LXXVII.—*Evaporation and Dissociation.* Part VII. *A Study of the Thermal Properties of a Mixture of Ethyl Alcohol and Ethyl Oxide.*

By WILLIAM RAMSAY, Ph.D., and SYDNEY YOUNG, D.Sc.

It has been shown in Part VI of this series of memoirs (*Phil. Mag.*, 1887, May, p. 435, and Aug., p. 196), that for both the gaseous and the liquid states the relation of pressure to temperature at constant volume may, in the case of methyl and ethyl alcohols, ethyl oxide, and carbon dioxide, and presumably in the case of all stable liquids, be expressed by the formula $p = bT - a$. That is, the isochoric lines, or lines of equi-volume for unit mass of the substance, are straight when mapped against pressures as ordinates and temperatures as abscissæ. We also showed that with the two dissociating substances, acetic acid and nitric peroxide, such isochoric lines are not straight, but are, at large volumes, tangential to the theoretical isochoric lines of minimum density at high temperatures, and at lower temperatures probably tangential to the theoretical isochoric lines of maximum density. A comparison of the behaviour of such stable and dissociable substances has shown the effect of chemical union on the relations of pressure, temperature, and volume.

But the mixture of two liquids, such as alcohol and water, is known frequently to be accompanied by contraction and by evolution of heat. It therefore appeared of interest to investigate thoroughly the behaviour of such a mixture, in order to throw light on the nature of this attraction.

Such a mixture must, in our opinion, be regarded as a solution of the one liquid in the other, and the meaning of the word "solution" must be so extended as to cover such instances. For while we speak

of the "solution" of a solid in a liquid, and of the "solution" of a gas in a liquid, it is customary to speak of the "mixture" of two liquids. A solid paraffin, of definite formula for example, dissolves in a liquid paraffin of lower molecular weight; but the solid paraffin may be melted, and then mixed with the liquid, and it cannot be denied that the end result is identical in both cases. It happens that it is, as a rule, impossible to mix a fused salt with liquid water; but that is owing merely to the difficulty of obtaining water at a sufficiently high pressure and temperature. Mr. Shenstone has recently shown that with the easily fusible salt, silver nitrate, mixture with water at high temperatures takes place in any desired proportion. The following results, we think, may therefore throw light on the vexed question of solution.

For a description of our apparatus and methods, we must refer to our memoir on ethyl oxide (*Phil. Trans.*, 1887, Part I, p. 57).

In filling the experimental tube, an attempt was made to obtain molecular proportions of ether and alcohol. A mixture of these liquids, weighed out in the desired proportions, was introduced by means of a pipette into the little apparatus, displacing the mercury with which the apparatus had been filled; a woodcut of this apparatus is shown on p. 61 of our memoir on ether (*loc. cit.*). After the mercury had been removed in great part by a Sprengel's pump, the exit from the bulb was sealed. There was, therefore, practically no air in the bulb or the experimental tube, its space being occupied by the mixed vapours. The liquid in the experimental tube was then repeatedly boiled in the usual manner, so as to displace the air-film adhering to its walls. We supposed that we had then the desired mixture in our tube. But data will be produced to prove that during the process of boiling, ether had escaped in greater proportion than alcohol; hence our final proportion was not molecular, but in the ratio of 63 mols. of alcohol to 37 mols. of ether.

The pressures were measured by two gauges, as usual, but the low pressure gauge was separately controlled (and its indications subsequently transferred to the high pressure gauge) by direct comparison of several readings against a column of mercury of known height and temperature. The comparison is as follows:—

Calculated. mm.	Found by direct reading. mm.
1008·7	1005·0
1182·8	1180·4
1299·9	1299·6
1339·9	1337·5

The mean difference is 0·2 per cent., and by taking the mean of all

the readings we assume that the probable error is not above 0.1 per cent.

The specimens of alcohol and ether were specially prepared as described in our former paper, and were dried finally with sodium. The boiling points, as before, were absolutely constant.

EXPERIMENTAL RESULTS.

Vapour-pressures.

As the vapour-pressures of a mixture of liquids is a function of the relative volumes of liquid and gas, we were precluded from experiments of this nature. There is no true vapour-pressure, and in the diagram on Plate II representing isotherms the lines corresponding to the vapour-pressures of a pure substance are given; and it is evident that with the mixture the pressure rises with decrease of volume. The vapour-densities at low temperatures were also omitted, inasmuch as the behaviour of such a mixture at low temperatures is deducible from measurements at higher temperatures and pressures.

Constants at High Temperatures.

This series includes a few determinations of compressibility at low temperatures. The usual corrections were employed for volume, pressure, and temperature, for details concerning which our memoir on ether may be consulted (*loc. cit.*, p. 65).

As before, three quantities were employed; the largest occupying 0.3558 c.c. at 13.5°; the middle quantity, 0.04765 c.c. at 15.6°; and the smallest quantity, about one-tenth of the middle quantity. With the largest quantity, the expansion of the liquid and the compressibility were measured; with the middle quantity, the behaviour at temperatures ranging between 190° and 275°, as regards pressure, temperature, and volume, both as liquid and gas; and with the smallest quantity, from 80° up to 275°, similar data were obtained for the gas. These measurements cover all the relations of pressure, temperature, and volume, from 350 c.c. per gram, down to 1.3 c.c. per gram.

So far, the two bodies had remained mixed. At 210°, the volume was increased as much as possible, in order to ascertain whether total evaporation would take place. The effect of this was to partially separate the alcohol from the ether, the more volatile ether occupying the top of the tube, while the less volatile alcohol remained mostly in the state of liquid. It will be seen from the numbers (p. 759), and from the diagram (Plate I), that the volumes are much influenced by mixture.

