

## Some Thermodynamical Relations - Part II

This content has been downloaded from IOPscience. Please scroll down to see the full text.

1885 Proc. Phys. Soc. London 7 307

(<http://iopscience.iop.org/1478-7814/7/1/334>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 142.132.1.147

This content was downloaded on 02/10/2015 at 16:08

Please note that [terms and conditions apply](#).

PROCEEDINGS  
OF  
THE PHYSICAL SOCIETY  
OF LONDON.

---

FEBRUARY 1886.

XXXIV. *Some Thermodynamical Relations.*—PART II.

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

IN a note at the conclusion of the first of this series of papers, it was stated that the absolute temperatures of certain nearly related bodies corresponding to equal vapour-pressures are constant at all pressures. Further investigation, however, has shown that although it is only in the case of nearly allied substances, such as chlorobenzene and bromobenzene, that the ratio of the absolute temperatures corresponding to the same vapour-pressure is a constant, whatever (within the limits afforded by experimental data) that pressure may be, yet a relation does exist between the ratios of the absolute temperatures of all bodies, whether solid or liquid and whether stable or dissociable, which may be expressed in the case of any two bodies by the equation

$$R' = R + c(t' - t),$$

where  $R$  is the ratio of the absolute temperatures of the two bodies corresponding to any vapour-pressure, the same for both;  $R'$  is the ratio at any other pressure, again the same

\* Read December 12, 1885.

for both ;  $c$  is a constant which may be 0 or a small + or — number ; and  $t'$  and  $t$  are the temperatures of one of the bodies corresponding to the two vapour-pressures.

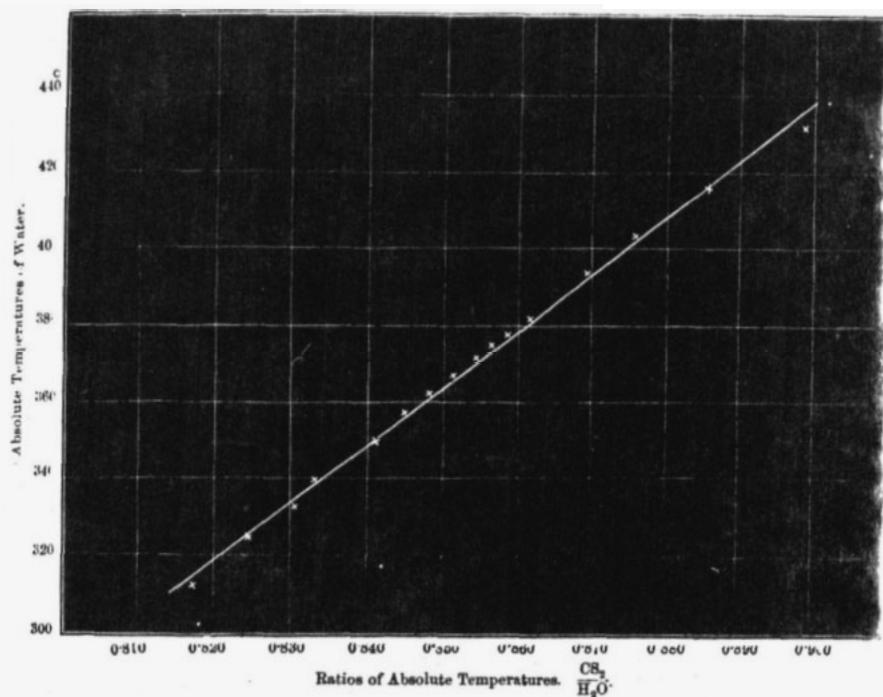
When  $c=0$ ,  $R'=R$ , or the ratio of the absolute temperatures is a constant at all pressures ; and where  $c$  is greater or less than 0, its value may readily be determined either by calculation, or graphically by representing the (absolute) temperatures of one of the two bodies as ordinates, and the ratio of the absolute temperatures at pressures corresponding to the absolute temperatures of that body as abscissæ. It is found that in all cases the points representing the relation of the ratio of the absolute temperatures of the two bodies to the absolute temperatures of one of them fall in a straight line. This is illustrated in some of the examples which are brought forward to prove the truth of the law. It follows from this that, if we know accurately the vapour-pressures of one substance, we only require two, or, better, three, accurate determinations of the vapour-pressure of any other substance, at temperatures moderately far apart, in order to be able to calculate the vapour-pressure of that substance at any required temperature, or, rather, to calculate the temperature corresponding to any vapour-pressure within the limits of pressure comprised in the determinations of the standard substance.

In the examples which follow, the same substance has not always been taken as the standard ; but generally, in the comparison of any two bodies, that one is taken as correct which is likely to have been the more accurately investigated. Twenty-two different bodies have been examined, and they are arranged in twenty-three couples. The absolute temperatures corresponding to definite vapour-pressures of a number of substances are given in the tables in a previous portion of this paper. For other substances, curves were drawn to represent the relation of temperature to pressure, and the temperatures corresponding to definite pressures read off.

