creased.[13] The predominating effect seems, therefore, to be a "tightening." The suggestion occurs in explanation that possibly the extra electrons when introduced in most cases tend to enter with the other electrons into stable groups or configurations which could not be formed to the same extent without them.

Summary

The apparent heat capacity of electrons, their partial molal heat capacity and the Thomson effect are defined and compared, and the conditions under which they might be numerically equal discussed. The available evidence is examined to determine whether such equality exists in actual cases. It is concluded that for a large majority of the metals studied the apparent heat capacity is not nearly equal to the Thomson effect, and probably not to the partial molal heat capacity. From comparisons of the magnitude of the last quantity with the first, certain tentative conclusions are drawn relating to the specific effects upon interatomic constraints of increasing the negative charge of metals.

BERKELEY, CALIFORNIA

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

THE ACCURATE MEASUREMENT OF HEATS OF VAPORIZATION OF LIQUIDS

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That the accurate measurement of heats of vaporization is one of considerable difficulty, is evident from the widely divergent values found in the tables of physical constants. The methods available may be divided into two general classes: (1) condensation methods and (2) evaporation methods.

One great difficulty with the condensation method is the correction required for the heat given out by the condensed liquid cooling from the boiling temperature (temperature of condensation in the calorimeter) to the temperature of the calorimeter. This correction involves an accurate knowledge of the specific heats of the liquids used over this range of temperature and such data are no more accurately known than the heats of evaporation which are being measured. The direct evaporation methods, which do not involve such a correction, have a distinct advantage in this respect. Also, since electrical quantities are susceptible of very accurate measurement, the direct method seems preferable. Another great

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[13] Whether these assumed reactions occur entirely in the surface regions of the metals or in the interior is not important from the present standpoint.

It should be noted also that other languages, including that of the quantum theory, may be used in describing these results.

difficulty in condensation methods is the prevention of premature condensation of the vapor before it enters the condensing chamber in the calorimeter. However, this error may be determined.[1]

In developing the direct electrical method used in this research the desirable features of certain methods employed in the past were incorporated and a number of sources of errors were eliminated. Obviously, an apparatus suitable for making accurate measurements of the heats of vaporization of a large number of liquids in a reasonable length of time should fulfil certain requirements, among which the following are important: (1) it should be as simple and compact in design as possible; (2) excessive amounts of liquids should not be required; (3) the construction should be such that the weight of the liquid distilled may be ascertained with certainty; (4) the vaporizer proper must be maintained under adiabatic conditions in order that all of the electrical energy expended may be used exclusively in producing vaporization of the liquid; (5) it must be possible to measure current, resistance and time accurately, in order to determine exactly the energy expended in the vaporization of a given weight of liquid.

Brown's apparatus[2] because of its simplicity and compactness, fulfils the first two requirements admirably and in designing the apparatus used in this research, some of the general features of Brown's apparatus were embodied. The method employed by A. C. Smith[3] to determine the weight of the liquid evaporated from the vaporizer, that is, by suspending the vaporizer in the vapor mantle from one arm of an analytical balance, satisfied the third requirement. However, Smith, while weighing the vaporizer and contents, allowed the terminals to suspend free, that is, not in the mercury cups, so that the moment the terminals were dropped back into the mercury cups and the current was switched through the heating coil, ebullition should commence at once or the determination would be worthless. To eliminate the uncertainty connected with this procedure a modification was incorporated in our method for ascertaining the weight of the liquid evaporated. By the method adopted, weighings can be made with certainty to 0.001 g. The general arrangement of the final apparatus is shown in Fig. 1.

The vaporizer B, containing the liquid whose heat of vaporization was to be determined, was a small glass tube, 26 mm. in diameter and 125 mm. long. At the top it was constricted to a small orifice 3 mm. in diameter. A reflecting surface, obtained by coating the outside of the vessel with silver, aided materially in preventing heat exchange to or from the vessel by radiation. Two heavy platinum wires L, No. 16 B. and S. gage, sealed into the base of the vaporizer, served as terminals of the heating coil. These two heavy platinum wires dip into mercury cups, in order to complete the elec-

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[1] See Richards and Mathews, THIS JOURNAL, **33**, 863 (1911). Mathews, *J. Phys. Chem.*, **21**, 536 (1917).

[2] Brown, *J. Chem. Soc.*, **83**, II, 987 (1903).

[3] Smith, *Proc. Roy. Soc. Edinburgh*, **24**, 450 (1903).

trical circuit. Some difficulty was experienced at first because of the inability of mercury to wet platinum; this resulted in the weighings being somewhat uncertain. The difficulty was entirely obviated by drilling holes in the end of the heavy platinum wires and inserting No. 26 B. and S. gage copper wires which were then well amalgamated. These "contactors" dip into the mercury, making excellent electrical contact and at the same time increasing the sensitivity of the balance so that the weighings are certain. The heating coil[4] (resistance 5 to 8 ohms) consists of a helix of fine platinum wire (No. 37 B. and S. gage) set in a vertical position. It is supported on a light mica frame, not shown in the diagram.

