# XIX. *On the Specific Heat and other Physical Characters of Mixtures of Ethylic Alcohol and Water.* *By* A. Dupré, *Ph.D., Lecturer on Chemistry at Westminster Hospital, and* F. J. M. Page, *B.Sc.* *Communicated by* Charles Brooke, *F.R.S.*

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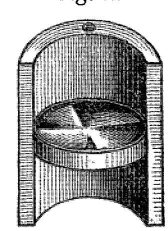
## Section I.—*Specific Heat.*

The authors, having recently had occasion to estimate carefully the specific heat of mixtures of alcohol and water, came in the course of these experiments to the unexpected result that the specific heat of such mixtures, up to an alcoholic strength of about 36 per cent., is sensibly higher than the specific heat of water itself. These experiments, to the best of their knowledge, furnish the first example of a liquid having a higher specific heat than water, which has always been considered to possess the highest specific heat of any substance solid or liquid. They therefore beg leave to lay their results before the Royal Society.

Two methods were employed for the estimation of the specific heat. The first method, and the one chiefly used, consisted in heating a metallic weight to a certain temperature, and then plunging it into the liquid whose specific heat was to be estimated; the rise in temperature thus produced in different liquids will, after the necessary corrections, be inversely proportional to the specific heat of these liquids.

Fig. 1.



Annular weight and fan-wheel, half of the former being cut away to show the fan-wheel.

Two weights were employed, one of brass, the other copper gilt, both well polished. They were made in the shape of stout rings—the internal diameter of the brass weight being 38·5 millims., its external diameter 49 millims., its height 39·5 millims., its weight 246·49 grms.; the internal diameter of the copper ring was 39 millims., its external diameter 61 millims., its height 39·5 millims., and its weight 614·49 grms. In the inner cylindrical space of each was inserted a small fan-wheel, resembling in its construction the wheel of a smoke-jack, so that, when the heated weight is caused to rotate rapidly in a liquid, a current is thus drawn through the ring, producing, first, a very complete mixture of the liquid, and, secondly, a more rapid cooling of the weight.

The weights were heated in an apparatus exactly similar to that employed by Regnault in his researches on the specific heat of solids—steam, or the vapour of boiling alcohol being employed for heating them.

The liquid whose specific heat is to be estimated is carefully measured in a narrow-necked flask, and poured into a calorimeter of very thin polished brass, supported on stretched silk cords and surrounded by a double cylinder of tin plate, to prevent as far as possible any gain or loss by radiation.

A thermometer, divided into tenths of a degree Centigrade, allowing $\frac{1}{100}$ of a degree to be read, was used to indicate the temperature of the steam-oven.

Two thermometers were employed to indicate the temperature of the calorimeter,—one having a range from 10° to 20° C., and divided into twentieths of a degree Centigrade, allowing $\frac{1}{200}$ of a degree to be read off by means of a telescope; the other had a range from 16° to 21°·5 C., divided into fiftieths of a degree C. and allowing $\frac{1}{500}$ of a degree to be read off.

The bulbs of both these thermometers were thin, and of such a length as to pass through nearly the entire depth of liquid contained in the calorimeter. A thermometer similar to the two last was employed to take the temperature of the air. All the thermometers were carefully compared with a standard, as well as calibrated by thread measurements.

The experiments are conducted as follows. As soon as the temperature of the steam-oven remains constant for at least ten or fifteen minutes, it is read off; a measured quantity of the liquid, cooled a few degrees below the temperature of the room, is poured into the calorimeter, and its temperature, after thorough mixture, read off by means of a telescope. On a given signal, one assistant pushes the calorimeter underneath the steam-oven; a second then, opening the slide-valve, lets down the weight which is detached from the string, and the calorimeter is brought back into its first position. The weight, which has of course been kept underneath the surface of the liquid after leaving the steam-oven, and has not been allowed to touch the sides or bottom of the brass vessel, is now hooked to a strand of worsted, previously twisted; on allowing this to untwist a rapid rotation of the weight ensues, and consequently a thorough mixture of the liquid by the fan-wheel*. The whole of these movements occupy from fifteen to twenty-five seconds.

The elevation of the temperature of the calorimeter is observed, which usually reaches a maximum one minute after the introduction of the brass weight, whilst with the copper weight a minute and a half elapsed before this was effected.

As soon as the temperature has attained its greatest elevation and the thermometer begins to sink, the time is noted; and in half a minute with the brass weight, or three quarters of a minute with the copper weight, the temperature is again read off; the fall of temperature during this interval is added, as a correction, to the highest temperature observed, as representing the loss due to radiation. This correction usually amounts only to a few hundredths of a degree.

* As a mean of several experiments, it was found that a rapid rotation of the weight during five minutes produced a rise in the temperature of the water in the calorimeter of 0°·005 C. In the course of an experiment on the specific heat of a mixture, the time during which the weight rotated at the above speed always fell short of one minute, consequently the effect thereby produced on the temperature of the calorimeter is somewhat less than 0°·001 C. The heat thus produced is moreover a nearly constant quantity, affecting all experiments alike, so that its ultimate influence on the specific heat of the various mixtures is reduced to an almost infinitesimal fraction; it has therefore been neglected throughout the calculations.

The following Tables give the results of the experiments.

$t''$ denotes temperature of air.

T denotes temperature of the steam-oven and consequently of the weight.

$t$ denotes temperature of calorimeter at beginning.

$t'$ denotes temperature of calorimeter at end.

$v$ denotes loss of temperature during $30^s$ or $45^s$.

$e$ denotes total corrected rise in temperature.

N denotes the number of degrees expended by the heated weight in raising the liquid in the calorimeter one degree, the heat expended in raising the temperature of the calorimeter and immersed part of thermometer having been previously deducted.

This figure, N, will therefore be directly proportional to the specific heat of the various liquids used, supposing equal weights taken in each case.

### Table I.

*Brass ring*, weight 264·49 grms.

*Brass value* of calorimeter and immersed part of thermometer 69·54 grms.

*Quantity* of liquid contained in calorimeter 449·53 cub. centims.

*Time* occupied in making each experiment, one minute.

*a.* Distilled Water.

| Experiment. | $t''$. | T. | $t$. | $t'$. | $v$. | $e$. | N. |
|---|---|---|---|---|---|---|---|
| 1. | 9·0 | 97·80 | 10·048 | 14·142 | 0·020 | 4·096 | 20·14 |
| 2. | 11·6 | 97·83 | 10·234 | 14·297 | 0·025 | 4·088 | 20·14 |
| 3. | 12·1 | 97·90 | 10·568 | 14·654 | 0·005 | 4·081 | 20·11 |
| 4. | 13·1 | 98·10 | 10·260 | 14·369 | 0·000 | 4·109 | 20·09 |

Mean value of N 20·12.

*b.* Spirit 10 per cent. Sp. gravity 0·9814.

| Experiment. | $t''$. | T. | $t$. | $t'$. | $v$. | $e$. | N. |
|---|---|---|---|---|---|---|---|
| 5. | 12·4 | 97·50 | 10·522 | 14·505 | 0·000 | 3·983 | 20·92 |
| 6. | 11·9 | 97·87 | 10·305 | 14·351 | 0·000 | 4·046 | 20·74 |
| 7. | 13·9 | 98·20 | 11·593 | 15·586 | 0·000 | 3·993 | 20·85 |

Mean value of N 20·836.

Specific heat of 10 per cent. spirit 103·55.

*c.* Spirit 20 per cent. Sp. gravity 0·9716.

| Experiment. | $t''$. | T. | $t$. | $t'$. | $v$. | $e$. | N. |
|---|---|---|---|---|---|---|---|
| 8. | 13·9 | 97·5 | 11·217 | 15·184 | 0·000 | 3·967 | 21·06 |
| 9. | 13·9 | 97·5 | 11·825 | 15·792 | 0·000 | 3·967 | 20·90 |
| 10. | 11·1 | 98·1 | 9·890 | 13·974 | 0·000 | 4·084 | 20·90 |
| 11. | 12·9 | 98·2 | 10·486 | 14·535 | 0·000 | 4·049 | 20·97 |

Mean value of N 20·957.

Specific heat of 20 per cent. spirit 104·16.

TABLE II.

*Copper ring*, weight 614·49 grms.
*Copper value* of calorimeter and immersed part of thermometer 51·08 grms.
*Quantity* of liquid contained in calorimeter 859·3 cub. centims.
*Time* occupied in making each experiment, 1·5 minute.

*a.* Distilled Water.

| Experiment. | *t″*. | T. | *t*. | *t′*. | *v*. | *e*. | N. |
|---|---|---|---|---|---|---|---|
| 12. | 12·4 | 97·9 | 10·609 | 16·025 | 0·007 | 5·423 | 15·01 |
| 13. | 11·7 | 98·71 | 10·543 | 16·040 | 0·010 | 5·507 | 14·92 |
| 14. | 15·4 | 98·15 | 12·656 | 17·945 | 0·015 | 5·304 | 15·03 |

Mean value of N 14·98.

*b.* Spirit 5 per cent. Sp. gravity 0·9914.

| Experiment. | *t″*. | T. | *t*. | *t′*. | *v*. | *e*. | N. |
|---|---|---|---|---|---|---|---|
| 15. | 10·9 | 98·00 | 10·162 | 15·545 | 0·015 | 5·398 | 15·31 |
| 16. | 12·8 | 98·22 | 10·188 | 15·654 | 0·010 | 5·476 | 15·10 |

Mean value of N 15·205.

Specific heat of 5 per cent. spirit 101·50.

