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ON THE THEORY OF SPECIFIC HEAT OF LIQUIDS

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ABSTRACT. Liquid is considered here as a sort of compressed gas in which the intermolecular forces play a role comparable to translational motion. On this basis the calculation of specific heat of liquids gives reasonable agreement with experimental results of hydrogen, argon, air and carbondioxide.

INTRODUCTION

Several attempts to explain the specific heat of liquids have been made in the past, but most of them are qualitative. Ghose (1924) had proposed an empirical formula which does not explain the nature of variation of specific heat with temperature. Prigogine and Suzanne (1942) have calculated the specific heat of liquid argon considering the model of Lennard-Jones, but they have not got good agreement with observed values. Later Ookawa (1947) has tried to deduce a relation on the basis that liquid consists of clusters of different sizes the magnitude of which varies with temperature. The final result obtained by him contains an unknown function of temperature and hence the values of specific heat have not been calculated.

When the molecules of a gas are forced to come very close to each other, the intermolecular forces come to operation, the influence of which is taken into account by the addition of a term to the pressure value of the gas equation as is apparent in Vander Waals' equation. This gas equation indicates the energy expression which is found to be modified on account of the potential energy due to intermolecular forces. The specific heat may now be deduced from such an expression. In this paper we have considered the liquid as a sort of compressed gas. So the result of the above deduction can be used to calculate the specific heat in case of liquid argon and liquid hydrogen for which only translatory motion should be considered within the temperature range under consideration. For air whose molecules are diatomic, we are to consider restricted rotations and for carbondioxide in addition vibrations of the atoms inside molecules are to be considered. To explain the specific heat of carbondioxide gas, we take 3 degrees of translation, 3 degrees of rotation and the vibration of atoms inside the molecule. This is also expected from the value of γ, the ratio of specific heats, which is nearly 1.30 at room temperature indicating the number of degrees of freedom to be 6.67 i.e. 3 degrees due to translation, 3 degrees due to rotation and one third of a degree due to vibration. But it is seen that in case of liquid carbondioxide we require in addition another 6 degrees of freedom for explaining the experimental data. This may be due to some motion caused by the deformation of molecules or may be due to the effect of interaction other than the effect of Vander Waals' forces. The results of our theoretical calculations are in good agreement with experimental findings. At the melting points of argon and air there is, however, some discrepancy.

DEDUCTION

If we neglect the extension of the molecules in space; and regard them as point masses Van der Waals' equation becomes

$$\left(P+\frac{a}{V^2}\right) V = RT = NKT$$

We write it as follows :

$$PV = N\left(KT-\frac{a}{VN}\right) \qquad \ldots \quad (1)$$

The above equation may also be used for liquids; however, the pressure P caused by the impact of molecules is very small in this case (Partington, 1949)

The constant a in the above equation, though originally regarded as independent of temperature, is found to depend on temperature when comparison is made with observational results. The exact nature of this function is not known. But it is clear that a should vanish at high temperatures and at low densities because the gas will become perfect then. At a temperature T_m where we shall get solid state, the product PV should be zero because solid does not give rise to any pressure due to impact of molecules. Considering these two limiting cases we suggest that

$$a = VRT\, e^{-2\theta(T^{1/2}-T_m{}^{1/2})}$$

where θ is a constant independent of temperature Substituting for a in (1) we get

$$PV = N[KT-KT\, e^{-2\theta(T^{1/2}-T_m{}^{1/2})}]$$

Energy of the system with translatory motion alone is known to be -

$$E = \tfrac{3}{2}PV = N[\tfrac{3}{2}kT-\tfrac{3}{2}kT\, e^{-2\theta(T^{1/2}-T_m{}^{1/2})}] \qquad \ldots \quad (2)$$

Hence $$C_v = \frac{dE}{dT} = \tfrac{3}{2}R[1-e^{-2\theta(T^{1/2}-T_m{}^{1/2})}(1-\theta T^{\frac{1}{2}})]. \qquad \ldots \quad (3)$$

In equation (2) we find that in case where there is translational energy only the average energy per particle per degree of freedom is

$$\tfrac{1}{2}kT[1-e^{-2\theta(T^{1/2}-T_m{}^{1/2})}]$$

In diatomic and polyatomic molecules we may expect rotation and molecular vibration which will give rise to new degrees of freedom. In case of liquids these motions are not free but restricted due to intermolecular intraction, hence the energy per particle per degree of freedom should not be taken as $\frac{1}{2}KT$. Assuming equipartition of energy we shall take the energy per particle for each of these new degrees of freedom also as $\frac{1}{2}KT[1-e^{-2\theta(T^{1/2}-T_m^{1/2}}]$. So the specific heat at constant volume C_v is given by

$$C_v = \frac{n}{2} R[1-e^{-2\theta(T^{1/2}-T_m^{1/2}(1-\theta T^{\frac{1}{2}})}] \tag{4}$$

where n stands for the number of degrees of freedom.

