A Critical Study of Physical Properties and Molecular Potential for Water

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CERTIFICATE

CERTIFIED that the thesis entitled " A CRITICAL STUDY OF PHYSICAL PROPERTIES AND MOLECULAR POTENTIAL FOR WATER" which is being submitted by Mr. OM SINGH in fulfilment of the requirements for the award of the degree of Doctor of Philosophy in Physics of the University of Roorkee, is a record of his own work carried out by him under my supervision and guidance. The matter embodied in this thesis has not been submitted for the award of any other degree or diploma.

This is further to certify that he has worked for a period of equivalent to 24 months full time research for preparing this thesis for Ph.D. Degree at the University.

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(OM SINGH)

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PREFACE

There are three distinct states of matter - solid liquid and gas. The liquid state is intermediate between the solid and the gaseous states and therefore it is to be expected that the thermodynamic properties of a liquid will be intermediate between those of its solid and gaseous states. But because of the peculiar properties of the liquid state and intensive interaction among the particles in strong disorder, the theoretical analysis of the problem becomes difficult and remains much less developed in contrast with the theory of gases and solids. This is not for want of trying. A vast number of researches have been devoted to attempts to analyze the structure of liquids, either directly by the diffraction methods which have proved so successful in crystalline solids, or indirectly, through the construction of models and their thermodynamic testing. But we still lack either an adequate picture of the arrangement of molecules in a liquid or the necessary quantitative theory to explain their thermal and other properties.

The attempts that have been made to formulate a theory of liquids fall into four broad classes :

(i) Simulation studies
(ii) Integral equation methods
(iii) Lattice theories
(iv) Perturbation theories.

None of the above theories is adequate description of the liquid state structure, and so far by no means the problem of liquid state is completely solved. Though the perturbation theories are in the process of developing into a consistent theory but so far only it has been proven that they are physically satisfying approach to the theory of the equilibrium properties only and that is too in case of simple liquids not for non simple liquids like water. That is why the liquid state research is an emerging field which will keep physicists attention occupied in the coming decades.

Most of the above theories now remain only of historical importance, because they are either "gas-like" approach or "Solid-like" approach. They do not treat the liquid state as an independent state. A real theory to come for liquids must have to treat it as an independent state.

An exact and a well developed theory of liquid state is not only of academic interest but also has many technical applications, for example in the pollution and entrophication problems, as well as is necessary for further advances in a number of branches of physics, Physical chemistry, Biophysics etc. This problem is of further importance because of biochemical interests, in that all living structures are mostly composed of water.

As a first step to understand the liquid state of matter, we have chosen to study the various thermodynamic and mechanical properties of liquids critically with respect to temperature. Since the different states of matter are nothing but a competition between the thermal energy and intermolecular forces. So in the preliminary stages the problem of liquid state resolves itself into two. First, to a relation which can give us the temperature variation of various properties of liquids and, secondly, to a choice of a suitable form of intermolecular potential.

This thesis devided into five Chapters. First Chapter is devoted to a survey review on intermolecular potentials. Special attention is paid towards 48 years of Lennard Jones (6: n) potential. It is concluded from the discussion that for a real pair potential, while keeping the simplicity of the L-J(6:n) potential some sort of flexibility in the potential parameters must be so introduced as to conform to the experimental data. It is then pointed out that a new line of approach could be to introduce a suitable temperature dependence of the force parameters.

In Chapter 2 our essense has been an idea to deal the liquid state as a real, van der waal gas of "molecular clusters" or microscopic "drops" . Such a model suggests itself if we try a mathematical decoupling of molecular clusters to avoid the complicated cluster integrals. An "effective" potential between the "drops" has been obtained, Starting from the experimental PVT-data for liquid water.

In Chapter 3 various empirical, semi-empirical expressions for properties of water have been examined and a single expression which represents the functional dependence of temperature of almost all properties of water is suggested. The expression has been interpreted in terms of two state theory of water. A more fundamental interpretation in terms of molecular interaction has been discussed.

In Chapter 4 a specific form of temperature-dependent molecular potential has been considered as trial. Compressibility, sound velocity and pressure dependence of bulk modulus for liquid water have been calculated from this potential. A good agreement with experimental results has been found. A speculative suggestion for future work on building a theory of liquid state **sui generis** without directly refering to gaseous or solid state has been mentioned basing it on a temperature-dependent molecular potential. According to this speculation the transformation of solid to liquid state would mean 'cluster' - formation of molecules, so that the liquid can be treated as a real van der waals gas of these 'clusters' or 'drops'. Such a description will correspond to the case already treated in Chapter 2.

Chapter 5 deals with a brief review of a number of theories of liquids. Calculation have been made for volume and two-state thermodynamic parameters alongwith some other physical properties of water on two-state approach. Furthermore a statistical theormodynamic theory is successfully applied to water based on the two -state model of liquid water which consists of two classes of molecular structures. Class I is constituted of hydrogen bonded molecules and Class II is constituted by unbonded monomers. The resulting partition function is formulated and calculated by using the two quantities, the energy difference between class I and class II, θ , and the fraction of close-packed specy.

CHAPTER I

A great deal of the current effort in science is directed towards relating the real-life properties of gases, liquids and solids to behaviour at the atomic and molecular level. Since the amount of information that one needs about the molecules and their interactions is much less than the information about the physical properties which is or should be derivable from them, a knowledge of the true intermolecular potential is thus a necessary step towards an understanding of these physical properties. A quite good number of the intermolecular potential functions is available in the literature. The purpose of the present review is not to deal with all these potentials in detail(which requires a large space) but with principles and attempts which have been made by various authors to determine a reasonable form of the pair potential and finally to suggest something which ought to be fundamental about a true pair potential.

One of the most common potential which has been used extensively in determining the various properties of the matter in the gaseous, liquid and solid states is the Lennard- zones (6 : n) potential Fig. (1). The general form of this potential energy function is

$$\phi(r) = \frac{\epsilon}{(1-\frac{m}{n})}\left[\frac{m}{n}\left(\frac{r^*}{r}\right)^n - \left(\frac{r^*}{r}\right)^m\right] \qquad (1.1)$$

or

$$\phi(r) = \epsilon\left[\left(\frac{r^*}{r}\right)^{12} - 2\left(\frac{r^*}{r}\right)^6\right]$$

Where ϕ (r) is the mutual pair potential-energy of interaction between two molecules, ϵ is the (-ve) minimum energy, r is the distance between molecular centres, r^* is the distance between molecular centres at the minimum molecular pair potential energy. n and m are the repulsive and attractive exponents. The choice of the repulsive exponent n = 12 is primarily one of the methamatical convenience, but by no means unique. A general survey of the literature reveals that n can have any value ranging from 8 to 30.

The potential is named after Lennard-jones, although, Mie (1) was the first to suggest that the interaction energy between a pair of atoms might usefully be expressed as the sum of two terms (Fig. 1), a negative term proportional to the power- m of the distance r and a positive term proportional to the power - n of the distance r with $n > m > 0$ (this form for the sake of bravity called the (m : n) interaction), he made many of the earlier calculations of the bulk properties of the gases and liquids in a series (2- 9) that started in 1924.

In 1924 Lennard-jones (10) showed that the experimental values of the second virial coefficient of Argon, and several other gases could be derived from a (4:n) interaction with n (repulsive exponent) having any of the values n = 8, 10, $13\frac{1}{3}$, 20, 24.

In 1930 London (11) proved by quantum theory that at large distances the interaction energy is proportional to r^{-6}. It is, therefore, natural to use the values m = 6 In 1931 Lennard-jones(2) **refitted** the experimental data with m = 6 and n = 9, 10,12.

One reason for the popularity of Lennard-jones (6:n) potential is that Lennard-jones has showed how the integration for the second virial coefficient could be carried out analytically to yield a power series that converged rapidly enough to be within the scope of a desk calculator. This was the non-trivial matter in the days before the fast electronic computers.

The properties which provide a convenient means of testing a potential-energy functions are : second and third virial coefficients of gases. Joule-Thomson coefficients, crystal properties (lattice spacing, heat of sublimation, mechanical constants), coefficient of viscosity thermal conductivity, diffusion, thermal diffusion and scattering of molecular beams. The parameters of a force model are determined by fitting experimental second virial coefficients and also from the viscosity data. We shall not discuss here the methods of fitting the data , which essentially are the following five methods,

(i) Selected points

(ii) Empirical equations

(iii) Parallel translation of axes

(iv) Curve intersections

(v) Least squares iteration

There are two general criteria which are used to give some measure of confidence in the reality of a true pair potential of the molecules. The first one is that the model must not conflict in any essential way with generally accepted theoretical results about intermolecular forces. The second criterion is that the model must be able to predict, in agreement with experiment, other properties besides those used to determine the parameters.

EXPRESSIONS FOR THE SECOND AND THE THIRD VIRIAL COEFFICIENTS FOR LENNARD-JONES (6:n) POTENTIAL :

The equation of state of a gas written as power series in density is :

$$\frac{PV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^4} + \frac{E(T)}{V^6} + \frac{F(T)}{V^8} + \ldots \qquad (1.2)$$

where B(T), C(T), D(T), E(T) ,F(T) etc. are the second, third, fourth, fifth and sixth virial coefficient respectively.

The second virial coefficient, B(T) , of the virial equation of state is related to the potential energy $\phi(r)$

as

$$B(T) = -\frac{2\pi N}{3kT}\int_0^{\infty} r^3 \frac{d\phi}{dr} e^{-\phi(r)/kT} dr$$

$$= 2 \quad N\pi \int_0^{\infty} r^2 (1- e^{-\phi/kT})dr \qquad (1.3)$$

Using the following reduced quantities,

$$r^* = r/\sigma \quad , \quad T^* = kT/\epsilon$$

$$B^* = \frac{B}{\frac{2}{3}\pi N \sigma^3} = \frac{B}{b_o}$$

Therefore $\phi(r^*) = 4\epsilon\left[r^{*-n} - r^{*-6}\right]$

$$B^*(T^*) = -\frac{4}{T^*}\int r^{*2}\left[-\frac{n}{r^{*n}} + \frac{6}{r^{*6}}\right] e^{-\frac{4}{T^*}(r^{*-n} - r^{*-m})} dr^*$$

Putting $A = \frac{4}{T^*}$

$$B^*(T^*) = n A \int_0^{\infty} r^{*-n+2} e^{\frac{A}{r^{*6}}} e^{-\frac{A}{r^{*n}}} dr^*$$

$$- 6 A \int_0^{\infty} r^{*-4} e^{\frac{A}{r^{*6}}} e^{-\frac{A}{r^{*n}}} dr^*$$

Which gives finally after carrying out the integration ,

$$B^*(T^*) = A \sum_{j=0}^{\infty} \frac{1}{j!} A^j A^{-(6j+n-3)/n} \Gamma\left(\frac{6j+n-3}{n}\right)$$

$$- 6 A \sum_{j=0}^{\infty} \frac{1}{j!} A^j \frac{1}{n} A^{-\left(\frac{6j+3}{n}\right)} \Gamma\left(\frac{6j+3}{n}\right)$$

$$B^*(T^*) = \sum_{j=0}^{\infty} b^{(j)} T^{*-(2j+1)/4} \qquad (1.4)$$

where $$b^{(j)} = -\frac{2^{j+\frac{1}{2}}}{4j!}\Gamma\left(\frac{2j-1}{4}\right) \qquad (1.5)$$

The third virial coefficient, C(T), of the virial equation of state is related to the potential energy, $\phi(r_{ij})$, of a pair of molecules i & j separated by a distance r_{ij} by

$$C(T) = -\frac{8\pi^2N^2}{3}\iiint f_{12}f_{13}f_{23}r_{12}r_{13}r_{23}dr_{12}dr_{13}dr_{23} \qquad (1.6)$$

where $$f_{ij} = \exp\left(-\frac{\phi(r_{ij})}{kT}\right) - 1$$

The integral may be evaluated by a method similar to that used for the evaluation of the second virial coefficient. The results obtained are

$$C^*(T^*) = \sum_{j=0}^{\infty} c^{(j)} T^{*-\frac{j+1}{2}} \qquad (1.7)$$

$$C(T) = b_0^2 C^*(T^*) \qquad (1.8)$$

Where the expansion coefficients $c^{(j)}$ for the third virial coefficient are complicated integrals and values are computed by numerical integration.