*c.* Spirit 10 per cent. Sp. gravity 0·9814.

| Experiment. | *t″*. | T. | *t*. | *t′*. | *v*. | *e*. | N. |
|---|---|---|---|---|---|---|---|
| 17. | 8·2 | 98·3 | 10·245 | 15·604 | 0·025 | 5·384 | 15·56 |
| 18. | 11·9 | 97·7 | 9·962 | 15·232 | 0·020 | 5·395 | 15·46 |
| 19. | 12·4 | 97·8 | 10·110 | 15·494 | 0·010 | 5·394 | 15·44 |

Mean value of N 15·503.
Specific heat of 10 per cent. spirit 103·49.

*d.* Spirit 20 per cent. Sp. gravity 0·9716.

| Experiment. | *t″*. | T. | *t*. | *t′*. | *v*. | *e*. | N. |
|---|---|---|---|---|---|---|---|
| 20. | 12·4 | 98·3 | 11·018 | 16·342 | 0·015 | 5·339 | 15·71 |
| 21. | 11·4 | 98·2 | 10·105 | 15·495 | 0·015 | 5·405 | 15·65 |
| 22. | 15·4 | 98·6 | 12·589 | 17·877 | 0·010 | 5·298 | 15·59 |
| 23. | 17·9 | 98·3 | 14·390 | 19·559 | 0·015 | 5·184 | 15·54 |

Mean value of N 15·622.
Specific heat of 20 per cent. spirit 104·27.

TABLE II. (continued).

*e.* Spirit 30 per cent. Sp. gravity 0·9578.

| Experiment. | *t''*. | T. | *t*. | *t'*. | *v*. | *e*. | N. |
|---|---|---|---|---|---|---|---|
| 24. | 11·9 | 98·3 | 10·188 | 15·743 | 0·020 | 5·575 | 15·36 |
| 25. | 13·9 | 98·5 | 10·414 | 15·975 | 0·020 | 5·581 | 15·34 |

Mean value of N 15·35.
Specific heat of 30 per cent. spirit 102·47.

*f.* Spirit 36 per cent. Sp. gravity 0·9470.

| Experiment. | *t''*. | T. | *t*. | *t'*. | *v*. | *e*. | N. |
|---|---|---|---|---|---|---|---|
| 26. | 9·8 | 98·6 | 10·635 | 16·379 | 0·025 | 5·769 | 14·95 |
| 27. | 11·9 | 98·4 | 10·327 | 16·049 | 0·025 | 5·747 | 15·03 |
| 28. | 11·9 | 98·5 | 10·471 | 16·231 | 0·030 | 5·790 | 14·91 |

Mean value of N 14·966.
Specific heat of 36 per cent. spirit 99·90.

TABLE III.

*Brass ring*, weight 246·49 grms.
*Brass value* of calorimeter and immersed part of thermometer 103·55 grms.
*Time* occupied in each experiment 1$^{m}$ 20$^{s}$.
*Quantity* of liquid contained in calorimeter 1155·767 cub. centims.

*a.* Distilled Water.

| Experiment. | *t''*. | T. | *t*. | *t'*. | *v*. | *e*. | N. |
|---|---|---|---|---|---|---|---|
| 29. | 20·0 | 98·3 | 19·068 | 20·560 | 0·000 | 1·492 | 51·684 |
| 30. | 20·0 | 98·3 | 19·083 | 20·580 | 0·000 | 1·497 | 51·497 |

Mean value of N 51·590.

*b.* Spirit 10 per cent. Sp. gravity 0·9814.

| Experiment. | *t''*. | T. | *t*. | *t'*. | *v*. | *e*. | N. |
|---|---|---|---|---|---|---|---|
| 31. | 19 | 98·54 | 18·510 | 19·985 | 0·005 | 1·480 | 53·509 |

Specific heat of 10 per cent. spirit 103·72.

TABLE III. (continued).

*c.* Spirit 20 per cent. Sp. gravity 0·9716.

| Experiment. | $t''$. | T. | $t$. | $t'$. | $v$. | $e$. | N. |
|---|---|---|---|---|---|---|---|
| 32. | 19·0 | 98·2 | 17·049 | 18·549 | 0·002 | 1·502 | 54·148 |
| 33. | 20·0 | 98·7 | 18·281 | 19·767 | 0·006 | 1·492 | 54·018 |

Mean value of N 54·083.

Specific heat of 20 per cent. spirit 104·83.

*d.* Spirit 30 per cent. Sp. gravity 0·9578.

| Experiment. | $t''$. | T. | $t$. | $t'$. | $v$. | $e$. | N. |
|---|---|---|---|---|---|---|---|
| 34. | 19·0 | 98·4 | 17·923 | 19·450 | 0·010 | 1·537 | 53·191 |

Specific heat of 30 per cent. spirit 103·10.

*e.* Spirit 40 per cent. Sp. gravity 0·9396.

| Experiment. | $t''$. | T. | $t$. | $t'$. | $v$. | $e$. | N. |
|---|---|---|---|---|---|---|---|
| 35. | 20·5 | 98·42 | 18·070 | 19·719 | 0·008 | 1·657 | 50·102 |
| 36. | 17·0 | 98·44 | 16·058 | 17·762 | 0·006 | 1·710 | 49·766 |
| 37. | 18·0 | 98·60 | 16·783 | 18·774 | 0·009 | 1·692 | 49·958 |

Mean value of N 49·942.

Specific heat of 40 per cent. spirit 96·805.

*f.* Spirit 45 per cent. Sp. gravity 0·9292.

| Experiment. | $t''$. | T. | $t$. | $t'$. | $v$. | $e$. | N. |
|---|---|---|---|---|---|---|---|
| 38. | 19·5 | 98·2 | 18·032 | 19·757 | 0·002 | 1·727 | 48·430 |
| 39. | 20·0 | 98·2 | 18·456 | 20·154 | 0·004 | 1·702 | 48·897 |
| 40. | 20·0 | 98·4 | 18·244 | 19·970 | 0·000 | 1·726 | 48·456 |

Mean value of N 48·594.

Specific heat of 45 per cent. spirit 94·192.

*g.* Spirit 50 per cent. Sp. gravity 0·9184.

| Experiment. | $t''$. | T. | $t$. | $t'$. | $v$. | $e$. | N. |
|---|---|---|---|---|---|---|---|
| 41. | 19·2 | 98·3 | 17·771 | 19·579 | 0·008 | 1·816 | 46·743 |
| 42. | 19·8 | 98·4 | 18·273 | 20·052 | 0·016 | 1·795 | 47·068 |
| 43. | 19·6 | 98·3 | 18·117 | 19·918 | 0·018 | 1·819 | 46·462 |

Mean value of N 46·758.

Specific heat of 50 per cent. spirit 90·633.

TABLE III. (continued).

*h*. Spirit 60 per cent. Sp. gravity 0·8956.

| Experiment. | $t''$. | T. | $t$. | $t'$. | $v$. | $e$. | N. |
|---|---|---|---|---|---|---|---|
| 44. | 17·5 | 98·35 | 16·076 | 18·105 | 0·016 | 2·045 | 43·345 |
| 45. | 18·5 | 98·48 | 17·535 | 19·538 | 0·006 | 2·009 | 43·405 |
| 46. | 19·5 | 98·40 | 17·447 | 19·435 | 0·005 | 1·993 | 43·771 |

Mean value of N 43·507.
Specific heat of 60 per cent. spirit 84·332.

*i*. Spirit 70 per cent. Sp. gravity 0·8721.

| Experiment. | $t''$. | T. | $t$. | $t'$. | $v$. | $e$. | N. |
|---|---|---|---|---|---|---|---|
| 47. | 16·5 | 98·3 | 17·165 | 19·369 | 0·024 | 2·228 | 40·141 |
| 48. | 19·0 | 98·2 | 17·087 | 19·275 | 0·008 | 2·196 | 40·730 |
| 49. | 19·0 | 98·4 | 16·881 | 19·088 | 0·010 | 2·217 | 40·539 |

Mean value of N 40·470.
Specific heat of 70 per cent. spirit 78·445.

*j*. Spirit 80 per cent. Sp. gravity 0·8483.

| Experiment. | $t''$. | T. | $t$. | $t'$. | $v$. | $e$. | N. |
|---|---|---|---|---|---|---|---|
| 50. | ...... | 98·2 | 17·370 | 19·820 | 0·012 | 2·462 | 37·034 |
| 51. | ...... | 98·1 | 17·167 | 19·636 | 0·012 | 2·481 | 36·786 |
| 52. | ...... | 98·1 | 17·167 | 19·602 | 0·022 | 2·459 | 37·135 |

Mean value of N 36·985.
Specific heat of 80 per cent. spirit 71·690.

*k*. Spirit 90 per cent. Sp. gravity 0·8228.

| Experiment. | $t''$. | T. | $t$. | $t'$. | $v$. | $e$. | N. |
|---|---|---|---|---|---|---|---|
| 53. | ...... | 97·60 | 17·293 | 20·000 | 0·020 | 2·727 | 34·074 |
| 54. | ...... | 97·55 | 18·277 | 20·960 | 0·020 | 2·703 | 33·927 |
| 55. | ...... | 98·05 | 15·795 | 18·587 | 0·024 | 2·816 | 33·785 |

Mean value of N 33·928.
Specific heat of 90 per cent. spirit 65·764.

*l*. Spirit 100 per cent. Sp. gravity 0·7936.

| Experiment. | $t''$. | T. | $t$. | $t'$. | $v$. | $e$. | N. |
|---|---|---|---|---|---|---|---|
| 56. | 20·0 | 98·25 | 17·215 | 20·306 | 0·006 | 3·097 | 31·128 |
| 57. | 19·0 | 97·60 | 17·674 | 20·708 | 0·012 | 3·046 | 31·266 |

Mean value of N 31·176.
Specific heat of 100 per cent. spirit 60·430.

