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AN IMPROVED METHOD FOR THE DETERMINATION OF THE TOTAL VAPOR PRESSURES OF THE VARIOUS MIXTURES IN THE SYSTEM, METHYL-ETHYL ALCOHOLS

- by -

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(B. S. University of North Dakota, 1931)

A thesis submitted to the Graduate Division
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degree
of
MASTER OF SCIENCE

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Grand Forks, North Dakota
May 24, 1934

This thesis, presented by Mr. Raymond G. Larson, in partial fulfillment of the requirements for the degree of Master of Science, is hereby approved by the Committee on Instruction in charge of his work.

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INTRODUCTION

The object of this investigation was to develop a simple method which could be used for determining accurately the vapor pressures of binary solutions. A survey of the literature on this subject reveals many methods together with the various difficulties to be overcome in work of this nature.

A brief review of the various methods used will aid in bringing to the readers attention the advantages and difficulties of each procedure.

The static method consists in observing the fall in height of mercury in a barometer tube due to the vapor pressure of the liquid introduced into the Torricellian vacuum. Tammann[1] has shown, however, that this method is open to serious errors due to small traces of air and volatile impurities unavoidably present in the solution and on the sides of the tubes. Furthermore, the concentration of the solution which is finally in equilibrium with the vapor in the space above the mercury is not exactly known since there is a variation in concentration of the solution due to evaporation. Michaud[2] and Schmidt[3] have used the static

[1] Tammann, Wied. Ann., <u>33</u>, 322 (1888). [Statement was taken from article by Pearce & Snow, J. Phys. Chem., <u>31</u>, 231 (1927)]

[2] Michaud, Ann. de Phys. <u>5</u>, 6 (1916).

[3] Schmidt, Z. fur physik. Chem. <u>99</u>, 71 (1921).

method in determining the vapor pressures of binary mixtures of various liquids. They recognized the chief problems of freeing the liquids of dissolved air and of preventing or determining the change of composition due to evaporation of the more volatile component and developed their apparatus and procedure accordingly. Smith and Menzies[1] quotes the following in regard to the static method: "Schmidt[2] after enumerating its difficulties, including one not noted by other observers, namely that a number of barometer tubes had to be rejected before one was found in which the pressures with small amounts of vapor were not larger than with greater amounts adds: 'The static method has so many disadvantages, when compared with the dynamic, that I can only warn [observers] not to use it' ". In spite of the fact that the static method is theoretically, completely unobjectionable, it is considered undesirable because of inherent sources of inaccuracy or because of excessive time necessary to get results. This method is more readily applied to pure substances and for comparative purposes than to volatile binary systems.

The dynamic method has been employed by most investigators. It may be divided into two classes, namely: the gas saturation or air bubbling method and the distillation procedure. The former class depends on the assumption that if air or some

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[1] Smith & Menzies, J. Am. Chem. Soc., <u>32</u>, 1412-34 (1910).
[2] Schmidt, Z. physik. Chem., <u>8</u>, 629.

inert gas is bubbled through a solution under conditions such that equilibrium is reached, the quantity of each volatile component present in the vapor is proportional to its partial vapor pressure in the solution. The work of Regnault[1] and others shows quite conclusively that the pressure of a saturated vapor in equilibrium with its liquid is lowered by the presence of an indifferent gas. Campbell[2], in particular, in a study of the saturated vapor pressures of eight different liquids in contact with air, hydrogen, and carbon dioxide, observed and measured this effect and showed that in certain cases it attained a considerable magnitude; the v.p. of chloroform and methyl alcohol in an atmosphere of carbon dioxide, for example, being only about three quarters of the values in the absence of the gas. It hence follows that the concentration of a saturated vapor in a gas is not a true measure of the vapor pressure of the liquid and, therefore, that the very large number of vapor pressure measurements which have been made by the gas saturation method are subject to an error, unknown in extent but, in some cases at least, of very considerable magnitude. Besides this difficulty, there are others which make the method undesirable. Menzies[3] found that there is a surface condensation error in certain measurements of vapor pressure by gas current saturation method

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[1] Regnault, Ann. Chim. Phys., 15, 129 (1845); Mem. Acad. Sci., 26, 679 (1862). [Taken from article by Sayce and Briscoe, J. Chem. Soc., 132, 1302-7 (1929).]

[2] Campbell, Trans. Faraday Soc., 10, 197 (1915). [Statement by Sayce and Briscoe, loc. cit.]

[3] Menzies, J. Am. Chem. Soc., 42, 978 (1920).

which is sufficiently great to largely account for unexplained irregularities recorded in the literature of measurements by this method.

Another criticism of the bubbling method is that the error due to change of composition may be particularly large if the components are very different in volatility. In addition there may be an error due to failure to obtain saturation of the gas stream with the vapor and also due to a difference in actual pressure in the bubblers where saturation takes place from that of the measured atmospheric pressure.

The partial distillation method consists in distilling off a small portion of liquid from a large volume of the binary mixture and then analyzing the distillate obtained. Zawidski's[1] objection to this method is that the volume of the mixture used is often too small and hence the composition and boiling point vary too much during the distillation. This error is particularly large if the components are very different in volatility. Rosanoff's[2] method, which is a decided improvement over the older distillation methods, consists in adding to the boiling mixture the more volatile component in such a manner that the temperature of the boiling mixture, electrically heated, does not change and a relatively small amount of distillate is analyzed. The chief criticism of this method is that it seems to be unsuitable for pairs of liquids

[1] Zawidski, Z. physik. Chem., <u>35</u>, 129 (1901). [From article by Nelson, J. Am. Chem. Soc., <u>54</u>, 1390-3 (1932).]