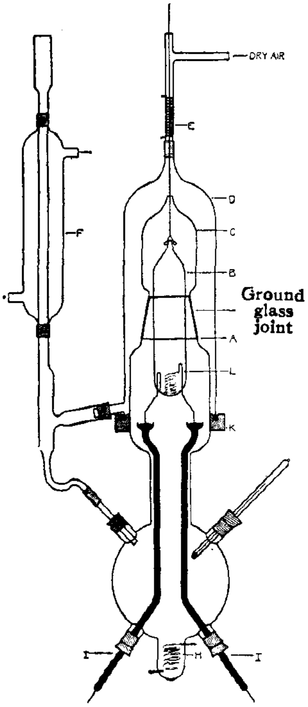

Fig. 1.

Two small platinum wires sealed into the neck of the vaporizer (forming small hooks) afforded a means of attaching the vaporizer to a fine brass suspension wire, which leads to one arm of an analytical balance placed above the entire apparatus. The vessel at the bottom serves as a boiler for the generation of the vapor used to jacket the vaporizer. This is sealed onto the chamber A in which the vaporizer is suspended. Some of the same liquid as that contained in the vaporizer is placed in the boiler and a current of from 6 to 8 amperes is passed through the resistance coil in the cistern H at the bottom of the boiler.

The cap C also is constricted at the top and has a 3mm. hole for the passage of the suspension wire. The outer vessel D consists of a large cylindrical tube open at the bottom and constricted at the top, with an orifice 3 mm. in diameter. By means of a tubulure on the boiler, connection is made with the condenser F. The outer vessel D rests in an annular ring of mercury contained in a channel cut in the cork K, and this vessel is also connected to the return condenser. The mercury seal prevents vapor from escaping from the outer vessel D.

Electrical contact with the terminals of the heating element in the vaporizer and the outside circuit is furnished through the two tubes I which are filled with mercury. Heavy amalgamated platinum wires, sealed into the lower ends of these tubes, extend into mercury cups providing contact with the outside electrical circuit (see Fig. 2). The upper ends of the tubes I are flanged out into cups 13 mm. in inside diameter, thus providing a fairly flat surface of mercury into which dip the platinum wires L from the vaporizer.

The brass suspension wire, as it emerges from the outer vessel D, leads up through the center of a coil of manganin resistance wire, No. 22 B. and S. gage, encased in the glass "chimney" E. By passing from 1 to 2 amperes of current through this heating coil, condensation on the suspension wire is prevented. To prevent the escape of vapor from the "chimney" E, a slow current of dry air is drawn into the apparatus by means of an aspirator bottle attached to the condenser F. An excess of dry air is passed into the "chimney" under slight pressure, the excess not needed passing out at the top. This procedure prevents loss of vapor and also at the same time prevents condensation of liquid on the suspension wire. Tests showed that no appreciable amount of heat was carried to the vaporizer by this procedure.

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[4] Several different vaporizers were used in the course of the investigation.

A small Anschütz thermometer projecting into the boiler through a small tubulure is used to ascertain the temperature at which vaporization is taking place. The Anschütz thermometer was accurately standardized by comparison with a standard Precision thermometer, which has been standardized at the Bureau of Standards.

Fig. 2 shows the electrical connections. There are three separate circuits, one leading to the terminals of the heating element L in the vaporizer, a second carrying current to the heating wire H in the boiler, and a third carrying current to the manganin resistance wire in the "chimney" E.

The electrical energy, supplied to the heating element in the vaporizer, is taken from a battery of five storage cells placed directly beneath the apparatus. By adjusting the sliding contact of the rheostat (18) the current flowing through this circuit is brought to approximately 1 ampere, as indicated by the ammeter (3). The current strength is then brought to *exactly* 1 ampere by adjustment with a rheostat consisting of a well amalgamated manganin resistance wire (5) dipping into a column of mercury (6). A micrometer adjustment enables the operator to control the current strength very exactly. The current strength is adjusted until the potential drop across the standard 1-ohm resistance (11) is exactly one volt, as determined by a Type K Leeds and Northrup potentiometer. Any slight fluctuation in the current, during the few minutes required for the evaporation of 10 or 15 g. of liquid, can be compensated immediately by means of the manganin-mercury rheostat. A very sensitive galvanometer throwing an image of a lamp filament from the mirror onto a scale on the wall was used to indicate zero current through the potentiometer.

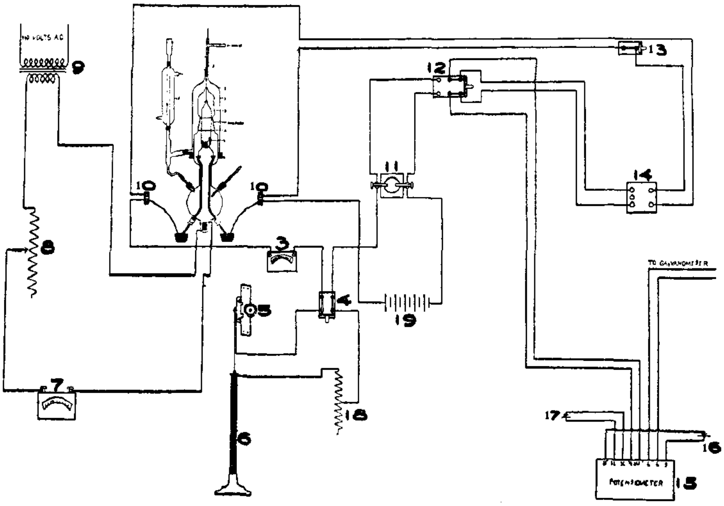

Fig. 2.

