XV. *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 their formation.*

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The pure methylic alcohol was prepared according to the following process, devised by Mr. Chapman. Rectified wood-spirit is mixed with its own bulk of a saturated solution of calcium chloride, the mixture is heated to boiling and allowed to stand over night. The layer of oil found floating on the surface is carefully removed, and the fluid underneath is mixed with about one volume per cent. of a saturated solution of lead acetate. An amount of sulphide of ammonium, not quite sufficient to precipitate all the lead, is next added, the precipitate, which carries down much colouring-matter and many minute globules of oil, is filtered off, or allowed to subside, and the clear fluid is distilled. To this distillate caustic soda in coarse powder is added, and after standing some time it is diluted with water and again distilled; much resinous matter is thus removed, and the acetate of methyl is decomposed. The specific gravity of this second distillate is now brought to about ·82 (if necessary, by treatment with potassium carbonate), after which it is mixed with one fourth of its bulk of a saturated solution of bisulphite of ammonium. The mixture is allowed to stand for several days, and is then filtered and distilled from a water-bath; to the distillate a little sulphuric acid is added, and it is then redistilled, also from a water-bath. Finally a slight excess of caustic soda is added, and the liquid is once more distilled, when pure methylic alcohol passes over, which is rendered anhydrous by several distillations over caustic lime. The purity of the spirit is tested by oxidizing 20 grammes of it with an excess of bichromate of potassium and sulphuric acid, when it should yield nothing but carbonic acid and water.

The spirit thus prepared was perfectly miscible with water in every proportion; it had at 10° C. a specific gravity of ·81371, boiled at 58°·6 C. at a pressure of 757·4 millims., and had a specific heat of 58·325 between the temperatures of 60° and 18°.

Section I.—*Specific Heat.*

The mixture*, the specific heat of which is to be estimated, is enclosed in a small annular brass vessel, which can be closed hermetically by means of a screw-plug. In the inner cylindrical space a fan-wheel is fixed, acting as a stirrer when the vessel is

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[*] For the method employed for the preparation of mixtures of the exact strength desired, see Section V.

rotated under water. This vessel, when filled, is heated in a REGNAULT'S steam-oven by the vapour of methylic alcohol; and when the temperature has become constant it is lowered into the calorimeter, hooked on to a wire, and made to spin round underneath the surface of the water; a second observer meanwhile watches the thermometer of the calorimeter. The temperature of this rises, rapidly at first, more slowly towards the end, and reaches a maximum in from two to three minutes. The thermometer is observed during the next succeeding 1 to 1½ minute, and the fall observed is added as a correction to the highest temperature reached. The results obtained are not quite as concordant as those yielded by the method chiefly employed in estimating the specific heat of mixtures of ethylic alcohol and water (Philosophical Transactions, 1869, p. 591), owing principally to the difficulty of keeping the temperature of the steam-oven constant for a sufficient length of time when the vapour of methylic alcohol, instead of steam, is used for heating. Methylic alcohol has, however, too low a boiling-point for the successful application of the former method.

From the data obtained the specific heat of the mixture is calculated by help of the following formula:—

$$\frac{C}{100}=\frac{W(t''-t)}{m(T-t')}-\frac{\mu}{m},$$

wherein C is the specific heat sought,

W the water value of calorimeter and contents (water, thermometer, and calorimeter itself),

t temperature of calorimeter at the beginning,

t'' temperature of calorimeter at end, correction added,

T temperature of steam-oven,

m weight of mixture employed,

μ water value of annular brass vessel,

t' temperature of calorimeter at end, without correction.

In the following Table the experiments marked with an asterisk were made with methylic alcohol of one preparation, those not so marked with spirit of another preparation.

TABLE I.

Amount of water in calorimeter 1156·666 grms.

Water value of calorimeter 8·565 grms.

Water value of annular brass vessel (μ) was 6·8337 grms. in all experiments with an asterisk, and 6·6572 grms. in the others.

Water value of immersed part of thermometer 1·139.

Time occupied in each experiment, 3 to 4½ minutes.

Spirit 10 per cent.

Experiment.	*m.*	*t'''*†.	T.	*t.*	*t.*	V‡.	*t''*.	C.
1.	52·140	12·7	52·65	11·003	12·965	0·000	12·965	97·828
2.	52·140	13·5	53·15	11·980	13·940	0·000	13·940	99·054
3*.	54·351	20·8	62·80	19·042	21·174	0·014	21·188	98·062
4*.	54·111	20·8	62·45	18·283	20·456	0·014	20·470	99·387

Mean specific heat of spirit of 10 per cent. 98·582.

Spirit 20 per cent.

Experiment.	*m.*	*t'''*.	T.	*t.*	*t'*.	V.	*t''*.	C.
5.	49·735	13·5	53·75	12·556	14·380	0·000	14·380	95·266
6.	49·735	14·7	55·15	13·728	15·589	0·000	15·589	96·935
7.	49·735	16·0	58·15	13·880	15·860	0·000	15·860	96·415
8*.	51·831	19·6	60·60	18·839	20·740	0·016	20·756	95·045

Mean specific heat of spirit of 20 per cent. 95·914.

Spirit 30 per cent.

Experiment.	*m.*	*t'''*.	T.	*t.*	*t'*	V.	*t''*.	C.
9.	51·390	11·0	55·62	10·296	12·279	0·010	12·289	91·413
10.	51·390	10·0	54·52	9·968	11·925	0·010	11·935	91·856
11*.	51·151	19·0	59·8	17·101	19·017	0·000	19·017	93·768
12*.	50·831	19·3	61·15	18·617	20·484	0·030	20·514	93·595

Mean specific heat of spirit of 30 per cent. 92·658.

Spirit 40 per cent.

Experiment.	*m.*	*t'''*.	T.	*t.*	*t'*.	V.	*t''*.	C.
13.	51·383	13·0	52·90	11·960	13·718	0·000	13·718	88·891
14.	51·145	15·0	52·80	12·703	14·412	0·000	14·412	88·410
15*.	50·025	17·3	61·54	17·079	18·963	0·005	18·968	89·784
16*.	49·580	19·9	60·30	18·856	20·598	0·006	20·604	89·793

Mean specific heat of spirit of 40 per cent. 89·219.