[2] Rosanoff and coworkers, J. Am. Chem. Soc., <u>31</u>, 953-87 (1909).

of very different volatility owing to the difficulty of controlling the addition of the more volatile component to the boiling mixture to maintain a constant composition.

Ferguson & Funnell[1] have developed a form of the dynamic method by which liquid is distilled into an all glass apparatus, its vapors circulated about till equilibrium is obtained, confined in a known volume, its temperature and pressure relations observed, the vapor condensed and liquid analyzed. The method is considered undesirable, however, because of its elaborate requirements for the apparatus, and because of the unknown effect due to the presence of air.

Nelson's[2] method is similar to that of Rosanoff[3]. The distillate, however, is returned to the boiler heated by an electrical heating element and is run for a period of time till the thermometer shows no change in temperature. The distillation is carried out at atmospheric pressure and the distillate is analyzed.

Martin & Collie's[4] method is an improvement over that of Sameshima's[5] which is a modification of Zawidski's[6] method. The modification included an air jacketed water cooled condenser in the thermostat to prevent the volatilization of the

[1] Ferguson and Funnell, J. Phys. Chem., <u>33</u>, 1-8 (1929).

[2] Nelson, J. Am. Chem. Soc., <u>54</u>, 1390-3 (1932).

[3] loc. cit.

[4] Martin and Collie, J. Chem. Soc., <u>135</u>, 2658-65 (1932).

[5] Sameshima, J. Am. Chem. Soc., <u>40</u>, 1482-1508 (1918).

[6] loc. cit.

returning distillate until the liquid (distillate) had a chance to mix with the boiling mixture. In both of these methods the distillate is returned to the boiling mixture. If the components differ much in volatility the returning distillate will constantly vary the composition of the boiling mixture and hence its boiling point. Both methods have yielded very satisfactory results.

The indirect method, as perfected by Ramsay and Young[1], consists in observing the temperatures at which solutions boil under various pressures. They have used the method extensively and their results are very reliable. Pearce & Snow's[2] criticisms of this method are (1) the liquid and the vapor are both liable to become superheated (2) in the case of solutions, the concentration is changed by the evaporation of the solvent and (3) the method is limited by the fact that many solutes decompose on boiling.

Calingaert & Hitchcock[3], Cunaeus[4], Hoover & Glassey[5], Culbertson[6], Barus[7], and others have used the indirect method

[1] Ramsay & Young, J. Chem. Soc., <u>47</u>, 45 (1885). [From Pickett, Ind. Eng. Chem., Anal. Ed., <u>1</u>, 36-8 (1929)]

[2] Pearce & Snow, J. Phys. Chem., <u>31</u>, 231-45 (1927).

[3] Calingaert & Hitchcock, J. Am. Chem. Soc., <u>49</u>, 750 (1927). [From Dornte, J. Phys. Chem., <u>33</u>, 1309-31 (1929).]

[4] Cunaeus, Z. physik. Chem., <u>36</u>, 232 (1901). [From Dornte, loc. cit.]

[5] Hoover & Glassey, Trans. Roy. Soc., Canada III, (3) <u>19</u>, 35 (1925); [From Dornte, loc. cit.]

[6] Culbertson, Proc. Roy. Soc., 85 A, 306 (1911). [From Dornte, loc. cit.]

[7] Barus, Proc. Nat. Acad. Sci., <u>14</u>, 939 (1928). [From Dornte, loc. cit.]

for binary mixtures and used the gas interferometer for gas or vapor analysis but the results are unreliable. Cunaeus attributes the unsatisfactory results to an adsorbed film on the glass surfaces of the interferometer chamber. Dornte[1] investigated the possibility of the use of the interferometer for the analysis of the vapors of binary systems and concluded that the interferometer method for the determination of partial pressures is unreliable unless an entirely empirical calibration is used.

Squire[2] has developed a rather unique indirect method for measuring the true vapor pressure of volatile liquids. The pressure observed in all types of apparatus is that exerted by the liquid in equilibrium with its vapor. Squire defines the true vapor pressure as that pressure which the liquid exerts when the first molecules leave the liquid. This method also involves the problems in that the samples must be free from dissolved air and gases, and that care must be taken that the composition does not change or that the composition can be accurately determined.

Pickett[3] used a modification of the Ramsay and Young[4] vapor pressure method and obtained very satisfactory results for pure substances. The method was very satisfactory in that it

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[1] Dornte, J. Phys. Chem., 33, 1309-31 (1929).

[2] Squire, Internat. Petroleum Tech., 8, 299-303 (1931).

[3] Pickett, Ind. Eng. Chem., Anal. Ed., 1, 36-8 (1929).

[4] loc. cit.

was economical in time and material. Linder[1] also used a slight modification of the Ramsay and Young method. The apparatus was made of glass with ground glass connections and was designed to measure the vapor pressures of pure hydrocarbons near 0°C. A Mc Leod gauge was used to measure the pressure. The results obtained were very satisfactory in comparison with other published results.

A good résumé of vapor pressure methods published up to 1926 is given by Reilly, Rae, and Wheeler[2] in the book entitled "Physico-Chemical Methods."