Calculations for the Lennard-jones potential have been made for various properties by various authors(38) such as : second virial coefficients (12-16), transport properties of dilute gases : viscosity, thermal conductivity, and coefficient of self-diffusion of the dilute gases(12,19, 20,58), lattice spacing, latent heat of sublimation and coefficient of thermal expansion of solid argon at low temperatures (19-25), with the same force parameters as are used to fit the second virial coefficients.

Numerical calculations have been made of the third virial coefficient for the Lennard-jones potential by Bird et al.(26), and some other authors (27-29). Rowlinson et al.(30) developed asymptotic expression for the Lennard-jones third virial coefficient valid at high and low temperatures.

With modern computers it is possible to reach the fifth virial coefficient E(T) for a Lennard-jones potential (31-33).

This potential has only two adjustable parameters and so conforms to the principle of corresponding states. The properties of the inert gases, in all states of matter, require a potential of this form.

However, Lennard-jones (6:n) potential which has been used extensively in the study of interaction of simple non-polar molecules since 1924, has severe faults. These were revealed by many independent failures which became apparent from 1960 onwards. The inadequacy of the L-J potential, even in case of simplest molecules (inert gases), has been corroborated (14-16, 34-37) by several independent authors and may be summarized as follows :

(i) The long range interaction potential between a pair of atoms is given by second-order perturbation theory (17) as $-C_{ab}r^{-6}$, where the interaction constant C_{ab} can be related to the oscillator strengths of electronic transitions which can be measured experimentally from the ultraviolet spectrum. Barker and Leonard (39) found that the coefficients so determined for simple gases (He, Ne, A, Kr and Xe) are roughly half those of Lennard-jones potential.

(ii) Munn (31) calculated the same dispersion-force coefficient for Argon and Neon from the low temperature viscosity measurements, which is a direct source of information concerning dispersion forces. Again the values so obtained are half those for the Lennard-jones (6:12) potential.

(iii) Weir, Wynn Jones, Rowlinson and Saville (40) pointed out that the Lennard-jones (6:12) potential is inadequate for wide ranges of temperature, and this becomes more obvious when the deviations are examined graphically. The minimum depth of the best L-J potential are $\epsilon/k = 116 \pm 1^{\circ}K$ for Argon and $163 \pm 1^{\circ}K$ for Krypton, which are too small to produce the rapid fall in B observed. Their measurement of the second virial coefficient at low temperature require a depth ϵ that is about one third larger than that of Lennard-jones potential. They do not stress the physical significance of any of these figures, but only put them forward as evidence that the depths of the true pair potential is certainly greater than the depths associated with the L-J potential.

(iv) Rowlinson (41), Sherwood and Prausnitz(42) calculated the third virial coefficient, as the third virial coefficient is more sensitive to the shape of the potential function than the second virial coefficient, for many gases e.g. Argon, Krypton, Xenon, Methane, Nitrogen, Co_2 etc. and compared with the experimental values. It is found that the calculated values of the third virial coefficient have a peak at low temperatures whose height cannot be reconciled with the experimental one.

(v) The experimental behaviour of the classical fluctuation discriminatnt of the configurational energy and the virial was examined by Rowlinson(43) for the fluid states of nitrogen and methane which shows that the discriminant must be essentially positive. But Lennard-Jones (6:12) potential leads to negative values of the discriminant for orthobaric liquids at low temperatures, for the liquids at high pressures and for the gases at high temperatures. Any how Rowlinson pointed out that the discriminant can be made positive in the low temperature region by choosing a value of $n = 13 - 14$, but at high temperatures, the value would have to be 20-30. It does mean that the best experimental results for gases at high temperatures are not compatible with a L-J potential with a reasonable repulsive index. So this also demonstrate the inadequacy of the L-J (6:12) potential at high densities and temperatures.

(vi) Guggenheim's and McGlashan's (44) investigations on the equilibrium properties of the crystal, namely, the variation of entropy with temperature, of energy with temperature, of density with temperature and of the density with pressure show that the interaction energy which best accords with all these properties is strikingly different from the commonly advocated difference between an inverse twelfth power and an inverse sixth power of the distance.

(vii) Kihara's (14-16) objections to the L-J(6:12) potential are :(a) It does not explain the absolute stability of the cubic structure, (b) The real intermolecular potential for rare gases has a wider bowl and a harder repulsive wall than the Lennard-jones potential.

(ix) For some time it has also been recognized that it does not give satisfactory description of dilute gas properties (15,45,46).

In the light of the above discussion, it has been recognized for some time that the inverse power (6:12) potential due to Lennard-jones is not an adequate representation of the intermolecular energy even of the inert gases which have several simplifying features, i.e. closed electronic shells, monoatomic molecules with spherical symmetry and they crystallize in the simple closed packed structure which make them a unique system for a detailed study of their molecular fields.

Nonetheless, the success of potential function is evaluated as much in terms of its simplicity as in accuracy. Lennard-jones(6:12) has remarkable simplicity although, of course, its accuracy has been in doubt for some time. But the modifications due to several authors most significant since 1960 onwards are advancement in this direction of making it more flexible so that its accuracy might increase, although at the cost of simplicity. Notable among these are, due to Kihara (15), Guggenheim-McGlashan (44), Boys and Shavitt (47), Dymond, Rigby and Smith (48), Pollara et al.(55), Dymond and Alder (54) and very recently due to Koo (57) etc. which are discussed in brief below :-

Kihara (15) proposed a three-parameter potential, in which third parameter is added to represent the molecular core size :

$$\phi(r) = A\left(\frac{m}{n}\right)\epsilon\left[\left(\frac{1-\nu}{\frac{r}{\sigma}-\nu}\right)^{n}-\left(\frac{1-\nu}{\frac{r}{\sigma}-\nu}\right)^{m}\right] \qquad (1.9)$$

where r, is the separation, σ is the collision diameter $(U(\sigma) = 0)$, $-\epsilon$ is the minimum value of U, $(\nu\sigma)$ is hard core within which U is supposed to be infinite and $A(m/n)$ is a pure number

$$A(x) = x^{-\frac{x}{1-x}} (1-x)^{-1} \quad \text{or } A(1/2) = 4 \qquad (1.10)$$

This potential can also be written in terms of the reduced separation (r/r_m), where r_m is the separation at which U is minimum,

$$\frac{r_m}{\sigma} - \nu = (1-\nu)\left(\frac{n}{m}\right)^{\frac{1}{n-m}} \qquad (1.11)$$

This potential reduces to that of Lennard-jones for $\nu = 0$ This can be written in terms of (r/σ) as in equation (1.9), or as,

$$\phi(r) = \frac{n\epsilon}{n-m}\left[\frac{m}{n}\left(\frac{r_m}{r}\right)^n - \left(\frac{r_m}{r}\right)^n\right] \qquad (1.12)$$

This potential has been used by Sherwood and Prausnitz (42) to fit the second virial coefficients of Argon and by Barker, Fock and Smith (49) to fit the second virial coefficient and the transport coefficients. The parameters suggested by them are close to each other,

S and P $n = 12$, $m = 6$, $\nu = 1/9$, $\sigma = 3.314$ Å, $\epsilon/k = 147.2$ °K (1.13)

B.F. and S. $n = 12$, $m = 6$, $\nu = 1/10$, $\sigma = 3.363$ Å, $\epsilon/k = 142.9$ °K (1.14)

The greater success of the Kihara potentials is due to their greater depth of the well.

It is generally agreed that the second virial coefficients alone cannot determine the form of the interaction energy. Any how the more detailed information concerning the interaction energy especially at distance r near to that at which the energy is minimum, should be obtainable from the equilibrium properties of the crystal, in particular the density, the energy and the entropy. Guggenheim and McGlashan (44) have correlated the interaction energy between argon atoms with the equilibrium and non-equilibrium experimental properties of argon, namely, the variation of entropy with temperature, of energy with temperature of density with temperature, of density with pressure, of the second virial coefficient of the gas with temperature , and of viscosity of the gas at high temperatures. Their curve of interaction energy in the neighbourhood of the minimum is expressed as a power series in $(r-r_0)$ which introduces additional anharmonic terms in the neighbourhood of potential minimum in order to explain the solid properties, namely

$$\omega = -\epsilon + K\left(\frac{r-r_0}{r_0}\right)^2 - \alpha\left(\frac{r-r_0}{r_0}\right)^3 + \beta\left(\frac{r-r_0}{r_0}\right)^4 \qquad (1.15)$$

where r_0 is the distance at which the energy is minimum, K, The greater success of the Kihara potentials is due to their greater depth of the well.

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$$\omega = -\epsilon + K\left(\frac{r-r_0}{r_0}\right)^2 - \alpha\left(\frac{r-r_0}{r_0}\right)^3 + \beta\left(\frac{r-r_0}{r_0}\right)^4 \tag{1.15}$$

where r_0 is the distance at which the energy is minimum, K, a parameter determines approximately the characteristic frequency ν, α is a parameter which plays an important role in determining the dependence of ν on the lattice constant and so indirectly the temperature dependence of all the equilibrium properties.

β, the importance of anharmonicity is determined mainly by the value of $\beta - \alpha$ and they have assumed for β a value between 0 & α so that anharmonicity is unimportant in the atomic vibrations. Calculations show that this potential gives considerably better fit tham (6:12) potential in some properties such as in case of entropy and lattice constants etc.

