Summary

It has been shown at the beginning of this paper that the substances dicyano-imide, tricyanomelamine, and hydromelonic acid may be looked upon as ammono-carbonic acids. In the present paper the preparation of these acids, as well as certain of their metallic salts, has been described. The preparation and properties of mercuric dicyano-imide have been recorded.

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

THE SPECIFIC HEATS OF BINARY MIXTURES

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A method for measuring the specific heats of liquids has been described in previous communications from this Laboratory.[1] In carrying the investigations to solutions, binary mixtures of nearly ideal liquids have been studied first, and in this paper are presented the results on mixtures of benzene and toluene; bromobenzene and chlorobenzene; carbon tetrachloride and chloroform; benzene and carbon tetrachloride; and of chloroform and acetone. The fourth pair is described in the literature as showing a minimum boiling point, the fifth as showing a maximum boiling point, but the other three pairs are generally classed as illustrations of ideal solutions. In such solutions, properties may be expressed in terms of the mole fractions of the components and the properties of the pure substances by simple addition.

Few solutions, if any, are strictly ideal and it becomes of interest to study the mechanism underlying the deviations from the ideal solution. One of the best approaches appears to be through investigations of specific heats at different temperatures.

The apparatus used in this work has been described before.[1a] The input of electrical energy (in international units) was converted into calories by dividing by 4.182. In weighing out the liquid to make solutions of definite composition the usual correction for the buoyancy of the air was made. A given solution (160 cc.) was used but once, for the evaporation of the warm liquid after completing an experiment caused a change in composition. In nearly every case the experimental points fall on a smooth curve within 0.001 calorie per degree.

Purification of Materials

The benzene, toluene, carbon tetrachloride and chloroform were purified in the manner described in the preceding papers and their physical constants were essentially

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[1] (a) Williams and Daniels, THIS JOURNAL, **46**, 903 (1924); (b) **46**, 1569 (1924).

the same as those previously reported. Inasmuch as larger quantities of material were needed for the mixture, it was not practicable to confine the distillate to such narrow ranges. The remaining liquids, obtained from the Eastman Kodak Company, were carefully dried and fractionated. The constants were as follows.

Substance	B. p. at 760 mm. °C.	n_D^{25}
Benzene	80.15– 80.24	1.49765
Toluene	110.5 –110.6	1.49735
Carbon tetrachloride	76.40– 76.55	1.45905
Chloroform	61.0 – 61.1	1.44660
Acetone	56.05– 56.10	1.36488
Chlorobenzene	131.85–132.10	.....
Bromobenzene	156.0 –156.4	.....

Experimental Results

The experimental work is summarized in Figs. 1 to 5, where specific heat is plotted against temperature. The heat capacities at different temperatures over the whole range of concentrations are shown in Figs. 6 to 10, together with the partial heat capacities per gram. The latter were obtained by the method of intercepts[2] in which heat capacities were plotted against percentage composition. The graphical extrapolation of the tangent to the ordinate for each of the pure liquids, was carried out on a large scale with curves similar to the full lines of Figs. 6–10.

The partial molal heat capacities, $\overline{C}_p$, of the dissolved liquids were calculated by multiplying the partial heat capacities per gram by their molecular weights. The values are shown in Cols. 3 and 5 of Tables I to V. The molal heat capacities of some of the pure liquids given in the tables were obtained from data which have been presented previously.[1] The heat capacities of the chlorobenzene, bromobenzene and acetone were determined, and the empirical equations which give the specific heat at constant pressure (C_p) as a function of the temperature (Centigrade) over the range studied are: acetone, $C_p = 0.5042 + 0.00030t + 0.0_419t^2$; bromobenzene $C_p = 0.3043 + 0.000101t + 0.0_544t^2$; chlorobenzene, $C_p = 0.2273 + 0.000042t + 0.0_525t^2$. In Cols. 4 and 6 are shown the differences between the molal heat capacities of the pure liquids (C_p), and the molal heat capacities of the same liquids in the dissolved state, that is the partial molal heat capacities ($\overline{C}_p$). These differences are of theoretical interest, for they give a measure of the so-called "ideality" of the solutions.