1. *Ratios of the Absolute Temperatures of Water and Carbon Bisulphide at Definite Vapour-pressures.*—As an example of the method employed, the whole of the data are given in this case, and also a diagram showing how the value of  $c$  may be obtained graphically. The absolute temperatures of water corresponding to the definite vapour-pressures are taken

to be correct, and are made the ordinates in fig. 1. The abscissæ are the ratios of the absolute temperatures of carbon bisulphide to those of water at those vapour-pressures. As

Fig. 1.



might be expected, some of the points representing the relation of the ratios of the absolute temperatures to the temperatures of water fall slightly to one or other side of the straight line drawn to pass through them. In order to find the error involved in these slight deviations from the straight line, points on the line itself corresponding to the same temperatures of water were read off, and these are given in the table as smoothed ratios. Lastly, the absolute temperatures of carbon bisulphide were calculated by multiplying those of water by the smoothed ratios; and the recalculated temperatures of carbon bisulphide are given together with the observed temperatures. It will be seen that the difference between the observed and recalculated temperatures is very small.

Pressures.	Absolute temperatures of water.	Ratios of absolute temperatures of CS <sub>2</sub> to those of H <sub>2</sub> O.	Smoothed ratios.	Recalculated absolute temperatures of CS <sub>2</sub> .	Observed absolute temperatures of CS <sub>2</sub> .
millim.					
50	311.3	.8161	.8160	254.0	254.05
100	324.7	.8245	.8242	267.6	267.7
150	333.1	.8301	.8296	276.3	276.5
200	339.6	.8339	.8338	283.2	283.2
300	348.9	.8403	.8400	293.1	293.2
400	356.0	.8448	.8449	300.8	300.75
500	361.7	.8485	.8483	306.8	306.9
600	366.5	.8517	.8519	312.2	312.15
700	370.7	.8545	.8545	316.8	316.75
800	374.45	.8567	.8571	320.9	320.8
900	377.8	.8589	.8590	324.5	324.5
1000	380.85	.8612	.8611	327.95	328.0
1500	393.2	.8695	.8692	341.8	341.9
2000	402.5	.8753	.8757	352.5	352.3
3000	416.5	.8852	.8850	368.6	368.7
5000	435.85	.8987	.8978	391.3	391.7

In the equation  $R' = R + c(t' - t)$  the value of  $c = .0006568$ .

The greatest difference between the observed and recalculated temperatures is at the highest pressure (5000 millim.), and is only  $0^{\circ}.4$ .

2. *Water and Ethyl Alcohol.*  $\frac{H_2O}{C_2H_5O}$ . Temperatures of water taken as correct, and made the ordinates.  $c = .0000962$ .

Pressures.	Ratios.	Smoothed ratios.	Absolute temp. of Alcohol.	
			Recalculated.	Observed.
10	1.058	1.0527	270.1	269.25
50	1.0553	1.0553	295.0	295.0
100	1.0559	1.0567	307.3	307.5
150	1.0565	1.0574	315.0	315.3
200	1.0580	1.0580	321.0	321.0
300	1.0579	1.0589	329.5	329.8
400	1.0595	1.0596	336.0	336.0
500	1.0604	1.0602	341.2	341.1
600	1.0609	1.0606	345.55	345.45
700	1.0619	1.0610	349.4	349.25
800	1.0618	1.0614	352.8	352.65
900	1.0624	1.0617	355.8	355.6
1000	1.0626	1.0620	358.6	358.4
1500	1.0633	1.0632	369.8	369.8
2000	1.0648	1.0641	378.25	378.0
3000	1.0663	1.0655	390.9	390.6
5000	1.0675	1.0673	408.4	408.3
10000	1.0687	1.0701	435.15	435.7
15000	1.0701	1.0720	452.7	453.5
20000	1.0715	1.0735	466.2	467.1

The only noticeable differences between the observed and recalculated temperatures are at the three highest pressures and at 10 millim. With regard to the error at the low pressure, it may be mentioned that a number of careful determinations of the vapour-pressure of alcohol at low temperatures were made by Ramsay and Young by the still method (see note at end of paper), and that their results differed slightly from those of Regnault. At a pressure of 50 millim. the difference was only  $0^{\circ}\cdot 05$ , but at 10 millim. the absolute temperature found by them was  $270^{\circ}\cdot 25$ , which is practically the same as that recalculated by means of the equation

$$R' = R + c(t' - t).$$

3. *Ethyl Alcohol and Methyl Alcohol.*  $\frac{C_2H_5O}{CH_4O}$ . Temperatures of ethyl alcohol taken as correct.  $c = \cdot 0001603$ .