Spirit 50 per cent.

Experiment.	*m.*	*t'''*.	T.	*t.*	*t'*.	V.	*t''*.	C.
17.	49·890	10·2	56·48	10·056	11·874	0·010	11·884	82·456
18.	50·220	13·0	50·90	11·601	13·203	0·000	13·203	85·443
19*.	49·491	21·0	60·95	19·840	21·494	0·000	21·494	84·867
20*.	49·281	21·0	61·00	19·605	21·278	0·000	21·278	85·817

Mean specific heat of spirit of 50 per cent. 84·645.

† *t'''*, temperature of air. ‡ V, correction added.

Spirit 60 per cent.

Experiment.	m.	t'''.	T.	t.	t'.	V.	t''.	C.
21.	47·930	12·5	58·85	11·379	13·137	0·010	13·147	80·228
22.	47·834	13·0	55·90	11·415	13·072	0·000	13·072	80·432
23*.	48·471	21·0	61·30	20·006	21·558	0·000	21·558	79·873

Mean specific heat of spirit of 60 per cent. 80·177.

Spirit 70 per cent.

Experiment.	m.	t'''.	T.	t.	t'.	V.	t''.	C.
24.	46·980	12·0	56·15	11·489	13·046	0·010	13·056	75·567
25.	46·980	11·5	56·65	10·092	11·704	0·000	11·704	74·872
26*.	45·921	18·4	60·18	17·087	18·560	0·005	18·565	75·491
27*.	45·311	19·1	58·10	18·020	19·383	0·008	19·391	76·071

Mean specific heat of spirit of 70 per cent. 75·500.

Spirit 80 per cent.

Experiment.	m.	t'''.	T.	t.	t'.	V.	t''.	C.
28.	44·180	11·1	55·65	10·335	11·756	0·000	11·756	70·399
29.	44·180	11·7	58·15	11·240	12·713	0·005	12·718	70·818
30*.	45·621	21·1	58·50	20·296	21·520	0·000	21·520	69·643
31*.	44·601	21·1	59·90	20·074	21·320	0·000	21·320	69·138

Mean specific heat of spirit of 80 per cent. 69·999.

Spirit 90 per cent.

Experiment.	m.	t'''.	T.	t.	t'.	V.	t''.	C.
32.	43·660	11·0	58·48	9·965	11·385	0·000	11·385	65·303
33*.	44·156	21·4	60·45	20·352	21·520	0·000	21·520	63·770
34*.	42·681	……	59·20	16·981	18·187	0·000	18·187	64·346
35*.	42·016	21·0	62·20	20·130	21·294	0·014	21·308	63·706

Mean specific heat of spirit of 90 per cent. 64·282.

Spirit 100 per cent.

Experiment.	m.	t'''.	T.	t.	t'.	V.	t''.	C.
36.	43·029	13·0	58·05	11·225	12·465	0·000	12·465	58·264
37.	42·679	13·2	59·65	12·465	13·695	0·000	13·695	57·548
38.	42·429	14·1	60·75	13·289	14·545	0·000	14·545	59·036
39*.	42·586	17·9	51·20	17·067	17·969	0·004	17·973	58·625
40*.	42·116	18·0	59·60	17·082	18·199	0·000	18·199	58·494
41*.	41·341	18·1	59·70	17·540	18·619	0·006	18·625	57·985

Mean specific heat of absolute methylic alcohol 58·325.

TABLE II.

Per cent., by weight, of absolute methylic alcohol.	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 II.—*Heat produced by the mixing of Methylic Alcohol and Water.*

The amount of heat produced is estimated as follows:—An annular vessel made of thin brass, such as described in the section Specific Heat, and capable of holding about 100 cub. centims., is immersed in the water of the calorimeter. The vessel has two openings provided with short tubes, which reach above the surface of the water when the whole body of the vessel is submerged. Through one of these tubes passes tightly a rod connected with an efficient stirrer moving up and down the annular space; the other tube carries a small glass funnel which can be closed by a stopper. The experiment is conducted as follows:—One of the two liquids is weighed out in the brass vessel, the other is weighed out in a thin glass bulb, the quantity of liquid remaining in the bulb when it is emptied, and that which adheres to the sides of the small funnel, which experience had shown to be a very constant quantity, being allowed for, so that the exact amount of liquid necessary is delivered into the brass vessel. The brass vessel is now fixed in its proper position in the calorimeter, which is then filled with water a little below the temperature of the room; and the glass bulb containing the other liquid is also immersed in the calorimeter. After the lapse of fifteen minutes, the water in the calorimeter having been stirred from time to time, the temperature of the various fluids has become equalized. The glass bulb is now taken out without touching it with the hand, and its contents are poured rapidly through the funnel into the brass vessel; the funnel is closed, and the two fluids in the brass vessel thoroughly mixed by means of the stirrer. The temperature of the water in the calorimeter, which is constantly stirred, reaches a maximum in from 4 to 5 minutes; it is observed during 2 or 2½ minutes longer, and any fall observed is added as a correction to the highest temperature reached. As, however, the whole rise is small, this correction usually amounts to very little, and frequently to nothing. From the data thus obtained the heat produced by mixing the liquids in the brass vessel is calculated, the water value of the mixture in the brass vessel being of course added to the water value of the calorimeter and contents.

TABLE III.

Water value of calorimeter 8·664 grms.
Water value of immersed part of thermometer and stirrer 2·024 grms.
Water value of annular brass vessel 5·362 grms.
Water contained in calorimeter 1156·666 grms.