Theoretical Discussion

In attempting to explain the properties of binary mixtures two fundamental factors have long been recognized, namely, the formation of com-

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[2] (a) Roozeboom, "Die Heterogenen Gleichgewichte," Braunschweig, **1904,** vol. II, pt. 1, p. 288. (b) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923,** p. 38.

pounds between the two components, and the breaking down of complex molecules present in one or both of the liquids. This matter has been studied by Hartung[3] and by Hildebrand.[4]

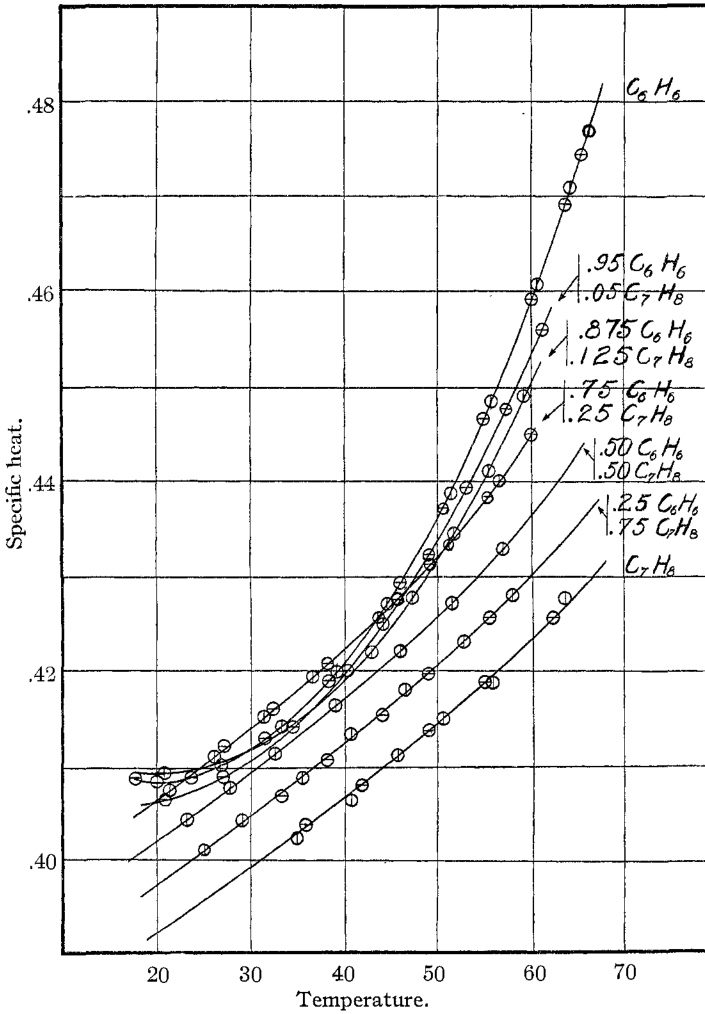

Fig. 1.—C_6H_6—C_7H_8.
Compositions are expressed in mole fractions.

The first of these factors should give a minimum in a vapor pressure-composition curve, and pressures less than those calculable on the basis of Raoult's law; for the escaping molecules are held more firmly by the attractive forces which tend to make a new compound. The combina-

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[3] Hartung, *Trans. Faraday Soc.*, **12**, 66 (1917).

[4] Hildebrand, "Solubility," Chemical Catalog Co., New York, **1924**, p. 86.

tion should be accompanied by an evolution of heat and a contraction in volume.

If the second effect takes place the vapor pressure-composition curve should exhibit a maximum, for the attractive force which tends to hold two or more molecules together in the pure liquid is weakened by the addition of the second liquid. The vapor pressures are then greater than those calculated by Raoult's law. This phenomenon should be accompanied by an absorption of heat and an expansion in volume.

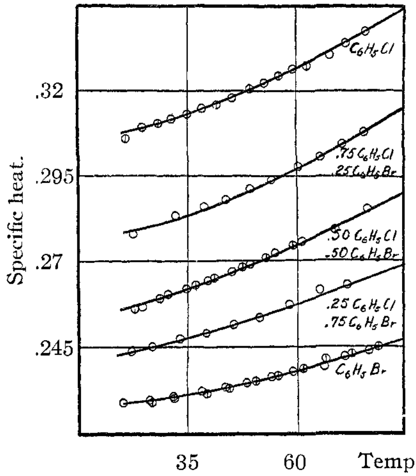

Fig. 2.
$C_6H_5Cl—C_6H_5Br$.

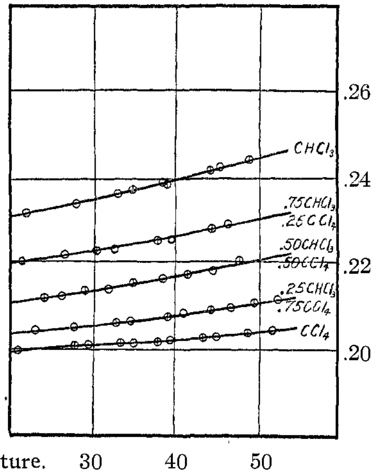

Fig. 3.
$CHCl_3—CCl_4$.