In all the methods used to determine the total or partial vapor pressures of binary mixtures, the chief problem has been to prevent or determine the change of composition due to evaporation. Considering the requirements as pointed out by Smith & Menzies[3] for accurate vapor pressure measuration and also the various difficulties and advantages as obtained by a survey of the literature, the authors decided to improve the indirect method of Ramsay & Young and modify it for the measurement of the total pressure of binary mixtures of methyl and ethyl alcohols.

[1] Linder, J. Phys. Chem., 35, 531 (1931).

[2] Reilly, Rae, Wheeler, "Physico-Chemical Methods", P.437 (1926).

[3] loc. cit.

EXPERIMENTAL

Vapor Pressure Apparatus The apparatus used by Linder has been modified by us and is shown in fig. 1[1]. A is an unsilvered Dewar tube with an evacuated ground glass stopcock B, at its base. C is an evacuated ground glass stopper in which are seated by ground glass joints a special thermometer D, with its bulb surrounded by cheesecloth, and a heating element E, fitting into a small tube extending down into chamber A. F are ground glass connections held together by rubber bands. G is a silvered Dewar tube containing a cooling mixture. H is a condensation tube with a small stopcock I, at its base. Both stopcocks B and I were lubricated with graphite and sealed with mercury wells. J is a stopcock through which the entire system may be evacuated. K is a rubber tubing which leads by means of a T tube connection to the hyvac-pump and atmosphere through calcium chloride drying towers. L is a five liter flask for the purpose of enlarging the volume of the system for reasons later to be explained. M is an ordinary mercury thermometer and N is an open mercury manometer. All joints or connections were sealed by mercury except stopcock J, which was lubricated by a thin film of vaseline and was found to maintain an air tight joint for the pressures under which the investigation was carried out.

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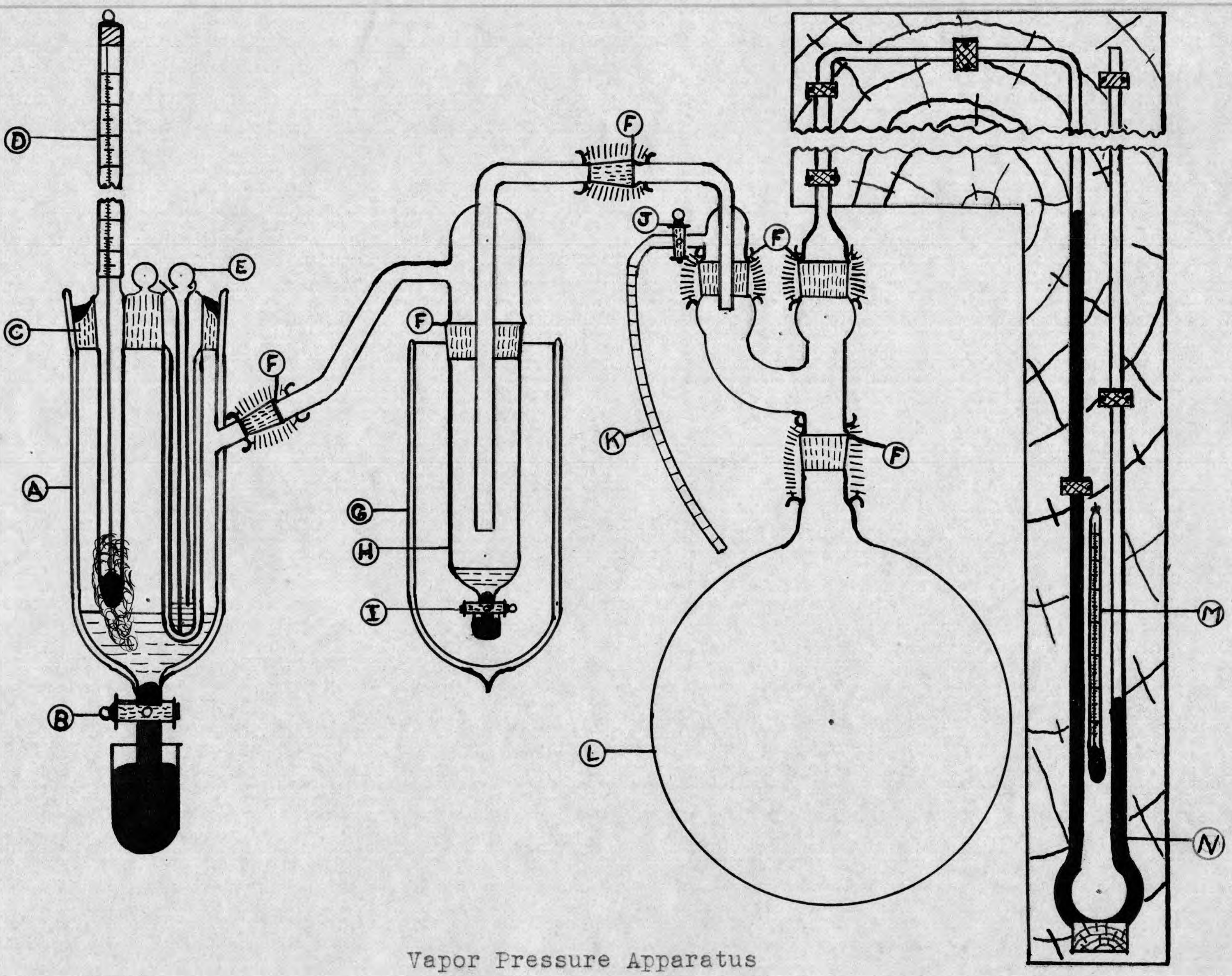
[1] Made by Scientific Glass Apparatus Co., Bloomfield, New Jersey.