By means of the two-way switch (12) the potentiometer can be placed in circuit with either the 1-ohm standard resistance or the heating element.

In order to measure the potential across the terminals of the heating element by means of the potentiometer, a "volt box" (14) with a ratio of 1 to 50.00 was introduced into the circuit so as to reduce the e.m.f. to a value within the capacity of the potentiometer and also to permit very accurate measurements to be made.

After taking the potential drop across the metal blocks (10) while the terminals of the heating element (L) were suspended in the mercury cups, the vaporizer was removed and a double strand of heavy well-amalgamated copper wire (No. 11, B. and S. gage) was connected across the cups to effect electrical contact. The potential across the two blocks was then again measured while a current of exactly 1 ampere flowed through the circuit. During this whole operation vapor was passed through the apparatus from the boiler, so that proper temperature conditions were maintained. The difference in the two readings divided by the current strength gave the resistance of the heating element and the entire length of the platinum terminals. Since 20 mm. of each of the heavy platinum terminals (L) project out of the vaporizer, the resistance of this portion, at the temperature of each experiment, must be subtracted from the value obtained for the resistance of the heating element and terminals, since any heat liberated in this portion of the circuit does not assist in the vaporization of liquid in the vaporizer. This calculation was made from the known resistance of platinum wire of this size, using the known temperature coefficient for the resistance of platinum. This correction must be made for all liquids on account of the differences in their boiling points.

The resistance of the mercury cups, blocks and connecting wires was also measured with a Wheatstone bridge. This method gave a value of 0.00910 ohm at 78.6°. The potentiometer method gave a value of 0.00918 ohm at the same temperature, a difference of only 0.00008 of an ohm. As the resistance of the fine platinum heating element is about 5 ohms, this difference would cause an error of less than 0.01 of a calorie in the heat of vaporization values of any of the liquids studied.[5]

Before carrying out a determination or a series of determinations, the apparatus is first thoroughly cleaned, dried and assembled. Further drying is effected by forcing a current of dry air through the entire apparatus for 10 to 24 hours so as to displace all moist air with dry air and to remove, as far as is possible by such procedure, moisture from the walls inside the boiler and inner and outer compartments.

The experimental liquid is then pipetted into the vaporizer as quickly as possible; a small capillary tube closed at the upper end is also introduced into the vaporizer to prevent bumping of the liquid when it starts to

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[5] An alternative procedure, used in the latter part of the work, was to remove the vaporizer and substitute a piece of platinum wire of the same length and diameter as the portion of heavy platinum wire projecting from the vaporizer.

boil,[6] and the apparatus is again assembled as shown in Fig. 1. Approximately 100 cc. of the same liquid is placed in the boiler. By means of a swivel and turnbuckle attached to the suspension wire, the vaporizer is so adjusted that the copper "contactors" suspend directly into the center of the mercury cups to a depth of about 4 mm. and the ends of the platinum electrodes suspend about 0.5 mm. above the surface of the mercury. The wooden frame supporting the apparatus is then so adjusted that the suspension wire hangs free and does not touch at any point. As soon as the proper alignment is attained, the liquid in the boiler is made to boil, the vapor rises and surrounds the vaporizer, passes out of the orifice at the top of the cap C, down through the space between C and D and out of the tubulure at the bottom of D to the condenser, where it condenses and flows back to the boiler through a trap. The return of material to the boiler is important for two reasons. It saves material and prevents possible slight changes in temperature which would result from a fractionation effect which would be experienced were the liquid not quite pure. In a few minutes the temperature of the liquid in the vaporizer is brought to the boiling point, the switch connecting the heating element of the vaporizer is closed, and the rheostat in the circuit adjusted so that about 1 ampere of current flows through the heating coil. The current is then brought to exactly 1 ampere by means of the sliding manganin wire, the manipulation of which has already been described. Several measurements of the potential drop across the blocks are then made while exactly 1 ampere of current flows through the heating coil. Sufficient weights are now placed on the balance pan to balance the weight of the vaporizer and confined liquid and a 1-g. weight is removed. The pointer of the balance is then set so as to coincide with the third small mark on the balance scale. When the pointer swings across the zero mark of the scale the chronometer is started. A 10g. weight is now removed from the balance pan and the pointer returns to its original position on the scale. The current is held constantly at *exactly* 1 ampere during the entire period required to evaporate 10 g. of liquid from the vaporizer. Any fluctuations in the current are immediately compensated by the operator, who constantly watches the spot of light on the galvanometer scale on the wall. When the balance pointer again swings past the zero mark the run is finished and the time is recorded. It will be noted that the liquid in the vaporizer is boiled for some time before the actual distillation of the 10g. sample. This is important as this procedure insures the removal of any dissolved air.

Sufficient data are thus obtained for the calculation of the latent heat of vaporization of the liquid from the formula, $Q = (R \times T \times I^2)/(W \times 4.186)$, where R is the resistance of the heating element, T the time

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[6] This procedure was particularly necessary in the earlier work before the mica frame was used to support the resistance wire.

necessary to evaporate *W* grams of liquid and *I* the current strength measured in amperes.

