

May 16, 1872.

FRANCIS GALTON, M.A., Vice-President, in the Chair.

The following communications were read:—

- I. "On the Specific Heat and other physical characters of Mixtures of Methylic Alcohol and Water, and on certain relations existing between the Specific Heat of a Mixture or Solution and the Heat evolved or absorbed in its formation." By A. DUPRÉ, Ph.D., Lecturer on Chemistry at the Westminster Hospital. Communicated by W. ODLING, M.B. Received April 4, 1872.

(Abstract.)

The pure methylic alcohol used in these experiments was prepared from rectified wood-spirit according to a process of E. Th. Chapman, being a modified chloride-of-calcium process as originally recommended by Sir Robert Kane. The anhydrous alcohol obtained had a specific gravity of $\cdot 81371$ at 10° C.; it boiled at a temperature of $58^{\circ}\cdot 6$ C. under a pressure of $757\cdot 4$ millims., had a specific heat of $58\cdot 325$ between the temperatures 60° and 18° , and was perfectly miscible with water in every proportion. When oxidized with excess of bichromate and sulphuric acid, it yielded nothing but carbonic acid and water.

Section 1. *Specific Heat.*

This is estimated in the usual manner, by heating a known weight of the liquid enclosed in a suitable vessel to a certain temperature, and plunging it, vessel and all, into the water of a calorimeter; the rise in temperature produced will, with the necessary corrections, furnish the data required for the calculation of the specific heat sought. This calculation was performed by help of the following formula:—

$$C = \frac{W(t'' - t)}{m(T - t')} - \frac{\mu}{m},$$

wherein C is the specific heat required;

W the water-value of the calorimeter and contents;

t the temperature of the calorimeter at the beginning;

t' the temperature of the calorimeter at the end;

t'' the temperature of the calorimeter at the end plus the necessary corrections;

T the temperature of the steam-oven;

m weight of fluid or mixture employed;

μ water-value of vessel holding the mixture.

The vessel to contain the mixture is an annular brass vessel, with a fan-

wheel in the inner cylindrical space to serve as stirrer. The steam-oven is heated by the vapour of methylic alcohol.

The mean results are given in the following Table :—

TABLE I.

Percentage of methylic alcohol, by weight.	Specific heat found.	Specific heat calculated.	Difference.
10	98·582	95·832	+2·750
20	95·914	91·665	4·249
30	92·658	87·497	5·161
40	89·219	83·330	5·889
50	84·645	79·162	5·483
60	80·177	74·995	5·182
70	75·500	70·827	4·673
80	69·999	66·660	3·339
90	64·282	62·492	1·790
100	58·325		

Section 2. *Heat produced by mixing Methylic Alcohol and Water.*

This is estimated by mixing the alcohol and water, in the required proportion, in an annular vessel similar to the one used for the estimation of the specific heat, and observing the elevation of temperature produced in the water of a calorimeter in which the annular vessel is immersed. The units of heat evolved in the formation of 5 grms. of each mixture were thus calculated and found to be :—

TABLE II.

10 per cent. spirit	20·930	60 per cent. spirit	41·493
20	„	37·276	70	„	34·456
30	„	44·744	80	„	22·448
40	„	45·384	90	„	13·164
50	„	44·429			

The temperature at which the mixing took place ranged between 16° and 20° C.

Section 3. *Boiling-points.*

The mixtures were boiled in a flask connected with a condenser, by which the vapours are condensed and made to run back into the flask; the composition of the mixture is thus kept as uniform as possible.

The cold liquid running back is prevented from disturbing the boiling by having to pass down a tube placed inside the flask, in which it becomes heated nearly to boiling before it flows into the boiling mixture. The following Table gives the results, the barometer standing at 757·4 millims. The numbers in column 3 are calculated on the assumption that the

boiling-point of a mixture is influenced by its components in proportion to their respective weights.

TABLE III.

Percentage of absolute methylic alcohol, by weight.	Boiling-point observed.	Boiling-point calculated.	Difference.
0	99.93	°	
10	82.57	95.80	-13.23
20	75.26	91.76	16.56
30	70.68	87.53	16.85
40	68.31	83.40	15.09
50	67.08	79.26	11.18
60	65.75	75.13	9.38
70	64.65	71.00	6.35
80	63.13	66.87	3.74
90	60.96	62.73	1.77
100	58.60		

Section 4. *Capillary Attraction.*

This is estimated by means of an apparatus similar to the one employed by Gay-Lussac, the height being measured by a cathetometer. Two capillary tubes are employed, and the mean taken. The third column in Table IV. gives the length of a column of water equal in weight to the thread of alcoholic mixture in the second column, and affords, therefore, a measure of the relative strength of the molecular attraction in the various mixtures. The heights in column 4 are calculated on the assumption that they will be proportional to the weight of the constituents.