COMPARISON WITH EXPERIMENTAL RESULTS

(i) *Liquid Hydrogen*

Below 50° abs. in case of hydrogen only translatory motion need be considered. So in eqn. (4) we take $n = 3$ in the temperature range considered and $\theta = 0.215$ (determined by trial). The calculated values of specific heat are shown against the experimental results obtained by Bartholomo and Eucken (1936).

Specific heat of liquid hydrogen

Temp. in abs	C_v (obs.) in Cal/degree cent	C_v (Cal) in cal/degree cent
15 33	2 54	2.55
15 86	2 56	2 61
16 23	2 63	2 64
16 87	2 70	2 70
17 22	2 70	2 73
17 88	2 78	2.78
18 92	2.84	2 84
19 50	2 89	2 89
20 00	2 92	2 92
20 50	2.98	2 94

The agreement here is quite satisfactory, the maximum deviation being less than 2%.

(ii) *Liquid Argon*

Argon is monatomic. So we take in equation (4). $n = 3$ and $\theta = 0.25$ (determined by trial) The experimental results are taken from Eucken and Hauck (1928).

Specific heat of Argon

Temp. in abs.	C_v (obs.) in cal/°C	C_v (calculation of Prigogine and Suzanne) in cal/°C	C_v (our calculation) in cal/°C
90	5.5	5.25	6.47
100	5.5		5.94
110	5.5	5.15	5.49
120	5.20		5.13
130	4.90	4.30	4.82
140	4.65		4.54
150	4.35	4.50	4.32
160	4.00	4.30	4.12
170	3.75	4.00	3.97

The agreement in this case is satisfactory beyond 110° abs. The maximum deviation is less than 4%. There is a tendency of deviation after 160° abs. This is expected because critical temperature for argon is only 151° abs. and at this temperature things are not normal.

(iii) *Liquid Air*

Air is a mixture of mostly diatomic molecules. So in equation (4) we are to take $n = 5$ (for translatory motion 3 and for rotatory motion 2) and $\theta = 0.33$ (determined by trial). The experimental results are taken from Eucken and Hauck (1928).

Specific heat of air

Temp in °abs.	Cv(obs.) in cal.°c.	Cv(cal.) in cal /°c.
80	7.8	10.00
90	7.8	8.85
100	7.7	7.90
110	7.35	7.30
120	6.85	6.75
130	6.50	6.40
140	6.10	6.10
150	5.70	5.85
160	5.03	5.70
170	5.55	5.55

The agreement here is satisfactory excepting at the melting point. The maximum deviation is less than 3%.

(iv) *Liquid Carbondioxide*

In this case we have vibration of atoms in the molecules. The energy due to this vibratory motion is to be calculated using the Einstein function for specific heat. The three characteristic temperatures (abs.) are 3400, 1900 and 960. Out of these three only the last one will have some contribution at the temperature under consideration, the effect of the other two will be negligibly small. We will have only N oscillators with 960 temperature. The contribution of these for specific heat (given in the second column in the table below) can be obtained in the usual way from the table for Einstein function. To explain the rest of energy we will take $n = 12$ in equation (4). The experimental results here are taken from Eucken and Hauck (1928).

Specific heat of carbondioxide

Temp. in °Abs	C_{960} in cal/°c.	C in cal/°c	$C + C_{960} -$ in cal /°c	cal /°c
230	0.541	10.116	10.657	10.4
240	0.604	10.38	10.984	10.9
250	0.66	10.620	11.280	11.25
260	0.706	10.836	11.542	11.45
270	0.76	11.028	11.788	11.75
280	0.80	11.244	12.044	12.10
290	0.86	11.292	12.152	12.25
300	0.9	11.892	12.792	12.75
310	0.94	12.024	12.964	13.10
320	0.98	12.156	13.136	13.35

For the last three readings we have taken $\theta = 0.057$ and for the rest, $\theta = .055$. Near the critical temperature a change in the value of θ is always expected because things are not normal then, a step anomaly is seen at 300° abs. The maximum deviation in this case is less than 2%.

DISCUSSION

It is usually expected that in specific heat measurements at low temperatures, there remains an error of 4%. So the theory suggested above gives very good agreement with experimental results in case of these four liquids. At the melting point and at the critical temperatures abnormal behaviour is always expected. So slight deviation at these points should not be considered as defect of the theory.

Equipartition principle which is deduced for perfect gases can be used, as we have seen, to restricted motions as well.

We may notice that equation (1) can also be written as

$$PV = KT\left(N - \frac{a}{VKT}\right)$$

Substituting for a in the above equation we notice that a liquid or a real gas can be looked upon as a perfect gas with $N[1-e^{-2\theta(T^{1/2}-T_m^{1/2})}]$ moving particles instead of N molecules and the rest of the particles can be assumed to be at rest. We can get all the above results with this idea also. We will discuss about this idea in our next paper which will deal with the variation of the coefficient of viscosity with temperature both in liquids and gases.

Heuse (1919) has observed a fall in the values of the specific heat of many gases at low temperature. Such a fall has been reported by him even in case of argon which is a monatomic gas. A fall of this type is, however, expected from eqn. (4) and it will be interesting to compare the calculated values of the specific heat from eqn. (4) with the experimental findings.

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