

## HEATS OF REACTION IN NON-AQUEOUS SOLUTIONS.

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Measurements of heats of reaction have long been considered of fundamental importance in thermo-chemistry, and of late years have played a considerable part in the theory of solutions. So far as the writer is aware, however, nothing has been published concerning the study of heats of reaction in other solvents than water. A few years ago Dr. F. L. Shinn, at the suggestion of Professor Kahlenberg, made some preliminary experiments along this line in this laboratory. The results of their work indicated that the solvent used seemed to influence the magnitude of the thermal effect produced. It is the purpose of our investigations, of which this paper describes only the preliminary part, to study various reactions in different solvents to ascertain what part the solvent plays in such reactions and perhaps to throw some further light on the somewhat perplexing problem of solutions.

In this paper but one reaction will be considered—the neutralization of pyridine (1 mol.) by acetic acid (1 mol.)—the heat of reaction having been measured in a number of solvents. The heat evolved by the reaction of the pure substances in the absence of any solvent was also measured.

The exact ratio of pyridine to acetic acid in pyridine acetate is immaterial for the case in hand, the essential condition being that the reaction be the same in each case. Therefore the ratio *one* mol. of pyridine to *one* of acetic acid was adopted, and great care was used to see that this ratio was maintained exactly. The product of this reaction is, fortunately, a liquid; and it is soluble in the solvents used, thus obviating complications due to precipitation and corrections therefor.

The object of this preliminary work was to obtain a comparison of values for the different solvents, keeping the conditions the same in each case, rather than to furnish absolute values of heats of neutralization as they are ordinarily measured. Ordinarily the acid and base are each dissolved in a large excess of solvent, the resulting solutions being of equal molecular concentration. These two solutions, when mixed, then give a certain quantity of heat, which, when gram equivalents are taken, is known as the heat of neutralization. In the first series of determinations to be described the experimental conditions were somewhat different. The base—pyridine—was dissolved in the solvent in question and the pure acid (not in solution) was run into this solution. Three procedures naturally presented themselves. Either the weight or volume of solvent might be kept constant for all the different solvents, or equimolecular quantities of the different solvents might be taken. The first alternative was chosen for the preliminary work, and in each case 96.4

grams of the solvent contained one molecule of pyridine. This is a much more concentrated solution than those ordinarily used. The small heat effect produced by this reaction, together with the cost of the materials, almost precludes the usual procedure. However, some measurements made in the usual way will be carried out.

*Materials Used.*—Naturally great care was exercised in the preparation of the materials used. For the most part they were substances which present no especial difficulties in purification.

*Pyridine.*—The pyridine used was Merck's "C. P." It was dried for weeks over fused caustic potash, after which potassium permanganate was added and the mixture boiled under a reflux condenser for several hours for the purpose of destroying the picolines and higher homologs. After this treatment it was distilled from the permanganate. The sample used for the measurements of the first series boiled at  $114^{\circ}$ – $115^{\circ}$  at 736 mm.

*Acetic Acid.*—Glacial acetic acid (99 per cent.) was fractionally recrystallized until a triplicate analysis showed it to be 100 per cent. pure.

*Acetone.*—The acetone available was of excellent quality. It had stood over anhydrous copper sulfate for several weeks. Upon distillation several liters were obtained within a temperature range of  $0.05^{\circ}$ . The boiling point of the sample used was  $54.4^{\circ}$  at 725 mm.

*Benzene.*—The benzene used (Merck's recrystallized) was fractionally recrystallized and redistilled. Its constancy of boiling point ( $78.0^{\circ}$ – $78.2^{\circ}$  at 737 mm.) showed it to be very pure.

*Carbon Tetrachloride and Nitrobenzene.*—These were both fractionally distilled, no further treatment being necessary, judging from the constancy of their boiling points. The carbon tetrachloride boiled at  $74.5^{\circ}$ – $74.8^{\circ}$  at 743 mm., and the nitrobenzene at  $209.0^{\circ}$  at 740 mm.

*Carbon Bisulfide.*—The carbon bisulfide had stood over copper foil for some time. It was then fractionated by distillation, using an electrical heating device to prevent superheating. The fraction used boiled at  $46.3^{\circ}$  at 751 mm.

*The Alcohols.*—The methyl alcohol had stood over anhydrous copper sulfate for several months. It was fractionated by distillation and the distillate showed no coloration upon standing with anhydrous copper sulfate. The fraction used boiled between  $64.3^{\circ}$ – $64.5^{\circ}$  at 742.5 mm.

The ethyl alcohol after standing over anhydrous copper sulfate for several months was distilled. The best boiling fractions were mixed and redistilled with metallic sodium. A distillate of almost constant boiling point ( $77.7^{\circ}$  at 740 mm.) was obtained.