The experiments are made at a temperature of 13°·5 C.

TABLE IV.

Percentage of methylic alcohol, by weight.	Height, assuming water = 100 millims.	Relative molecular attraction.	Height calculated.	Difference.
0	100.000	100.000		
10	68.820	67.818	93.334	-25.416
20	58.830	57.264	86.667	29.403
30	52.463	50.381	80.001	29.620
40	48.947	46.252	73.335	27.083
50	46.538	43.136	66.668	23.532
60	46.467	42.170	60.002	17.832
70	45.176	40.034	53.336	13.302
80	43.997	37.955	46.669	8.714
90	42.612	35.671	40.003	4.332
100	40.970	33.337		

Section 5. *Specific Gravity and Rate of Expansion.*

Table V. gives the specific gravities of the various mixtures at the temperatures of 10° and 20° C., water at 4° C. taken as unit, together with the calculated specific gravities at 10° C., and the difference between the specific gravities as observed and calculated.

Table VI. gives the expansion of 100 volumes of the mixtures when heated from 10° to 20° C., calculated from the data of the previous Table. The figures in column 4 are calculated on the assumption that the expansion is proportional to the volumes of the constituents, the contraction taking place on mixing being allowed for.

TABLE V.

Percentage of methylic alcohol, by weight.	Specific gravity at 10° C.	Specific gravity at 20° C.	Specific gravity at 10° C., calculated.	Difference.
0	99973	99819		
10	98632	98384	97762	+ 870
20	97478	97080	95622	1856
30	96222	95675	93573	2649
40	94729	94054	91611	3118
50	92991	92205	89727	3264
60	91048	90207	87923	3125
70	88933	88035	86188	2745
80	86598	85655	84520	2078
90	84054	83079	82916	1138
100	81371	80334		

TABLE VI.

Percentage of methylic alcohol, by weight.	Volume at 10° C.	Volume at 20° C., found.	Volume at 20° C., calculated.	Difference.
0	100	100.154		
10	100	100.252	100.293	-0.041
20	100	100.410	100.429	-0.019
30	100	100.571	100.562	+0.009
40	100	100.718	100.689	+0.029
50	100	100.853	100.809	+0.044
60	100	100.932	100.922	+0.010
70	100	101.019	101.028	-0.009
80	100	101.101	101.124	-0.023
90	100	101.173	101.212	-0.039
100	100	101.290		

Section 6. *Compressibility.*

This is estimated by means of an apparatus similar to the one employed by Regnault and Grassi. Instead of a reservoir of compressed air a

vessel holding liquid carbonic acid was employed, by means of which any required pressure could be obtained with great facility.

TABLE VII.

Percentage of methylic alcohol, by weight.	Temperature in degrees Centigrade.	Compressibility for 1 atmosphere.		Difference.
		Found.	Calculated.	
0	16.8	0.00004741		
10	16.5	.00004368	0.00005497	-0.00001129
20	16.0	.00004365	.00006303	.00001938
30	15.4	.00004289	.00007052	.00002763
40	17.4	.00004781	.00007758	.00002977
50	16.5	.00004916	.00008420	.00003504
60	16.4	.00005541	.00009029	.00003488
70	15.7	.00006167	.00009586	.00003419
80	16.3	.00007416	.00010083	.00002667
90	15.2	.00009103	.00010511	.00001408
100	15.0	.00010879		

All relations pointed out in the former paper as existing between the various properties of mixtures of ethylic alcohol and water find their parallel in the mixtures now under consideration. Certain sets of properties come to a maximum deviation from the calculated mean at the same strength; in some cases the values found are always below, in others always above the calculated mean; and in both mixtures the rate of expansion shows the same singular peculiarity, viz. of being for certain mixtures below, for others above the mean. In this, as in the previous mixture, the specific heat and the heat evolved during mixture not only come to a maximum deviation from the mean in mixtures of the same strength, but all mixtures evolving the same amount of heat during their formation possess a specific heat elevated to the same amount above the mean; and, moreover, the numerical relation between these two values is the same for mixtures of every degree of strength. Hence, if the heat evolved in the formation of 5 grms. of any of the mixtures be divided by 7.9, the elevation of the specific heat of this particular mixture above its calculated mean value is obtained. Between the boiling-point and the capillary attraction a somewhat similar relation is found. If in this case the observed depression of the capillarity of any mixture below its calculated mean value be divided by 1.9 (the capillarity of pure water taken as 100), the depression of the boiling-point of this mixture below the mean is obtained.

It has been pointed out above that an intimate relation exists between the heat evolved during the formation of a mixture and its specific heat. A closer study of this relation has led the author to the following conclusions, which seem not only to hold good for the two mixtures now under consideration, but to be of very general application; they may be formulated as follows.

