THE CONSTITUTION OF HEAVY WATER

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ABSTRACT. The Raman band of heavy water is found to be similar to that of ordinary water both in diffuseness and extent. The variations with temperature in the structure of this band are also similar to those of ordinary water. These changes are attributed to changes in the relative proportions of D_2O, $(D_2O)_2$ and $(D_2O)_3$ molecules which are assumed to be in thermal equilibrium. By an analysis of the intensity curves of the band, the proportions of the three polymers at different temperatures are calculated. The results are compared with those of water and the points of similarity and differences explained on the basis of their other physical properties.

1. INTRODUCTION

Soon after the discovery of heavy water, Wood[1] studied its Raman spectrum and found that it gives rise to a broad and diffuse band with a maximum of intensity having Raman frequency equal to $2517 \, cm^{-1}$. Later Ananthakrishnan[2] reported that in addition to the principal band which actually consists of three components with frequencies 2363, 2515 and $2662 \, cm^{-1}$ there are two comparatively fainter bands at 1110 and $1250 \, cm^{-1}$. Bauer and Magat,[3] however, found only two components in the principal band at 2389 and $2509 \, cm^{-1}$. The other bands reported by them are at 170, 350, 500 and $1207 \, cm^{-1}$, the one at 1110 found by Ananthakrishnan not being observed in their spectra. Rank, Larson and Bordner[4] studied the Raman spectrum of D_2O in the vapour state, which revealed a comparatively sharp line at 2666. On account of the similiarity in the general features of the Raman spectra of D_2O outlined above and those of water extensively investigated by a number of workers, we undertook a study of D_2O on lines similar to the work[5] of one of us on water in its various phases. The results reveal not only certain points of resemblance in general, but some interesting differences in detail which are described in the succeeding parts of this communication.

2. EXPERIMENTAL TECHNIQUE

Since the D_2O available to us was small in quantity, it was found necessary to adopt an arrangement by which wastage of the substance is avoided as far as possible, particularly during our study at the higher temperatures where loss due to evaporation may be considerable. Hence the heavy water was kept in a tube sealed under vacuum. This procedure was necessary for other considerations also. The sample supplied by Norsk Hydro-Electric Company when studied directly gave a strong continuous background in the Raman spectrum, possibly due to slight traces of fluorescent impurities. It was therefore found necessary to distil it in vacuum. On account of certain convenient features in the arrangement which may be adopted for investigation of similar substances, the details of the technique are briefly outlined in figure 1.
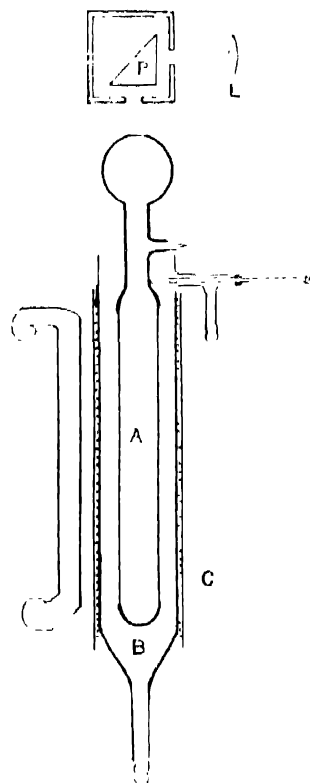

