **52**, 171 (1858).

chromatic light are all alike and the displacement must be carefully followed on the cross hairs of a telescope.

IV. Length of Cell.—The maker of the instrument supplies cells varying in length from 0.1 cm. to 8 cm. The observation has been confirmed that the micrometer reading, that is, the displacement of the bands, is proportional to the length of the cell. The longer cell, therefore, increases the accuracy of the measurements.

In the case of benzene derivatives the longer cell increases the optical effects which have just been described. For example, using a 4cm. cell the breaks in the calibration of thymol occurred regularly with each increase in concentration of about 200 mg. per liter. When using an 8cm. cell this phenomenon occurred at about every 100 mg. per liter.

The writer wishes to express his thanks to Dr. A. L. Kibler, Chief of the Physical Chemistry Department for his advice, and to Mr. G. A. Sachs for his assistance in the laboratory.

Summary

Some observations are reported on the use of the Zeiss interference refractometer as a means of determining the concentrations of dilute solutions.

EDGEWOOD, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

SELENO COMPOUNDS OF TUNGSTEN[1]

BY VICTOR LENHER AND AUGUST G. FRUEHAN

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Since selenium is similar to sulfur in many respects, it was believed to be possible to prepare some new compounds of selenium which would be analogous to known compounds of sulfur. Thus, seleno-antimonates, seleno-arsenates and seleno-stannates are known which are analogous to the thio-antimonates, thio-arsenates and thio-stannates. Many mixed compounds such as $Na_3SbSeS_3 \cdot 9H_2O$ and $Na_3AsSe_2S_2 \cdot 9H_2O$ have also been prepared. Thio-compounds of tungsten, molybdenum and vanadium such as $(NH_4)_2WS_4$, $(NH_4)_2WO_2S_2$, $(NH_4)_2MoS_4$ and $(NH_4)_3VS_4$ are known, but analogous seleno compounds have not been reported. It is the purpose of this investigation to attempt the preparation of seleno compounds which are analogous to the thio-tungstates.

Uelsmann[2] prepared tungsten triselenide by saturating a tungstate with hydrogen selenide and then acidifying the solution with sulfuric acid, when the tungsten triselenide was precipitated. It was logical to

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[1] From part of a thesis to be submitted by August Fruehan in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[2] Uelsmann, *Jahresbericht*, **1860**, 92.