

from the solubility data by this method is 0.56 ± 0.05 , the internal pressure of naphthalene being taken as 1.00, as is done by Mortimer.

Discussion

With the exception of the highly polar system: water-alcohol-acetamide, the results may be summarized as follows.

When a non-volatile solute is added to a mixture of two volatile solvents, the partial pressure of that solvent in which the solute is more soluble (in terms of mole fractions) is lowered by the greater percentage.

The solute is, in general, more soluble in the solvent with internal pressure nearer its own. It will be noted that the selective action of the solute is as marked in cases where it is highly soluble in both solvents, as in those where the solubility in one of the liquids is low. For example, camphor had a stronger selective action on the partial pressure of benzene than did benzil, although the ratio of the relative solubilities in the two separate liquids was much less in the first case, and the solutions were further from saturation. The effects observed are of the same order as those observed by Wright with solutes chosen for insolubility in one of the liquids. No quantitative relation could be established from the available data.

Summary

1. The change in partial pressures produced by addition of a non-volatile solute to binary liquid mixtures at the boiling point has been measured for eight systems at several compositions.

2. The selective action of a non-volatile solute on the partial pressures of a liquid mixture has been found to be measurable in systems which, as a whole, obey the laws of dilute solution; it is roughly correlated with relative solubility in the separate solvents.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

EBULLIOSCOPIC MEASUREMENTS IN MIXED SOLVENTS¹

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From the experimental standpoint, the fundamental problems of ebullioscopy are measurement of temperature differences, the attainment of true and therefore permanent and reproducible temperature equilibria, and knowledge of the concentration of the solution. The first may be satisfactorily solved by the differential mercury thermometer of the Beck-

¹ Prepared from portions of theses submitted to the Faculty of the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degrees of Doctor of Philosophy (B. H. Carroll, 1922) and of Master of Arts (G. K. Rollefson, 1921).

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mann type. The second depends on the prevention of superheating and a constant rate of heating and heat losses. The most general solution of the superheating difficulty is probably by use of the Cottrell apparatus.³ The apparatus here described is better adapted for use with small quantities; a Cottrell "pump" could be used in its boiling tube, if desired. The last point mentioned above has been neglected in all but one published investigation, the concentration being calculated from the weight of materials introduced into the apparatus with at best an approximate correction for vapor and liquid in the condenser. Sampling the liquid during the determination was independently developed by Mathews and Haverstick⁴ and by Washburn and Read.⁵

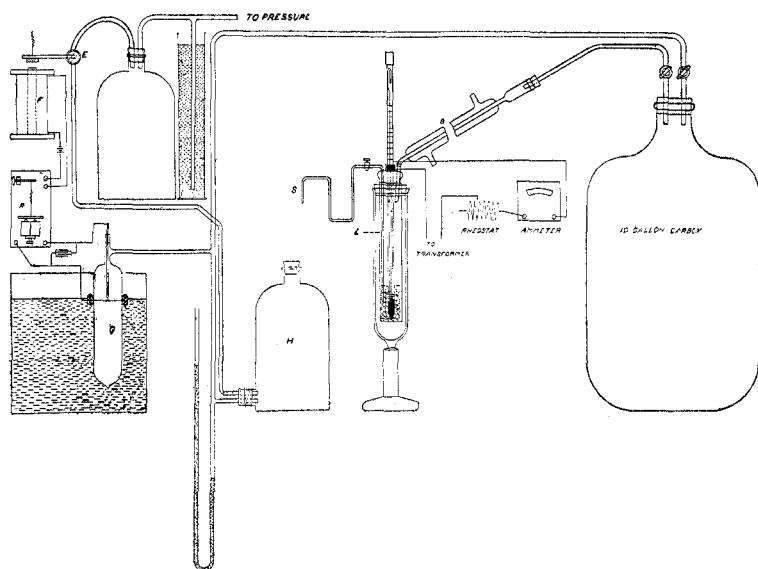


Fig. 1.