FIGURE 1

The glass tube A, 2 cm. in diameter, is 15 cm. long and has a narrow stem at the top at the end of which is blown a spherical bulb with its surface as clear as possible. The bottom of the tube is closed and the side tube indicated in the diagram is connected to another bulb not shown in the figure. After pouring the D_2O in this bulb, it is exhausted and sealed. After repeated distillation of

heavy water into A, the side tube is sealed off at the constriction previously provided. It is placed vertically in an outer jacket B through which water is circulated. This is surrounded by a heating coil which is protected from the atmosphere by the glass tube C. A vertical type of mercury arc is placed as near as possible to the outermost jacket C. The tube A, containing heavy water up to the side tube, is painted black all over leaving a clear portion at the centre for the liquid column to be exposed to the mercury arc light. A small circular clear space is provided at the top of the bulb to transmit the scattered radiation which after total reflection through the right-angled prism P is concentrated on to the slit of the spectrograph by the achromatic lens L. The current through the coil is so adjusted and the water circulated through B so regulated that a steady desired temperature is reached. The temperature of the circulating water was noted by a thermometer introduced through the side tube and after it was steady for a considerable period, the spectrum of the scattered radiation was taken. The narrow tube a a top of A served the purpose of a diaphragm to cut off parasitic light from the sides of the tube. The bottom of A and the surface of the liquid layer were protected from the direct mercury arc light to eliminate the intense scattering from them.

For temperatures lower than that of the laboratory, the tube containing heavy water is dipped in a transparent thermos flask containing cold water, which is kept at a constant temperature by adding ice and stirring.

3 STRUCTURE OF THE D_2O AND H_2O BANDS

The Raman spectrum of heavy water reveals a broad diffuse band as for ordinary water, with three clear maxima having Raman frequencies equal to 2394, 2534 and 2674 cm^{-1}. The following table contains the frequencies as given by different authors on this band :—

TABLE I

Raman frequencies of the D_2O band

Author.	Raman frequencies of maxima.		
Wood	—	2517	—
Ananthakrihsnan	2358	2507	2680
Bauer and Magat	2389	2509	—
Authors	2394	2534	2674

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Except for slight differences in the frequencies of maxima there is general agreement as to the existence of at least two components in the band. Wood used the 2537Å line of the mercury arc for exciting the band and might have measured its wavelength by a micrometer, which gives only an approximate value on account of the diffuseness of the band. The other two sets of values for excitation by the 4047Å line are also the result of micrometric measurements. In a case like this where a spectral line is very diffuse it is always desirable to take a microphotometric curve for finding the exact position of the maxima. This is what we have done and the values given by us are the result of such a measurement.

By a study of the D_2O band at different temperatures which will be described in detail later, we found large variation in the relative intensities of the three components, the one of lower frequency increasing in intensity with diminishing temperature, the highest frequency component at the same time diminishing in intensity, the central component remaining approximately constant. This explains the absence of the third frequency in Bauer and Magat's results as the temperature of their laboratory must have been much lower than that of the tropical laboratories where Ananthakrishnan and the authors work. This discrepancy should not therefore be taken as a genuine difference in the structure of the bands as was the case with water. In the later, there was controversy for a long time as to whether Raman band of water consists of three or two components, the continental workers finding only two clear maxima, while the workers in India observed a third faint component. In a work of this kind where variation in the structure varies considerably with temperature, it is therefore always desirable to make note of the temperature at which the investigation is carried.
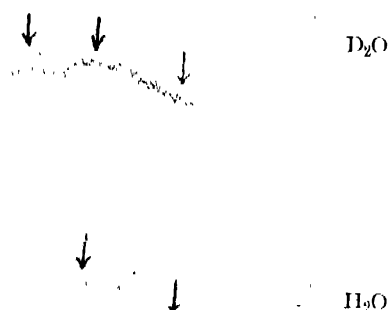
D_2O

H_2O

FIGURE 2

Before giving our results with variation in the structure of the D_2O band with temperature, a comparative study of the microphotometric curves of this band and that for H_2O at the same temperature, are given below. Both the bands are very broad and diffuse. While the H_2O band extends from about 3052 cm^{-1} to 3834 cm^{-1}, a range of about 782 wave numbers, that of D_2O ranges from 2254 to 2784 with a width of 530 wave numbers. This indicates that the width of the D_2O band is decidedly smaller than that of H_2O. For a comparison of the two bands, their microphotometric curves are given in figure 2.