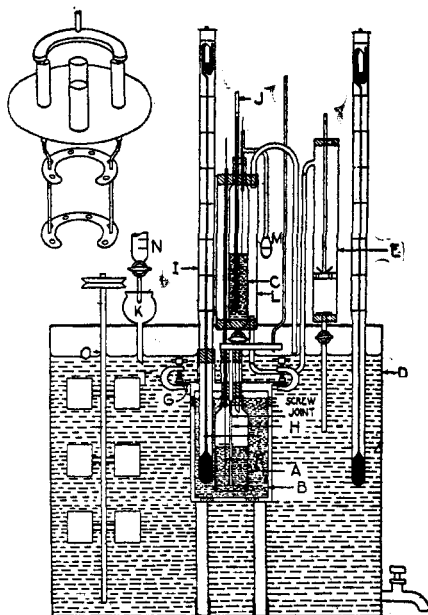
The isoamyl alcohol was subjected to fractional distillation only. Its very constant boiling point ( $129.2^{\circ}$ – $129.3^{\circ}$  at 750 mm.) showed no other treatment to be necessary.

*Ethyl Acetate.*—Kahlbaum's C. P. ethyl acetate was treated with a large quantity of phosphorus pentoxide, and after standing a few days it was distilled therefrom. The fraction used boiled at  $75.9^{\circ}$ – $76.1^{\circ}$  at 743 mm.

*Chloroform.*—The chloroform was fractionated by distillation and that portion having a boiling point of  $60.15^{\circ}$ – $60.2^{\circ}$  at 744 mm. was used.

*Method.*—The method of measurement of heat values was practically that developed by Richards and Rowe<sup>1</sup> for the measurement of specific heats of liquids. The new form of adiabatic bath described by Richards and Burgess<sup>2</sup> and by Richards and Jesse<sup>3</sup> was used instead of the earlier form. The new bath was found to be far superior, as it simplifies the manipulations greatly and makes possible a much more exact control of temperature. The accompanying diagram shows the apparatus in cross section.

The reaction takes place in the small platinum bottle *A*, which is suspended in a weighed amount of water in the platinum vessel *B* (of about 600 cc. capacity) constituting the calorimeter proper. The solution of the base was placed in the platinum bottle and the acid run into it from the jacketed cylindrical separatory funnel, *C*, placed above. In order that the initial temperature of acid and alkali might be the same at the moment of mixing, the alkali contained in the large outer bath *D* was caused to circulate through the jacket *L*, surrounding the funnel containing the acid, by means of the small pump *E*, run by an electric motor. In this way the temperature of the acid, which was constantly stirred by means of a small spiral platinum stirrer surrounding the thermometer, could be brought quickly to the temperature of the mixture in the calorimeter. The temperature of the acid was taken by means of an excellent thermometer *I*, graduated to  $0.01^{\circ}$  and capable of being read to  $0.001^{\circ}$ . This thermometer had been compared previously with the Beckmann at each  $0.1^{\circ}$  and a table was always at hand giving



<sup>1</sup> *Z. physik. Chem.*, 64, 187 (1908).

<sup>2</sup> *THIS JOURNAL*, 32, 431 (1910).

<sup>3</sup> *Ibid.*, 32, 268 (1910).

the readings of one thermometer in terms of the other. It was therefore possible to ascertain at a glance when the temperature of alkali and acid were the same. Having brought the temperature of each to the same point before mixing, no correction for difference in temperature was necessary. In a number of these preliminary measurements this ideal condition was not realized exactly, but in such cases the correction, always slight in value, was accordingly made.

At the moment when it was desired that the substances react, the circulation of alkali through the jacket around the acid compartment was stopped by closing the valve on the pump, and the large bored stopcock on the acid funnel *C* was opened. Sulfuric acid was run from a buret *N* into the outer compartment at such a rate that the temperatures of the mixture within the calorimeter and the contents of the outer compartment, as indicated by the two Beckmann thermometers whose zeros had been set together, rose simultaneously. Loss or gain of heat by the calorimeter through radiation was thus eliminated. Not more than two seconds were required for the acid to run into the platinum bottle. A few moments thereafter the rubber bulb *M* was compressed so as to force out the last drop of acid hanging in the delivery tube.

It seems unlikely that an appreciable error could have arisen from gain or loss of heat in transference of the acid into the bottle for the following reasons: The length of the delivery tube exposed between the jacketed acid container and alkali bath below was not greater than three-fourths of an inch. The system was always at about the room temperature and had always stood for a considerable time, with everything in place, preceding the moment of mixing. The delivery of acid into the alkali was practically instantaneous.

The rate of stirring is very important, as has been pointed out by Richards and Burgess.<sup>1</sup> In the earlier part of this work somewhat erratic results were obtained, which were traced later to inefficient stirring. In the work here described the calorimeter stirrers, both in calorimeter and in bottle, were driven at the rate of from 70 to 80 strokes per minute, thus assuring prompt and thorough mixing. The maximum rise of temperature was generally reached in about five or six minutes after mixing. The stirrer in the platinum bottle *P* consisted of two disks of sheet platinum attached to a short, stout platinum rod suspended from the plunger of the calorimeter stirrer by means of a fine platinum wire. The calorimeter stirrer (shown in detail in the smaller diagram) consisted of two flat, perforated rings of pure silver held in position by two silver rods, each of which screwed into a thin rod of celluloid attached to the cross-bar above. The joint between silver and celluloid was just above the surface of the water. The celluloid rods were used to reduce the

<sup>1</sup> *Loc. cit.*

liability of conduction of heat into or out of the calorimeter, and to render the calculation of the water equivalent more certain.

The acid in the funnel C was stirred by means of a thick spiral of braided platinum wire surrounding the thermometer and attached to the plunger of the calorimeter stirrer.