The apparatus used in this investigation depends for its accuracy on pressure control, elimination of superheating by internal electrical heating, and the means of sampling the solution and of reducing heat losses to a minimum. It was of the Beckmann type, with the thermometer immersed in the liquid.

Referring to the diagram (Fig. 1), the boiling tube L was shielded thermally by an unsilvered Dewar tube in which it was supported by a cork. The tube, 4 cm. in diameter, was made flat-bottomed to reduce dead space and insure better stirring; the heating wire of heavy platinum with roughened surface was brought close to the bottom for the same reasons. The ends of the wire were sealed into glass tubes carried by the

³ Cottrell, *THIS JOURNAL*, **41**, 721 (1919).

⁴ Haverstick, *Thesis*, University of Wisconsin, 1916.

⁵ Washburn and Read, *THIS JOURNAL*, **41**, 734 (1919).

ground stopper of the boiling tube. The stopper also carried the capillary sampling tube S, reaching nearly to the bottom, the connection with the reflux condenser and the thermometer. The thermometer was of the Beckmann type, and was sealed with dental cement into a smaller stopper ground into the main stopper. A buzzer attached to the thermometer was used to prevent sticking and readings were estimated to 0.001° .

The pressure regulator may best be described in terms of operation. The bulb G was immersed in a thermostat, constant to $\pm 0.02^\circ$. It was made in two parts, each cemented with de Khotinsky cement into a heavy, flat brass ring; these were bolted together with a thin spring-steel diaphragm between, and the joints made tight by gaskets of rubber dam. The lower portion contained air at constant temperature and, therefore, constant pressure. The upper portion was connected by a side tube to the rest of the apparatus. A small piece of platinum foil was soldered to the upper side of the diaphragm; a threaded brass rod, working through a nut sealed into the upper part of the bulb, carried a sharp platinum wire which could be brought into contact with the foil.

Assume a fall of pressure in the apparatus. The diaphragm bulges, making contact with the wire. This actuates the relay R, energizing the electromagnet F and opening the valve E, which admits air under pressure into the system until the contact again opens. A condenser was connected across the contact to reduce sparking. The opening through the valve E was small, and the volume of the system was increased by introducing the carboy and the bottle H to reduce the rate of change in pressure. The connecting tubing should be at least 8 mm. in diameter. With the apparatus described, the diaphragm being 5 cm. in diameter and about 0.1 mm. thick, the change in pressure on operation was barely visible on the water manometer M which indicated difference in pressure between the apparatus and the atmosphere, that is, less than 0.02 mm. of mercury. The temperature of the boiling liquid in L. could be maintained constant to 0.001° for over an hour at a time. It is advisable to have sufficient leakage (best deliberately introduced by a capillary outlet) so that the valve operates several times a minute. The necessity of the pressure regulator is evident when one considers that the boiling point of most solvents is changed 0.001° by 0.03 to 0.04 mm. change in pressure. Its use seemed better than duplication of the apparatus. Since the elevation of the boiling point is a function of the external pressure varying with the solvent, as first pointed out by Washburn and Read,⁵ the use of a fixed pressure in all determinations is a further advantage.

Three of the earlier series were made with a slightly different regulator working on the same principle but using a U-tube filled with mercury, instead of the diaphragm.

The independence of atmospheric pressure removed the necessity of rapid determinations. The solvent was weighed into the tube L, and brought to

boiling. The pressure in the apparatus was then raised to 760 mm. and the regulator adjusted to hold it there. When the temperature had become constant, the equilibrium was temporarily disturbed by a change in pressure, or by a large change in the heating current. If after this disturbance the temperature did not return to the same point, $\pm 0.001^\circ$, and remain there ten minutes more (upon restoration of the former current strength), the process was repeated until the temperature had twice been proved correct to $\pm 0.001^\circ$. The solute was then introduced, and the temperature of the boiling solution established in the same manner. A sample was taken by chilling the bend of the sampling tube with a freezing mixture,

