

ON AN IMPROVED METHOD OF DETERMINING LATENT HEAT OF EVAPORATION AND ON THE LATENT HEAT OF EVAPORATION OF PYRIDINE, ACETONITRILE AND BENZONITRILE

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The latent heats of evaporation of liquids at their boiling-points have become of much greater importance since the determination of molecular weights by means of the boiling-point method has come into general use. Arrhenius and Beckmann¹ have shown that the so-called boiling-point constant of a solvent, i. e. the rise in the boiling-point caused by one gram-molecule of solute in 100 grams of solvent may be calculated according to the formula, $K = \frac{0.02 T^2}{H}$, where K is the boiling-point constant, T the absolute boiling-point, and H the latent heat of evaporation. These investigators were led to develop this formula by van't Hoff's² deduction of the formula for the freezing-point constant, which has exactly the same form as the formula above given, the K being in this case the freezing-point constant, T the absolute freezing-point and H the latent heat of fusion.

In 1897, Alfred Werner³ investigated the molecular weights of a number of inorganic salts in pyridine and benzonitrile as solvents by means of the boiling-point method. Among these

¹ Zeit. phys. Chem. 4, 550 (1889).

² Ibid. 1, 481 (1887).

³ Zeit. anorg. Chem. 15, 1 (1897).

salts was silver nitrate. In these solvents silver nitrate yielded normal molecular weights, and yet these solutions were found to be fairly good conductors of electricity.¹ Again Dutoit and Friderich² determined the conductivity of solutions of silver nitrate in acetonitrile and found that the conductivity was of the order of that of the aqueous solutions. It was consequently of interest to ascertain the molecular weight of silver nitrate in acetonitrile. This work, together with the verification of Werner's results, was undertaken in this laboratory and will be reported upon soon: suffice it to say in this connection, that Werner's experimental work has been confirmed. The boiling-point constants used by Werner were empirically determined by assuming the molecular weight of diphenylamine to be normal in these solvents, and then calculating the K from the well-known formula, $M = 100 K \frac{S}{\Delta L}$, where M is the molecular weight of the solute, S the amount of solute, Δ the rise in boiling-point, and L the amount of solvent. Inasmuch as salts dissolved in these solvents generally yield normal molecular weights and yet conduct electricity well—a fact which cannot be harmonized with the theory of electrolytic dissociation—it seemed highly desirable that the boiling-point constants of these solvents should be determined not simply empirically, or calculated according to the Tronton-Schiff rule,³ but that they should be deduced from the latent heats of vaporization of these solvents according to the formula of Arrhenius and Beckmann (above given) which in turn is founded upon thermodynamics.

In seeking a method by means of which to determine the latent heats of evaporation of these liquids, the method of Berthelot⁴ and also that of Schiff⁵ suggested itself, inasmuch as both

¹ Kahlenberg and Lincoln. *Jour. Phys. Chem.* **3**, 33 (1889); also Lincoln. *Ibid.* **3**, 457 (1889). Solutions of other salts in these solvents also conduct electricity to some extent.

² *Bull. Soc. Chim. Paris*, (3) **19**, 391 (1893).

³ The calculation according to this rule was also made by Werner, l. c.

⁴ *Comptes rendus*, **85**, 647 (1877); also *Mécanique Chimique*, **8**, 288-299. *Liebig's Ann.* **234**, 338 (1886).

of these methods are simple and admit of operating with relatively small quantities of substance. The peculiarity of Schiff's apparatus consists of a trap which he interposes between the retort and the condenser, which is located in the calorimeter. The object of this trap is to prevent any vapors that may be prematurely condensed to liquid from getting into the condenser. This trap is reproduced in the accompanying Fig. 1 and needs