Shavitt and Boys (47) (Fig. 7) introduces a new expression with unlimited number of adjustable parameters, namely,

$$\phi(r) = \frac{4\epsilon}{(r^2 + B^2)^3} \sum_{i=0} C_{2i} \left[r^{2i} e^{A(1-r^2)} \right] \quad (1.16)$$

Here $r = R/R_0$, where R is the intermolecular distance and R_0 is the distance for which U = 0, A, B^2 and C_{2i} $(i=0,1,2,..)$ are the parameters, and it is suggested that A and B^2 be assigned definite values while the linear coefficients C_{2i} be varied to fit the experimental or theoretical data. The scale factor ϵ can be made equal to the maximum depth of the potential well by a simple 'normalization' of the parameters C_{2i}. It is shown that the choice $A = 4$, $B^2 = 0.1$ makes the basic function of the system Equation (1.16) namely that for which $C_o = 1$ and all other $C_{2i} = 0$, practically indistinguishable from the L-J potential.

$$\phi_L(r) = 4\epsilon\left(\frac{1}{r^{12}} - \frac{1}{r^6}\right) \qquad (1.17)$$

Three cases of the potential function equation (1.16) given by assigning three sets of values of the C_{2i} have been examined. The second, third and fourth virial coefficients for the three potentials u_1, u_2, & u_3 have been calculated at various temperatures. The second virial coefficient was evaluated by a straightforward numerical integration, the third and fourth virial coefficients by the method of expansion in Gaussian functions.

Dymond, Rigby and Smith (48) proposed a two parameter, five term, potential function of a polynomial form, namely,

$$\phi(R) = \epsilon\left[0.331\left(\frac{R_m}{R}\right)^{28} - 1.2584\left(\frac{R_m}{R}\right)^{24} + 2.07151\left(\frac{R_m}{R}\right)^{18} - 1.74452\left(\frac{R_m}{R}\right)^{8} - 0.39959\left(\frac{R_m}{R}\right)^{6}\right] \qquad (1.18)$$

Where R_m is the intermolecular separation at the minimum energy ϵ, and are different for different gases. The power of the main attractive term (in R^{-6} and R^{-8}) were chosen on theoretical grounds. The attractive term has no theoretical basis , but was found necessary to give a broad bowl to the potential function as required by the experimental data. The potential function is illustrated in Fig. (6). This potential fits well the second virial coefficient of a wide range of gases. The heat of sublimation and lattice parameters of the inert gases have been calculated using the parameters obtained from the fitting of the second virial coefficients. And when the correction of non-pairwise additivity in the solid phase are applied, the agreement is excellent. The heat of sublimation calculated in this way are considerably superior to those estimated from other two parameters intermolecular potentials in common use. The third virial coefficients of Ar,Kr and Xe have been calculated making allowance for the non-pairwise additivity (42,48). In the case of Kr the calculated results are 10% low than the experimental results. Any how this potential has got certain limitations namely, as five terms are involved in the potential function it is unlikely that the coefficients of the various powers of R can be regarded as meaningful. Thus the coefficients of R^{-6} and R^{-8} cannot be used to evaluate theoretical approaches to the theory of dispersion forces, and secondly at small separations the repulsion forces predicted by the potential are clearly much greater than those suggested by scattering experiments.

Pollara et al (55) proposed a three parameter potential function, to avoid the Kihara's objection against the Lennard-jones (6:12) potential, as shown in Fig. (4). of the form,

$$\begin{array}{lll} \phi = \infty & 0 \leq r \leq \sigma & \\ \phi = -\epsilon & \sigma \leq r \leq & \quad (1.19) \\ \phi = -\epsilon \dfrac{\nu^6}{r^6} & \nu \leq r \leq \infty & \end{array}$$

which includes an adjustable bowl, a hard repulsion and a realistic (r^{-6}) attraction term, a hybrid potential of the square well potential, and the Sutherland potential. In order to test the proposed model they calculated the second virial coefficient by the usual methods of statistical mechanics using Equation(1.20) given below :-

$$B(T) = \left[\left(\frac{2}{3}\right) \pi \tilde{N} \sigma^3 \exp\left(1/T^* \right) - \left(\frac{2}{3}\right) \pi \tilde{N} \nu^3 \left(\exp\left(1/T^*\right) - 1 \right) + \sum_{n=1}^{\infty} \frac{T^{*-n}}{(2n-1)n!} \right] \qquad (1.20)$$

Where N is the Avogadro number, r is the intermolecular distance $T^* = kT/\epsilon$, ϵ, σ, r are as defined in Fig. (4) The results so obtained were compared to those of Hamann and Lambert (56) (7:28) potential energy function.

Recently, Dymond and Alder (54) dealt with the problem in a more systematic way. They studied the effect of variations in the interatomic potential of argon on the calculated properties of the dilute gas. They modified the L-J (6:n) potential as follows :

(a) Changes in the long range attraction.

(b) Potential energy functions with different slopes to the outer wall of the attractive bowel.

(c) Potential energy functions with different bowl width.

(d) Potential energy function with different repulsive energy.

Pictorially these changes are shown in Figs (3a to 3e) Further they found that changing different regions of the potential simultaneously leads to the same results as combining the separate changes. And a potential function which does provide a reasonable fit to the experimental data. The general features of this numerical potential are that it has a smaller attractive tail, a wider bowl with a steeper outer wall, and a weak repulsive region than previously postulated potentials, to overcome the Kiharas criticisms against the Lennard - Jones (6:12) potential.

Very recently to remove these criticism Ronald Y. Koo (57) et al. modified the Lennard-Jones potential as shown in Fig. (5) and expressed mathematically as :

$$\phi(r) = \left[\frac{n\epsilon}{(n-6)}\right]\left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^6\right] \quad \text{for } 0 < r < r_{\min}$$

$$\phi(r) = -\epsilon \qquad \text{for } r_{\min} \leq r \leq \gamma r_{\min}$$

$$\phi(r) = \left[\frac{n\,\epsilon}{(n-6)}\right]\left(\frac{1}{6}n\right)^{\frac{6}{n-6}} \left(\frac{\gamma\sigma}{r}\right)^n - \left(\frac{\gamma\sigma}{r}\right)^6 \quad \text{for } \nu r_{\min} \leq r < \infty$$

(1.21)

where $r_{\min} = \left(\frac{1}{6}n\right)^{\frac{1}{n-6}} . \sigma$

and ϵ, σ, n, γ are the maximum energy of attraction, the collision diameter, hardness of the repulsion and width of the bowl respectively. Substituting the modified L-J (6 :n: ν) potential function in to the expression for the second virial coefficient given by,

$$B(T) = 2\pi N \int_0^\infty \left[1 - e^{-\phi(r)/kT}\right] r^2 \, dr \qquad (1.22)$$

The reduced second virial coefficient is obtained for the modified L-J (6:n: ν) potential as :

$$B^*(T^*) = -A^{3/n} \sum_{j=0}^{\infty} (j!)^{-1} A^{j/\beta} \; F(T^*, n, r_{\min}, \nu)$$

(1.23)

$$\text{Where, } F(T^*, n, r_{\min}, \;) = \left\{ \frac{6}{n} A^{\frac{1}{\beta}} \left[\gamma^3 \Gamma(K_1, M_1) + \Gamma(K_1+1) - \Gamma(K_1, M_2) - \gamma^3 \Gamma(K_2, M_1) - \Gamma(K_2+1) + \Gamma(K_2, M_2) \right\} \right.$$

(1.24)

in which,

$B^{*} = B \,/\, (\frac{2}{3} \pi N \sigma^{3})$

$T^{*} = KT / \epsilon$

$A = \beta \, r^{*6}_{min} \,/\, T^{*}$

$\beta = n \,/\, n-6$

$r^{*}_{min} = r_{min} / \sigma$

$\Gamma(x+1) = x!$

$\Gamma(x+1,\ y+1) = (x, y)! = \int_{0}^{y} e^{-t} \, t^{x} \, dx$

$K_{1} = (6j+3-n)/n$

$K_{2} = (6j-3)/n$

$M_{1} = A \left(\frac{Y}{r^{*}_{min}}\right)^{n}$

$M_{2} = A \left(\frac{1}{r^{*}_{min}}\right)^{n}$

When $Y = 0$ Equation (1.23) reduces to the form of the Lennard- Jones (6:n) potential i.e.

$$B^{*}(T^{*}) = \frac{3}{n} A^{\frac{3}{n}} \sum_{j=0}^{\infty} (j!)^{-1} A^{j/\beta} \, \Gamma\left(\frac{6j-3}{n}\right) \qquad (1.25)$$

Equation (1.23) and Equation (1.25) were used to calculate the second virial coefficient for six gases , nitrogen, CO_2 , ethane, n-butane, ethylene, and benzene. They found that the modified potential $(6{:}n\ ;\ \nu)$ has an improvement over the (6:n) potential.

However, none of these potentials has been found to be flexible enough to reproduce all the known low-density properties of the inert gases within experimental error. This is true inspite of the fact that recent measurements of the coefficient of viscosity at high temperatures (50) indicate that values (51-53) derived from the earlier experiments were significantly too low.

1.2 POLARMOLECULES

For polar molecules Stockmayer (59) modified L-J (6-n) potential by adding some extra term which corresponds to direct and induced electrostatic terms. It describes well the interaction between those polar molecules for which interactions (dipole-quadropole and higher multipoles) other than dipole-dipole are unimportant just like H_2O and NH_3 molecules. The form of this potential energy function is,

$$\phi = \lambda r^{-S} - C r^{-6} - \mu^2 r^{-3} g \, , \; (S > 6 \;\&\; \mu_1 = \mu_2)$$

where $g = 2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos (\phi)$

or
$$\phi (r, \theta_1, \theta_2, \phi_2 - \phi_1) = 4 \epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] - \frac{\mu_1 \mu_2}{r^3} g (\theta_1, \theta_2, \phi_2 - \phi_1) \qquad (1.26)$$

Where $g(\theta_1, \theta_2, \phi_2 - \phi_1) = 2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos (\phi_2 - \phi_1)$

is the angular dependence of the dipole-dipole interaction. μ_1 and μ_2 are the permanent dipole moment, ϕ_1 and ϕ_2 are the inclinations of the two dipole axes to the intermolecular axis, and ϕ is the azimuthal angle between them as shown in the Fig.(10). This potential (59) has been widely used to represent the effective intermolecular force between a pair of polar molecules. The second virial coefficient was calculated by Pople (60) using a perturbation method for this potential function. Additional examples are summarized by Hirschfelder, Curtiss and Bird (12). No transport-property calculation is available for this potential function. The limitations of this simple model is obvious, however, first, the polar molecules are spherically unsymmetric and therefore, the charge overlap and dispersion forces for a pair of them can only fortuitously be represented by a central force field such as the Lennard-jones potential, second, the nature of charge distribution in a real polar molecule may not be adequately described by a centrally located permanent point dipole alone.

Though the model, that has been used most widely for the interpretation of the properties of polar gases in terms of molecular parameters, is due to Stockmayer (59), yet it is unsatisfactory in many respects e.g.,

(i) The collision diameters obtained from the application of the Stockmayer potential to the second virial coefficients of polar gases are frequently found to be unrealistically small.

(ii) The model predicts only positive values of the dielectric second virial coefficient for all polar gases while there are many polar gases known to show negative dielectric second virial coefficient (61) e.g. $-600\ cm^6/mole^2$ for CH_3F at 50°C (63). It is impossible to explain such negative values on the basis of the Stockmayer model.

(iii) In certain mixtures, large positive enhancements of dielectric second virial coefficient are observed e.g., β (* 10^{-3}) for the mixture $Me_2O + SO_2$ is $45.5\ cm^6/mole^2$ (71), whereas the value calculated from the Stockmayer potential is $3.0\ cm^6/mole^2$.