Measurements with the Largest Quantity. (Plate I.)

Temp.	Pressure.	Vols. of 1 gram.	Temp.	Pressure.	Vols. of 1 gram.
	mm.	c.c.		mm.	c.c.
20	1500	1·3197	140	9300	1·6309
	9559	1·3171		10880	1·6295
	43306	1·3105		16370	1·6229
30	800	1·3365		22050	1·6163
	22020	1·3306		27360	1·6094
	48800	1·3242		34130	1·6030
40	800	1·3540		39760	1·5964
	11630	1·3506	150	11890	1·6768
	33510	1·3441		17040	1·6695
50	800	1·3720		21470	1·6630
	6880	1·3706		25850	1·6562
	26890	1·3641		30780	1·6497
	51280	1·3576		35740	1·6430
60	800	1·3931		40870	1·6364
	7535	1·3904		46500	1·6299
	26560	1·3839	160	14180	1·7354
	46400	1·3772		16680	1·7294
70	1000	1·4159		19670	1·7227
	11620	1·4106		23120	1·7161
	26560	1·4040		26270	1·7095
	44240	1·3976		29850	1·7028
80	2291	1·4348		34280	1·6962
	11910	1·4303		38210	1·6896
	22410	1·4237		42510	1·6830
	40330	1·4173		46510	1·6764
90	2863	1·4608	170	17010	1·8015
	5305	1·4581		18470	1·7962
	10920	1·4570		20650	1·7896
	22040	1·4502		23300	1·7830
	36030	1·4436		25860	1·7763
100	3679	1·4889		28200	1·7697
	5950	1·4861		30950	1·7630
	13240	1·4836		33630	1·7564
	23340	1·4769		36840	1·7498
	35040	1·4704		39800	1·7432
110	4730	1·5199		42420	1·7366
	8070	1·5166		46400	1·7299
	17810	1·5099		50150	1·7233
	27330	1·5045	180	22240	1·8710
	38530	1·4969		24280	1·8630
120	5925	1·5511		26020	1·8564
	9300	1·5498		27530	1·8497
	17020	1·5432		29360	1·8430
	24400	1·5366		31200	1·8364
	34400	1·5300		33480	1·8297
	43300	1·5234		35500	1·8232
130	6745	1·5895		38160	1·8166
	13640	1·5828		39970	1·8100
	20840	1·5762		42630	1·8033
	27370	1·5696		44890	1·7966
	34760	1·5629		47800	1·7900
	42870	1·5564	190	25700	1·9770

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
190	mm.	c.c.	200	mm.	cc.
	27450	1·9635		32430	2·0864
	29870	1·9501		33560	2·0711
	31930	1·9368		34810	2·0576
	34680	1·9234		36260	2·0443
	37200	1·9100		37840	2·0309
	40140	1·8969		39450	2·0175
	43390	1·8835		41300	2·0040
200	46970	1·8702		43340	1·9907
	30940	2·1047		45490	1·9778
	31410	2·0980		47860	1·9639

The following series may be held to relate to partially separated liquids:—

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
210	mm.	c.c.	210	mm.	c.c.
	35820	2·3272		37850	2·2434
	35860	2·3150		38980	2·2201
	36200	2·3014		40460	2·1931
	36840	2·2742			

This series formed the conclusion of a day's work. The tube was necessarily allowed to cool, and again heated up, when thorough mixture was obtained by the violent convection currents. A repetition gave the following numbers:—

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
210	mm.	c.c.	210	mm.	c.c.
	34880	2·3096		40920	2·1795
	35570	2·2877		42910	2·1526
	36520	2·2606		45220	2·1256
	37650	2·2337		47790	2·0986
	39180	2·2066		51090	2·0717

The volume was then greatly increased, so as to reproduce a separation. On compressing to a small volume, no meniscus was visible, owing to the fact that the ether, which had now accumulated at the top of the tube, was above its critical temperature. Two readings were taken here. The pressure being 37810 mm., the volume was

2·5456 c.c. per gram, and at 38140 mm. the volume was 2·4778 c.c. The volume was again increased to about 4·5 c.c. per gram, and again decreased.

The following series was obtained :—

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
210	mm. 37070 37640 39700 40450 41230 42400	c.c. 2·5456 2·4099 2·2877 2·2607 2·2337 2·2066	210	mm. 43650 45380 47400 49850 52570	c.c. 2·1796 2·1526 2·1256 2·0986 2·0717

The volume was then slightly increased, and a few readings were taken.

Pressures 40350 mm. 39530 mm. 37610 mm.
Volumes 2·2607 c.c. 2·2877 c.c. 2·4099 c.c.

It is evident that these readings closely correspond with those of the last series.

The liquid was then allowed to cool partially, and then heated again. Partial mixture had taken place.

Pressure.. 39750 mm. Volume.. 2·2607 c.c. (A).

The process was repeated, and the following readings taken :—

Pressures 39510 and 39350 mm.
Volumes 2·2580 ,, 2·2594 c.c. per gram.

These are indicated on the diagram, Plate II, as (B).

After a further separation had been effected by heating the lower portion of the tube, while allowing the upper portion to cool, the volume being large in order to favour distillation, the temperature was equalised, and the volume reduced. It was then found that in addition to the meniscus formed by the alcoholic ether at the top of the liquid, a second meniscus was visible at the junction of the two heterogeneous liquids. Two readings were taken; and it will be seen that the pressure corresponding to these volumes is much higher than previously.

Pressures 40570 mm. 41340 mm. (C).
Volumes 2·2877 c.c. 2·2607 c.c. (C).