While there is a significant similarity in the two curves with regard to diffuseness and structure, there is a fundamental difference in their extent and relative intensities of the components. The extent of the D_2O curve in the figure is decidedly smaller than that of H_2O. This disparity in the extent of the two bands is actually greater than what is recorded in the figure on account of the lower dispersion of the prism spectrograph in the region where the H_2O band falls. It is also clear from the curves that for heavy water, the components (marked with arrows) are better resolved, the first component with $\Delta v = 2394$ cm^{-1} being of the same intensity as the second, whereas for ordinary water, the first component is not only not well resolved from the second, but is also less intense.

4. STRUCTURAL VARIATION OF THE D_2O BAND WITH TEMPERATURE

On account of the close similarity in the nature of the D_2O and H_2O bands, we investigated the structure of the D_2O band at 6, 30, 65 and 100°C on lines similar to the work on H_2O by one of us.[6] The microphotometric curves of the Raman band for D_2O at different temperatures are taken and the intensities at different points on the bands are calculated by the usual method. The results are given in table II, in which the intensities against the corresponding frequencies are recorded for the four different temperatures.

For a clear understanding of the variations in the structure of the band with temperature, the results in table II are graphically represented in figure 3, with the frequencies along the abscissa and the corresponding intensities along the ordinate.

TABLE II.

Intensity distribution of the Raman band of D_2O at different temperatures

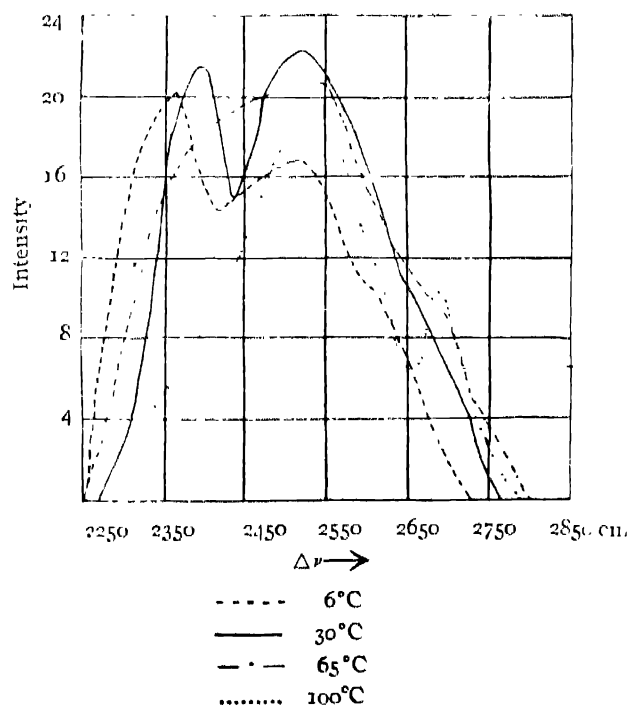| 6°C.		30°C.		65°C.		100°C.	
$\Delta\nu$ in cm⁻¹	Int.	$\Delta\nu$ in cm⁻¹	Int.	$\Delta\nu$ in cm⁻¹	Int.	$\Delta\nu$ in cm⁻¹	Int
2254	0	2251	0	2254	0	2204	0
2314	16·7	2314	4·0	2314	0·0	2314	2·6
2354	19·4	2354	16·8	2354	18·3	2354	6·2
2374	20·0	2374	18·3	2390	18·1	2390	7·0
2390	15·5	2390	21·4	2404	18·1	2404	10·0
2412	19·1	2404	21·1	2500	20·4	2470	11·7
2484	16·3	2420	18·5	2515	20·6	2514	19·0
2530	16·7	2434	15·1	2501	15·7	2545	19·6
2580	11·8	2470	18·3	2674	9·7	2580	14·9
2630	9·9	2484	21·4	2600	9·7	2630	8·2
2690	3·9	2534	22·2	2720	1·8	2660	6·1
2750	0·6	2564	20·2	2750	1·7	2701	11·6
2781	0	2630	12·5	2784	0	2690	12·2
		2660	11·6			2720	4·8
		2704	6·3			2781	2·2
		2781	0			2800	0