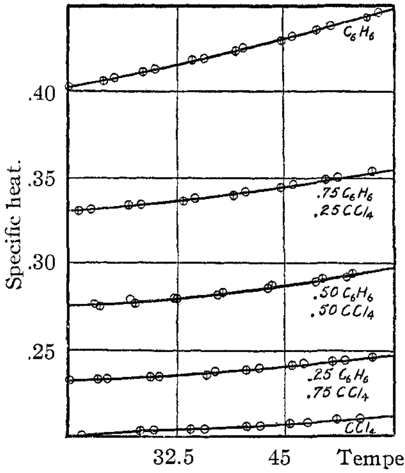

Fig. 4.
$C_6H_6—CCl_4$.

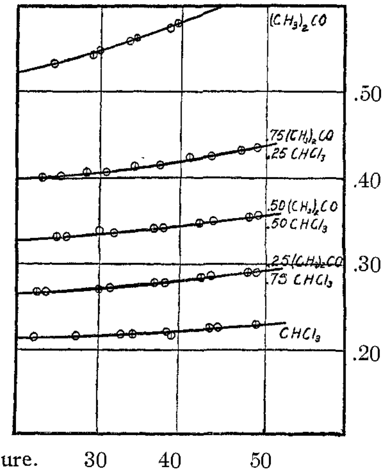

Fig. 5.
$CHCl_3—(CH_3)_2CO$.

Compositions are expressed in mole fractions.

A pure liquid which contains associated molecules may have an abnormally large heat capacity, for as the temperature is raised, the associated molecules are broken down and heat is absorbed. When associated molecules are broken down on mixing two liquids, heat is absorbed and this heat, which was responsible for the abnormally large heat capacity of the pure liquid, can no longer be included as part of the heat capacity. Thus it is possible for an associated liquid, with a large temperature coefficient of de-association, to give a decreased heat capacity in solution.

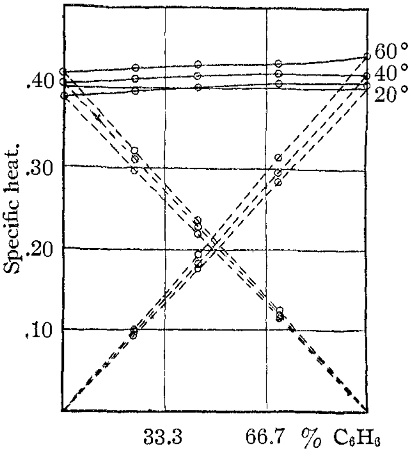

Fig. 6.
C_6H_6—C_7H_8.

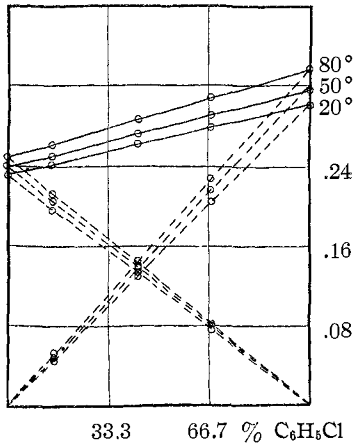

Fig. 7.
C_6H_5Cl—C_6H_5Br.

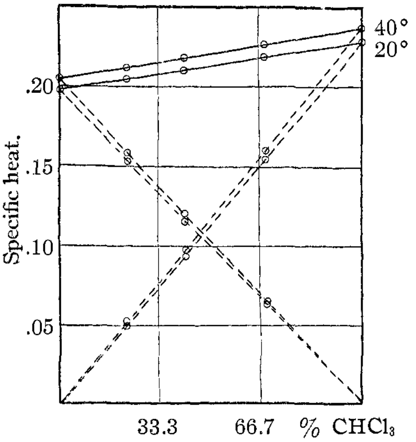

Fig. 8.
$CHCl_3$—CCl_4.

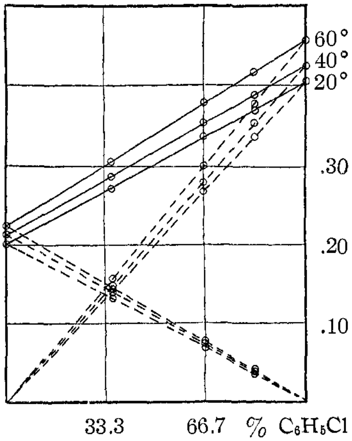

Fig. 9.
C_6H_6—CCl_4.

