

CLXXXVI.—*Latent Heats of Vaporisation of Mixed Liquids. Part I.*

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THE physical properties of mixed liquids have, for the most part, been fairly completely studied, and the general result that has been discovered is that for normal mixtures of unassociated liquids, the physical properties, as a general rule, are approximately linear functions of the composition, and in the cases of mixtures of associated liquids deviations from this additive law appear. One

physical property, however, seems to have been completely neglected, namely, the latent heat of vaporisation. It is not known whether or not the latent heat of a normal mixture is an additive quantity. When a mixture of two liquids is boiled, both its temperature and composition vary as the vaporisation proceeds, and hence its latent heat must also vary. It is clearly necessary to define the meaning of the latent heat of a mixture. Now a mixture of two liquids has, in two perfectly legitimate senses, two latent heats of vaporisation defined as follows:

(1) The latent heat of vaporisation of a mixture of two liquids is the heat required to evaporate one gram from an infinitely large quantity of the mixture of definite composition.

(2) The latent heat of a mixture of two liquids is the heat required to vaporise completely one gram of the mixture at constant temperature.

In the first definition no regard is paid to the composition of the vapour. Since an infinitely large quantity of the liquid is taken, both the temperature and composition of the parent liquid remain constant.

In the second definition the composition of the vapour is the same as the liquid, since all the liquid started with is assumed to have been vaporised. In order that the vaporisation may take place at constant temperature, the external pressure must be continually diminished as the vaporisation proceeds.

Since in the first case the external pressure is constant, we may term it the latent heat of vaporisation at constant pressure, and denote it by the symbol L_p .

In the second case the composition of vapour and liquid are the same, so we may term it the latent heat of vaporisation with constant composition, and denote it by L_c .

That the two quantities are quite separate and different in magnitude may be shown as follows:

Consider an infinitely large quantity of a mixture of two liquids A and B at its boiling point T . Let the composition in terms of the constituent A be C . Let one gram be evaporated, say, to avoid complications, under a negligibly small external pressure. The heat absorbed is L_p .

Now take one gram of the same mixture, and allow it to evaporate slowly in a vacuum at the same temperature T . Imagine the vaporisation to proceed in infinitely small successive quantities each of mass dm . The heat required to evaporate the first elementary portion will obviously be $L_p \cdot dm$. Let us suppose, in the first place, that the constituent A is the one of higher boiling point, and also possesses the higher latent heat. Then as the evaporation of the

gram of liquid proceeds, the composition in terms of A will increase, and hence the heat required to vaporise successive elementary portions will continually increase until the heat required to evaporate the last portion will be $L_A dm$, where L_A is the latent heat of vaporisation in a vacuum of pure A at the temperature T .

Obviously, the total heat required to vaporise the gram of liquid of composition C is equal to

$$L_c = - \sum_{L=L_A}^{L=L_p} L dm,$$

and must be much greater than L_p .

Expressing L as a function of the mass m of the unevaporated liquid, we can write:

$$L_c = \int_0^1 f(m) dm.$$

If, on the other hand, the constituent of higher boiling point, A , has the lower latent heat at the temperature T , the heat required to vaporise successive fractions will continually diminish, and L_p will be greater than L_c .

In this work latent heats at constant pressure (L_p) only have been measured.

Method of Determination and Apparatus.

