PHYSICAL PROPERTIES OF BINARY LIQUID MIXTURES.

By J. C. Hubbard.

Introduction.

THE study of a solution, a salt in water, for example, is in general, complicated by electrolytic dissociation, and by the probable formation of hydrates. These two effects may more or less effectually mask other effects, which, if they exist, would cause apparent deviations from a theory of solutions which takes only the two mentioned into account. There are, however, certain binary liquid mixtures the physical properties of which present such simple and small deviations from the properties of the pure substances added together, that it may be hoped by an investigation of them to be able to trace minutely the condition of each component in the mixture, thereby gaining new insight into some of the second order effects in solutions and also, possibly, learning something of the mechanism of the liquid state itself.

For the study here summarized are chosen such simple properties as could be measured with great precision, as density and index of refraction; and, in order to secure as wide a basis of comparison as possible, it seemed best to choose for study those pairs of liquids for which the partial and total vapor pressures have already been so carefully investigated by Zawidzki.[1]

The specific volumes are given for the temperatures at which he measured the vapor pressures. In addition are given the specific volumes at 25° C. and the indices of refraction at the same temperature for the lines C, D, F and G', thus securing data for determining the mean temperature coefficient of expansion, and for the dispersion. It is unfortunate that the indices of refraction could not also have

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[1] J. von Zawidzki, Uber die Dampfdrucke binärer Flussigkeitsgemische, Zs. phys. Chem., 35, p. 129, 1900. See also Rosanoff and Easley, Amer. Chem. Soc. Jour., XXXI., No. 9, p. 953, 1909; Zs. für phys. Chem., p. 641, 1910.

been measured for the same temperature as the vapor pressures, but, on account of the great volatility of most of the substances, it was found that such determinations required facilities not available.

The methods of obtaining results such as are given here call for nothing original in principle, but it is hoped that the procedure evolved has produced results of greater accuracy than hitherto obtained for such mixtures.

APPARATUS.

On account of the excessive volatility of the substances studied, and of the difference, in general, of composition of liquid and vapor, it is very difficult to prevent changes of composition through evaporation. Each point of the procedure was carefully examined, and the process was finally reduced to a certain rigid, mechanical routine, which, though arbitrarily varied in detail, is capable of giving results usually reproducible to from two to five parts in one hundred thousand, depending upon the volatility of the substances.

After much preliminary work in measuring specific volumes, involving a trial of specially designed pyknometers, it was found that the most reliable results were to be secured by the use of the common specific gravity bottle with graduated neck and solid glass stopper. The bottles were each of 10 c.c. capacity; the necks were about 4 cm. in length, graduated in millimeters and of about 1.5 mm. internal diameter. The glass stoppers were ground until no loss by evaporation of any of the liquids contained in the bottles could be detected in an interval of several hours. The volume of each bottle was calibrated for about twenty points along the scale at both temperatures at which the density was to be measured. It was found that where the temperature changes to which the bottles were subjected varied in a regular cycle the calibration values could always be reproduced to 2×10^{-4} cm.^{3}, or to two parts in one hundred thousand of the capacity of the bottle. When the bottle was to be used at a new temperature it was recalibrated. Much of interest came of the calibration of these bottles. The calibration curves finally settled down into a state very nearly independent of temperature changes between 0° and 60° C.

Two thermostats, each of five gallons capacity, regulated and heated electrically, were used in connection with the specific volume measurements. One of these was kept at 25°.00 ± .002 C. throughout the series, and the other at either 35°.17 ± .001 or 50° ± .001 to agree with Zawidzki's temperatures as the case required. The thermometers read to .001° and were compared from time to time with a standard (Baudin, calibrated at the International Bureau of Weights and Measures) loaned by Professor Webster.

The pyknometer bulbs were held in the thermostats by means of wire stages. The stopper, with a few millimeters of neck of a bulb, was allowed to protrude from the water, and over this was placed a heating coil which kept the stopper and the upper part of the neck several degrees warmer than the water in the thermostat. This was found necessary to prevent the condensation of liquid mixture in the top part of the neck, causing a lowering in the meniscus reading of the pyknometer. The mensicus reading was made by means of a mirror held below the surface of the water, obviating the necessity of disturbing the heating coil about the neck of the bulb.

From the thermostat at 25° was led a stream of water through thick walled, jacketed tubing for the temperature regulation of the Pulfrich refractometer (new construction) which was used in the measurement of the indices of refraction. The room being at about 20° made necessary a small amount of heating to compensate the slight loss by radiation. This was accomplished by passing the tubing through the core of a small rheostat which could be warmed any desired amount. By this arrangement the refractometer could be kept at 25° C. without sensible deviation. The thermometer scale of the refractometer reads to .01° C.

PREPARING VOLATILE MIXTURES OF KNOWN COMPOSITION.

The largest error, and the one most difficult of estimation, is to be found in the determination of the composition of the mixture. As this subject seems to have received very little attention it may be worth while to enter into it here, the object being to show that large systematic errors may be produced unless proper precautions are taken.

In the first place, all weighings must be reduced to vacuo, otherwise there will be a systematic error in the "per cent. composition," amounting in some cases to 0.1 per cent, due to the difference of density of the two components.

A quantity a of liquid A is first weighed out in the weighing bottle, then a quantity b of the second liquid B is poured into the bottle and the total amount, $a + b$, is determined. The proportion of A in the mixture is then supposed to be $z = a/(a + b)$. If a series of observations be obtained, say of the deviation from the additive law of specific volume for the mixture $A - B$, as

$$\Delta v = v - v_C = v - [zv_A + (1 - z)v_B]$$

(where v is the observed, and v_C the calculated specific volume), z being determined as described above, a smooth curve for Δv and z may be obtained. If, now, a second series of observations be made, always weighing out first the liquid B, a smooth curve is again obtained, but this curve will not coincide with the first. The discrepancy is caused by the evaporation of the first liquid when the cover of the weighing bottle is removed to add the second liquid. The numerator of the composition fraction for the liquid first weighed out will be too large.

The error due to this cause may be brought down to the other errors of the determination by subtracting from the weight of the first component a quantity determined by many trials as a suitable evaporation correction. This number is obtained by placing a quantity of the liquid A, for example, in the weighing bottle and making repeated weighings, between each weighing removing the stopper in the same manner and for the same length of time (five seconds) as was done when actually making up the mixture. The amount of evaporation so measured is surprisingly constant. Let it be Δa; then, instead of $z = a/(a + b)$, we have $z' = (a - \Delta a)/w$ where w is the total weight. In these experiments a had values from 6 in a very few cases to 60 gr., and Δa varied from .0006 gr. in the case of acetic acid to .018 gr. in the case of carbon disulphide; the calculated fraction z thus having a correction of from 1 in 10^5 to 1 in 300, usually however about 1 in 10^4. When the correction is applied the above mentioned discrepancy disappears.