Full lines—Total heat capacity.
Broken lines—Partial heat capacities of components.

In such a case the partial molal heat capacity, $\overline{C}_p$ in solution is less than the molal heat capacity of the pure liquid, C_p. If the two liquids unite chemically, and the new chemical compound is broken down with the absorption of heat, when the temperature is raised the mixture will possess an abnormally large heat capacity. In this case, $\overline{C}_p$ is greater than C_p.

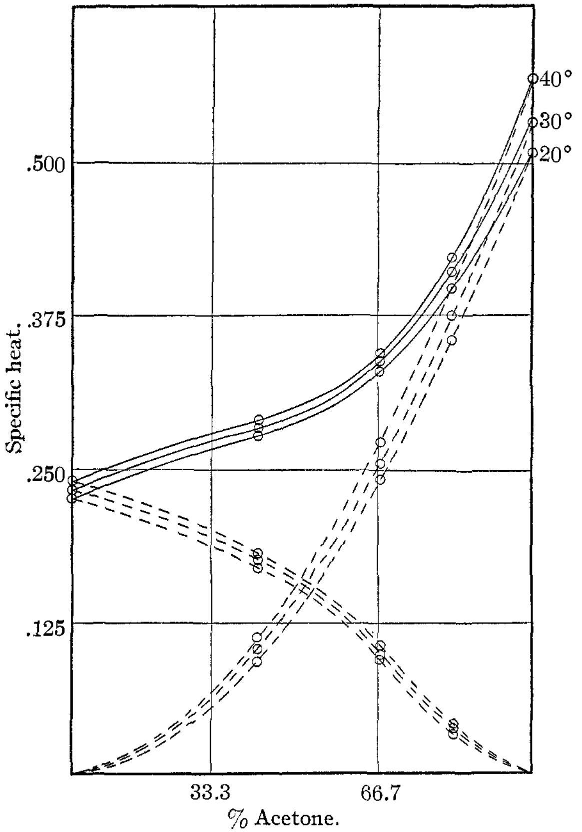

Fig. 10.—Heat capacities of $CHCl_3$—CH_3COCH_3 mixture.
Full lines—Total heat capacity.
Broken lines—Partial heat capacities of components.

It is necessary to consider another factor which leads to opposite effects. Since heat capacity is increased by merely increasing the number of molecules, even though the total weight remains unchanged, the liquid in the unassociated state may have the greater heat capacity, $(\overline{C}_p > C_p)$. Likewise, compound formation may cause a decrease in the heat capacity, $(\overline{C}_p < C_p)$. It does not seem possible, at present, to predict whether a liquid will have a greater or lesser heat capacity in solution since the same mechanism may be used to explain either an increase or a decrease. When the temperature coefficient of dissociation is high the effects suggested in the preceding paragraphs are large, and when the dissociation caused by mixing is complete the effects described in this paragraph become large. With these general considerations in mind each of the binary systems is discussed briefly.

Benzene-Toluene.—Large deviations from the law of ideal solutions are not to be expected, since the two components of this[5] system are similar chemically. Vapor-pressure measurements indicate that they give a solution which is practically ideal.

The abnormally low specific heat of pure benzene between 20° and 45° has been discussed in a previous paper. This abnormality leads to an interesting consideration. From Fig. 1 it is evident that pure benzene at 30° has a lower specific heat than a solution of 0.75 mole fraction of benzene with 0.25 mole fraction of toluene, although benzene has a higher specific heat than toluene. The effect of a small amount of toluene is to increase the heat capacity of the solution, but further addition of toluene decreases it. In an attempt to explain this apparent anomaly, the specific heats of two other solutions were determined, containing, respectively, 0.95 and 0.875 mole fractions of benzene.

It is interesting to suggest a mechanism that may show why the benzene and toluene do not form an ideal solution at the lower temperatures. When benzene is mixed with toluene, some of the associated molecules are broken down according to the reaction: $(C_6H_6)_n \longrightarrow nC_6H_6$. In support of this hypothesis it was found that a considerable absorption of heat occurs when toluene is added to benzene. This cooling effect on mixing benzene and toluene has been reported by Young and Fortey.[5a] Benzene in the "de-associated" state has a higher specific heat, because the number of molecules is increased, and the partial molal heat capacity of benzene in solution is greater than the molal heat capacity of pure

TABLE I

SPECIFIC HEATS AND PARTIAL MOLAL HEAT CAPACITIES ($\bar{C}_p$) OF MIXTURES OF BENZENE AND TOLUENE

Mole fraction C_6H_6	Sp. heat	C_6H_6		C_7H_8	
		$\bar{C}_p$	$\bar{C}_p - C_p$	$\bar{C}_p$	$\bar{C}_p - C_p$
		20°			
1.00	0.4076	31.81	.....	...	....
0.95	.4058	31.76	−0.05	37.42	+1.33
.875	.4088	31.73	− .08	37.75	+1.66
.75	.4066	32.08	+ .27	36.35	+0.26
.50	.4020	32.08	+ .27	36.28	+ .19
.25	.3973	32.27	+ .46	36.12	+ .03
.00	.3920	...	....	36.09	....