By suitable heating, a partial mixture was obtained, and the following readings taken:—

Pressures	39450 mm.	38490 mm. (D).
Volumes	2·2607 c.c.	2·2871 c.c. (D).

The volume was lastly kept small, to prevent boiling, and the upper part of the tube was cooled. The meniscus at the division of the ether and alcohol was seen to descend the tube, until it became lost at the surface of the mercury. The whole of the tube was again heated, and readings were taken.

Pressures	36670 mm.	35520 mm. (E).
Volumes	2·2607 c.c.	2·2877 c.c. (E).

It will be seen that these readings agree perfectly with those of the second series.

It is obvious from these observations, that the volume of the substances when thoroughly mixed is smaller than when they are separate, under these conditions of temperature and pressure. On increasing the volume slightly, the meniscus at the top of the thoroughly mixed liquids was perfectly visible, and there was no sign of junction in the body of the liquid. Experiments were also made at 220° with partial mixture, and with complete mixture, with the same general results, although much less marked.

Series I.

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
220	mm. 39130 39160 39200 39230	c.c. 3·7160 3·6480 3·6201 3·5123	220	mm. 39310 39460 39530 39570	c.c. 3·4441 3·3761 3·3081 3·2269

Series II.

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
220	mm. 44860 45700 46590 47740 48960 50500 52140	c.c. 2·4106 2·3835 2·3563 2·3292 2·3021 2·2750 2·2478	220	mm. 50500 48960 47640 46590 45710 44860 43170	c.c. 2·2750 2·3021 2·3292 2·3563 2·3835 2·4106 2·4785

Series II.

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
220	mm. 41950 41150 40550 39800 39410 39340 39200 39130 39110 39220 39180 39220 39260	c.c. 2·5522 2·6143 2·6826 2·8189 2·9549 3·0908 3·2269 3·3761 3·6480 3·5123 3·4480 3·4123 3·3761	220	mm. 39280 39360 39670 39820 40230 40650 41340 42150 43370 45090 39120 39130	c.c. 3·2269 3·0908 2·9549 2·8189 2·7508 2·6826 2·6143 2·5522 2·4785 2·4106 3·6480 4·3319

After the second last measurement was taken, the volume was increased and a small quantity of liquid appeared at the bottom of the tube; on still further enlarging the volume, this liquid increased, and then began to decrease. If the volume was increased very slowly to the same amount, no liquid appeared. This behaviour is probably due to cooling and consequent separation of alcohol.

Measurements with the Middle Quantity. (Plate II.)

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
190	mm. 13370 13700 14 80 14460 14860 15270 15690 16170 16680 17180 17750 18310 18900 19530 20190 20870	c.c. 32·41 31·37 30·35 29 33 28·33 27·29 26 27 25·25 24·14 23·12 22·11 21·09 20·06 19·04 18·04 17·02	190	mm. 21570 22070 22370 22620 22820 23060 23210 23340 23560 23640 23870 24000 24200 24330 24780	c.c. 16·04 15·00 14·00 13·00 12·01 11·04 10·06 9·070 8·092 7·113 6·136 5·163 3·218 2·250 1·961

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
200	mm. 29300 30760 13850 14600 15430 16350 17410 18580 19840 21300 22840 24610	c.c. 2·089 2·069 32·42 30·36 28·31 26·28 24·15 22·11 20·07 18·04 16·02 14·00	200	mm. 26440 27060 27300 27570 27680 27910 28020 28130 28330 28410 28740	c.c. 12·02 11·04 10·06 9·072 8·094 7·115 6·138 5·164 4·189 3·219 2·250
210	33670 35610 34650 14340 15130 16010 16970 18120 19350 20750 22310 24070	2·344 2·267 2·298 32·44 30·38 28·33 26·29 24·17 22·12 20·08 18·05 16·03	210	26070 28240 30540 31630 32590 32860 32900 33060 33340 33380 37200	14·01 12·03 10·07 9·077 8·099 7·120 6·143 5·167 4·192 3·224 2·253

At 219·5°, with small volumes, no meniscus was visible, and the substance became clouded on slightly increasing volume, presenting the usual appearance of a body at its critical point. On still further increasing volume, a permanent meniscus appeared. It appears therefore that 219·5° is the critical temperature of this particular

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
220	mm. 14800 15630 16540 17570 18790 20090 21600 23350 25230 27480 29980 32770	c.c. 32·45 30·39 28·34 26·30 24·17 22·13 20·08 18·05 16·03 14·01 12·03 10·07	220	mm. 34150 35600 36820 38050 38830 38960 39510 40420 42110 43850 46280 51390	c.c. 9·075 8·099 7·120 6·140 5·167 4·192 3·219 2·736 2·541 2·444 2·349 2·251

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
	mm.	c.c.		mm.	c.c.
230	15270	32·44	230	34730	10·07
	16130	30·38		36540	9·080
	17100	28·34		38240	8·102
	18170	26·30		40140	7·123
	19450	24·17		41800	6·146
	20830	22·13		43310	5·173
	22450	20·08		44840	4·193
	24230	18·06		46440	3·224
	26390	16·03		49710	2·736
	28840	14·01		51050	2·638
	31610	12·02		47730	2·929
240	38810	9·080	240	48070	5·172
	41050	8·102		50680	4·192
	43200	7·123		52060	3·709
	45620	6·146		54340	3·224
250	16130	32·46	250	31340	14·02
	17090	30·40		34720	12·03
	18120	28·35		38770	10·07
	19310	26·29		41100	9·080
	20710	24·18		43710	8·102
	22230	22·15		46160	7·123
	24000	20·10		49340	6·146
	26100	18·07		52590	5·173
	28480	16·04			
275	17150	32·48	275	31060	16·05
	18230	30·42		34380	14·03
	19350	28·37		38440	12·04
	20650	26·33		43400	12·09
	22250	24·20		46280	9·090
	23900	22·15		49820	8·110
	25870	20·11		53930	7·129
	28220	18·08			

mixture. On increasing volume, the relative amount of alcohol in the liquid is increased, when the critical temperature would be higher.