Vapor Pressure Apparatus

Figure 1

Procedure   The method of determining the total vapor pressures of both pure and binary mixtures in this apparatus is as follows: All parts of the apparatus proper were cleaned with hot dichromate-sulfuric acid solution, washed with distilled water, ethyl alcohol, and ether, and then dried in an oven before the parts were assembled. With all connections sealed with mercury except stopcock J, the system was tested for leaks by evacuating it for a period of an hour or more and then pressure and temperature readings were taken of both the manometer and barometer. No appreciable leak could be noticed over a period of five days.

The liquid to be tested was drawn into chamber A, through stopcock B, by means of a partial vacuum in the system and also enough pure mercury to seal securely the connection. Dewar tube G, was then filled with a cooling mixture, depending on the kind of liquid in chamber A, so that the vapors drawn over from A would be immediately condensed. For water, the cooling mixture consisted of ice-calcium chloride solution; for the alcohols, a cooling mixture of carbon dioxide-ether slush may be used. The thermometer in chamber A has, wrapped around its bulb, layers of cheesecloth, in such a manner that the cloth dips into the liquid while the base of the thermometer bulb is not in the liquid. In such a condition, the thermometer will indicate the temperature of the liquid in equilibrium with its vapor.

The following manner was used in making a trial: With the liquid to the proper level in A, and H, surrounded by a cooling mixture which is capable of condensing all vapors and with all joints and connections well sealed, the system is opened to an exhaust pump by means of stopcock J. Evacuation will cause evaporation and hence a cooling of the liquid in chamber A. The vapors will be condensed in tube H and the dissolved gases and air in the liquid will pass over into the big flask L, and out by way of the pump.

When the temperature at which the vapor pressure is to be determined, has been reached, as indicated by the thermometer D, the system is closed. Evaporation, however, will continue since H condenses the vapors from A and the liquid thus formed will have a lower vapor pressure than that in A since it is at a lower temperature. After about five minutes an equilibrium is reached as determined by the fact that the temperature recorded by thermometer D, remains constant to 1/100 of a degree for perhaps five minutes or so and then rises very slowly. Equilibrium then is a condition during which the rate of evaporation is equal to the rate of condensation. The cooling produced by this evaporation must be compensated by the slight heat transfer from the surroundings.

The pressure readings, as observed on manometer N by means of a cathetometer, are usually taken about 10 minutes after evacuation has been stopped. The readings on thermometer D are observed both before and after the pressure readings are taken and the average temperature used in the calculations. In most cases these readings are identical. Thermometer M gives the room temperature used for manometer corrections. In the case of binary mixtures, the system must be carefully opened to dry air and a sample of the liquid in A must be carefully withdrawn for analysis. The binary mixtures of ethyl-methyl alcohols may be examined for their composition by means of a refractometer. The metal beaker of the Zeiss dipping refractometer is used to hold a representative sample withdrawn from A and is immediately clamped on to the prism. The refractive index may then be determined and its composition calculated from the refractive index-composition curve for the particular mixture. The barometric pressure and temperature readings are observed shortly before or after the manometer readings are taken.

Theory At equilibrium the pressure in the entire system must be equal. The condensing tube H separates the system into two parts. To the left of it the pressure is due to the vapor pressure of the liquid investigated. To the right the pressure is due to air and dissolved gases removed from the liquid and apparatus. Both these pressures must be equal and hence the vapor pressure of the liquid may be measured indirectly by measuring the pressure exerted by the air and dissolved gases.

This method has several fine advantages which make it very practical and efficient. Dissolved gases which are invariably a constant source of error are easily removed from the liquid. The matter of temperature regulation is a simplified matter since no thermostat is needed. The composition of the liquid whose vapor pressure is measured may be accurately determined by analysis. And the range of pressure measuration may be varied to suit the individual needs.

Calculations The manometer readings as observed with the cathetometer were corrected for Bureau of Standards corrections, temperature correction of the brass scale to 20°C, and reduction of millimeters of mercury to 0°C. The barometric pressure was corrected for B. S. correction, temperature scale correction, reduction to mm. of mercury at 0°C. and a correction for difference in height of manometer and barometer. The difference between the corrected pressures gives the vapor pressure of the solution in A at the temperature indicated on D. It was not necessary to make a correction for gravity since for these pressures the correction is about the same for both mercury columns and hence they are compensating when determining the vapor pressure.

<u>Purification of Materials</u>

(a) <u>Air-equilibrium Water</u> This was obtained from a copper still with a block tin condenser by distilling distilled water containing alkaline permanganate solution.

(b) <u>Ethyl Alcohol</u> Absolute ethyl alcohol was obtained by a method described by G. Frederick Smith[1]. Two-liter portions of 93% ethyl alcohol were refluxed for a period of two hours with 800 grams of barium oxide in an all-glass distillation apparatus. The liquid was then distilled and the retained middle portion was next refluxed with 50 grams of calcium metal turnings per liter of alcohol till a gelatinous gray precipitate of calcium ethylate was formed. This was distilled and the middle portion was again retained. The procedure of refluxing and distilling was repeated three more times with a little calcium metal. During the last treatment the distillate was delivered directly into a flask which was part of the apparatus used for making up the binary mixtures of the two alcohols.

