

arising, for example, from a somewhat abnormal osmotic pressure, or a change in the migration velocities of the ions, as has been assumed by most authors.

In conclusion, I desire to express to the authorities of the Carnegie Institution my great indebtedness for the assistance rendered me in the prosecution of these researches; for without such aid little progress could have been made up to the present time.

BOSTON, December, 1907.

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[CONTRIBUTION FROM THE LABORATORY OF THE MALLINCKRODT CHEMICAL WORKS.]  
**THE REFRACTIVE INDICES OF ALCOHOL-WATER MIXTURES.<sup>1</sup>**

BY LAUNCELOT W. ANDREWS.

Received January 15, 1908.

To Leach and Lythgoe belong the credit of having first determined, by means of the Zeiss immersion refractometer, the refractive powers of aqueous solutions of methyl and ethyl alcohols and of publishing the results<sup>2</sup> in tabular form for the entire range from zero per cent. to one hundred per cent. for the temperature of 20°. An earlier table<sup>3</sup> by B. Wagner comprises the range for ethyl alcohol only from zero to three hundred and thirty, expressed in grams per liter.

The method used by the first-named authors for fixing the concentration of the solutions of which they observed the refraction, is not mentioned in their publication, but the inference is that they deduced the concentrations from density determinations by means of Hehner's tables.

Since, in case of nearly absolute and of very strong alcohol, the refractometer and density constants bear such a relation to one another that the concentration may be much more accurately inferred from the former than from the latter, it follows, that the refraction constants should be fixed independently of observations of specific gravity. For this and other reasons, I decided to prepare absolute alcohol, and from this to make, by dilution with known weights<sup>4</sup> of water, the solutions needed for the refractometric work.

#### Preparation of the Absolute Alcohol.

Three methods came into consideration for the preparation of the absolute alcohol required, *viz.*, the usual quick-lime process; the method of Winkler<sup>5</sup> with metallic calcium, and the Evans and Fetsch<sup>6</sup> and Konek<sup>7</sup>

<sup>1</sup> Read before the American Chemical Society, January 2, 1908.

<sup>2</sup> This Journal, 27, 964 (1905).

<sup>3</sup> Dissertation, Jena (1903).

<sup>4</sup> The weighings were not reduced to vacuum.

<sup>5</sup> Ber., 38, 3612 (1905).

<sup>6</sup> This Journal, 26, 1158 (1904).

<sup>7</sup> Ber., 39, 2263 (1906).

process with magnesium amalgam. It was decided to operate by all three methods and to compare the refractive indices of the products.

The plan contemplated the continuance or repetition of each process until no further change occurred in the constants, and was carried out in that way. Two criteria of complete hydration were made use of, first, the constancy of the refractive index, which falls rapidly as the last portions of the water are extracted, second, the constancy of the critical temperature of solution. The latter method, devised by Crismer,<sup>1</sup> cannot be too highly recommended. It consists, as is well known, in cooling a mixture of equal volumes of the alcohol and of kerosene until the mixture becomes turbid, a sign of the critical temperature having been reached, and observation of the temperature. It was found advisable to free the kerosene from its more volatile constituents by passing a current of steam through it for some time, after which it was dried. This treatment obviated the appearance of a preliminary haze before the critical temperature was reached, a phenomenon that slightly diminished the sharpness of the observations. The following table shows the relation between the C. T. S. (critical temperature of solution) and the percentage of alcohol, as found for the kerosene used by me. It may be seen that if the temperature be read to 0.1°, a difference of 0.005 per cent. in the amount of water present may be easily detected, a fact previously demonstrated by Crismer. With proper precautions, a much closer temperature determination may be secured, but is hardly necessary.

TABLE I.