Measurements with the Smallest Quantity.

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
80	mm. 1042 1104 1150 1195 1228 1263 1306 1360	c.c. 350·3 306·0 273·0 238·9 216·9 194·9 173·1 151·3	80	mm. 1422 1496 1590 1705 1763 1830 1899 1978	c.c. 129·9 108·7 87·47 66·35 55·81 45·28 34·78 24·31
liquid present			liquid present		
100	1158 1317 1468 1665 1822 2012 2188 2305	350·5 306·1 273·1 239·0 217·0 195·0 173·2 151·4	100	2397 2493 2619 2784 2885 2996 3112 3239	130·0 108·8 87·54 66·40 55·85 45·32 34·81 24·33
130	1263 1439 1608 1827 2004 2220 2433 2808	350·7 306·4 273·3 239·2 217·2 195·1 173·3 151·5	130	3237 3808 4619 5573 5835 6022 6270 6543	130·1 108·8 87·58 66·43 55·88 45·34 34·82 24·34
160	1344 1533 1714 1949 2144 2373 2664 3027	355·1 310·2 276·8 242·3 219·9 197·6 175·5 153·4	160	3498 4136 5054 6470 7519 8961 10975	131·7 110·2 88·69 67·25 56·58 45·91 35·26
170	1393 1590 1778 2045 2227 2465 2765 3143 3643	351·1 306·7 273·6 239·4 217·4 195·3 173·5 151·7 130·2	170	4306 5266 6751 7873 9409 11612 13081 14939	108·9 87·66 66·49 55·93 45·38 34·86 29·62 24·37

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
180	mm. 1424 1628 1827 2074 2280 2527 2832 3224 3734	c.c. 351·2 306·7 273·7 239·5 217·4 195·4 173·5 151·7 130·2	180	mm. 4431 5398 6981 8187 9748 12100 15826 18410	c.c. 109·0 87·68 66·50 55·94 45·39 34·87 24·38 19·13
200	1487 1701 1903 2172 2388 2654 2975 3383 3931	351·3 306·9 273·8 239·6 217·5 195·5 173·6 151·8 130·3	200	4674 5711 7387 8643 10410 13000 17300 20500	109·0 87·73 66·54 55·97 45·42 34·88 24·39 19·13
220	1541 1768 1980 2259 2488 2763 3105 3536 4100	351·5 307·0 273·9 239·7 217·7 195·6 173·7 151·9 130·4	220	4877 5997 7777 9130 11000 13860 18730 22450	109·1 87·77 66·57 56·00 45·44 34·90 24·40 19·14
230	1561 1806 2010 2295 2532 2811 3160 3614	351·6 307·1 274·0 239·8 217·7 195·6 173·7 151·9	230	4201 4981 6152 7966 9356 11310 14300 19330	130·4 109·1 87·79 66·58 56·01 45·45 34·91 24·41
250	1682 1935 2167 2474 2740 3048 3425 3914 4553	339·0 296·1 264·2 231·2 209·9 189·1 167·5 146·5 125·7	250	5438 6680 8689 10225 12397 15700 21320 26010	105·1 84·65 64·19 54·00 43·82 33·66 23·53 18·46

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
275	mm. 1732 2019 2252 2586 2855 3186 3598 4113 4792	c.c. 339·2 296·3 264·4 231·4 210·1 188·8 167·6 146·6 125·8	275	mm. 5706 6958 9213 10840 13290 16710 22920 28100	c.c. 105·2 84·71 64·24 54·04 43·85 33·68 23·54 18·48

Weight of Substance employed.—To ascertain the volume of 1 gram of the mixture, it is necessary to know the weight. That was obtained by assuming that when the product of pressure and volume is constant, the gases present have their normal density. But the problem of ascertaining the weight is a complex one, inasmuch as the accurate relative proportions of the alcohol and ether are unknown. And it is still further complicated by the fact that on two occasions, small traces of liquid found their way up the experimental tube, thereby increasing the mass of the smallest quantity. There is, however, no possibility of a mistake having occurred by such small additions, for after each day's work the temperature was brought back to that at which the first determinations were made, and identical results were obtained except in the two cases where liquid was seen to ascend. The amount of liquid remained constant at the following temperatures:—160°, 170°, 180°, 200°, 220°, and 230°; and the products of pressure into volume at the largest volumes are as follows:—

160°.	170°.	180°.	200°.	220°.	230°.
1601·3 1599·3 1598·3 —	1639·4 1634·7 1630·9 1641·8	1676·3 1674·1 1676·2 —	1751·7 1750·0 1747·2 1745·0	1815·9 1820·0 1818·5 1815·9 1815·6	1842·0 1859·2 1846·4 1844·8 —
Vol. decreased from 4 to 3 between ex- tremes.	decrease 3 to 2.	decrease 4 to 3.	decrease 3 to 2.	decrease 8 to 5.	decrease 3 to 2.

It is evident from these numbers that we are justified in regarding the vapour-density as normal. But in order to know the weight, we must know the vapour-density; and in order to ascertain the vapour-density, we must know the relative proportion of each constituent.

The vapour-densities of mixtures of alcohol and ether in the proportions of x molecules of alcohol to $100-x$ molecules of ether were calculated; and also the corresponding weights from the mean value of $\frac{pv}{t}$, and these vapour-densities. The weights were then mapped against values of x . It will be seen later that the true weight was obtained from the intersection of this line with another, which must now be explained.