Pressures.	Ratios.		Absolute temperatures of Methyl Alcohol.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
10 }	<i>a</i> 1·0372 }	1·0475	256·5 }	°
10 }	<i>b</i> 1·0428 }	1·0473	257·9 }	259·0
50	1·0424	1·0433	282·8	283·0
100	1·0424	1·0414	295·3	295·1
150	1·0406	1·0400	303·2	303·0
200	1·0392	1·0392	308·9	308·9
300	1·0384	1·0379	317·75	317·6
400	1·0371	1·0368	324·1	324·0
500	1·0358	1·0359	329·3	329·3
600	1·0346	1·0351	333·75	333·9
700	1·0335	1·0346	337·4	337·8
800	1·0339	1·0340	341·05	341·1
900	1·0334	1·0336	344·05	344·1
1000	.....	1·0331	346·9	.....
1500	1·0304	1·0314	358·5	358·9
2000	1·0297	1·0300	367·0	367·1
3000	1·0276	1·0280	380·0	380·1
5000	1·0256	1·0251	398·3	398·1

Two values are given for 10 millim.:—(*a*) the ratio calculated from Regnault's values, and (*b*) the ratio obtained by employing the recalculated temperature of ethyl alcohol. The only noticeable difference between the observed and recalculated temperatures is at a pressure of 10 millim.; and by taking the recalculated temperature of ethyl alcohol it is greatly reduced.

4. *Carbon Bisulphide and Ethyl Oxide.*  $\frac{\text{CS}_2}{\text{C}_4\text{H}_{10}\text{O}}$ . Temperatures of carbon bisulphide taken as correct.  $c = \cdot 0001621$ .

Pressures.	Ratios.		Absolute temp. of Ethyl Oxide.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
100	1·0284	1·0283	260·3	260·3
150	1·0298	1·0298	268·5	268·5
200	1·0306	1·0307	274·8	274·8
300	1·0324	1·0325	284·0	284·0
400	1·0335	1·0337	290·95	291·0
500	1·0344	1·0346	296·65	296·7
600	1·0353	1·0355	301·45	301·5
700	1·0361	1·0361	305·7	305·7
800	1·0372	1·0369	309·4	309·3
900	1·0371	1·0375	312·8	312·9
1000	1·0380	1·0380	316·0	316·0
1500	1·0408	1·0402	328·7	328·5
2000	1·0423	1·0420	338·1	338·0
3000	1·0451	1·0446	352·95	352·8
5000	1·0490	1·0484	373·6	373·4

In this series the greatest difference between the observed and recalculated temperatures is only  $0^{\circ} \cdot 2$ .

5. *Carbon Bisulphide and Ethyl Bromide.*  $\frac{\text{CS}_2}{\text{C}_2\text{H}_5\text{Br}}$ . Temperatures of carbon bisulphide taken as correct.  $c = \cdot 0001185$ .

Pressures.	Ratios.		Absolute temperatures of Ethyl Bromide.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
50	1·0162	1·0172	249·75	250·0
100	1·0186	1·0188	262·8	262·8
150	1·0203	1·0199	271·1	271·0
200	1·0224	1·0206	277·5	277·0
300	1·0223	1·0218	286·9	286·8
400	1·0233	1·0228	294·05	293·9
500	1·0237	1·0234	299·9	299·8
600	1·0244	1·0241	304·8	304·7
700	1·0251	1·0247	309·1	309·0
800	1·0249	1·0251	312·9	313·0
900	1·0259	1·0256	316·4	316·3
1000	1·0263	1·0260	319·7	319·6
1500	1·0274	1·0276	332·7	332·8
2000	1·0280	1·0289	342·4	342·7
3000	1·0299	1·0308	357·7	358·0
5000	1·0327	1·0335	379·0	379·3

6. *Carbon Bisulphide and Ethyl Chloride.*  $\frac{\text{CS}_2}{\text{C}_2\text{H}_5\text{Cl}}$ . Temperatures of carbon bisulphide taken as correct.  $c = \cdot 0001050$ .

Pressures.	Ratios.		Absolute temperatures of Ethyl Chloride.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
150	1·1118	1·1135	248·3	248·7
200	1·1136	1·1142	254·2	254·3
300	1·1152	1·1152	262·9	262·9
400	1·1164	1·1160	269·5	269·4
500	1·1164	1·1166	274·9	274·9
600	1·1174	1·1172	279·4	279·3
700	1·1181	1·1177	283·4	283·3
800	1·1178	1·1181	286·9	287·0
900	1·1186	1·1185	290·1	290·1
1000	1·1194	1·1189	293·15	293·0
1500	1·1210	1·1203	305·2	305·0
2000	1·1209	1·1215	314·1	314·3
3000	1·1224	1·1232	328·25	328·5
5000	1·1253	1·1256	348·0	348·1

7. *Chlorobenzene and Water.*  $\frac{\text{H}_2\text{O}}{\text{C}_6\text{H}_5\text{Cl}}$ . Temp. of water taken as correct.  $c = \cdot 000598$ .