(iv) For such mixtures, second virial coefficient may have large negative values. For the mixture $Me_2O + SO_2$ second virial coefficient $B_{12} = -1220\ cm^3/mole$, the Stockmayer potential predicts $-470\ cm^3/mole$.

Efforts have been made to extend its validity and to increase the accuracy as well, by several authors by introducing various modifications to the stockmayer potential function. Notable among these are the Buckingham and Pople (62-63), Dymond and Smith (64) Suh and Storvick(65), Sweet and Steele(66-68) and Chang Lyoul Kong (69-70) etc., they are discussed in brief below : -

Buckingham and Pople (62,63) considered the effects of separately adding the induced-dipole energy, the quadropole energy, and an arbitrary and simple version of the molecular shape factor into the stockmayer potential.

Dymond et al. (64) refined the off-centre model, which in conjunction with a hard-sphere central potential could provide a semi-quantitative interpretation of the four points discussed above and was especially successful for mixtures, by the addition of a Lennard-jones central potential, and applied to the compressibility and dielectric virial coefficients of single component systems of polar gases. They found that off-centre dipole model, when applied to the properties of polar gases, has certain advantage over the Stockmayer potential. For almost all polar molecules (CH_3F, NH_3 , $CHCl_3$, AsF_3, CHF_3, Me_2O, SO_2, HCl) the dielectric virial coefficients are negative, or less positive than would be expected from a central dipole model. This provides strong evidence for the applicability of the off-centre dipole model.

Suh and Storvick (65) extended the Kihara core model to include non-spherical polar molecules. The polar contribution to the molecular pair forcefield is represented by a permanent point dipole located at the centre of the core. The molecular cores for the polar molecules were selected on the basis of the cores for the hydrocarbon homomorph of the polar molecules. Pople's perturbation method was then used to obtain an expression for the second virial coefficient of a polar gas. The potential function parameters for nine polar gases ($CHCl_3$, C_2H_5Cl , $CHCl_3$, $CHCl_2F$, CCl_2F_2, CH_3COCH_3, CH_3OH , CH_3F , NH_3) were then evaluated by numerical methods. The second virial coefficient datas.For these gases are well represented by this potential.

Sweet and Steele'(66-68) investigated the interaction between a pair of Linear symmetric molecules using the two simple models . The two models consists of a linear Kihara core potential, and a diatomic model(a model made up by placing two centres of interaction on the axis of each molecule, and the sum of all the pair interactions between the centres on the adjacent molecules is taken as the overall intermolecular potential energy). They extended this model then, to the systems of linear polar molecules by adding simply the usual dipole-dipole interaction to their potential function.

Chang Lyoul Kong (69-70) refined the Stockmayer potential a step further, by taking into consideration a more realistic molecular shape factor and including the induction effect for axially symmetric polar molecules. This model basedon the following assumptions:-

(i) A polar molecule with axial symmetry has two constituent and,

$$U_2 = \mu_0^2 R^{-3} \left[2 \operatorname{Cos} \theta_1 \operatorname{Cos} \theta_2 + \operatorname{Sin} \theta_1 \operatorname{Sin} \theta_2 \operatorname{Cos} (\phi_1 + \phi_2) \right]$$
$$- (\alpha_e \mu_0^2/2)\ R^{-6}\ (3 \operatorname{Cos}^2\theta_1 + 3 \operatorname{Cos}^2\theta_2 + 2) \qquad (1.29)$$

α_e and μ_0 are the mean polarizability and the permanent dipole moment respectively. The terms dipole-quadropole and higher multipoles are neglected. The coordinate system defined in Fig. (10).

This potential was used to evaluate the second virial coefficient of the polar gases (methyl flouride and fluoroform) by a perturbation treatment. But the merit of a potential function cannot be judged simply on the basis of its ability to reproduce the observed second virial coefficients because the ordinary second virial coefficients of polar gases are quite insensitive to the orientation dependences of intermolecular potential functions. So the potential function is further tested by computing the dielectric second virial coefficients (which is very sensitive to the orientation dependences of intermolecular potential functions) for polar gases (CH_3F and CHF_3).

In the light of the above discussion one may say that the search for a true pair potential is still not complete. **Heuristic** approaches are still justified and occasionally rewarding. Even for the inert gases for which L-J potential is fairly good there is a scope for modifications the basis of the cores for the hydrocarbon homomorph of the polar molecules. Pople's perturbation method was then used to obtain an expression for the second virial coefficient of a polar gas. The potential function parameters for nine polar gases ($CHCl_3$, C_2H_5Cl, $CHCl_3$, $CHCl_2F$, CCl_2F_2, CH_3COCH_3, CH_3OH, CH_3F, NH_3) were then evaluated by numerical methods. The second virial coefficient datas.For these gases are well represented by this potential.

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Chang Lyoul Kong (69-70) refined the Stockmayer potential a step further, by taking into consideration a more realistic molecular shape factor and including the induction effect for axially symmetric polar molecules. This model basedon the following assumptions:-

(i) A polar molecule with axial symmetry has two constituent atomic groups located on the molecular axis. Each atomic group, which may be an atom or group of atoms has a centre of Lennard-jones (6:12) interaction.

(ii) The potential energy between a pair of the molecules due to the charge-overlap and dispersion force is the sum of all the pair interactions between all constituent atomc groups on the adjacent molecules.

(iii) The molecules are polarized and each molecule has a point dipole located at its centre. The centre of molecule is assumed to be the centre of gravity.

(iv) There is uncorrelated, free rotation of the molecules on their axes.

The form of the potential energy function is,

$$\phi\,(R,\theta_1,\,\theta_2\,,\,\phi_1,\,\phi_2) = U_1(R,\theta_1,\,\theta_2,\,\phi_1,\,\phi_2)+U_2(R,\theta_1,\,\theta_2,\phi_1,\phi_2)$$

where U_1 is the sum of all the pair interactions between the constituent atomic groups, and U_2 represents the energies of dipole-dipole and dipole-induced dipole interactions and expressed as,

$$U_1 = 4\,\epsilon_{AB}\left[\left(\frac{\sigma_{AB}}{r_{AB}}\right)^{12} - \left(\frac{\sigma_{AB}}{r_{AB}}\right)^{6}\right] + 4\,\epsilon_{ab}\left[\left(\frac{\sigma_{ab}}{r_{ab}}\right)^{12} - \left(\frac{\sigma_{ab}}{r_{ab}}\right)^{6}\right]$$

$$+ 4\,\epsilon_{Ab}\left[\left(\frac{\sigma_{Ab}}{r_{Ab}}\right)^{12} - \left(\frac{\sigma_{Ab}}{r_{Ab}}\right)^{6}\right] + 4\,\epsilon_{aB}\left[\left(\frac{\sigma_{aB}}{r_{aB}}\right)^{12} - \left(\frac{\sigma_{aB}}{r_{aB}}\right)^{6}\right]$$

and,

$$U_2 = \mu_o^2 R^{-3} \left[2 \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos (\phi_1 + \phi_2) \right]$$
$$- (\alpha_e \mu_o^2/2)\, R^{-6} \,(3 \cos^2\theta_1 + 3 \cos^2\theta_2 + 2) \qquad (1.29)$$

α_e and μ_o are the mean polarizability and the permanent dipole moment respectively. The terms dipole-quadropole and higher multipoles are neglected. The coordinate system defined in Fig. (10).

This potential was used to evaluate the second virial coefficient of the polar gases (methyl flouride and fluoroform) by a perturbation treatment. But the merit of a potential function cannot be judged simply on the basis of its ability to reproduce the observed second virial coefficients because the ordinary second virial coefficients of polar gases are quite insensitive to the orientation dependences of intermolecular potential functions. So the potential function is further tested by computing the dielectric second virial coefficients (which is very sensitive to the orientation dependences of intermolecular potential functions) for polar gases (CH_3F and CHF_3).

In the light of the above discussion one may say that the search for a true pair potential is still not complete. Heuristic approaches are still justified and occasionally rewarding. Even for the inert gases for which L-J potential is fairly good there is a scope for modifications by altering any or all of the characteristics of the potential, viz. the hard core , the depth of the bowl and the width and slope of the tail of the bowl. Thus, for example Dymond et al (54) find a numerical potential, as modification, to agree better for some properties of inert gases.

It emerges from this discussion, then , that in search for a real pair-potential while keeping the simplicity of the L-J potential some sort of flexibility in the potential parameters must be so introduced as to conform it to the experimental data. A new line of approach could be to introduce a suitable temperature dependence of the parameters, as mentioned above. We shall return to this topic again in Chapter IV.

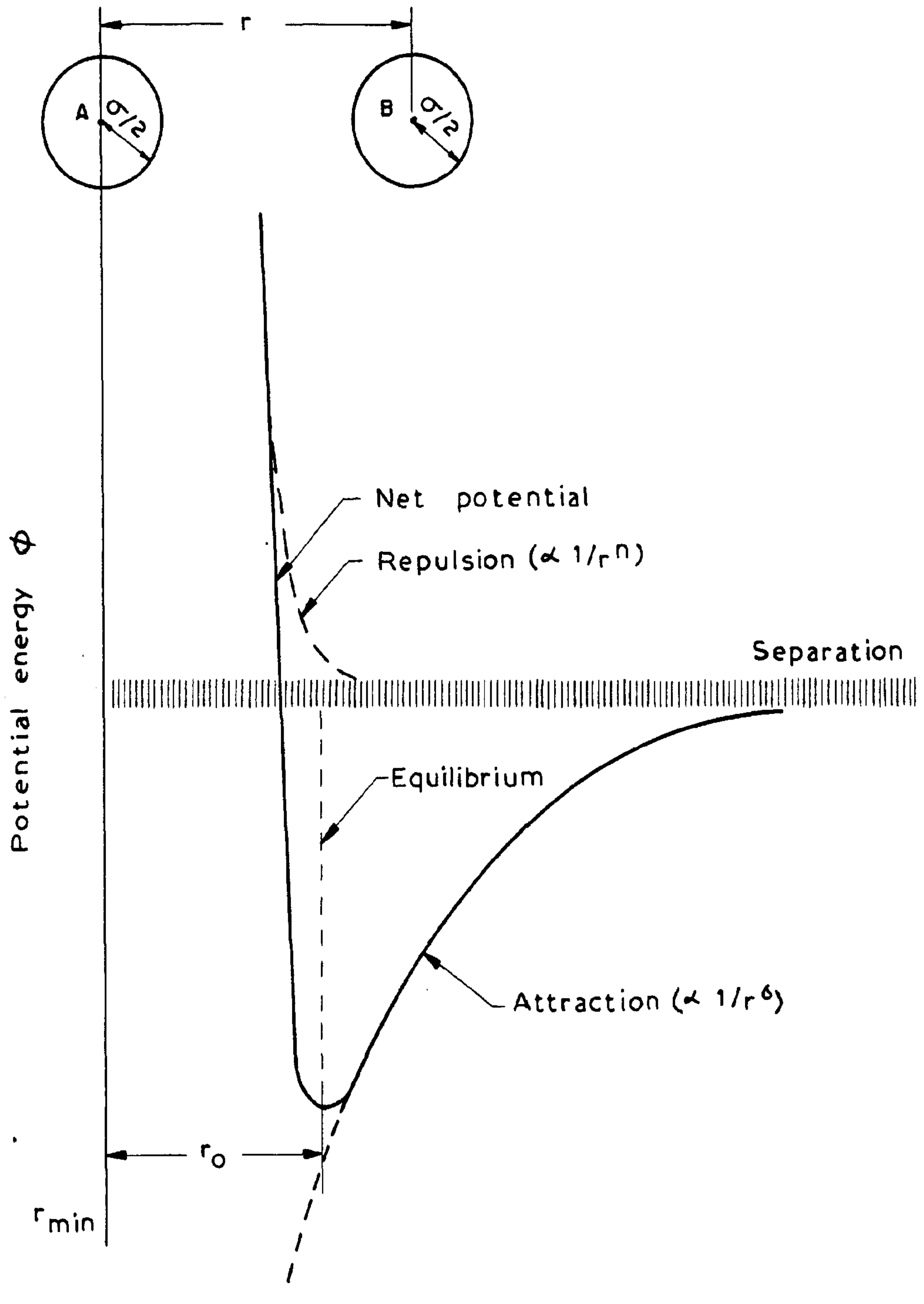

r
A
$\sigma/2$
B
$\sigma/2$
Net potential
Repulsion ($\propto 1/r^n$)
Separation
Potential energy Φ
Equilibrium
Attraction ($\propto 1/r^6$)
r_0
r_{min}