Relation existing between the specific heat of mixtures and the heat evolved during their formation :—

1. The difference between the number of heat-units evolved during the mixing of given weights of two substances, at the temperatures t and t' respectively, is equal to the difference between the number of heat-units required to raise the mixture, and that required to raise the two constituents taken separately, from the lower to the higher temperature. Or let U and U' be the units of heat evolved by mixing x and y at the temperatures t and t' respectively, S , S' , and S'' the specific heat of the mixture z and its constituents x and y respectively, then

$$U - U' = z \cdot S(t - t') - \{x \cdot S'(t - t') + y \cdot S''(t - t')\}.$$

2. If more units of heat are evolved at the higher than at the lower temperature, the specific heat of the resulting mixture will be below the calculated mean; on the other hand, the specific heat of the mixture will be above the calculated mean, if the greater number of heat-units be evolved at the lower temperature*.

3. The absorption of a lesser number of heat-units will be of course equivalent to the evolution of a greater number, while the absorption of a greater number will be equivalent to the evolution of a smaller number of heat-units.

A series of Tables are next given showing that the following mixtures, namely, ethylic alcohol and water, methylic alcohol and water, prussic acid and water, ethylic alcohol and bisulphide of carbon, aqueous solutions of potassium chloride, sodium chloride, potassium nitrate, and potassium hydrate, conform to proposition 2, and all, except the mixture of ethylic alcohol and bisulphide of carbon, also conform as closely as can be expected with proposition 1. Perfect agreement is only possible if the specific heat of each constituent, as well as that of the mixture, has been accurately determined between the two temperatures for which the heat evolved on mixing has been estimated; and this has not, in the majority of cases, been done as yet.

The author next points out that, at first sight, the above observations may be explained by assuming that a difference in the chemical constitution of the mixture is produced by a change of temperature†. In some cases a rise in temperature may produce a certain amount of decomposition or dissociation, while a fall would be accompanied by recombination; the apparent specific heat of the mixture would thereby become raised. In some other cases the reverse may happen, and the specific heat of the mixture would fall below the mean. This supposition seems, however, incompatible with the observed rate of expansion of mixtures, both of ethylic and methylic alcohol and water. In these the rate of expansion is in some of the mixtures below the mean, indicating apparently that a more intimate union takes place on heating, in others the rate of expansion

* This relation had already been suggested by Berthelot.

† This has already been pointed out by Pfaundler, as well as by Marignac.

is above the mean, indicating dissociation. The specific heat of these mixtures does not, however, show any corresponding alterations.

The author finally shows that if these propositions should prove to be an exposition of a general law, they will enable us to calculate the specific heat of one constituent of a mixture or solution, if we know the specific heat of the other constituent, the specific heat of the mixture, and the heat evolved or absorbed at two different temperatures between which these specific heats have been estimated. It may thus be possible to compare the specific heat of liquid and solid substances when both are placed under similar conditions, and relations may be discovered which at present are masked in consequence of the difference in the physical conditions of the substances to be compared.

II. "On Supersaturated Saline Solutions. Part III.—On a relation between the Surface-tension of Liquids and the Supersaturation of Saline Solutions." By CHARLES TOMLINSON, F.R.S., and G. VAN DER MENSBRUGGHE. Received April 6, 1872.

It was stated by one of us in Part II.* that when a drop of a liquid is deposited on the surface of a supersaturated saline solution, it will do one of three things :—(1) mingle with the solution without any nuclear action ; (2) spread out into a film with powerful nuclear action ; or (3) assume the form of a lens, without any separation of salt. It was further stated that when a liquid forms a film or a lens, it does so according to the general proposition, that if a drop of a liquid B, with the surface-tension b , be placed on the surface of another liquid A, with the surface-tension a , the drop will spread into a film, if $a > b + c$ (c being the tension of the common surface of the liquids A and B) ; but if, on the contrary, $a = < b + c$, the drop will remain in the form of a lens. Hence if B spread on A, A will not spread on the surface of B. When the liquids A and B mingle in all proportions, c has no value. The spreading of the drop may also be interfered with by the superficial viscosity of the solution, or the greater or less difficulty in displacing the superficial molecules.

It was also stated that if a greasy smear be made upon the clean interior surface of a flask above the solution, and the flask be inclined so as to bring a portion of the solution against such smear, the liquid does one of two things :—(1) it breaks up into well-defined globules, which roll over the smear without loss of tension, in which case the smear has no nuclear action ; or (2) as soon as the solution reaches the smear its edge flattens and becomes ragged, in which case the smear is nuclear and the salt separates.

A glass rod drawn through the hand becomes covered with a smear or film ; or the same rod, by exposure to the air, contracts a film by the

* Philosophical Transactions for 1871, p. 52.