Pressures.	Ratios.		Absolute temperatures of Chlorobenzene.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
100	1·0579	1·0573	343·3	343·5
150	1·0625	1·0623	353·85	353·9
200	1·0654	1·0660	362·0	361·8
300	1·0711	1·0716	373·9	373·7
400	1·0753	1·0760	383·05	382·8
500	1·0788	1·0791	390·3	390·2
600	1·0819	1·0820	396·55	396·5
700	1·0845	1·0845	402·0	402·0



8. *Bromobenzene and Water.*  $\frac{\text{C}_6\text{H}_5\text{Br}}{\text{H}_2\text{O}}$ . Temperatures of water taken as correct.  $c = \cdot 000609$ .

Pressures.	Ratios.		Absolute temperatures of Bromobenzene.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
50	1·1156	1·1124	346·3	347·3
100	1·1220	1·1206	363·9	364·3
150	1·1255	1·1258	375·0	374·9
200	1·1284	1·1297	383·65	383·2
300	1·1344	1·1353	396·1	395·8
400	1·1388	1·1396	405·7	405·4
500	1·1427	1·1431	413·45	413·3
600	1·1460	1·1460	420·0	420·0
700	1·1489	1·1486	425·8	425·9
800	1·1516	1·1509	430·95	431·2

9. *Aniline and Water.*  $\frac{\text{C}_6\text{H}_5\text{NH}_2}{\text{H}_2\text{O}}$ . Temperatures of water taken as correct.  $c = \cdot 000345$ .

Pressures.	Ratios.		Absolute temperatures of Aniline.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
50	1·2046	1·2048	375·05	375·0
100	1·2100	1·2094	392·7	392·9
150	1·2129	1·2124	403·85	404·0
200	1·2144	1·2145	412·45	412·4
300	1·2174	1·2176	424·8	424·75
400	1·2197	1·2201	434·4	434·2
500	1·2217	1·2221	442·1	441·9
600	1·2237	1·2239	448·55	448·5
700	1·2254	1·2253	454·2	454·25
800	1·2269	1·2266	459·3	459·4

10. *Methyl Salicylate and Water.*  $\frac{C_6H_4(OH)COO(CH_3)}{H_2O}$ .

Temperatures of water taken as correct.  $c = \cdot 000459$ .

Pressures.	Ratios.		Absolute temperatures of Methyl Salicylate.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
50	1·3026	1·3008	404·9	405·5
100	1·3067	1·3069	424·35	424·3
150	1·3101	1·3107	436·6	436·4
200	1·3118	1·3136	446·1	445·5
300	1·3170	1·3179	459·8	459·5
400	1·3204	1·3212	470·35	470·05
500	1·3235	1·3239	478·9	478·7
600	1·3261	1·3260	486·0	486·0
700	1·3283	1·3280	492·3	492·4
800	1·3302	1·3298	497·95	498·1

11. *Bromonaphthalene and Water.*  $\frac{C_{10}H_7Br}{H_2O}$ . Temperatures of water taken as correct.  $c = \cdot 000612$ .

Pressures.	Ratios.		Absolute temperatures of Bromonaphthalene.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
150	1·4587	1·4592	486·05	485·9
200	1·4623	1·4631	496·9	496·6
300	1·4689	1·4690	512·5	512·5
400	1·4733	1·4732	524·45	524·5
500	1·4766	1·4769	534·2	534·1
600	1·4797	1·4798	542·3	542·3
700	1·4823	1·4821	549·4	549·5
800	1·4846	1·4847	555·95	555·9

12. *Sulphur and Carbon Bisulphide.*  $\frac{S}{CS_2}$ . Temperatures of carbon bisulphide taken as correct.  $c = -\cdot0006845$ .

Pressures.	Ratios.		Absolute temperatures of Sulphur.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
300	2.2783	2.2779	667.9	668.0
400	2.2733	2.2727	683.5	683.7
500	2.2681	2.2685	696.2	696.1
600	2.2650	2.2649	707.0	707.0
700	2.2607	2.2617	716.4	716.1
800	2.2588	2.2588	724.6	724.6
900	2.2558	2.2563	732.2	732.0
1000	2.2530	2.2540	739.3	739.0
1500	.....	2.2444	767.4	.....
2000	2.2373	2.2372	788.15	788.2
3000	2.2262	2.2262	820.8	820.8

The close agreement between the observed and recalculated temperatures of such a high-boiling substance as sulphur is very striking.

13. *Carbon Bisulphide and Ethylene.*  $\frac{CS_2}{C_2H_4}$ . Temperatures of carbon bisulphide taken as correct.  $c = \cdot000274$ .

Pressures.	Ratios.		Absolute temperatures of Ethylene.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
50	1.8212	1.8208	139.5	139.5
100	1.8242	1.8244	146.8	146.75
150	1.8263	1.8268	151.35	151.4
200	1.8283	1.8287	154.9	154.9
300	1.8325	1.8315	160.1	160.0
400	1.8339	1.8336	164.0	164.0

Here again the agreement is very remarkable, considering the difficulty of measuring very low temperatures accurately.

14. *Water and Oxygen.*  $\frac{H_2O}{O}$ . Temperatures of water taken as correct.  $c = -\cdot0003932$ .