Quantities taken of		Per cent., by weight, of alcohol in mixture produced.	Temperature of calorimeter at		Loss by radiation.	Corrected rise.	Units of heat evolved by 5 grms. of the mixture.	Mean.
Methylic alcohol.	Water.		Beginning.	End.				
7·850	70·650	10	19·655	19·930	0·000	·275	21·896	20·930
5·984	53·856	10	19·179	19·353	0·020	·194	19·965	
12·428	49·712	20	16·204	16·560	0·004	·360	35·647	37·276
11·350	45·400	20	16·584	16·944	0·000	·360	38·912	
22·434	52·346	30	16·342	16·862	0·004	·523	43·432	44·744
18·590	43·376	30	17·449	17·913	0·000	·464	46·056	
30·786	46·179	40	16·443	17·020	0·004	·577	46·532	45·384
30·636	45·954	40	17·344	17·886	0·000	·546	44·236	
35·406	35·406	50	16·083	16·578	0·000	·495	43·481	44·429
32·112	32·112	50	17·415	17·890	0·000	·475	45·377	
50·141	33·427	60	16·508	17·071	0·000	·563	41·763	41·493
33·030	22·020	60	17·531	17·904	0·000	·373	41·224	
52·120	22·336	70	16·944	17·356	0·000	·412	34·000	34·456
31·950	13·692	70	17·920	18·184	0·000	·264	34·912	
57·435	14·358	80	17·061	17·338	0·010	·287	24·424	22·448
30·464	7·616	80	19·442	19·562	0·010	·130	20·474	
62·325	6·925	90	19·301	19·446	0·008	·153	13·444	13·164
23·498	2·611	90	18·570	18·619	0·008	·057	12·984	

SECTION III.—*Boiling-points.*

For methods and instruments employed in estimating the boiling-points, specific gravity and rate of expansion, and the compressibility* (Sections III., V., and VI.), see the paper "On the Specific Heat and other Physical Characters of Mixtures of Ethylic Alcohol and Water," by A. DUPRÉ, Ph.D., and F. J. M. PAGE, B.Sc., Phil. Trans. 1869, p. 591, Sections III., V., and VI.

Table IV. gives the boiling-points found, the barometer standing at 757·4 millims. The third column gives the boiling-points calculated on the assumption that they are proportional to the weight of the constituents.

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* Instead of using an air-pump for forcing air into the apparatus, an iron bottle containing liquid carbonic anhydride was employed. The water in the apparatus being covered with a layer of oil, to prevent absorption of carbonic anhydride, any desired pressure could easily be obtained by simply turning the screw-valve of the iron bottle to the requisite extent and time.

TABLE IV.

Per cent., by weight, of absolute methylic alcohol.	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 IV.—*Capillary Attraction.*

The capillary attraction is estimated as follows:—A somewhat wide glass cylinder, the rim of which is accurately ground, stands on a metal frame with three levelling-screws, by means of which the rim of the cylinder can be placed perfectly horizontal. On the rim rests a stout metal bar, through which are drilled three holes exactly at right angles to the lower face of the bar, so that a tube or screw fitting into one of these holes will stand vertical when the rim of the cylinder is horizontal. Two of these holes carry capillary tubes; in the third a long fine screw, pointed at both ends, can be screwed up and down. A mark is etched on each capillary tube, and by depressing or raising the tube the liquid under examination is always made to rise exactly to this mark; the influence of any irregularity in the bore of the tube is thus avoided. The experiment is conducted as follows:—The perfectly clean capillary tubes are put into their respective holes in the plate, and this is placed on the levelled rim of the cylinder. The mixture to be examined is poured into the glass, and a small quantity of the liquid is sucked through each of the tubes by means of a suction-tube. The height of the tubes is then adjusted so that the lower part of the menisci just touches the marked point of the tubes. The screw is now carefully screwed down until the point just touches the surface of the liquid in the cylinder; this contact can be made with the utmost nicety. It now only remains to determine the vertical distance between the upper point of the screw and the lowest part of the two menisci in the tubes, when, the total length of the screw being known, the elevation of the liquid in the capillary tubes becomes known. The vertical distances are measured by means of a very excellent cathetometer, which allows the reading of 0·025 millim.

Table V. gives the results obtained.

Column 1 gives the percentage of methylic alcohol by weight.

Columns 2 and 3 give the observed heights of the threads in millims.

Columns 4 and 5 give the heights supposing water stood at 100 millims.

Column 6 gives the mean of columns 4 and 5.

Column 7 gives the length of a column of water equal in weight to the thread of alcoholic mixture in column 6, and affords, therefore, a measure of the relative strength of the molecular attraction in the various mixtures.

Column 8 gives the heights calculated on the assumption that they will be proportional to the weight of the constituents of each mixture.

Column 9 gives the difference between columns 7 and 8.

The observed heights given are in each case the mean of two closely concordant experiments. The temperature at which the experiments were made was 13°·5 C.

TABLE V.

1.	2.	3.	4.	5.	6.	7.	8.	9.
Alcohol per cent.	Heights observed.		Heights, assuming water 100 millims.		Mean of columns 4 and 5.	Relative molecular attraction.	Height calculated.	Difference.
	Tube 1.	Tube 2.	Tube 1.	Tube 2.				
0	74·575	51·050	100·000	100·000	100·000	100·000		
10	51·875	35·225	68·645	69·001	68·820	67·818	93·334	−25·416
20	44·400	30·075	58·749	58·912	58·830	57·264	86·667	29·403
30	39·550	26·850	52·332	52·595	52·463	50·381	80·001	29·620
40	36·975	25·000	48·942	48·971	48·947	46·252	73·335	27·083
50	34·925	23·925	46·212	46·865	46·538	43·136	66·668	23·532
60	34·925	23·650	46·212	46·327	46·269	42·170	60·002	17·832
70	34·050	23·125	45·054	45·298	45·176	40·034	53·336	13·302
80	33·270	22·500	44·022	43·973	43·997	37·955	46·669	8·714
90	32·100	21·825	42·474	42·750	42·612	35·671	40·003	4·332
100	30·650	20·850	41·099	40·842	40·970	33·337		

SECTION V.—*Specific Gravity and Rate of Expansion.*

The mixtures are made by accurately weighing out the required quantities of absolute methylic alcohol and water. This is done in two separate flasks, which are afterwards joined together, air-tight, by a short india-rubber tube; and the thorough mixture is effected by repeatedly pouring the fluids from one flask into the other through the tube. In some of the mixtures a considerable rise in temperature takes place; but as the mixing is effected in a closed vessel no loss of alcohol is experienced. The flasks, still kept connected, are allowed to cool; the mixture is put into a bottle, which should not be less than three quarters filled, and the air is exhausted from the bottle. In this state the bottle is allowed to stand over night, by which means the air dissolved in the mixture is got rid of without appreciable loss of spirit.