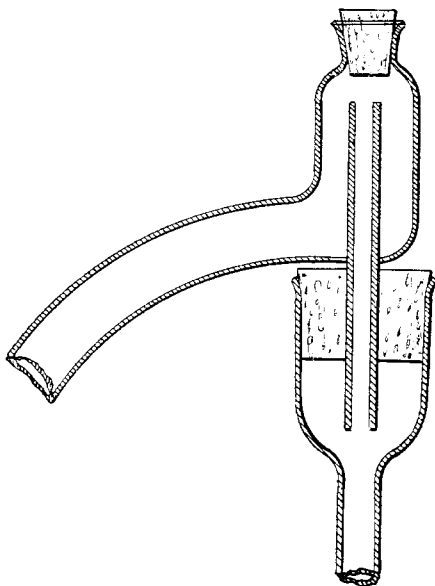


Fig. 1

no further explanation. Schiff constructed this part of his apparatus of silver and the calorimeter and condenser of thin silver-plated brass. Schiff states that he assured himself that no prematurely condensed vapors got into the condenser, by using a glass trap; he does not, however, state with which liquid he made this test. Inasmuch as he tested his apparatus with water, I assume that it is with this liquid that he made the test. I have repeated Schiff's experiment with water and am able to confirm his statements fully. However, when I attempted to operate with pyridine, which has a higher boiling-point than water and

at the same time a much lower latent heat of vaporization and specific heat, I found that a considerable amount of pyridine had to be condensed in the trap before the latter assumed the temperature of the vapor, and that finally so much liquid was formed that some of it ran over into the condenser, it being sufficiently prevented from running back into the retort by the copious vapors that were being evolved in the latter during the process of boiling.

After this experience it was decided to resort to the ingenious method of Berthelot. The apparatus was constructed as described by Berthelot¹ and the method of procedure that he outlined was closely followed, special care being taken to make the proper correction for the heating of the calorimeter by direct radiation from the burner. A Beckmann's thermometer was employed which had been carefully compared with a normal thermometer calibrated by means of an air thermometer at the Physikalisch-technische Reichsanstalt at Charlottenburg. The thermometer was carefully screened from the hot retort by means of an asbestos screen; and an effective stirrer was used to stir the calorimeter water. These latter details are the only ones in which the apparatus differed from that of Berthelot.

In order to test the apparatus as to whether it was in good working condition, preliminary experiments were made in finding the latent heat of evaporation of water. (Berthelot originally thus tested his apparatus with water, and after finding a value for this substance that agreed sufficiently well with that found by Regnault in his classical experiments, he considered his apparatus thoroughly approved.) Three determinations in each of which about nine and one-half grams of water were evaporated at a barometric pressure of 741 mm, yielded the following results as the latent heat of evaporation of one gram at the boiling-point: 538.4 cal, 535.2 cal, 539.5 cal — average 537.7 cal. (Berthelot found 536.2 and Regnault 536.6.) It may be well to state in this connection that the capacity of the calorimeter was 1120 cc approximately, and that the water value of calorimeter and

¹ l. c.

other utensils was 26.54 cal, thus making the observed rise of temperature about five degrees in each case. After finding these results, I felt that the apparatus worked fairly satisfactorily; nevertheless I thought it advisable to subject it to a further test by determining the latent heats of at least two other substances that could easily be obtained in the pure state, and as such ethyl alcohol and benzene were selected. The latter was Kahlbaum's crystallizable thiophene-free product and had a remarkably constant boiling-point. The alcohol was thoroughly dried by standing over anhydrous copper sulphate for a long time; it was then distilled, and finally treated with metallic sodium and redistilled. Two determinations were made with the alcohol at 744 mm of barometric pressure, about twenty grams being evaporated in each case, thus raising the temperature of the calorimeter about five degrees. The results obtained are 234.7 cal and 232.5 cal respectively, as the latent heat of evaporation of one gram at the boiling-point; whereas Andrews¹ found 202.4 cal, Wirtz² 205.07 cal, and Marshall and Ramsay³ 216.5 cal. It is evident from this that my results were considerably too high. With benzene, four determinations were made at a barometric pressure of 741 mm. The amounts evaporated varied between 32 and 35 grams, thus giving a rise of about 3.7 degrees in the temperature of the calorimeter in each case. The results obtained are 106.5 cal, 106.3 cal, 99.3 cal, and 101.5 cal respectively for the latent heat of evaporation of one gram at the boiling-point. Schiff⁴ found 93.43 cal, Wirtz 92.91 cal, and Griffiths and Marshall⁵ 94.37 cal, which indicates that my results were again too high. It will be further noted that while two of the results obtained with benzene agree well, the other two are considerably lower. Again the two results obtained with alcohol differ rather more than they ought to for two perfectly similar experiments. The agreement of the three results obtained for water is also hardly