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[5] (a) Young and Fortey, *J. Chem. Soc.*, **83**, 45, 68 (1903). (b) Schulze, *Ann. Physik*, **59**, 82 (1919).

TABLE I (*Concluded*)

Mole fraction C_6H_6	Sp. heat	C_6H_6		C_7H_8	
		$\bar{C}_p$	$\bar{C}_p - C_p$	$\bar{C}_p$	$\bar{C}_p - C_p$
		30°			
1.00	.4115	32.12	....	...	....
0.95	.4108	32.11	−0.01	36.97	+ .22
.875	.4110	31.98	− .14	38.62	+2.13
.75	.4140	32.36	+ .24	36.90	+0.15
.50	.4090	32.75	+ .63	36.85	+ .10
.25	.4044	32.86	+ .74	36.78	+ .03
.00	.3992	...	....	36.75	....
		40°			
1.00	.4210	32.86	....	...	....
0.95	.4204	32.81	− .05	37.78	+ .57
.875	.4195	32.75	− .11	38.85	+1.44
.75	.4220	33.02	+ .16	38.20	+0.74
.50	.4167	33.38	+ .52	37.50	+ .09
.25	.4120	33.49	+ .63	37.47	+ .06
.00	.4065	...	....	37.41	....
		50°			
1.00	.4357	34.01	....	...	....
0.95	.4340	33.96	− .05	37.38	− .78
.875	.4326	33.79	− .22	39.30	+1.14
.75	.4317	34.03	+ .02	38.58	+0.42
.50	.4255	34.15	+ .14	38.20	+ .04
.25	.4204	34.20	+ .19	38.20	+ .04
.00	.4145	...	....	38.16	....
		60°			
1.00	.4575	35.71	....	...	....
0.95	.4520	35.68	− .03	38 00	− .96
.875	.4505	35.63	− .08	38.20	− .76
.75	.4455	35.60	− .11	38.42	− .54
.50	.4365	35.25	− .46	39.00	+ .04
.25	.4302	35.38	− .33	38.95	+ .01
.00	.4232	...	....	38.96	....

benzene. The fact that this increase is brought about by a liquid that has a lower heat capacity than the benzene explains the apparent anomaly mentioned above.

Chlorobenzene—Bromobenzene.—The vapor-pressure relations of this system, as well as the heats of mixing and volume changes have been carefully studied by Young,[6] who concludes that the various solutions of chlorobenzene and bromobenzene are "ideal within the limits of experimental error."

The specific-heat data presented in Table II support this statement in an approximate way, but the deviations are large enough to show that even this solution is not absolutely ideal. In general, the molal heat capacity

[6] Young, *J. Chem. Soc.*, **81,** 768 (1902).

TABLE II

SPECIFIC HEATS AND PARTIAL MOLAL HEAT CAPACITIES ($\bar{C}_p$) OF MIXTURES OF CHLOROBENZENE AND BROMOBENZENE

Mole fraction C_6H_5Cl	Sp. heat	C_6H_5Cl		C_6H_5Br	
		$\bar{C}_p$	$\bar{C}_p - C_p$	$\bar{C}_p$	$\bar{C}_p - C_p$
		20°			
1.00	0.3093	34.80	....	...	....
0.75	.2802	34.67	−0.13	34.38	−1.80
.50	.2580	33.76	−1.04	35.95	−0.23
.25	.2438	33.65	−1.15	36.20	+ .02
.00	.2305	...	....	36.18	....
		40°			
1.00	.3153	35.47	....	...	....
0.75	.2862	35.35	−0.12	36.28	− .29
.50	.2650	35.10	− .37	36.35	− .22
.25	.2487	35.10	− .37	36.42	− .15
.00	.2330	...	....	36.57	....
		60°			
1.00	.3258	36.65	....	...	....
0.75	.2970	36.68	+ .03	36.90	− .46
.50	.2730	36.33	− .32	37.29	− .07
.25	.2565	36.25	− .40	37.53	+ .17
.00	.2380	...	....	37.36	....
		80°			
1.00	.3405	38.31	....	...	....
0.75	.3110	38.60	+ .29	38.47	+ .02
.50	.2864	38.40	+ .09	38.53	+ .08
.25	.2662	38.30	− .01	38.78	+ .33
.00	.2450	...	....	38.45	....

of the pure liquid is slightly greater than that of its partial molal heat capacity in solution, the heat capacity in the latter case being reduced by the process of solution because of the loss of heat-absorbing complexes.