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

Table VII. gives the expansion of 100 volumes of the mixture 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.

To facilitate this calculation (as also the compressibility), Table VIII. gives in columns 2 and 3 the volumes of water and methylic alcohol respectively contained, at a temperature of 10° C., in 100 volumes of a spirit of the strength given in column 1. Columns 4 and 5 give the combined volumes of the two, before and after mixture respectively; and, lastly, column 6 gives the differences between 4 and 5, thus showing the amount of contraction having taken place in the formation of 100 volumes of the various mixtures. The figures in this Table are calculated from those given in Table VI. By help of this Table the numbers contained in column 4, Table VII., have been calculated thus:—

Let w be the volume per cent. of water contained in the mixture at 10° C.,

m the volume per cent. of methylic alcohol present at the same temperature, and

C the amount of contraction which has taken place in the formation of 100 volumes of this mixture at 10° C.,

Then 100 volumes of this mixture at 10° C. would occupy at 20°

$$\frac{w \times 100{\cdot}154}{100} + \frac{m \times 101{\cdot}290}{100} - \mathrm{C}$$

volumes, on the assumption that the expansion is proportioned to the volumes of the constituents.

The capacity of the specific-gravity bottle employed was at 10° C. = 545·4985 cub. centims., at 20° C. = 545·6585 cub. centims.

This bottle was brought to the exact temperature desired by immersion in a water-bath of special construction, for details of which see Philosophical Transactions, 1869, p. 608.

TABLE VI.

Per cent. 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 VII.

Per cent. 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		

TABLE VIII.

1. Per cent., by weight, of absolute methylic alcohol.	2. Volumes of water.	3. Volumes of methylic alcohol.	4. Combined volumes.	5.	6. Contraction.
			Before mixture.	After mixture.	
10	88·793	12·121	100·914	100	·914
20	78·003	23·985	101·962	,,	1·962
30	67·373	35·475	102·848	,,	2·848
40	56·852	46·566	103·418	,,	3·418
50	46·507	57·139	103·646	,,	3·646
60	36·428	67·135	103·563	,,	3·563
70	26·687	76·505	103·192	,,	3·192
80	17·322	85·139	102·460	,,	2·460
90	8·408	92·967	101·374	,,	1·374

SECTION VI.—*Compressibility.*

Table IX. gives the compressibility of the various mixtures for the pressure of one atmosphere.

The numbers in column 5 are calculated on the assumption that the compressibility of a mixture is proportional to the volumes of its constituents. To the compressibilities found directly, 0·000002 is always added as a correction for the compressibility of the piézomètre.

TABLE IX.

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

Per cent. of methylic alcohol, by weight.	Depression of gauge, in millims. *	Temperature, in degrees Centigrade.	Compressibility for 1 atmosphere.		Difference.
			Found.	Calculated.	
0	10·10	16·8	0·00004741		
10	9·29	16·2	·00004377	0·00005497	−0·00001129
10	9·25	16·8	·00004359		
20	9·28	15·9	·00004372	·00006303	·00001938
20	9·29	16·2	·00004359		
30	9·12	15·3	·00004300	·00007052	·00002763
30	9·07	15·6	·00004278		
40	10·19	17·4	·00004781	·00007758	·00002977
50	10·49	16·5	·00004916	·00008420	·00003504
60	11·88	16·4	·00005541	·00009029	·00003488
70	13·27	15·7	·00006167	·00009586	·00003419
80	16·05	16·3	·00007416	·00010083	·00002667
90	19·80	15·2	·00009103	·00010511	·00001408
100	23·75	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.

Undoubtedly all the various physical characters of mixtures must, to a certain extent, be dependent on each other, and no explanation of the relation existing between any two of them can be received which is not compatible with every other property observed. The relation existing between some of these characters seems, however, to be more intimate and direct than it is between others. Thus 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),

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* In the paper on Mixtures of Ethylic Alcohol and Water, previously quoted, the numbers in the corresponding column (column 2, Table XIII.) should be divided by four.

the depression of the boiling-point of this mixture below the mean is obtained. A similar, though less direct relation appears to exist between the compressibility of a mixture and the amount of contraction taking place in its formation. The numerical relation between these two values differs, however, in different mixtures, both being evidently governed by some additional factor. Lastly, it is also worthy of note that the compressibility of weak mixtures of methylic, as well as of ethylic alcohol and water, is less than that of water, rises to that of water at an alcoholic strength of about 30 per cent., and continues greater for all stronger mixtures.

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. This relation may be formulated as follows, in accordance with the principles of the mechanical theory of heat, as first pointed out by KIRCHHOFF in 1858 ("Ueber einen Satz der mechanischen Wärmetheorie und einige Anwendungen desselben; von G. KIRCHHOFF," Pogg. Ann. vol. xiii. p. 177). 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, provided the condition of the mixtures when they have been brought to the same temperature is the same in both cases. 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

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

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.

Ethylic Alcohol and Water.