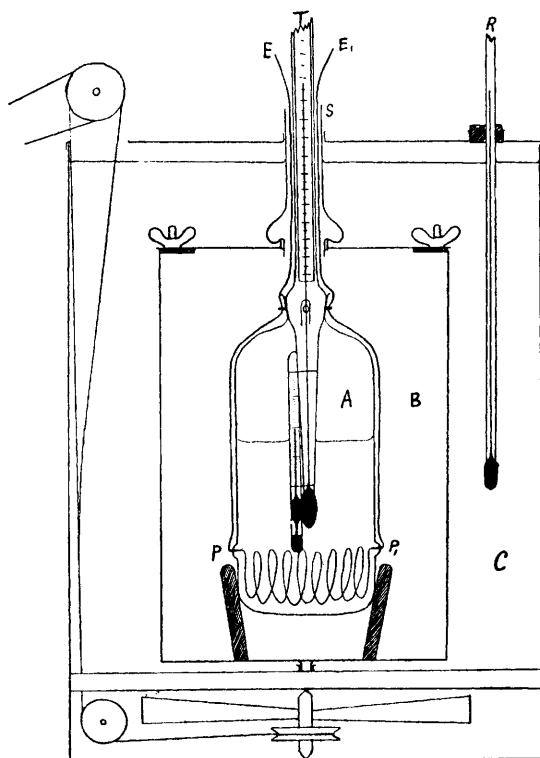
The latent heat of a pure liquid is a quantity which is by no means easy of measurement with accuracy, as a comparison of results obtained by different observers for the same liquid will show. With mixed liquids the difficulties are increased, for account has to be taken of changing composition and changing temperature as the vaporisation proceeds. There are two general methods of determining latent heats which have been fully worked out, namely, (1) condensation of vapour in a calorimeter, and observation of the heat evolved; (2) measurement of heat required to vaporise, by an electrically-heated wire, a weighed quantity of a liquid. An adaptation of the second method to mixed liquids is described in this paper.

The general principle of the method adopted is as follows: A known quantity of electricity is passed through a coil of platinum wire of known resistance, which is immersed in the liquid the latent heat of which is to be measured, first heated to its boiling point by an external bath. The amount of liquid evaporated is found by weighing before and after. This gives all the data necessary.

When, however, a mixed liquid is partly evaporated, the boiling point rises, and a certain amount of heat is used up in raising the

temperature of the liquid. To determine this correction a separate experiment is made to find the heat capacity of the liquid and the containing vessel, and the total rise in temperature is found by having a thermometer dipping into the liquid. In order that this rise in temperature may be small, a comparatively large quantity of the liquid is taken, and only a small quantity evaporated.

FIG. 1.



The general form of the apparatus is shown in the accompanying diagram.

The liquid the latent heat of which is to be measured is placed in the evaporating bottle *A*, which is about 250 c.c. capacity. This bottle is provided with a coil of platinum wire (about 1 metre of 0.02 cm. diameter), the ends of which are fused to two stout pieces of platinum, which are fused through the sides of the bottle at the points *P*, *P*₁. Stout pieces of copper wire are soldered to the platinum terminals, and pass outside to the ends *E*, *E*₁, which can

be attached to circuit leads. A thermometer T is ground into the neck of the bottle, and has a groove impressed in it, which can be turned opposite to a small hole pierced in the neck of the bottle, thus allowing it to be opened or closed to the external pressure. The bottle is made to stand on rubber-covered rods, as shown, in a copper insulating vessel B . This vessel is provided with a lid and two windows front and back (not shown in sketch). The lid and the panes of glass of the windows are screwed down on rubber to render the vessel perfectly water-tight. The vessel B is pivoted inside a large bath C , made of sheet copper, and provided with two windows (not shown). It contains water (or for temperatures higher than 100° , a high boiling liquid), and is heated by burners from below. It is provided at the bottom with a rotatory stirrer connected by a cord passing over pulleys to a small motor outside. The temperature of this bath is registered by a thermometer R . The vessel B can be rotated rapidly backwards and forwards by turning the glass tube S , and this serves to give the liquid in the evaporating bottle a rotatory motion, and continually sweeps fresh liquid over the platinum coils as the evaporation proceeds. Inside the bottle, attached to the thermometer, is a very small manometer, which serves to indicate when the pressure in the bottle has reached the atmospheric pressure.

The thermometers T and R are graduated in $1/5$ ths, and are readable to 0.02° with accuracy.

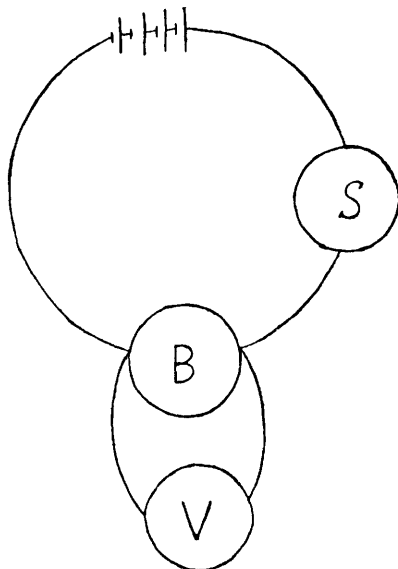
The current used is obtained from secondary cells (about eight cells are necessary), and is quite steady. The current passed through the circuit is accurately measured by means of a silver voltameter. The general arrangement of the apparatus is indicated in the accompanying diagram.