At first the authors were inclined to attribute the high specific heat observed in the weaker spirits to evaporation, which, if it took place to any extent, would, of course, make the specific heat appear higher than it really is.

To test this point, they undertook some experiments in which the weight of the calorimeter with its liquid contents was carefully taken before and after the experiments, so that if any loss took place by evaporation it might become apparent. The following results were obtained.

First, with distilled water, twelve minutes intervened between the first weighing of the calorimeter before the experiment and the second weighing after the experiment.

First experiment, loss observed during the experiment . . 0·16 grm.
Second experiment, loss observed during the experiment . . 0·125 grm.

On allowing the calorimeter to stand exposed to the air for twelve minutes, a loss of 0·17 grm. in the first case, and 0·12 grm. in the second, took place, due to spontaneous evaporation. Thus the loss which could fairly be ascribed to evaporation produced by the introduction of the heated weight is quite inappreciable. Two similar experiments, made with 10 per cent. spirit, gave respectively 0·25 grm. and 0·20 grm. loss in the twelve minutes during which the experiment was made, and a loss of 0·21 and 0·21 grm. during the twelve succeeding minutes, when the calorimeter was allowed to stand exposed to the air, showing an evaporation of 0·04 grm and 0·00 grm. respectively, due to the introduction of the heated weight, a quantity which will not account for one-tenth of the effect observed.

Four experiments were then made in which the copper ring, instead of being heated to about 97° C., was heated to about 42° C.; the results are given in the following Table.

TABLE IV.

*Copper ring*, weight 614·49 grms.
*Copper value* of calorimeter and immersed part of thermometer 69·12 grms.
*Quantity* of liquid contained in the calorimeter 420·69 cub. centims.
*Time* occupied in each experiment 1·5 minute.

*a.* Distilled Water.

| Experiment. | $t''$. | T. | $t$. | $t'$. | $v$. | $e$. | N. |
|---|---|---|---|---|---|---|---|
| 58. | 14·0 | 41·64 | 12·925 | 16·246 | 0·025 | 3·342 | 7·485 |
| 59. | 14·7 | 41·94 | 12·957 | 16·335 | 0·020 | 3·398 | 7·422 |

Mean value of N 7·453.

*b.* Spirit 10 per cent. Sp. gravity 0·9814.

| Experiment. | $t''$. | T. | $t$. | $t'$. | $v$. | $e$. | N. |
|---|---|---|---|---|---|---|---|
| 60. | 14·00 | 43·00 | 13·449 | 16·832 | 0·025 | 3·408 | 7·708 |
| 61. | 13·25 | 41·81 | 12·339 | 15·693 | 0·020 | 3·374 | 7·771 |

Mean value of N 7·739.
Specific heat of 10 per cent. spirit 103·83.

It will be seen that the specific heat of the 10 per cent. spirit, deduced from these experiments, is as much above that of water as in the former experiments. To explain the results obtained in both cases as an effect of evaporation, we must make the very improbable hypothesis that the amount of liquid which evaporates during the introduction of a heated metallic body into a liquid is exactly proportional to the temperature of the body, whether it be heated to the boiling-point of the liquid or be considerably below it—an assumption obviously untenable.

Apart, however, from these experimental data, a little consideration will show that the effect observed is not due to evaporation.

The evaporation, if any, which affects the result must take place during the moment when the weight is in the act of entering the fluid; when once fairly underneath the surface, the large mass of cold liquid prevents the superheating of any part of it, whilst the effect produced by any evaporation taking place from the surface of the liquid spontaneously, is already provided for in the correction obtained by observing the fall in temperature for some time after the temperature of the calorimeter has reached its maximum.

The amount of evaporation, then, not included in this correction will depend, in the first place, on the temperature of the heated metal, which, being nearly the same in all the experiments, affects all alike; secondly, upon the time which the weight takes in actually entering the fluid, which is also alike in all the experiments, and is but a small fraction of a second; and lastly, all other circumstances being the same, this evaporation will be proportional to the surface of the heated body submerged. From the dimensions of the two weights, which have been previously given, the total surface of each, including the fan-wheel, can be calculated. It amounts to 182·4 square centimetres in the case of the copper ring, and 153·1 square centimetres in the case of the brass ring. The former weighs 614·49 grms., the latter 246·49 grms. The proportion of surface to weight is thus twice and ·1 as great in the brass weight as in the copper weight; in other words, the evaporation from the surface of the brass weight (153·1 square centimetres) will have twice and ·1 as much effect on its temperature as the evaporation from the surface of the copper weight (182·1 square centimetres) has on its temperature; yet the results obtained with the two weights are almost identical.

A series of experiments has nevertheless been undertaken, in which the specific heat of the 10 per cent. and 20 per cent. spirit was estimated, by observing the heating-effect of a known weight of either liquid, heated to a known temperature, upon a known weight of distilled water contained in a calorimeter. The liquid was at first enclosed in a thin glass bulb, which was heated with its contents to the desired point, by being immersed in a mercury-bath as recommended by Professor Kopp. The results, though generally confirming the previous experiments, did not agree among themselves as well as could be wished. This seemed chiefly owing to the fact that a globular body, having the greatest cubical capacity for a given surface, is not well adapted for the rapid cooling of its contents. In consequence of this, when about 50 cub. centims. of liquid were employed, from fifteen to twenty minutes were required to bring the temperature of the calorimeter to a maximum, or rather to the point whence the temperature began to sink; for the calorimeter frequently remained stationary at its maximum temperature for five or six minutes. On this account the correction applied amounted to a considerable fraction of the total rise observed, and great uncertainty was thereby introduced.

Having observed the beneficial effect, as regards rapidity of cooling, produced by the ring-shaped form of the weights, a hollow vessel of a similar shape was made of very thin brass, the liquid being contained in the annular space between the two sides. The external diameter of this annular vessel was about 60 millims., its internal diameter 40 millims., its height 70 millims. The annular space containing the liquid was thus about 10 millims. broad, and its capacity about 99 cub. centims.

The liquid was introduced by means of two openings at the upper part, which could be closed by small taps. The total weight of the vessel amounted to 49·66 grms.

The weight of water contained in the calorimeter, together with a weight of water equivalent, as regards the specific heat, to the vessel itself, stirrer, and immersed part of thermometer, amounted to 1165·905 grms.; and, as a mean of several concordant results, it was found that for every degree Centigrade lost by the empty annular vessel, the calorimeter and its contents gained 0°·004 C.

The annular vessel, after being filled with the liquid to be examined, was heated to the desired temperature in an oven, similar to the one used in the previous experiments, except that warm water instead of steam was used. By a simple arrangement the temperature of the water could be kept constant, whilst an effective stirrer preserved a uniform temperature in every part.

When the annular vessel, thus heated, was introduced into the calorimeter, the latter reached the maximum elevation of its temperature in five minutes, and did not remain stationary, but began to fall at once. The annular vessel was then taken out, the temperature of the calorimeter again read off at the end of three minutes, and the loss in temperature added to the highest temperature previously observed. During the whole of the experiment, the water in the calorimeter was kept thoroughly mixed by means of a stirrer. In all other respects the experiments were conducted as usual. The results are given in Table V.; they agree very well with those obtained in previous experiments; $m$ denotes the quantity of liquid heated, in grammes.

TABLE V.

*Water value* of calorimeter, contents, &c. 1165·905 grms.

*For each* degree Centigrade lost by the annular brass vessel the temperature of the calorimeter was raised 0°·004 C.

*Time* occupied by each experiment 5 minutes.

*a.* Distilled Water.

| Experiment. | *m.* | *t''.* | T. | *t.* | *t'.* | *v.* | *e.* | Specific heat. |
|---|---|---|---|---|---|---|---|---|
| 62. | 87·485 | ...... | 64·32 | 10·630 | 14·540 | 0·020 | 3·930 | 99·90 |
| 63. | 87·485 | 14·9 | 63·70 | 12·646 | 16·389 | 0·020 | 3·763 | 100·06 |
| 64. | 87·485 | 15·4 | 63·20 | 12·480 | 16·217 | 0·020 | 3·757 | 101·20 |
| 65. | 91·890 | 14·0 | 62·64 | 10·759 | 14·762 | 0·010 | 4·013 | 101·28 |

Mean specific heat of distilled water 100·61. In the following experiments, however, which were made under similar conditions, the specific heat of water is assumed to be 100·00.

*b.* Spirit 10 per cent. Sp. gravity 0·9814.

| Experiment. | *m.* | *t''.* | T. | *t.* | *t'.* | *v.* | *e.* | Specific heat. |
|---|---|---|---|---|---|---|---|---|
| 66. | 92·375 | 14·9 | 60·015 | 12·535 | 16·285 | 0·035 | 3·785 | 104·19 |
| 67. | 92·375 | 13·9 | 59·30 | 12·343 | 16·059 | 0·030 | 3·746 | 104·25 |
| 68. | 89·490 | 13·2 | 62·30 | 11·578 | 15·485 | 0·030 | 3·937 | 104·36 |
| 69. | 89·490 | 13·7 | 61·80 | 12·252 | 16·076 | 0·030 | 3·854 | 104·60 |

Mean specific heat of 10 per cent. spirit 104·35, or, assuming water to be 100·00, specific heat of 10 per cent. spirit 103·71.