Some of the liquids used were quite volatile. Care was taken to prevent evaporation, not only because of the resulting loss of material but also in order to prevent the thermal effect which would be produced by such evaporation. The thermometer and delivery tube passed through tightly fitting corks. The fine platinum wire from the bottle stirrer passed through a glass guiding tube which was of very small bore at each end. The celluloid rods of the calorimeter stirrer worked through corked sleeves, which reduced the size of the necessary opening to a minimum. By using these precautions no difficulty from evaporation of material was experienced.

The outer alkali compartment was stirred by a powerful 10-bladed stirrer, *O*, as indicated, run at a rate of several hundred revolutions per minute. Complete admixture of the concentrated sulfuric acid with the alkali liquid was practically instantaneous. The whole system of stirrers and the pump were driven by a  $1/30$  h. p. electric motor, through a suitable adjustment of pulleys. The speed of the motor was controlled by a rheostat with sliding contact.

The calorimeter thermometer used was an excellent, large-bulbed Beckmann of Goetze's manufacture, having a clearly marked scale. It was most carefully standardized by comparison with a  $0.01^\circ$  thermometer which had been standardized by the Reichsanstalt. During the comparison both thermometers were placed in the adiabatic calorimeter with bulbs close together. Readings were recorded only after they had become constant on each thermometer. The scales were compared at intervals of every  $0.1^\circ$  throughout the entire length of the Beckmann scale. Two such series of comparisons were made in the same manner and from the average of these nearly identical series a curve and table for the instrument were prepared. The excellent concordance of values obtained for the amount of heat liberated by the neutralization of a definite quantity of a certain strength hydrochloric acid solution, to be described later, and the additional fact that these measurements were made at slightly different parts of the Beckmann scale, attested to the fact that the standardization was most carefully made and was satisfactory.

Since there is no indicator known for the reaction between pyridine and acetic acid it was necessary to rely on weighing to ascertain the end-point, *i. e.*, to ascertain whether the ratio of one mol. of pyridine to one mol. of acetic acid had been maintained exactly. The procedure was as follows: Exactly 19.77 grams of pyridine (*i. e.*, 0.25 mol.) were weighed

out in the platinum bottle. 24.1 grams of the solvent were then added. 14.55 cc. of pure acetic acid were run into the jacketed acid compartment. After the determination had been made the stirrer, bottle and contents were again weighed in order to determine how much acid had actually been used in the reaction. Care was taken to keep this amount as constant as possible, because further addition of acid would be accompanied by a heat effect. It was found possible to deliver almost exactly the theoretical quantity (15.01 grams) to the platinum bottle.

In order to calculate the heat of neutralization we must know the water equivalent of the solution formed in the platinum bottle, since this is also warmed by the reaction and therefore takes up a part of the heat liberated. This makes necessary a determination of the specific heat of the mixture. The manipulation was the same as for the heat of neutralization, except that a weighed quantity of the pyridine acetate solution was placed in the platinum calorimeter and an accurately weighed quantity (40.86 grams) of a 1.366 *N* hydrochloric acid solution was always placed in the platinum bottle; and the acid was just neutralized by running into it the requisite quantity of 2.732 *N* sodium hydroxide solution. After the rise in temperature had been recorded the apparatus was taken apart, the bottle, stirrer and contents weighed and the very slight excess of sodium hydroxide solution determined by titration. The quantity of sodium hydroxide solution used was always so adjusted that the neutralization was complete and that the excess should not amount to more than 0.1 cc. It was in fact generally less. The heat of dilution of this small amount of sodium hydroxide solution is so small as to be negligible.

In order to determine the exact quantity of heat liberated by the exact neutralization of 40.86 grams of this particular acid solution, the following series of four determinations were made, the first of which is given in detail to show the method of calculation:

TABLE I.

DETERMINATION OF AMOUNT OF HEAT LIBERATED BY EXACT NEUTRALIZATION OF 40.86 GRAMS OF 1.366 *N* HYDROCHLORIC ACID.

Data concerning temperature:

Initial temperature of sodium hydroxide solution.....	0.949°
Initial temperature of calorimeter.....	0.949°
Final temperature of calorimeter.....	2.412°
Rise in temperature during experiment.....	1.463°

Data concerning heat capacity, expressed in terms of water equivalent:

Water in calorimeter.....	450.00 grams
Calorimeter and fittings, equivalent to.....	8.11 grams
62.96 grams of sodium chloride solution (sp. ht. 0.94).....	59.18 grams

Total water equivalent..... 517.29 grams

Total heat liberated = 517.29 × 1.463 = 756.79 cal.

The data for the entire series of four determinations are given in the following table:

TABLE II.

No.	Total water equivalent. Grams.	Initial temp. NaOH.	Initial temp. calorimeter.	Rise in temperature.	Total heat liberated. Cals.
1	467.18	0.816°	0.816°	1.620°	756.83
2	517.29	0.949°	0.949°	1.463°	756.79
3	517.26	0.771°	0.772°	1.463°	756.75
4	517.26	0.670°	0.672°	1.463°	756.75
Average.....					756.78

Examples of the method of handling the data for the determination of heat of reaction and the specific heat of the resulting mixture will also be given at this point for the purpose of illustration. The data for specific heat are given first, as these values must be used in the other calculation:

TABLE III.