In the formation of 5 grms. of a 10 per cent. mixture of ethylic alcohol and water are evolved, at a temperature of

17°·295 C.,	26·68	units of heat.
71·15 C.,	7·97	,, ,,
Difference	18·71	,, ,,

To raise 5 grms. of the mixture from 17°·295 C. to 71°·15 requires		278·86 units.
,, 4·5 grms. water through same interval . . .	242·35	
,, 0·5 grm. alcohol ,, ,, . . .	16·27	
Total for constituents separately	258·62	258·62 ,,
Difference between mixture and constituents		20·24 ,,

In the formation of 5 grms. of a 30 per cent. mixture are evolved, at a temperature of

17°·337 C.,	47·98 units.
52·3 C.,	22·16 ,,
70·9 C.,	10·34 ,,

To raise 5 grms. of this mixture from

17°·337 to 52°·30 requires 179·36 units,
17·337 to 70·90 ,, 274·79 ,,

To raise 3·5 grms. water from 17°·337 to 53°·30 requires	122·37 units.
,, 1·5 grm. alcohol ,, ,,	31·62 ,,
Total units required to raise constituents	153·99 ,,
To raise 3·5 grms. water from 17°·337 to 70°·90 requires	187·47 ,,
,, 1·5 grm. alcohol ,, ,,	48·55 ,,
Total units required to raise constituents	236·02 ,,

47·98 − 22·16 = 25·82 = difference in units of heat evolved.
179·36 − 153·99 = 25·37 = ,, ,, required.
47·98 − 10·34 = 37·64 = ,, ,, evolved.
274·79 − 236·02 = 38·77 = ,, ,, required.

The differences between theory and experiment are, therefore, in the above cases at least, extremely small and quite within the limits of almost unavoidable experimental error.

The number of units of heat evolved during the mixing of ethylic alcohol and water becomes therefore less the higher the temperature at which the mixing takes place. Assuming, then, that the above given formula (No. 1) is correct, it is easy to calculate a temperature at which the mixing of alcohol and water would not be accompanied by evolution of heat. U' becomes zero when $U = z \, . \, S(t'-t) \sim \{x \, . \, S'(t'-t) + y \, . \, S''(t'-t)\}$.

Let U be the units of heat evolved in the formation of 5 grms. of mixture at the temperature t, then the temperature T, at which no heat is evolved on mixing, will be

$$T = \frac{U}{5S - (xS' + yS'')} + t.$$

On making this calculation for the various mixtures examined, this temperature was found to be 88°·2, 87°·6, 83°·5, 88°·3, 86°, 84°·9, 78°·4, 92°, and 129°·6 C. for mixtures of

10, 20, 30, 40, 50, 60, 70, 80, and 90 per cent. alcoholic strength respectively. Excluding the last temperature, as in this case a slight experimental error would greatly influence the result, the agreement between the rest is close enough to warrant the conclusion that the actual variations observed are due only to slight experimental error; and we may therefore look upon the mean of all, namely 86°·1, as being approximately the temperature at which no heat at all would be evolved, whatever be the proportion in which the alcohol and water are mixed.

The idea at once suggests itself that the whole of the phenomena under consideration are due to dissociation. For every given temperature an equilibrium may exist between the free alcohol and water on the one hand, and the compound formed between the two on the other. A rise in temperature might be accompanied by dissociation of some of the compound present, and consequent absorption of heat; a fall of temperature, on the other hand, would then be accompanied by reunion and consequent liberation of heat, whereby the apparent specific heat of the mixture would be augmented. The same idea has already been advanced by PFAUNDLER, and also by MARIGNAC, to account for the observed deviations of the specific heat of many mixtures from their calculated mean value.

A closer examination of some of the other properties of these alcoholic mixtures does not, however, tend to confirm this supposition. Thus, as is well known, considerable contraction in volume follows the mixing of alcohol and water; but this contraction is not, as might be supposed, in any degree proportional to the amount of heat evolved. Thus the maximum contraction takes place in a mixture containing about 45 per cent. of alcohol, whereas the maximum amount of heat is evolved at an alcoholic strength of about 30 per cent. The maximum elevation of the specific heat above its calculated mean value is also observed at this strength of 30 per cent.; and hence, in order to reconcile the above theory with fact, we must assume on the one hand that the amount of combination taking place at any given temperature is greatest when 30 parts of alcohol are mixed with 70 parts of water, and on the other that a given rise of temperature will produce in this mixture of alcohol and water a greater amount of decomposition or dissociation than in any other. We should thus have the maximum amount of chemical action and the feeblest union both occurring with one and the same proportion of alcohol and water.

The rate of expansion of the various mixtures seems also opposed to the supposition that dissociation is the cause of the high specific heat observed. It is to be supposed that the greater the amount of dissociation the more nearly would the specific gravity observed correspond to its calculated value. In other words, the rate of expansion of all the mixtures should be above its mean value, and this excess should stand in some relation to the observed elevation of the specific heat. The following Table will show that this is by no means the case. It gives for spirits of 30, 20, and 10 per cent. strength by weight, the specific gravities as found and as calculated for the temperatures 0°, 10°, 20°, 30°, and 70° C. The specific gravities for the temperatures 0, 10, 20, and 30 are taken from the Tables of MENDELEJEFF.

TABLE X.

Temperature, in degrees Centigrade.	Specific gravity.		Difference.
	Found.	Calculated.	
	30 per cent. spirit.		
0	96540	93268	+3272
10	95998	92907	3091
20	95403	92490	2913
30	94751	91988	2763
70	91669	89389	2280
	20 per cent. spirit.		
0	97566	95407	+2159
10	97263	95142	2121
20	96877	94805	2072
30	96413	94386	2027
70	93863	92024	1839
	10 per cent. spirit.		
0	98493	97643	+ 850
10	98409	97508	901
20	98191	97259	936
30	97892	96914	978
70	95815	94815	1000

The specific gravity of the 30 per cent. spirit thus really approaches more and more to its calculated value; in the case of the 20 per cent. spirit this approach, though still perceptible, is, however, considerably less, both absolutely and proportionally. Finally, with the 10 per cent. spirit, the phenomenon is actually reversed, the observed specific gravity gradually receding from the specific gravity as calculated; and so far from any dissociation being indicated, the opposite rather seems to take place.