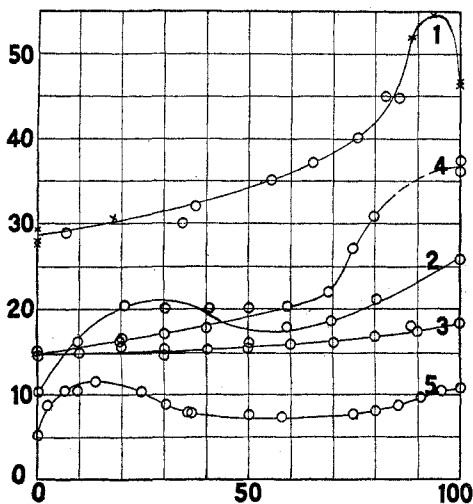


Fig. 2.—“Molecular elevation” as ordinates; percentages of first component as abscissas. 1, Carbon tetrachloride—ethyl acetate. 2, Benzene—ethyl alcohol. 3, Ether—acetone. 4, Chloroform—acetone. 5, Ethyl alcohol—water.

“molecular elevations” (“*K*”) as with pure solvents, is for convenience in presentation only.

The solutes were chosen for normal behavior in both solvents, the criterion of normality being proportionality of elevation of the boiling point to concentration. This is not a proof of the ideal nature of the solution. As the two components of the mixture were generally quite dissimilar, it was a matter of considerable difficulty to find a material that acted as a normal solute in both solvents, and which could be determined analytically in their mixture. No case was found in which the solute acted normally in the pure solvents and abnormally in the mixture, in spite of the extraordinary changes in “molecular elevation” with composition of solvent. The maximum mole fraction of solute was 0.04.

and permitting the excess of pressure in the apparatus to force out a portion of the liquid into chilled weighing bottles. The process was repeated with further additions of solute.

Mixed solvents for some reason displayed a tendency to superheat to an extent not characteristic of either of the pure liquids. Further, in the case of mixtures containing 90% or more of benzene or chloroform, there was a continuous change in boiling point which could not be explained by leakage.

The elevation of the boiling point in mixed solvents generally depends on the solute. It is desired to emphasize at this point that the calculation of results as

Materials

The solvents were purified by standard methods of chemical purification, followed by careful fractionation in a constant-pressure still.⁶ The maximum range in boiling point of the fractions selected was 0.15°. Purity was checked by boiling point and density or refractive index, or both.

The solutes were c. p. chemicals, recrystallized or resublimed. The methods of analysis were identical with those used by the authors⁷ and described elsewhere.