SPECIFIC HEAT OF PYRIDINE ACETATE (1 MOL. PYRIDINE + 1 MOL. ACETIC ACID)  
DISSOLVED IN 96.4 GRAMS OF CARBON TETRACHLORIDE.

Weight of 1.366 <i>N</i> hydrochloric acid solution used.....	40.86 grams
Excess of sodium hydroxide (determined by titration).....	0.05 cc.
Weight of pyridine acetate solution taken.....	500.00 grams
Data concerning temperature:	
Initial temperature of sodium hydroxide.....	1.289°
Initial temperature of calorimeter.....	1.287°
Final temperature of calorimeter.....	4.348°
Rise in temperature during experiment.....	3.061°
Data concerning heat capacity, expressed in terms of water equivalent:	
62.83 grams of sodium chloride solution (sp. ht. 0.94), equivalent to.....	59.06 grams
Calorimeter and fittings, equivalent to.....	8.11 grams
Total water equivalent.....	67.17 grams

Heat absorbed exclusive of pyridine acetate solution =  $67.17 \times 3.601 = 205.61$  cal.

Heat liberated by neutralization of 40.86 grams acid = 756.78 cal.

Heat taken up by pyridine acetate solution =  $756.78 - 205.61 = 551.17$  cal.

Specific heat of solution =  $551.7 \div (500.00 \times 3.061) = 0.3601$ .

TABLE IV.

DETERMINATION OF AMOUNT OF HEAT LIBERATED BY NEUTRALIZATION OF 1 MOL. OF  
PYRIDINE IN 96.4 GRAMS OF CARBON TETRACHLORIDE BY 1 MOL. OF ACETIC ACID.

Weight of pyridine taken.....	19.77 grams
Weight of carbon tetrachloride taken.....	24.14 grams
Weight of acetic acid used.....	15.02 grams
Theoretical quantity of acetic acid required.....	15.01 grams
Data concerning temperature:	
Initial temperature of acetic acid.....	1.016°
Initial temperature of calorimeter.....	1.016°
Final temperature of calorimeter.....	2.152°
Rise of temperature during experiment.....	1.136°







TABLE VI (Continued).

Solvent.	Weight of solvent.	Initial temp. of acid.	Initial temp. of calorimeter.	Heat brought in by acid.	Rise in temp.	Water equivalent.	Heat evolved.	Heat evolved for 1 mol.
Carbon tetrachloride . . . . .	24.11	1.016°	1.016°	.....	1.136°	479.34	544.5	2177.0
Carbon tetrachloride . . . . .	24.11	0.945°	0.933°	+0.09	1.138°	479.35	545.4	2181.6
Carbon tetrachloride . . . . .	24.11	1.208°	1.196°	+0.09	1.134°	479.35	543.5	2174.0
Average . . . . .								2177.5
Nitrobenzene . . . . .	24.10	2.027°	2.022°	+0.04	1.194°	482.71	576.3	2305.2
Nitrobenzene . . . . .	24.11	2.031°	2.029°	.....	1.194°	482.71	576.4	2305.6
Average . . . . .								2305.4
Carbon bisulfide . . . . .	24.10	0.610°	0.607°	.....	1.070°	480.25	513.9	2055.6
Carbon bisulfide . . . . .	24.10	0.622°	0.618°	.....	1.070°	480.25	513.9	2055.6
Average . . . . .								2055.6
Ethyl acetate . . . . .	24.10	0.727°	0.727°	.....	1.165°	485.78	565.9	2263.6
Ethyl acetate . . . . .	24.10	0.803°	0.799°	.....	1.165°	485.77	565.9	2263.6
Average . . . . .								2263.6
Methyl alcohol . . . . .	24.10	0.834°	0.834°	.....	0.591°	489.17	289.1	1156.4
Methyl alcohol . . . . .	24.11	0.964°	0.964°	.....	0.590°	489.12	288.6	1154.4
Average . . . . .								1155.4
Ethyl alcohol . . . . .	24.10	2.449°	2.455°	-0.04	0.640°	489.18	313.1	1252.4
Ethyl alcohol . . . . .	24.10	1.931°	1.873°	+0.42	0.642°	489.17	313.6	1254.4
Average . . . . .								1253.4
Isoamyl alcohol . . . . .	24.10	0.819°	0.824°	.....	0.841°	487.44	409.9	1639.6
Isoamyl alcohol . . . . .	24.10	0.665°	0.665°	.....	0.841°	487.42	409.9	1639.6
Average . . . . .								1639.6

For convenience in reference the final results for each solvent used in the first series are summarized in the following table:

TABLE VII.

Solvent.	Sp. ht.	Heat evolved for 1 mol. of pyridine. Cals.
None . . . . .	0.4455	2286.1
Acetone . . . . .	0.4886	2100.6
Water . . . . .	0.7307	1758.0
Benzene . . . . .	0.4441	2168.3
Carbon tetrachloride . . . . .	0.3603	2177.5
Nitrobenzene . . . . .	0.4173	2305.4
Carbon bisulfide . . . . .	0.3760	2055.6
Ethyl acetate . . . . .	0.4689	2263.6
Methyl alcohol . . . . .	0.5260	1155.4
Ethyl alcohol . . . . .	0.5271	1253.4
Isoamyl alcohol . . . . .	0.4967	1639.6

It will be observed that in but one instance, *viz.*, nitrobenzene, was the heat evolved greater than in the case where no solvent was used. It is also interesting to note that the value obtained with water as the solvent is considerably less than the values for the other solvents, excepting the alcohols, which are not comparable because of esterification. The considerable difference in the values obtained with different solvents seems to indicate that the role of the solvent cannot be neglected, *i. e.*, it is not justifiable to think of the reaction as taking place quite independently of the solvent.