Vapour-pressures of oxygen have been determined by Olszewski and by Wroblewski, but their results do not agree

well together. Olszewski measured his temperatures by means of a hydrogen-thermometer; Wroblewski by a thermopile. It was found that the curve showing the relation of temperature to pressure was very fairly regular when constructed from Olszewski's numbers, and the temperatures corresponding to definite pressures were therefore read from this curve. The temperature corresponding to a pressure of 9 millim. is a single observation by Olszewski. The temperatures corresponding to 50, 100, and 150 millim. are taken from Wroblewski's results.

Pressures.	Ratios.		Absolute temperatures of Oxygen.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
9	4.5967	4.454	63.5	61.5
50	4.0534	4.349	71.6	76.8
100	3.9353	4.2845	75.8	82.5
150	4.0132	4.253	78.6	83.0
300	.....	4.191	83.2	.....
400	.....	4.182	85.1	.....
500	.....	4.1405	87.4	.....
600	.....	4.120	89.0	.....
700	.....	4.1025	90.4	.....
800	4.0701	4.090	91.6	92.0
1000	4.0732	4.064	93.7	93.5
1500	4.0536	4.0175	97.9	97.0
2000	4.0520	3.980	101.1	100.0
3000	3.9478	3.924	106.1	105.5
5000	3.8267	3.849	113.2	113.9
10000	3.7044	3.733	124.7	125.7
15000	3.6489	3.656	132.7	133.0
20000	3.6242	3.5975	139.1	138.1

It is hardly to be expected that the measurement of such extremely low temperatures could be very exact, and the difference of  $2^{\circ}\text{C}$  at an absolute temperature of about  $60^{\circ}$ , is not more than might be expected. It will be seen that the three temperatures given by Wroblewski differ considerably from those calculated from Olszewski's results.

The vapour-pressures of oxygen are given up to the critical point, at which the pressure is 38,600 millim., but those of water have only been determined up to 20,000 millim. The absolute temperatures of oxygen were therefore compared with those of alcohol, in order to find whether the value of  $c$  remains constant up to the critical point.

15. *Alcohol and Oxygen.*  $\frac{C_2H_5O}{O}$ . Temperatures of alcohol taken as correct.  $c = -0.00040075$ .

Pressures.	Ratios.		Absolute temperatures of Oxygen.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
300	...	3.940	83.7	.....
400	...	3.913	85.9	.....
500	...	3.894	87.6	.....
600	...	3.879	89.1	.....
700	...	3.861	90.4	.....
800	3.8331	3.848	91.6	92.0
1000	3.8332	3.824	93.7	93.5
1500	3.8123	3.780	97.8	97.0
2000	3.7800	3.7485	100.8	100.0
3000	3.7024	3.694	105.7	105.5
5000	3.5848	3.621	112.8	113.9
10000	3.4662	3.514	124.0	125.7
15000	3.4098	3.441	131.8	133.0
20000	3.3824	3.388	137.9	138.1
30000	3.3189	3.300	147.9	147.1
40000	3.2698	3.240	155.6	*154.2

The absolute temperatures of oxygen recalculated from the smoothed ratios with alcohol agree well with those calculated from the ratios with water. It was thought worth while to compare these temperatures with those of sulphur, oxygen being the most and sulphur the least volatile of all the substances examined.

\* The last pressure, 40,000 millim., is a little above the critical point, but sufficiently near to allow of the continuation of the vapour-pressure curve without sensible error. This was done instead of calculating the absolute temperature of alcohol corresponding to 38600 millim., the critical pressure of oxygen. It is to be remarked that the last two or three points representing the experimentally determined vapour-pressures of oxygen at the highest temperatures lie a little above the curve which was drawn. If more weight had been given to these points, the agreement between the observed and recalculated numbers would have been much closer. Thus Olszewski gives 154°.2 as the absolute temperature at the critical pressure 38600 millim., whereas from the curve this would be the temperature at 40000 millim. If the curve were raised so as to pass through the point representing the observed critical pressure and temperature, the interpolated temperature would become 155.3, or only 0°.3 lower than that recalculated from the smoothed ratio.

In any case, the agreement seems to be close enough to show that the equation  $R' = R + c(t' - t)$  holds good up to the critical point.

16. *Sulphur and Oxygen.*  $\frac{S}{O}$ . Temperatures of Sulphur taken as correct.  $c = -.0001652$ .