It might have been expected that the various physical constants for these solutions would show greater deviations from those calculable on the basis of Raoult's law, since they are associated liquids. The dielectric constants for both liquids are comparatively high (C_6H_5Cl = 11 and C_6H_5Br = 5.2), and Hildebrand[7] has suggested that the dielectric constant may be considered to be the most direct evidence of polarity or association. It may be pointed out that the mere existence of association in a pure liquid is not a sufficient cause for the formation of a non-ideal solution. The extent of association must be changed by the process of solution if the liquid is to have different properties in the dissolved state.

Chloroform—Carbon Tetrachloride.—Chloroform and carbon tetrachloride form solutions that are nearly ideal. Table III shows that in this case, as in the case of chlorobenzene and bromobenzene, the molal

[7] Ref. 4, p. 88.

heat capacity of each pure liquid is greater than its partial molal heat capacity in solution. Carbon tetrachloride has been shown to contain more than one kind of molecule and it is probable that chloroform is of a similar nature, since its dielectric constant is twice as great as that of carbon tetrachloride. "De-association" taking place upon solution may deprive the components of some of the associated molecules existing in the pure liquids, and reduce the quantity of heat necessary to raise the temperature.

TABLE III

SPECIFIC HEATS AND PARTIAL MOLAL HEAT CAPACITIES ($\bar{C}_p$) OF CHLOROFORM AND CARBON TETRACHLORIDE

Mole fraction $CHCl_3$	Sp. heat	$CHCl_3$		CCl_4	
		$\bar{C}_p$	$\bar{C}_p - C_p$	$\bar{C}_p$	$\bar{C}_p - C_p$
		20°			
1.00	0.2312	27.60	....	...	....
0.75	.2198	27.52	−0.08	29.85	−0.76
.50	.2118	27.34	− .26	30.47	− .14
.25	.2040	27.28	− .32	30.39	− .22
.00	.1990	...	....	30.61	....
		30°			
1.00	.2343	27.97	....	...	....
0.75	.2226	28.00	+ .03	30.39	− .84
.50	.2140	27.92	− .05	30.39	− .84
.25	.2055	26.80	−1.17	30.84	− .39
.00	.2030	...	....	31.23	....
		40°			
1.00	.2382	28.44	....	...	....
0.75	.2262	28.33	− .11	30.70	− .68
.50	.2170	28.33	− .11	30.70	− .68
.25	.2075	27.47	− .97	31.00	− .38
.00	.2040	...	....	31.38	....
		50°			
1.00	.2431	29.02	....	...	....
0.75	.2307	29.02	....	31.08	− .53
.50	.2207	29.02	....	31.08	− .53
.25	.2102	28.37	− .65	31.30	− .31
.00	.2055	...	....	31.61	....

Benzene—Carbon Tetrachloride.—There is some evidence in the literature that benzene and carbon tetrachloride give a vapor-pressure curve exhibiting a maximum at 0.90 mole fraction of carbon tetrachloride. Using Zawidski's[8] data, Dolezalek[9] explained these deviations of the vapor pressures from the additivity law as being due to the association of carbon tetrachloride. An absorption of heat on mixing these liquids has been reported by Young and Fortey.[5a]

[8] Zawidski, *Z. physik. Chem.*, **35**, 129 (1900).

[9] Dolezalek, *ibid.*, **64**, 727 (1908).