*c.* Spirit 20 per cent. Sp. gravity 0·9716.

| Experiment. | *m.* | *t''.* | T. | *t.* | *t'.* | *v.* | *e.* | Specific heat. |
|---|---|---|---|---|---|---|---|---|
| 70. | 88·510 | 14·7 | 63·22 | 12·950 | 16·891 | 0·024 | 3·965 | 105·09 |
| 71. | 88·490 | 15·5 | 61·62 | 13·757 | 17·502 | 0·030 | 3·775 | 105·18 |

Mean specific heat of 20 per cent. spirit found 105·13; or, assuming water to be 100·00, specific heat of 20 per cent. spirit will be 104·49.

After the foregoing experiments had been concluded, it was found that a somewhat similar series of experiments on the specific heat of mixtures of alcohol and water had been made by A. SCHNIDARITSCH in the year 1859, and published in Wien. Akad. Ber. vol. xxxviii. p. 39, and KOPP and WILL, Jahrb. 1859, p. 440. SCHNIDARITSCH gives the specific heat of mixtures, from 10 per cent. to 10 per cent. by volume, from water to absolute alcohol; his results, however, differ considerably from those given in this paper. From the latter it appears that the specific heat of such alcoholic mixtures, up to a strength of 36 per cent. of alcohol, is above that of water; according to SCHNIDARITSCH the specific heat of all is below that of water. In fact the specific heat obtained by him for mixtures, up to an alcoholic strength of 60 per cent., is below that obtained in the present series of experiments, whilst for all stronger mixtures and absolute alcohol his results are higher.

SCHNIDARITSCH'S paper, though of some length, does not give the requisite data to check the results obtained by him, inasmuch as the correction applied in each case is not given. In his statement, however, as to how the corrections were made, there is an obvious error, as he uses REGNAULT'S formula for the amount of cooling observed in his (REGNAULT'S) calorimeter, though his (SCHNIDARITSCH'S) calorimeter is of different shape and one-fourth of the size. Any correction thus calculated which SCHNIDARITSCH has applied to his experiments will be obviously too small. Moreover SCHNIDARITSCH has experimented with but comparatively small quantities, about 10 grms. of spirit enclosed in a glass tube, whilst his calorimeter only contained 100 cub. centims.

Lastly, the thermometer employed to take the temperature of the calorimeter could only be read to $\frac{1}{50}$ of a degree, which is rather too large a fraction of the total rise observed.

His method of heating the glass tube and contents seems rather objectionable; and although the same glass tube and the *same portion* of the mixture, hermetically sealed in the glass tube, were used by him throughout the series of experiments on that mixture, yet the results obtained do not agree very well; with the 20 per cent. spirit there is a difference of nearly 3 per cent.

The authors nevertheless thought it advisable to repeat some of the experiments on the 20 per cent. spirit, estimating its specific heat between the same limits as those used by SCHNIDARITSCH. Instead of using a glass tube they employed an annular vessel (similar to the one previously described, but smaller and made of thinner brass) to enclose the spirit to be heated. This heating was effected in the same apparatus as that employed to heat the metallic weights, but the vapour of boiling alcohol was used instead of steam. In all other respects the experiments were conducted as usual.

The results of these experiments are given in Table VI.

The letters have the same signification as in previous Tables.

TABLE VI.

*Amount* of water in calorimeter 1155·766 grms.
*Water value* of calorimeter and immersed part of thermometer 9·734 grms.
*Water value* of annular brass vessel 2·597 grms.
*Time occupied* in each experiment $2^{m}$ $30^{s}$.

*a.* Distilled Water; amount taken 32·3475 grms.

| Experiment. | $t''$. | T. | $t$. | $t'$. | $v$. | $e$. | Specific heat. |
|---|---|---|---|---|---|---|---|
| 72. | 17·30 | 75·5 | 16·502 | 18·220 | 0·008 | 1·721 | 100·55 |

*b*. Spirit 20 per cent.; amount taken 33·6255 grms.

| Experiment. | *t''*. | T. | *t*. | *t'*. | *v*. | *e*. | Specific heat. |
|---|---|---|---|---|---|---|---|
| 73. | 18·0 | 75·60 | 16·723 | 18·549 | 0·008 | 1·834 | 104·55 |
| 74. | 17·3 | 75·45 | 16·500 | 18·329 | 0·008 | 1·837 | 104·59 |

Mean specific heat 104·570.

Relying on these experiments and the considerations above mentioned, the authors have no hesitation in saying that some undetected error must have vitiated the elaborate research of SCHNIDARITSCH.

Lastly, a few experiments have been made in which the copper weight, instead of being heated, was cooled to zero Centigrade, by enclosing it in a well-fitting metal box of very thin brass, the whole being placed in a vessel filled with small fragments of ice. In about two hours the lid of the box was taken off and the copper weight rapidly transferred to the calorimeter, which had been previously filled with liquid. The lowering of temperature produced is inversely proportional to the specific heat of the liquid in the calorimeter. All evaporation which the introduction of a heated body could produce is thus entirely avoided.

*Weight* of copper gilt ring 614·49 grms.

*Amount* of liquid in calorimeter 859·3 cub. centims.

*Copper value* of calorimeter and thermometer 58·70 grms.

a. *Distilled water.*

In three experiments the value of N was 15·450, 15·510, and 15·901. Mean 15·62.

b. 20 *per cent. spirit.*

In three experiments the value of N was 16·549, 16·112, and 16·365. Mean 16·342.

Specific heat of 20 per cent. spirit 104·62.

The temperature of calorimeter at beginning was about 19° C.

The weight produced a depression of about 1°·15 C.

The results of these experiments do not agree among themselves as well as those obtained in previous experiments, chiefly from the temperature of the cooled weight not being ascertained, but being assumed to be zero Centigrade in each case.

The following Table (Table VII.) gives the mean result of all the foregoing experiments, the theoretical specific heat of each mixture being given as calculated from the proportions of alcohol and water present in each mixture.

TABLE VII.

| Per cent. by weight of absolute alcohol. | Specific heat, found. | Specific heat, calculated. | Difference. |
|---|---|---|---|
| 5 | 101·502 | | |
| 10 | 103·576 | 96·043 | + 7·533 |
| 20 | 104·362 | 92·086 | 12·276 |
| 30 | 102·602 | 88·129 | 14·473 |
| 40 | 96·805 | 84·172 | 12·633 |
| 45 | 94·192 | 82·193 | 11·999 |
| 50 | 90·633 | 80·215 | 10·418 |
| 60 | 84·332 | 76·258 | 8·074 |
| 70 | 78·445 | 72·301 | 6·144 |
| 80 | 71·690 | 68·344 | 3·346 |
| 90 | 65·764 | 64·387 | 1·377 |
| 100 | 60·430 | | |

## Section II.—*Heat produced by the mixing of Alcohol and Water.*

The amount of heat produced by mixing alcohol and water in various proportions was estimated as follows:—

The liquid which formed the smallest portion of any given mixture was enclosed in a very thin glass bulb with a long narrow stem, the bulb and contents being carefully weighed.

The necessary quantity of the other liquid was then weighed out in a small calorimeter, made of very thin polished brass; into this calorimeter, supported as usual on stretched silk cords, surrounded by a cylinder of tin plate, and with a delicate thermometer immersed in the liquid, the glass bulb with its contents was introduced, and allowed to remain for ten minutes, the bulb itself being used to stir the liquid. At the end of that time the temperature of the calorimeter was observed; the glass bulb was then raised partly above the surface of the liquid in the calorimeter, broken by a smart tap with a file, and, by means of the portion of the broken bulb remaining attached to the stem, the contents of the calorimeter were thoroughly mixed.

In less than a minute the thermometer in the calorimeter reached a maximum, and at once began to fall; this fall was observed for thirty seconds, and added to the rise of temperature observed.

From the data thus obtained, the specific heat of the mixture formed being known, the number of units of heat evolved by 5 grms. of the mixture was calculated.

TABLE VIII.

Water value of calorimeter employed 1·248 grm.
Water value of thermometer employed 0·632 grm.
Specific heat of glass of bulb 0·19.

| Quantities taken of | | Per cent. by weight of alcohol contained in the mixture produced. | Weight of glass bulb immersed. | Temperature of calorimeter at | | Loss in thirty seconds. | Corrected rise. | Units of heat evolved by 5 grms. of the mixture. |
|---|---|---|---|---|---|---|---|---|
| Alcohol. | Water. | | | Beginning. | End. | | | |
| grms. | grms. | | | | | | | |
| 79·830 | 8·870 | 90 | 1·7529 | 18·091 | 20·265 | 0·083 | 2·257 | 7·7025 |
| 73·2300 | 18·4075 | 80 | 1·6049 | 17·365 | 20·700 | 0·034 | 3·369 | 12·4775 |
| 81·1280 | 34·7690 | 70 | 2·6649 | 17·128 | 21·763 | 0·041 | 4·676 | 18·8200 |
| 62·1660 | 41·4440 | 60 | 3·6849 | 17·309 | 23·348 | 0·241 | 6·280 | 27·2620 |
| 46·1850 | 46·1850 | 50 | 9·3634 | 17·567 | 24·815 | 0·277 | 7·525 | 35·5850 |
| 37·0070 | 45·2308 | 45 | 7·1494 | 17·420 | 25·053 | 0·277 | 7·910 | 38·8095 |
| 36·6375 | 54·9562 | 40 | 4·0449 | 17·420 | 26·001 | 0·419 | 9·000 | 44·8630 |
| 29·2340 | 68·2125 | 30 | 2·3544 | 17·337 | 26·227 | 0·250 | 9·140 | 47·9800 |
| 22·8025 | 91·2100 | 20 | 1·5069 | 16·106 | 24·202 | 0·177 | 8·273 | 43·9545 |
| 11·2345 | 101·1105 | 10 | 1·3419 | 17·295 | 22·286 | 0·069 | 5·060 | 26·6850 |

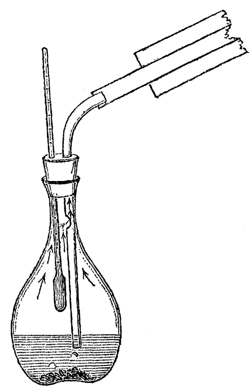
Section III.—*Boiling-points.*

About 100 cub. centims. of the mixture whose boiling-point was to be estimated were placed in a flask of about 200 cub. centims. capacity, closed by a doubly perforated cork.