¹ Pogg. Ann. 75, 501 (1848).

² Wied. Ann. 40, 438 (1890).

³ Phil. Mag. [5] 41, 49 (1896).

⁴ l. c.

⁵ Phil. Mag. [5] 41, 37 (1896).

as good as might have been expected. It is clear from these experiments that while acceptable results may be obtained with Berthelot's apparatus, as in the case of water, for instance, in other cases, those of alcohol and benzene, for example, the results may be much too high. The cause of this was soon found in the superheating of the vapors just before they enter the condenser, as they pass from the retort through that part of the tube which goes through the center of the ring burner.¹ By covering the flame of the ring burner with a wire gauze, as is done in the experiment, and holding a thermometer in the zone through which the vapors must pass in going from the retort to the condenser, I have convinced myself that the temperature of this zone generally becomes much higher than the boiling-points of the liquids commonly tested, during the time of experimentation. This was found to be the case even after the thermometer had been protected by two small concentric cylinders of asbestos paper. Now obviously the extent of the superheating would depend upon the specific heat of the vapors, upon the rate with which they pass through this hot zone (i. e., upon the rate of boiling) and upon the height of the flame and the exact position of the retort. It is very difficult to get the retort in exactly the same position each time, and it is also difficult to get the height of the flame exactly the same in different experiments; it is to these two circumstances that the variations in the results of individual experiments with one and the same substance are to be ascribed. It may be well to state here that I have always endeavored to have the retort in as nearly the same place as possible and the flame of the same height. It is clear that when the vapors have a high specific heat the superheating would be relatively less than when the specific heat is low, and so it becomes evident why fairly acceptable results were obtained with

¹ The reader will understand this explanation perfectly by referring to the cut of Berthelot's apparatus in *Comptes rendus*, **85**, 647 (1877), or *Mécanique Chimique* I, 292, or Müller-Pouillet's *Lehrbuch der Physik*, 9 Aufl., 2 H., 410. As these books are generally available, it seemed unnecessary to reproduce the cut in this connection.

water and not with the two other substances. After this experience, it was concluded that there is great uncertainty in making determinations of latent heat of evaporation with Berthelot's apparatus to say the least. The fact that superheating of the vapors may readily occur in working with this apparatus was also clearly pointed out by Schiff¹ who, however, did not assure himself by actual experiment that such superheating does occur.

A new apparatus was now constructed which, while retaining the good points of Berthelot's apparatus, did not have the objectionable features. The real point in which the new apparatus differs from that of Berthelot lies in the construction of the retort. The latter is so made that the heating is accomplished by means of an electric current instead of with a flame. The construction of this retort is shown in Fig. 2, in which it is represented rather large in proportion to the rest of the apparatus so as to show the details somewhat better. The retort consists of a test-tube 17 cm long and 3.5 cm in diameter, into the bottom of which is fused the tube *a*, which fits into the condenser with a ground glass joint at *b*. At *c* there are two large lateral openings. The glass tubes *e* and *f* pass through a good cork *d*. Into these tubes are fused the ends of the spiral of platinum wire *g*. This spiral consists of about 40 cm of fairly stout platinum wire, to the ends of which are welded short heavy pieces of platinum rod; and these rods in turn are fused into the glass tubes. Long, rather heavy copper wires pass down into the glass tubes at the bottom of which they are connected with the ends of the platinum rods by means of a few drops of mercury. Two small binding screws serve to connect the copper wires with the ends of other wires that lead to the source of electricity, as indicated in the cut. It is obviously essential that the lower end of the tube of the retort which connects with the condenser at *b* be made short so as to guard against premature condensation of the vapors in this part of the tube. In the figure this protruding part of the tube has been represented rather longer relatively

