

Some Thermodynamical Relations - Part I

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characterized by the fewness and simplicity of the apparatus required, it was thought undesirable to mar that simplicity by the addition of something not essential.

In conclusion, I desire to thank Professor Ayrton, F.R.S., for his kindness in suggesting the simple way of describing the method adopted in this note, and also for the statement of a problem which led to the results herein stated.

XXXIII. *Some Thermodynamical Relations.*—PART I.

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

THE relations to be considered in the following pages are, we believe, well founded; but we hope to confirm them by more exact experiments than have as yet been made.

It appears advisable here to state the share which each of the authors has had in this work. For our purpose, the equation

$$\frac{L}{s_1 - s_2} = \frac{dp}{dt} \cdot \frac{t}{J}$$

will be employed. The relations of the first term of this equation were the subject of a communication to the Chemical Section of the Philosophical Society of Glasgow in the year 1877 by Dr. Ramsay, which, however, he considered too incomplete to be published; while the application of the last term of the equation to the vapour-pressures of substances, which formed the subject of a joint research by both authors, was independently discovered by Dr. Young. It is also right here to mention that some of the relations discovered by Dr. Ramsay have been pointed out subsequently and independently by Trouton (*Phil. Mag.* 1884, vol. xviii. p. 54).

The term $\frac{L}{s_1 - s_2}$ (where L represents the heat of vaporization of a liquid or solid substance at its boiling- or volatilizing-point, and where s_2 is the volume of the liquid or solid at these temperatures, and s_1 that of the gas into which one or other is converted), if stated in words, denotes the heat

* Read November 28, 1885.

expressed in units required to produce unit increase of volume of substance at the temperature of ebullition of the liquid or volatilization of the solid.

Two laws have been discovered, representing certain relations between different liquids.

The first law may be stated thus :—*The amount of heat required to produce unit increase of volume in the passage from the liquid to the gaseous state at the boiling-point under normal pressure is approximately constant for all bodies; or* $\frac{L}{s_1 - s_2} = C$.

The data on which this law is based are imperfect. The heats of vaporization of but few bodies have been determined with accuracy; and we have recently shown in a communication to the Royal Society that the results obtained by Favre and Silbermann, by Regnault, and by Andrews for ethyl alcohol are only approximations to truth. It is probable that the data given for other substances less easy to obtain in a pure state are still less to be relied on. We have also shown in that paper that the density of saturated vapour of alcohol is normal, or nearly so, only at temperatures below 50°. Nevertheless, in calculating by means of the above-mentioned formula the constant for alcohol, it has been assumed that the saturated vapour of alcohol possesses normal density at 78°·4; and from want of knowledge it has similarly been assumed that at their boiling-points the saturated vapours of the other liquids to be considered have also normal density. It must therefore be acknowledged that considerable doubt rests on both the expressions in the term $\frac{L}{s_1 - s_2}$, and this doubt prevented the previous publication of these relations; but it will be seen in the sequel that the much more trustworthy determinations of vapour-pressures amply confirm the law which has been stated.

The following table exhibits these relations at normal pressure:—

Substance.	$s_1 - s_2$.	L.	$\frac{L}{s_1 - s_2}$.
Water	1695	537	0.3166
Methyl alcohol	865.9	263.7	0.3046
Ethyl alcohol.....	624.7	202.4	0.3240
Ethyl oxide	322.3*	90.5	0.2808
Methyl formate.....	417.1	117.1	0.2808
Methyl acetate	362.5	110.2	0.3040
Ethyl acetate.....	323.0	92.7	0.2870
Ethyl oxalate	256.2	72.7	0.2835
Amyl alcohol (?)	375.5	121.4	0.3238
Acetic acid.....	318.0†	101.9	0.3204
Benzene	370.6	92.3	0.2491
Bromine.....	169.2	45.6	0.2695
Phosphorus chloride..	209.5	51.4	0.2453
Carbon disulphide ...	343.3	86.7	0.2526
Methyl iodide	181.5	46.1	0.2539
Ethyl iodide	180.5	46.9	0.2598
Ethyl chloride	361.9	100.1	0.2767
Carbon tetrachloride .	186.3	46.9	0.2515
Chloroform	229.1	61.2	0.2673
Mercury.....	258.0	77.5	0.3004
Nitric peroxide	309.6‡	93.48	0.3019

It will be seen that these numbers vary between 0.2453 for phosphorus chloride and 0.3240 for ethyl alcohol. The alcohols, water, and acetic acid give all nearly 0.32; and benzene, and bodies containing halogens and sulphur give lower numbers, averaging 0.2564.

