SPECIFIC HEATS OF LIQUIDS IN RELATION TO RAMAN EFFECT DATA.

By S. Bhagavantam.

(*From the Department of Physics, Andhra University, Waltair.*)

1. Introduction.

Since the discovery of the Raman effect, various attempts have been made to utilise the observed Raman frequencies for the purpose of explaining the specific heats of substances. Mention may be made here of the work of Andrews and Southard (1930), Bhagavantam (1930) and Paramasivan (1931). The subject may be broadly divided into two distinct parts; one relating to the specific heats at low temperatures and the other to the specific heats at the room temperatures. In the former case, the major part of the specific heat is explained with the help of the Debye theory and the investigation should therefore proceed on the lines of ascertaining the exact relationship, if any, between the Debye elastic spectrum and the low frequency oscillations recorded in the Raman scattering by solids. On the other hand, at comparatively higher temperatures all Debye functions based on low frequencies reach their limiting values and therefore the exact frequencies on which they are based are not of much significance. The contribution from internal frequencies, however, becomes appreciable at these temperatures and a full knowledge of these is therefore necessary to predict the specific heat and its variation with temperature. The present paper deals with this latter aspect and the specific heats for benzene, carbon tetrachloride and carbon disulphide are calculated at several temperatures in the neighbourhood of the room temperature. These liquids have been chosen as their internal frequencies are now reliably known. Certain interesting conclusions are arrived at by considering the results of such calculations and these are set forth here.

2. Choice of Debye Limits and Internal Frequencies.

Lord, Ahlberg and Andrews (1937) have recently satisfactorily explained the specific heat data in respect of solid benzene at low temperatures by assuming a mean characteristic temperature $\theta = 150$ to represent the contribution of the benzene lattice to the specific heat. The three degrees of

translational freedom are taken to give rise to compressional waves and the three degrees of rotational freedom are taken to give rise to torsional waves and these waves are assumed to take up energy in the manner described by the Debye function. The contribution to specific heat on account of these six degrees of freedom will then be $6RD\left(\dfrac{\theta}{T}\right)$ at T. The exact relationship between the Debye limit corresponding to $\theta = 150$ and the observed low frequency Raman lines in solid benzene has not been discussed by these authors. They even seem to be of the opinion that there is no justification for expecting such a relationship to exist (Blackman, 1935). The internal frequencies of the benzene molecule have been given by Lord and Andrews (1937) after a careful consideration of the Raman effect and infra-red data as 406 (2), 538 (1), 606·4 (2), 670 (1), 849·7 (2), 992·6 (1), 1008 (1), 1025 (2), 1145 (1), 1160 (2), 1176·0 (2), 1190 (1), 1477 (2), 1520 (1), 1595 (2), 1854 (1), 3048·3 (2), 3061·5 (1), 3063 (1), 3077 (2). The number in the bracket in each case represents the degeneracy of the corresponding oscillation and the total number of degrees of freedom comes out as 30 as it ought to. To each of these is assigned an Einstein function, and the aggregate specific heat is calculated. The good agreement obtained by these authors in the entire range in which they have investigated (0 to 270° K.) is convincing proof of the fact that the choice of the fundamental frequencies has been correctly made. We may therefore write down equations (1) and (2) to represent respectively the specific heats of solid and vapour benzene :

$$C_v = 6RD\left(\frac{\theta}{T}\right) + \sum_{i=1}^{i=30} RE\left(\frac{h\nu_i}{KT}\right) \tag{1}$$

$$C_v = 3R + \sum_{i=1}^{i=30} RE\left(\frac{h\nu_i}{KT}\right) \tag{2}$$

θ in equation 1 is equal to 150.

In the case of vapour, each of the three translational and three rotational degrees of freedom has assigned to it a mean energy of $\dfrac{KT}{2}$ per molecule. In the case of a liquid, we do not know whether (1) or (2) will be applicable and hence we will examine both these equations.