One example is given here (Table I., Fig. 1) to show the manner of applying the evaporation correction.

Table I.[1]

Evaporation Correction for Carbon Disulphide-Methylal. 25° C.

$\Delta a\ (CS_2) = .018 \pm .001\ gr.$ $v_1\ (CS_2) = .79621.$
$\Delta b\ (Meth.) = .017 \pm .001\ gr.$ $v_2\ (Meth.) = 1.17233.$

Wt. CS_2	Wt. Meth.	Total.	% CS_2	Δv	% Corr.	Corr. to Δv.
	11.318	12.978	12.793	.00525	+.128	+.00049
	10.001	13.999	28.560	993	+.122	+ 43
	8.963	14.525	38.290	1129	+.118	+ 45
6.506		14.885	43.708	1248	−.120	− 45
	8.029	14.736	45.513	1188	+.117	+ 44
	7.187	15.300	53.026	1179	+.113	+ 41
	6.224	15.531	59.92	1130	+.110	+ 43
	6.024	15.892	61.12	1097	+.109	+ 41
9.862		15.781	62.493	1189	−.113	− 42
10.542		16.126	65.371	1157	−.109	− 41
12.544		16.670	75.251	966	−.110	− 42
15.087		17.431	86.553	632	−.104	− 38

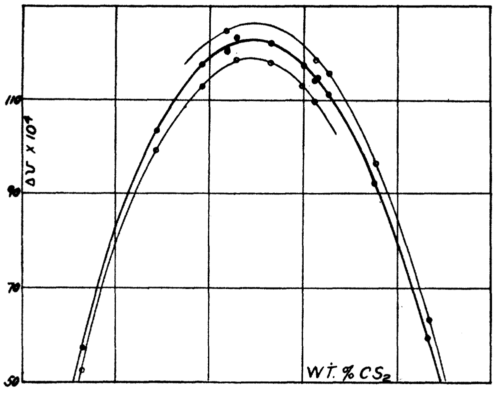

Fig. 1.

This case represents the greatest extreme, both in volatility and in the small quantity of liquid used, giving by far the largest corrections obtained in any of the results.

The sixth column of the table shows the corrections obtained for the percentage composition, while the last column gives the corresponding corrections to Δv. When the carbon disulphide is weighed

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[1] For complete data see Table II. All the weights given in the table were made to 0.1 mmg. but as the evaporation correction could not be determined so accurately the weights are given only to the nearest milligram. All weights reduced to vacuo.

out first the percentage number is too great, and since the specific volume of CS_2 is smaller than that of methylal the calculated volume is too small, making the deviations of the specific volume from the additive law too large. The reverse is true when methylal is first weighed out; the deviations are too small. It will be seen that two curves are obtained which are brought together into one (the heavy curve of the figure) when the corrections are applied. The consideration of these systematic errors, due to errors in the percentage composition, applies, not only to densities, but to all other properties as well, and it is unfortunate that so little care has thus far been bestowed upon it.

OPERATION.

When a given mixture has been made up it must be thoroughly shaken, and this must be done without wetting the space between the rim and the stopper of the weighing bottle, in order to insure all of each component being present. (Much time was lost in the beginning in locating errors finally found to be due to imperfect mixing, or to the loss of liquid in the rim space before mixing had become complete.) The stopper is then quickly removed, about 15 c.c. of the mixture is withdrawn by gentle suction from the bottom of the bottle into a slender stemmed pipette of just sufficient capacity. The pipette tube is then inserted into the pyknometer bulb to the bottom and the mixture is forced out gently until the bottle is full. Some of the liquid is allowed to run over; about 3 c.c. are left in the transferring tube. This procedure insures that very little of the liquid now in the pyknometer has been exposed to air, and until it was adopted it was found impossible to get concordant results. Some of the liquid is next removed from the graduated neck by inserting a capillary tube connected to a suction pump, and the exposed interior of the neck is dried. The stopper is inserted, and the bulb is placed in position in the thermostat at the lower temperature. When the meniscus reading has become constant the bulb and contents are weighed, more liquid is removed from the neck, as before, and the bulb is placed in the thermostat at the higher temperature, when similar observations are made. These observations give the specific volumes at the two temperatures.

The mixture is next brought to the refractometer temperature by placing the bulb in the first thermostat, after which three successive samples are taken from the bottom of the bulb for the determination of the indices of refraction with the sodium and three principal hydrogen lines. About 90 minutes are necessary for the completion of all the observations of a mixture of given composition.

THE "ADDITIVE LAWS." NOTATION.

Vapor Pressure.—When the vapor pressure of pairs of liquids are plotted against the molecular proportion of one of the components, three types of curves are obtained. The simplest is a straight line, such as would be expected if the components exerted neither physical nor chemical influence on each other, but mixed in all proportions. Besides this curve are curves convex toward the axis, and curves concave toward the axis. The former are conceivably caused by a lessening of the number of evaporating molecules, on account of a union or by increased cohesion; the latter by an increased number of evaporating molecules, possibly caused by dissociation of polymerized molecules, or by a lessening of cohesion due to the mixing.[1] In any case the deviation from the straight line serves as a valuable criterion for the classification of binary mixtures, and, taken in connection with the deviation of other properties, may be expected to throw some light on the theory.

We shall consider the deviations from the simple additive law.

$$p_c = xp_1 + (1 - x)p_2,$$

where x is the number of mols of A in one mol of mixture, p_1 and p_2 being the respective vapor pressures of A and B in the pure state.

$$\Delta p = p - p_c, \tag{1}$$

where p is the observed total pressure.

Specific Volume.—Let v_1 and v_2 be the respective specific volumes of the substances A and B, and v_c the calculated specific volume of the mixture, and let w_1 and w_2 be the weights of the two substances in the mixture. Then, assuming that there is no change

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[1] See Zawidzki, loc. cit., p. 157 et seq.; also Ostwald, Allg. Chemie, II., p. 617; Dolezalek, Zeit. f. phys. Chem., 64, p. 727, 1908.

of volume on mixing, the total calculated volume is

$$V_c = w_1 v_1 + w_2 v_2 = (w_1 + w_2) v_c$$

whence

$$v_c = z v_1 + (1 - z) v_2$$

where z is the weight of A in one gram of the mixture. If v is the observed specific volume of the mixture then

$$\Delta v = v - v_c \tag{2}$$

gives the deviation of the volume from the additive law.