The sequel will show that these numbers cannot be regarded as experimental deviations from a constant; but that they have significance can hardly be denied. It would also appear that the nature of the element in the compound, and its amount influence the absolute value; though the nature and extent of this influence can hardly be formulated.

The second law is :—*If the amounts of heat required to produce unit increase of volume in the passage from the liquid to the gaseous state be compared at different pressures for any two bodies, then the ratio of the amount at the boiling-point under a pressure p_1 , to the amount at another pressure p_2 , is approximately constant for all liquids.*

Or, $\frac{L}{s_1 - s_2}$ at p_1 , bears a constant proportion to $\frac{L}{s_1 - s_2}$ at p_2 , for all liquids, and probably for all solids.

* Determined by Horstmann, *Annalen*, 1868, Suppl. vi. p. 64.

† Determined by Ramsay and Young.

‡ Density taken as 39 ($H=1$) as an approximation.

In support of this statement the facts to be adduced are as follows :—

Water.					Chloroform.			
P. mms.	T.	$s_1 - s_2$ ccs.	L.	$\frac{L}{s_1 - s_2}$	T.	$s_1 - s_2$ ccs.	L.	$\frac{L}{s_1 - s_2}$
300	76°·4	402·2	552·1	0·137	35°·0	535	64·65	0·121
760	100·0	169·5	556·5	0·317	61·0	229	61·2	0·267
1000	107·1	131·3	531·5	0·405	69·3	178	60·4	0·339
2000	129·3	69·5	515·6	0·742	92·5	95·3	58·2	0·611
3000	143·3	47·9	505·7	1·055	108·5	66·3	56·6	0·854
4000	154·2	36·9	497·7	1·350	121·0	51·4	55·4	1·079
5000	162·8	30·1	491·6	1·633	131·0	42·1	54·5	1·294
6000	170·1	25·5	486·1	1·906	140·0	35·9	53·6	1·493
7000	177·0	22·2	481·3	2·168	148·0	31·4	52·8	1·684
8000	182·9	19·7	477·0	2·424	155·0	27·9	52·2	1·871

The ratios, placing $\frac{L}{s_1 - s_2}$ at 300 millims. pressure = 1·0 for each substance, are :—

P	300	760	1000	2000	3000	4000	5000	6000	7000	8000
Water	1·00	2·30	2·94	5·40	7·68	9·81	11·88	13·86	15·77	17·63
Chloroform...	1·00	2·22	2·81	5·06	7·07	8·94	10·72	12·38	13·96	15·51

Another method of comparison is to regard the value of $\frac{L}{s_1 - s_2}$ for water as equal to unity at each pressure, when the numbers for chloroform become

1·00 0·962 0·953 0·938 0·922 0·911 0·903 0·893 0·885 0·850.

Similar results may be obtained on comparing other bodies with water; it may be, however, remarked that the instance chosen is one of those in which least concordance is to be noticed. It is evident that here also the concordance is merely approximate.

Another point worthy of notice is this. The heat of vaporization is expended in at least two channels :—it produces expansion against pressure, thus doing external work; and it is partly expended in internal work on the molecules of the body. Now it follows from what has preceded that the internal and total work bear an approximately constant proportion to each other for any one pressure, whatever be the liquid. Thus at a pressure of approximately 760 millims. the ratio of external to total work is shown as follows :—

Substance.	Total work. External work.	Substance.	Total work. External work.
Bromine	11.09	Ethyl acetate	11.81
Phosphorus chloride ...	10.09	Ethyl oxalate	11.67
Carbon disulphide	10.39	Amyl alcohol	13.32
Methyl alcohol	12.53	Ethyl chloride	11.39
Ethyl alcohol	13.33	Benzene	10.25
*Ethyl oxide (ether)	11.55	Chloroform	10.99
Water	13.02	Carbon tetrachloride ...	10.35
Methyl iodide	10.45	Mercury	12.36
Ethyl iodide	10.69	*Nitric peroxide	12.42
Methyl formate	11.55	Acetic acid	13.18
Methyl acetate	12.51	Water	13.02

* Vapour-density found at a few degrees above boiling-point.

