Some Thermodynamical Relations - Part IV

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

SINCE the first portions of this research were published Professors Ayrton and Perry have criticised our work, and while we would thank them for the appreciative way in which they speak of our labours, we must differ entirely from their conclusion that "there is nothing further to be said about the four laws in question." This conclusion rests on a complete misapprehension of the whole scope of our papers, and for the obvious reason that, while we have endeavoured by a method of what may be termed approximation to arrive at a workable plan¹ of deducing from the known vapour-pressures of a substance like water the unknown vapour-pressures of any other substance with as little expenditure of experimental work as possible, and have in our research made the statement, which is only a very rough approximation to truth, that the ratios of the absolute temperatures of any two liquids at any given pressure are equal to the ratios at any other pressure, but have materially modified this statement, and asserted next, what is a very close approximation to truth, that when the statement given does not hold (as in by far the majority of cases), the relation of the ratios is 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 pressure ; t and t' the temperatures of one of the two bodies corresponding to those vapour-pressures ; and c is a constant). Professors Ayrton and Perry have based all their reasoning on the first statement, which laid no claim to exactitude, and have informed us, what we already knew, that Dalton's law gives better results. The data given in our previous papers, however, show how nearly our generalization agrees with fact.

To refute the accusation of having performed useless labour would be really to repeat the substance of our previous papers ; but the members of the Physical Society would hardly thank

* Read May 8, 1886.

us were we to do so. There are, however, two or three remarks made by our critics which call for special reply.

1. It is suggested that our obvious course would have been to employ Rankine's formula, which, our critics state, is not empirical, but based on Rankine's molecular theory. We have been informed that the formula deduced by Rankine from his molecular theory was found by him not to agree with the experimental results; and that, in order to secure agreement, an empirical term was added. We would ask if this was not the case, and, if so, whether the whole formula is not thereby rendered empirical?

2. We are told that our labours might have been reduced by 75 per cent. had we recognized the fact that our four laws are identical. Now we do not anywhere state that our "laws" are absolute, in which case only would the identity necessarily hold; but indeed give methods for calculating their deviation from constancy. It is moreover desirable to test the truth of such statements in every possible way, inasmuch as different determinations by different observers are thereby introduced.

3. That it is by no means impossible to obtain with accuracy the specific volumes of saturated vapour will appear from memoirs on the thermal behaviour of ethyl alcohol and ether, which are in the hands of the Royal Society; indeed such measurements can be made at temperatures when a direct determination of L would be extremely difficult, if not impossible. To show the necessity of using determinations from all sources, we may point out that if Regnault's values of L and of $\frac{dp}{dt}$ for alcohol and for ether are employed, and the vapour-density calculated by the thermodynamic equation

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

impossible values are obtained, unless it is supposed that chemical dissociation takes place, which is absurd.

4. We are told that the equation numbered (6) (p. 371 of the 'Proceedings'), $t = \alpha \psi(p)$, is identical with our four "laws;" and that "if (6) is true, then it follows that the ratio of the absolute temperatures of two vapours to one another at

any pressure is the same as at any other pressure, or $\theta = \kappa t$ (7). In fact, then, we can test laws I., II., III., and IV. by simply testing (7); and as we find from Regnault and Rankine's formula that (7) is untrue, there is nothing further to be said about the four laws in question." We hope that no one has, like Professors Ayrton and Perry, so misunderstood our papers as to suppose that we imagine that "the ratio of the temperatures of two vapours at any pressure is always the same as at any other pressure." We do, indeed, notice that this statement holds with very close approximation for like bodies, such as chloro- and bromo-benzene; but the whole of the second and third parts of our memoir are devoted to an attempt, which we deem not unsuccessful, to give a method whereby the *deviation from the above statement can be estimated*.

The didactic remarks so kindly directed to us at the beginning of Messrs. Ayrton and Perry's critique, lead us to suppose that the great importance of such problems in Chemistry is not so generally known as we had imagined; and we would cordially agree that the cooperative principle may here with advantage be applied, and physicist and chemist mutually assist each other.

The problem of dissociation has for long invited the attention of chemists. Many compounds decompose at a moderately high temperature, and their constituents reunite when the temperature is lowered. It is argued that, were it possible to attain a sufficiently high temperature, all the simpler compounds at least would exhibit the phenomena of dissociation.

From the nature of gases, it is to be expected that a study of the behaviour of dissociating gases would be the simplest way of arriving at a knowledge of the subject. An obvious criterion of the amount of dissociation is given by the vapour-density of the partially dissociated body; for if the dissociating gas, and the simpler gases resulting from its dissociation, obey Boyle's and Gay-Lussac's laws, then it is easy to calculate from the density of the gas the percentage number of molecules decomposed. But there is no means of knowing whether the dissociating substance, as such, does or does not obey these laws; hence it is evidently desirable to ascertain the behaviour of substances which do not dissociate as regards

expansion and compressibility; so that some idea may be gained as to the influence exerted by molecular attraction between like molecules on the volume they occupy. An investigation of this nature is best carried out by ascertaining the behaviour of gases when they are becoming increasingly subject to molecular attraction, *i. e.* when they are approaching the condition of saturated vapours. The pressure of saturation is, under normal circumstances, identical with the vapour-pressure; hence the importance of a knowledge of this quantity. We have before remarked, that we have communicated to the Royal Society the results of experiments on alcohol and ether with this view.