Indices of Refraction.—The theory of dispersion for liquids is not as yet in a satisfactory state. The most common expression for the refractivity $R = N/d = (n^2 - 1)/(n^2 + 2)d$ (Lorenz-Lorentz), has strong theoretical support, and preserves a fair constancy even for change of state. Planck's theory gives the same expression with the assumption of a single absorption band for the substance, but does not lead to a simple expression for the refractivity when there is more than one absorption band.[1]

The well-known additive law

$$R_c = z R_1 + (1 - z) R_2, \tag{3}$$

where z is the weight of A per gram of the mixture, has been experimentally studied by a great number of observers, usually without much question as to whether the liquids investigated followed the dispersion formulæ. As, however, deviations from (3) tend to show the need, and perhaps indicate the direction, of further investigations both into the theory of dispersion and into the dispersion of particular liquids, such work has a distinct value.

The deviation of refractivity is

$$\Delta R = R - R\,. \tag{4}$$

If we multiply (3) by d_c, the calculated density, remembering that $R = N/d$, we have

$$N_c = y N_1 + (1 - y) N_2, \tag{5}$$

y being the volume of A in 1 c.c. of mixture.

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[1] On the dispersion of liquids see also A. Trowbridge, Phys. Rev., XXVIII., p. 389, 1909.

Pulfrich gives the empirical equation

$$\frac{N - N_c}{N} = \alpha\frac{d - d_c}{d} = \alpha c = \alpha\frac{v_c - v}{v_c}, \tag{6}$$

or

$$\alpha = -\frac{\Delta N}{N}\Big/\frac{\Delta v}{v_c}, \tag{7}$$

in which α is supposed to be constant, and $N = (n^2 - 1)/(n^2 + 2)$. Eq. (6) leads to the expression

$$R\frac{1 - \alpha c}{1 - c} = R_c = zR_1 + (1 - z)R_2,$$

which is Pulfrich's modification of the additive law.[2] We also have from (6)

$$\Delta R = (\alpha - 1)(v_c - v)N = -(\alpha - 1)N\Delta v. \tag{8}$$

In the following tables the values of α are calculated from (7), and ΔR from (8) except in two cases, where Δv being too small, ΔR is calculated from (4).

The Substances.

The substances benzol, ethyl acetate, ethyl iodide, carbon tetrachloride, acetic acid, chloroform, acetone, methylal and carbon disulphide were generously furnished by the Department of Chemistry of Clark University, and I am indebted to Mr. C. W. Bacon, a graduate student of that department, for carrying out their purification. It was obviously important to have had the substances in a state of high purity. The methods of purification, as carried out by Mr. Bacon, will be given in connection with each substance.

Results.

In the case of each mixture are given three tables. In the first table of each set, besides the proportions by weight of one of the substances, are given in order the values of v_{25} and $v_{35.17}$, or v_{50} as the case may be, and n_C, n_D, n_F and $n_{G'}$. In the second table are given the deviations of specific volume Δv_{25}, $\Delta v_{35.17}$ or Δv_{50}, and the deviation of refractivity for the D line, ΔR_D, beside the constants

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[1] Pulfrich, Zeit. f. phys. Chem., 4, 561, 1889; see also Winkelmann, Handbuch, 6, p. 650.

α, of the Pulfrich equation, for each of the wave-lengths. In the last table of each set are given the molecular and weight proportions of the mixtures and the total vapor pressures as given by Zawidzki (*loc. cit.*), and the deviation Δp of these total pressures from the simple additive law. Finally for each set of results has been drawn a figure showing the deviations of pressure, specific volume and refractivity plotted as functions of the weight composition of the mixture.

I. *Carbon Disulphide — Methylal.*

The carbon disulphide was washed with 5 per cent. sodium hydroxide solution and set away over quicklime for twenty-four hours being occasionally shaken. It was then poured into a bottle containing mercury and shaken frequently until the disagreeable odor had disappeared, decanted from mercury and distilled.

The fraction was collected boiling within 0°.2 C.

The methylal was dried with $CaCl_2$ and distilled over within a small fraction of a degree. The sample chosen came over within 0°.2 C.

The evaporation correction for CS_2 is $.018 \pm .001$ gr. and for methylal $.017 \pm .001$ gr. The total amount of mixture was about 15 gr.; thus the error in the weight composition is about 7×10^{-5}.

Remarks on Tables II., III. and IV. — This was the first set of observations completed, and as the temperature regulation of the refractometer had not been made perfect, readings for the same samples varied as much as 2′, which corresponds to about 2 units in the fourth decimal place of the index of refraction. As every determination in the table is a mean of at least three, the probable error is considerably less. The asterisk (*) after specific volume determinations indicates a slight amount of boiling in the pyknometer during the measurement at the higher temperature. The disturbance affected the meniscus to the extent of 1 division, introducing an uncertainty of 3 in 10^{-4} in the four results marked. The other volume errors are subject to the reading errors already mentioned of 2×10^{-5}. The composition error of 7×10^{-5} produces uncertainty in the values of v of 3×10^{-5}.

The value of α diminishes with the amount of CS_2 present, and with diminishing wave-length.

TABLE II.

Carbon Disulphide—Methylal.

No.	z(wt)CS_2	v_{25}	$v_{35.17}$	n_C	n_D	n_F	$n_{G'}$
	0.00000	[1.17233]	1.19043	1.34850	1.35018	1.35425	1.35759
	0.00000	1.17214	1.19044	1.34845	1.35018	1.35420	1.35759
	0.00000	1.17216	1.19043	1.34916	1.35078	1.35489	1.35832
	Mean.	1.17215	1.19043	1.34870	1.35038	1.35444	1.35783
1	.12921	1.12932	1.14685	1.36939	1.37164	1.37730	1.38206
2	.28682	1.07469	1.09108	1.39871	1.40178	1.40954	1.41639
3	.38408	1.03949	1.05500*	1.41928	1.42294	1.43220	1.44037
4	.43588	1.02031	1.03538	1.43107	1.43502	1.44524	1.45440
5	.45630	1.01293	1.02807	1.43595	1.44005	1.45054	1.45986
6	.53139	.98458	.99905	1.45459	1.45922	1.47115	1.48179
7	.60034	.95819	.97243*	1.47286	1.47810	1.49146	1.50325
8	.62226	.94959	.96319*	1.47937	1.48471	1.49857	1.51091
9	.62380	.94911	.96265	1.47964	1.48497	1.49889	1.51123
10	.65262	.93797	.95114*	1.48798	1.49357	1.50815	1.52061
11	.75141	.89891	.91140	1.51859	1.52508	1.54205	———
12	.86449	.85309	.86443	1.55901	1.56665	1.58690	1.60505
	1.00000	.79620	.80611				
	1.00000	.79623	.80611				
	1.00000	.79621	.80609				
	Mean.	.79621	.80610	1.61440[1]	1.62357	1.64830	1.67073

[1] It was impossible to get accurate readings for CS_2 in the refractometer. The values are reduced from Landolt & Börnstein's tables.

TABLE III.

Carbon Disulphide—Methylal.