[1] G. Frederick Smith, "Rapid Dehydration of Alcohol Using Barium Oxide and Metallic Calcium", Ind. Eng. Chem., (Analytical Edition) <u>1</u>, 72-74, (1929).

Its refractive index was: $n_D^{25} = 1.35940$.

This value compares exactly with that obtained by Andrews[1] who prepared the absolute alcohol by three different methods.

(c) Methyl Alcohol This was obtained by a method used by Eastman Kodak Company. To two-liter portions of Merck's "acetone free" absolute methanol were added six grams of sodium metal. The liquid was refluxed and then distilled. The retained middle portion was treated twice more with a little sodium and the distillate of the last distillation was delivered directly into the other flask of the apparatus for making up the solutions.

Its refractive index was: $n_D^{25} = 1.32633$.

Glazunov[2] obtained a value $n_D^{25} = 1.32773$ and Lifschitz & Beck[3] found $n_D^{25} = 1.32663$ for 100% alcohol. Neither of these values check with my value. The author, however, feels that his results are dependable for three reasons; namely,(1) the refractive indices[4] of aqueous solutions are all greater than that of the pure alcohol,(2) the refractive index of formaldehyde, an oxidation product of methyl alcohol, is much greater than that of the pure alcohol,and (3) the general trend of the weight per cent-refractive index curve for the authors solutions of methyl and ethyl alcohols, indicated such a value to be very probable.

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[1] Andrews, J. Am. Chem. Soc., 30, 353, (1908).

[2] Glazunov, I.C.T., Vol.VII, 67, #22.

[3] Lifschitz & Beck, I.C. T., Vol. VII, 79, #256.

[4] I. C. T., Vol. VII, 67, #22.

Solution Mixing Apparatus The mol per cent mixture of absolute ethyl alcohol and absolute methyl alcohol were made up by the use of the apparatus shown in fig. 2. A and B are six-liter flasks which contain the pure liquids. C and D are 100 c.c. burettes which have been standardized by the United States Bureau of Standards. They are connected to the solution bottle F, of one liter capacity, by means of an adapter E. The tubes G, containing phosphorus pentoxide, in series with the Drexel wash bottles H, containing concentrated sulfuric acid, protect the entire system from moist air. Except for the solution bottles and Drexel wash bottles, the apparatus is made of pyrex glass with ground glass connections held together and further sealed with a wax. The joint between E and F, however, is merely the ground glass connection. I and J are sealed tubes through which the pure liquids were distilled directly into the flasks A and B. L and M are rubber pressure bulbs. N is an iron ring for holding bottle F to adapter E.

The procedure for making up the solutions is as follows: The entire apparatus was well cleaned with hot dichromate-sulfuric acid solution, washed with distilled water, ethyl alcohol, and ether, and then dried in an oven before the parts were assembled. With the apparatus assembled and the pure liquids distilled into flasks A and B, the tubing, burettes, and adapter were rinsed out with the absolute alcohols. When the entire system was at a constant temperature as indicated by a thermometer reading accurately to one-tenth of a degree, the volumes of each of the pure liquids to make a certain mol per cent of solution was calculated by means of their densities.

The equation[1]