Measurements of time were made by means of an Agassiz chronometer, which was frequently checked by comparison with the time signals sent out by radio from Arlington. The variations did not exceed 1 second in 24 hours. The resistance of the heating coil could always be determined to 0.0025 ohm on a total resistance of about 5 ohms. An error of this magnitude would produce an error of not greater than 0.04 of a calorie in the case of most of the liquids investigated. In most instances, however, the resistance of the heating coil could be determined to 0.0005 ohm. The weight of the liquid evaporated could be determined to 0.001 g. on a total of 10 g. and the current could be maintained to about one part in one thousand. The possibilities for error by this method are, therefore, very small. There is, of course, a possibility of slight error due to radiation of energy from the fine platinum wire used as the heating coil in the vaporizer, as this coil must obviously be at a somewhat higher temperature than the liquid bathing it. Tests were made in which a thin cylindrical platinum shield inclosed the heating coil, without touching it. The results obtained were the same with and without this additional reflecting surface, so it was concluded that the energy being lost by radiation through the silvered surface on the vaporizer was negligible.

In the course of the development of the method here described, about 100 determinations of the heat of vaporization of benzene were made. Inasmuch as the value for benzene is probably the most certain value we have for any organic liquid, it was chosen as the trial liquid for testing the method. The last eight determinations on benzene, made after the apparatus had been perfected, are given in Table I.

TABLE I

BENZENE

Current strength = 1.000 amp.

Wt., corr. to vac., g.	Resistance of coil Ohms	Time		Temp., °C.	*L*, cal. per g.	*L'*, at 80.2°
		Min.	Sec.			
10.032	7.4335	8	53.9	79.5	94.51	94.40[a]
10.032	7.4335	8	53.7	79.5	94.48	94.37
10.032	7.4325	8	53.7	79.2	94.46	94.30
10.032	7.4312	8	53.3	79.2	94.37	94.22
15.048	7.4405	13	21.3	79.1	94.65	94.48
15.048	7.4340	13	19.5	79.1	94.35	94.24
15.048	7.4280	13	21.3	79.1	94.49	94.38
15.048	7.4255	13	22.1	79.1	94.55	94.44
					Av. =	94.35
					Mean error =	± 0.03

This value of 94.35 calories for the latent heat of vaporization of benzene is only 0.02 calorie lower than that obtained by Griffiths and Marshall and agrees exactly with that found by Tyrer at 80.35°.

TABLE I (*Concluded*)

VALUES OBTAINED BY OTHER EXPERIMENTERS

Temp., °C.	L	Observer
80.2	94.37	Griffiths and Marshall
80.35	94.35	Tyrer
80.35	93.45	Schiff
80.2	94.40	Marshall and Ramsay
..	92.97	Louguinin
80.0	93.90	Nagornow and Rotinjanz
80.2	94.93	Brown
80.0	95.45	Young

[a] The values for L' are calculated from the formula, $L = 107.05 - 0.1581\theta$, where L is the heat of vaporization at the temperature of distillation, θ. (Griffiths and Marshall.)

Purification of Liquids

As a test of the purity of the liquids used, their boiling points at 760 mm. pressure, their refractive indices and their densities were determined. The boiling points were corrected to 760 mm. pressure either by the use of Young's formula, $C = c\,(760-P)(273 + \text{b. p.})$, where C is the correction to be added to the reading at pressure P, and c is Young's factor, depending

TABLE II

PURIFICATION AND PROPERTIES

Substance	Source	Purification	d_4^{20}	n_D^{20}	B. p. (760 mm.)
Benzene	Kahlbaum	Method of Richards and Shipley[7]	....	.....	80.2
Ethylbenzene	Wis. Lab.	Dried by P_2O_5 and fr.[b]	0.8672	1.49593	136.1
Toluene	Mallinckrodt	H_2SO_4, NaOH, Hg, P_2O_5 and fr.	.8661	1.49675	110.65–110.70
Heptane	Wis. Lab.	Method of Kremers[8]	.6838	1.38746	98.56–98.57
4-Methylheptane	Chem. Eng. Lab., Michigan	P_2O_5, fr.	.7165	1.40063[a]	117.9–118.1
o-Xylene	Kahlbaum	H_2SO_4, NaOH, Hg, P_2O_5 and fr.	.8745	1.50265	142.6–142.8
m-Xylene	Kahlbaum	Same as above	.8657	1.49788	139.3–139.4
p-Xylene	Kahlbaum	Same as above and also crystallized 6 times	.8616	1.49577	138.4
Cyclohexene	Eastman	P_2O_5, fr.	.8094	1.44554[a]	82.45–82.85
Cyclohexane	Eastman	P_2O_5, fr.	.7447	.....	80.9–81.1
Methylcyclohexane	Univ. of Brussels	P_2O_5, fr.	.7697	.....	100.5–101.1
Methylene chloride	Wis. Lab.	Aq., Na_2CO_3, $CaCl_2$ and fr.	....	.....	41.4–42.2
Ethylene chloride	Kahlbaum	$CaCl_2$, fr. 4 times	1.2541	1.44268	83.65–83.70
Ethylene bromide	Kahlbaum	$CaCl_2$, and fr.	2.1767	.....	131.6–131.8
Ethyliodide	Kahlbaum	Aq. NaOH, $CaCl_2$, fr. 10 times	1.9321	1.51357[a]	72.35–72.40
n-Butyl iodide	Wis. Lab.	Aq. NaOH, $CaCl_2$, fr. 3 times	1.5981	1.49523[a]	130.5–130.9
Tetrachloro-ethane	Eastman	Aq. K_2CO_3, K_2CO_3 and fr.	1.5966	1.49415	146.2–146.8
Trichloro-ethylene	Eastman	Method of Veley[9]	1.4655	1.47758	87.0–87.2

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[7] Richards and Shipley, THIS JOURNAL, **36**, 1825 (1914).