Pressures.	Ratios.			Absolute Temperatures of Oxygen.				
	From observed temperatures.	From mean of recalculated temperatures.	Smoothed.	a. $\frac{H_2O}{O}$ . From	b. $\frac{C_2H_6O}{O}$ . From	c. Mean of a & b.	$\frac{S}{O}$ . From	Observed.
millim. 300	...	8.005	8.005	83.2	83.7	83.45	83.45	...
400	...	7.9965	7.980	85.1	85.9	85.5	85.7	...
500	...	7.955	7.937	87.4	87.6	87.5	87.5	...
600	...	7.9395	7.9395	89.0	89.1	89.05	89.05	...
700	...	7.921	7.9245	90.4	90.4	90.4	90.4	...
800	7.876	7.910	7.910	91.6	91.6	91.6	91.6	92.0
1000	7.904	7.887	7.8675	93.7	93.7	93.7	93.7	93.5
1500	7.9155	7.847	7.840	97.9	97.8	97.85	97.9	97.0
2000	7.882	7.808	7.8055	101.1	100.8	100.95	101.0	100.0
3000	7.780	7.750	7.7525	106.1	105.7	105.9	105.9	105.5

It will be seen that the temperatures of oxygen recalculated from those of sulphur, when  $c = -\cdot0001652$ , agree remarkably well with the mean of the temperatures recalculated from the ratios with water and alcohol.

17. *Acetic Acid and Water.*  $\frac{C_2H_4O_2}{H_2O}$ . Temperatures of water taken as correct. For liquid acetic acid  $c = \cdot0003186$ ; for solid acetic acid  $c = -\cdot000852$ .

In the 'Philosophical Transactions,' Part II., 1884, it was shown experimentally by Ramsay and Young that the vapour-pressures of solid acetic acid were lower than those of the liquid acid at the same temperature, and curves were constructed showing the relation of temperature to pressure for both the solid and the liquid acid. The absolute temperatures corresponding to definite pressures were read from these curves. For pressures below 5 millim. the vapour-pressures of water

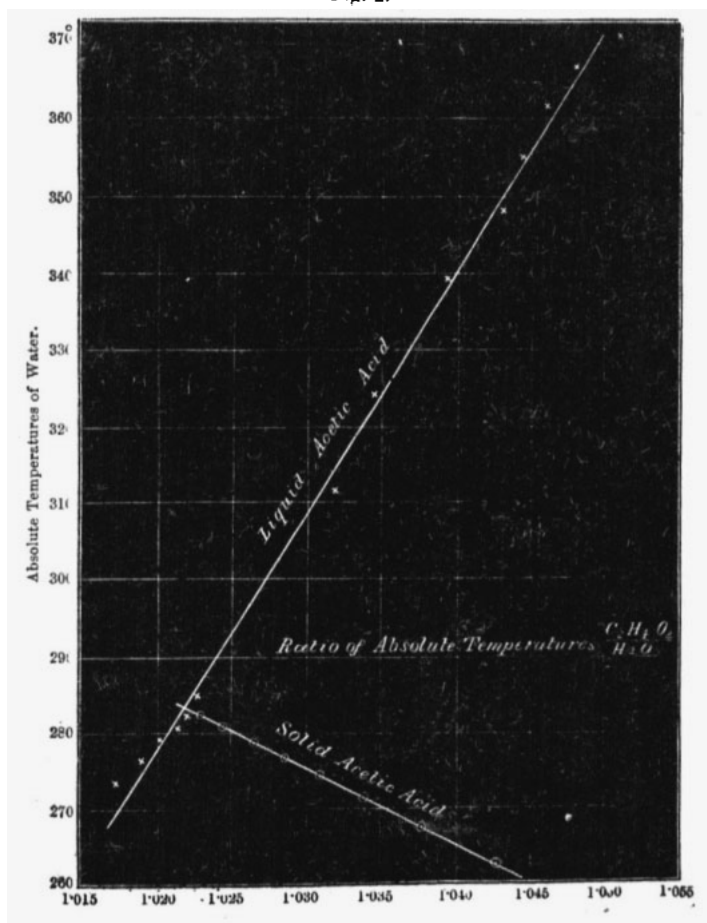
a. Liquid Acetic Acid and Water.				
Pressures.	Ratios.		Absolute temperatures of Acetic Acid.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
5	1·0175	1·0188	279·35	279·01
6	1·0193	1·0195	282·2	282·14
7	1·0202	1·0202	284·6	284·64
8	1·0212	1·0209	286·8	286·01
9	1·0219	1·0215	288·8	288·88
10	1·0222	1·0220	290·55	290·6
50	1·0311	1·0305	320·8	321·0
100	1·0345	1·0347	336·0	335·9
150	1·0369	1·0375	345·6	345·4
200	1·0392	1·0395	353·0	352·9
300	1·0426	1·0424	363·7	363·75
400	1·0447	1·0447	371·9	371·9
500	1·0455	1·0465	378·5	378·15
600	1·0478	1·0480	384·1	384·0
700	1·0506	1·0495	389·05	389·45
b. Solid Acetic Acid and Water.				
2	1·0423	1·0422	272·9	272·89
3	1·0372	1·0374	277·15	277·10
4	1·0335	1·0335	280·15	280·14
5	1·0306	1·0307	282·6	282·60
6	1·0284	1·0284	284·7	284·67
7	1·0264	1·0261	286·3	286·37
8	1·0244	1·0244	287·8	287·8
9	1·0226	1·0226	289·1	289·03

adopted by Regnault were not employed, the values calculated from his empirical formula representing the relation of temperature to pressure of water between  $0^{\circ}$  and  $100^{\circ}$  being probably more correct.