In the case of CS_2 and CCl_4, we will assume similar equations. As has already been mentioned, the exact value of θ is not very important as for all low values which are ordinarily met with in such cases, the Debye function nearly reaches its limit at the room temperature. Thus the first term of (1) may be put equal to 12 calories in CCl_4. In CS_2, it should, however, be taken as 10 calories as out of a total of 9 degrees of freedom, only 5 are taken

over by the lattice, the other 4 being internal. The vibrational frequencies and their degeneracies in each case are given below :

CCl_4: 217 (3), 313 (2), 459 (1), 777 (3)

CS_2: 397 (2), 655 (1), 1523 (1).

3. Results.

TABLE I.

Specific Heat of Liquid Benzene at Constant Volume.

Tempe-rature °C.	Contribution of the lattice	Contribution of internal frequencies	Total calc. as if it were a solid	Total calc. as if it were a gas	Observed (Mills and McRae)	Observed (Williams and Daniels)
0	11·72	9·68	21·40	15·68	21·15	..
20	11·76	11·01	22·77	17·01	22·09	21·57
40	11·78	12·44	24·22	18·44	23·00	23·13
60	11·80	13·83	25·63	19·83	24·06	25·22
90 (vapour)	..	16·0	..	22·0	23·4*	..

* Observed C_p is taken from *I.C.T.* and C_v obtained therefrom by subtracting 2 calories.

TABLE II.

Specific Heat of Liquid CCl_4 at Constant Volume.

Tempe-rature °C.	Contribution of the lattice	Contribution of internal frequencies	Total calc. as if it were a solid	Total calc. as if it were a gas	Observed (Mills and McRae and Williams and Daniels)
0	12	11·53	23·53	17·53	21·24
20	,,	12·05	24·05	18·05	21·50
40	,,	12·52	24·52	18·52	21·69
60	,,	12·94	24·94	18·94	22·41
80	,,	13·32	25·32	19·32	22·82

TABLE III.

Specific Heat of Liquid CS₂ at Constant Volume.

Temperature °C.	Contribution of the lattice	Contribution of internal frequencies	Total calc. as if it were a solid	Total calc. as if it were a gas	Observed (Regnault)
0	10	3·64	13·64	8·64	11·70
20	,,	3·89	13·89	8·89	11·70
40	,,	4·12	14·12	9·12	11·77
97 (vapour)	..	4·66	..	9·66	9·95†

† C_p is taken from *I.C.T.* and C_v obtained therefrom by subtracting 2 calories.

In the above tables, the observed values of C_v for benzene are obtained from the work of Mills and McRae (1910) and Williams and Daniels (1924). These authors have given C_p at different temperatures and C_v is calculated therefrom by reducing it in the ratio of the adiabatic and isothermal compressibilities as determined by Tyrer (1913). The results of Mills and McRae at higher temperatures are consistently lower than those obtained by Williams and Daniels and the differences in the case of benzene are appreciable. The data of both authors are given in Table I. The results of the latter authors however appear to be more reliable at high temperatures. In the case of CCl_4, the differences are not so prominent and at the two lower temperatures (0 and 20) the values of Mills and McRae and at all the other temperatures those of Williams and Daniels are given. In the case of CS_2, results of very early work of Regnault are the only ones available and these are given. In both these cases also C_v is calculated from the observed C_p in the manner described above. C_p for the vapours of benzene and CS_2 is available and C_v is obtained therefrom and given in Tables I and III. No reliable value for the specific heat of CCl_4 vapour is available.

4. Discussion of Results.

The following features may first be noted :

1. The agreement between the calculated and the observed specific heats is very satisfactory in the case of benzene and CS_2 vapours.

2. The specific heat observed in the vapour state is less than that obtained in the liquid.

3. In all the three cases, the observed specific heats for the liquid state at all temperatures lie between those calculated on the one hand by treating the liquid as a solid and on the other by treating it as a gas.

4. In the case of benzene the observed values are much closer to the solid values than in the other two cases where they are midway between the two sets of calculated values.