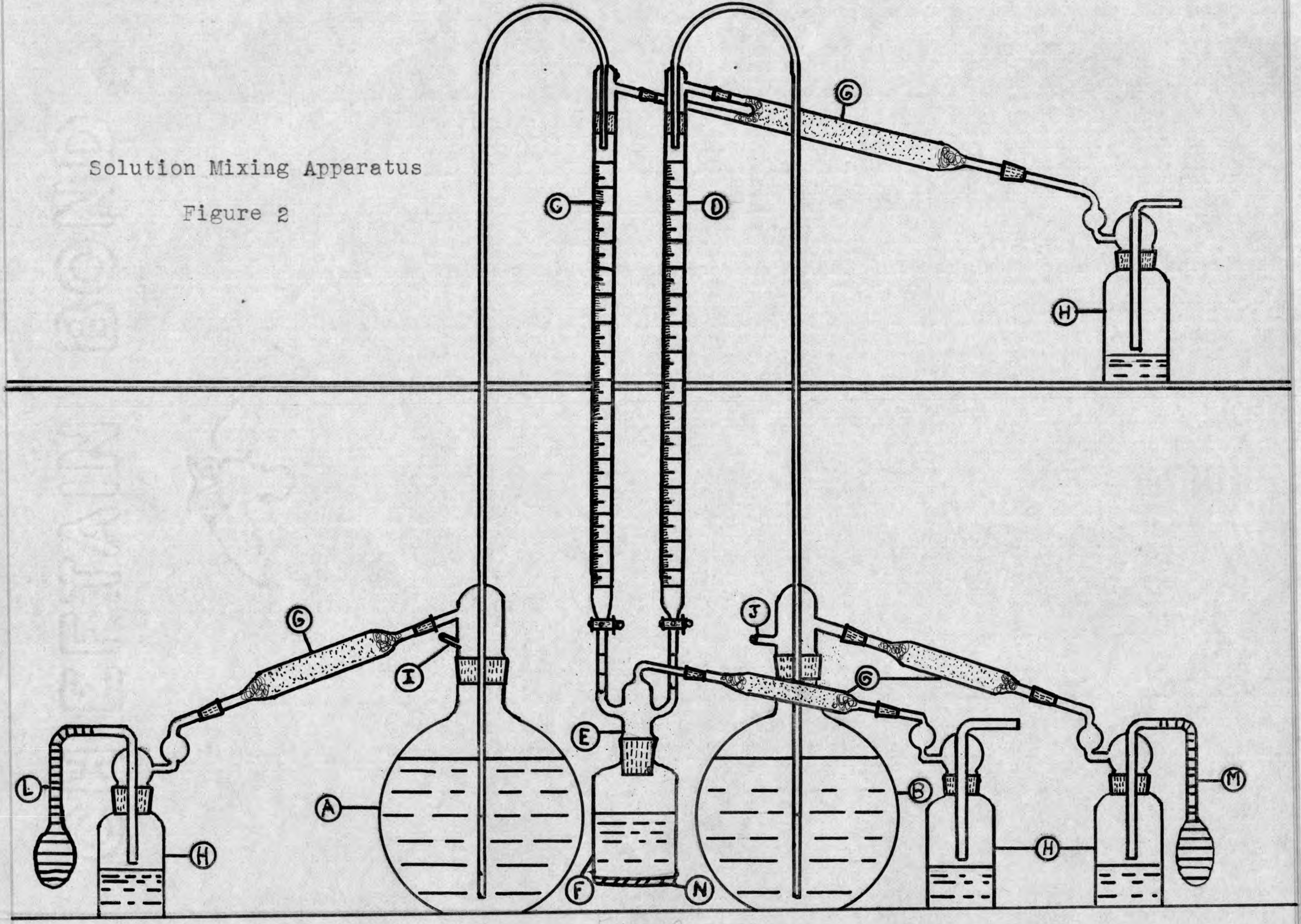
$$d_4^t = 0.80999 - 0.0_3 9253t - 0.0_6 41t^2$$

gives the density of methyl alcohol which reproduces the experimental values of several investigators to 0.00002 for a temperature range of 0 to 30°C. The equation[1]

$$d_4^t = 0.78506 - 0.0_3 8591\ (t-25) - 0.0_6 56\ (t-25)^2 - 0.0_8 5\ (t-25)^3$$

gives the density of ethyl alcohol saturated with air for a temperature range of 10 to 40°C. The temperature is maintained constant, a labeled solution bottle is connected firmly to the adapter E, the pure alcohols are forced into the burettes, and the desired volumes of each liquid are drained into the bottle F. The bottle is then quickly detached from the adapter E and stoppered with a ground glass plug. The liquid is further protected by means of an inverted beaker sealed to the bottle by paraffin. Eleven solutions were made, varying in mol per cent from 100% methyl - 0% ethyl to 0% methyl - 100% ethyl, by intervals of 10 mol per cent. About 800 c.c. of solution were contained in each bottle. The maximum possible error involved in the reading of the burettes was calculated to be about .1%. The solutions were then stored in a dark place until they were used.

[1] International Critical Tables, III, 27.



Solution Mixing Apparatus

Figure 2

Fig 2

Thermometers D was a special mercury thermometer reading to tenths of a degree with a scale range of -17 to 75°C. It was certified by the U. S. Bureau of Standards so that there is no emergent stem correction to be made at 25°C., the temperature at about which our measurements were carried out. The Beckman thermometer used in the refractometer water bath was compared with a Bureau of Standards thermometer. M was an ordinary mercury thermometer compared with an accurate one.

Cathetometer The scale of this instrument has been certified by the Bureau of Standards. The instrument itself was mounted on an iron platform with its iron supports embedded in concrete.

Refractometer This instrument was a Zeiss dipping refractometer. A metal beaker was used to hold the liquid to be analyzed and to protect it from access of air. The temperature of the refractometer bath was 25.00 ± .02°C. as observed on a Beckman thermometer. The instrument was calibrated by using air-equilibrium water. The refractometer was allowed to remain in the bath for ten minutes before readings were taken. In determining the points for the refractive index composition curve, of the ethyl-methyl alcohol mixtures, three check readings for three different trials on the liquid were obtained.

Barometer This instrument was compared with another mercurial barometer by the U. S. Bureau of Standards.

EXPERIMENTAL RESULTS

In table 1 are tabulated the results obtained in the determination of the refractive indices of the binary solutions of methyl and ethyl alcohols. Column 1 gives the number of the solution as labeled on the bottle. Columns 2, 3, and 4 give the corresponding mol, weight, and volume per cent of methyl and ethyl alcohols, and in column 5 is shown the experimentally determined refractive index values at 25°C.

In figure 3, curves I and II show the relationships when plotting the refractive indices against the mol per cent and weight per cent compositions respectively for the binary solutions as given in table I.

The author desired to standardize his vapor pressure apparatus and procedure by determining the vapor pressure of water at various temperatures. Because of lack of time he could not satisfactorily do this and hence he is unable to present any data in regard to the vapor pressures of the binary mixtures of methyl-ethyl alcohols.