Per cent. of water.	Per cent. of alcohol.	C. T. S. kerosene.	Diff. per cent. for 1° C.
0.0	100.0	4.0°	0.050
0.2	99.8	8.0°	54
0.4	99.6	11.6°	57
0.6	99.4	15.1°	59
0.8	99.2	18.4°	60
1.0	99.0	21.7°	0.061
0.2	98.8	24.9°	64
0.4	98.6	28.0°	66
0.6	98.4	31.1°	69
0.8	98.2	34.0°	72
2.0	98.0	36.8°	0.075
0.2	97.8	39.4°	77
0.4	97.6	42.0°	83
0.6	97.4	44.4°	91
0.8	97.2	46.6°	0.100
3.0	97.0	48.6°	

The raw material employed for the preparation was that commercially known as "double Cologne spirit." This was digested for three

<sup>1</sup> "Les températures critiques de dissolution," Bruxelles (1904).

weeks, being frequently stirred, with good quicklime, and then distilled, the first and last tenths being rejected. To the intermediate fraction, which contained about 99 per cent. of alcohol, silver nitrate was added<sup>1</sup> in the proportion of about five grams to each liter and the solution boiled for about eight hours, under reflux condensation and exclusion of moist air. Then, after standing cold for two or three days, it was distilled. The distillate contained about 0.3 per cent. of water. No reaction for aldehydes could be obtained from it. Various portions of this intermediate product were used for the further dehydration with, first, fresh lime from marble, second, turnings of metallic calcium, third, magnesium amalgam.

It soon appeared that a too prolonged treatment with either of the last-named reagents gave an alcohol which, on distillation, was less dry (judged by the C. T. S.) than that secured by a briefer treatment. The true explanation of this department is uncertain, although it would be not difficult to suggest an hypothetical one. The proper period of digestion is shown by the appearance of a pale yellowish tint throughout the liquid. When this point is distinctly reached, no matter which of the drying agents be used, if the alcohol is distilled with the usual precautions,<sup>2</sup> the following phenomena were observed.

The first portion of the distillate contained a little water and had a C. T. S. (with the standard kerosene referred to above) of about 6°. After approximately ten per cent. had distilled off, in each case the C. T. S. rose to 4° or 4.15° and remained at that point till nearly all had come over. In some instances, especially when magnesium amalgam was present in the distilling vessel, the C. T. S. fell again toward the close of the distillation. Hence, the middle portion alone was used for the determinations. It may be remarked, however, that the first fraction (tenth) was not distinguishable in density from the middle one. In several instances, the intermediate fraction was subjected a second and a third time to the action of the same desiccating agent as before, but in no case was it possible to reduce the C. T. S. below 4° or to obtain a product of which the density or refractive index pointed to greater dehydration than that of the 4° material.

It was repeatedly observed that the alcohol dehydrated by prolonged

<sup>1</sup> Winkler, Ber., 38, 3612 (1905).

<sup>2</sup> The remark of Winkler (*Loc. cit.*), that the hygroscopic character of absolute alcohol "has been exaggerated" should not be interpreted in the sense that any precautions to exclude moist air may safely be neglected. This author must have been favored with exceptionally dry atmospheric conditions, or the remark quoted would never have been made. I can fully confirm the observations of Crismer (*Loc. cit.*, p. 7) on the rapid absorption of water by dry alcohol on exposure to humid air and have not been able under the conditions of my experiments to confirm the divergent observations of Winkler.

contact with either calcium or with magnesium amalgam possessed a peculiar foreign odor, which persisted even after dilution with a little water. The nature of the substance giving this odor is entirely unknown, but its presence does not appreciably influence either of the constants determined. Its amount is, therefore, probably, extremely minute.

The desiccation with calcium or with magnesium amalgam may be effected by contact at the ordinary temperature for several days or at the boiling point of alcohol in half an hour or two hours. The amalgam was prepared by agitating magnesium powder with its own weight of mercury under the surface of 98 per cent. alcohol, acidified with a little hydrochloric acid. When etched in this manner, the mercury soon flows over the surface of the magnesium particles. The alcoholic acid is poured off and the magna washed with absolute alcohol. Other methods of preparation were experimented with, but this was found most efficient and has the advantage of rendering a greater amount of magnesium available in proportion to the mercury.

#### Apparatus.

The refractometer used was a Zeiss instrument of the immersion type. Its scale was subject to a small correction ( $-0.24^\circ$ ) which was determined by a series of observations on pure water at  $25^\circ$ . All the readings presented in this paper have been so corrected.