S is the silver voltameter, B is the evaporating bottle, and V is a Weston voltameter to measure the potential difference between the terminals of the platinum coil. This latter instrument covers a range of 8–13 volts, is graduated in 0.05 volt divisions, and is readable with accuracy to less than 0.01 volt. All the electrical contacts, where possible, were soldered to ensure perfect contact, and the switches were made tight, and were of a heavy type. The contacts were quite without resistance.

The composition of the mixed liquid is found before and after an experiment by determining the specific volumes of the liquid at a constant temperature, a table having been prepared beforehand, representing the relation between the composition and the specific volume. The specific volumes were determined with a quartz pyknometer immersed in a thermostat at about 20° , and the measurements were made to the fifth decimal place. The calculated

compositions contain an error not greater than 0.01 unit for mixtures the constituents of which differ moderately in their densities, whilst for mixtures like chloroform and benzene, which show a large variation of specific volume, an even greater degree of accuracy is obtained. About 5 to 12 grams of liquid are evaporated in each experiment. With mixtures like carbon tetrachloride and ether this causes a variation in composition of about 2 units, but with chloroform and benzene the variation is only about 0.2 unit. It is then assumed that over this small range the latent heat is a linear function of the composition, and the mean com-

FIG. 2.



position is taken as the point for which the latent heat is as determined in the experiment. The error of this assumption is negligibly small.

In carrying out an experiment, the boiling point of the mixed liquid is first determined approximately, and then its composition is found by determining with accuracy its specific volume. The evaporating bottle is about two-thirds filled, and weighed. The air is then pumped out of the bottle by pressing the end of the rubber tube which is attached to a strong water pump against the open orifice in the neck of the bottle, and when the liquid has boiled for a few seconds closing the bottle by turning the thermometer stem. The ground joint at the neck is lubricated with a

mixture of fused dextrose and glycerol. This lubricant is quite insoluble in organic solvents, and when made up to a proper consistency it answers the purpose admirably. It has the advantage over phosphoric acid as a lubricant, that it is more adhesive, and is not so easily squeezed out by pressure. It is also hygroscopic, but not to so great a degree as phosphoric acid.

After the air has been pumped out of the bottle it is again weighed to determine loss of liquid during the evacuation. A small correction is made to account for the very small change in the composition caused by this loss. The bottle is then placed in position in the inner copper vessel, and the external bath is heated to the boiling temperature of the mixture. The bottle and contents are slowly warmed by the passage through the platinum coil of a small shunted current. When the pressure inside the bottle has reached the external atmospheric pressure, as is indicated by the small manometer inside the bottle, and it has remained at a constant temperature for some minutes, the bottle is opened by turning the thermometer stem. The current is then switched on, and the boiling should commence immediately. The potential difference between the ends of the platinum coil should be from about 10 to 12.5 volts. As the temperature rises (usually about 1—1.5°) the temperature of the outside bath is raised correspondingly. A difference of a few tenths of a degree between the temperature of the boiling liquid and the outside bath makes no material difference during the time of an experiment, which only lasts about four or five minutes. As the boiling proceeds it is observed that the needle of the voltmeter always falls slightly, but this is only small (about 0.8 per cent.), and by taking readings at regular small intervals and finding the mean, the error in the voltage is reduced to about 0.07 per cent.

The total current passed through the coil is found by weighing the silver deposited on the platinum basin of the voltmeter. About 0.3 to 0.45 gram of silver is usually deposited, and the error in weighing is not greater than 0.1 milligram. The temperature of the bath and bottle is allowed to fall about 3°, and the experiment is repeated with the bottle closed, and with a voltage of about 8.5. The rise in temperature is observed (about 4°), and the range covers that through which the temperature rose in the first experiment. This gives the heat capacity of the bottle and contents. The bottle is then weighed to determine the amount of liquid vaporised in the first experiment.

