The specific heat of water vapour and the theory of the dissociation of water vapour at high temperatures. By W. H. McCrea, B.A., Trinity College.

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1. The following is an attempt to account theoretically for the observed specific heat of water vapour. The usual theory of the vibrational specific heat together with the theory of the dissociation of the H_2O molecule at high temperatures is found to account satisfactorily for the observed facts. It is shown, also, that at temperatures near 100° C. there is an effect due to polymerisation.

The experimental values of the specific heat at constant volume (C_v) at a pressure of one atmosphere are given by Partington and Shilling*. Some of them are given here in Table II and plotted in the figure.

2. The first point that arises is to explain the minimum appearing near the beginning of the curve.

In working out specific heats theoretically the molecules are always assumed to be independent systems and so, for purposes of comparison, observed values must be reduced to the ideal state of infinitely low pressure. The equation

$$\left(\frac{\partial C_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v \quad \text{.....................(1)}$$

is used. The effect is, of course, zero if the perfect gas equation is obeyed, but for steam the equation of state which fits the facts best is Callendar's, viz.

$$v = \frac{RT}{p} - \frac{C}{T^n} + b \text{........................(2)},$$

which, using (1), leads to

$$C_v(p) - C_v(0) = \frac{n(n-1)CR}{T^n v} \quad \text{...............(3)},$$

and here $n = \frac{10}{3}$,

$$C = 1{\cdot}769 \times 10^8 \text{ litres/gm. mol.}$$

The calculated value is given in Table II for the first three temperatures, after which it is inappreciable. The "C" term in (2) is due to the association of the water vapour molecules and this correction to the apparent specific heat measures the amount of heat spent in separating them.

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* *The Specific Heats of Gases* (Benn, 1925), Table C.

3. It is necessary to remark here that in Shilling's* more recent work the minimum is more pronounced and occurs at about 600° abs. It cannot be explained by the above method. If the values are correct the only possible explanation would seem to lie in some peculiar behaviour of the rotational specific heat. It is well known that certain expressions for the latter given by the Quantum Theory predict a maximum above the equipartition value. It is clear that such an expression added to one for the vibrational heat could yield a minimum in the total specific heat. For any measurable values of the molecular moments of inertia this could, however, only happen at about 100° abs. or lower, unless the rotational heat approached its asymptotic (equipartition) value from below by passing through a minimum after the maximum. Even then it is extremely unlikely that it would differ appreciably from equipartition at temperatures as high as 600° abs. But a number of calculations were made on different expressions given by the Quantum Mechanics and none (even allowing for the symmetry of the molecule) showed such a behaviour. It therefore seems likely that this minimum is spurious and is probably due to some difficulty in the velocity of sound method of finding specific heats.

4. Two of the fundamental frequencies of vibration of the H_2O molecule are known from band spectra data to be

$$\nu_1 = 4{\cdot}785 \times 10^{13} \text{ and } \nu_2 = 11{\cdot}235 \times 10^{13}.$$

The third (which must exist) is not definitely known, but it must be high and Dennison has suggested for it

$$\nu_3 = 21{\cdot}720 \times 10^{13}.$$

This gives for the vibrational specific heat, in the usual way,

$$C_{vib}/R = \phi\left(\frac{2283}{T}\right) + \phi\left(\frac{5362}{T}\right) + \phi\left(\frac{10360}{T}\right) \quad \ldots\ldots(4),$$

where
$$\phi(x) = x^2 \frac{e^x}{(e^x - 1)^2}.$$

The values of the specific heat from (4), assuming that the rotations have attained equipartition, are given in Table II and shown by the broken line in the graph.

There is obviously no agreement between this simple theory and experiment.

Clearly we could not have expected this theory to be sufficient since it predicts a specific heat rising asymptotically to

$$6R \, (= 12 \text{ approx.})$$

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* *Phil. Mag.* (7), 3, p. 273 (Feb. 1927).

and the experimental curve rises well above this. Now there is known to be a certain amount of dissociation in steam at high temperatures and so some of the heat will be spent in bringing it about. It may mean, however, that there is a large general departure from the simple harmonic type of vibration since this is certain to be the case with those molecules that are just about to split up.