In the equation $\frac{L}{s_1 - s_2} = \frac{dp}{dt} \cdot \frac{t}{J}$, both terms are approximately known for a number of substances. But before comparing them it is necessary to reduce the pressures which have been given in the previous part of this paper in millimetres of mercury, to grams per square centimetre. The comparison has been made for water, with the following results :—

Pressures, in millim. of mercury.	$\frac{L}{s_1 - s_2}$	$\frac{dp}{dt} \cdot \frac{t}{J}$
300 . . .	0.137	0.1395
1000 . . .	0.405	0.414
2000 . . .	0.742	0.770
3000 . . .	1.055	1.110
5000 . . .	1.633	1.743

The non-equality of these numbers may be ascribed to various causes : want of accuracy in experiment, most probably in determination of the heats of vaporization, and the assumption that the density of the saturated vapour of water is normal at high pressures, are among the most likely. With such results for water, it was thought unnecessary to compare these terms for other liquids, where the constants are probably less accurately determined. These numbers, however, suffice to prove that the relations pointed out in the first part of this paper, although derived from observations and assumptions not always trustworthy, agree fairly well with those deduced from the vapour-pressures, which have been determined with a high degree of accuracy.

We now proceed to exhibit the relations between the vapour-pressures of various liquids. The constants of the bodies considered were determined by Regnault, Olszewski, Naumann, Isambert, Moitessier and Engel, and by ourselves.

If a curve be constructed to represent the relation of temperature to pressure for any substance, and if tangents be drawn to touch the curve at various points corresponding to certain temperatures, these tangents will give the rate of increase of pressure per unit rise of temperature ; in other words, the value $\frac{dp}{dt}$ for those temperatures.

If we construct curves for a number of substances, and determine the value of $\frac{dp}{dt}$ for each of them at the same temperature, it is clear that the values obtained will differ widely, and will be greater for volatile substances than for those which are less volatile. But if we determine the values of $\frac{dp}{dt}$ for the same series of bodies, not at the same temperature, but at the same pressure, the conditions under which the comparison is made will be more similar, and the resulting values may be expected to differ much less.

In the calculation of the vapour-pressures of a number of substances for each degree between certain limits of pressure, it became evident that at any given pressure the rate of increase was generally, though not always, greater for the volatile substances than for the less volatile.

It was found that the product of the absolute temperature into the rate of increase of pressure $\left(\frac{dp}{dt} \cdot t\right)$ at any given pressure was approximately the same for the bodies examined, but the differences were evidently too great to be ascribed to errors of experiment or of calculation. That this product should be approximately the same for different substances might perhaps be anticipated from the following considerations :—If there are two bodies, the absolute temperatures of which must be raised to 200° and 400° respectively, in order to produce a certain effect, the same for both, it might be expected that a further rise of temperature of 1° would produce a greater effect on the substance whose temperature was

200° than on that at 400°; for the rise of temperature in the first case is greater in proportion to the temperature to which the body has already attained than it is in the second, the rise in the one case being from 200° to 201°, and in the other from 400° to 401°. The rise of temperature would perhaps rather be proportional if the temperature of the hotter body were raised from 400° to 402°, or if the rise of temperature in each case were made proportional to the absolute temperature. In order, then, to make the conditions as similar as possible in the calculation of the value of $\frac{dp}{dt}$ for different substances, the magnitude of the unit degree of temperature should be made to vary in the same ratio as the absolute temperature of those substances, corresponding to the particular pressure at which they are compared; or, in other words, keeping the unit degree constant, the value $\frac{dp}{dt}$ should be multiplied by the absolute temperature t .

The values of $\frac{dp}{dt} \cdot t$ were determined for a number of liquids at several different pressures; and it was found that the products obtained for different stable substances at the same pressure were always approximately the same, whatever that pressure might be. Thus at a pressure of 400 millims. the following values were obtained:—

Carbon bisulphide	4436	1·000
Alcohol	5873	1·324
Chlorobenzene	4724	1·065
Bromobenzene	4703	1·060
Aniline	5124	1·155
Methyl salicylate	4959	1·112
Bromonaphthalene	4930	1·111
Mercury	4812	1·085

This may be better seen by making one of these values equal to unity, and reducing the others in the same ratio. The second column is thus calculated.

Repeating this operation at another pressure, a second series of values was obtained; and these were reduced in the same

way. It was at once noticed that the reduced numbers at the new pressure were identical within the limits of error of experiment and calculation with those at the first pressure.