It may be well here to recall to mind that 5 grms. of a 30 per cent. spirit, when heated from 0° to 70° C., require about 25 units of heat in excess of what would be necessary to raise the constituents separately through the same interval. This excess amounts to about 21 units with the 20 per cent. spirit, and to about 13 units in the case of the 10 per cent. spirit. No apparent connexion, therefore, seems to exist between the rate of expansion and the high specific heat.

Methylic Alcohol and Water.

The great volatility of methylic alcohol presents considerable difficulties to the accurate estimation of the various properties of these mixtures, more particularly as regards the specific heat and the heat evolved on mixing. In addition to this, the elevation of the specific heat of the various mixtures above the calculated value is but small, and therefore even slight errors will have a much greater influence on any calculations based on the difference between the values as found and as calculated.

10 per cent. mixture.

In the formation of 5 grms. of a 10 per cent. mixture are evolved, at a temperature of

5°·8 C.,	23·65	units of heat.
19·64 C.,	20·93	„ „
Difference	2·72	„ „

30 per cent. mixture.

In the formation of 5 grms. of this mixture are evolved, at a temperature of

6°·4 C.,	45·75	units.
17·38 C.,	44·74	„
Difference	1·01	„

Endeavours to estimate the heat evolved at higher temperatures led to still less satisfactory results. At the end of every experiment the mixture was found to be weaker in spirit than it should have been, from the amounts of water and alcohol taken; and this loss of alcohol of course diminished the amount of heat evolved. This loss took place although the mixing was effected in a closed vessel. Nevertheless these experiments show distinctly that less heat is evolved at the higher temperature.

Calculating, as in the previous mixture, the temperature at which no heat would be evolved on mixing, the following temperatures are obtained:—152°, 175°, 173°, 154°, 162°, 160°, 147°, 175°, and 146° for strengths of 10, 20, 30, 40, 50, 60, 70, 80, and 90 per cent. respectively; the mean of these temperatures is 156° C. These temperatures differ apparently somewhat widely, and yet the maximum deviation from the mean found corresponds to a small error only in the estimation of the specific heat of the corresponding mixture. Thus the maximum differences are found at an alcoholic strength of 20 and 80 per cent. The specific heat of these two mixtures as found is 95·91 and 69·99, whereas the specific heat corresponding to the above mean temperature of 156° would be 96·42 and 69·54; the difference in either case is less than $\frac{1}{150}$ of the total value. A glance at Table II. will show that in this, as in the previous mixture, the rate of expansion seems incompatible with the supposition that the high specific heat observed is caused by dissociation. For weak and for strong mixtures the rate of expansion is below the mean, for mixtures of middle strength above the mean; in the first two cases the amount of contraction is greater, in the last case it is less, the higher the temperature. The specific heat does not, however, show any corresponding change.

Water and Prussic Acid.*

CNH one part.
H_2O one part.

Specific heat of prussic acid	·2940
,, ,, ,, mixture found . .	·8317
,, ,, ,, ,, calculated .	·6470

In the formation of 5 grms. of this mixture are absorbed, at a temperature of

0° C.,	26·61 units.
14 C.,	40·54 ,,
Difference	13·93 ,,

To heat 5 grms. of the mixture from 0° to 14° requires 58·219 units.
,, 2·5 ,, of water requires 35·00 units.
,, 2·5 ,, prussic acid requires 10·29 ,,
45·29 45·290 ,,
Difference 12·929 ,,

Ethylic Alcohol and Bisulphide of Carbon.*

CS 62·3 parts.
C_2H_6O 37·7 ,,

Specific heat of bisulphide	·2381
,, ,, ,, alcohol	·5790
,, ,, ,, mixture found . .	·3903
,, ,, ,, ,, calculated .	·3666

In the formation of 5 grms. of this mixture are absorbed, at a temperature of

0° C.,	5·850 units.
21·9 C.,	10·925 ,,
Difference	5·075 ,,

To heat 5 grms. of the mixture from 0° to 21°·9 requires 42·735 units.
,, ,, the constituents separately from 0° to 21°·9 ,, 40·142 ,,
Difference 2·593 ,,

Solutions of Potassium Chloride.

KCl one molecule, or 12·12 per cent.
H_2O thirty molecules, or 87·88 ,,

Specific heat of solution, according to THOMSON, ·850.

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* BUSSY and BUIGNET, Ann. Chem. Phys. [4], 5.

In the formation of 5 grms. of this solution are absorbed, at a temperature of

8°·9,	34·25	units of heat.
66·55,	21·00	,, ,,
Difference	13·25	,, ,,

To heat 5 grms. of the solution from 8°·9 to 66°·55 requires 24·500 units.

To heat the water contained in the 5 grms. to the same extent requires 253·30 units.

KCl one molecule, or 7·952 per cent.
H_2O fifty molecules, or 92·048 ,,

Specific heat of solution, according to THOMSON, ·904.

In the formation of 5 grms. of this solution are absorbed, at a temperature of

9°·0,	23·85	units of heat.
64·3,	13·95	,, ,,
Difference	9·90	,, ,,

To heat 5 grms. of the solution from 9° to 64°·3 requires 249·95 units.
To heat the water alone ,, ,, ,, 254·50 ,,

Solution of Sodium Chloride.

$NaCl$ one part.
H_2O 7·28 parts.

Specific heat of the solution, as calculated from THOMSON'S Tables, ·8747.

In the formation of 5 grms. of this mixture are absorbed, at a temperature of

0°·2 C.,	11·25	units of heat.
10·3 C.,	9·00	,, ,,
17·1 C.,	8·15	,, ,,
70 C.,	0·00	,, ,,

To heat 5 grms. of this solution from 0°·2 to 70° requires 305·25 units.
To heat the water alone ,, ,, ,, 306·85 units.

Solutions of Potassium Nitrate.

KNO_3 one molecule, or 9·09 per cent.
H_2O fifty-six molecules, or 90·91 per cent.

Specific heat of this solution, calculated from THOMSON'S Tables, ·909.