No.	Δv_{25}	$\Delta v_{35\ 17}$	ΔR_{D25}	a_C	a_D	a_F	$a_{G'}$
1	.00574	.00607	.00030	.773	.767	.734	.742
2	1036	1088	91	.650	.638	.630	.566
3	1174	1219	126	.595	.579	.574	.561
4	1203	1248	136	.576	.565	.545	.503
5	1232	1301	151	.548	.534	.529	.515
6	1220	1285	166	.519	.503	.492	.472
7	1173	1273	170	.518	.488	.472	.472
8	1138	1189	161	.463	.444	.425	.410
9	1147	1196	175	.483	.467	.449	.432
10	1116	1152	179	.469	.448	.424	.475
11	924	976	163	.452	.425	.400	——
12	594	626	143	.293	.261	.221	.204

TABLE IV.

Carbon Disulphide—Methylal (Zawidzki). 35°.17 C.

z and x CS_2	$p_{35.17}$	Δp	z and x CS_2	$p_{35.17}$	Δp
0.0000	587.7	0.0	.6060	695.5	152.1
.0496	613.3	29.2	.6803	685.4	147.5
.1044	638.9	58.9	.7353	675.4	141.5
.1651	660.1	84.5	.7927	661.6	132.0
.2719	686.0	118.2	.8421	644.6	118.5
.3480	696.7	134.5	.8573	634.7	109.7
.3904	700.4	141.2	.9130	603.2	82.4
.4542	703.2	148.7	.9576	564.2	46.6
.4942	701.4	149.8	1.0000	514.5	0.0
.5377	700.3	152.0			

The values of $\Delta p_{35.17}$, Δv_{25}, $\Delta v_{35.17}$ and ΔR_{D25} are plotted in Fig. 2.

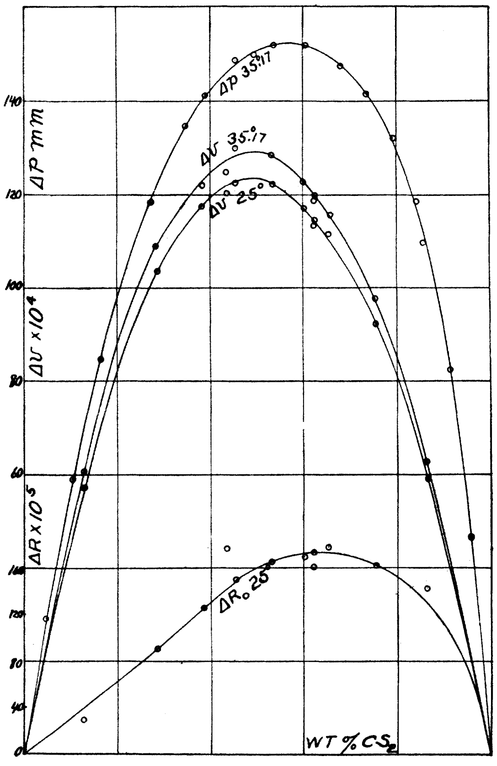

Fig. 2.

II. *Carbon Disulphide—Acetone.*

The same CS_2 was used as in the last case. The acetone was mixed with 6 per cent. solid $KMnO_4$, boiled in a reflux condenser over a water bath for three hours, distilled off rapidly, dried over freshly ignited K_2CO_3 and distilled in the usual manner. Boiled at 56°.0 to 56°.3 C.

Evaporation correction for $CS_2 = .018 \pm .001$ gr.; for acetone, $.010 \pm .001$ gr. Corresponding probable error in the weight composition is 7×10^{-5}.

Table V.

Carbon Disulphide—Acetone.

No.	z(wt)CS_2.	v_{25}	$v_{35.17}$	n_C	n_D	n_F	$n_{G'}$
	0.00000	[1.26913]	[1.28810]	1.35450	1.35636	1.36112	1.36509
	0.00000	1.26906	1.28824	1.35450	1.35636	1.36112	1.36509
	0.00000	1.26903	1.28821	1.35475	1.35662	1.36140	1.36540
	Mean.	1.26905	1.28823	1.35458	1.35645	1.36121	1.36519
1	.13245	1.21357	1.23204	1.37333	1.37576	1.38177	1.38701
2	.29326	1.14319	1.16040	1.40047	1.40364	1.41171	1.41887
3	.40329	1.09304	1.10938	1.42182	1.42567	1.43533	1.44390
4	.51761	1.03962	1.05502	1.44776	1.45253	1.46387	1.47471
5	.51799	1.03937	1.05478	1.44794	1.45253	1.46417	1.47522
6	.51902	1.03847	1.05389	1.44819	1.45271	1.46439	1.47471
7	.64733	.97694	.99106	—	—	—	—
8	.71137	.94547	.95867	1.50093	1.50692	1.52263	1.53661
9	.83283	.88407	.89605	1.54325	1.55043	1.56942	1.58644
10	.86892	.86551	.87711	1.55702	1.56465	1.58477	1.60291
	1.00000	.79620	[.80590]				
	1.00000	.79623	.80609				
	1.00000	.79619	.80611				
	Mean.	.79621	.80610	1.61440	1.62357	1.64830	1.67073

Remarks on Tables V., VI. and VII.—Owing to the uncertainty of the evaporation correction to .001 gr. the compositions z (V., VI.) are again subject to an error of 7×10^{-5} which makes the calculated volumes and Δv subject to an error of 3×10^{-5}. The observed volumes are measured to 2×10^{-5}. The indices are measured to the errors of the instrument (see "Operation"). The values of the deviations are plotted with the proportions by weight in Fig. 3.

III. *Chloroform—Acetone.*

The acetone was purified as in the previous case. The chloroform was shaken with 5 per cent. NaOH solution, separated and shaken three times with distilled water. It was next dried over $CaCl_2$ for twenty-four hours, filtered and distilled. The distillate smelled

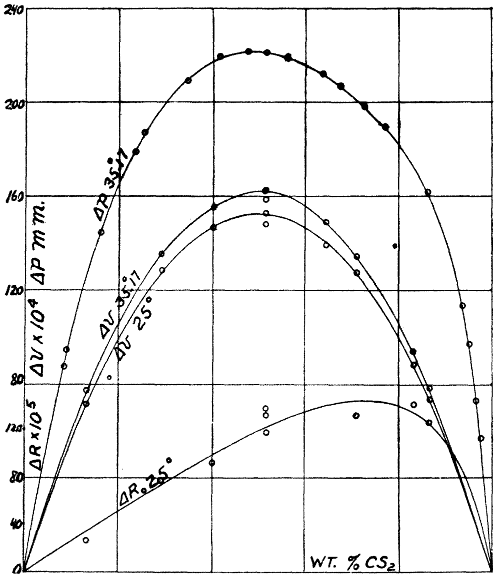

Fig. 3.