The calculations were therefore continued so as to include the widest attainable ranges of pressure, and at every pressure the value of $\frac{dp}{dt} \cdot t$ for one substance was made equal to unity; and the others reduced in the same ratio. The values of $\frac{dp}{dt} \cdot t$ for water were made = 1, because the vapour-pressures of this substance have been determined by Regnault between wide limits of temperature with very great care; but it was noticed that the values for both water and alcohol were very much higher than for the other substances examined; and a similar comparison was therefore made by taking the values for carbon bisulphide as equal to unity.

It was then found that for pressures ranging between 150 and 1500 or 2000 millim. the reduced values for each substance, with the exception of mercury, were very nearly constant for all pressures.

In the case of alcohol and water, employing the vapour-pressures of water as determined by Regnault (*Mémoires de l'Académie*, vol. xxv.), and of alcohol as determined by Ramsay and Young, the ratio of the values $\frac{dp}{dt} \cdot t$ was seen to be the same at pressures between 150 and 20,000 millin.

Two methods of calculation were adopted. In the first and more accurate method the vapour-pressures for each degree were calculated by the method of differences; and from these numbers the value of $\frac{dp}{dt}$ at any pressure could easily be calculated with very small error. The time required by this process is very great; and it was only adopted in the case of water, for which the pressures for each degree between -32° and 230° have already been calculated (Balfour Stewart, 'Treatise on Heat'), and of carbon bisulphide, alcohol, chlorobenzene, bromobenzene, aniline, methyl salicylate, bromonaphthalene, and mercury between certain limits of pressure, generally 150 or 200 to 700 millim. (Ramsay and Young, *Chem. Soc. Journ.* 1885, p. 640).

In all other cases tangents were drawn to touch the vapour-pressure curves at points corresponding to definite pressures, several curves being required for each substance on different scales to admit of this being done. With care, this method yields fairly satisfactory results.

It has been mentioned that the identity of the reduced numbers for any one substance holds at pressures ranging between about 150 and 1500 to 2000 millim. At lower pressures it is much more difficult to determine the values of $\frac{dp}{dt}$ with accuracy, and the influence of experimental errors is greater. Moreover, it has been necessary provisionally to adopt the method of tangents for all substances except water and carbon bisulphide at low pressures; and it is doubtful, therefore, whether much confidence is to be placed in the values at pressures below 150 millim.

As regards high pressures, with the exception of alcohol all the substances have been investigated by Regnault; and it may be worth while to mention one or two facts which appear to throw some little doubt on the accuracy of some of his determinations at pressures above 2000 or 3000 millim. In vol. xxvi. of the *Mémoires de l'Académie* Regnault gives the vapour-pressures of a large number of substances for each 5°, calculated from his empirical formulæ. Many of these series have been examined by the method of differences; and it has been found that in several cases the numbers forming the third set of differences increase slowly up to pressures of from 2000 to 3000 millim., but decrease at higher pressures. This is notably the case with alcohol; and it has been shown by Ramsay and Young, in a paper read before the Royal Society in May 1885, that the higher vapour-pressures of this substance as determined by Regnault are too low. It has also been pointed out by Vincent and Chappuis (*Compt. Rend.* vol. c. p. 1216) that the vapour-pressures of methyl chloride above 7 atmospheres are much higher than those calculated from Regnault's formula, the difference at 140° amounting to no less than 11·3 atmospheres.

Where this decrease is observable in the third set of differences, it seems therefore justifiable to doubt the accuracy of the results at the higher pressures.

It may be stated in conclusion:—(1) That the values of $\frac{dp}{dt} \cdot t$ are approximately the same for all stable substances at the same pressure, but that the differences are real, and are not due to errors of experiment or calculation; and (2) that the rate of increase of this value $\frac{dp}{dt} \cdot t$ with rise of pressure is the same for all stable bodies, at any rate for pressures between 150 and 2000 millim., while for alcohol and water it is the same for all pressures between 150 and 20,000.

In the tables which follow, the values of $\frac{dp}{dt}$, t (absolute temperature), and $\frac{dp}{dt} \cdot t$ are given for a number of stable substances at definite pressures, also the reduced values of $\frac{dp}{dt} \cdot t$, that for (1) water and (2) carbon bisulphide being made = 1.000 at each pressure, the values for other substances at the same pressure being reduced in the same ratio.