FIG. 1

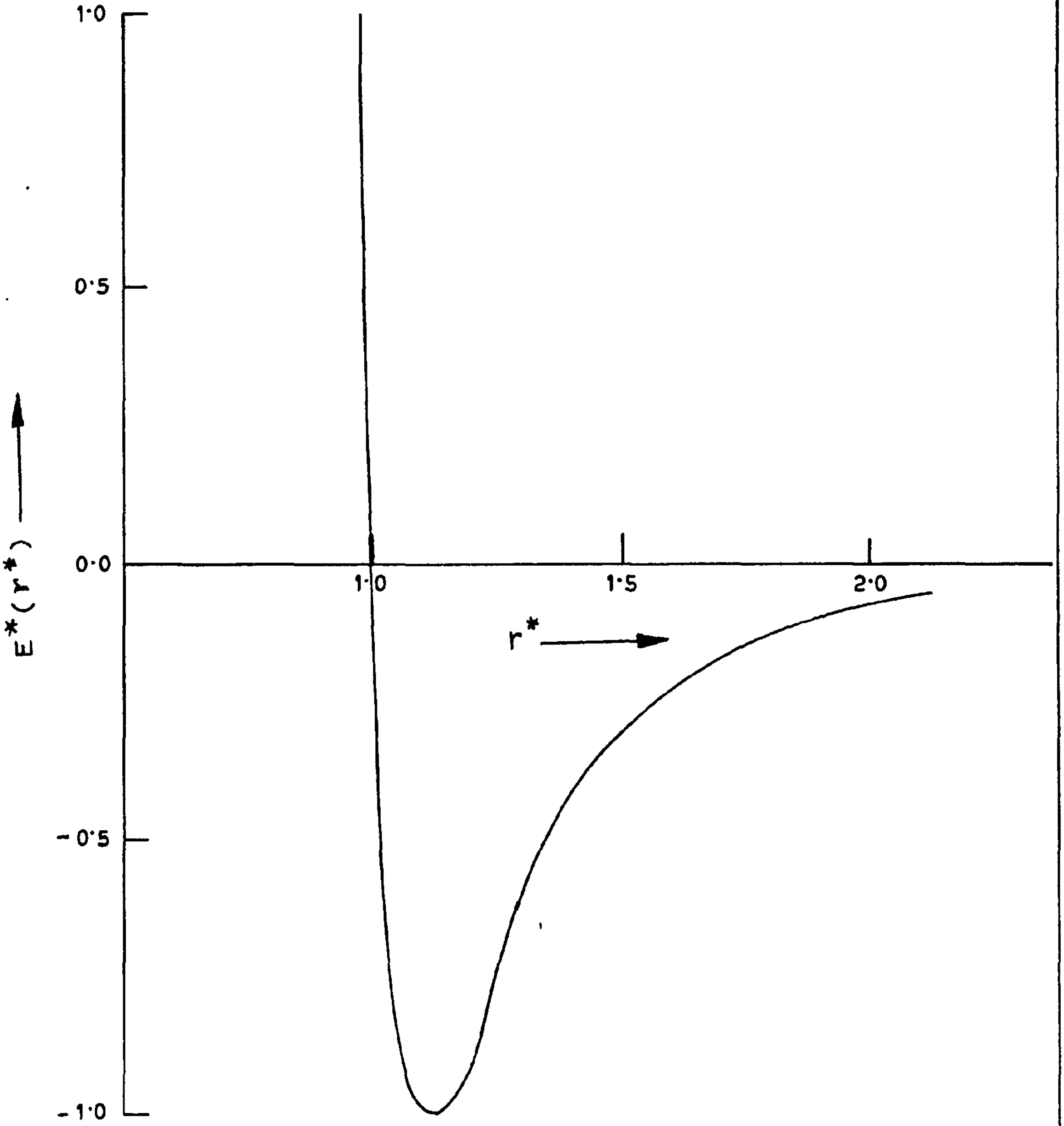


FIG. 2

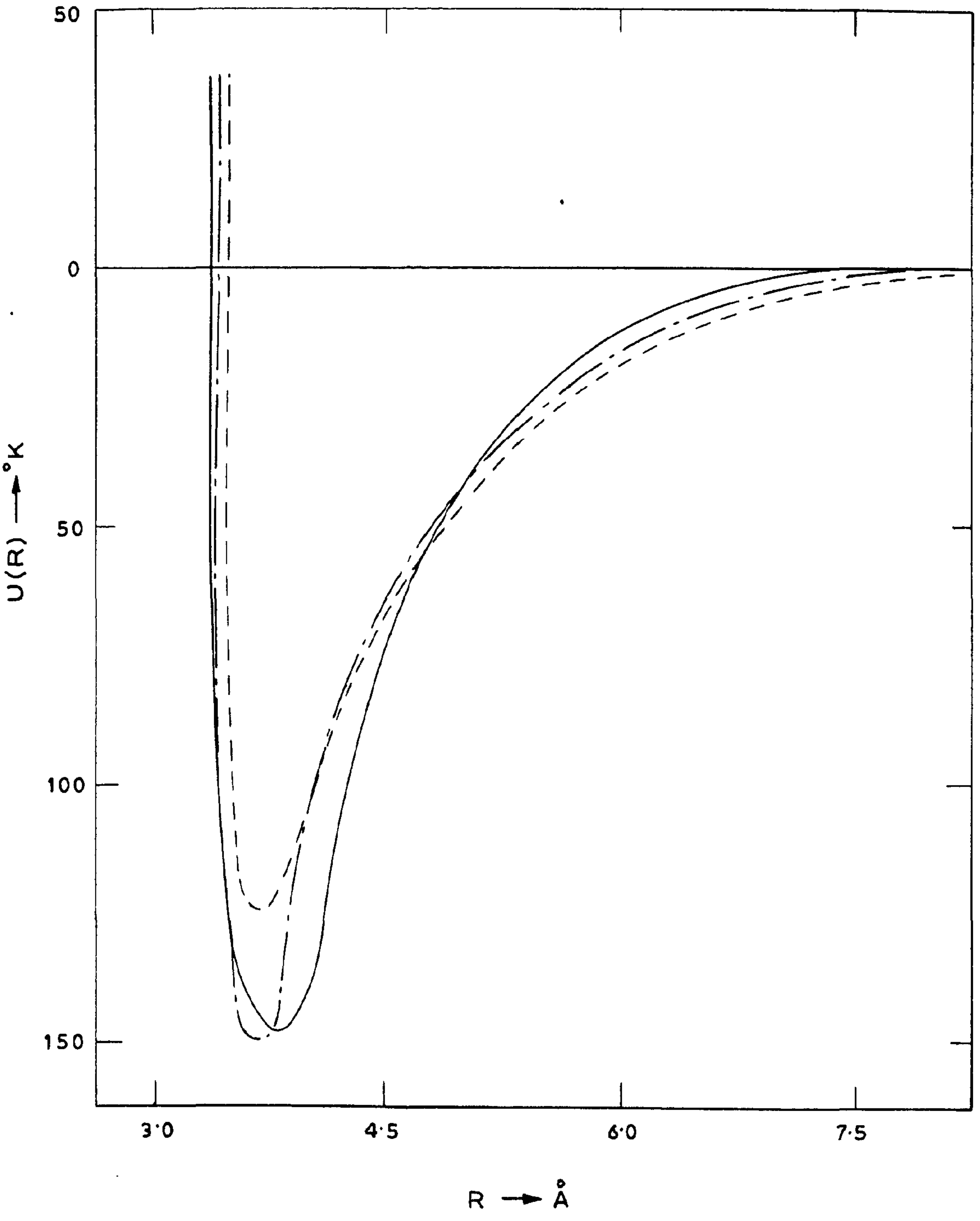


FIG. 3(a)