These results may be interpreted as follows :—

The thermal motion of liquid molecules which goes to make up its heat content is neither wholly disorganised in the form of random movements as in a gas nor wholly organised in the form of elastic waves as in the case of a solid. This important conclusion emerging out of the present investigation is not entirely new but has already been indicated recently from other branches of work mainly in light scattering. Particular attention may be drawn to the work of Raghavendra Rao (1935) on the fine structure of Rayleigh scattering. The presence of two displaced Brillouin components in the light scattered by liquids can only be explained by assuming that part of the thermal movements in the liquid are in an organised form constituting high frequency sound waves and causing the shift in the scattered light. On the other hand, the presence also of a central undisplaced component is to be associated with the fluctuations in density caused by the random movements of the molecules. Quantitative data regarding the relative intensities of these components are not available but a significant observation of Raghavendra Rao that the central component in CCl_4 is unusually bright in relation to the outer components when compared to the other cases such as benzene and toluene, may be cited here. It is particularly gratifying that the same result is arrived at from a study of the specific heats of liquids, a branch which is directly concerned with the manner in which heat energy is taken up by the molecules. It cannot be a mere accident that the observed specific heat of benzene liquid at various temperatures is quite close to that calculated on the assumption that the entire translational and rotational thermal energy is in the form of elastic waves whereas in the case of CCl_4 the observed value is well below the value so calculated and is as near to the gas value as to that of the solid. A good portion of the thermal energy is therefore taken up by a disorganised movement of the CCl_4 molecules in the liquid and hence we should expect a relatively strong, central or undisplaced scattering.

A quantitative investigation of the relative intensities of these components in relation to the observed specific heats is likely to throw considerable light both on the theories of specific heats as applied to liquids and nature

of the liquid state. Recent work of Raman and Raghavendra Rao (1937) on the viscous liquids is of great significance in this respect and the variation of specific heats of such liquids with temperature is likely to reveal interesting facts. Reliable data are, however, not available in these cases but work is in progress in this laboratory. There is also the additional difficulty of uniquely fixing the fundamental frequencies in such cases but by choosing substances for which complete Raman effect data are available, some progress may be expected.

5. Summary.

The specific heats of liquid benzene, CCl_4 and CS_2 are calculated with the help of the known fundamental frequencies in each case at different temperatures. Two alternative methods of evaluating the contribution to specific heat of translational and rorational degrees of freedom are adopted. In the first, a Debye function is assumed as in the case of a solid and in the second, a mean energy of $\dfrac{KT}{2}$ per degree of freedom per molecule is assigned as in the case of a gas. The observed specific heats are found to lie between these two extremes. It is therefore concluded that in liquids thermal movements of molecules are partly in an organised manner constituting Debye elastic waves as in a solid and partly in a random manner as in a gas. Analogy is drawn between this conclusion and the results obtained in light-scattering in respect of the fine structure of the Rayleigh line in liquids where two displaced Brillouin components and one undisplaced central component are usually observed.

REFERENCES.

Andrews, D. H., and Southard, J. C., *Phys. Rev.*, 1930, **35**, 670.

Bhagavantam, S., *Ind. Jour. Phys.*, 1930, **5**, 573.

Blackman, *Proc. Roy. Soc.*, 1935, **148 A**, 365 and 384.

Lord, R. C., Ahlberg, J. E, and Andrews, D. H., *Jour. Chem. Phys.*, 1937, **5**, 649.

———————, *Jour. Phys. Chem.*, 1937, **41**, 149.

Mills and McRae, *ibid.*, 1910, **14**, 797 ; 1911, **15**, 54.

Paramasivan, S., *Ind. Jour. Phys.*, 1931, **6**, 413.

Raghavendra Rao, B. V., *Proc. Ind. Acad. Sci.*, 1935, **1**, 261, 473 and 765.

Raman, C. V., and Raghavendra Rao, B. V., *Nature*, 1937, **139**, 584.

Regnault, *Mem. de L'Acad.*, 1862, **26**, 262.

Tyrer, D., *Jour. Chem. Soc.*, 1913, **103**, 1975.

Williams, J. W., and Daniels, F., *Jour. Amer. Chem. Soc.*, 1924, **46**, 903.