In one of the perforations a thermometer was fixed in such a manner that its bulb was about $\frac{1}{2}$ inch above the surface of the liquid, whilst nearly the whole thread of mercury was surrounded by the vapour of the boiling liquid.

The steady boiling of the mixture was ensured by the introduction of broken pieces of tobacco-pipes, previously ignited, into the flask.

Fig. 2.



In the second perforation a tube of moderately large diameter was inserted, which passed down to just beneath the surface of the liquid, the upper end being connected with a LIEBIG's condenser. In this tube a lateral opening is made, by means of a blowpipe-flame, just beneath the cork; and through the opening thus made the vapour from the flask passes into the condenser, whilst the condensed liquid runs down the tube, and is discharged just below the surface of the boiling liquid, having been raised nearly to the boiling-point in its passage down the heated tube. In this manner the composition of the liquid in the flask can be kept constant for a sufficient length of time to allow a tolerably accurate estimation of the boiling-point to be made.

It was found that the boiling-points of distilled water and absolute alcohol did not vary $\frac{1}{100}$ of a degree, whether the vapour was allowed to escape freely into the atmosphere, or was condensed and made to run back into the flask. It is, however, necessary to have the glass tube and condenser of a diameter large enough to allow the condensed liquid to run down on one side while the vapour escapes on the other. If this precaution is not taken, the condensed liquid is apt to block up the tube and prevent the free escape of the vapour; should this occur, the pressure in the flask is slightly increased, and a corresponding rise in the boiling-point at once takes place.

The thermometer employed had a range from 65° to 100° C., divided into tenths of a degree; and thus $\frac{1}{100}$ of a degree could be read off.

The following Table gives the result of the experiments, the barometer standing at 744·4 millims.

The third column gives the boiling-points calculated on the assumption that the two bodies, alcohol and water, influence the boiling-points of the several mixtures in proportion to the weights of each which those mixtures respectively contain.

TABLE IX.

| Per cent. by weight of absolute alcohol. | Boiling-point observed. | Boiling-point calculated. | Difference. |
|---|---|---|---|
| 0 | 99·4 | | |
| 10 | 90·98 | 97·25 | −6·27 |
| 20 | 86·50 | 95·10 | −8·60 |
| 30 | 84·01 | 92·95 | −8·94 |
| 40 | 82·52 | 90·90 | −8·38 |
| 45 | 81·99 | 89·72 | −7·73 |
| 50 | 81·33 | 88·60 | −7·27 |
| 60 | 80·47 | 86·50 | −6·03 |
| 70 | 79·61 | 84·35 | −4·74 |
| 80 | 78·84 | 82·20 | −3·36 |
| 90 | 78·01 | 80·05 | −2·04 |
| 100 | 77·89 | | |

## Section IV.—*Capillary Attraction.*

A capillary tube of convenient size and length is chosen, carefully cleaned with sulphuric acid, alcohol, and water, and then thoroughly rinsed out with the mixture under examination.

The capillary tube, thus prepared, is fixed vertically in an ordinary universal screw-clamp.

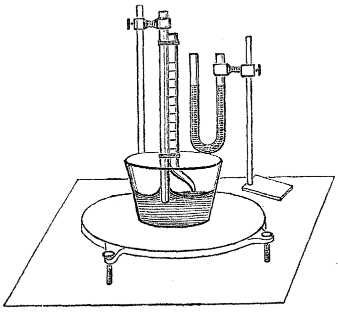
A glass rod is taken, about the same length as the capillary tube; its lower extremity is drawn out and bent aside, so that it terminates in a point at some distance from the axis of the rod. A millimetre-scale is etched on the glass rod, and the vertical distance of the point from the lowest division of the millimetre-scale is carefully measured. This glass rod is fixed to the capillary tube by two india-rubber bands, the point of the glass rod being some little distance above the lower extremity of the capillary tube.

The liquid whose capillarity is to be estimated is placed in a small capsule, underneath the capillary tube. The capsule is supported on a stand, whose height can be delicately adjusted by means of three screws.

The stand is raised at first rapidly, then slowly, until the point of the glass rod just touches the surface of the liquid in the capsule. The moment when this contact between the point and the surface takes place can be observed with the greatest accuracy; and as the point is bent aside, it touches the surface beyond the influence of the capillary action of the external portion of the tube.

The height of the thread of liquid in the capillary tube is now to be read off by means of the scale etched on the glass rod. To do this with sufficient accuracy, a telescope, capable of horizontal and vertical movement, and furnished with cross wires in the eyepiece, is used.

Fig. 3.



A small U-tube, containing spirit, is fixed near the capillary tube; the eyepiece of the telescope is turned round till one of the cross wires just touches the two menisci in the U-tube; thus the cross wire is placed accurately horizontal. On slightly turning the telescope horizontally, and, if necessary, raising it vertically, the horizontal wire can be made to touch the meniscus in the capillary tube, and at the same time cut the divisions etched on the glass rod; the point where the wire thus crosses the millimetre-scale is read off, and thus the height of the thread above the surface of the liquid is determined.

This method gives very accurate results, if care be taken in the various adjustments.

The following Table gives the results obtained.

Column 1 gives the percentage of alcohol by weight.

Column 2 gives the observed height of the thread, in millims.

Column 3 gives the height supposing water stood at 100 millims.

Column 4 gives the length of a column of water equal in weight to the thread of alcoholic mixture in column 3, and affords, therefore, a measure of the relative strength of the molecular attraction in the various mixtures.

Column 5 gives the heights calculated on the assumption that they will be proportional to the weight of the constituents of each mixture.

Column 6 gives the difference between Columns 4 and 5.

## Table X.

A thread of mercury in the capillary tube, 121·5 millims. long, weighed 0·4426 grm., giving 0·584 millim. as the diameter of the tube.

The temperature at which the experiments were made was 16° C.

| 1. Alcohol per cent. | 2. Height observed. | 3. Height, assuming water=100 millims. | 4. Relative molecular attraction. | 5. Height calculated. | 6. Difference. |
|---|---|---|---|---|---|
| 0 | 49·47 | 100 | 100 | 100 | |
| 10 | 34·22 | 69·17 | 68·07 | 93·11 | −25·04 |
| 20 | 27·92 | 56·43 | 54·83 | 86·22 | 31·39 |
| 30 | 23·84 | 48·19 | 46·15 | 79·34 | 33·19 |
| 40 | 22·41 | 45·30 | 42·56 | 72·45 | 29·89 |
| 45 | 21·64 | 43·74 | 40·64 | 69·00 | 28·36 |
| 50 | 21·24 | 42·93 | 39·43 | 65·56 | 26·13 |
| 60 | 20·93 | 42·30 | 37·89 | 58·68 | 20·79 |
| 70 | 20·66 | 41·76 | 36·42 | 51·79 | 15·37 |
| 80 | 20·43 | 41·29 | 35·03 | 44·90 | 9·87 |
| 90 | 20·06 | 40·54 | 33·35 | 38·02 | 4·67 |
| 100 | 19·40 | 39·21 | 31·13 | 31·13 | |

## Section V.—*Rate of Expansion.*

The rate of expansion is determined by carefully estimating the specific gravity of the different mixtures, at the temperatures 10°, 15°·5, and 20° C.

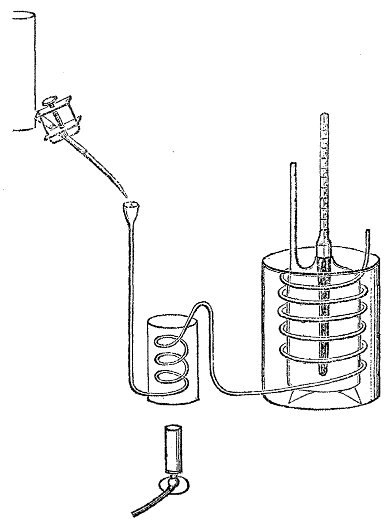
The specific-gravity bottle employed is a rather large two-necked bottle of thin glass. In one of the necks a delicate thermometer is fixed, serving as a stopper; the other neck ends in a capillary tube about 120 millims. long; 100 millims. from the upper end a mark is etched on the tube, and the capacity of the bottle, when filled up to this mark, is carefully measured. As it is difficult to fill such a bottle exactly up to the mark at a particular temperature, the level of the liquid in the capillary tube is only roughly adjusted, and the distance of the surface of the liquid from the mark accurately measured. It was found that 1 millim. of the tube contained 0·00195 cub. centim.; this being known, the quantity of liquid contained in the tube above the mark could be calculated, and its weight subtracted from that found, in order to get the weight of the contents of the flask when filled up to the mark.

The thermometer is carefully ground in to fit the neck of the flask; it has a long thin bulb passing through almost the entire depth of the specific-gravity bottle. Its range was from 8° to 25° C., divided into twentieths of a degree; and with a telescope $\frac{1}{200}$ degree Centigrade could be read off.