In the case of the alcohols it was to be expected that the values would be quite different from the others since there is the possibility that the acetic acid would be partially taken up by the solvent, to form the corresponding ester, thus leaving the pyridine incompletely neutralized. In this connection it is interesting to note that in the case of ethyl acetate, where no such side reaction is possible, the value obtained is approximately the same as that where no solvent was used. Furthermore, as we go up in the series of alcohols the values become higher, as would be expected, since the tendency for the solvent to be reacted upon by the acid becomes less, and the reaction taking place is more nearly the action of the acid on the pyridine alone.

In the case of carbon bisulfide, benzene, ethyl acetate and carbon tetrachloride no side reactions would be expected, and in these cases, together with that of acetone, the values obtained are more nearly of the same order as the value obtained where no solvent was used, the differences probably being due in great measure to differences in heats of solution of the pyridine acetate formed. In order that the acetic acid may act upon the dissolved pyridine, the latter must be taken away from the solvent, and it is only natural that the pyridine would be held more tenaciously by some solvents than by others, and, therefore, that more energy would be required to effect this separation in some cases than in others. The pyridine acetate formed by the reaction in dissolving in different solvents would be likely to produce heat effects of different magnitude. It is therefore not at all surprising that the values fluctuate from solvent to solvent as they do.

#### Second Series.

In the second series of measurements the method of operation was changed so as to conform more nearly to the usual procedure, in that both the acid and the base were dissolved in the solvent before neutralization took place, the concentration of both the acid and base in the solvent being precisely the same. The concentration adopted was 1 mol. in 100 grams of solvent.

The requisite quantity of pyridine, *viz.*, 19.77 grams (0.25 mol.), was weighed out into the platinum bottle and exactly 25.00 grams of the

solvent added. The acid solution was prepared similarly and run into the jacketed acid compartment, a very slight, determined excess over the theoretical amount being added to make up for the loss of liquid remaining on the walls when this compartment was emptied into the bottle beneath. After the neutralization had taken place and the temperature data were obtained the solution in the platinum bottle was carefully weighed to ascertain whether the proper quantity of acid solution had been used, and also in order that the water equivalent of the solution formed might be calculated exactly. The remainder of the calculation was precisely the same as those in the first series and therefore need not be repeated.

The materials used were purified with great care, as before. The pyridine was digested with barium oxide<sup>1</sup> for a number of hours before dis-

TABLE VIII.

Solvent.	Weight of solution in calorimeter.	Initial temp. of NaOH.	Initial temp. of calorimeter.	Rise in temp. during expt.	Total water equivalent.	Sp. ht.
Water.....	480.0	0.766°	0.766°	1.660°	67.74	0.8087
Water.....	480.0	0.728°	0.730°	1.656°	67.73	0.8110
Average.....						0.8099
Acetone.....	420.0	0.567°	0.567°	2.705°	67.72	0.5048
Acetone.....	420.0	0.019°	0.016°	2.706°	67.66	0.5048
Average.....						0.5048
Chloroform.....	550.0	0.845°	0.849°	2.932°	67.61	0.3464
Chloroform.....	550.0	1.003°	1.003°	2.928°	67.71	0.3468
Average.....						0.3466
Carbon tetrachloride..	490.0	1.501°	1.501°	3.384°	67.75	0.3181
Carbon tetrachloride..	485.0	1.879°	1.881°	3.389°	67.79	0.3207
Average.....						0.3194
Benzene.....	400.0	0.661°	0.661°	3.133°	67.68	0.4347
Benzene.....	400.0	0.535°	0.535°	3.140°	67.61	0.4335
Average.....						0.4341
Ethyl acetate.....	400.0	1.289°	1.287°	2.954°	67.77	0.4710
Ethyl acetate.....	400.0	0.017°	0.017°	2.962°	67.68	0.4695
Ethyl acetate.....	400.0	0.760°	0.760°	2.946°	67.66	0.4731
Ethyl acetate.....	400.0	0.540°	0.539°	2.970°	67.71	0.4677
Average.....						0.4703

(It should be noted that in this series the temperatures of acid and base were so nearly the same that no correction was necessary.)

<sup>1</sup> Wilcox, *J. Physic. Chem.*, 14, 576 (1910).

tillation in order to dry it more thoroughly. The product so obtained boiled very constantly, the fraction used coming over between  $113.8^{\circ}$  and  $114.3^{\circ}$  at 729 mm.

The data concerning the specific heats of the solutions formed in the neutralization experiments appear in Table VIII. The quantity of hydrochloric acid used was 40.86 grams in every case.

In the following table are given the data concerning the determination of the quantity of heat evolved by the addition of 1 mol. of acetic acid + 100 grams of solvent to 1 mol. of pyridine + 100 grams of solvent. In each determination exactly 19.77 grams of pyridine + 25.00 grams of solvent were taken, and the weight of water in the calorimeter was, in each case, 450.00 grams:

TABLE IX.