¹ I. c.

than it ought to be. The calorimeter is covered with a heavy piece of asbestos board coated with tin foil and shaped so as to fit snugly. The small space between the bottom of the retort and the cover of the calorimeter is nicely packed with cotton

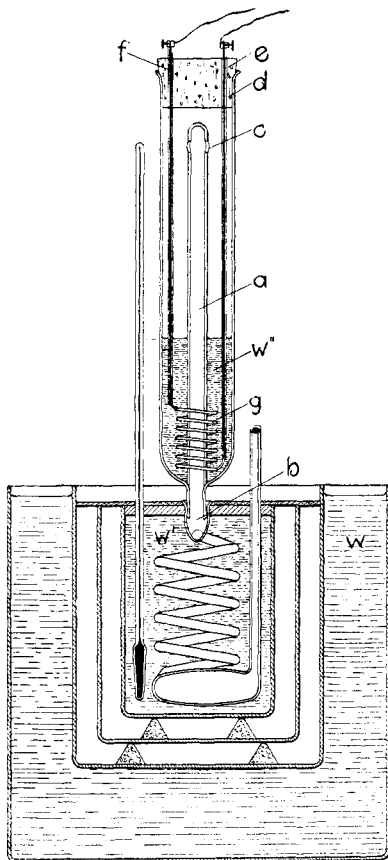


Fig. 2

batting, and in fact the whole retort is enclosed in cotton batting during the progress of the experiment, a few peep-holes only being left through which the boiling can be observed. This cotton batting covering of the retort, which has not been represented in the figure, serves very effectively to screen the thermome-

ter and calorimeter from the hot retort; at the same time it prevents the latter from becoming chilled, thus materially aiding the progress of the experiment. This screen can be made very easily by gluing a layer of cotton batting on thin asbestos paper. By placing the screen so as to rest on the calorimeter cover it may be bent so as to enclose the retort, remaining in position without any further support.

The calorimeter of about 1250 cc capacity was made of very thin nickel-plated sheet copper. It was somewhat elliptical in form, which permitted the thermometer to be placed at a greater distance from the retort than would have been possible by using a dish of the same capacity but of circular cross section. The stirrer, which is not represented in the figure, was made of thin copper. It was provided with a hard rubber handle, by means of which an up and down motion was imparted to it. The parts

of the stirrer were so shaped as to ensure very thorough mixing of the calorimeter water. The thermometer employed was the Beckmann instrument above mentioned. The condenser was made of glass. It is no doubt better to construct it of metal, provided the latter is not attacked by the liquids to be tested. Platinum is of course the best material out of which to make the condenser, but it is so very costly.

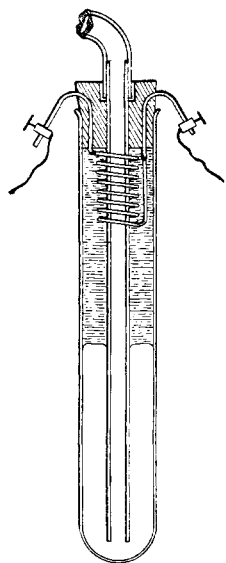


Fig. 3

Figure 3 shows a simpler form of the retort. Here the test-tube is inverted, the lower end being closed with a good rubber stopper through which the glass tube passes, connecting with the condenser as indicated. The ends of the spiral of platinum wire are welded to rather heavy platinum rods which pass through the rubber stopper as represented in the figure. The ends of these

rods are connected with the wires leading to the source of electricity by means of small binding screws. This form of the

retort is much simpler than that in Fig. 2, and it is consequently to be preferred whenever the liquid tested does not attack the stopper. Rubber being a poor conductor of heat, the rubber stopper itself serves to screen the calorimeter from the hot liquid in the retort. The spiral wires need not necessarily be made of platinum in all cases, any metal will of course answer, provided it is ductile and not attacked by the liquid to be tested. The apparatus fitted out with the retort pictured in Fig. 3 may be used for a goodly number of liquids; it is so simple in construction and so easily operated that it is to be recommended for use in laboratories where students are taught physical and physico-chemical measurements.