The specific-gravity bottle is placed in a water-bath, surrounded by a double cylinder of tin plate.

The temperature of this water-bath is under perfect control by means of the following arrangement.

Fig. 4.



The water-bath contains a coil of metal tube like an ordinary condenser. The lower end of this coil is connected with a second and smaller worm, which is contained in a small water-bath. The latter is heated by a lamp and kept gently boiling. The lower end of this second worm is bent upwards, and terminates in a long funnel. Any water poured into this funnel will pass, first through the worm, surrounded by boiling water, and be thus heated, and then through the tube in the water-bath containing the specific-gravity bottle, when it will give up its heat and raise the temperature of the water-bath. By regulating the flow of water, the temperature of this water-bath can be raised quickly, or kept constant at any desired point; so that with a little care the temperature can be raised in a few minutes from 10° to 20°, and kept within $\frac{1}{20}$ of a degree of the latter temperature for any length of time. To ensure a uniform temperature, the water is constantly agitated by the passage of a rapid current of air from below upwards.

The temperature of the bath is taken by a thermometer exactly similar to the one inside the specific-gravity bottle.

It was found that the temperature of the specific-gravity bottle could be kept within about $\frac{1}{40}$ of a degree of the temperature of the water-bath; a more exact coincidence is not required, as the possible error thus made is quite within the unavoidable errors in filling, weighing, &c.

The bottle was weighed on a balance which turned readily with 0·0005 grm., the empty bottle being counterpoised by a second bottle of the same size and shape, to avoid any errors from hygrometric moisture.

The thermometer and barometer were observed every time a weighing was made, and the true weight *in vacuo* calculated in each case.

The mixtures were made by gradually diluting the stronger mixtures, from nearly absolute alcohol downwards; and after being made, the mixtures were exposed for twenty-four hours in the exhausted receiver of an air-pump, so that any air present might be removed.

Owing to a slight mistake in making some of the mixtures, they are not of the exact strength desired.

Weight of distilled water in specific-gravity bottle

at 10°·0 C. 545·3507 grms.,
15°·5 C. 545·0540 grms.,
20°·0 C. 544·6705 grms.

The volume of the bottle will therefore be, adopting MATTHIESSEN'S results for the expansion of water,

at 10°·0 C. 545·4985 cub. centims.,
15°·5 C. 545·5843 cub. centims.,
20°·0 C. 545·6585 cub. centims.

TABLE XI.

| Per cent. of alcohol, by weight. | Specific gravity at 10° C. | Specific gravity at 15°·5 C. | Specific gravity at 20° C. |
|---|---|---|---|
| 10 | 98396 | 98298 | 98189 |
| 20 | 97261 | 97054 | 96866 |
| 30 | 95995 | 95666 | 95392 |
| 40 | 94253 | 93854 | 93520 |
| 45 | 93262 | 92846 | 92496 |
| 50 | 92185 | 91745 | 91390 |
| 59·77 | 89994 | 89545 | 89179 |
| 69·70 | 87695 | 87219 | 86844 |
| 79·81 | 85271 | 84797 | 84410 |
| 89·89 | 82712 | 82240 | 81851 |
| 100·00 | 79792 | 79317 | 78932 |

TABLE XII.

| Per cent. of alcohol, by weight. | Volume at 10° C. | Volume at 20° C. Found. | Volume at 20° C. Calculated. | Difference. |
|---|---|---|---|---|
| 0 | 100 | 100·154 | 100·154 | |
| 10 | 100 | 100·212 | 100·272 | −0·060 |
| 20 | 100 | 100·405 | 100·386 | +0·019 |
| 30 | 100 | 100·632 | 100·489 | +0·143 |
| 40 | 100 | 100·783 | 100·601 | +0·182 |
| 45 | 100 | 100·827 | 100·652 | +0·175 |
| 50 | 100 | 100·868 | 100·700 | +0·168 |
| 59·77 | 100 | 100·914 | 100·789 | +0·125 |
| 69·70 | 100 | 100·980 | 100·874 | +0·106 |
| 79·81 | 100 | 101·020 | 100·954 | +0·066 |
| 89·89 | 100 | 101·052 | 101·034 | +0·018 |
| 100·00 | 100 | 101·088 | 101·088 | |

## Section VI.—*Compressibility.*

The compressibility was estimated in an apparatus similar to the one employed by REGNAULT and GRASSI, but of simpler construction.

The piézomètre is a cylindrical glass tube with spherical ends, and has a long capillary tube attached at one end; it is about 150 millims. long and 32 millims. in diameter. The weight of water contained in it at 4° C. is 114·9727 grms.; and 1 millimetre of the capillary tube has a capacity of 0·000517173 cub. centim.

Air was forced into the apparatus by means of a small pump, and thus pressure was applied simultaneously to the inside and outside of the piézomètre; the amount of pressure is ascertained by the length of a column of mercury supported by it. The compression produced is read off by a millimetre-scale etched on the capillary tube.

To the compressibilities thus found, 0·000002 was always added as a correction for the compressibility of the piézomètre, this number being about the mean of the effect observed by GRASSI when a glass piézomètre was employed.

The numbers in the following Table are calculated for a pressure of one atmosphere.

TABLE XIII.

Weight of water contained in Piézomètre at 4° C. 114·9727 grms.
1 millim. of capillary gauge = 0·000517173 cub. centim.

| Per cent. of alcohol, by weight. | Depression, in millims. | Temperature, in degrees Centigrade. | Compression. | Calculated. | Difference. |
|---|---|---|---|---|---|
| 0 | 40·68 | 9 | 0·00004774 | 0·00004774 | |
| 10 | 36·92 | 11·2 | 0·00004351 | 0·00005387 | − 0·00001036 |
| 20 | 33·00 | 11·5 | 0·00003911 | 0·00005998 | 0·00002087 |
| 30 | 32·92 | 10·2 | 0·00003902 | 0·00006584 | 0·00002682 |
| 40 | 36·88 | 9 | 0·00004347 | 0·00007118 | 0·00002771 |
| 45 | 39·20 | 8 | 0·00004608 | 0·00007364 | 9·00002756 |
| 50 | 41·60 | 9 | 0·00004878 | 0·00007600 | 0·00002722 |
| 59·77 | 48·20 | 10 | 0·00005620 | 0·00008029 | 0·00002409 |
| 69·70 | 53·25 | 10·1 | 0·00006159 | 0·00008426 | 0·00002267 |
| 79·81 | 59·96 | 9·6 | 0·00006942 | 0·00008775 | 0·00001833 |
| 89·89 | 68·76 | 11·1 | 0·00007950 | 0·00009140 | 0·00001190 |
| 100·00 | 81·36 | 9·7 | 0·00009349 | 0·00009349 | |

Without entering into any theoretical speculations, sufficient data for which they do not at present possess, the authors would point out certain relations, more or less intimate, which connect the various physical properties of mixtures of alcohol and water, and which have been brought out by the above series of experiments.

It will be seen by a glance at Plate LXIV. that, with one exception (*i. e.* expansion of 17 to 18 per cent. spirit), the numbers found never coincide with those calculated, as explained in the foregoing paper; in fact all the characters examined fall naturally into two classes—I. containing those which, at an alcoholic strength of 30 per cent. by weight, reach a maximum deviation from the number calculated, and II. those which reach a maximum deviation at 40 per cent. Each of these classes may be divided into two subclasses—one containing those properties in which the numbers found are above those calculated, and a second containing those in which they are below.

Class I.

*a.* Specific heat.
Heat produced by mixing.

*b.* Boiling-points.
Capillary attraction.

Class II.

*c.* Rate of expansion.

*d.* Compressibility.

On examining these in detail some remarkable facts will be noticed. In subclass *a*, Specific Heat, it will be seen, by Table VII. and Plate LXIV., that the first addition of alcohol to water, though alcohol has a specific heat much less than that of water, actually raises the specific heat; so that a mixture between 30 per cent. and 40 per cent. has the same specific heat as water.

On comparing the elevation of specific heats found, above the theoretical specific heats calculated as above, with the amount of heat produced by mixing, it will be seen (Plate LXIV.) that mixtures producing the same amount of heat possess the same elevation of specific heat; and further, if the number of units of heat produced in the formation of any mixture be divided by 3·411 in each case, a number is obtained which expresses the elevation of the specific heat of such mixture above its theoretical specific heat.

By thus calculating the specific heat from the units of heat evolved, or *vice versâ*, numbers are obtained which agree so closely with the numbers found, that the difference is quite within the limits of experimental error (*vide* Table XIV.).

TABLE XIV.

| Percentage of alcohol, by weight. 1. | Theoretical specific heat (Table VII.). 2. | Units of heat divided by 3·411. 3. | Specific heat thus calculated by adding columns 2 and 3. | Specific heat found by experiment. |
|---|---|---|---|---|
| 10 | 96·043 | 7·823 | 103·866 | 103·576 |
| 20 | 92·086 | 12·885 | 104·971 | 104·362 |
| 30 | 88·129 | 14·060 | 102·189 | 102·620 |
| 40 | 84·172 | 13·152 | 97·324 | 96·805 |
| 45 | 82·193 | 11·377 | 93·570 | 94·192 |
| 50 | 80·215 | 10·432 | 90·647 | 90·633 |
| 60 | 76·258 | 7·992 | 84·250 | 84·332 |
| 70 | 72·301 | 5·517 | 77·818 | 78·445 |
| 80 | 68·344 | 3·658 | 72·002 | 71·690 |
| 90 | 64·387 | 2·258 | 66·645 | 65·764 |

In subclass *b* a somewhat similar relation exists between the boiling-points and capillary attraction. Mixtures having the same depression of boiling-point have also the same depression of capillarity below that calculated; and the depression of the boiling-point may be obtained by dividing the depression of capillarity, when water rises to 100 millims., by 3·410 (Tables IX. & X. and Plate LXIV.); or the curve giving the depression observed in capillarity will be nearly the same as that giving the depression of the boiling-point, if water be taken as rising to 29·3 millims. The numbers, however, thus obtained do not agree quite so closely as do those obtained in a similar manner with the specific heat and heat produced by mixing; but it must be remembered that the boiling-point cannot be estimated with the same amount of accuracy as the specific heat, whilst it also varies with the height of the barometer, and the capillary attraction with the temperature. It might thus be possible to select a temperature and pressure in which the relation between the two properties would be as perfect as that existing between the specific heat and the heat produced by mixing.