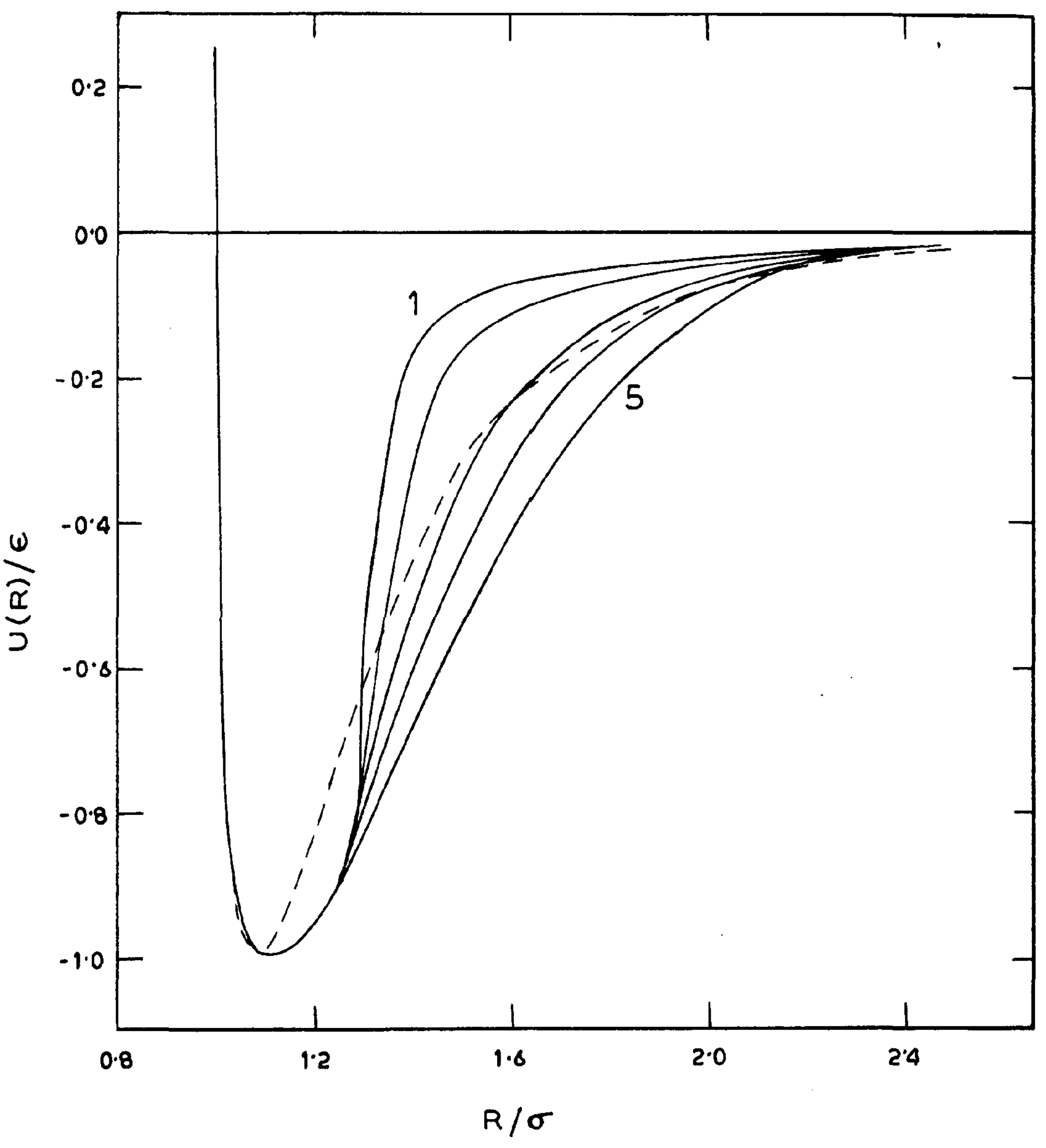


FIG. 3(b)

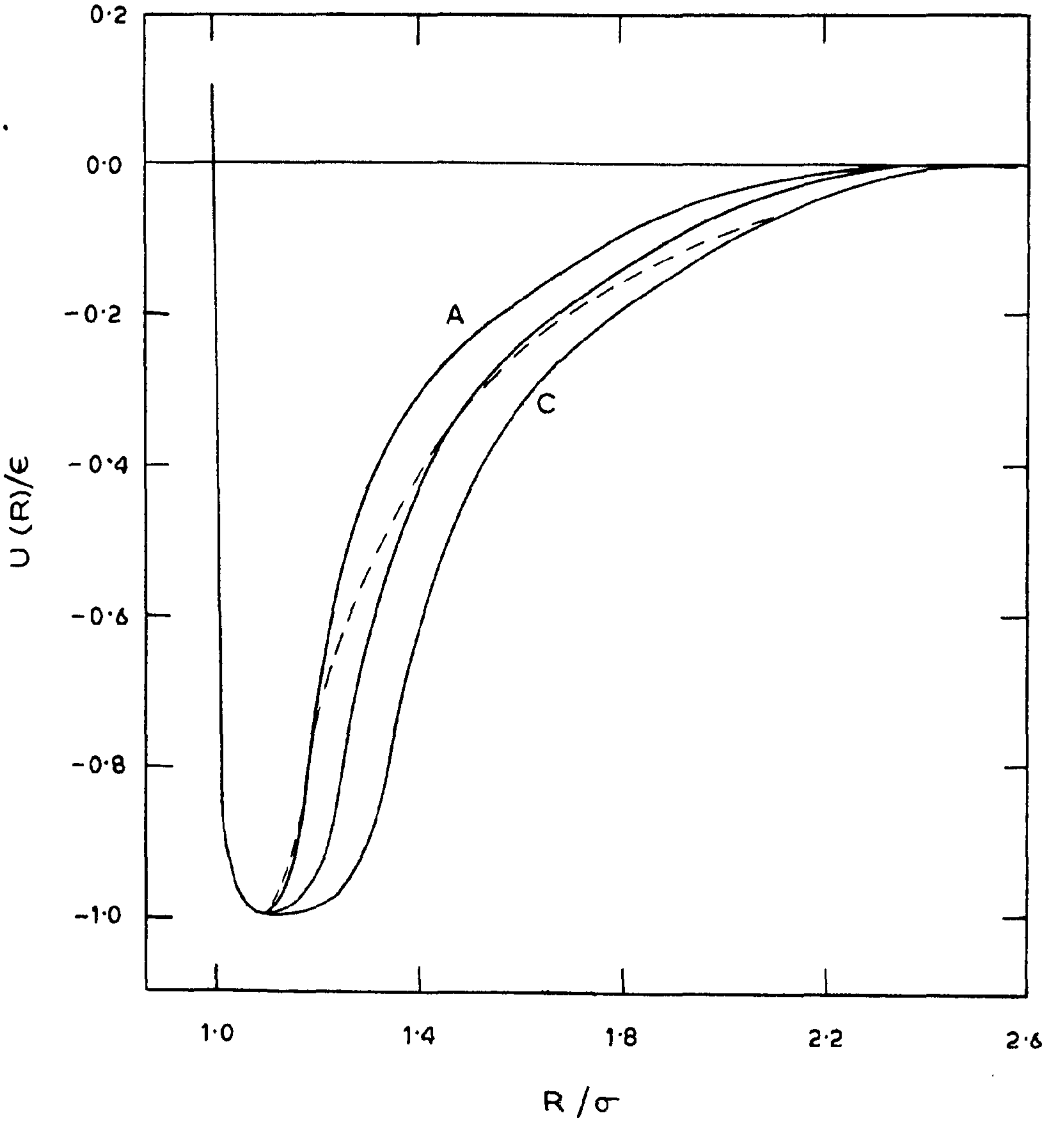


FIG. 3(c)

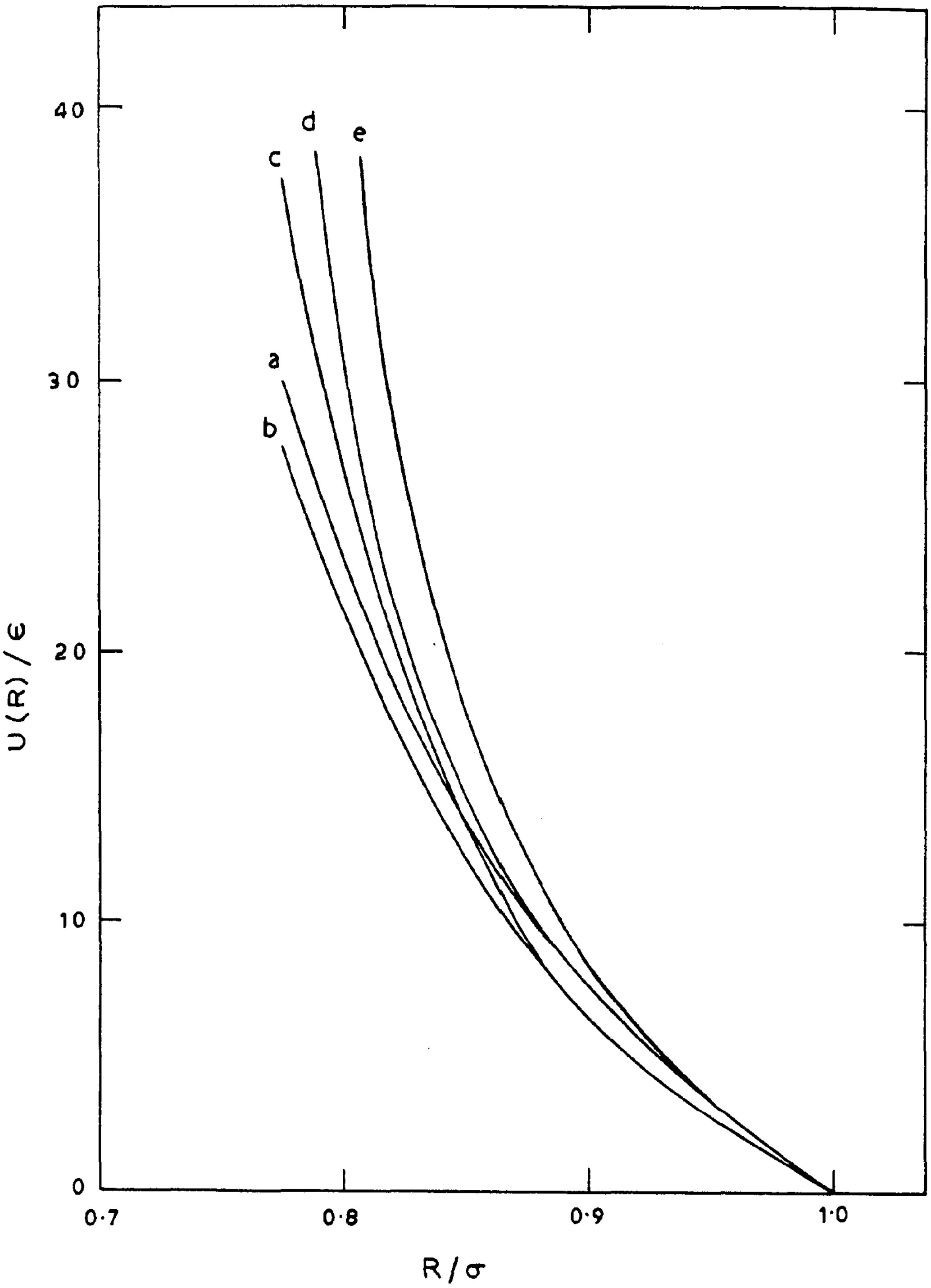


FIG.3(d)