The differences between the recalculated and observed absolute temperatures of solid acetic acid are extremely minute. If the vapour-pressures of water given by Regnault were employed, the value of  $c$  would be slightly altered, and in that case the agreement would not be quite so close, the greatest difference amounting to  $0^{\circ}\cdot 15$ .

The results for both the solid and the liquid acid are shown in the diagram (fig. 2).

Fig. 2.





*Dissociating Substances.*

Five of these bodies have been examined, three liquid and two solid. In all of them the value of  $c$  is constant, while in the case of nitrogen peroxide, when compared with water it is  $=0$ , or at any rate it is a very small number.

18. *Nitrogen Peroxide and Water.*  $\frac{\text{N}_2\text{O}_4}{\text{H}_2\text{O}}$ . Water taken as correct.  $c=0$ .

Pressures.	Ratios.		Absolute temperatures of $\text{N}_2\text{O}_4$ .	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
100	0.7884	0.790	256.5	256.0
150	0.7899	"	263.15	263.1
200	0.7895	"	268.3	268.1
300	0.7908	"	275.6	275.9
400	0.7904	"	281.25	281.4
500	0.7904	"	285.75	285.9

Considering the nature of the substance, these differences may probably be considered within the limits of experimental error.

19. *Chloral Ethyl-alcoholate and Water.*  $\frac{\text{CCl}_3\text{CH} \begin{Bmatrix} \text{OH} \\ \text{OC}_2\text{H}_5 \end{Bmatrix}}{\text{H}_2\text{O}}$ .

Temperatures of water taken as correct.  $c = -0.005119$ .

Pressures.	Ratios.		Absolute temperatures of Chloral Ethyl-alcoholate.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
50	1.0729	1.0728	334.0	334.0
100	1.0659	1.0659	346.1	346.1
150	1.0619	1.0615	353.6	353.7
200	1.0545	1.0582	359.4	358.1
300	1.0530	1.0535	367.6	367.4
400	1.0500	1.0499	373.8	373.8
500	1.0470	1.0470	378.7	378.7

20. *Chloral Methyl-alcoholate and Water.*  $\frac{\text{CCl}_3\text{CH} \begin{Bmatrix} \text{OH} \\ \text{OCH}_3 \end{Bmatrix}}{\text{H}_2\text{O}}$

Temperatures of water taken as correct.  $c = -\cdot0005392$ .

Pressures.	Ratios.		Absolute temperatures of Chloral Methyl-alcoholate.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
50	1·0639	1·0641	331°·25	331°·2
100	1·0573	1·0570	343·2	343·3
150	1·0532	1·0546	351·3	350·8
200	1·0486	1·0489	356·2	356·1
300	1·0439	1·0439	364·2	364·2
400	1·0402	1·0400	370·2	370·3

The last two substances examined are solid throughout, and, at the higher temperatures at any rate, dissociate completely on being converted into vapour.

21. *Ammonium Chloride and Water.*  $\frac{\text{NH}_4\text{Cl}}{\text{H}_2\text{O}}$ . Temperatures of water taken as correct.  $c = -\cdot0006667$ .

Pressures.	Ratios.		Absolute temperatures of $\text{NH}_4\text{Cl}$ .	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
50	1·6855	1·6809	523°·3	524°·7
100	1·6717	1·6720	542·9	542·8
150	1·6650	1·6664	555·1	554·6
200	1·6587	1·6620	564·4	563·3
300	1·6546	1·6560	577·8	577·3
400	1·6514	1·6511	587·8	587·9
500	1·6478	1·6475	595·9	596·0
600	1·6453	1·6441	602·6	603·0

The determinations of the vapour-pressures and temperatures of volatilization of ammonium chloride were attended with great difficulties, and the agreement between the calculated and observed temperatures is as near as could be expected. The volatilizing-point at the atmospheric pressure, calculated from the equation  $R' = R + c(t' - t)$ , would be  $338^{\circ}\cdot6$  C., which agrees well enough with the temperature found by experiment.

22. *Ammonium Carbamate and Water.*  $\text{CO} \left\{ \begin{array}{l} \text{NH}_2 \\ \text{ONH}_2 \end{array} \right. \cdot \text{H}_2\text{O}$ . Tem-  
peratures of water taken as correct.  $c = -0.000696$ .

Pressures.	Ratios.		Absolute temperatures of Ammonium Carbamate.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
10	0.9529	0.9510	270.4	270.9
50	0.9313	0.9321	290.2	289.9
100	0.9221	0.9230	299.7	299.4
150	0.9159	0.9170	305.45	305.1
200	0.9122	0.9126	309.9	309.8
300	0.9060	0.9061	316.15	316.1
400	0.9017	0.9011	320.8	321.0

It is thought that these twenty-two examples, including twenty-one different bodies—solid, liquid, stable, and dissociable—are sufficient to prove that the equation  $R' = R + c(t' - t)$  is applicable to all classes of bodies, and that by the determination of the constant  $c$ , which involves only a small amount of experimental work, it becomes possible to calculate the vapour-pressures of any substance, assuming those of water or some other body to be accurately known, within the limits of pressure included in the experimental determinations of the standard substance.