The thermostat used in the work was kept at  $25^\circ \pm 0.6^\circ$ . Its temperature never varied more than  $0.05^\circ$  during an observation and very rarely by so much. Each sample of alcohol was observed at least five times after the temperature of the thermostat was attained, and the mean of the concordant readings taken. This mean was corrected for  $25^\circ$  by the temperature coefficient given in Table II.

Two thermometers were used. One was divided in  $1/5^\circ$  and had divisions wide enough to enable  $0.01^\circ$  to be estimated with considerable accuracy. This thermometer was made by Geissler Nachfolger in 1880, of unknown glass. The second thermometer was made of Jena normal glass, divided into  $1/10^\circ$  and read to  $0.01^\circ$ . In order to insure taking the readings on a rising meniscus, in case of all definitive observations, the thermometer was removed from the thermostat, waved in the air a moment to cool it about  $1^\circ$  and then replaced.

Fixed points were determined for both instruments at  $0^\circ$  and at the transition point of sodium sulphate (after Richards). The intermediate scale was calibrated by two mercury threads and the reading corrected accordingly and reduced to the international or hydrogen scale by the table of Marck.<sup>1</sup>

With these corrections applied, the two instruments agreed, on direct comparison, for temperatures between  $20^\circ$  and  $30^\circ$  within the limits of

<sup>1</sup> Landolt and Bernstein Tabellen, 44.

the observation errors. A third thermometer was used for some of the density determinations. It was fused into one of the pycnometers. It was compared with the others by filling the pycnometer with mercury and immersing the whole in a mercury bath containing the other instruments and placed in the thermostat.

Two pycnometers were employed, one of about 50 cc. of the Sprengel type, the other of 35 cc. with fused-in thermometer. The errors of a density determination of alcohol amounted to about two units of the fifth place of decimals. It is hardly possible to secure greater accuracy on a liquid of this kind with pycnometers so small as this. The determination of density was not, however, a main object of this investigation.

To obtain a degree of precision in the measurement of this constant commensurate with present means of obtaining pure absolute alcohol, pycnometers or sinkers of not less than 250 cc. should be used.

In all these determinations, except as previously noted, correction to vacuum was made for weights and substances weighed, and the errors of the weights were corrected.

### Experimental.

1. Absolute alcohol made by the quicklime method gave C. T. S.  $3.9^\circ$ . Density  $_{4^\circ}^{25^\circ}$  0.785103, 0.785087, 0.785107. C. T. S. after each density determination,  $4.1^\circ$ ,  $4.1^\circ$ ,  $4.0^\circ$ . Refractometer, mean of 7 observations,  $85.30^\circ$ . Another preparation of the same gave: refractometer readings, mean of 5,  $85.33^\circ$ . C. T. S.  $4.15^\circ$ . Density  $_{4^\circ}^{25^\circ}$  0.785111.

2. Absolute alcohol made by calcium method, digested at about  $35^\circ$ , gave C. T. S.  $4.05^\circ$ . Density  $_{4^\circ}^{25^\circ}$  0.785091, 0.785112, 0.785108. Refractometer, mean of ten readings,  $85.29^\circ$ . A second preparation, made at the boiling-point of alcohol: C. T. S.  $3.9^\circ$ . Density  $_{4^\circ}^{25^\circ}$  0.785105. A third preparation, made with an alcohol from another source, dried in the same manner: C. T. S.  $4.1^\circ$ ; refractometer, mean of 5,  $85.32^\circ$ .

3. Absolute alcohol made by cold magnesium amalgam process gave: C. T. S.  $4.18^\circ$ . Density  $_{4^\circ}^{25^\circ}$  0.785102, 0.785110, 0.785095; refractometer, mean of six,  $85.35^\circ$ .

A second lot of the same, but digested hot: C. T. S.  $4.03^\circ$ . Density  $_{4^\circ}^{25^\circ}$  0.785091, 0.785105, 0.785106; refractometer, mean of five observations,  $85.30^\circ$ .

A third preparation, made like the last: C. T. S.  $3.95^\circ$ . Density  $_{4^\circ}^{25^\circ}$  0.785085; refractometer,  $85.28^\circ$ .