Before discussing the dissociation itself it is, therefore, interesting to see if this latter phenomenon is likely in itself to cause the specific heat to increase above its equipartition value. The only way of doing so seemed to be by considering the phenomenon in the case of hydrogen. Kemble and van Vleck* have given an expression which takes account of the interaction of rotation and vibration and of the departure from simple harmonic type for the H_2 molecule. I find that for a temperature of 2537° abs., which is higher than those for which they give numerical results, their formula yields a specific heat of $3{\cdot}54R$ (equipartition value $\frac{7}{2}R$; value on elementary theory $3{\cdot}03R$). Thus a law of force between the nuclei in the molecule, which gives good agreement with observation, is, in fact, capable of accounting for an excess above equipartition values.

In the figure the curves given by the elementary theory and Kemble and van Vleck's theory for H_2 are drawn for comparison with H_2O results.

5. We now consider the effect of dissociation on the specific heat. We cannot treat it by any reduction to an ideal state because the only ideal state would be that in which all the molecules were dissociated and we should then obtain the specific heat of a mixture of 1 gram molecule of H_2 and $\frac{1}{2}$ gram molecule of O_2, or even rather of 2 gram atoms of H-atoms and one of O-atoms. The only reason that we could get results this way before was that our equation of state assumed there to be no dissociation and so could be used to find the specific heat supposing the molecules removed from each other's range of influence but undissociated. As soon as the equation of state allows for dissociation it must be such as to give complete dissociation for zero pressure.

Thus the only method is to calculate the amount of heat used in splitting up the molecules at the pressure at which the specific heat is measured. This could be done empirically from experimental dissociation curves, but it is more instructive to work out the theory in the following manner, which at the same time checks the observed values.

We shall assume that, apart from dissociation, the assembly behaves as a perfect gas.

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* *Phys. Rev.* XXI, p. 653 (1923).

The Dissociation of H_2O.

Suppose that the whole assembly we are considering is formed out of X atoms of oxygen and $2X$ atoms of hydrogen, and suppose that, at any instant, it consists of

M_1 free atoms of oxygen (O),
M_2 free atoms of hydrogen (H),
N_1 molecules of oxygen (O_2),
N_2 molecules of hydrogen (H_2),
N_3 molecules of water vapour (H_2O).

Then we must have

$$\left.\begin{aligned} M_1 + 2N_1 + N_3 &= X \\ M_2 + 2N_2 + 2N_3 &= 2X \end{aligned}\right\} \quad \text{..................(1)}.$$

We neglect changes in the internal energies of the atoms and take as the zero energy state of the assembly that in which all the molecules are dissociated and all the atoms are at rest. The zero state of any molecule is taken to be rest in its lowest quantum state, and its heat of dissociation χ the work required to resolve it from such a state into its constituent atoms at rest at infinite separation.

Let $g_1(z)$, $g_2(z)$ be the partition functions for translatory motion of the atoms; $h_1(z)$, $h_2(z)$, $h_3(z)$ those for the molecules; $b_1(z)$, $b_2(z)$, $b_3(z)$ the partition functions for the internal motions (rotations and vibrations) of the molecules; and σ_1, σ_2, σ_3 the symmetry numbers of the molecules which are each two in the present case. Then the equilibrium state at any temperature, defined by $\theta = e^{-1/kT}$, is given by*

$$\frac{\overline{N}_1}{\overline{M}_1^{\,2}} = \frac{h_1(\theta)\, b_1(\theta)}{\sigma_1 \theta^{\chi_1} [g_1(\theta)]^2} \quad \text{.....................(2)},$$

$$\frac{\overline{N}_2}{\overline{M}_2^{\,2}} = \frac{h_2(\theta)\, b_2(\theta)}{\sigma_2 \theta^{\chi_2} [g_2(\theta)]^2} \quad \text{.....................(3)},$$

$$\frac{\overline{N}_3}{\overline{M}_1 \overline{M}_2^{\,2}} = \frac{h_3(\theta)\, b_3(\theta)}{\sigma_3 \theta^{\chi_3} g_1(\theta) [g_2(\theta)]^2} \quad \text{...............(4)}.$$