In Class II. subclass *c* (see Table XII. Plate LXIV.), the rate of expansion, is remarkable, inasmuch as the first addition of alcohol, up to nearly 20 per cent., causes the rate of expansion to be below that calculated, whilst in all the rest of the mixtures the rate of expansion remains constantly above that calculated; and so a mixture about 17 or 18 per cent. has a rate of expansion identical with its theoretical expansion.

In subclass *d* it will be noticed (Table XIII. Plate LXIV.) that the first additions of alcohol, although the latter is much more compressible than water, produce mixtures which are less compressible than water, so that a mixture between 45 and 50 per cent. has the same compressibility as water.

Other characters, which have been examined by previous experimenters, are:—

1. *Vapour-Tension.*—This falls under Class I. subclass *b*, reaching a maximum deviation below the mean, calculated in a similar way, at 30 per cent. of alcohol, according to the researches of DRONKE, 'Ueber die Spannkraft der Dämpfe aus Flüssigkeitsgemischen. Inaugural-Dissertation, Marburg 1862; and WÜLLNER, Pogg. Ann. cxxix. 353.

2. *Specific Gravity*; and 3. *Index of Refraction.*—The two latter form a new class,

as they both reach a maximum deviation from the calculated mean at 45 per cent. These two properties have been shown to be connected with each other by DEVILLE and HOEK, Ann. de Chim. et de Phys. 3rd series, v., and Pogg. Ann. cxii.

Properties which are more nearly chemical than physical, as the solubility of various salts, have also been examined; some of these salts, as potassic chloride, reach a maximum deviation from the mean solubility at 30 per cent. alcohol; others seem to reach the maximum deviation at 40 per cent. and 45 per cent.; but the subject requires further investigation.

Thus the whole of the physical characters of mixtures of alcohol and water come to a maximum deviation from their theoretical values somewhere between 30 per cent. and 45 per cent. alcohol by weight; the 30 per cent. alcohol nearly corresponds to the formula $C_2H_6O+6OH_2$, which actually gives 29·87 per cent.; whilst 45 per cent. is nearly represented by the formula $C_2H_6O+3OH_2$, which really gives 46 per cent.

Some of the physical characters examined seem to be especially connected with each other; these are:—

1. Specific heat and heat produced by mixing; for by dividing the number of units of heat evolved by 5 grms. of any mixture by 3·411, the elevation of the specific heat of such mixture above the theoretical specific heat is obtained.
2. Boiling-point and capillary attraction, which in a similar way can be calculated from each other.

DEVILLE and HOEK have shown the specific gravity and index of refraction to be connected with each other.

Whether these relations hold good with other similar substances, whether in fact these experiments have brought forward one example of a general law, or only discovered a singular anomaly, must be left for further research to decide.

## EXPLANATION OF THE PLATE.

## PLATE LXIV.

### UPPER HALF.

Curve 1 gives the specific heats; the vertical lines represent the percentage by weight of alcohol in this and all the following curves.

The horizontal line gives the specific heat, water=100.

Curve 2. The horizontal lines give the boiling-points in degrees Centigrade.

Curve 3. The horizontal lines give the capillarity in millims., water=100 millims.

Curve 4. The horizontal lines give the expansion for 10,000 volumes.

Curve 5. The horizontal lines give the compressibility in millionths.

### LOWER HALF.

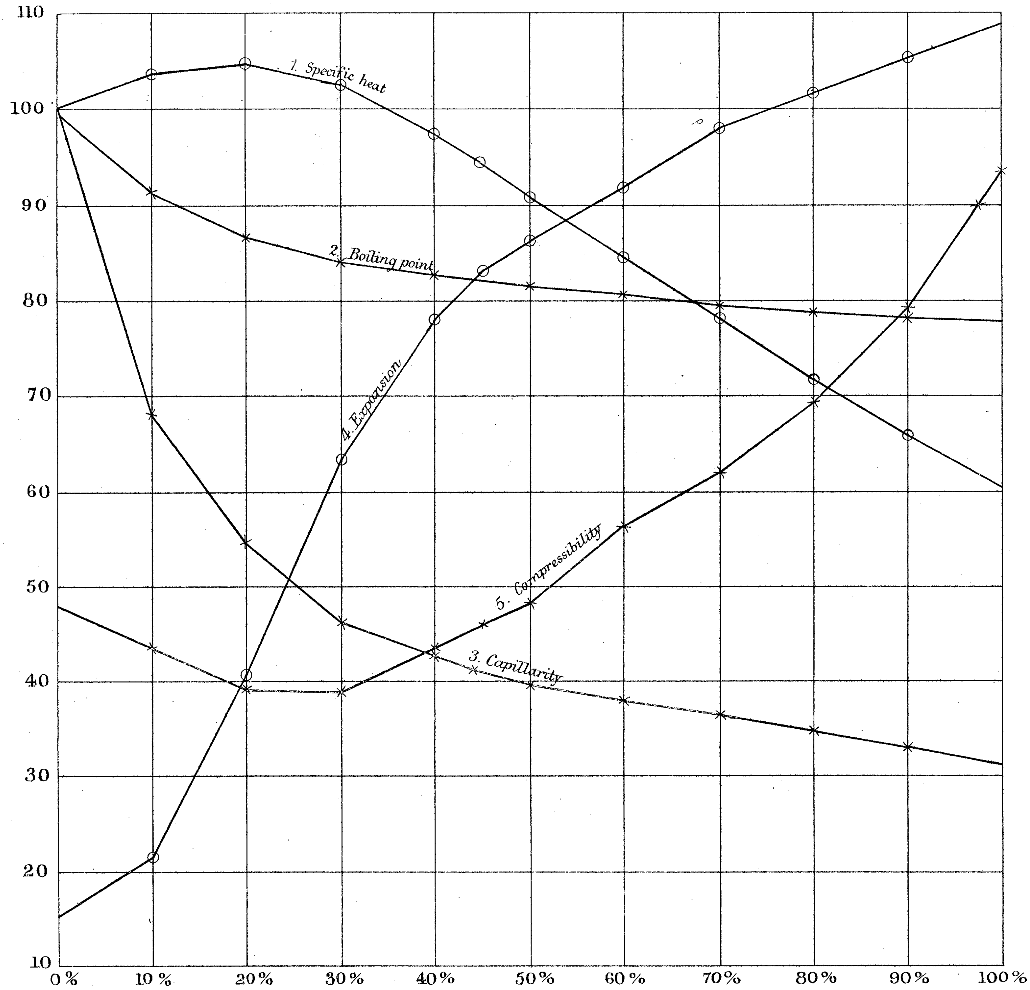
The vertical lines, as in the upper half of the Plate, give the percentage of alcohol.

The horizontal lines in Curves 1–5 have the same significance as in the upper half, except that they give the deviations of the numbers found from the theoretical mean, instead of the numbers themselves.

Curve 6 gives the heat produced by mixing, the horizontal lines representing units of heat.

The zero line represents the mean value of all the properties.

Those belonging to subclasses *a* and *c*, specific heat, heat produced by mixing, and rate of expansion, are distinguished by a small circle round the points directly ascertained by experiment; while those belonging to subclasses *b* and *d*, boiling-point, capillary attraction, and compressibility, are similarly distinguished by a cross.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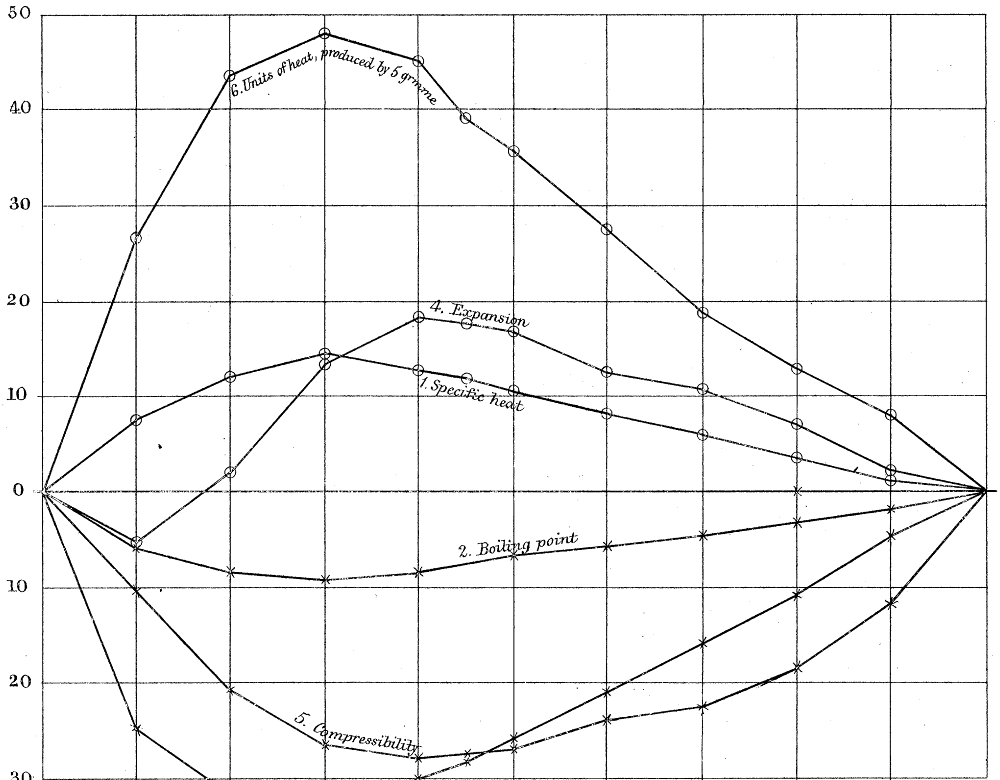
1. Specific heat
2. Boiling point
3. Capillarity
4. Expansion
5. Compressibility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1. Specific heat
2. Boiling point
5. Compressibility