4. Total mean of all observations on absolute alcohol:

Density,  $0.78510 \pm 0.00001$ ,  $_{4^\circ}^{25^\circ}$ . Refractometer (weighted mean)  $85.30^\circ \pm 0.02$  Z,  $25^\circ$ . Index of refraction ( $\mu_D$ ) against air,  $1.359408 \pm 0.00001$ ,  $25^\circ$ . Refractive power,  $\frac{n_D - 1}{d} = 0.45833$ ;  $\frac{\mu_D - 1}{d} = 0.45779$ .

5. From the absolute alcohol, a series of dilutions with distilled water were made by weighing, at intervals of about two per cent., except in the neighborhood of absolute alcohol, where the intervals were closer. Each of these dilute alcohols was observed with the refractometer, at least five observations being taken at each dilution. Subsequently further dilutions, about ten in all, were made from different preparations. These observations were reduced by a graphic method and independently by a series of quadratic equations, which were found to fit the various parts of the curve closely. The plotting served as a check on the mathematical work and to detect clerical errors in the computations. In this manner the scale readings and the refractive indices given in the following table were separately computed as they appear in Table II. When completed, no individual point observed was found to differ

TABLE II.—REFRACTION INDICES AND SCALE READINGS OF THE IMMERSION REFRACTOMETER FOR AQUEOUS ALCOHOLS.

% H <sub>2</sub> O.	$\mu_{25}^{\circ}$ .	Diff.	Zeiss Deg.	Diff.	$\Delta z$ for 5° C.
0	1.35941—	....	85.30°	....	5.55
1	984—	43.0	86.49°	1.19	5.57
2	6024—	40.0	87.60°	1.11	5.59
3	061—	36.9	88.63°	1.03	5.61
4	094+	33.8	89.58°	0.95	5.63
5	125—	30.7	90.45°	0.87	5.64
6	153—	27.7	91.23°	0.78	5.65
7	178—	25.0	91.93°	0.70	5.65
8	200+	22.5	92.55°	0.62	5.66
9	221—	20.3	93.10°	0.55	5.67
10	239—	18.1	93.59°	0.49	5.67
11	255—	15.9	94.03°	0.44	5.65
12	269—	13.8	94.42°	0.39	5.62
13	280+	11.9	94.76°	0.34	5.60
14	290—	9.6	95.05°	0.29	5.57
15	297+	7.5	95.29°	0.24	5.55
16	305—	7.3	95.49°	0.20	5.52
17	312—	7.1	95.68°	0.19	5.49
18	319—	7.1	95.88	0.20	5.46
19	326—	6.8	96.07°	0.19	5.42
20	331—	5.2	96.22°	0.15	5.38
Max. 20.7	1,363,315	0.5	96.24°	....	....
21	3,313	...	96.23°	....	5.34
22	3,302	1.2	96.20°	0.03	5.30
23	3,286	1.6	96.16°	0.04	5.26
24	3,265	2.1	96.10	0.06	5.23
25	3,239	2.6	96.03°	0.07	5.20
26	3,208	3.1	95.94°	0.09	5.17
					5.06
30	3,038	...	95.47°	....	....

NOTE.—The percentages of water in the first column are by weight. The refractive indices are against air ( $\mu$ ). The temperatures are given in terms of the inter-

national (hydrogen) scale. The figures of the last column give approximately only the differences of the scale readings between  $20^{\circ}$  and  $25^{\circ}$ . They may be used for calculating the corrections when the temperature differs by one or two degrees from  $25^{\circ}$ . The readings presupposed adjustment to read  $13.63^{\circ}$  in water at  $25^{\circ}$ . Practically the use of the table is restricted to alcohols stronger than 88 per cent. by weight.

from the corresponding value of the table by an amount larger than could be accounted for by an error in the temperature of  $0.03^{\circ}$  and in the averaged refractometer reading of  $0.04^{\circ}$ , and the mean difference was less than half this amount. It is of course possible, and probable, that there are constant errors of greater magnitude. In these, as in previous determinations of the same sort, there is no direct proof that the alcohol may not have contained traces of higher alcohols sufficient to affect the results appreciably, though this seems unlikely. Further, it is not known what may be the magnitude of the errors in the Zeiss table of the relation of the refractometer degrees and the corresponding refractive indices.