We eliminate M_1, M_2 (dropping the bars for convenience), which for finite χ_1, χ_2, χ_3 will never be zero, though from experiment they must be negligible compared with N_1, N_2, N_3 for the temperatures we are considering†. We find

$$\begin{aligned} \frac{N_1^{\frac{1}{2}} N_2}{N_3} &= \sqrt{\frac{h_1 b_1}{\sigma_1 \theta^{\chi_1} g_1^{\,2}}} \cdot \frac{h_2 b_2}{\sigma_2 \theta^{\chi_2} g_2^{\,2}} \cdot \frac{\sigma_3 \theta^{\chi_3} g_1 g_2^{\,2}}{h_3 b_3} \\ &= \frac{h_2 b_2 h_1^{\frac{1}{2}} b_1^{\frac{1}{2}}}{2^{\frac{1}{2}} h_3 b_3}\, \theta^{\chi_3 - \chi_2 - \frac{1}{2}\chi_1} \quad \text{.....................(5)}. \end{aligned}$$

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* R. H. Fowler, *Phil. Mag.* (6), 45, p. 1 (1923).

† I have calculated that, for the amount of dissociation found experimentally, the value of $\frac{M_2}{N_2}$ at 1700° K is very nearly $\frac{1}{1000}$.

Neglecting M_1, M_2 in equation (1) we have $N_2 = 2N_1$. Also for the most part we are concerned with less than 1 per cent. dissociation, so that it is sufficiently accurate to consider N_3 as constant in (5) and we shall take it as applying to one gram molecule of H_2O.

To a first approximation we can write $b_i(\theta) = r_i(\theta)\, v_i(\theta)$, where $i = 1, 2$ or 3, and $r_i(\theta)$, $v_i(\theta)$ are the partition functions for rotational and vibrational motions considered separately. This is the usual first approximation used in specific heat and band spectrum theory.

For the temperatures considered all rotations will have their equipartition values, so that

$$r_j(T) = \frac{8\pi^2 I_j kT}{h^2}, \quad j = 1, 2 \quad \text{..............(6)},$$

for the diatomic molecules with moments of inertia I_1 and I_2, and

$$r_3(T) = \frac{8\pi^2 AkT}{h^2}\sqrt{\frac{8\pi^2 CkT}{h^2}} \quad \text{..............(6')}$$

for the triatomic molecule H_2O, assuming that its moments are A, A and C*. The values of the moments are not known very accurately, so we take $I_2 = 0{\cdot}4 \times 10^{-40}$, $A = 3 \times 10^{-40}$, $C = 10^{-40}$ gm. cm.^{2}, which must be approximately correct, and, since estimates of I_1 have hitherto varied greatly, we shall take it to be $\alpha \times 10^{-40}$ and use our theory as a means of finding α which we can then compare with other estimates. [We have written $r(T)$ for the function of T obtained by substituting $e^{-1/kT}$ for θ in $r(\theta)$.]

In $v_i(\theta)$ we consider each normal mode of vibration as equivalent to a Planck oscillator of the same frequency (ν, say). Each one contributes a factor

$$1 + e^{-\frac{h\nu}{kT}} + e^{-2\frac{h\nu}{kT}} + \ldots + e^{-p\frac{h\nu}{kT}} \quad \text{..............(7)},$$

where the "p" state is the highest that is physically possible. It is found that $h\nu/kT$, for the values of ν in each of the three molecules and for nearly the whole range of T considered, is sufficiently large to make the expression (7) nearly unity.

Also we have†

$$h_i(\theta) = \frac{(2\pi m_i)^{\frac{3}{2}} V}{h^3 (\log 1/\theta)^{\frac{3}{2}}} = \frac{(2\pi m_i kT)^{\frac{3}{2}} V}{h^3} \quad \text{...........(8)},$$

where m_i is the mass of a molecule and we take

$$m_1 = 32 \times 1{\cdot}65 \times 10^{-24}, \quad m_2 \simeq 2 \times 1{\cdot}65 \times 10^{-24},$$

$$m_3 = 18 \times 1{\cdot}65 \times 10^{-24} \text{ gm.},$$

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* There is no simple expression for the energy levels when all the moments are unequal, but the form of $r_3(T)$ must be very similar. If two of the moments of H_2O are 3 and 1×10^{-40} the other should strictly be taken as 4 or 2×10^{-40}.