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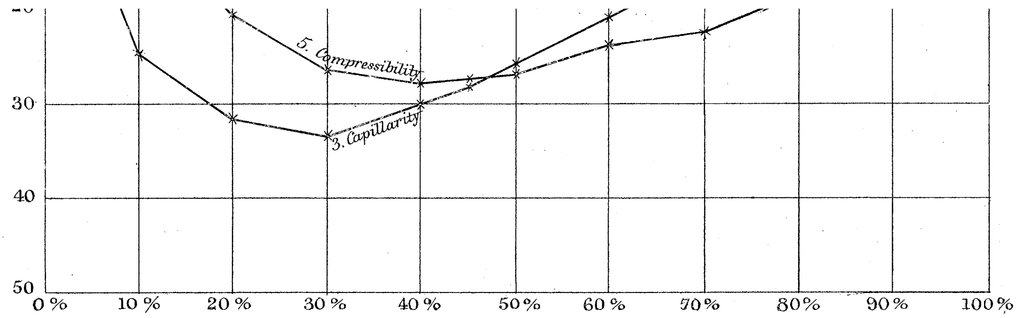
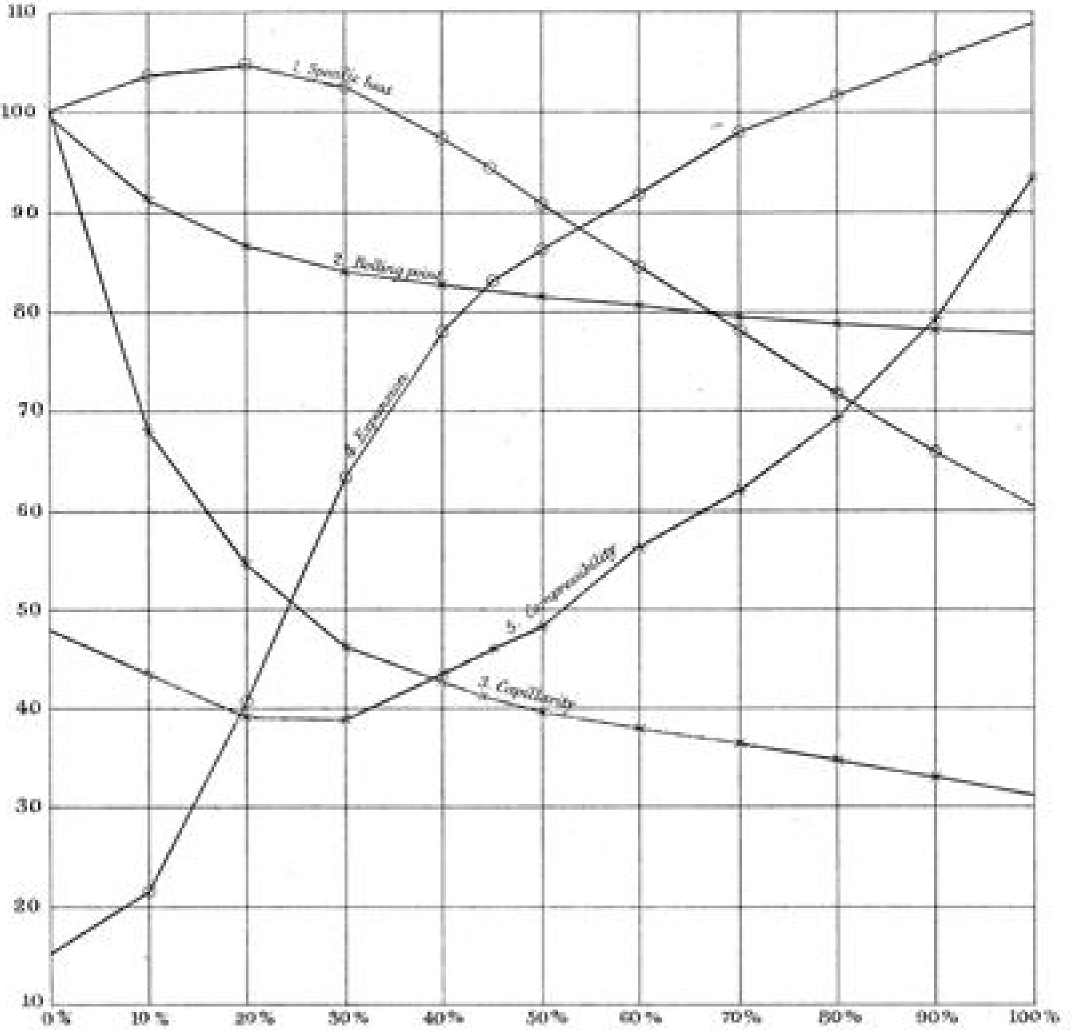



W. H. Wesley lith.


W. West imp.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1. Specific heat
2. Boiling point
4. Expansion
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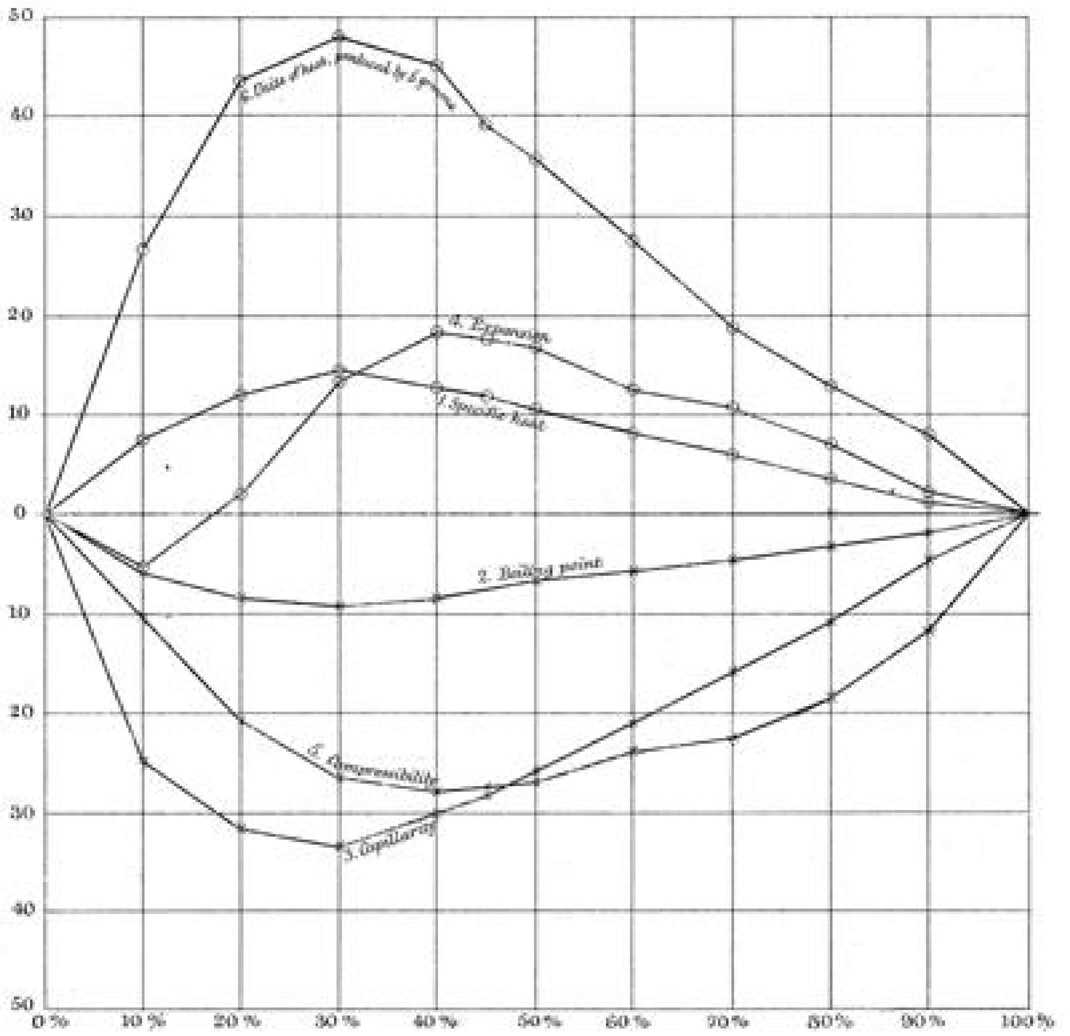
3. Capillarity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6. Units of heat, produced by 1 gramme
4. Expansion
1. Specific heat
2. Boiling point
5. Compressibility
3. Capillarity