In the case of the retort represented in Fig. 2 the ends of the platinum spiral might be fused into the sides of the test-tube and the top of the latter closed as in the form of Fig. 3, thus avoiding the use of cork. This arrangement, though no doubt better while it lasts, makes it more difficult to fill the retort, and above all the latter becomes very breakable, and hence this form is hardly to be recommended. It needs scarcely to be stated that but little change in the apparatus is necessary to make it available for measuring latent heats of vaporization at other than atmospheric pressures.

A current of from 8 to 15 amperes, according to the nature of the liquid tested, served to heat the liquid to boiling. This current was taken from twelve large storage cells, representing then an E. M. F. of about 24 volts. A rheostat placed in the circuit permitted the current to be adjusted as desired, the strength of the latter being indicated by a Weston ammeter. The liquids were brought to a boil rather slowly, but were kept boiling vigorously when once ebullition had begun. The boiling usually continued from three to five minutes. The liquids were not evaporated so far as to expose the platinum spiral. The amount of liquid evaporated was ascertained by weighing both the retort and the condenser on an analytical balance before and after the experiment. The weights thus obtained act as a check upon each other; they generally agreed to

within a few centigrams. The practice of Berthelot was followed in taking the average of the two weights. Corrections for loss of heat by radiation during the progress of the experiments were made according to the well known method of Regnault-Pfaundler. The temperature of the room during all the experiments was $18^{\circ} \pm 0.5^{\circ}$. The total water value of calorimeter, condenser, stirrer and thermometer plus the calorimeter water was 1190.19 grams. It was found that by screening the calorimeter carefully from the retort as above described the temperature of the former was not appreciably raised by direct radiation of heat from the latter, so that no special correction had to be made, which is absolutely necessary in working with Berthelot's apparatus. In thus heating the liquid by means of electricity, there is no tendency to bumping; the boiling may be perfectly regulated at will; and there is no flame, an object of a very high temperature, in the neighborhood of the apparatus. We have here then all the advantages of Berthelot's apparatus without its disadvantages, the danger of superheating the vapors in particular being entirely removed.

Before working with substances of unknown latent heats of evaporation, the apparatus was thoroughly tested with substances readily obtainable in the pure state, whose heats of evaporation have been determined by other investigators. As such substances water, ethyl alcohol, benzene, and ethyl iodide were selected. These substances represent various heats of vaporization, ranging from over 500 to less than 50. The water used was the distilled water of the laboratory; its specific conductivity was 3×10^{-6} . The alcohol was dried with anhydrous copper sulphate for days; it was then distilled. Finally it was treated with metallic sodium and redistilled. The benzene was Kahlbaum's crystallizable, thiophene-free product. It had a remarkably constant boiling-point, -79.5° at 750 mm. The ethyl iodide was also of Kahlbaum's make. It was dried with fused calcium chloride and then redistilled. At 752 mm barometric pressure it boiled at 71.4° . In addition to these substances the latent heats of vaporization of two esters, ethyl

formate and ethyl acetate, were also determined. These substances are by no means easily obtained in a very pure condition, it being difficult to free them entirely from water and especially from traces of free alcohol; however, as I have worked with them in testing the apparatus, I thought it best to give the results obtained. The ethyl acetate was of Schuchardt's manufacture. It was repeatedly dried with fused calcium chloride and finally redistilled, when it boiled fairly constantly at 75° at 744 mm barometric pressure. The ethyl formate was prepared by treating very concentrated formic acid with the proper quantity of absolute alcohol together with some strong sulphuric acid and distilling the mixture, after having digested it for a time on the water-bath. The product was repeatedly dried with fused calcium chloride and finally redistilled. It boiled constantly at 53.5° under a barometric pressure of 730 mm. In all work on latent and specific heat it is highly desirable to get the substances as pure as possible, especially free from water.

