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XVIII. *Some Thermodynamical Relations.*—PART III.
*By WILLIAM RAMSAY, Ph.D., and SYDNEY YOUNG, D.Sc.**

IN the first of this series of papers (Phil. Mag. Dec. 1885) two relations between the vapour-pressures of different substances were described:—1. The product of the rate of increase of pressure per unit rise of temperature $\left(\frac{dp}{dt}\right)$ into the absolute temperature (t) is approximately the same for all bodies at the same pressure, but the differences are real, and are not due to errors of experiment or of calculation. 2. The rate of increase of this value $\frac{dp}{dt} \cdot t$ with rise of pressure is very nearly the same for all bodies. This was shown in the tables by making the product $\frac{dp}{dt} \cdot t$ for one substance equal to unity at each pressure, and reducing the values for other substances at the same pressure in the same ratio. It was pointed out that, at pressures between 150 or 200 millim. and 1500 or 2000 millim., the variations from constancy are very small, but that they are frequently greater at lower and at higher pressures; and it was suggested that these variations might possibly be due either to errors of experiment or of calculation.

In the second paper a relation was proved to exist between the absolute temperature of any two bodies corresponding to equal vapour-pressures, which may be expressed by the equation

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

where R' is the ratio of the absolute temperatures of any two bodies at a given pressure, R the ratio at another given pressure, t' and t are the temperatures of one of the two bodies corresponding to those vapour-pressures, and c is a constant. The value of c may be determined graphically by making the temperatures (absolute or Centigrade) of one of the bodies (A) ordinates and the ratios of the absolute temperatures of the two bodies (A and B) at pressures corresponding to the temperatures of (A) abscissæ, when the points representing this relation fall in a straight line.

In the case of nearly related bodies such as chlorobenzene and bromobenzene, $c=0$ and $R'=R$ at all pressures, and in those cases the ratios of the products $\frac{dp}{dt} \cdot t$ are also equal at

* Communicated by the Physical Society : read December 12, 1885.

all pressures; and it appeared likely that if the variations from constancy of the reduced values of $\frac{dp}{dt} \cdot t$ for other substances were real, they would be related in some way to the variations from constancy of the ratios of the absolute temperature. This is indeed the case; for if we compare the values of $\frac{dp}{dt} \cdot t$ for any two substances, and make the temperatures of one of them ordinates, and the ratios of the products $\frac{dp}{dt} \cdot t$ abscissæ, we again find that the points representing the relation of the ratios of the product $\frac{dp}{dt} \cdot t$ at definite pressures to the temperatures of one of the bodies corresponding to those pressures, fall in a straight line. We therefore obtain a similar equation,

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

R' and R in this case representing the ratios of the products $\frac{dp}{dt} \cdot t$. The cause of the apparently greater deviation from constancy at low and at high pressures is simply this—that at low pressures a small change of pressure corresponds to a large change of temperature, while at high pressures the intervals of pressure taken are very great, and therefore the intervals of temperature are also great. This is clearly seen by referring to the table of absolute temperatures corresponding to the pressures taken. Taking water as an instance, we have the following numbers:—

P.	t absolute.	Interval of t .	P.	t absolute.	Interval of t .
millim.			millim.		
10	284.3	0	600	366.5	0
50	311.3	27.0	700	370.7	4.2
100	324.7	13.4	800	374.45	3.75
150	333.1	8.4	900	377.8	3.35
200	339.6	6.5	1000	380.85	3.05
300	348.9	9.3	1500	393.2	12.35
400	356.0	7.1	2000	402.5	9.3
500	361.7	5.7	3000	416.5	14.0
600	366.5	4.8	5000	435.85	19.35

The determinations of the products $\frac{dp}{dt} \cdot t$ are, however, necessarily less accurate than those of the temperatures, especially at low pressures, for the sources of error are more numerous and have greater influences on the results; yet the

values calculated directly from the vapour-pressure curves generally agree very well with those recalculated from the equation

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

as will be seen in the following table. With the exception of chlorobenzene and bromobenzene, the comparison is only made for those substances which have been investigated through a large range of pressure, for otherwise it is impossible to determine the value of c with sufficient certainty.

1. *Water and Carbon Bisulphide.* Ratios of the products $\frac{dp}{dt} \cdot t$ for CS_2 to those of water at the same pressures taken as abscissæ, and the temperatures of water corresponding to those pressures taken as ordinates. $c = -0.000399$.