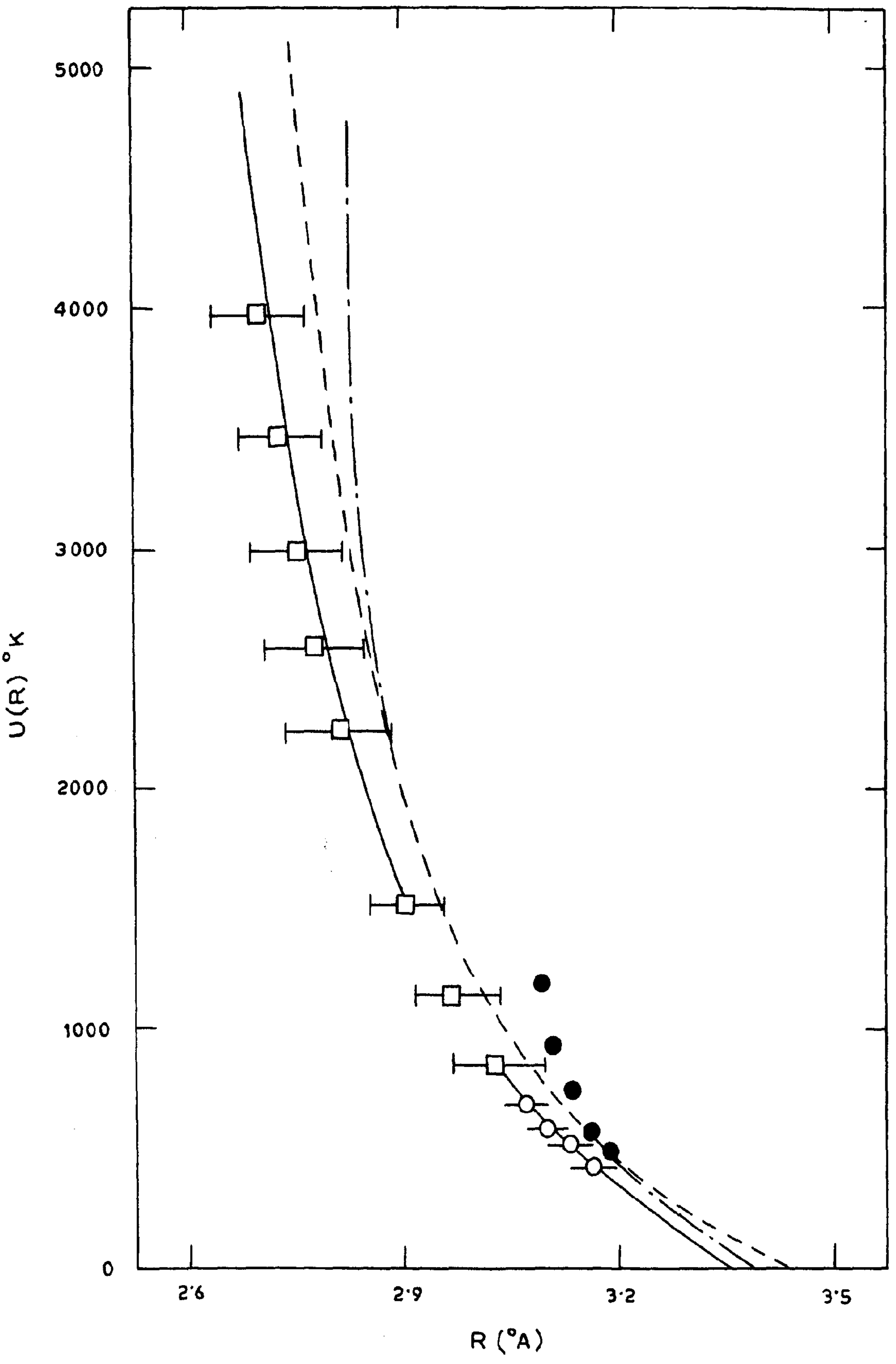


FIG. 3(e)

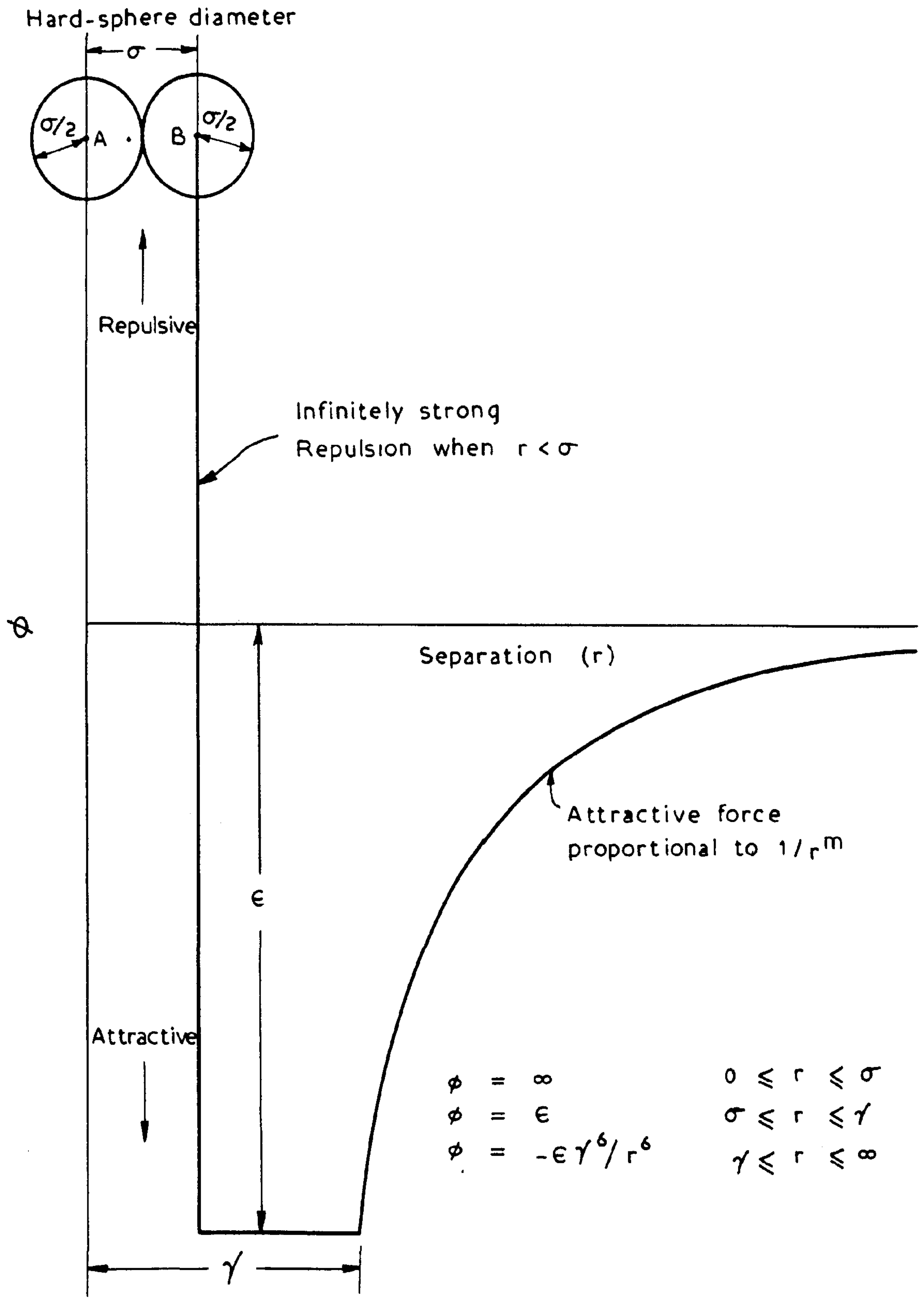

Hard-sphere diameter
σ
σ/2
A
B
σ/2
Repulsive
Infinitely strong
Repulsion when r < σ
Φ
Separation (r)
ε
Attractive force
proportional to $1/r^m$
Attractive
$\phi = \infty \quad 0 \leqslant r \leqslant \sigma$
$\phi = \epsilon \quad \sigma \leqslant r \leqslant \gamma$
$\phi = -\epsilon\gamma^6/r^6 \quad \gamma \leqslant r \leqslant \infty$
γ

FIG. 4

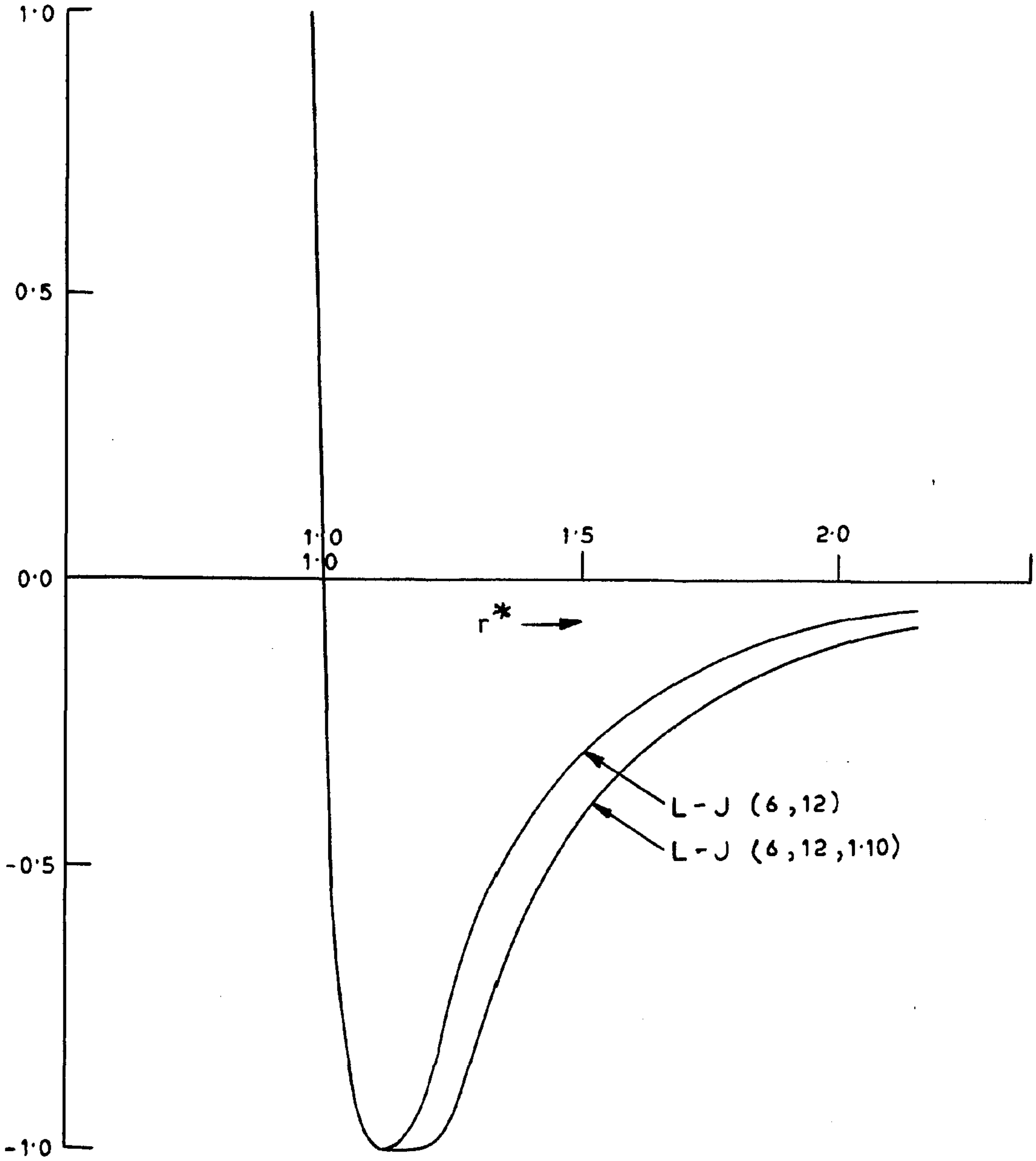
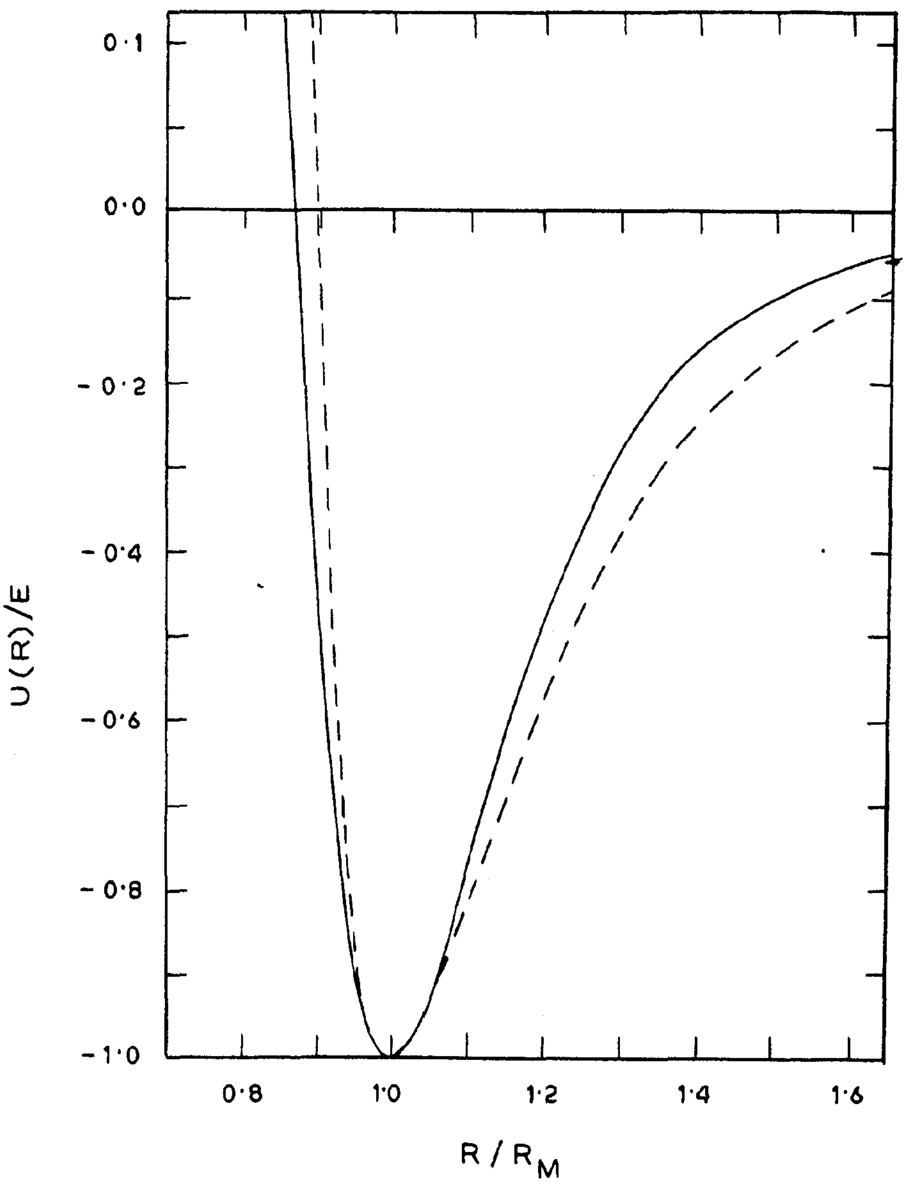