Again, if the body exerting vapour-pressure be one capable of partial dissociation on passage from the solid or liquid to the gaseous state, its apparent vapour-pressure will really consist of its real vapour-pressure, and also of the pressure due to its dissociation into its constituents. It is evidently of importance to determine the latter independently of the former; and it is only by the employment of some law applicable to all bodies, and deduced from the behaviour of stable substances, that an idea can be formed of the pressure due to the second cause.

In the *Philosophical Magazine* for April 1886, p. 299 (*ante*, p. 22), Professor Unwin also comments on our papers, and, unlike Professors Ayrton and Perry, has appreciated our motive in bringing forward the subject. We have to thank him for pointing out the relation of the ratio of the total heat of vaporization to the heat expended in external work, deduced from the second half of the thermodynamic equation. We agree with him that the approximate constancy there observed lies at the basis of all the relations found by us.

We have taken the liberty of applying his formula

$$\frac{t^{n+1}}{p} \times \frac{dp}{dt}$$

to alcohol, ether, and mercury, using the vapour-pressures determined by us over a wide range of temperatures in the first two cases; and for mercury, the results given in the *Journ. Chem. Soc.* 1886, p. 37.

We have taken the value of $(n+1)$ for alcohol as 2·248, for ether as 2·23, and for mercury as 2·21.

The values of the expression $\frac{t^{n+1}}{p} \cdot \frac{dp}{dt}$ at different pressures are as follows :—

Alcohol.				Ether.			
Press. millim.	Temp. abs.	$\frac{dp}{dt}$	$\frac{t^{2.248}}{p} \cdot \frac{dp}{dt}$	Press. millim.	Temp. abs.	$\frac{dp}{dt}$	$\frac{t^{2.23}}{p} \cdot \frac{dp}{dt}$
23·733	283	1·516	20700	184·9	273	8·843	12950
540·91	343	22·750	20376	921·18	313	31·16	12393
1692·3	373	58·175	20721	2293·9	343	62·84	12341
2359·8	383	75·95	20592	7495·7	393	153·95	12156
5686·6	413	151·75	20226	13281	423	234·9	12715
14764	453	315·45	19931	21804	453	336·4	12921
22182	473	430·8	19966				
45519	513	763·7	20703				

Mercury.

Pressures, millim.	Temp. abs.	$\frac{dp}{dt}$	$\frac{t^{2.21}}{p} \cdot \frac{dp}{dt}$
10·0	457·30	0·350	26486
100·0	534·20	2·506	26743
200·0	563·44	4·470	26833
500·0	608·03	9·40	26703
1000·0	647·20	16·37	26697
3000·0	723·10	38·61	26811
5000·0	765·60	56·90	26904

With mercury, the value of n is much more nearly constant than if Regnault's numbers be employed.

It will be noticed that this number is much higher than that given by Professor Unwin (0·69, while ours is 1·21); but it is worthy of remark, that if the values of n be calculated for the stable substances mentioned in our first paper, taking the highest and lowest pressures, and the corresponding values of $\frac{dp}{dt}$, the value of n varies between the narrow limits 1·15 and 1·52. Although we have not verified these values for intermediate pressures except in the examples already given, it may be of interest to reproduce them.

Substance.	Pressures from which n was calculated.	Value of n .
Carbon disulphide	50 and 5000	1·147
Ethyl bromide	50 and 5000	1·316
Ethyl chloride	50 and 5000	1·243
Carbon tetrachloride . . .	50 and 5000	1·326
Bromobenzene	50 and 800	1·475
Chlorobenzene	100 and 700	1·480
Chloroform	200 and 5000	1·376
Ethylene	10 and 400	1·235
Sulphur	300 and 3000	1·251
Bromo-naphthalene . . .	150 and 800	1·196
Methyl salicylate	50 and 800	1·517
Aniline	50 and 800	1·218
Methyl alcohol	50 and 5000	1·395

It was found impossible to obtain a constant value for n with dissociating substances when different pressures were employed.

The whole subject of vapour-pressure is one that cannot well be considered on its own merits, for they must evidently be intimately related to other physical properties; and although we have already accumulated data for alcohol and ether bearing on this subject, we prefer to reserve a general consideration of the question until an investigation, as regards the thermal behaviour of other bodies, on which we are at present engaged, shall have been finished.

X. *Some Thermodynamical Relations.*—PART V.

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

IN the first two of the series of papers on "Some Thermodynamical Relations," published in the previous volume of the 'Proceedings' (vol. vii.), it was shown by one of us that the ratio of the absolute temperatures of nearly related bodies, such as chlorobenzene and bromobenzene, or ethyl chloride and ethyl bromide, is constant for equal vapour-pressures; and that a relation exists between the ratios of the absolute temperatures of all bodies which may be expressed

* Read May 22, 1886.