It was supposed, as has been mentioned, that the tube was originally filled with a mixture of ether and alcohol in molecular proportions. In order to obtain the weight of the largest quantity of mixed liquids in the experimental tube, two methods of determining specific gravity were resorted to; (1) direct determination of the specific gravity of the mixture; and (2) measurement of the contraction on mixing the alcohol and ether in molecular proportions at 0° . From the known specific gravities of the two liquids at 0° , the specific gravity of the mixture can be deduced from the second method. The first method proved unsatisfactory owing to the extreme difficulty, if not impossibility, of filling any form of specific gravity apparatus without evaporating some of the ether; the results obtained were for this reason

always too high. We therefore avoid giving details; but it may be mentioned that the specific gravity found at 12.9° , with all corrections for a vacuum, &c., introduced, was 0.07564. To determine the contraction on mixing, an apparatus (shown in the accompanying woodcut) was employed.

Two bulbs, A and B, communicate by a wide capillary. To the top bulb a graduated stem C was sealed, near the upper end of which a small bulb was blown. The apparatus was calibrated and weighed; and the capacity of the lower bulb was reduced to such an amount by addition of mercury, that the amount of alcohol which it contained up to the constriction at 0° , bore a molecular proportion to the ether contained in the upper bulb and the stem. While the apparatus was kept in melting ice, alcohol was introduced so as to fill the lower bulb to the constriction, and ether was then poured in so as to fill the upper bulb and the stem up to a calculated mark. The upper tube above the small bulb was then closed by sealing. The apparatus now contained alcohol and ether in molecular proportions, unmixed. By inverting and shaking the apparatus, mercury was made to pass repeatedly from one bulb into the other, thus being replaced by the mixed liquids. After 20 inversions, no further contraction took place, and the altered volume was then read, again at 0° . The following results were obtained:—

First measurement.....	0.725	per cent. contraction.
Second ,, 	0.731	,, ,,
Mean.....	0.728	,, ,,

With 0.728 per cent. contraction, the specific gravity of the mixture is 0.7671, and its specific volume, 1.3036, the specific volume of alcohol at 0° being taken as 1.2403, and that of ether 1.3583 (see our previous memoirs on alcohol and ether). It has been assumed that the percentage contraction does not greatly vary when the proportions of alcohol and ether are considerably altered. We are justified at least in supposing that the result of the following calculations, giving the weight, would not be appreciably affected.

The next step was to obtain the ratios of the weights of the second and third quantities to the first, by comparison of the volumes at the same temperatures and pressures, both in the liquid and gaseous states with the smallest quantity; and in the gaseous state with the smallest quantity. The following ratios were obtained between the largest and middle quantities:—

Ratios.—0.13235; 0.13096; 0.13256; 0.13218; 0.13385; 0.13524; 0.13362; 0.13333; 0.13273; 0.13302; 0.13421. Mean, 0.1331.

The ratios between the middle quantity and the smallest quantity were also determined:—

Ratios.—0·09224; 0·09238; 0·09285; 0·09290; 0·09222. Mean, 0·09252.

Ratio between smallest and largest quantities, 0·0132.

Since the weight of the largest quantity is calculated from its specific gravity, and the ratio between that and the smallest is known, that of the smallest also depends on the relative proportions of alcohol and ether. It may be confidently assumed that all three portions have the same composition; for, in order to obtain the middle quantity, the tube was inverted after thorough mixture had been ensured, and a portion of the mixed liquid allowed to escape through the mercury; and the smallest quantity was obtained in a similar manner.

We have now two means of calculating the weights of the smallest quantity for different molecular proportions; first from the normal vapour-density, by the method already described; and, second, from the specific gravities of the liquid, also calculated for different molecular proportions.

The results of the first process are as follows, where x is the number of molecules of alcohol in 100 of the mixture:—

	Vapour-density.	Weight.	Vol. of 1 gram liquid at 0°.	Weight.
$x = 50$	30·0	0·003566	1·3036	0·003312
55	29·3	0·003483	1·2979	0·003326
60	28·6	0·003400	1·2920	0·003342
65	27·9	0·003316	1·2857	0·003358
70	27·2	0·003233	1·2791	0·003375

On mapping the weights obtained by both methods against values of x , the point of intersection of the two curves gives the value of x as 63, and of the weight as 0·003352 gram, and the volume of 1 gram of the mixed liquid at 0° is consequently 1·2882 c.c.

From the ratios previously stated it follows that the weight of the middle quantity is 0·03623 gram, and that of the largest, 0·27204 gram.

Similar comparisons of the smallest quantities among themselves gave the weight of that portion used for the isothermals 160°, 0·003313 gram, and for the isothermals 250° and 275°, 0·003479 gram.

REDUCTION AND ARRANGEMENTS OF RESULTS.

Vapour-pressures.

It has already been pointed out that the vapour-pressures of a mixture vary with the volume, and that pressure continues to rise, on diminution of volume, even after liquid has begun to appear. For example, at 190° liquid begins to be visible at a pressure of 22000 mm., and the last bubble of gas disappears at about 24600 mm. The pressure has thus risen 2600 mm., or over 10 per cent. of its total amount during condensation. The rise of pressure is even more remarkable at lower temperatures. At 80°, condensation begins at a pressure of about 1200 mm., and the last trace of gas is condensed at 2290 mm. The pressure is therefore nearly doubled during condensation. It is clear from this that any attempt (and attempts have been made) to determine the vapour-pressure of a mixture by the statical method must lead to wholly erroneous, and indeed uninterpretable results, inasmuch as the relative quantities of the two substances in the residual liquid would alter with each alteration of volume. Moreover, by the dynamical method, the results can only be even approximately correct when the volume of liquid is very large compared with the volume of vapour.