TABLE I

DATA

CARBON TETRACHLORIDE-ETHYL ACETATE							
% of solvent	G. of solute per 100 g. of solvent	Δt °C.	K °C.	% of solvent	G. of solute per 100 g. of solvent	Δt °C.	K °C.
100.0	4.04 thymol	1.244	46.4	55.5	2.43 camphor	0.563	35.0
100.0	3.03 thymol	0.942	46.8	37.4	4.09 camphor	.864	32.1
93.5	3.00 thymol	1.073	54.4	34.25	3.53 camphor	.702	30.2
88.7	2.99 thymol	1.024	52.3	18.1	4.15 thymol	.843	30.7
85.8	2.96 camphor	0.875	44.9	6.9	3.53 camphor	.669	28.9
82.5	2.87 camphor	.848	45.0	0	1.76 thymol	.343	29.3
75.9	3.29 camphor	.866	40.1	0	3.17 thymol	.580	27.5
65.1	2.75 camphor	.672	37.2	0	2.04 thymol	.390	28.1
BENZENE-ETHYL ALCOHOL							
100	1.85	0.315	25.9	40.6	5.24	0.693	20.1
100	3.58	.604	25.7	30.1	5.95	.787	20.1
80.25	3.31	.458	21.2	20.3	4.18	.562	20.5
69.8	4.48	.555	18.6	9.7	4.17	.446	16.25
59.0	3.45	.408	18.0	0	5.90	.396	10.15
50.0	5.18	.547	16.1				
ETHER-ACETONE							
100.0	5.38	0.810	18.27	30.0	5.61	0.700	15.21
100.0	5.74	.912	18.35	30.0	4.73	.563	14.6
90.0	4.90	.701	17.44	20.0	4.89	.628	15.69
88.4	4.72	.699	18.09	20.0	4.70	.638	16.57
80.0	4.92	.679	16.9	10.1	4.49	.540	14.70
70.1	5.31	.649	16.1	0	6.98	.840	14.68
60.0	5.37	.700	15.9	0	6.05	.725	14.62
50.1	4.81	.610	15.5	0	6.12	.758	15.14
40.3	4.85	.620	15.45	0	6.82	.833	14.60
					Succinic acid		
CHLOROFORM-ACETONE							
100.0	2.66	0.653	36.6	50.0	5.48	0.725	...
100.0	4.98	1.218	...	40.2	2.06	.252	17.83
79.7	1.78	0.395	30.85	40.2	3.82	.515	...
79.7	3.39	.703	...	40.2	6.35	.743	...
79.7	5.43	1.104	...	30.1	2.55	.302	17.15
74.7	2.42	0.419	27.15	30.1	5.04	.574	...
74.7	4.61	.824	...	30.1	7.22	.815	...

⁶ Mathews and Faville, *J. Phys. Chem.*, **22**, 1 (1918).

⁷ See preceding paper, *THIS JOURNAL*, **47**, 1785 (1925).

TABLE I (Concluded)

% of solvent	G. of solute per 100 g. of solvent	Δt °C.	K °C.	% of solvent	G. of solute per 100 g. of solvent	Δt °C.	K °C.
68.9	1.14	0.152	22.0	19.9	3.89	.414	16.40
68.9	2.75	.378	...	19.9	6.85	.739	...
68.9	4.13	.598	...	10.3	4.82	.466	14.92
59.2	1.62	.210	20.22	10.3	8.64	.847	...
59.2	3.82	.502	...	0	4.04	.395	14.80
59.2	5.26	.698	...	0	8.29	.811	...
50.0	1.90	.257	20.15	0	12.37	1.209	...
50.0	3.45	.446	...				

ETHYL ALCOHOL-WATER

100	3.20	0.582	...	36.5	2.45	0.324	..
100	6.27	1.141	10.71	36.5	4.70	.622	7.80
95.4	3.19	0.512	...	35.5	3.23	.439	..
95.4	6.17	1.067	10.22	35.5	6.52	.881	7.98
90.4	1.61	0.256	...	30.2	3.19	.476	..
90.4	3.16	.518	...	30.2	6.08	.903	8.79
90.4	4.78	.778	9.60	24.3	2.07	.402	..
85.4	2.88	.419	..	24.3	4.31	.778	..
85.4	6.15	.915	8.79	24.3	5.92	1.045	10.40
80.1	2.02	.269	..	13.7	2.34	0.467	...
80.1	4.76	.649	8.03	13.7	4.54	.881	11.48
74.8	2.15	.271	..	9.31	3.52	.632	...
74.8	4.31	.570	..	9.31	6.84	1.198	10.32
74.8	6.93	.917	7.80	6.44	2.46	0.442	...
57.8	2.07	.261	..	6.44	4.90	.859	10.35
57.8	4.73	.600	7.48	2.1	2.14	.307	...
50.2	2.01	.238	..	2.1	4.10	.608	8.71
50.2	3.55	.448	..	0	2.07	.176	..
50.2	5.18	.662	7.57	0	4.55	.409	..
				0	6.86	.601	5.15

Discussion

The reproducibility of the results was about 1%; the limit on the accuracy was, in general, that of the analysis of the solution, since the elevation of the boiling point could be measured to $\approx 0.002^\circ$, or less.