TABLE VI.

Carbon Disulphide—Acetone.

No.	Δv_{25}	$\Delta v_{35.17}$	ΔR_{D25}	a_C	a_D	a_F	$a_{G'}$
1	.00715	.00767	.00027	.855	.836	.895	.899
2	1280	1356	77	.762	.755	.766	.747
3	1469	1559	92	.779	.755	.764	.755
4	1531	1633	140	.710	.662	.698	.626
5	1525	1628	133	.700	.676	.675	.579
6	1483	1589	118	.720	.705	.700	.696
7	1397	1493	——	——	——	——	——
8	1278	1341	133	.666	.650	.640	.637
9	881	936	141	.516	.497	.485	.479
10	732	781	124	.508	.477	.458	.438

TABLE VII.

Carbon Disulphide—Aceton (Zawidzki). 35°.17 C.

$x\mathrm{CS}_2$	$z\mathrm{CS}_2$	$p_{35.17}$	Δp	$x\mathrm{CS}_2$	$z\mathrm{CS}_2$	$p_{35.17}$	Δp
0.0000	0.0000	343.8	0.0	.5716	.6363	652.2	212.1
0.0624	.0802	441.7	87.4	.6144	.6760	653.7	206.4
.0690	.0885	449.6	94.2	.6713	.7278	655.0	198.1
.1271	.1602	510.0	144.8	.7208	.7720	654.6	189.4
.1857	.2323	553.8	178.7	.8280	.8630	645.1	161.8
.2038	.2511	564.9	186.8	.9216	.9391	612.2	113.1
.2815	.3392	600.7	209.5	.9378	.9520	598.4	96.6
.3526	.4165	622.8	219.6	.9584	.9679	578.1	72.8
.4100	.4766	634.6	221.7	.9692	.9764	564.0	56.9
.4502	.5176	641.2	221.5	1.0000	1.0000	512.3	0.0
.4953	.5625	646.1	218.9				

strongly of phosphine and also gave the test for chlorine. The whole material was then shaken up with NaOH, washed with water and dried as before. It gave no test for chlorine and after filtration was used without further distillation. Boiling point 61°.2 C. Evaporation corrections: Chloroform, .015 ± .001 gr.; acetone, .010 ± .001 gr.

TABLE VIII.

Chloroform—Acetone.

No.	z Chl	v_{25}	$v_{35.17}$	n_C	n_D	n_F	$n_{G'}$
	0.00000	1.27403	1.29334	1.35436	1.35620	1.36096	1.36495
	0.00000	1.27401	1.29330	1.35436	1.35621	1.36087	1.36483
	0.00000	1.27402	1.29325	1.35434	1.35621	1.36091	1.36474
	Mean.	1.27402	1.29330	1.35435	1.35621	1.36091	1.36484
1	.16664	1.17445	1.19201	1.36261	1.36454	1.36941	1.37344
2	.33039	1.07637	1.09208	1.37211	1.37417	1.37920	1.38334
3	.45832	.99950	1.01378	1.38122	1.38332	1.38848	1.39275
4	.56298	.93643	.94957	1.38982	1.39196	1.39728	1.40171
5	.64507	.88682	.89911	1.39721	1.39943	1.40494	1.40949
6	.72276	.83976	.85122	1.40531	1.40757	1.41319	1.41790
7	.79884	.79411	.80483	1.41385	1.41618	1.42196	1.42676
8	.88409	.74349	.75348	1.42451	1.42692	1.43287	1.43784
9	.94292	.70889	.71839	1.43237	1.43487	1.44097	1.44605
	1.00000	.67573	.68472	1.44042	1.44296	1.44919	1.45444
	1.00000	.67570	.68470	1.44063	1.44316	1.44939	1.45460
	1.00000	.67570	.68474	1.44064	1.44316	1.44939	1.45462
	Mean.	.67571	.68472	1.44057	1.44309	1.44932	1.45455

TABLE IX.

Chloroform—Acetone.

No.	Δv_{25}	$\Delta v_{35.17}$	ΔR_{D25}	a_C	a_D	a_F	$a_{G'}$
1	+.00013	+.00013	+.00017	——	——	——	——
2	+ 2	− 15	+ 22	——	——	——	——
3	− 30	− 59	+ 34	5.4	5.8	5.8	5.4
4	− 75	− 111	+ 38	3.13	3.17	3.18	3.12
5	− 125	− 161	+ 28	1.89	1.94	2.04	2.02
6	− 183	− 222	+ 26	1.57	1.58	1.62	1.64
7	− 195	− 231	+ 20	1.39	1.42	1.45	1.44
8	− 157	− 178	+ 17	1.42	1.42	1.45	1.44
9	− 97	− 107	+ 9	1.29	1.36	1.38	1.36

TABLE X.

Chloroform—Acetone (Zawidzki). 35°.17 *C.*

x Chl.	z Chl.	$p_{35.17}$	Δp	x Chl.	z Chl.	$p_{35.17}$	Δp
0.0000	0.0000	344.5	0.0	.4934	.6672	255.5	−63.6
.0595	.1152	332.2	− 9.2	.5083	.6802	252.9	−65.5
.1217	.2218	319.9	−18.4	.5135	.6847	252.7	−65.4
.1835	.3162	307.6	−27.5	.5523	.7174	250.1	−66.0
.2630	.4234	291.0	−40.0	.5812	.7407	248.4	−66.2
.2897	.4563	285.9	−43.7	.6622	.8014	249.0	−61.5
.3613	.5379	272.9	−53.0	.8022	.8930	262.2	−41.0
.4008	.5792	267.1	−56.8	.9177	.9583	279.8	−17.6
.4240	.6023	263.1	−59.6	1.0000	1.0000	293.1	0.0

Remarks on Tables VIII., IX. and X.—A great deal of trouble was experienced in getting the results for this case. The acetone apparently absorbed moisture from the air every time the bottle was opened. The observations were repeated three times before satisfactory results were obtained. The results given are from the last set which alone are retained because they were made with acetone kept in several small bottles and also because great care was taken to thoroughly mix the liquids. These precautions seem to have entirely eliminated irregularities greater than ordinary errors of observation from the results. The error of .001 gr. in the evaporation correction implies an error of 3×10^{-5} in z, since the amount of mixture made up in each case was never less than 30 gr. This implies an error well under the errors of observation for Δv and ΔR.

The errors in n_D are about as before, but the agreement for differences of the indices for the different wave-lengths in any given case was excellent, seldom amounting to more than 3 or 4×10^{-5}. The deviations for this case are plotted in Fig. 4.