Pres- sures.	Reduced ratios of $\frac{dp}{dt} \cdot t$, calc. from curves.	Reduced ratios of $\frac{dp}{dt} \cdot t$, recal- c. from equa- tion.	Products $\frac{dp}{dt} \cdot t$ for CS_2 , calc. from curves.	$\frac{dp}{dt} \cdot t$ for CS_2 , recalc. from values for water and recalc. ratios.	Δ per cent.
millim.					
50	.804	.8042	675.7	675.9	+0.03
100	.796	.7989	1280.0	1281.0	+0.31
150	.794	.7955	1839	1842	+0.16
200	.787	.7929	2373	2391	+0.75
300	.787	.7892	3430	3442	+0.35
400	.784	.7864	4436	4451	+0.34
500	.784	.7841	5417	5417	0.0
600	.782	.7822	6361	6364	+0.05
700	.780	.7805	7317	7320	+0.04
800	.783	.7790	8235	8197	-0.46
900	.785	.7777	9281	9196	-0.92
1000	.780	.7764	10102	10054	-0.48
1500	.781	.7715	14507	14325	-1.27
2000	.767	.7678	18460	18481	+0.11
3000	.750	.7622	26056	26476	+1.59
5000	.755	.7545	41128	41106	-0.05

There are only two cases in which the difference between the calculated and recalculated values amounts to 1 per cent., and these two cases occur close together and are in opposite directions. Generally the differences are much smaller than 1 per cent., while the differences between the

highest and lowest of the reduced values of $\frac{dp}{dt} \cdot t$ (calculated or recalculated) exceeds 6 per cent.

2. *Bromo-benzene and Chloro-benzene.* The values for these substances appeared to be identical. They were therefore taken together and compared both with carbon bisulphide

and with water, to find whether the recalculated values would be the same in the two comparisons. This is shown by the table opposite to be the case.

3. *Carbon Tetrachloride and Water.* Values of $\frac{dp}{dt} \cdot t$ for H_2O taken as unity at each pressure. Temperatures of water as ordinates. $C = -0.0006945$.

Pressures.	Reduced ratios of $\frac{dp}{dt} \cdot t$.		$\frac{dp}{dt} \cdot t$ for CCl_4 .	
	Calculated.	Recalculated.	Calculated.	Recalculated.
millim.				
50	.859	.8455	722	710.6
100	.830	.8362	1333	1344
150	.827	.8304	1915	1922
200	.832	.8258	2510	2491
300	.811	.8194	3537	3573
400	.809	.8145	4580	4610
500	.823	.8105	5684	5599
600	.819	.8072	6669	6567
700	.794	.8042	7446	7543
800	.799	.8016	8403	8435
900	.789	.7993	9330	9452
1000	.785	.7972	10170	10323
1500	.779	.7886	14470	14642
2000	.780	.7822	18783	18828
3000	.765	.7724	26564	26830
5000	.759	.7590	41344	41351

4. *Ether and Water.* Values of $\frac{dp}{dt} \cdot t$ for H_2O taken as unity at each pressure. Temperatures of water as ordinates. $c = -0.0003194$.

Pressures.	Reduced ratios of $\frac{dp}{dt} \cdot t$.		$\frac{dp}{dt} \cdot t$ for $(\text{C}_2\text{H}_5)_2\text{O}$.	
	Calculated.	Recalculated.	Calculated.	Recalculated.
millim.				
100	.811	.8305	1304	1335
150	.833	.8278	1928	1916
200	.839	.8257	2531	2490
300	.825	.8228	3598	3588
400	.840	.8205	4752	4644
500	.812	.8187	5612	5655
600	.826	.8171	6723	6648
700	.818	.8158	7673	7651
800	.811	.8146	8530	8571
900	.808	.8135	9559	9620
1000	.812	.8126	10513	10523
1500	.798	.8086	14819	15013
2000	.822	.8057	19787	19393
3000	.798	.8012	27730	27830
5000	.795	.7950	43314	43313

a. Values of $\frac{dp}{dt} \cdot t$ for CS₂ taken as unity at each pressure. Temperatures of CS₂ as ordinates. C = -0.0007626.

b. Values of $\frac{dp}{dt} \cdot t$ for H₂O taken as unity. Temperatures of H₂O as ordinates. C = -0.0009850.

Pres- sures.	CS ₂ =1.		H ₂ O=1.		$\frac{dp}{dt} \cdot t$ for chloro- benzene. Calculated.	$\frac{dp}{dt} \cdot t$ for bromo- benzene. Calculated.	Mean values of $\frac{dp}{dt} \cdot t$ for chloro- and bromo- benzene.	$\frac{dp}{dt} \cdot t$ for chloro- and bromo-benzene. Recalculated.	
	Mean of re- duced ratios of $\frac{dp}{dt} \cdot t$ for chloro- and bromo- benzene. Calculated.	Reduced ratios of $\frac{dp}{dt} \cdot t$ for chloro- and bromo-benzene. Recalculated.	Mean of re- duced ratios of $\frac{dp}{dt} \cdot t$ for chloro- and bromo- benzene. Calculated.	Reduced ratios of $\frac{dp}{dt} \cdot t$ for chloro- and bromo-benzene. Recalculated.				CS ₂ =1.	H ₂ O=1.
	millim.								
50	1.095	1.0974	0.880	0.8785	...	740	740	741.5	738.4
100	1.086	1.0870	0.8645	0.8663	1384	1395	1390	1391	1391
150	1.068	1.0803	0.848	0.8570	1982	1946	1964	1987	1984
200	1.071	1.0752	0.8425	0.8506	2558	2525	2542	2551	2565
300	1.068	1.0675	0.8405	0.8415	3670	3657	3664	3662	3670
400	1.0625	1.0618	0.833	0.8345	4724	4703	4714	4710	4723
500	1.057	1.0571	0.829	0.8289	5728	5724	5726	5726	5726
600	1.055	1.0531	0.8245	0.8241	6740	6678	6709	6699	6705
700	1.050	1.0496	0.8195	0.8200	7678	7688	7683	7680	7691
800	1.045	1.0465	0.818	0.8163	...	8602	8602	8618	8589

5. *Chloroform and Water.* Values of $\frac{dp}{dt} \cdot t$ for water taken as unity at each pressure. Temperatures of water as ordinates. $c = -0.0006701$.