FIGURE 3

The extent of the band is almost the same for all temperatures, but the variations in the distribution of intensity from one temperature to another are very conspicuous. While the intensity curve for $6°C$ shows two clear maxima at 2365 and 2530 with an inflection at 2645 cm^{-1}, that for $30°C$ contains the maxima and inflection at 2395, 2535 and 2655 cm^{-1} respectively. At $60°C$ there is only one clear maximum at 2550 cm^{-1} with a small inflection at 2695 cm^{-1}, while at $100°C$ again there are two well defined maxima at 2540 and 2690 cm^{-1} with an inflection at 2350 cm^{-1}.

It is evident from the above observations that the clear maximum of lowest frequency at about 2395 cm^{-1}, changes very rapidly in intensity with increasing temperature, the frequency changes, however, being negligible and within the order of accuracy with which they can be determined. This maximum which is most intense at $6°C$ is reduced to almost equal intensity with the second at $30°C$ diminishing further at $60°C$ and almost disappearing at $100°C$, excepting for a small inflection in the curve for this temperature.

The central maximum, however, persists with equal intensity at all temperatures. The third maximum which makes its appearance clearly at $100°C$ with a frequency equal to 2690 cm^{-1} is perceptible, at other temperatures as a mere inflection, the prominence of this inflection diminishing with falling temperature.

5. EXPLANATION OF THE ABOVE RESULTS.

The close resemblance between the D_2O and H_2O Raman bands, not only in their diffuseness and structure, but also in respect of changes in the distribution of intensity in the bands with temperature, leads naturally to the conclusion that the explanation given by one of us[7] for these phenomena in H_2O applies equally well to the case of D_2O. The three components in the H_2O bands were attributed to three polymers of water, H_2O, $(H_2O)_2$ and $(H_2O)_3$ and the changes in the relative intensities of these components were explained as arising out of changes in the relative proportions of these polymers with temperature. The arguments put forward by some authors against this hypothesis were fully dealt with in another paper.[8] The hypothesis of the existence of polymers in water is not a new one and the explanation of the above phenomena for H_2O on this hypothesis is so natural that it is extended to the case of D_2O as well, which is its isotopic analogue.

By studying the Raman spectrum of D_2O vapour, Rank, Larson and Bordner found a single line at 2666 cm^{-1} similar to the single line in H_2O vapour at 3650 cm^{-1}. This indicates that in the vapour state heavy water consists entirely of single molecules. The component in nearly the same position (2690 cm^{-1}) for this substance in the liquid state at $100°C$ is therefore attributed to D_2O molecules, the other two components of smaller frequencies in the band

being assigned to $(D_2O)_2$ and $(D_2O)_3$ molecules as in the case of ordinary water.

The diminution with increasing temperature in the intensity of the 2394 cm^{-1} component, attributed to the $(D_2O)_3$ molecules, is explained as due to diminution in the proportion of these molecules which with increasing temperature change to the other polymers. The increasing intensity of the third component 2690 cm^{-1} with increasing temperature is ascribed to the increasing propoition of the single molecules to which this component is assigned. The approximate constancy in the intensity of the central component 2534 cm^{-1} is taken as an indication that the proportion of the double molecules giving rise to this component is nearly constant. This is also taken as indicating the comparatively greater stability of the double molecules.

It would have been interesting to study the Raman spectrum of heavy ice, but on account of the difficulty in maintaining it in the solid condition at a steady temperature, the work could not be undertaken.

6. RELATIVE PROPORTIONS OF THE POLYMERS IN HEAVY WATER

With a view to determine roughly the relative proportions of the three polymers in heavy water at different temperatures, the intensity curves of the heavy water band are analysed on lines similar to the analysis of the corresponding curves for ordinary water.[9] The curves for 6, 30, 65 and 100°C as analysed are given in figures 4, 5, 6 and 7 respectively.