In the formation of 5 grms. of this solution are absorbed, at a temperature of

5°·5,	36·45	units.
28·8,	34·85	,,
Difference	1·60	,,

To heat 5 grms. of this solution from 5°·5 to 23°·8 requires 83·17 units.
To heat the water alone „ „ „ 83·17 „

KNO_3 one molecule, or 4·76 per cent.
H_2O 112·3 molecules, or 95·24 „

Specific heat of this solution, calculated from THOMSON'S Tables, ·943.

In the formation of 5 grms. of this solution are absorbed, at a temperature of

	$\overset{\circ}{5}\cdot 7$,	20·57 units.
	19·7,	19·16 „
Difference		1·41 „

To heat 5 grms. of the solution from 5°·7 to 19°·7 requires 66·01 units.
To heat the water alone „ „ „ 66·66 „

The data for calculating the heat absorbed in this and in the preceding solution are taken from GRAHAM, OTTO'S 'Chemie,' vol. i. part 2, by H. KOPP.

Solution of Potassium Hydrate.

KHO one molecule, or 9·4 per cent.
H_2O thirty molecules, or 90·6 „

Specific heat of solution, according to THOMSON, ·876.

In the formation of 5 grms. of solution are evolved, at a temperature of

	$\overset{\circ}{4}\cdot 0$,	54·05 units.
	31·6,	61·75 „
Difference		7·70 „

To raise 5 grms. of solution from 4° to 31°·6 requires 120·885 units.
To raise the water alone „ „ „ 125·030 „

Every one of the preceding eight mixtures conforms with proposition 2, and most of them also fairly enough with proposition 1, the only signal exception being the mixture of ethylic alcohol and bisulphide of carbon. A very close correspondence can only be expected where all the necessary data have been estimated with accuracy and at the required intervals of temperature. Some amount of error is, however, unavoidable; and that mixture which is least affected by such small errors, will serve best to bring out the real connexion existing between the various properties. Now none of the eight sets of mixtures considered equals the mixtures of ethylic alcohol and water in this respect, and we find accordingly that these most nearly conform to the law. These mixtures have therefore been chosen, not only as the best illustrations of the law, but also as a guide in tracing similar relations between the corresponding properties of other mixtures and solutions, relations which, being in those cases more liable to be masked by small experimental errors, might otherwise have been overlooked.

Apart from all speculation as to the cause of these phenomena, for which the existing data seem insufficient, a more extended study of the relations pointed out cannot fail to throw much light on the vexed question of the constitution of solutions and mixtures.

It is also evident that proposition 1 will enable us to calculate the specific heat of one constituent of a mixture if we know the specific heat of the other, the specific heat of the mixture, and the units of heat evolved or absorbed at the two different points of temperature between which these specific heats have been determined.

This calculation will serve not only as a check on the accuracy of the various experimental data involved, but may in certain cases enable us to calculate the specific heat of an element in a condition in which this could not be directly determined. If, for example, we can estimate the heat evolved or absorbed at two different temperatures during the combination of two elements, of which one is, say, in the nascent state, the specific heat of the element in that condition could be calculated.

Lastly, these considerations show how important it is to give, in all cases in which the heat of combination &c. is estimated, not only the quantities of substance employed, but also the exact temperature at which the experiment was performed. Without this the results are well nigh valueless.

Let z be the weight of a mixture, x and y the weights of its two constituents, U and U′ the units of heat evolved at the temperatures t and t', of which t is the lower, and S, S′ and S″ the specific heat of the mixture and of its two constituents x and y respectively; then, if S and S′ are known, we have

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

If heat is absorbed in the formation of the mixtures, U and U′ may be taken as representing the units of heat absorbed at t and t', and the above equation becomes correct if the signs for U and U′ are reversed.

The specific heats of the four solids above considered, calculated with the help of this formula, are as follows:—

Potassium chloride from the weaker solution	·147
,, ,, ,, ,, stronger ,,	·135
,, ,, as estimated by KOPP directly	·173
Sodium chloride calculated	·229
,, ,, as estimated by KOPP	·214
Potassium nitrate from the weaker solution	·227
,, ,, ,, ,, stronger ,,	·192
,, ,, as estimated by KOPP	·2388
Potassium hydrate calculated	·274

Potassium hydrate has not yet been directly estimated.

EXPLANATION OF THE PLATE.

In the Plate the abscissæ represent the percentage by weight of alcohol.

PLATE XLVII.

Upper Half.

Curve 1. The ordinates give the specific heats, water taken as 100.

Curve 2. The ordinates give the boiling-points in degrees Centigrade, at 757·4 millims. pressure.

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

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

Curve 5. The ordinates give the compressibility in millionths.

Under Half.

The ordinates in Curves 1 to 5 have the same significance as in the upper half, except that they give the deviation of the numbers found from the theoretical mean instead of the numbers themselves.

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

Curve 7. The ordinates give the deviation of the specific gravity from the mean, for 1000 volumes of mixture, at a temperature of 10° Centigrade.

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

The points directly ascertained by experiment are marked either by a circle or a cross.

Dupré

Phil. Trans. MDCCCLXXII. Plate 47.

Fig. 1.