The second series of tables contains similar data for several substances which dissociate more or less completely on their passage into the gaseous state. It will be seen that for such bodies the values of $\frac{dp}{dt} \cdot t$ at any pressure are considerably higher than for stable substances at the same pressure.

The initial letter of the name of the observer of the vapour-pressure of each substance is given in the table containing the values of $\frac{dp}{dt}$ at the foot of the vertical columns. R. stands for Regnault, R. and Y. for Ramsay and Young, O for Olszewski, N. for Naumann, I. for Isambert, M. & E. for Moitessier and Engel.

Values of $\frac{dp}{dt}$ for various Stable Substances at Definite Pressures.

Pressure in millims.	Carbon bisulphide. CS ₂ .	Ethyl iodide. C ₂ H ₅ I.	Ethyl bromide. C ₂ H ₅ Br.	Ethyl chloride. C ₂ H ₅ Cl.	Carbon tetrachloride. CCl ₄ .	Ether. C ₄ H ₁₀ O.	Bromo- benzene. C ₆ H ₅ Br.	Chloro- benzene. C ₆ H ₅ Cl.	Chloroform. CHCl ₃ .	Mercury. Hg.	Ethylene. C ₂ H ₄ .	Sulphur. S.	Bromo- naphthalene. C ₁₀ H ₇ Br.	Methyl salicylate. C ₉ H ₉ O ₃ .	Aniline. C ₆ H ₅ NH ₂ .	Methyl alcohol. CH ₃ OH.	Water. H ₂ O.	Ethyl alcohol. C ₂ H ₅ OH.	
10	2.66	4.52	2.86	2.57	2.13	0.302	1.43	0.738	0.65	0.68	
50	2.76	4.52	5.19	4.52	5.01	3.63	4.03	1.31	4.54	1.93	2.00	3.04	2.70	2.89	
100	4.78	6.28	7.15	6.30	7.18	5.19	5.60	2.47	9.67	3.49	3.77	5.48	4.95	5.35	
150	6.65	8.00	8.80	8.07	9.21	6.59	7.07	3.45	12.41	4.12	4.65	6.76	6.95	7.62	
200	8.38	11.03	12.25	9.94	10.99	9.24	9.82	4.40	15.97	5.24	6.05	9.41	8.88	9.83	
300	11.70	14.08	15.47	13.45	16.94	11.60	12.34	6.26	22.67	7.38	8.30	13.40	13.77	13.77	
400	14.75	18.86	16.90	18.91	13.85	14.68	8.06	30.07	9.40	10.55	17.16	15.90	17.48	
500	17.65	21.65	20.08	22.30	15.35	15.25	9.78	11.35	12.65	20.56	19.10	21.10	
600	20.38	24.39	22.90	25.45	16.80	16.16	13.05	13.10	14.53	23.71	22.20	24.80	
700	23.10	27.33	25.94	27.68	18.05	17.00	14.60	14.75	16.30	27.41	25.30	28.20	
800	25.67	29.70	28.28	30.55	19.10	17.65	16.35	18.40	30.63	28.10	31.46	
900	28.60	32.45	30.57	33.27	20.40	33.25	31.30	35.42	
1000	30.80	35.12	32.83	35.27	36.88	34.00	38.58	
1500	42.43	44.25	48.25	45.11	50.52	47.22	53.32	
2000	52.40	55.00	60.90	58.54	65.59	59.80	66.61	
3000	70.67	75.10	83.80	78.60	88.57	83.40	92.09	
5000	105.00	108.9	119.80	116.00	134.24	125.00	138.28	
10,000	215.30	238.40	258.00
15,000	294.00	327.40	365.00
20,000	365.00	408.40	450.00
R.	R.	R.	R.	R.	R.	R. & Y.	R. & Y.	R.	R.	O.	R.	R. & Y.	R. & Y.	R. & Y.	R.	R.	R. & Y. (above 1000 mm.).	

Values of $\frac{dp}{dt} \cdot t$ (where t is the absolute temperature) for various Stable Substances at Definite Pressures.