Solvent.	Initial temp. of calorimeter.	Initial temp. of acid solution.	Rise in temp. during expt.	Sp. ht. of solution formed.	Weight of solution formed.	Total water equivalent.	Heat evolved.	Heat evolved for 1 mol.
Water.....	1.121°	1.121°	1.289°	0.8099	84.78	527.22	679.6	2718.4
Water.....	1.444°	1.446°	1.286°	0.8099	84.72	527.18	678.0	2712.0
Average.....								2715.2
Acetone.....	0.659°	0.660°	0.896°	0.5048	84.72	501.33	449.2	1796.8
Acetone.....	0.657°	0.656°	0.894°	0.5048	84.77	501.35	448.2	1792.8
Average.....								1794.8
Chloroform.....	0.668°	0.668°	1.206°	0.3466	84.51	487.85	588.4	2353.6
Chloroform.....	0.478°	0.478°	1.211°	0.3466	84.59	487.88	590.8	2363.2
Average.....								2358.4
Carbon tetrachloride....	0.818°	0.818°	1.138°	0.3194	84.74	485.63	552.5	2210.0
Carbon tetrachloride....	0.822°	0.822°	1.138°	0.3194	84.81	485.65	552.7	2210.8
Average.....								2210.4
Benzene.....	0.431°	0.431°	1.146°	0.4341	84.82	495.38	567.7	2270.8
Benzene.....	0.507°	0.506°	1.150°	0.4341	84.74	495.35	569.6	2278.4
Average.....								2274.6
Ethyl acetate.....	0.363°	0.365°	1.072°	0.4703	84.82	498.45	534.3	2137.2
Ethyl acetate.....	0.227°	0.227°	1.075°	0.4703	84.79	498.43	535.8	2143.2
Average.....								2140.2

(It will be noted that in all the determinations reported in the above table the temperatures of acid and base were so nearly the same that no correction was necessary.)

For convenience in reference the final results of this series are summarized in the following table:

TABLE X.

Solvent.	Sp. ht. of solution formed.	Heat evolved in neutralization, 1 mol. of pyridine.
Water.....	0.8099	2715.2
Acetone.....	0.5048	1794.8
Chloroform.....	0.3466	2358.4
Carbon tetrachloride.....	0.3194	2210.4
Benzene.....	0.4341	2274.6
Ethyl acetate.....	0.4455	2286.1
None <sup>1</sup> .....	0.4703	2140.2

It is very evident that the value of the thermal effect produced when pyridine and acetic acid react in different solvents is dependent on the solvent used. Indeed the differences are not very considerable except for the solvents water and acetone, but still they are far greater than the experimental error. Naturally the question arose as to whether these differences might not be due, in considerable part at least, to differences in the heat of solution of the resulting pyridine acetate in the differ-

TABLE XI.

## DATA CONCERNING MEASUREMENTS OF HEATS OF SOLUTION.

Solvent.	Weight of solution formed, Grams.	Total water equivalent, Grams.	Rise in temperature.	Heat evolved per mol. Cals.
Water.....	84.68	527.15	+0.913°	+1925.2
Water.....	84.77	527.21	+0.916°	+1931.6
Average.....				+1928.4
Acetone.....	84.47	501.20	-0.165°	-330.7
Acetone.....	84.75	501.34	-0.165°	-330.8
Average.....				-330.75
Chloroform.....	84.49	487.84	+0.618°	+1205.9
Chloroform.....	84.49	487.84	+0.618°	+1205.9
Average.....				+1205.9
Carbon tetrachloride.....	84.53	485.56	-0.055°	-106.8
Carbon tetrachloride.....	84.57	485.58	-0.055°	-106.8
Average.....				-106.8
Benzene.....	84.50	495.24	-0.103°	-204.0
Benzene.....	84.58	495.28	-0.106°	-210.0
Average.....				-207.0
Ethyl acetate.....	84.71	498.40	-0.119°	-237.2
Ethyl acetate.....	84.54	498.33	-0.118°	-235.2
Average.....				-236.2

<sup>1</sup> Value taken from first series, for comparison.

ent solvents. Consequently a series of determinations of the heat of solution of pyridine acetate in these different solvents were undertaken, the results of which, together with the data, appear in Table XI.

In these measurements the concentration of the final solution was the same as in the neutralization determinations. Fifty grams of the solvent were weighed out into the platinum bottle and the requisite quantity of pyridine acetate was placed in the jacketed compartment above so as to deliver 0.25 mol. into the solvent when temperature equilibrium had been attained.

The following table gives the values for the heats of neutralization after correction has been made for the heat absorbed or evolved in the process of solution of the pyridine acetate formed in the reaction, together with the uncorrected values, and the specific heats of the solutions:

TABLE XII.

## SUMMARIZED TABLE.

Solvent.	Sp. ht. of solution formed.	Apparent heat of neutralization. Cals.	Heat of solution of acetate. Cals.	Heat of neutralization (corrected). Cals.
None.....	0.4469	2279.6	.....	+2279.6
Water.....	0.8099	2715.2	+1928.4	+786.8
Acetone.....	0.5048	1794.8	-330.8	+2125.6
Ethyl acetate.....	0.4703	2140.2	-236.2	+2376.4
Benzene.....	0.4341	2274.7	-207.0	+2481.7
Chloroform.....	0.3466	2358.4	+1205.9	+1152.5
Carbon tetrachloride....	0.3194	2210.4	-106.8	+2317.2

It will be noted at once that the values for the heats of solution in the various solvents are not only very different but are sometimes of opposite sign, the individual values varying from +1928 cal. to -331 cal.