[8] Kremers, *J. Am. Pharm. Assoc.*, **9**, 857 (1920).

[9] Veley, *Proc. Roy. Soc.* (London), **82**, 217 (1909).

Table II (*Concluded*)

Substance	Source	Purification	d_4^{20}	n_D^{20}	B. p. (760 mm.)
Tetrachloro-ethylene	Eastman	$CaCl_2$, and fr.	1.6207	1.50566	121.1
Chlorobenzene	Eastman	$CaCl_2$, and fr.	1.1064	1.52462	131.7
Bromobenzene	Eastman	Fr. repeatedly	1.4956	1.55989	155.2
o-Chlorotoluene	Eastman	Hg, $CaCl_2$, fr.	1.0785	1.52221[a]	159.45–159.55
p-Chlorotoluene	Eastman	Hg, $CaCl_2$, and fr.	1.0700	1.51895[a]	161.5–161.9
Nitromethane	Wis. Lab.	P_2O_5 and fr.	1.1319[d]	.....	100.95–101.10
Chloroform	Mallinckrodt	H_2SO_4, Aq. KOH, $CaCl_2$, P_2O_5 and fr. 4 times	1.4889	1.44637	61.20–61.25
Carbon tetrachloride	Merck	Hg(reflux) H_2SO_4, aq. NaOH, H_2O, $CaCl_2$, fr.	1.5944	1.46048	76.70–76.74
Carbon disulfide	Mallinckrodt	Hg, P_2O_5 and fr.	1.2632	.....	46.23
Pyridine	Merck	See Note *c*	0.9832	1.51012	115.3–115.4
Ethylene chlorohydrin	Eastman	Na_2SO_4, Na_2CO_3 and fr.	1.2022	1.44208	127.9–128.1
Methyl alcohol	Baker Chem. Co.	Cryst. with $CaCl_2$, dist. with H_2O, then with CaO, BaO, and Na, and fr.	0.7917	1.32863	46.65–64.70
Ethyl alcohol	......	See Note *e*	.78992	1.36170[f]	....
*iso*Propyl alcohol	Wis. Lab.	Digested with fused $CaCl_2$, dist., digest. BaO and fractionated 3 times	.7830[a]	1.37592[a]	82.16–82.26
n-Butyl alcohol	Kahlbaum	Method of Brunel, Crenshaw and Tobin[10]	.8099 .8061[a]	1.39759[g]	117.7–117.9
*iso*Butyl alcohol	U. S. Ind. Alcohol Co.	Digested repeatedly with BaO and fractionated	.8027	1.39436[a]	107.6–107.7
sec.-Butyl alcohol	Gen. Motors Lab.	Sample small, not purified	....	.....	98.6–99.8
iso-Amyl alcohol	Kahlbaum	Same as for *n*-butyl	.8105	.....	131.35
Benzyl alcohol	Kahlbaum	Fractionated out of contact with air	1.0453	.....	205.6–206.0
Acetone	Mallinckrodt	Method of Shipsey and Werner[11]	0.7916	1.35788[f]	56.0
Methylethyl ketone	Wis. Lab.	Bisulfite purification	.8052	1.37876	79.5–79.9
Ethyl ether	Mallinckrodt	Concd. H_2SO_4, washed, dried with $CaCl_2$, and Na, and fr.	.7142	.....	34.66

[a] At 25°.

[b] fr. = fractionated.

[c] The double salt of C_5H_5N and $ZnCl_2$ was prepared and recrystallized from absolute alcohol. The requisite amount of concd. NaOH was added to free the base. This was then dried with fused KOH and fractionated.

[d] At 25.3°.

[e] Aldehydes were removed by allowing fine colloidal silver oxide to settle slowly through a column of the liquid until a negative test with fuchsine was obtained. Then the material was brought to approx. 99% with unslaked lime and completely dehydrated with finely divided metallic calcium.

[f] Using D_3 line = 587.6 $\mu\mu$.

[g] Using D_3 line at 25°.

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[10] Brunel, Crenshaw and Tobin, This Journal, **43**, 572 (1921).

[11] Shipsey and Werner, *J. Chem. Soc.*, **103**, 1255 (1903).

upon the liquid; or (in most cases), by distilling the liquid at 760 mm., using the barostat described by Mathews and Faville.[12] In order to determine the densities, an Ostwald-Sprengel pycnometer, provided with ground glass caps, was used. A Pulfrich refractometer made by Zeiss was used for determining the refractive indices. As a source of illumination for the refractometer either a sodium flame (D = 589.3 $\mu\mu$) or a Geissler helium tube (D_3 = 587.6 $\mu\mu$) was used.