† Darwin and Fowler, *Phil. Mag.* (6), 44, p. 450 (1922).

and V is the volume at 1 atmosphere, the pressure at which the dissociation and specific heats are measured. We may write

$$V = T\frac{V_0}{273},$$

where V_0 is the theoretical volume at 273° abs.

Now let $\kappa(T)$ be the percent. dissociation at temperature T° abs., then

$$N_1 = \frac{1}{2}\frac{\kappa}{100}N_3.$$

Therefore $$\frac{N_1^{\frac{1}{2}}N_2}{N_3} = \frac{2}{N_3}\left(\frac{\kappa N_3}{200}\right)^{\frac{3}{2}} \quad \text{....................(9).}$$

Substituting from (6), (6′), (8) and (9) and writing unity for each $v_i(\theta)$, we eventually obtain from equation (5)

$$\kappa = 200\left(\frac{3\,.\,8}{81}\right)^{\frac{2}{3}}\frac{\pi^{\frac{1}{6}}(1{\cdot}65\times 10^{-24})^{\frac{1}{2}}k^{\frac{1}{2}}\alpha^{\frac{1}{3}}}{(2{\cdot}705\times 10^{19})^{\frac{1}{3}}h}\frac{T^{\frac{5}{6}}}{T_0^{\frac{1}{3}}}e^{\frac{2}{3}\left(\frac{\chi_3-\chi_2-\frac{1}{2}\chi_1}{kT}\right)} \quad \text{.........(10),}$$

giving $$\log_{10}\kappa = \tfrac{5}{6}\log_{10}T - \frac{b}{T} + A \quad \text{..............(11),}$$

where A and b are constants.

Partington and Shilling* give a table of values of κ which we can use successively in equation (11). By subtracting each of the resulting equations from that immediately succeeding it we get a series of values for b and can test its constancy. The results are contained in the following Table. The experimental values of κ

TABLE I.

Temp. T (abs.)	κ observed (1 atmosphere)	b	A
1300°	·0029	—	—
1397	·0084	8162	1·244
1480	·0185	8032	1·052
1500	·0221	8033	1·054
1561	·0368	7932	0·986
1705	·108	8069	1·074
2155	1·18	7780	0·903
2257	1·79	7814	0·919
		Mean = 7975	Mean = 1·033

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* *The Specific Heats of Gases*, p. 178.

extend to higher temperatures, but the corresponding values of b do not agree with those given below. The disagreement is so irregular that one concludes that the observations must be at fault whether or not the theory is beginning to fail. But we should, in fact, expect the theory to have to be modified since $v_3(\theta)$ is beginning to differ widely from unity.

The constancy of b and A is satisfactory, but it is not sensitive to changes in the coefficient of $\log T$ in (11) which cannot, therefore, be altogether established by it. However $(\chi_3 - \chi_2 - \frac{1}{2}\chi_1)$, and hence

TABLE II.

Abs. Temp. T	C_v observed (1 atmosphere)	Correction due to polymerisation	C_v calc. on elem. theory	Heat employed in dissociation (1 atmosphere)	Sum of last two columns
° 373	6·65	−0·24	6·13	—	—
473	6·61	−0·10	6·34	—	—
573	6·61	−0·04	6·58	—	—
673	6·65	—	6·83	—	—
773	6·74	—	7·06	—	—
873	6·88	—	7·19	—	—
1073	7·30	—	7·70	—	—
1273	7·90	—	8·08	—	—
1473	8·70	–	8·40	·093	8·49
1673	9·67	—	8·72	—	—
1873	10·84	—	9·00	1·007	10·01
2073	12·17	—	9·26	2·285	11·55
2273	12·95	—	9·51	4·398	13·91
2473	13·45	—	9·72	—	—
2573	13·57	—	—	—	—
2673	—	—	9·92	—	—

the heat of dissociation of water vapour at 0° abs., can be calculated from b. The above value of b gives for the latter quantity

$$D_0 = 54{,}760 \text{ cals. per gm. mol.},$$

and the empirical formula for the heat of formation at any temperature is*

$$D_T = 57{,}095 + 0{\cdot}249T + 0{\cdot}0_3 9975T^2 - 0{\cdot}0_6 7798T^3 \quad \ldots(12).$$