G. N. Lewis⁸ has derived the following equation for the change in boiling point, dT , on adding dN moles of a non-volatile solute to a mixture of n_1 moles of one solvent and n_2 moles of another, the partial pressures being respectively p_1 and p_2 and the change in partial pressure of the first from p_1 to p_1' , produced by addition of the solute, being dp_1 ($n_1/p_1 - n_2/p_2$) $dp_1/dN = L/Rt_2 dT/dN - 1$.

L in this case is the heat of vaporization of one mole from a large quantity of the mixture. The equation reduces for pure solvents and constant-boiling mixtures to the familiar van't Hoff relation. The necessary partial-pressure data have been obtained by vapor-pressure measurements at

⁸ Lewis, THIS JOURNAL, 28, 766 (1906).

the boiling point on the same systems that were used in the ebullioscopic measurements.⁷ These data also indicate that dp_1/dN is sufficiently constant so that for purposes of calculation it may be replaced by $\Delta p_1/\Delta n$. As the ebullioscopic measurements prove the constancy of dT/dN for the solutes chosen, calculation of ΔT for finite increments of ΔN is permissible. L may be calculated as the sum of the heats of vaporization of the components, corrected for the temperature of vaporization. In three of the systems, chloroform-acetone, benzene-alcohol and alcohol-water, the heat effects on mixing condensed vapor with the liquid cannot be neglected. These may be calculated from the simple heats of mixing⁹ by the method of partial molal quantities.¹⁰

It is, therefore, possible for these systems to compare dT as calculated by the Lewis equation with experimental values. For the sake of uniformity, this has been done for a concentration of 5 g. of solute per 100 g.

TABLE II
COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF dT

ETHER-ACETONE			CHLOROFORM-ACETONE		
% Solvent in liquid	dT Calcd. °C.	dT Obs. °C.	dT Calcd. °C.	dT Obs. °C.	
0	0.726	0.612	0.590	0.493	
10	.578	.614	.585	.516	
20	.484	.618	.558	.540	
30	.620	.622	.595	.566	
40	.591	.630	.708	.599	
50	.695	.638	.756	.633	
60	.760	.650	.809	.672	
70	.739	.667	.871	.760	
80	.796	.690	1.046	1.032	
90	.854	.718	1.298	...	
100	.915	.749	1.240	1.222	

CARBON TETRACHLORIDE-ETHYL ACETATE			BENZENE-ETHYL ALCOHOL		
% Solvent in liquid	dT Calcd. °C.	dT Calcd. by integral form °C.	dT Obs. °C.	dT Calcd. by integral form °C.	dT Obs. °C.
0	0.925	0.902	0.952	0.403	0.344
10	.970	.941	.980	.525	.519
20	1.011	.570	.558
30	1.061	1.043	1.045	.660	.648
40	1.088	1.112	1.090	.653	.638
50	1.176	1.132	1.135	.641	.629
60	1.282	1.230	1.198	.593	.596
70	1.359	1.272	1.275	.562	.543
80	1.540	1.460	1.39	.534	.530
90	1.749	1.645	1.78	.441	.440
100	1.725	1.645	1.56	.866	.846

⁹ Carroll and Mathews, *THIS JOURNAL*, **46**, 30 (1924).

¹⁰ Lewis and Randall, *ibid.*, **43**, 237 (1921).

TABLE II (Concluded)
 ETHYL ALCOHOL-WATER

% Alcohol in liquid	dT Calcd.	dT Calcd. by integral form °C.	dT Obs. °C.	% Alcohol in liquid	dT Calcd.	dT Calcd. by integral form °C.	dT Obs. °C.
0	0.440	0.426	0.436	60	0.625	0.637	0.636
10	1.486	1.369	.932	70	.686	.669	.648
20	1.275	1.110	.991	80	.765	.743	.688
30	1.042	1.030	.770	90	.874	.839	.809
40	0.550	0.519	.655	100	1.025	.983	.908
50	.570	.560	.640				

of solvent in all cases. The equation may also be integrated, giving $n_1 \ln p_1' / p - n_2 / p_2 (p_1' - p_1) = L/R(1/T_1 - 1/T_2) - N$. This may be arranged for convenience in calculation, without serious error, as $T_2 - T_1 = RT_1^2/L [n_1 \ln p_1' / p_1 - n_2 / p_2 (p_1' - p_1) + N]$. ΔT as calculated from this form is in good agreement with the values from the differential form.