The observations show the existence of a maximum of the refractive index at 20.7 per cent. of water. This corresponds very accurately, perhaps by accident, with a hydrate of the composition represented by the formula  $3C_2H_6O \cdot 2H_2O$ . It is very unlikely that the position of this maximum is incorrectly located by a larger amount than 0.3 per cent.

The view has recently found expression that improvements in the technique of making absolute alcohol have reduced the densities found for this substance from the figures obtained by Mendeléeff to those of recent authors. That this view is incorrect is shown by the fact that Crismer obtained exactly the same density numbers as Mendeléeff, although he used the critical temperature of solution method for determining when his alcohol was dry, and this is without doubt the most searching criterion for the purpose yet employed.

The results of Mendeléeff and of Crismer,  $D_{40}^{25} = 0.78522$  are given in terms of the mercury-glass thermometer, those of Winkler, Konek, Klason and Norlin, and of the present writer, in terms of the hydrogen thermometer.

Since we do not know the expansion curve for the glass of the thermometers employed by Mendeléeff or by Crismer, it is impossible to say exactly what the difference is. We may, however, assume, with probably a very small error, that the correction to be applied at  $25^{\circ}$  is  $0.11^{\circ}$  or  $-0.000095$  on the density. Applying this to Mendeléeff's figure, we have for the density reduced to the international standard,  $0.78512$ . Morley<sup>1</sup> has recently recalculated Mendeléeff's table in part, reducing the densities to the hydrogen temperature standard and he finds for absolute alcohol, at  $22^{\circ}$ ,  $0.78763$ . This corresponds to  $0.78508$  at  $25^{\circ}$ .

<sup>1</sup> This Journal, 26, 1185.

It therefore appears that the absolute alcohol of Mendeléeff was just as pure and free from water as that obtained by the most modern methods.

### Summary.

It is demonstrated that the absolute alcohol, prepared by the use of calcined marble and freed from aldehydes, has the same density, the same refractive index and the same critical temperature of solution as that which has been dried by the use of magnesium amalgam or of metallic calcium.

The observations of Crismer, to the effect that the critical temperature of solution of alcohol in kerosene is the best criterion of the dryness of absolute alcohol, is fully confirmed.

Absolute alcohol was found to have the following constants:

Density  $^{25}_{4}$  0.78510  $\pm$  0.00001.

Zeiss immersion refractometer,  $85.30^{\circ}$   $\pm$  0.02 at  $25^{\circ}$  H.

Index of refraction ( $\mu$ ) against air, 1.35941  $\pm$  0.00001 at  $25^{\circ}$  H.

Refractive power  $\frac{n_D - 1}{d} = 0.45833$ ;  $\frac{\mu_D - 1}{d} = 0.45779$ .

A table is presented of the refractive indices against air and of the refractometer readings of aqueous alcohols for each per cent. of water from 0 to 30, accompanied by an approximate table of temperature coefficients of refraction through the same range.

The existence is demonstrated of a maximum refractive index of 1.363315 at  $25^{\circ}$  for the mixture containing 20.7 per cent. of water and 79.3 per cent. of alcohol, a composition which very closely corresponds by chance or otherwise, with the formula  $3C_2H_6O \cdot 2H_2O$  (calculated, 20.69 per cent.).

ST. LOUIS, MISSOURI.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY;  
NO. 149.]

## THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. THE DETERMINATION OF THE MOLECULAR WEIGHTS AND CRITICAL TEMPERATURES OF LIQUIDS BY THE AID OF DROP WEIGHTS.<sup>1</sup>

BY J. LIVINGSTON R. MORGAN AND RESTON STEVENSON.

Received December 26, 1907.

### Introduction. Object of the Investigation.

In 1864, Thomas Tate,<sup>2</sup> as the result of his experiments with water, announced the following laws:

<sup>1</sup> Extract from the Dissertation of Reston Stevenson. Our thanks are due to Mr. E. Higgins for kind assistance in the latter part of the work.

<sup>2</sup> Phil. Mag., 4th Ser., 27, 176 (1864). All other references to drop weight will be found in the bibliography of that subject at the end of this paper.