The latent heat is then calculated from the following equation :

$$L = \frac{J.S.V.}{A.M.},$$

where L is latent heat, J is electrical heat equivalent, S is weight of silver deposited during the experiment, V is the volts recorded on the voltmeter, A is the electrochemical equivalent of silver, and M is the weight of liquid vaporised. M is equal to the loss in weight of the bottle + the weight of vapour occupying the space vacated by the vaporised liquid at the boiling point. The latter, which is a small correction, can be approximately calculated.

A correction has now to be subtracted for the heat required to raise the temperature of the liquid during the vaporisation. This is:

$$H = \frac{C \times t \times W}{M},$$

where C is the heat capacity of liquid and bottle, t is the rise in temperature observed, and W is the mean weight of bottle and contents. C is found from the second experiment, and is given by:

$$C = \frac{J \times S_1 \times V_1}{A \times t_1 \times W_1},$$

where S_1 is weight of silver deposited, V_1 the voltage, t_1 the rise in temperature, and W_1 is the final weight of bottle and contents.

The corrected latent heat is then given by the following:

$$L_p = \frac{J}{A.M.} \left(SV - \frac{t}{t_1} \cdot \frac{W}{W_1} \cdot S_1 V_1 \right).$$

The correction need not exceed about 6 units, and is known with accuracy. The constant J/A has the value 213.60.

Three mixtures have been investigated, namely, ether and carbon tetrachloride; benzene and *n*-hexane; chloroform and benzene.

The results obtained are set forth in the remaining portion of the paper.

An idea of the general accuracy and practicability of the method is obtained by a comparison of results obtained for pure liquids with standard results obtained by other investigators.

The values given in the following tables for the latent heats refer to a mean pressure a few mm. above 760 mm. Without knowing variation of latent heat with variation of atmospheric pressure it is impossible to reduce all the values to one standard pressure. The difference, however, caused by a moderate change in external pressure makes but a very slight difference to the latent heat. The error is in any case well within total error of results.

Mixtures of Benzene and n-Hexane.

The benzene used in these experiments was prepared from Kahlbaum's pure material by refractionation over phosphoric oxide. It

was quite free from thiophen, and a litre distilled at constant temperature. Its specific volume at $20^{\circ}00'$ was 1.13815.

Kahlbaum's pure hexane from petroleum was refractionated. Its specific volume at $20^{\circ}00'$ was 1.47471.

Latent Heat of Benzene:—Three consecutive experiments gave the results:

	94.43 calories
	94.31 ,,
	94.31 ,,
Mean.....	94.35 ,,

These values refer to a mean pressure of 763 mm., and a temperature of $80^{\circ}35'$. Griffiths and Marshall (*Phil. Mag.*, 1896, [v], **41**, 1) obtained the value 94.37. This result is probably the most accurate latent heat determination that has been made. J. C. Brown (*Trans.*, 1905, **87**, 265) obtained the result 94.93.

Latent Heat of Hexane:—Two consecutive results gave:

	81.59 calories
	82.11 ,,
Mean.....	81.85 ,, Temperature = $66^{\circ}88'$.

Mabery and Goldstein (*Amer. Chem. J.*, 1902, **28**, 66) obtained the result 79.4 , which is rather considerably lower than the above.

Latent Heats of Mixtures of Benzene and Hexane:—The experimental results were plotted on cross-section paper against the composition, and the results given in the following table were read off from the smoothed curve. In the table also is given the boiling points of the mixtures for a mean pressure of about 766 mm.

Percentage of C_6H_6 in the mixture.	Latent heat in calories.	Boiling point.	Percentage of C_6H_6 in the mixture.	Latent heat in calories.	Boiling point.
0	81.85	66.88°	60	85.60	71.8°
10	81.93	67.55	70	87.20	73.2
20	82.15	68.6	80	89.03	75.1
30	82.55	69.1	90	91.27	77.4
40	83.24	69.9	100	94.35	80.45
50	84.26	70.8			

The above results for the latent heats of the mixtures contain estimated accidental errors of about 0.05 unit, but the series may contain a constant error of about 0.2 unit. The results are discussed at the end of the paper.