Esters

All the esters listed below were obtained from Kahlbaum with the exception of ethyl acetate, which was purchased from the Mallinckrodt Chemical Company, and *n*-butyl formate, which was obtained from the Eastman Kodak Laboratories. Practically the same procedure was followed in their purification. Any free acid was removed by shaking the ester with a concentrated solution of potassium carbonate. The potassium salt of the fatty acid and the lower alcohols were removed by washing with water, that is, those that were not appreciably soluble in water. A rough drying was then effected with anhydrous potassium carbonate and the ester completely dehydrated with phosphorus pentoxide. The esters were then subjected to a series of fractionations until constant boiling specimens were obtained.

The boiling points, densities and refractive indices are given in Table III.

TABLE III

PROPERTIES OF ESTERS

Substance	B. p. (760 mm.), °C.	d_4^{20}	n_D^{20}
Ethyl formate	54.1–54.2	0.9194	1.35994
Methyl acetate	57.0–57.2	.9337	1.36143
Ethyl acetate	77.06	.9004	1.37302
Methyl formate	31.8–31.9	.9708	1.34332
Propyl propionate	122.5–122.8	.8764	1.39076
n-Butyl propionate	145.9	.8769	1.40127
Propyl acetate	101.35–101.6	.8820	1.37771
*iso*Butyl formate	97.9–98.3	.8850	1.38536
Ethyl propionate	99.3–99.45	.8897	1.38415
*iso*Butyl acetate	116.2–116.8	.8718	.....
Ethyl *iso*butyrate	110.0–110.2	.8709	1.38708
Ethyl butyrate	119.9–120.5	.8789	1.38650
Methyl propionate	79.78–79.98	.9155	1.37724
Methyl *iso*butyrate	92.2–92.4	.8096	1.38333
Propyl formate	80.9–81.0	.9038	1.37696
n-Butyl formate	106.7	.8807	1.39052 (sodium flame)

The results of the measurements made appear in Table IV. The temperatures given represent the average of the closely agreeing temperatures

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[12] Mathews and Faville, *J. Phys. Chem.*, **22**, 1 (1918).

at which vaporization took place. The mean error was calculated by the customary formula. For a number of these liquids no values for heat of vaporization appear in the literature; for many others the values found by different investigators are widely discordant.

TABLE IV

RESULTS OF MEASUREMENTS

Substance	No. of detns.	Temp., °C.	L (cal. per g.)	Mean error (in cal.)
Benzene	8	80.20	94.35	±0.03
Ethylbenzene	5	135.17	81.08	± .04
n-Heptane	8	97.23	76.35[a]	± .04
4-Methylheptane	3	117.20	70.86	± .02
Cyclohexane	3	80.00	85.62	± .07
Methylcyclohexane	2	99.90	76.92	± .00
Cyclohexene	3	81.60	88.70	± .06
Toluene	4	109.66	86.50	± .01
o-Xylene	5	141.41	82.89	± .09
m-Xylene	4	138.30	81.85	± .09
p-Xylene	4	137.12	81.03	± .02
Methylene chloride	4	40.48	78.74	± .23[b]
Ethylene chloride	6	82.21	77.34	± .03
Ethylene bromide	3	130.80	46.24	± .04
Ethyl iodide	7	71.16	45.62	± .04
n-Butyl iodide	3	129.50	45.93	± .03
Trichloro-ethylene	7	85.69	57.24	± .03
Tetrachloro-ethylene	8	120.69	50.04	± .03
Tetrachloro-ethane (*sym.*)	6	145.03	55.02	± .07
Ethylene chlorohydrin	4	126.55	122.97	± .08
Chlorobenzene	7	130.56	77.61	± .08
Bromobenzene	8	154.79	57.63	± .05
o-Chlorotoluene	9	158.07	72.61	± .10
p-Chlorotoluene	3	160.38	73.14	± .03
Chloroform	6	60.14	58.80	± .05
Carbon tetrachloride	4	75.40	46.55[a]	± .02
Carbon disulfide	6	45.29	84.07	± .03
Nitromethane	4	99.90	134.94	± .35[c]
Pyridine	6	114.13	107.38	± .07
Methyl alcohol	6	63.81	263.31[a]	± .31
Ethyl alcohol	8	77.42	201.88	± .09
*iso*Propyl alcohol	4	81.25	159.23	± .04
n-Butyl alcohol	6	116.78	141.31	± .18
*iso*Butyl alcohol	4	106.84	138.25	± .03
sec.-Butyl alcohol	3	98.13	134.41	± .48[b]
iso-Amyl alcohol	6	130.17	119.84	± .06
Benzyl alcohol	4	204.25	111.58	± .09[d]
Acetone	4	56.00	122.09	± .02
Methylethyl ketone	3	78.20	105.95	± .04
Furfural	6	160.55	107.51	± .21[c]
Ethyl ether	6	33.99	86.08	± .06
Propionic acid	3	139.30	98.83	± .06