The agreement is quite good and it is found that D_0 is fairly sensitive to changes in the above coefficient which could not therefore be very different from that derived here.

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* Partington and Shilling, *loc. cit.*, p. 169. [There seems to be a misprint in their final result for D_T, $0{\cdot}449T$ occurring in place of $0{\cdot}249T$.]

From the value of A we have found, and from equation (11), a comes out to be 34·53, giving for the moment of inertia of the oxygen molecule

$$34{\cdot}53 \times 10^{-40} \text{ gm. cm.}^2.$$

This is about twice the value given by Mecke*, which is probably a reliable determination by the band spectrum using the latest theories. In view of the data the agreement here is not unsatisfactory.

The contribution to the apparent specific heat due to dissociation will be

$$\frac{D_T}{100}\frac{d}{dT}\kappa(T) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(13).$$

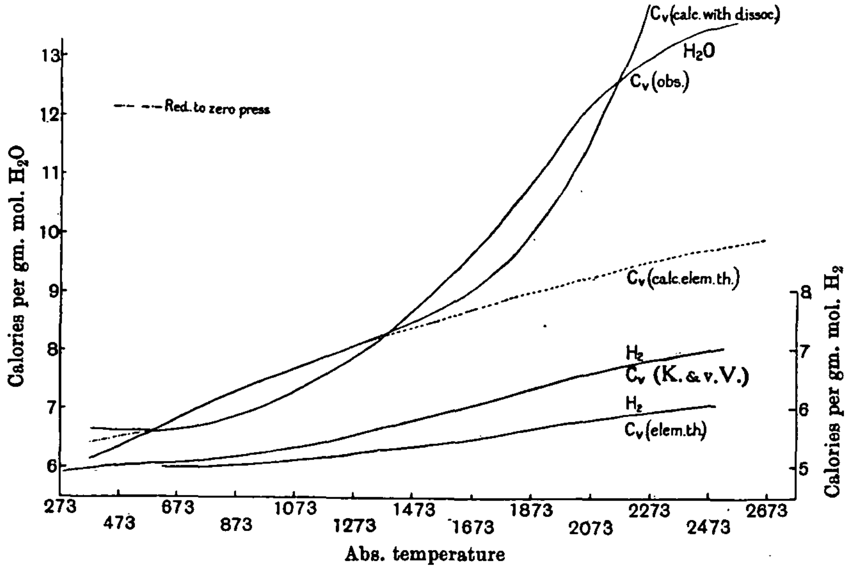

Fig. 1.

We obtain from (11) using the calculated b and A

$$\left.\begin{aligned}\log_{10}\kappa &= \tfrac{5}{8}\log_{10}T - \frac{7975}{T} + 1{\cdot}033\\ \frac{{\cdot}4343}{\kappa}\frac{d\kappa}{dT} &= \tfrac{5}{8}({\cdot}4343)\frac{1}{T} + \frac{7975}{T^2}\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots(14).$$

The values of (13) for certain temperatures were calculated using D_T given by (12)† and the results are given in Table II and

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* *Zeit. für Phys.* vol. 42, p. 396 (1927).

† D_T is derived from the observed specific heat of steam and it would be better to use the calculated specific heat based on the elementary theory since we now see that a large part of the former is due to dissociation. The variation of D_T with T is not, however, large.

shown in the figure. The agreement is good over the range in which we expect the theory to hold.

We conclude that the difference between the specific heats observed and given by the ordinary theory is due almost entirely to dissociation.

I wish to express my thanks to Mr R. H. Fowler for his interest and advice in this subject.