The results obtained with these substances are given in Table I., the headings of which are self-explanatory. It was thought best to indicate in each case the actual amount evaporated and to give the change in temperature suffered by the calorimeter, as it will aid the reader in forming an opinion as to the accuracy of the work. The specific heats used in the calculations are also indicated; they have been taken from the tables of Landolt and Börnstein. To facilitate comparison, the results of other observers are placed in the last column. Regnault's results refer to the "total" heat of vaporization, i. e., the specific heats between 0° and the boiling-points have not been subtracted.

After having obtained the results in Table I., the ap-

¹ REFERENCES: Andrews. Pogg. Ann. 75, 501 (1848). Brix. Pogg. Ann. 55, 341 (1842). Despretz. Ann. Chim. Phys. 24, 323 (1823). Favre and Silbermann. Ann. Chim. Phys. (3) 37, 461 (1853). Schall. Ber. Chem. Ges. Berlin, 17, 2199 (1884). Wirtz. Wied. Ann. 40, 438 (1890). Louguine. Ann. Chim. Phys. (7) 7, 251 (1896). Marshall and Ramsay. Phil. Mag. [5] 41, 49 (1896). Regnault Mémoires de l'Acad. 26, 761 (1862). Schiff. Liebig's Ann. 234, 338 (1886). Griffiths and Marshall. Phil. Mag. [5] 41, 37 (1896). Berthelot. Ann. Chim. Phys. (5) 12, 529 (1877). Berthelot and Ogier. Comptes rendus, 92, 669 (1881).

Determining Latent Heat of Evaporation

TABLE I

Substance	Barometer	Amount evaporated	Rise in temp. of calorimeter	Specific heat	Latent heat of evaporation for one gram	Results of other observers ¹
Ethyl alcohol	751 mm	25.264 g	5.241°	0.680	203.0	202.4 Andrews; 227 Brix; 208 Despretz; 208.9 Favre and Silbermann; 206.4 Schall; 205 Wirtz; 201.4 Longuinine; 216.5 Marshall and Ramsay.
"	"	24.750	5.130	"	203.1	
Av.					203.05	
Benzene	750 mm	35.476	3.514	0.4277	93.2	109 Regnault; 93.4 Schiff; 92.9 Wirtz; 94.37 Griffiths and Marshall.
"	"	31.399	3.102	"	93.9	
Av.					93.55	
Water	739	12.471	6.422	1	535.6	535.9 Andrews; 636.6 Regnault; 540 Brix; 531 Despretz; 536 Favre and Silbermann; 536.2 Berthelot; 537.7 Schiff; 536.6 Marshall and Ramsay.
"	743	12.715	6.517	"	534.0	
"	740	11.101	5.725	"	537.6	
"	726	11.753	6.028	"	535.6	
Av.					535.7	
Ethyl iodide	752	56.140	2.578	0.164	46.2	58.95 Regnault; 46.87 Andrews.
"	747	64.564	2.940	"	45.8	
Av.					46.0	
Ethyl formate	730	30.927	3.022	0.513	99.7	105.3 Andrews; 100.7 Berthelot and Ogier; 92.2 Schiff; 94.4 Marshall and Ramsay.
"	724	30.261	2.924	"	98.0	
Av.					98.9	
Ethyl acetate	744	31.787	3.111	0.474	90.8	92.7 Andrews; 83.1 Schiff; 84.3 Wirtz; 88.1 Marshall and Ramsay.
"	744	37.420	3.656	"	91.0	
Av.					90.9	

paratus was regarded as sufficiently tested. The latent heats of evaporation of pyridine, acetonitrile and benzonitrile were therefore next determined.