In table III are collected the frequencies of the positions of maxima and extents of the three components of the curves as obtained by the analysis.

TABLE III.

Frequencies of maxima and extent of the D_2O, $(D_2O)_2$
and $(D_2O)_3$ Components

Temp.	$(D_2O)_3$ component.		$(D_2O)_2$ component.		D_2O component.	
	Position of Max".	Extent.	Position of Max".	Extent.	Position of Max".	Extent.
6°C.	2365	2254-2540	2530	2413-2645	2645	2575-2725
30°C.	2395	2270-2535	2535	2430-2645	2640	2535-2765
65°C.	2400	2254-2535	2545	2400-2700	2695	2550-2785
100°C.	2420	2295-2535	2540	2420-2650	2690	2590-2800

$- \cdot - (D_2O)_3$ $\longrightarrow (D_2O)_2$ $\cdots D_2O$

FIGURE 4.

2250   2359   2450   2530   2650   2750   2850 cm⁻¹

$\Delta \nu \longrightarrow$

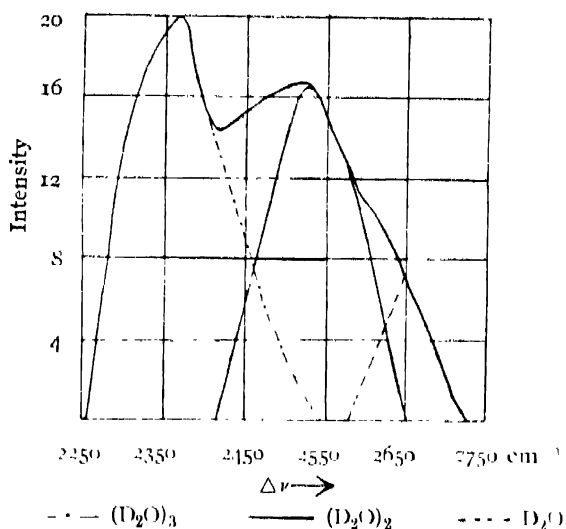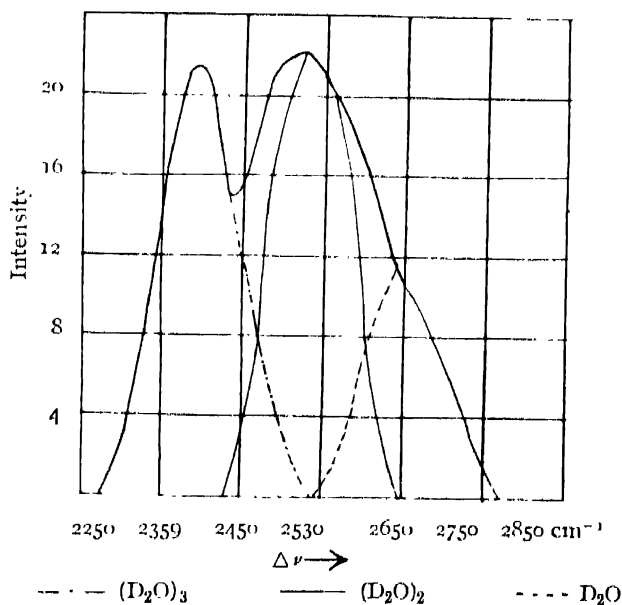$- \cdot - (D_2O)_3$ $\longrightarrow (D_2O)_2$ $\cdots D_2O$

FIGURE 5

Considering the roughness of the analysis, it can be asserted from the table that the maxima and extent of the components are very nearly constant.