Furthermore, when the individual values for the heats of neutralization are corrected for the thermal effect produced by the solution of the pyridine acetate formed, the resulting numbers do not agree as well as before the correction was made. Naturally the percentage error is considerably greater in the measurements of the heats of solution, because the thermal effect is so small, yet these discrepancies are by no means to be attributed to experimental error, for the latter are of far lesser magnitude.

It therefore becomes evident that the amount of heat given up in the reaction between pyridine and acetic acid in these various solvents is not a constant quantity, and that the thermal effect is sometimes greater and sometimes less than when the two pure substances interact with each other in the absence of any solvent.

These differences cannot be explained by differences in electrochemical behavior, for in the case of all the solvents other than water and acetone the solutions are practically insulators. The specific conductivities of pyridine acetate solutions in the various solvents used were determined,

and the data appear in the following table. The concentration of the solutions was the same as that obtained in the neutralization measurements, and the temperature of observation was 20°:

Solvent	Spec. conductivity.
Water.....	1.427
Acetone.....	0.0005626
Chloroform.....	0.0001036
Carbon tetrachloride.....	0.00003338
Ethyl acetate.....	0.00001844
Benzene.....	0.00001210

The aqueous solution conducts well and the acetone fairly well. In the former the heat evolved is approximately one-third the heat evolved when no solvent is used, while in the latter the heat evolved with and without the solvent is about equal. If a low value for the heat of neutralization signifies electrolytic dissociation, then the acetone in chloroform should be highly dissociated and should conduct well, but it does not. If the considerable evolution of heat obtained in the solution of pyridine acetate in water is assumed to be largely due to electrolytic dissociation of the acetate, we must at the same time assume a large negative heat of dissociation when the acetate is dissolved in acetone, where a conducting solution is also obtained. This assumption of a positive heat of electrolytic dissociation of a substance in one solvent and a negative heat of electrolytic dissociation in another is hardly justifiable.

As to the completeness of the reaction between pyridine and acetic acid in the different solvents, it can be said that there are a number of indications that the reaction is complete. In the first place, pyridine is a fairly strong base. Also, it has been found that salts of organic bases of ring series are, in general, "hydrolyzed" (*i. e.*, split apart in solution) to but a very slight extent.

Reactions in solution which are not complete reach the point of equilibrium but slowly, as a rule. With all of the solvents here used, however, it was always observed that the final temperature was attained very quickly indeed—as fast as the thermometer could acquire the new temperature. In fact the final temperature was attained just as quickly when pyridine and acetic acid were used in the various solvents as when hydrochloric acid and sodium hydroxide reacted with each other in aqueous solution. The considerable evolution of heat and the promptness with which the heat is liberated would argue for the completeness of the reaction.

Unfortunately we have not many methods for determining the state of substances in solution, and of those which we have but few are applicable to the case in hand. The boiling point of pyridine acetate is too near



that of the solvents to make the ebullioscopic method applicable, and the cryoscopic method is available for but two of the solvents used, *viz.*, water and benzene. Measurements of the molecular weight of pyridine acetate in these two solvents were accordingly made by this method, the results of which appear in the accompanying table:

TABLE XIV.  
MOLECULAR WEIGHT OF PYRIDINE ACETATE IN BENZENE.  
(By depression of the freezing point.)

Weight of solvent. Grams.	Weight of solute. Grams.	Depression of F. P.	Molecular weight.
20.56	0.9010	1.652°	132.5
20.56	1.7634	3.635°	140.0
20.56	2.3574	4.159°	137.8
20.56	2.7497	4.751°	140.7
Average.....			137.8

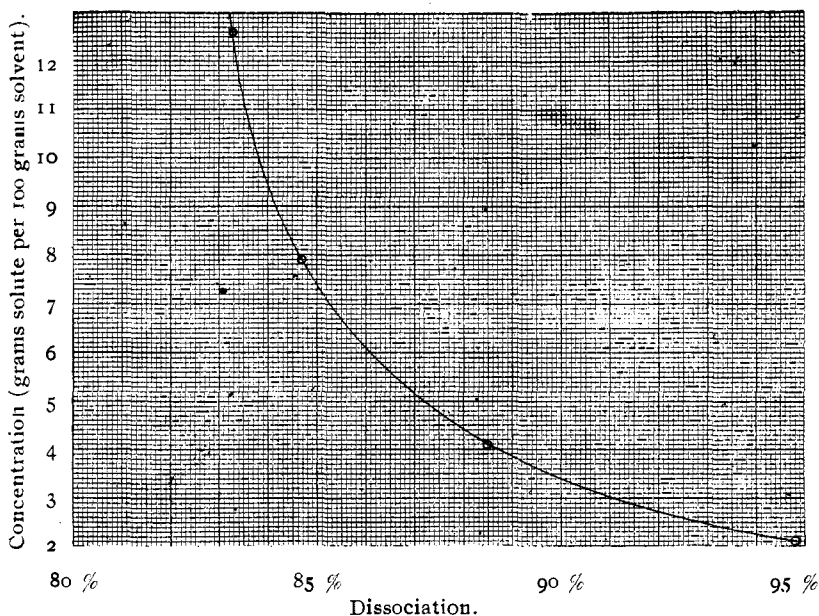
TABLE XV.  
MOLECULAR WEIGHT OF PYRIDINE ACETATE IN WATER AND THE "DEGREE OF DISSOCIATION" CALCULATED THEREFROM.  
(By depression of the freezing point.)