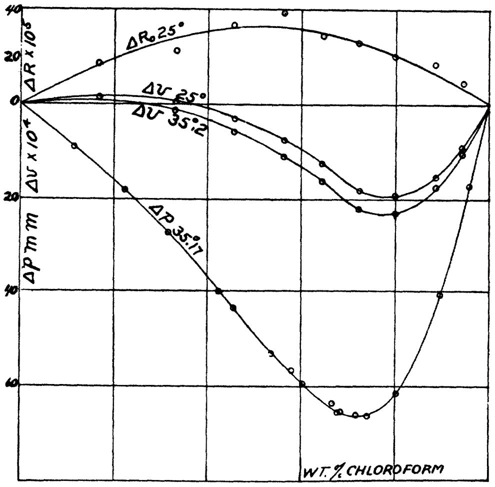

Fig. 4.

IV. *Ethyl Iodide — Ethyl Acetate.*

The ethyl iodide was washed with water to remove alcohol, dried over $CaCl_2$ with molecular silver, filtered and distilled in the usual way. It was kept in a black bottle containing a little silver — boiling point 72°.2 C. The ethyl acetate was dried with freshly ignited K_2CO_3, filtered and distilled with a micro-burner in the usual manner. Boiling point 77°.2 C. The measurements were carried out at 25° and at 50° C., the latter being sufficiently near Zadwizki's temperature (49°.99) for the pressure measurements.

Evaporation corrections: Ethyl iodide, .0075 ± .0005 gr.; ethyl acetate, .0042 ± .0005 gr.

Remarks on Tables XI., XII. and XIII. — The very great reluctance of ethyl iodide and ethyl acetate to mix is noteworthy. The smallest amount of any one mixture was 30 gr. The evaporation correction error of 5×10^{-4} gr. implies an error in the composition of less than 2×10^{-5}, which is negligible in calculating Δv and ΔR. The remarks in the preceding case concerning indices hold

TABLE XI.

Ethyl Iodide—Ethyl Acetate.

No.	z Iod.	v_{25}	v_{50}	n_C	n_D	n_F	$n_{G'}$
	.00000	1.11838	1.15874	1.36821	1.37004	1.37452	1.37822
	.00000	1.11829	1.15866	1.36822	1.37006	1.37458	———
	.00000	1.11821	1.15859	1.36822	1.37006	1.37456	1.37831
	Mean.	1.11829	1.15866	1.36822	1.37005	1.37455	1.37826
1	.19082	1.00742	1.04358	1.37943	1.38150	1.38657	1.39077
2	.35007	.91416	.94654	1.39162	1.39393	1.39964	1.40438
3	.49517	.82845	.85737	1.40563	1.40822	1.41465	1.42004
4	.59741	.76738	.79377	1.41808	1.42090	1.42800	1.43394
5	.68529	.71454	.73880	1.43092	1.43402	1.44176	1.44833
6	.74566	.67763	.70040	1.44119	1.44447	1.45274	1.45977
7	.82792	.62746	.64814	1.45757	1.46121	1.47032	1.47811
8	.89093	.58845	.60749	1.47253	1.47646	1.48639	1.49489
9	.94970	.55183	.56927	1.48898	1.49318	1.50398	1.51323
	1.00000	.52008	.53619	1.50535	1.50992	1.52159	1.53163
	1.00000	.52005	.53623	1.50534	1.50992	1.52158	1.53160
	1.00000	.52006	.53623	1.50533	1.50992	1.52158	1.53157
	Mean.	.52007	.53622	1.50534	1.50992	1.52158	1.53160

TABLE XII.

Ethyl Iodide—Ethyl Acetate.

No.	Δv_{25}	Δv_{50}	ΔR_{D25}	a_C	a_D	a_F	$a_{G'}$
1	+.00328	+.00369	−.00020	1.266	1.263	1.294	1.330
2	+ 529	+ 577	− 22	1.174	1.175	1.196	1.213
3	+ 638	+ 692	− 25	1.152	1.156	1.177	1.197
4	+ 647	+ 697	− 20	1.113	1.120	1.132	1.154
5	+ 620	+ 669	− 10	1.065	1.065	1.081	1.091
6	+ 540	+ 587	− 14	1.096	1.102	1.118	1.131
7	+ 444	+ 481	− 5	.993	1.041	1.060	1.070
8	+ 313	+ 337	− 4	1.049	1.047	1.054	1.060
9	+ 167	+ 174	− 0	.970	1.000	1.007	1.010

here also. The deviations of specific volume, refractivity and vapor pressure form their respective additive laws are shown in Fig. 5.

V. *Acetic Acid—Benzol.*

The acetic acid was Kahlbaum's best, and was further purified by fractional freezing. The benzol was boiled for three hours with

10–15 per cent anhydrous aluminum chloride under a reflux condenser. Distilled off and washed with NaOH to remove HCl, then washed with water, and, after drying over $CaCl_2$, was distilled. The fraction was collected boiling at 80°.5 C.

Evaporation corrections: Acetic acid, .0006 ± .0001 gr.; benzol, .0050 ± .0005 gr.

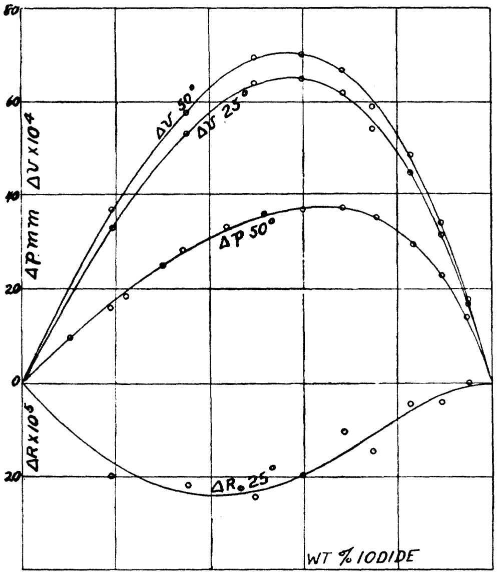

Fig. 5.

TABLE XIII.

Ethyl Iodide—Ethyl Acetate (Zawidzki). 49°.99 *C.*

x-Iod.	z-Iod.	$p_{49.99}$	Δp	x-Iod.		$p_{49.99}$	Δp
0.0000	0.0000	280.4	0.0	.4588	.6001	350.7	36.8
.0590	.0999	294.3	+ 9.6	.5486	.6827	357.4	37.0
.1148	.1867	304.7	15.9	.6340	.7541	361.7	35.0
.1376	.2202	308.7	18.3	.7388	.8335	363.5	29.2
.1946	.2996	319.5	24.9	.8253	.8932	363.5	22.9
.2288	.3443	325.2	28.1	.9098	.9470	360.7	13.9
.3057	.4380	335.4	32.7	1.0000	1.0000	353.4	0.0
.3745	.5158	343.4	35.7				

Remarks in Tables XIV., XV. and XVI.—The specific volumes and indices for the mixture acetic acid—benzol were easiest of all

TABLE XIV.