Pressure in mms.	Carbon bisulphide. CS ₂ .	Ethyl iodide. C ₂ H ₅ I.	Ethyl bromide. C ₂ H ₅ Br.	Ethyl chloride. C ₂ H ₅ Cl.	Carbon tetrachloride. CCl ₄ .	Ether. C ₄ H ₁₀ O.	Bromobenzene. C ₆ H ₅ Br.	Chlorobenzene. C ₆ H ₅ Cl.	Chloroform. CHCl ₃ .	Mercury. Hg.	Ethylene. C ₂ H ₄ .	Sulphur. S.	Bromo- naphthalene. C ₁₀ H ₇ Br.	Methyl salicy- late. C ₉ H ₉ O ₃ .	Aniline. C ₆ H ₅ NH ₂ .	Methyl alcohol. CH ₃ OH.	Water. H ₂ O.	Ethyl alcohol. C ₂ H ₅ OH.	
10	675.7	...	715	...	722	...	740	136	176	191	184.8	183	
50	1280	1315	1364	...	1333	1304	1395	1384	...	664	634	783	750	860	840.5	853	
100	1839	1884	1938	...	1915	1928	1946	1982	...	1320	1419	1481	1481	1617	1607	1642	
150	2373	2456	2438	2528	2510	2531	2525	2558	...	1903	1879	...	2002	2029	2174	2251	2315	2403	
200	3430	3504	3513	3536	3537	3596	3657	3670	2575	2483	2474	...	2502	2695	2788	2947	3016	3155	
300	4436	4586	4547	4564	4580	4752	4703	4724	3646	3650	3627	3754	3782	3814	4014	4256	4361	4541	
400	5417	...	5654	5520	5684	5612	5724	5728	4772	4812	4920	4868	4930	4959	5124	5560	5660	5873	
500	6361	...	6597	6697	6669	6723	6678	6740	5829	5948	...	6063	6062	6056	6231	6770	6908	7197	
600	7317	...	7337	7624	7446	7673	7688	7678	6850	7067	...	7049	7104	7110	7311	7917	8136	8567	
700	8235	...	8554	8372	8403	8530	8602	...	7862	8168	...	8113	8105	8125	8358	9259	9379	9845	
800	9281	...	9394	9430	9330	9559	8812	9243	...	9239	9089	9165	9372	10448	10522	11094	
900	10102	...	10371	10290	10170	10513	9709	10173	...	10210	11441	11825	12595	
1000	14507	...	14726	14716	14470	14819	10846	13891	...	15203	12685	12949	13827	
1500	18469	...	18848	19141	18783	19787	15191	16463	...	15733	18131	18567	19718	
2000	26056	...	26886	27528	26564	27730	19364	20706	24004	24070	25179	
3000	41128	...	41306	41702	41344	43314	27813	29015	32666	34736	35970	
5000	42320	53440	54482	56460	
10,000	100250	103870	108370
15,000	142680	148480	158780
20,000	182680	190770	...

Values of $\frac{dp}{dt}$ for various Dissociable Substances at definite Pressures.

Pressure in millim.	Nitrogen peroxide. N_2O_4 .	Ammonium chloride. NH_4Cl .	Ammonium carbamate. $CO_2N_2H_6$.	Chloral methyl-alcoholate. $CCl_3.CH \begin{cases} OH \\ OCH_3 \end{cases}$.	Chloral ethyl-alcoholate. $CCl_3.CH \begin{cases} OH \\ OC_2H_5 \end{cases}$.
10	0.99
50	...	1.91	3.75	2.97	2.94
100	5.2	3.63	7.02	5.46	5.47
150	8.1	4.98	10.13	8.26	7.91
200	11.3	6.26	12.71	10.23	10.17
300	15.6	8.39	18.57	14.33	14.08
400	20.47	10.74	23.48	19.30	18.06
500	24.27	13.25	22.34
600	...	15.70
	R. and Y.	R. and Y.	N., I., and M and E.	R. and Y.	R. and Y.

Absolute Temperatures (t) of various Dissociable Substances corresponding to definite Vapour-pressures.

Pressure in millim.	Nitrogen peroxide. N_2O_4 .	Ammonium chloride. NH_4Cl .	Ammonium carbamate. $CO_2N_2H_6$.	Chloral methyl-alcoholate. $CCl_3.CH \begin{cases} OH \\ OCH_3 \end{cases}$.	Chloral ethyl-alcoholate. $CCl_3.CH \begin{cases} OH \\ OC_2H_5 \end{cases}$.
10	270.9
50	...	524.7	289.9	331.2	334.0
100	256.0	542.8	299.4	343.3	346.1
150	263.1	554.6	305.1	350.8	353.7
200	268.1	563.3	309.8	356.1	358.1
300	275.9	577.3	316.1	364.2	367.4
400	281.4	587.9	321.0	370.3	373.8
500	285.9	596.0	378.7
600	...	603.0

Products of $\frac{dp}{dt}$ into Absolute Temperatures ($\frac{dp}{dt} \cdot t$) for various Dissociable Substances at definite Pressures.