The pyridine used was obtained from Kahlbaum. It was thoroughly dried with fused caustic potash and then distilled, the fraction boiling between 116° and 117.5° being used in Experiments 1, 2, and 3, — see Table II. I then sought to obtain a very pure sample of pyridine by means of the process described by Ladenburg.¹ Accordingly about 250 cc of the above-mentioned fraction of pyridine was dissolved in the required amount of dilute hydrochloric acid, and this solution was treated with enough mercuric chloride to form the double salt. Upon cooling the hot solution, this salt crystallizes out in beautiful needles. The crystals were thoroughly drained, redissolved in boiling water and again allowed to crystallize out in the cold. This process was once more repeated. These crystals were then distilled with caustic potash. The pyridine so obtained was redistilled and dried with fused caustic potash until no more of the latter would liquefy. The sample was then redistilled, and again allowed to stand over fused caustic potash. Not even the finest edges of the latter suffered any change in the liquid for days. The pyridine was then once more distilled, when it was found that a very large fraction of it passed over at 114° . There was, however, a small fraction that came over below 114° and also one above that temperature. Ladenburg states that after he had purified his sample its boiling-point remained constant at 114° to the last drop. Ladenburg only purified 20 cc in this manner, whereas I had about ten times that amount after purification. To be sure it is rather inconvenient and laborious to purify such a large quantity by this method. The fraction that came over at 114° was redistilled and it was found that it boiled quite constantly at the temperature mentioned under a barometric pressure of 734 mm. This sample was used in Experiments 4 and 5 of Table II. The odor of this sample was not as disagreeable as that of the unpurified pyridine.

¹Liebig's *Annalen*, 247, 1 (1888).

The acetonitrile used was also of Kahlbaum's manufacture. A small quantity of phosphorus pentoxide was added to the substance and it was then redistilled. Two determinations, Experiments 6 and 7, Table II., were made with this sample. A large excess of phosphorus pentoxide was then added to this acetonitrile and it was again distilled. This sample was used in Experiments 8 and 9, Table II. Finally this acetonitrile was once more treated with an excess of phosphorus pentoxide and redistilled. This last sample was used in Experiments 10 and 11 of Table II. It will be seen by referring to the table that the first sample gave a latent heat that is somewhat higher than the others; it was very likely not quite free from water. The samples after the second and third treatment, on the other hand, it will be noted, gave the same results within the limit of error of experimentation.

Two samples of benzonitrile were used. One was obtained from Kahlbaum and the other from Schuchardt. Their boiling-points were constant, and practically the same, — 189° at 748 mm of barometric pressure. The results obtained with these two samples are given in Experiments 12 and 13, respectively, of Table II.

In order to calculate the latent heats of evaporation of these liquids at their boiling-points, their specific heats had to be determined. This was done by means of the simple and excellent method of Berthelot.¹ The averages of three closely agreeing determinations gave the following results: specific heat of pyridine 0.4313 between 108° and 21° ; specific heat of acetonitrile 0.5333 between 66° and 21° ; specific heat of benzonitrile 0.4369 between 180° and 22° . Table II. now follows, the headings of which require no further explanation.

Inasmuch as Experiments 4 and 5 were made with the purified pyridine, the result 104.0 is to be regarded as the correct value of the latent heat of evaporation of pyridine at its boiling-point, 114° .

Experiments 8 to 11 were made with thoroughly dry

¹ *Mécanique Chimique*, I, 275-278.