Acetic Acid—Benzol.

No.	z-Acetic.	v_{25}	v_{50}	n_C	n_D	n_F	$n_{G'}$
	.00000	1.14459	1.18091	1.49331	1.49794	1.50985	1.52019
	.00000	1.14458	1.18093	1.49328	1.49794	1.50985	1.52012
	Mean.	1.14458	1.18092	1.49329	1.49794	1.50985	1.52015
1	.11634	1.12768	1.16362	1.47782	1.48218	1.49323	1.50276
2	.23614	1.10923	1.14433	1.46225	1.46628	1.47644	1.48517
3	.34008	1.09194	1.12633	1.44890	1.45265	1.46208	1.47020
4	.44857	1.07299	1.10638	1.43516	1.43861	1.44724	1.45460
5	.54459	1.05549	1.08773	1.42300	1.42618	1.43414	1.44086
6	.63968	1.03692	1.06822	1.41131	1.41418	1.42150	1.42765
7	.73819	1.01687	1.04693	1.39907	1.40172	1.40827	1.41375
8	.82321	.99858	1.02776	1.38875	1.39119	1.39712	1.40206
9	.91338	.97830	1.00627	1.37803	1.38023	1.38552	1.38983
	1.00000	.95797	.98468	1.36779	1.36977	1.37440	1.37819
	1.00000	.95799	.98460	1.36774	1.36974	1.37443	1.37818
	1.00000	.95789	.98461	1.36783	1.36977	1.37444	1.37816
	Mean.	.95795	.98463	1.36779	1.36976	1.37442	1.37818

TABLE XV.

Acetic Acid—Benzol.

No.	Δv_{25}	Δv_{50}	ΔR_{D25}	a_C	a_D	a_F	$a_{G'}$
1	.00481	.00554	−.000041	1.043	1.030	1.030	1.030
2	872	976	− 12	1.010	1.005	1.011	1.014
3	1082	1217	− 82	1.032	1.028	1.029	1.019
4	1212	1351	− 115	1.037	1.036	1.041	1.042
5	1255	1370	− 157	1.048	1.049	1.050	1.053
6	1172	1286	− 184	1.051	1.063	1.058	1.054
7	1006	1091	− 229	1.088	1.093	1.100	1.102
8	764	843	− 216	1.117	1.119	1.130	1.127
9	419	464	− 118	1.114	1.121	1.126	1.195

to measure because of the low vapor pressure of acetic acid. The readings for the indices were especially sharp and constant, successive readings for a mixture agreeing within the error of the instrument, viz., 0′.5 or 5×10^{-5}, and the probable error of the measurements which are given in the tables is still smaller as they are all means of at least three; the sixth place is therefore retained for ΔR_{D25}. The relative values of the indices for a given composition

TABLE XVI.

Acetic Acid—Benzol (Zawidzki). 49°.99 *C.*

x-Acetic.	z-Acetic.	$p_{49.99}$	Δp	x-Ac.	z-Ac.	$p_{49.99}$	Δp
0.0000	0.0000	267.1	0.0	.3493	.4136	228.0	34.8
.0160	.0170	265.9	+2.2	.3696	.4365	224.3	35.4
.0364	.0413	265.2	5.8	.5834	.6530	189.5	45.8
.0439	.0504	264.4	6.6	.6125	.6801	184.0	46.5
.0835	.0996	261.1	11.7	.6604	.7242	175.3	48.0
.1138	.1377	259.0	16.0	.8435	.8809	126.0	37.4
.1714	.2088	250.2	19.4	.9797	.9851	68.0	8.3
.2089	.2535	245.2	22.3	.9931	.9949	59.2	2.4
.2979	.3566	236.0	32.0	1.0000	1.0000	55.4	0.0

are subject, as in the preceding case, to an error of about 2×10^{-5}, and the specific volumes are subject to a like error the error of the evaporation correction being negligible. From 30 to 60 gr. of mixture were used each time. For deviations, see Fig. 6.

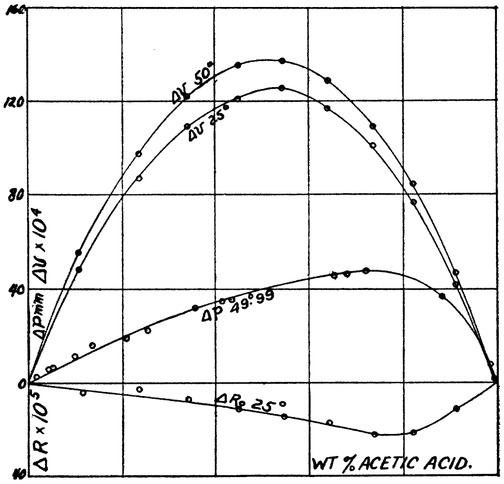

Fig. 6.

VI. *Carbon Tetrachloride — Benzol.*

The benzol used was the same as in the preceding case.

The carbon tetrachloride was dried with $CaCl_2$ and distilled. It was allowed to stand over lime to remove traces of sulphur.

Evaporation correction: CCl_4, .0090 ± .0005 gr.; C_6H_6, .0050 ± .0005 gr.

TABLE XVII.

Carbon Tetrachloride—Benzol.

No.	$z\cdot CCl_4$	v_{25}	v_{50}	n_C	n_D	n_F	$n_{G'}$
	0.00000	1.14451	1.18089	1.49332	1.49794	1.50985	1.52016
	0.00000	1.14455	1.18090	1.49327	1.49794	1.50981	1.52011
	0.00000	1.14454	1.18093	1.49330	1.49794	1.50985	1.52014
	Mean.	1.14453	1.18091	1.49330	1.49794	1.50984	1.52014
1	.16873	1.05794	1.09171	1.48973	1.49420	1.50562	1.51547
2	.31954	.98046	1.01198	1.48602	1.49030	1.50120	1.51058
3	.43419	.92179	.95150	1.48261	1.48674	1.49718	1.50613
4	.55495	.85969	.88749	1.47843	1.48232	1.49223	1.50070
5	.64704	.81251	.83881	1.47476	1.47849	1.48788	1.49592
6	.71042	.77966	.80492	1.47197	1.47555	1.48461	1.49231
7	.79671	.73562	.75943	1.46775	1.47109	1.47954	1.48668
8	.87639	.69470	.71713	1.46320	1.46629	1.47409	1.48069
9	.93504	.66449	.68589	1.45941	1.46230	1.46961	1.47576
	1.00000	.63110	.65131	1.45465	1.45733	1.46401	1.46953
	1.00000	.63109	.65133	1.45460	1.45731	1.46397	1.46952
	1.00000	.63107	.65133	1.45467	1.45733	1.46403	1.46958
	Mean.	.63109	.65132	1.45464	1.45732	1.46400	1.46954

TABLE XVIII.