Compressibilities of Liquid.

The isothermals for the liquid state, showing decrease of volume on increase of pressure, were for purposes of smoothing mapped on curve-paper, and isobars were drawn representing the relations of volume to temperature. The isothermals are shown on Plate I. The circles on the diagram are the experimental points; the crosses are retransferred from the isochors.

The results are given in the table (p. 772).

Orthobaric Volumes of 1 gram of Liquid.

Temp.	Volume.	Temp.	Volume.	Temp.	Volume.
0°	1·288	80°	1·4365	150°	1·6785
10	1·302	90	1·461	160	1·733
20	1·3195	100	1·489	170	1·7965
30	1·3365	110	1·520	180	1·874
40	1·354	120	1·552	190	1·976
50	1·373	130	1·590	200	2·107
60	1·393	140	1·6305	210	2·327
70	1·413				

Pressure in Millimetres.

T.	1500.	5000.	10000.	15000.	20000.	25000.	30000.	35000.	40000.	42500.	45000.	47500.	50000.	55000.
20°	1·320	1·319	1·318	1·317	1·316	1·314	1·313	1·312	1·311	1·311	1·311	1·310	1·310	1·310
30	1·336	1·335	1·334	1·332	1·331	1·330	1·3285	1·327	1·3265	1·326	1·3255	1·325	1·324	1·3235
40	1·354	1·352	1·351	1·3495	1·348	1·3465	1·345	1·3435	1·3425	1·342	1·341	1·340	1·3395	1·3385
50	1·3725	1·371	1·369	1·368	1·366	1·364	1·362	1·361	1·360	1·359	1·358	1·357	1·356	1·3545
60	1·393	1·3915	1·389	1·387	1·3855	1·3835	1·381	1·380	1·3785	1·378	1·3765	1·3755	1·374	1·372
70	1·416	1·413	1·410	1·408	1·406	1·402	1·4015	1·400	1·398	1·397	1·396	1·395	1·3935	1·3915
80	—	1·436	1·433	1·4305	1·428	1·426	1·4235	1·421	1·420	1·418	1·417	1·416	1·414	1·412
90	—	1·462	1·458	1·4555	1·452	1·4495	1·447	1·4445	1·4425	1·441	1·440	1·4385	1·437	1·434
100	—	1·4895	1·4855	1·482	1·4785	1·4755	1·4725	1·470	1·468	1·466	1·465	1·4635	1·4615	1·459
110	—	1·520	1·516	1·5115	1·508	1·504	1·501	1·4985	1·496	1·494	1·492	1·490	1·488	1·485
120	—	—	1·5495	1·545	1·5405	1·536	1·5325	1·530	1·526	1·524	1·522	1·520	1·517	1·514
130	—	—	1·5875	1·582	1·5775	1·571	1·5675	1·564	1·559	1·5565	1·554	1·552	1·549	1·545
140	—	—	1·631	1·624	1·6195	1·6115	1·606	1·6015	1·596	1·593	1·590	1·588	1·585	1·580
150	—	—	—	1·672	1·666	1·658	1·6505	1·6445	1·638	1·634	1·631	1·6285	1·624	1·619
160	—	—	—	1·723	1·723	1·712	1·7025	1·694	1·685	1·6815	1·678	1·674	1·670	1·6635
170	—	—	—	—	1·792	1·778	1·765	1·752	1·741	1·735	1·732	1·729	1·724	1·715
180	—	—	—	—	—	1·860	1·840	1·826	1·810	1·803	1·7965	1·7905	1·784	1·771
190	—	—	—	—	—	1·980	1·949	1·920	1·8965	1·888	1·878	1·869	1·860	1·841
200	—	—	—	—	—	—	2·055	2·014	1·996	1·996	1·980	1·967	1·954	1·933
210	—	—	—	—	—	—	—	2·193	2·157	2·157	2·128	2·101	2·080	2·051
220	—	—	—	—	—	—	—	2·305	2·275	2·2516	2·205	2·234	2·283	2·210
230	—	—	—	—	—	—	—	—	—	—	—	2·960	2·711	2·444

These numbers are calculated from volumes directly read after the last trace of vapour had disappeared at the top of the experimental tube. It is questionable whether the word "orthobaric" should be used; but by the method of measurement, the true vapour-pressure of the mixture must have been nearly obtained. The volumes were plotted against temperature, smoothed graphically, and reproduced as above.

Inasmuch as it is impossible to detect the volume at which the first trace of liquid makes its appearance in the experimental tube, it is impossible to give the volumes of the saturated vapour. These numbers cannot be read from the curves, for the transition from gas to liquid is accompanied by gradual rise of pressure; there is no definite angle between the line representing volumes in the gaseous condition, and that representing the state in which liquid and gas are both present at once. For the same reason, it is impossible to calculate the heats of vaporisation.

Two points of interest present themselves. In the case of pure stable liquids, the isochoric lines, or lines of equal volume, are straight, both for the liquid and the gaseous states. It is an interesting question whether the isochoric lines of a mixture are similar to those of a pure substance, or whether they are sinuous curves, in some way resembling those of a dissociable body (see *Phil. Mag.*, 1887, May and July). Another question is, what alteration occurs in the volumes of the two liquids or gases on mixing? How do the volumes of the mixture compare with the sums of the volumes of the constituents? We shall consider these points in their order.

Isochoric Lines.