It should be pointed out that those dissociable substances which have been investigated, are either, as in the case of ammonium carbamate and chloride and the compounds of chloral, wholly or almost wholly dissociated on their passage into the gaseous state at the temperatures of observation, or the amount of dissociation is very small, as with nitric peroxide. Until reliable data are obtained, it is perhaps premature to make any complete statement in reference to the behaviour of dissociable bodies.

#### *On the Vapour-Pressures of Mercury.*

It will have been observed in the tables in Part I. of this series of papers that mercury appears to differ from all the other substances examined, inasmuch as the values of  $\frac{dp}{dt} \cdot t$ , when

compared with either water or carbon bisulphide, are not even approximately constant at different pressures, but rise steadily and somewhat rapidly. Again, the absolute temperatures of mercury cannot be calculated from those of water by means of the equation  $R' = R + c(t' - t)$ , for if Regnault's data are correct,  $c$  is not a constant. There appeared, however, to be good reason to believe that Regnault's values were not reliable, and he himself admits that great difficulties were experienced in the investigation of this substance.

It was, therefore, considered desirable to attempt a re-determination of the vapour-pressures of mercury with the greatest possible accuracy at a few temperatures. This has been accomplished, and the results are fully described in *Trans. Chem. Soc.* Jan. 1886. It will be sufficient here to mention that new determinations were made at the boiling-points of methyl salicylate and of sulphur under atmospheric pressure ( $220^\circ$  and  $450^\circ$  approximately). Two other determinations at the boiling-point of bromonaphthalene under atmospheric and reduced pressure ( $280^\circ$  and  $270^\circ$ ), described in the *Trans. Chem. Soc.* xlvii. p. 640, and four determinations of the boiling-point of mercury under atmospheric pressure by Regnault (*Mémoires de l'Académie*, xxi. p. 230), were also made use of in the calculations.

On comparing the absolute temperatures of water with those of mercury at these five pressures, it was found that the value of  $c$  in the equation  $R' = R + c(t' - t)$  was constant, and that mercury did not form an exception to the law, which has been proved to hold good for all the other substances examined.

By making the absolute temperatures of mercury ordinates, and the ratios of the absolute temperatures of mercury to those of water at the same pressures abscissæ, and drawing a straight line through the five experimentally-determined points, the value of  $c$  was ascertained, and vapour-pressures of mercury were calculated for each  $5^\circ$ , from  $270^\circ$  to  $520^\circ$  C. It should be mentioned that slightly different results were obtained when the absolute temperatures of water were made the ordinates; but within the limits of temperature just mentioned, the difference was unimportant.

With the absolute temperatures of mercury as ordinates, the value of  $c$  is  $\cdot 0004788$ .

The values of  $\frac{dp}{dt} \cdot t$  for mercury were then determined; for the most part by the method of tangents, but between 150 and 700 mm. from the vapour-pressures calculated for each degree of temperature, and were compared with those of water and of carbon bisulphide. The results are given in the following table:—

Pressure.	$\frac{dp}{dt}$	$t$ .	$\frac{dp}{dt} \cdot t$ .	Water made = 1·000	Carbon bi- sulphide made = 1·000
millim.					
10	0·350	457·3	160	0·866	
50	1·405	508·5	714	0·850	1·057
100	2·506	534·2	1339	0·833	1·046
150	3·54	550·97	1950	0·843	1·061
200	4·47	563·44	2519	0·835	1·061
300	6·25	582·21	3639	0·834	1·061
400	7·85	596·44	4682	0·827	1·055
500	9·40	608·03	5715	0·827	1·055
600	10·91	617·87	6741	0·829	1·060
700	12·34	626·48	7731	0·824	1·057
800	13·75	634·0	8717	0·829	1·059
900	15·01	641·0	9621	0·814	1·037
1000	16·37	647·2	10595	0·818	1·049
1500	22·38	673·1	15064	0·811	1·038
2000	28·33	693·0	19633	0·816	1·064
3000	38·61	723·1	27919	0·804	1·071
5000	56·90	765·6	43562	0·800	1·059

It will be seen that the agreement with carbon bisulphide is extremely close throughout, and that with water the variation is not greater than with some of the other substances examined.

The variations from constancy in the reduced values of  $\frac{dp}{dt} \cdot t$  will be considered in Part III.

*Note.*—Reference has been made to the vapour-pressures of alcohol at high and low temperatures determined by ourselves. The data are contained in a paper presented to the Royal Society in May 1885. The vapour-pressures of dissociable substances are given in a paper read before the Royal Society in November 1885. Neither of these papers is as yet published.