Table II is, however, presented as a sample vapor pressure work sheet. It indicates the general method of determining the vapor pressure, and also gives a comparison of the results obtained for water with values obtained by the International Bureau of Weights and Measures. The meaning of the various symbols is:

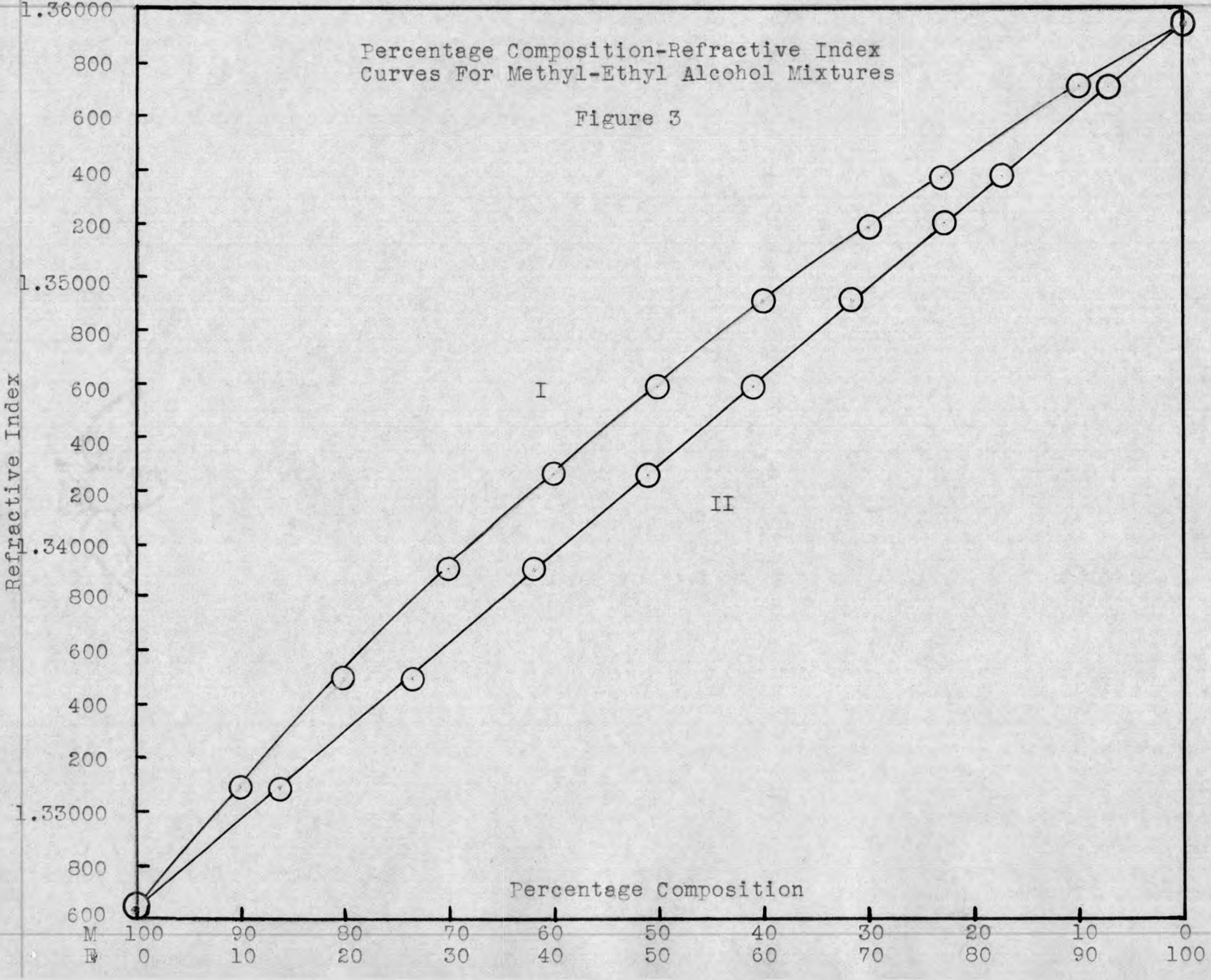
T_S	Temperature at which vapor pressure of liquid was determined (°C.).

M_L & M_R	Cathetometer readings of height of mercury columns in left and right arms of manometer (mm.).
$(M_L - M_R)$	Uncorrected difference of cathetometer readings (mm.).
T_M	Temperature of manometer = temperature of room ($^\circ$C.).
B	Barometric pressure uncorrected (mm.).
T_B	Temperature of barometer ($^\circ$C.).
H_B	Time at which barometric pressure was observed.
$(B)_C$	Corrected barometric pressure in mm. of mercury at 0°C.
$(M_L - M_R)_C$	Corrected difference in height of mercury in manometer in mm. of mercury at 0°C.
V_S	Vapor pressure of solution in mm. of mercury at 0°C. at a temperature of T_S.
R. I. (n_D^{25})	Refractive index of liquid in chamber A having vapor pressure V_S.
C_S	Composition of solution having vapor pressure of V_S corresponding to R. I.