The isochors for the liquid state were constructed from the isobars; they are represented on Plate III. From this it will be seen that from volumes of 1.32 c.c. per gram up to 2.7 c.c. per gram, the isochoric lines are straight between wide limits of pressure. As the volumes increase, the isochors, which were constructed from the isotherms, begin to show curvature which increases with rise of volume; and the curvature of each individual isochor increases with fall of pressure and temperature. This is evident on the diagram at volumes between 9 c.c. per gram and 30 c.c. per gram. It is probable that if measurements could have been made at still higher temperatures, these lines would also have become straight. Towards 30 c.c. per gram, the isochors are again becoming straighter, and at still larger volumes deviation from straightness becomes imperceptible at high temperatures. It is to be noticed, however, that at lower temperatures, these isochors exhibit curvature on approaching the vapour-pressure band.

It has been already remarked that the pressure of the vapours of a mixture of liquids depends on their relative amounts, which again depends on the relative volumes of the liquid and vapour. As these are continually changing during evaporation, the vapour-pressures are representable not by a line but by a band. This is well seen in the diagram of isochoric lines (Plate III); and, as has been remarked, the isochors show curvature before reaching this band, whereas with a pure liquid the isochors remain perfectly straight, and indeed can be induced to cut the vapour-pressure line. This curvature of the isochoric lines appears to be sudden for small volumes (liquid), but is gradual at large volumes (gas).

It is a question of interest whether such isochoric lines for a mixture of liquids can be conceived to cut through the vapour-pressure band. It may be remembered that in the case of pure liquids this is experimentally possible. In order that it may be experimentally realised it is necessary to work with liquid almost absolutely free from air; and our test, applicable in the case of pure liquids, was the absolute constancy of vapour-pressure through the whole process of condensation. But with a mixture this test is clearly inapplicable; and the only test which we have to rely on is to notice whether or not the pressure rises greatly during the condensation of the last small bubble of gas. So far as we could judge, this test gave fairly satisfactory results; when the liquids were mixed, the small bubble disappeared quickly. But it was found impossible to reduce pressure to any great extent without the bubble again appearing. It may have been the case, therefore, that a little air was present, preventing the partial realisation of the continuous passage from liquid to gas.*

Alteration of Volume on Mixing.

The second point of interest is as regards the alteration of volume on mixing alcohol and ether at any given temperature and pressure. From previous experiments, we know the volume of 1 gram of alcohol and also the volume of 1 gram of ether at any given temperature and pressure; and we also know the proportion of alcohol to ether in the mixture. The volume of the alcohol, supposing it to be unmixed, will clearly be proportional to its weight in a gram of the mixture, and similarly with ether. For purposes of comparison, three isobars were constructed, one for alcohol, one for ether,

* From this it is evident that Wroblewski's conclusion (*Monats. f. Chem.*, 1886, p. 383) regarding a pure liquid is realisable only in the case of a mixture, viz., that the isochoric lines, after approaching the vapour-pressure line, run parallel with it.

and one for the mixture; and from these isobars the volumes corresponding to particular temperatures were read off. The volumes of alcohol and ether were then reduced so as to be proportional to their relative weights in the mixture. For example, at a pressure of 40000 mm., and at a temperature of 190°, the volume of 1 gram of ether is 2.211 c.c.; and that of 1 gram of alcohol is 1.690 c.c. The volume of 0.4858 gram of ether is therefore 1.074 c.c., and of 0.5142 gram of alcohol 0.8690 c.c. The sum of these is 1.943 c.c., while the volume of 1 gram of the mixture at the same pressure and temperature is 1.897 c.c. The actual contraction is 0.046 c.c., and the percentage contraction on mixing is 2.37 per cent.

Three pressures were chosen: the first, 50000 mms., is above the critical pressure of all; the second, 40000 mms., is above the critical pressure of ether and of the mixture, but below that of alcohol; and the third, 5000 mms., is below that of all. The comparisons in the first case are all from experimental data; they are given in the following table, and are graphically represented on Plate IV.

Tempera- ture.	Vol. of 0.4858 gram of ether.	Vol. of 0.5142 gram of alcohol.	Sum.	Vol. of 1 gram of mixture.	Percentage alteration.
	c.c.	c.c.	c.c.		
150	0.8793	0.7739	1.6532	1.624	-1.77
170	0.9352	0.8124	1.7476	1.724	-1.35
190	1.0226	0.8639	1.8865	1.860	-1.40
200	1.0858	0.8947	1.9805	1.954	-1.34
210	1.1708	0.9281	2.0989	2.080	-0.90
220	1.2850	0.9770	2.2620	2.283	+0.93
230	1.4501	1.0515	2.5016	2.710	8.33
234	1.559	1.098	2.657	3.150	18.55
236	1.584	1.126	2.710	3.505	29.34
238	1.627	1.157	2.784	3.950	41.88
240	1.681	1.201	2.882	4.410	53.04
242	1.732	1.260	2.992	4.785	59.93
244	1.790	1.365	3.155	5.100	61.65
246	1.846	2.139	3.985	5.400	35.51
248	1.904	2.915	4.819	5.675	17.76
250	1.972	3.330	5.302	5.930	11.85
255	2.138	4.011	6.149	6.490	5.55
260	2.283	4.522	6.805	6.965	2.35
270	2.536	5.265	7.801	7.740	-0.78
275	2.655	5.574	8.229	8.040	-2.30

The pressure of 40000 mm. is below the critical pressure of alcohol. A portion of the isobar, therefore, takes the serpentine form characteristic of the continuous passage from the liquid to the gaseous state; and between the temperatures 231° and 236° there are for each temperature three possible volumes, two of which are realisable at the boiling point corresponding to that pressure, but

only one at any other temperature. The isobar, however, was constructed from the known values of a and b for alcohol in the equation $p = bt - a$, and the required volumes were read from its graphic representation. The following table summarises the results, which are also shown graphically in Plate IV:—