The general relation between boiling-point elevation and composition of solvent is represented by the equation to a degree which is gratifying in view of the unusual nature of the curves. The discrepancies between observed and calculated values are of the same order for the pure solvents and for the mixtures. The values of K calculated by the van't Hoff equation, and obtained experimentally with "normal" solutes in the pure solvents, are collected in Table III. The discrepancy is obviously much greater than the experimental error.

 TABLE III
 COMPARISON OF CALCULATED AND OBSERVED VALUES OF K

Liquid	$RT^2/100^w$ °C.	K Obs. °C.	Solute
Chloroform	37.8	36.1	Camphor
Acetone	17.13	14.80	Camphor
		14.60	Benzoic acid
		14.4	Succinic acid
		10.94 ^a	Benzoic acid
Ethyl alcohol	11.95	10.71	Acetamide
		10.3	Camphor
		7.88 ^a	Benzoic acid
Methyl alcohol	9.11	7.85	Benzoic acid
		5.13	Acetamide
Water	5.13	5.15	Acetamide
Ether	21.8	18.24	Benzoic acid
Ethyl acetate	27.8	28.6	Thymol
Carbon tetrachloride	51.9	46.8	Thymol
Benzene	26.2	25.7	Camphor

^a Determined by Haverstick, *Thesis*, University of Wisconsin, 1916.

It is interesting to note that, presumably due to compensating errors, solutions may follow the dil. solution laws more closely than those of the ideal solution. For example, the observed elevations of the boiling point for solutions of acetamide in alcohol and camphor in acetone, are more

nearly proportional to the weight concentration than to the elevations calculated by the Washburn general boiling-point law.

TABLE IV

Solvent	RATIO OF Δt OBSERVED CALCULATED	
	Ratio of weight concns.	Observed Ratio of Δt Calcd.
Alcohol	1:1.961	1:1.955
Acetone	1:2.06:3.075	1:2.06:3.06
		1:2.045:3.02

Summary

1. An ebullioscopic apparatus capable of an accuracy of 1% has been constructed. One of its principal features is a simple pressure regulator capable of other applications in physics and chemistry.

2. The Lewis equation for change in boiling point of a binary mixture on addition of a non-volatile solute has been tested experimentally and found to have the same order of accuracy as other laws of dilute solutions.

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

THE ELECTRICAL CONDUCTANCE OF SELENIUM OXYCHLORIDE SOLUTIONS¹

By A. P. JULIEN

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Introduction

This paper deals with the specific electrical conductance of selenium oxychloride and the molecular conductance of certain metallic chlorides in this solvent. The lack of quantitative experimental conductance data in non-aqueous solvents and the importance of such data in studying the laws of solution, render valuable any additional contributions in this field.

The literature contains but two references to earlier determinations of the electrical conductance of selenium oxychloride. Lenher² used carbon electrodes and found the specific conductance to be approximately 9.6×10^{-5} mhos. and Wildish³ stated that in the determination of the dielectric constant of selenium oxychloride he used a product having a conductance of about one-tenth that of conductivity water. Since the values reported for the specific conductance of selenium oxychloride are in such wide variance, there is an obvious necessity for establishing a method for the preparation of that compound which will yield a product having a constant electrical conductance.

¹ This paper is an abstract of a thesis submitted by A. P. Julien in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

² Lenher, *THIS JOURNAL*, **43**, 29 (1921).

³ Wildish, *ibid.*, **42**, 2607 (1920).