TABLE IV *(Concluded)*

Substance	No. of detns.	Temp., °C.	L (cal. per g.)	Mean error (in cal.)
Methyl formate	4	31.32	112.38	± .07
Ethyl formate	6	53.33	97.21	± .04
Propyl formate	5	80.01	88.15	± .11
n-Butyl formate	4	105.12	86.76	± .07
*iso*Butyl formate	3	97.03	78.51[a]	± .05
Methyl acetate	4	56.34	98.11	± .09
Ethyl acetate	3	76.00	87.63	± .10
Propyl acetate	5	100.42	80.29[a]	± .05
*iso*Butyl acetate	4	115.47	73.76	± .06
Methyl propionate	4	79.00	87.59	± .04
Ethyl propionate	5	97.64	80.07[a]	± .04
Propyl propionate	4	120.62	73.18	± .03
n-Butyl propionate	4	144.87	71.75	± .08
Methyl *iso*butyrate	4	91.05	78.15	± .04
Ethyl butyrate	3	118.90	74.72	± .10
Ethyl *iso*butyrate	4	109.22	72.08	± .04
β-Chloro-ethyl acetate	3	141.50	80.84	± .34

[a] Unpublished measurements made on these substances several years ago by the condensation method, using the technique described by the author [*J. Phys. Chem.*, **21**, 536 (1917)] gave the following results.

Substance	Temp., °C.	L (cal. per g.)
Benzene	79.3	94.0
n-Heptane	96.90	76.5
Carbon tetrachloride	75.22	46.4
Methyl alcohol	65.3	264.3
*iso*Butyl formate	96.51	79.5
Propyl acetate	100.06	79.7
Ethyl propionate	97.80	79.7
Ethyl butyrate	119.39	73.2

Although the results agree well, on the whole, the author believes that the results obtained by the new electrical method are more dependable, particularly because a knowledge of the specific heats is not required for the calculations and no extrapolations are used.

[b] Inaccuracy probably due to smallness of sample.

[c] Difficulty was experienced in keeping the current at a constant value.

[d] Evidently there was some oxidation of the alcohol.

Heats of Vaporization from Vapor-Pressure Data

In looking through the literature for heat of vaporization values as determined by other investigators, it was noted that the value given by Mills[13] for acetone is about 5.6 calories higher than our value. Since Mills' value was obtained by calculation from the specific volumes of vapor and liquid and the slope of the vapor-pressure curve at the boiling point it seemed desirable to repeat Mills' work on acetone and to make similar calculations for one or two other liquids. The equation used is

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[13] Mills, THIS JOURNAL, **31,** 1099 (1909).

the familiar one, $L/[(V-v)T] = \mathrm{d}P/\mathrm{d}T$, where L is the latent heat of vaporization, V the specific volume of the vapor at its boiling point, v the specific volume of the liquid at its boiling point and $\mathrm{d}P/\mathrm{d}T$ is the slope of the vapor-pressure curve at the boiling point.

The apparatus used was essentially that of Young;[14] hence no detailed description is necessary. The barometer was checked against the United States Weather Bureau barometer at the Madison Station. The thermometer used had been standardized by the United States Bureau of Standards.

After the vapor-pressure data had been taken, a graph was made by plotting the absolute temperature against the logarithms of the corresponding pressures, but this method did not give the slope with the accuracy desired. The curve was of service only in checking values for the vapor pressure. In order to get the slope of the curve the general equation, $\log P = C + A/T + B/T^2$, was used instead of the graphic method. By substituting three values of P and T in the equation, three simultaneous equations were obtained and the values for the constants A, B and C were determined. By differentiating this equation an equation for the slope of the curve at any point was obtained. From the value for the slope of the curve and the specific volumes of the liquid and vapor, the heat of vaporization was calculated.

For the measurement of the specific volume of the vapor the method of Dumas was chosen because of its accuracy and simplicity. The volume was reduced by means of the Berthelot equation to the volume occupied

TABLE V

ACETONE

VAPOR PRESSURE OF ACETONE

Temp., °C.	55.95	50.3	45.25	39.8	35.1	30.0	25.0
P (obs.), mm.	746.9	614.9	511.3	415.5	344.8	279.6	226.3
P (calcd. fr. eq.), mm.	746.9	614.2	511.3	415.7	344.8	279.0	224.5

Equation for curve: $\log P = 5.78247 - 324.58/T - 208188/T^2$

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \left[\frac{324.58}{T^2} + \frac{2(208188)}{T^3}\right] P \times 2.303$$

Specific volume of acetone vapor at 57° and 738.2 mm. (exptl.) = 462.8; specific volume of acetone vapor at 56° and 750.0 mm. (calcd.) = 454.1; specific volume of liquid acetone at 56.0° = 1.3.

$$L/[(V - v)T] = \mathrm{d}P/\mathrm{d}T$$

$$\frac{L}{(454.1 - 1.3)\ 329.1} = \left[\frac{324.58}{(329.1)^2} + \frac{2 \times 208188}{(329.1)^3}\right] \frac{750 \times 2.303 \times 24.21}{760 \times 1000}$$

$$L = \frac{4.829 \times 750 \times 2.303 \times 452.84 \times 24.21}{760 \times 1000}$$

$$L = 120.32 \text{ cal. per g.}$$

$$L \text{ (by vaporization method)} = 122.06 \text{ cal.}$$

$$\text{Diff.} = -1.74 \text{ cal.}$$

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[14] Young, *Sci. Proc. Roy. Soc. Dublin*, **12**, 374 (1910).