Pressures.	Reduced ratios of $\frac{dp}{dt} \cdot t$.		$\frac{dp}{dt} \cdot t$ for CCl_3H .	
	Calculated.	Recalculated.	Calculated.	Recalculated.
millim.				
200	.854	.8545	2575	2577
300	.836	.8183	3646	3699
400	.843	.8436	4772	4775
500	.844	.8397	5829	5801
600	.842	.8365	6850	6806
700	.838	.8337	7862	7819
800	.838	.8311	8812	8745
900	.821	.8289	9709	9802
1000	.838	.8269	10846	10708
1500	.818	.8186	15191	15199
2000	.805	.8123	19364	19552
3000	.801	.8030	27813	27893
5000	.777	.7900	42320	43041

6. *Ethyl Bromide and Ethyl Chloride with Water.* Values of $\frac{dp}{dt} \cdot t$ for water taken as unity at each pressure, and compared with mean values of $\frac{dp}{dt} \cdot t$ for ethyl bromide and ethyl chloride. Temperatures of water as ordinates. $c = -0.0006335$.

Pressures.	Mean of reduced ratios of $\frac{dp}{dt} \cdot t$.		Mean values of $\frac{dp}{dt} \cdot t$ for $\text{C}_2\text{H}_5\text{Br}$ and $\text{C}_2\text{H}_5\text{Cl}$.	
	Calculated.	Recalculated.	Calculated.	Recalculated.
millim.				
50	.851	.8449	715	710.1
100	.849	.8364	1364	1344
150	.829	.8311	1919	1924
200	.823	.8271	2483	2495
300	.8085	.8211	3525	3581
400	.8045	.8166	4555	4622
500	.8085	.8130	5587	5616
600	.817	.8099	6647	6589
700	.8085	.8073	7580	7572
800	.8045	.8049	8463	8469
900	.7955	.8028	9407	9493
1000	.798	.8008	10330	10370
1500	.793	.7930	14721	14723
2000	.790	.7871	18994	18946
3000	.7835	.7783	27207	27035
5000	.7615	.7660	41504	41733

7. *Mercury and Water.* From determinations of vapour-pressures of mercury by Ramsay and Young *. If Regnault's values are correct, the equation $R' = R + c(t' - t)$ does not hold good. Values of $\frac{dp}{dt} \cdot t$ for water taken as unity at each pressure. Temperatures of water as ordinates. $c = -0.0004236$.

Pressures.	Reduced ratios of $\frac{dp}{dt} \cdot t$.		$\frac{dp}{dt} \cdot t$ for Mercury.	
	Calculated.	Recalculated.	Calculated.	Recalculated.
millim.				
10	.866	.8600	160	158.9
50	.850	.8486	714	713.2
100	.833	.8429	1339	1355
150	.843	.8393	1950	1943
200	.835	.8366	2519	2523
300	.834	.8326	3639	3631
400	.827	.8296	4682	4696
500	.827	.8272	5715	5714
600	.829	.8252	6741	6714
700	.824	.8234	7731	7723
800	.829	.8218	8717	8647
900	.814	.8204	9621	9701
1000	.818	.8191	10595	10697
1500	.811	.8139	15064	15112
2000	.816	.8099	19633	19494
3000	.804	.8040	27919	27928
5000	.800	.7958	43562	43356

8. *Mercury and Carbon Bisulphide.* Employing the values of $\frac{dp}{dt} \cdot t$ for mercury and carbon bisulphide, both recalculated from their ratios with those of water, these values bear an almost constant ratio to each other at all pressures, or $c = 0$. The calculated ratios vary only between 1.0547 and 1.0552.

XIX. Mechanical Integration of the Product of two Functions.

To the Editors of the *Philosophical Magazine and Journal*.

GENTLEMEN,

IN connection with my paper (Phil. Mag. August 1885) on the mechanical integration of the product of two functions, Professor Nanson, of the Melbourne University, has sent me the following suggestion by which the necessity for the special piece of mechanism there described is obviated.

Let $\int_{a_1}^{a_2} \phi(\theta)\psi(\theta)d\theta$ be required; plot the two curves
 $r = \phi(\theta) + \psi(\theta), \quad r = \phi(\theta) - \psi(\theta);$

* The data for these determinations are to be found in the 'Journal of the Chemical Society,' January 1886.