TABLE IV

SPECIFIC HEAT AND PARTIAL MOLAL HEAT CAPACITIES ($\bar{C}_p$) OF MIXTURES OF BENZENE AND CARBON TETRACHLORIDE

Mole fraction C_6H_6	Sp. heat	C_6H_6		CCl_4	
		$\bar{C}_p$	$\bar{C}_p - C_p$	$\bar{C}_p$	$\bar{C}_p - C_p$
			20°		
1.00	0.4080	31.84	....	...	....
0.75	.3315	32.15	+0.31	30.65	+0.04
.50	.2720	31.75	− .09	30.92	+ .31
.25	.2298	31.85	+ .01	31.02	+ .41
.00	.1990	...	....	30.61	....
			30°		
1.00	.4150	32.39	....	...	....
0.75	.3345	32.63	+ .24	30.90	− .33
.50	.2768	32.46	+ .07	31.31	+ .08
.25	.2320	32.36	− .03	31.33	+ .10
.00	.2030	...	....	31.23	....
			40°		
1.00	.4212	32.87	....	...	....
0.75	.3395	33.10	+ .23	31.45	+ .07
.50	.2818	32.96	+ .08	31.55	+ .17
.25	.2350	32.86	− .01	31.75	+ .37
.00	.2040	...	....	31.38	....
			50°		
1.00	.4340	33.87	....	...	....
0.75	.3480	34.10	+ .33	31.75	+ .14
.50	.2875	33.96	+ .09	32.00	+ .39
.25	.2400	33.80	− .07	32.15	+ .54
.00	.2055	...	....	31.61	....
			60°		
1.00	.4550	35.51	....	...	....
0.75	.3620	35.77	+ .26	32.55	− .14
.50	.2960	35.40	− .11	32.70	+ .01
.25	.2480	35.30	− .21	33.15	+ .46
.00	.2125	...	....	32.69	....

From Table IV it is evident that the solutions are nearly ideal according to the specific-heat criterion, since the heat capacities are but slightly changed by the process of mixing. The fact that the heat capacity in solution is slightly greater in general than that of the pure liquid suggests that association has been diminished and the number of molecules increased, as in the case of benzene and toluene.

Chloroform—Acetone.—This system has been classed as "non-ideal." When the two liquids are mixed there is a considerable evolution of heat.[10]

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[10] This evolution of heat has been quantitatively measured by Young ["Fractional Distillation," The Macmillan Co., **1913,** p. 40], and by Carroll and Mathews, [THIS JOURNAL, **46,** 30 (1924)].

This is considered to be evidence of compound formation. A contraction in volume has been observed also.[11]

The vapor-pressure relations are due to Zawidski[8] and to Rosanoff and Easley.[12] The system shows a minimum vapor pressure at a concentration of approximately 0.6 mole fraction of chloroform.

TABLE V

SPECIFIC HEATS AND PARTIAL MOLAL HEAT CAPACITIES ($\bar{C}_p$) OF MIXTURE OF CHLOROFORM AND ACETONE

Mole fraction $CHCl_3$	Sp. heat	$CHCl_3$		CH_3COCH_3	
		$\bar{C}_p$	$\bar{C}_p - C_p$	$\bar{C}_p$	$\bar{C}_p - C_p$
20°					
1.00	0.2312	27.60	....	...	....
0.75	.2800	28.68	+1.08	30.80	+0.75
.50	.3240	29.98	+2.38	27.65	−2.40
.25	.4028	26.90	−0.70	30.12	+0.07
.00	.5176	...	....	30.05	....
30°					
1.00	.2343	27.97	....	...	....
0.75	.2827	29.18	+1.21	30.30	−0.40
.50	.3290	29.63	+1.66	28.65	−2.05
.25	.4064	27.10	− .87	30.83	+ .13
.00	.5333	...	....	30.70	....
40°					
1.00	.2382	28.44	....	...	....
0.75	.2860	29.63	+1.19	30.83	−0.98
.50	.3355	30.62	+2.18	28.83	−3.02
.25	.4170	23.30	−5.14	32.58	+0.73
.00	.5660	...	....	31.85	....

Table V shows that the partial molal heat capacity of the chloroform in solutions containing that substance in the larger mole fractions is greater than the molal heat capacity of the pure liquid; in dilute solutions it is less.

In the articles referred to, the general opinion seems to be that there is a compound formed between the constituents in equimolar proportions which may be represented by a formula, $(CH_3)_2C.CCl_3.OH$. The rather large negative value of the deviation, $\bar{C}_p < C_p$, obtained would seem to indicate that the number of molecules is decreased, and that the new compound is sufficiently stable to resist decomposition at higher temperatures.

Conclusions

It has been shown in most cases that the pure liquids contain more than one molecular species and that the equilibrium between these species is altered by the addition of a second liquid. This evidence together with

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[11] Hubbard, *Z. physik. Chem.*, **74**, 217 (1910).

[12] Rosanoff and Easley, THIS JOURNAL, **31**, 753 (1909).

that obtained in the study of the pure liquids presented before,[1a,1b] and the studies of Baker[13] (on dry liquids) suggests that truly normal liquids and ideal solutions are exceedingly rare.