Table V *(Concluded)*

Benzene

Vapor Pressure of Benzene

Temp., °C	80.2	79.25	75.1	70.1	65.1	60.15	55.15	50.15
P (obs.), mm	760.0	737.2	645.6	548.8	464.5	389.9	325.9	271.0
P (calcd. fr. eq.), mm	760.0	737.7	646.4	548.8	463.4	389.9	325.6	270.2

Equation for curve for vapor pressure of benzene = $\log P = 7.26210 - 1402.46/T - 51387.5/T^2$.

$$\frac{dP}{dT} = \left[\frac{1402.46}{T} + \frac{2(51387.6)}{T^3}\right] P \times 2.303$$

Specific volume of benzene vapor at 82.2° and 742.0 mm. (exptl.) = 366.84; specific volume of benzene vapor at 80.2° and 760 mm. (calcd.) = 356.11; specific volume of liquid benzene at 80.2° = 1.2.

$$\frac{L}{(355.5 - 1.2)\ T} = \left[\frac{1402.46}{T^2} + \frac{2 \times 51387.6}{T^3}\right] \frac{2.303 \times 24.21}{1000}$$

$$\begin{aligned} L &= 94.68 \text{ cal.} \\ L \text{ (by vaporization method)} &= 94.36 \text{ cal.} \\ \text{Difference} &= +0.32 \text{ cal.} \end{aligned}$$

Normal Heptane

Vapor Pressure of Normal Heptane

Temp., °C	98.57	97.8	95.0	90.0	85.0	80.0	75.0	70.0	60.0
P (obs.), mm	760	741.9	682.7	585.5	497.5	421.2	355.9	298.6	206.2
P (calcd. fr. eq.), mm	760	742.7	682.1	583.9	497.5	421.9	355.9	298.6	206.7

The equation for vapor-pressure curve = $\log P = 7.36624 - 1534.34/T - 49341/T^2$.

$$\frac{dP}{dT} = \left[\frac{1534.34}{T^2} + \frac{2(49341)}{T^3}\right] P \times 2.303$$

Specific volume of heptane vapor at 99.6° and 737.9 mm. pressure (exptl.) = 300.4; specific volume of heptane vapor at 97.5° and 736.1 mm. (calcd.) = 298.0 cc.; specific volume of liquid heptane at 97.5° = 1.5.

$$\frac{L}{(300.0 - 1.5)\ 370.6} = \left[\frac{1534.34}{(370.6)^2} + \frac{2 \times 49341}{(370.6)^3}\right] \frac{736.1 \times 2.303 \times 24.21}{760 \times 1000}$$

$$\begin{aligned} L &= 78.32 \text{ cal.} \\ L \text{ (by vaporization method)} &= 76.33 \text{ cal.} \\ \text{Difference} &= +1.99 \text{ cal.} \end{aligned}$$

by 1 g. at the temperature and pressure at which the heat of vaporization was actually determined with the electrical apparatus. It was assumed that the ratio of the actual volume to the volume calculated by the Berthelot equation was the same at the two temperatures and pressures. The densities of the liquids at their boiling points were determined in the usual way, by hanging a filled pycnometer of known capacity in the vapor above the boiling liquid until temperature equilibrium had been obtained, cooling, weighing and making necessary corrections. By use of the equation, $L = [dP/dT] \times [P(V-v)T \times 24.21]/[760 \times 1000]$, the heat of vaporization is given in calories. Table V gives the results obtained for the three liquids, acetone, benzene and heptane.

The vapor-pressure method cannot be said to be as accurate as the direct experimental method, notwithstanding the soundness of the thermo-

TABLE VI

SUMMATION OF RESULTS BY VAPOR-PRESSURE METHOD

Liquid	Temp. °C.	Heat of vaporization from v.-p. data, cal.	Heat of vaporization det. exptlly., cal.	Diff. cal.
Acetone	56.0	120.32	122.06	−1.74
Benzene	80.2	94.68	94.36	+0.34
Heptane	97.5	78.32	76.33	+1.99

dynamics involved. Small errors in the determination of vapor pressure result in relatively large errors in the value obtained. The measurement of the density of the saturated vapor at the boiling point must be known very exactly. Since these measurements check closely with the values calculated by means of the Berthelot equation, they cannot be seriously in error.

It is concluded from these investigations and a comparison with Young's work that the heat of vaporization of a liquid may now be determined by direct calometric methods more accurately than it can be calculated from data which involve the measurement of vapor pressures.

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Summary

1. The advantages of a direct electrical method over the condensation method for measuring heats of vaporization of liquids has been pointed out.
2. An accurate direct, electrical method has been developed and is here described.
3. It is believed that this new method gives a degree of accuracy not obtainable by the methods heretofore in general use, the order of accuracy being 0.1 cal., or less.
4. The heats of vaporization of 59 liquids have been measured and reported. For a number of these liquids values have not heretofore appeared in the literature.
5. While there is general agreement between the new values and values obtained by the author for some of these liquids by use of the condensation method developed by Richards and the author, it is believed that the new values are more reliable.
6. It is believed that the limit of accuracy in heat of vaporization values is henceforth a question of reproducibility of chemical materials.
7. The direct measurement of heats of vaporization by the new method is considered to be more reliable than the calculation from the most accurate vapor-pressure data obtainable.

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