Mixtures of Carbon Tetrachloride and Ether.

Kahlbaum's carbon tetrachloride was refractionated; its specific volume at 20° was 0.62724. The ether used was prepared from absolute alcohol in the ordinary way. It was purified by washing

with acid, alkali, and water, and drying over calcium chloride and sodium. It was then fractionated, dried further over phosphoric oxide, and again fractionated; 500 c.c. distilled over constantly within 0.01° . Its specific volume at 20° was 1.40154 (Ramsay and Young's value=1.4015).

Latent Heat of Carbon Tetrachloride:—Three consecutive results gave:

	47.04 calories
	46.86 "
	46.84 "
Mean.....	46.85 " Temperature= 77.75° .

The first result was considered rather less accurate than the other two, and is excluded from the mean value.

Wirtz (*Wied. Ann.*, 1890, **40**, 446) obtained the result 46.35.

Latent Heat of Ether:—Three experiments gave the values:

	86.74 calories
	86.06 "
	86.52 "
Mean.....	86.44 " Temperature= 34.74° .

The following are results by other observers:

Wirtz (<i>Wied. Ann.</i> , 1890, 40 , 438)	...	88.39 calories.
Brown (<i>Trans.</i> , 1903, 83 , 987)	...	84.78 "
Ramsay and Young (<i>Phil. Trans.</i> , 1887, 178 , A, 90)	...	84.5 "
Brix (<i>Pogg. Ann.</i> , 1842, 55 , 341)	...	90.0 "
Andrews (<i>Quart. Journ. Chem. Soc.</i> , 1849, 1 , 27)	...	90.45 "
Favre and Silbermann (<i>Compt. rend.</i> , 1846, 23 , 413)	...	91.11 "

The results for ether appear to be very discordant. The latent heat of ether seems to be greatly affected by small amounts of impurities.

Latent Heats of Mixtures of Carbon Tetrachloride and Ether:—The following results were read from a smoothed curve of experimental values:

Percentage of carbon tetra-chloride mixture.	Latent heat in calories.	Boiling point.	Percentage of carbon tetra-chloride in mixture.	Latent heat in calories.	Boiling point.
0	86.44	34.75°	60	76.75	47.25°
10	86.30	36.15	70	73.00	50.80
20	85.50	37.60	80	68.47	55.77
30	84.05	39.40	90	61.60	64.65
40	82.15	41.65	100	46.85	77.75
50	79.85	44.25			

The above results are similar in point of accuracy to those in the previous case.

Mixtures of Chloroform and Benzene.

The chloroform was prepared from commercially "pure" material as follows. It was washed with acid, alkali, and water, and then distilled under a layer of dilute alkaline solution of potassium permanganate. The product was dried over calcium chloride, fractionated, dried further over phosphoric oxide, and again fractionated. About 2 litres distilled over within 0.03° . Its specific volume at 20° was 0.67219 , and it boiled at $61.40^{\circ}/758$ mm.

Latent Heat of Chloroform.—Three experiments gave the results:

	59.38	calories
	59.27	"
	59.24	"
Mean.....	59.29	" Temperature = 61.52° .

Wirtz (*Wied. Ann.*, 1890, **40**, 446) obtained the value 58.49 .

Data concerning the benzene have already been given.

Latent Heat of Mixtures of Chloroform and Benzene.—The results given in the following table were obtained from a smoothed curve of experimental results.

Percentage of chloroform in the mixture.	Latent heat in calories.	Boiling point.	Percentage of chloroform in the mixture.	Latent heat in calories.	Boiling point.
0	94.35	80.65°	60	70.13	71.75°
10	90.00	79.58	70	67.15	69.50
20	85.55	78.40	80	64.50	67.00
30	81.25	77.12	90	61.83	64.30
40	77.15	75.58	100	59.29	61.52
50	73.40	73.80			

Discussion of Results.

The relation between the latent heat at constant pressure and the composition is best shown graphically.