In some cases there are at least two reactions taking place when liquids are mixed—a "de-association" of the liquids and a combination between the two liquids. These lead to opposing tendencies in any physical property. If the endothermic and exothermic heat effects happen to counterbalance, there is no heat of mixing and by this criterion the solutions are ideal. There is no reason to expect, however, that the opposing tendencies will exactly counterbalance in some other physical property, such as vapor pressure, volume, heat capacity, viscosity, etc. Since there is more than one factor at work it is not surprising that when such properties are plotted against composition, maxima and minima do not necessarily correspond to definite chemical compounds even if such compounds are known to exist. It is not possible at present to do more than point out, in a qualitative way, the factors that must be considered in predicting the heat capacities or other properties of solutions.

This research makes possible a detailed study of the temperature coefficient of the partial molal heat capacities of dissolved substances—perhaps for the first time.[14] It is disappointing to find, however, that no important conclusions concerning this quantity can be drawn. It was thought that an increase in temperature would tend to make the solutions more ideal, but most of the systems are too complex to permit such a generalization. If all the complexes were broken down, both in the pure liquids and in solution, at the high temperatures the solutions would become ideal, but within the temperature range of this investigation, it is evident that a sufficient number of complexes are left to cause deviations from the laws of ideal solutions. In fact, the solutions may become less ideal as the temperature is raised if a certain complex which has withstood the "de-association" process at the lower temperatures is destroyed at the higher temperatures.

Summary

1. The specific heats of five binary liquid mixtures have been determined at various concentrations from 20° to about 60°. The systems studied are benzene-toluene, chloroform-carbon tetrachloride, chlorobenzene-bromobenzene, benzene-carbon tetrachloride and chloroform-acetone. Of these the first four may be considered to be *nearly* ideal solutions.

2. The partial molal heat capacities of the constituents at various temperatures have been calculated for each of the systems studied.

3. The specific heats of pure acetone, chlorobenzene and bromoben-

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[13] Baker, *J. Chem. Soc.*, **121**, 508 (1922).

[14] Ref. 2 b, pp. 107, 393.

zene have been determined and the results have been recorded as graphs and as empirical equations.

4. Each of the systems studied has been critically discussed, and an attempt made to explain the nature of the deviations between the molal heat capacities of the pure liquids and the partial molal heat capacities in solution. It is evident that the changes taking place on solution are intricate, and that dissociation phenomena are probably more important than has been recognized.

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THE ELECTRONEGATIVE POTENTIAL SERIES IN LIQUID AMMONIA

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Introduction

As has been pointed out by Kraus[2] the elements may be arranged in two electropotential series, or series of electro-affinity, depending upon whether the element functions as cation or as anion. In general, an element in the electropositive series will displace a less electropositive element from solutions of its salts; similarly, in the electronegative series, an element will in general displace a less electronegative element from solutions containing this latter as homo-atomic anion.[3] It is the purpose of the present investigation to establish the order of electro-affinities of the elements in the negative condition by means of a study of such replacement reactions.

The order of replacement of the elements in the electronegative state in water is but incompletely known, because salts of homo-atomic anions of many of the elements are unstable in this solvent. A few well-known reactions will serve for illustration:[4] $F_2 + 2KCl = 2KF + Cl_2$; $Cl_2 + 2NaBr = 2NaCl + Br_2$; $Br_2 + 2NaI = 2NaBr + 2I$; $2(Cl,Br)_2 + Na_2S = 2Na(Cl,Br) + S$.

Homo-atomic anions containing lead, tin, arsenic, antimony, bismuth and phosphorus, as well as the more electronegative elements tellurium, selenium, sulfur, iodine, bromine and chlorine are stable in liquid ammonia solution.[5] Accordingly, this solvent was chosen in order to make a more

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[1] National Research Fellow.

[2] Kraus, *Trans. Am. Electrochem. Soc.*, **45**, 175 (1924).

[3] Such as Br^-, I^-, S_5^{--}, Se_x^{--}, etc. (Nomenclature of Kraus.)

[4] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans and Co., London, **1922**, vol. II, pp. 13, 92, 93, 113. Friend, "Text Book of Inorganic Chemistry," Griffin and Co., London, vol. VIII, pp. 9, 28, 69, 205.

[5] Hugot, *Compt. rend.*, **121**, 206 (1895); **129**, 299, 388, 603 (1899). Joannis, *ibid.*, **113**, 795 (1891). Peck, THIS JOURNAL, **40**, 335 (1918). Smyth, *ibid.*, **39**, 1299 (1917). Kraus, *ibid.*, **29**, 1557 (1907); **44**, 1221 (1922).