Temperature.	Vol. of 0·4858 gram of ether.	Vol. of 0·5142 gram alcohol.	Sum.	Vol. of 1 gram of mixture.	Percentage alteration.
	c.c.	c.c.	c.c.		
100	0·7768	0·7091	1·4859	1·468	— 1·20
120	0·8123	0·7307	1·5430	1·526	— 1·10
140	0·8589	0·7600	1·6189	1·596	— 1·41
160	0·9206	0·7955	1·7161	1·686	— 1·75
180	1·0085	0·8412	1·8497	1·810	— 2·14
190	1·074	0·8690	1·9430	1·897	— 2·37
200	1·170	0·9024	2·0724	2·014	— 2·82
210	1·341	0·9430	2·2840	2·193	— 3·98
215	1·478	0·968	2·446	2·350	— 3·90
218	1·608	0·986	2·589	2·559	— 1·16
220	1·700	1·001	2·701	2·776	+ 2·78
222	1·777	1·017	2·794	4·795	+ 71·62
223	1·807	1·026	2·833	5·380	+ 89·87
230	2·220	1·112	3·332	7·120	+ 113·74
231	2·274	3·466	5·740	7·300	+ 27·18
"	"	2·890	5·164	"	+ 41·36
"	"	1·131	3·405	"	+ 114·39
232	2·322	3·913	6·235	7·440	+ 19·32
"	"	2·509	4·831	"	+ 54·00
"	"	1·144	3·466	"	+ 114·66
233	2·371	4·196	6·567	7·600	+ 15·73
"	"	2·247	4·618	"	+ 64·57
"	"	1·170	3·541	"	+ 114·63
234	2·414	4·412	6·826	7·740	+ 13·39
"	"	2·026	4·440	"	+ 74·32
"	"	1·193	3·607	"	+ 114·58
235	2·461	4·582	7·043	7·900	+ 12·17
"	"	1·846	4·307	"	+ 83·42
"	"	1·229	3·690	"	+ 114·10
236	2·507	4·746	7·253	8·010	+ 10·44
"	"	1·635	4·142	"	+ 93·39
"	"	1·280	3·787	"	+ 111·51
237	2·550	4·890	7·440	8·140	+ 9·41
240	2·677	5·281	7·958	8·510	+ 6·94
250	3·041	6·278	9·319	9·550	+ 2·48
275	3·789	7·610	11·399	11·400	0

As we have been unable to discover a formula representing the behaviour of the mixture, we are precluded from giving results at a low pressure in the unrealisable portion of the passage from gas to liquid, if indeed it is conceivable in the case of a mixture. We have therefore calculated only the gaseous portions at a pressure of 5000 mm. We append the results:—

MIXTURE OF ALCOHOL AND ETHER. VOLUMES OF 1 GRAM.

MIXTURE OF ALCOHOL AND ETHER. ISOTHERMS AND ISOCHORS.

MIXTURE OF ALCOHOL AND ETHER. ISOCHORS.

PERCENTAGE INCREASE OF VOLUME ON MIXING ALCOHOL AND ETHER AT CONSTANT PRESSURES AND TEMPERATURES.

Temperature.	Vol. of 0.4858 gram of ether.	Vol. of 0.5142 gram alcohol.	Sum.	Vol. of 1 gram of mixture.	Percentage alteration.
	c.c.	c.c.	c.c.		
130	28.69	50.55	79.24	79.3	+ 0.76
160	31.72	56.46	88.18	90.0	2.06
170	32.74	58.36	91.10	92.1	1.10
180	33.85	60.12	93.97	95.7	1.84
200	35.80	63.81	99.61	101.1	1.50
220	37.75	67.36	105.11	105.9	0.75
230	38.72	69.06	107.78	108.1	0.30
250	40.54	72.50	113.04	114.1	0.94
275	42.85	76.72	119.57	120.2	0.53

It may appear remarkable that on mixing two bodies at the same pressure and temperature, a great expansion should be produced. But a familiar and somewhat analogous instance is at hand. Imagine a litre of dry air at a given temperature and pressure. Let a drop of liquid water be introduced; the sum of the volumes does not differ appreciably from 1 litre. But the water will evaporate into the dry air, and the volume of the "mixture" will be considerably greater than the sum of the volumes of the "constituents." The greatest expansion, at 232° under a pressure of 40000 mm., occurs precisely in this manner; the liquid alcohol is gasified by expansion into the space occupied by the ether. Above the critical pressure of alcohol at 50000 mm., a similar, though not so great, expansion is noticeable, even if the alcohol cannot be termed a "liquid."

DESCRIPTION OF PLATES.

Plate I shows the compressibilities of the liquid. The circles represent actual observations with the largest quantity of substance. The crossed circles show the effect of incomplete mixture, with the exception of those marked E. The crosses are points read from the isochors, on the apparently well-grounded assumption that in this region the isochors are straight lines.

Plate II represents the experiments with the middle quantity. The circles trace out the isotherms. The crossed circles represent observations with either the largest or the smallest quantity, the former at small volumes, the latter at large. The lines radiating from the vapour-pressure band are isochors for volumes between 2 c.c. per gram and 34 c.c. per gram. The vapour-pressure band is shown by the dotted lines.

Plate III gives the isochors, from volumes of 1.32 to 300 c.c. per gram. The general course of the vapour-pressure band is here well seen.

Plate IV represents the percentage alteration of volume on mixing the alcohol and ether at constant temperature and pressure. The lines are isobars for 5000, 40000, and 50000 mm.