TABLE II¹

No. of Expt.	Substance	Barometer	Boiling-point	Amount evaporated	Rise in temp. of calorimeter	Specific heat	Latent heat of evaporation of one gram
1	Pyridine	741 mm	116°-117.5°	30.289	3.726°	0.4313	101.1
2	"	"	"	29.084	3.468	"	101.9
3	"	742	"	32.035	3.802	"	101.3
4	"	735	114	30.754	3.719	"	Av. 101.4
5	"	"	"	27.684	3.355	"	104.1
6	Acetonitrile	742	81	27.772	4.896	0.5333	103.9
7	"	"	"	25.806	4.562	"	Av. 104.0
8	"	735.5	80.5	28.506	4.908	"	180.7
9	"	"	"	25.055	4.321	"	180.9
10	"	733	"	28.338	4.833	"	Av. 180.8
11	"	"	"	25.200	4.308	"	173.4
12	Benzonitrile	748	189	29.878	4.052	0.4369	173.9
13	"	"	"	25.456	3.525	"	173.5
							173.8
							Av. 173.6
							88.0
							87.4
							Av. 87.7

acetonitrile which had an exceedingly constant boiling-point. The average of these results, 173.6, is to be regarded as the correct value of the latent heat of evaporation of acetonitrile at its boiling-point, 80.5°.

Finally, Experiments 12 and 13 give the average value 87.7 as the latent heat of evaporation of benzonitrile at its boiling-point, 189°.

The boiling-point constant K for pyridine was empirically determined to be 30.07 by Werner. The latter also calculated K according to the Trouton-Schiff rule. The result he obtained was $0.00096 \times 389 \times 79 = 29.5$. According to the Arrhenius-Beckmann formula as given above, $K = \frac{0.02 (114 + 273)^2}{104.0}$

28.8. The agreement of these values for K must be pronounced fairly satisfactory.

Werner's empirical determination gave 36.55 as the boiling-point constant of benzonitrile. According to the Trouton-Schiff rule Werner calculated K to be $0.00096 \times 463 \times 103 = 45.70$, which does not agree at all with the empirically determined value. Werner states plainly that he is not able to explain this discrepancy. The application of the Arrhenius-Beckmann formula gives $K = \frac{0.02 (189 + 273)^2}{87.7} = 48.67$, a value which corresponds more nearly to the one deduced according to the Trouton-Schiff rule.

For acetonitrile the constant K calculated according to the Arrhenius-Beckmann formula is equal to $\frac{0.02 (80.5 + 273)^2}{173.6}$, or

¹ After the results contained in this table had been obtained, it was found that W. Louguinine [Archiv. des Sciences Naturelles de Genève, 9, 5-26 (1899)] had also determined the latent heats of evaporation of these three substances, his results being as follows: 101.39 for pyridine, 170.68 for acetonitrile, and 87.71 for benzonitrile. The latter value agrees well with that in the table. The figure for pyridine agrees well with that of the sample not specially purified. It may be well to state in this connection that the presence of picoline in pyridine lowers the latent heat of evaporation. The measurements for picoline have recently been made in this laboratory, and the results will be reported together with others in the near future. Louguinine's value for acetonitrile is about 1.8 percent lower than that given in the above table.

14.39. According to the Trouton-Schiff rule, $K = 0.00096 \times 353.5 \times 41 = 13.91$. The agreement must be pronounced fairly satisfactory. Werner has not made any boiling-point determinations using acetonitrile as solvent, and has consequently not found the constant of this solvent. I have, however, determined the boiling-points of solutions of various substances in acetonitrile, and while the complete presentation and discussion of the results obtained must be reserved for another article, it may be well to state in this connection that an average of five determinations in which diphenylamine was used as solute, yielded 19.69; on the other hand, an average of four determinations in which naphthalene was used as solute, gave 12.83 as the value of the boiling-point constant. The latter corresponds more nearly to the value obtained according to the Arrhenius-Beckmann formula. It is interesting to note that while the empirical constant for phenylcyanide (when diphenylamine is solute) is less than that calculated from the latent heat of evaporation, the empirical constant for methyl cyanide (when diphenylamine is solute) is much greater than that calculated from the latent heat of evaporation. This point will be discussed further in the article on molecular weight determinations in these solvents, which will be published ere long, when the bearing of these investigations upon the theory of electrolytic dissociation will also receive consideration.

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