On the supposition that the probability of excitation of the three polymers is the same and that the contribution to the intensity of the band by the D_2O molecules is the same as that of the $(D_2O)_2$ or $(D_2O)_3$, the relative intensities of the components are assumed to be proportional to the relative number of the polymerised molecules, as was done for water. This is justifiable by the fact that a quantum of light incident upon a group of molecules can excite either the

internal oscillations of one of the constituent molecules, or the external oscillations between one molecule, and another of the same group, but cannot excite the internal oscillations of all the molecules lying in a single group. Also, the probability of three different quanta, exciting the three different constituent molecules in a group at one and the same time is bound to be negligibly small.
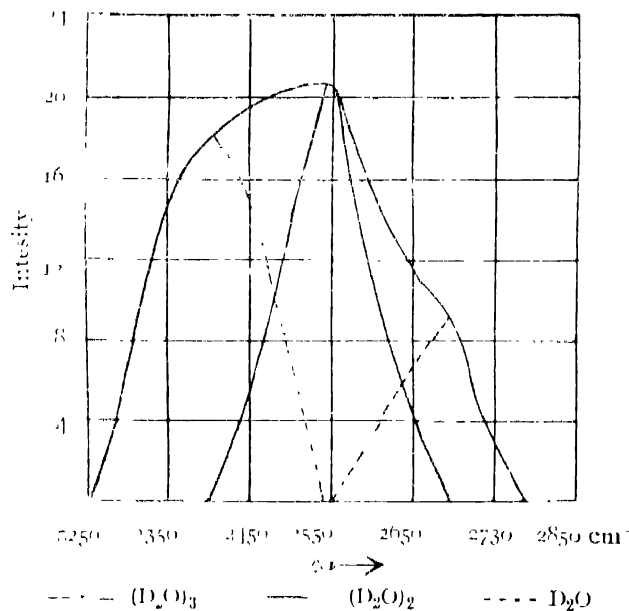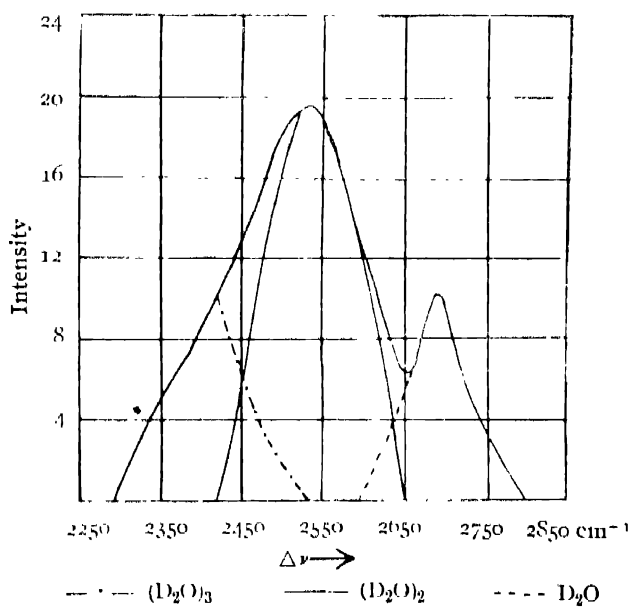

FIGURE 6

FIGURE 7

Since the extents of the three components are nearly the same, the ratio of the heights of their peaks, are assumed to give the direct ratio of the three polymers. The relative proportions of the polymers as calculated by this method are given in table IV.

TABLE IV

Relative proportions of D_2O, $(D_2O)_2$ and $(D_2O)_3$ in heavy water at different temperatures

Temp.	Relative intensity.			Percentage by numbers.			Percentage by weight.		
	$(D_2O)_3$	$(D_2O)_2$	D_2O	$(D_2O)_3$	$(D_2O)_2$	D_2O	$(D_2O)_3$	$(D_2O)_2$	D_2O
6°C	20	16·5	7	46	38	16	60	33	7
30°C	20·4	23	11·2	39	41	20	53	37	10
65°C	18	20·6	9	38	42	20	52	39	11
100°C	10	19·5	12	21	48	28	37	49	14

It is evident from the above table that while the percentage of the triple molecules is nearly halved and of the single molecules nearly doubled from the lowest to the highest temperature, the change in the double molecules is comparatively small. These changes are similar to those in ordinary water. For comparison the proportions for ordinary water taken from a previous paper[10] of one of us are given in table V.