It will be seen from the figure that the latent heat is by no means a linear function of the composition, as might have been expected. There is a relation which holds fairly closely in two cases between the latent heat and the boiling point. This can be shown by testing the well known relation of Trouton:

$$\frac{LM}{T} = K,$$

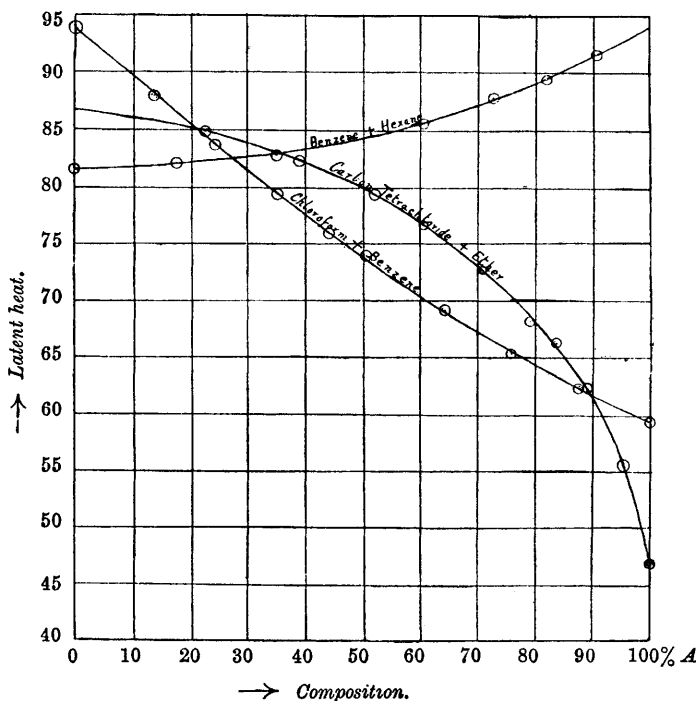
where L is the latent heat, M the molecular weight, and T is the temperature of boiling on the absolute scale.

In the case of mixtures, M must be taken as the mean molecular weight given by the formula:

$$M = \frac{100}{\frac{C}{M_A} + \frac{100-C}{M_B}},$$

where C is the composition in terms of the constituent A , and M_A and M_B are the molecular weights of the pure constituents. In

FIG. 3.



the following table are given the values of the constant $K = LM/T$ for the three cases.

While the value for K in the first and third cases is fairly constant, there is an entire lack of constancy for the case of carbon tetrachloride and ether.

Now Trouton's equation is directly deducible from the relation:

$$LM = K_1 T \log \frac{V_v}{V},$$

Composition C.	Values of K for mixtures of benzene and hexane.	Values of K for mixtures of carbon tetrachloride and ether.	Values of K for mixtures of chloroform and benzene.
0	20·74	20·85	20·83
10	20·51	21·86	20·66
20	20·31	22·75	20·42
30	20·15	23·60	20·24
40	20·07	24·40	20·05
50	20·07	25·08	20·01
60	20·13	25·77	20·04
70	20·23	26·23	20·24
80	20·35	26·36	20·48
90	20·52	25·34	20·84
100	20·83	20·55	21·06

where T is the temperature, V_v and V_L are the specific volumes of vapour and liquid respectively at T , and K_1 is a constant. This relation, moreover (see Crompton, *Proc.*, 1901, **17**, 61; and Klee-man, *Phil. Mag.*, 1910, [vi], **20**, 665), depends on the assumption that the composition of the vapour is the same as that of the liquid. We should expect, therefore, that Trouton's equation will only hold for mixtures when the difference between the composition of the liquid and the saturated vapour is comparatively small. Of the above cases this difference is greatest in the case of carbon tetrachloride and ether, and this case, as has been seen, shows the greatest divergence.

It is fairly clear that the latent heat of a liquid at constant pressure, although it is a function of the composition of the mixed liquid, is, at the same time, largely a property of the vapour, and dependent on the composition of the vapour.

It is hoped in subsequent papers to extend the present investigations to other classes of mixtures, and to study the relation between the latent heat and the composition of the vapour which is in equilibrium with the liquid of known composition.

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