Carbon Tetrachloride—Benzol.

No.	Δv_{25}	Δv_{50}	$\Delta R_{D\cdot 5}$
1	+.00004	+.00016	+.000225
2	− 1	+ 30	+ 398
3	+ 19	+ 54	+ 523
4	+ 10	+ 47	+ 497
5	+ 20	+ 56	+ 518
6	− 10	+ 23	+ 491
7	+ 16	+ 45	+ 438
8	+ 13	+ 34	+ 318
9	+ 4	+ 17	+ 179

Remarks on Tables XVII., XVIII. and XIX.—Owing to the very small values of Δv for this case the values of α have not been calculated. The magnitude of errors is in all respects as in the preceding case. For the plots of the deviations see Fig. 7.

Table XIX.

Carbon Tetrachloride—Benzol (Zawidzki). 49°.99 *C.*

$x\cdot CCl_4$	$z\cdot CCl_4$	$p_{49.99}$	Δp	$x\cdot CCl_4$	$z\cdot CCl_4$	$p_{49.99}$	Δp
0.0000	0.0000	268.0	0.0	.3953	.5630	294.5	10.7
.0507	.0952	271.8	+1.8	.5587	.7138	301.0	10.7
.1170	.2070	277.6	4.9	.6755	.8041	305.2	10.2
.1758	.2959	281.5	6.5	.7652	.8653	306.8	8.2
.2515	.3983	285.4	7.3	1.0000	1.0000	308.0	0.0
.2947	.4515	288.3	8.5				

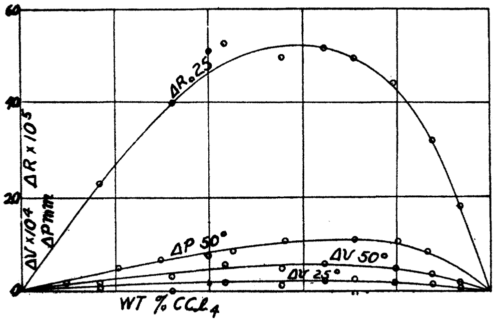

Fig. 7.

General Discussion. Summary.

From an inspection of the tables and figures it is seen that, for the cases studied and in the given temperature interval:

1. The deviations of the specific volumes from additivity increase in absolute value with the temperature.

A possible exception to this conclusion is found in the case of chloroform — acetone, which for a small portion of the curve seems to show a deviation diminishing with rise of temperature. This is the only mixture of the present series which shows a systematic negative deviation and the only one in which the temperature coefficient of deviation is negative. It is interesting to note in connection with this case the great heat developed on mixing which is also exceptional among the mixtures here considered. Carbon tetrachloride — benzol, according to Brown[1] shows a small negative deviation at 20° C. In the measurements here given the deviation is slightly

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[1] F. D. Brown, Trans. Chem. Soc., 39, p. 202, 1881.

positive at 25° and more so at 50° C. The results for these two mixtures indicate that further study is desirable to show more completely the nature of the temperature coefficient of specific volume deviation. It seems very probable that there are mixtures in which the deviations are negative at all temperatures, others in which the deviations are always positive, other in which the deviations grow from positive to negative, still others which show the reverse, and, possibly a few which show a mixture of effects. These possibilities must be settled before binary mixtures are understood

In this connection should be noticed the interesting analogous behavior of the partial and total vapor pressures; *i. e.*, that their deviations from additivity also increase in absolute value with the temperature. This was brought to my attention by Professor Rosanoff who has kindly furnished the following proof. Let P_1 and P_2 be the respective vapor pressures of the pure liquids A and B, and let p_1 and p_2 be the respective partial vapor pressures of A and B in the mixture A-B. Also let p_1' and p_2' be the respective partial pressures calculated on the assumption of simple additivity, thus, $p_1' = P_1x$ and $p_2' = P_2(1 - x)$. We have

$$p_1 = P_1 f(x),$$

hence

$$p_1 - p_1' = P_1\{f(x) - x\} = P_1\varphi(x).$$

Rosanoff and Easley (*loc. cit.*) have shown that $f(x)$ and, accordingly, $\varphi(x)$, in those cases in which the heat of dilution is moderate, is practically independent of the temperature. Hence, where this is true, for any given value of x, the deviation of the partial vapor pressure p_1 from additivity is

$$\Delta p_1 = p_1 - p_1' = kP_1,$$

where k is constant. Since P_1 increases with the temperature, therefore must Δp_1 increase in absolute value with the temperature. Similarly for $\Delta p_2 = p_2 - p_2'$; and hence, also, *the deviation of total vapor pressure, $\Delta p = \Delta p_1 + \Delta p_2$ must increase in absolute value with the temperature.* The analogous behavior of specific volume deviations in these mixtures is striking and suggestive.

2. The algebraic sign of the deviation of specific volume is the same as that of the vapor pressure at the same temperature.

This conclusion, together with (1), suggests the possibility of the vapor pressure deviation changing sign as the temperature is varied, and also, judging from the vapor pressure and volume curves of chloroform – acetone, that there may exist curves of the mixed type, part positive and part negative. These curves have already been predicted but have not as yet been found.[1] It is possible that chloroform – acetone may yield such a curve at a low temperature.

3. The deviations of refractivity are of the same sign as the deviation of vapor pressure and specific volume in the cases of CS_2 – methylal, CS_2 – acetone and $CCl_4 - C_6H_6$, and of opposite sign in the others. The deviations show an increase in absolute value with diminishing wave-length. The Pulfrich constant α is seen, in some cases to vary within wide limits. The Pulfrich equation is empirical and the constant α has no theoretical significance. The expression for the refractivity has not as yet taken a final form (see above), and until we know more about the dispersion of pure liquids it would seem to be very difficult to correlate deviations of refractivity ΔR with the deviations of density and vapor pressure. The values of ΔR are accordingly given here for but one wave-length, that of sodium. On account of the excellent uniformity shown by the differences of the indices for different wave-lengths the indices for all the wave-lengths are given in the hope that they may be useful for further calculation. Greater knowledge of the dispersion of binary mixtures may be expected from a study of their absorpton bands in the ultra-violet and in the infra-red.

It is the intention of the author to add results for other mixtures, making available for further study the binary systems *A-B*, *B-C*, *A-C*, to settle the question whether the deviations are additive from mixture to mixture or whether they depend upon the specific action of two given liquids upon each other.

The present results have been considered from the standpoint of Dolezalek's theory (*loc. cit.*), which attempts to explain all deviations by assuming dissociation of polymerized molecules, or combination of the two components, *i. e.*, putting the matter upon a

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[1] See Zawidzki, Zs. für phys. Chem., LXIX., p. 630, 1909.

chemical basis. The results of these calculations will be published in a subsequent paper.

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