Table I

PERCENTAGE COMPOSITION CONVERSION TABLE AND CORRESPONDING REFRACTIVE INDICES

(1) No. of Solution	(2) Mol %		(3) Wt. %		(4) Vol. %		(5) Refractive Index n_D^{25}
	M.	E.	M.	E.	M.	E.	
1.	100.000	0.000	100.000	0.000	100.000	0.000	1.32633
2.	90.000	10.000	86.227	13.773	86.206	13.794	1.33096
3.	80.000	20.000	73.562	26.438	73.528	26.472	1.33493
4.	70.000	30.000	61.877	38.123	61.833	38.167	1.33906
5.	60.000	40.000	51.063	48.937	51.017	48.983	1.34258
6.	50.000	50.000	41.025	58.975	40.979	59.021	1.34589
7.	40.000	60.000	31.682	68.318	31.643	68.357	1.34906
8.	30.000	70.000	22.966	77.034	22.933	77.067	1.35188
9.	23.085	76.915	17.272	82.728	17.249	82.751	1.35373
10.	10.000	90.000	7.174	92.826	7.164	92.836	1.35705
11.	0.000	100.000	0.000	100.000	0.000	100.000	1.35940



Percentage Composition-Refractive Index Curves For Methyl-Ethyl Alcohol Mixtures

Figure 3

Table II

VAPOR PRESSURE WORK SHEET

Trial No.	16	17	18	19	20	21
Date	4/16/34	4/16/34	4/16/34	4/18/34	4/18/34	4/18/34
Sol.	Water	Water	Water	Water	Water	Water
T_S	9.98	6.29	5.05	16.18	12.15	8.18
M_L	976.50	977.85	978.17	975.15	976.79	978.38
M_R	252.88	251.42	250.95	253.34	251.84	250.39
$(M_L - M_R)$	723.62	726.43	727.22	721.81	724.95	727.99
T_M	24.7	24.5	24.6	23.3	23.3	23.1
B	734.35	734.80	734.80	737.00	737.05	738.00
T_B	24.6	24.6	24.5	24.4	24.6	24.8
H_B	2:40 P.M.	4:00 P.M.	4:15 P.M.	12:40P.M.	1:05 P.M.	2:15 P.M.
$(B)_C$*	730.41	730.86	730.86	733.08	733.12	734.02
$(M_L - M_R)_C$*	720.72	723.55	724.33	719.10	722.22	725.27
V_S	9.69	7.31	6.53	13.98	10.90	8.75
R. I. (n_D^{25})						
C_S						
T_S	9.98	6.29	5.05	16.18	12.15	8.18
V_S (Exp.)	9.69	7.31	6.53	13.98	10.90	8.75
V_S (Tables)#	9.13	7.11	6.53	13.66	10.54	8.09
Diff.	+.56	.20	.00	.32	.36	.66

* "Smithsonian Meteorological Tables" were used in making the temperature corrections for millimeters of mercury at 0°C. and for a correction due to difference in height of barometer and manometer.

\# From tables of International Bureau of Weights and Measures given in "Handbook of Chemistry and Physics" by Hodgman & Lange, Sixteenth Edition, P. 943.

DISCUSSION OF RESULTS

The curves shown in figure 3, indicate a certain definite relationship between the composition of the binary mixture and its refractive index. Curve I, which is obtained by plotting the refractive index against the mol per cent composition of the mixture, is symetrically convex upward.

Schmidt[1] states that in the mixture methyl-ethyl alcohols the former consists of simple molecules and the latter is more or less associated. According to the Dolezalek theory as reviewed by Schmidt, curve I might be interpreted then as indicating a slight dissociation of the ethyl alcohol, the higher refractive liquid, providing, of course, the refractive index of the liquid is a direct function of the number of effective molecules. Schmidt considers this mixture an ideal system since on plotting the mole fraction against the vapor pressure he obtained a straight line.

Curve II is obtained by plotting the refractive index against the weight per cent composition and then joining the values for the pure alcohols by a straight line. It can be seen that almost all of the points lie on the line. Doroszewskii[2] has determined the refractive indices of ethyl-methyl alcohol mixtures at 15°C. and obtained the same relationship when plotting the refractive index against the weight per cent composition. In fact, on assum-

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[1] Schmidt, Z. physik. Chem. 99, 71 (1921).

[2] Doroszewskii, J. Russian Physico-Chemical Soc., 43, 46 (1911). [From International Critical Tables, Vol. VII, 79, #257.]

ing a perfectly straight line relationship, it was determined that the deviations of Doroszewskii's and the authors experimental results from the calculated values are almost all of the same sign. Such a comparison tends to indicate the accuracy of the two investigations. Doroszewskii presented the following equation as an expression of this relationship:

$$100\ n = n_A\ (\%\ A) + n_B\ (\%\ B).$$

n, n_A and n_B are the refractive indices of the mixture, and the two alcohols respectively. (% A) and (% B) are the weight per cent compositions of the two alcohols in the mixture. The accuracy of n is given as ± 1 or 2 in the fourth decimal place.

In comparing the author's results for the vapor pressure of water with that obtained by interpolation from tables of the International Bureau of Weights and Measures, one notes that his values are all a little bit too high. Such a difference may be attributed to some error in technique not yet acquired. The author, however, feels that this obstacle may be overcome in time and that this method will be very practicable in determining the vapor pressures of binary mixtures as well as of the pure liquids.

SUMMARY

A simple indirect method of measuring the vapor pressures of binary mixtures has been developed.

An apparatus has been described and used for making up binary solutions of methyl and ethyl alcohols in the absence of moist air.

The refractive indices of methyl-ethyl alcohol mixtures have been determined at 25°C. The refractive index-weight per cent curve for the binary system shows an almost perfectly straight line relationship.

The vapor pressure apparatus was not satisfactorily standardized because of lack of time in doing the work. A sample vapor pressure work sheet for some trials on water were, however, included to indicate the general procedure.

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