Pressure in millim.	Nitrogen peroxide. N_2O_4 .	Ammonium chloride. NH_4Cl .	Ammonium carbamate. $CO_2N_2H_6$.	Chloral methyl-alcoholate. $CCl_3.CH \begin{cases} OH \\ OCH_3 \end{cases}$.	Chloral ethyl-alcoholate. $CCl_3.CH \begin{cases} OH \\ OC_2H_5 \end{cases}$.
10	268
50	...	1002	1087	984	983
100	1331	1970	2102	1866	1893
150	2131	2762	3091	2898	2798
200	3030	3526	3938	3635	3642
300	4304	4844	5870	5219	5173
400	5787	6314	7537	7147	6751
500	6939	7897	8460
600	...	9467

Reduced Values of $\left(\frac{dp}{dt} \cdot t\right)$; that for Water being made = 1·000 at each pressure, and the values for other substances at the same pressure reduced in the same ratio.

Pressure in millim.	Nitrogen peroxide. N_2O_4 .	Ammonium chloride. NH_4Cl .	Ammonium carbamate. $\text{CO}_2\text{N}_2\text{H}_8$.	Chloral methyl-alcoholate. $\text{CCl}_3\cdot\text{CH} \left\{ \begin{smallmatrix} \text{OH} \\ \text{OCH}_3 \end{smallmatrix} \right.$	Chloral ethyl-alcoholate. $\text{CCl}_3\cdot\text{CH} \left\{ \begin{smallmatrix} \text{OH} \\ \text{OC}_2\text{H}_5 \end{smallmatrix} \right.$
10	1·451
50	1·193	1·293	1·170	1·170
100	0·828	1·226	1·308	1·161	1·178
150	0·921	1·193	1·335	1·252	1·209
200	1·004	1·169	1·306	1·205	1·208
300	0·987	1·110	1·346	1·197	1·186
400	1·018	1·116	1·332	1·263	1·193
500	1·004	1·143	1·225
600	1·164

Reduced Values of $\left(\frac{dp}{dt} \cdot t\right)$; that for Carbon-bisulphide being made = 1·000 at each pressure, and the values for other substances reduced in the same ratio.

Pressure in millim.	Nitrogen peroxide. N_2O_4 .	Ammonium chloride. NH_4Cl .	Ammonium carbamate. $\text{CO}_2\text{N}_2\text{H}_8$.	Chloral methyl-alcoholate. $\text{CCl}_3\cdot\text{CH} \left\{ \begin{smallmatrix} \text{OH} \\ \text{OCH}_3 \end{smallmatrix} \right.$	Chloral ethyl-alcoholate. $\text{CCl}_3\cdot\text{CH} \left\{ \begin{smallmatrix} \text{OH} \\ \text{OC}_2\text{H}_5 \end{smallmatrix} \right.$
10
50	...	1·483	1·609	1·456	1·456
100	1·043	1·540	1·643	1·458	1·480
150	1·159	1·502	1·681	1·576	1·522
200	1·277	1·486	1·659	1·532	1·535
300	1·255	1·412	1·711	1·521	1·508
400	1·238	1·423	1·699	1·611	1·522
500	1·281	1·458	1·562
600	...	1·488

A relation may be observed between the two substances bromobenzene and chlorobenzene, and also between ethyl chloride, ethyl bromide, and ethyl iodide. The ratio of the absolute temperatures of the bodies in either group corresponding to any given vapour-pressure is a constant. Thus the ratio of the absolute temperature of bromobenzene to that of chlorobenzene when the vapour-pressure of both is 100 millim. = $\frac{364\cdot3}{343\cdot5}$, or 1·061; and at the other pressures up to 700 millim. the ratio remains absolutely constant at 1·059.

The ratio of the absolute temperatures of ethyl bromide and ethyl chloride has been determined for pressures between 150 and 5000 millim., and the numbers found vary only between 1.089 and 1.091. The data for ethyl iodide are much less complete; the comparison with ethyl chloride can only be made at pressures between 150 and 500 millim., and with ethyl bromide between 50 and 500 millim. In the first case the ratio of the absolute temperatures varies between 1.206 and 1.209, and in the second case between 1.105 and 1.108.