Weight of solvent. Grams.	Weight of solute. Grams.	Depression.	Molecular weight.	"Dissociation." Per cent.
25.85	0.5330	0.537°	71.42	94.8
25.85	1.0589	1.033°	73.76	88.5
19.73	1.5618	1.956°	75.27	84.7
19.73	2.4919	3.095°	75.90	83.3

It will be noted that in benzene solutions pyridine acetate showed a normal molecular weight—approximately 139—and that the individual determinations vary no more than do corresponding measurements of the molecular weight of such substances as sugar in water. Evidently pyridine acetate in benzene solutions is not split apart into its constituents but is a stable substance, and therefore the reaction between pyridine and acetic acid in benzene solutions may be considered as going to completion. While similar measurements are impossible in the case of acetone, ethyl acetate, chloroform, and carbon tetrachloride, it seems safe to conclude that in these cases also the reaction is complete, for they are substances which do not react with pyridine acetate nor with the base or acid composing it.

Where water is the solvent, the values for the molecular weight of pyridine acetate, in dilute solution, are approximately one-half the normal molecular weight, just as when any ordinary bivalent salt is used for such measurements in aqueous solution, and where, accordingly, a dissociation of the salt is assumed. The so-called degree of dissociation was calculated from the molecular weight determinations, and was found to decrease in a regular manner with increasing concentration, as it does

ordinarily. For the very dilute solutions the dissociation was practically complete. The change with concentration is shown in the accompanying graph:



These measurements tend to show that the condition in solution is what should be expected in case the reaction is complete.

Attempts were also made to measure the degree of dissociation of pyridine acetate in aqueous solution at  $0^{\circ}$  by the conductivity method, but this was found to be impracticable, as the values for the molecular (or equivalent) conductivity continually increased with dilution without ever attaining a maximum value, although the dilution was carried out to over a million liters. Similar difficulties are encountered with many other acetates, as is well known.

If we consider that neutralization is a process which includes only the acid and the base, then the differences in the final values for the heats of neutralization in different solvents are undoubtedly to be explained by the difference in the tenacity with which the reacting pyridine and acetic acid are held by the solvents in question. It is evident that the energy required to separate them from the solvent must be considerable in some cases.

If, on the other hand, the solutions of acid or of base in the particular solvent in question be considered as a new chemical complex, *i. e.*, a new chemical substance not following the law of definite proportions,<sup>1</sup> but

<sup>1</sup> Kahlenberg, *Science*, 31, 41 (1910).

with definite acidic and basic properties, it is not at all strange that the heat of neutralization should vary considerably from solvent to solvent.

#### Summary.

1. Measurements of heats of reaction in non-aqueous solutions have been made and reported for the first time.

2. The amount of heat liberated for a given reaction in different solvents has been found to vary greatly from solvent to solvent.

3. These considerable differences cannot be explained as being due to any electrolytic dissociation of the acetate, nor are they due to differences in the heats of solution of the acetate in the different solvents.

4. The chemical nature of the solvents does not seem to give any clue as to the magnitude of the heat of neutralization in the cases investigated, nor of the magnitude or sign of the heat of solution of the resulting acetate.

It is proposed to continue this line of work, using such other reactions as may be found available.

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## THE VAPOR PRESSURE OF HYDRATES, DETERMINED FROM THEIR EQUILIBRIA WITH AQUEOUS ALCOHOL.

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The measurement of the small pressures of dissociation common to hydrated salts is a problem that presents many difficulties and has been the subject of numerous researches. The most general plan has been to place the salt in the Torricellian vacuum, and measure the depression of the mercury of the barometric column. On this plan were the methods of Debray,<sup>1</sup> Wiedemann,<sup>2</sup> Pareau,<sup>3</sup> Lescoeur,<sup>4</sup> and others, using various means for complete removal of the air from the barometric space. Lescoeur<sup>4</sup> also devised a method for measuring these pressures by getting the dew-point of the atmosphere which was in equilibrium with the salt in a closed space, and the vapor pressure of water at that dew-point gave the required pressure. Müller-Erzbach,<sup>5</sup> who has contributed a great deal of work on this subject, attacked the problem in two ways: One way, which he afterwards abandoned, was by comparing the losses of water from tubes containing water and the hydrate respectively, when placed for a time over concentrated sulfuric acid. This gave him the

<sup>1</sup> *Compt. rend.*, 64, 603 (1867).

<sup>2</sup> *Pogg. Ann.*, Jubelband, 474 (1873).

<sup>3</sup> *Wied. Ann.*, I, 55 (1877).

<sup>4</sup> *Ann. chim. phys.*, [6] 16, 378 (1889).

<sup>5</sup> *Ber.*, 14, 1093 (1881); *Z. physik. Chem.*, 2, 113 (1888).