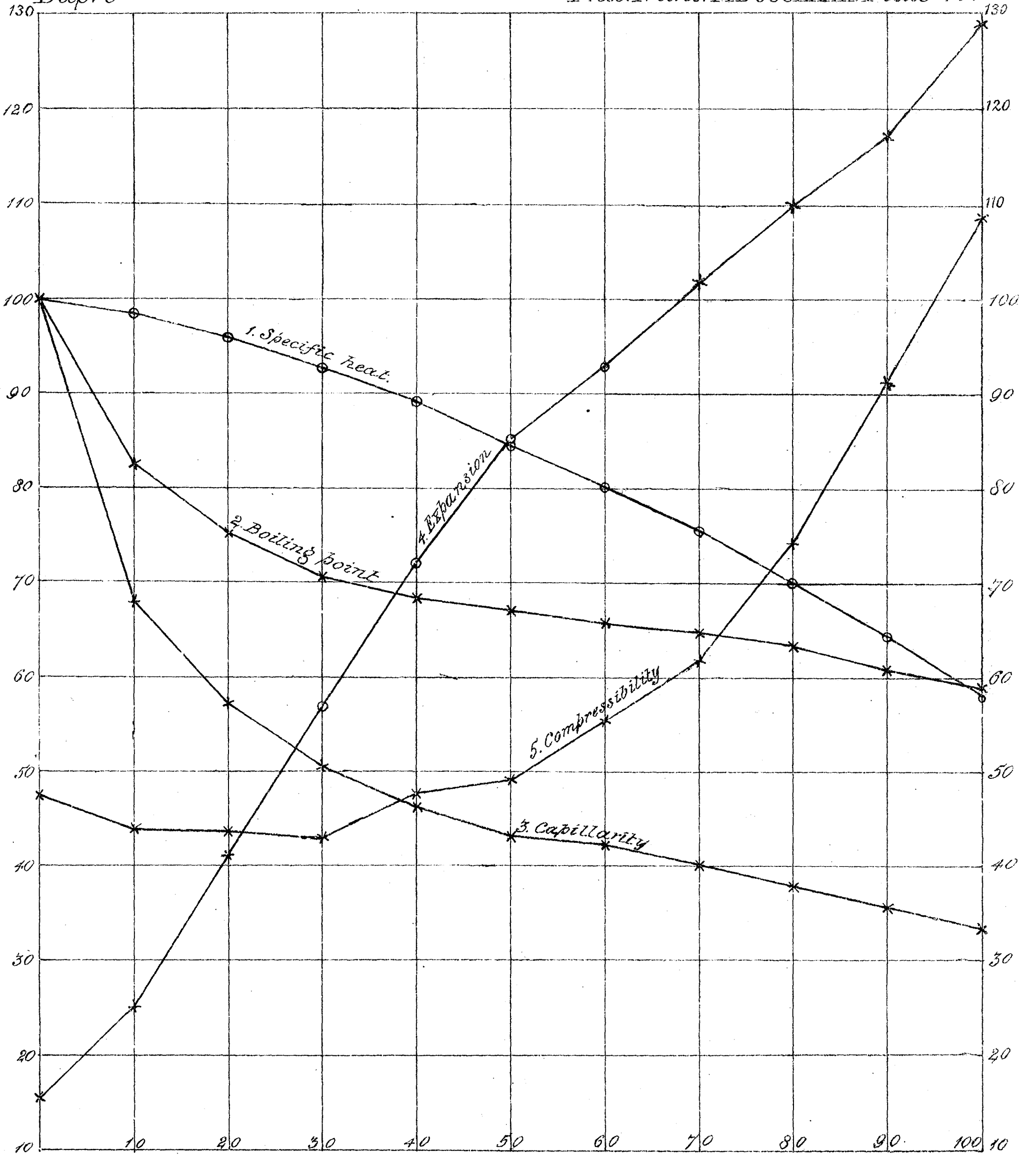
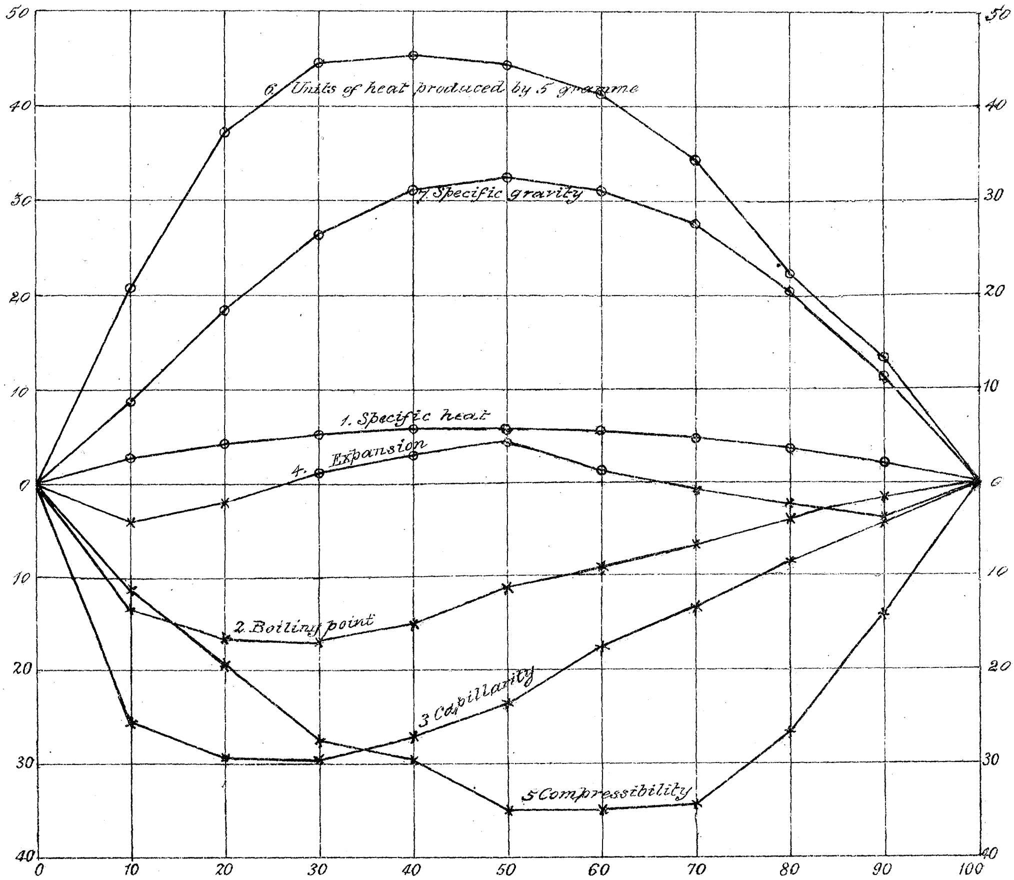


Fig. 2.



W. H. Wesley lith.

W. West & Co. imp.