TABLE V

Relative proportions of $(H_2O)_3$, $(H_2O)_2$ and H_2O molecules in water at different temperatures

Temp.	Percentage by numbers.			Percentage by weight.		
	$(H_2O)_3$	$(H_2O)_2$	H_2O	$(H_2O)_3$	$(H_2O)_2$	H_2O
9°C	23	58	19	34	57	9
4°C	22	58·5	19·5	32	58	10
38°C	21	50	29	32	52	16
98°C	13	51	36	21	58	21

7 DISCUSSION OF RESULTS

The similarity not only in the structure of the bands of D_2O and H_2O but also in their variations with temperature leads us to the conclusion that the explanation of one of us[11] for water applies equally well to heavy water. The objections

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by Sutherland[12] to the existence of triple molecules in water were met in another paper.[13] In a recent communication[14] Cross, Burnham and Leighton, agree with us as to the triplet structure of the water band, but "attach little or no significance to the existence of definite polymolecular structures such as $(H_2O)_2$ and $(H_2O)_3$" to which we attribute the two lower frequencies of the water band. They assume in liquid water "a broken down ice structure" having "different coordination types of water molecules," the two coordinated structure predominating in the liquid state. We are unable to understand how their coordinated types of molecules are different from our polymerised or associated types. It is well known that polymerisation is a result of coordination between molecules and we believe that their coordinated types are the same as our associated molecules, though they seem to differentiate between them. Our results with water agree with theirs in indicating a predominance of the double type over the others.

We therefore postulate the existence of single, double and triple molecules even in heavy water, the proportions of which change with temperature. From a comparison of tables IV and V, it is evident that the proportion of triple molecules at any temperature is greater for heavy water than for the lighter one. So the polymerisation appears to be larger in heavy water. This explains generally its higher freezing and boiling points and also its higher temperature of maximum density. There is another conspicuous feature in the variations in the • relative proportions of the polymers with temperature. For heavy water the change in the proportions of the three types of molecules from 6° to 30°C and from 65° to 100°C is much larger than from the intermediate range 30° to 65°C. This seems to indicate that the equilibrium between the three polymers is more stable at intermediate temperatures than at temperatures nearer the freezing and boiling points. This explains the minimum specific heat of heavy water approximately in this range as obtained by Brown, Bornes and Mass.[15] Also the higher degree of polymerisation in heavy water than in ordinary water explains its higher specific heat.

REFERENCES

1 *Phys. Rev.*, **46**, 392 (1934).

2 *Proc. Ind. Acad. Sciences*, **2** A, 291 (1935).

3 *C. R.*, **201**, 667 (1935).

4 *Journ. Chem. Phys.*, **2**, 464 (1934).

5 Rao, I.R., *Proc. Roy. Soc.*, *A*, **146**, 489-509 (1934).

6 Rao, I.R., *loc. cit.* •

7 Rao, I.R., *Proc. Roy. Soc.*, *A*, **130**, 498 (1931).

8 Rao, I.R. *Proc. Roy. Soc.*, *A*, **146**, 496 (1934).

9 *Loc. cit.*, p. 500.

10 Rao, I.R., *Proc. Roy. Soc.*, *A.*, **146**, 506 (1934).

11 *Loc. cit.*

12 Sutherland, *Proc. Roy. Soc.*, *A.*, **141**, 535 (1933).

13 *Loc. cit.*

14 Cross, Burnham, and Leighton, *Jour. Am. Chem. Soc.*, **59**, 1134 (1937).

15 *Can. J. Research.*, **13**, 167 (1933).