FIG. 5



$$U(R) = \varepsilon\left\{0{\cdot}331\left(\frac{R_M}{R}\right)^{28} - 1{\cdot}2584\left(\frac{R_M}{R}\right)^{24} + 2{\cdot}07151\left(\frac{R_M}{R}\right)^{18} - 1{\cdot}74452\left(\frac{R_M}{R}\right)^{8} - 0{\cdot}39959\left(\frac{R_M}{R}\right)^{6}\right\}$$

FIG. 6

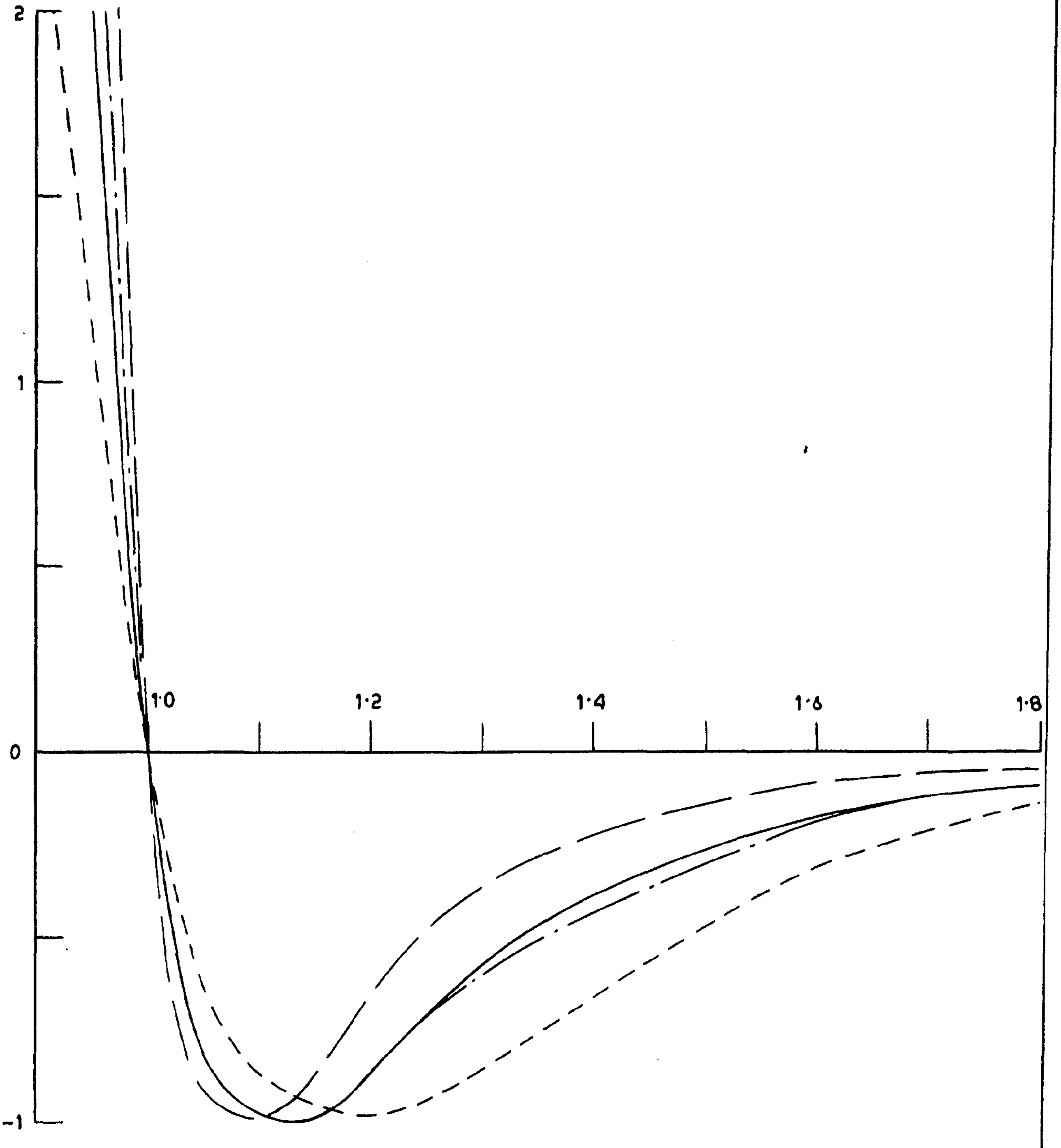


FIG. 7

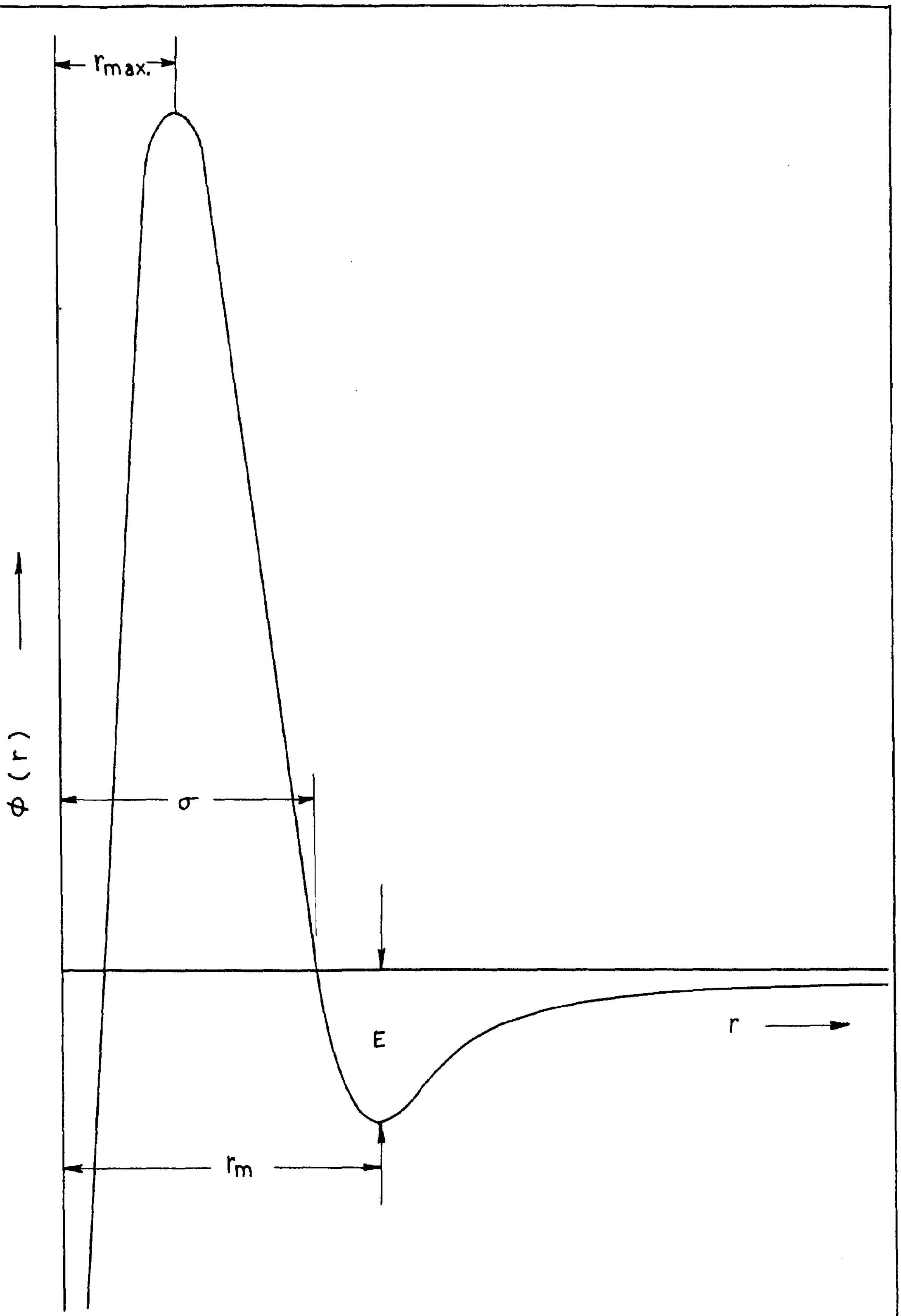


FIG. 8

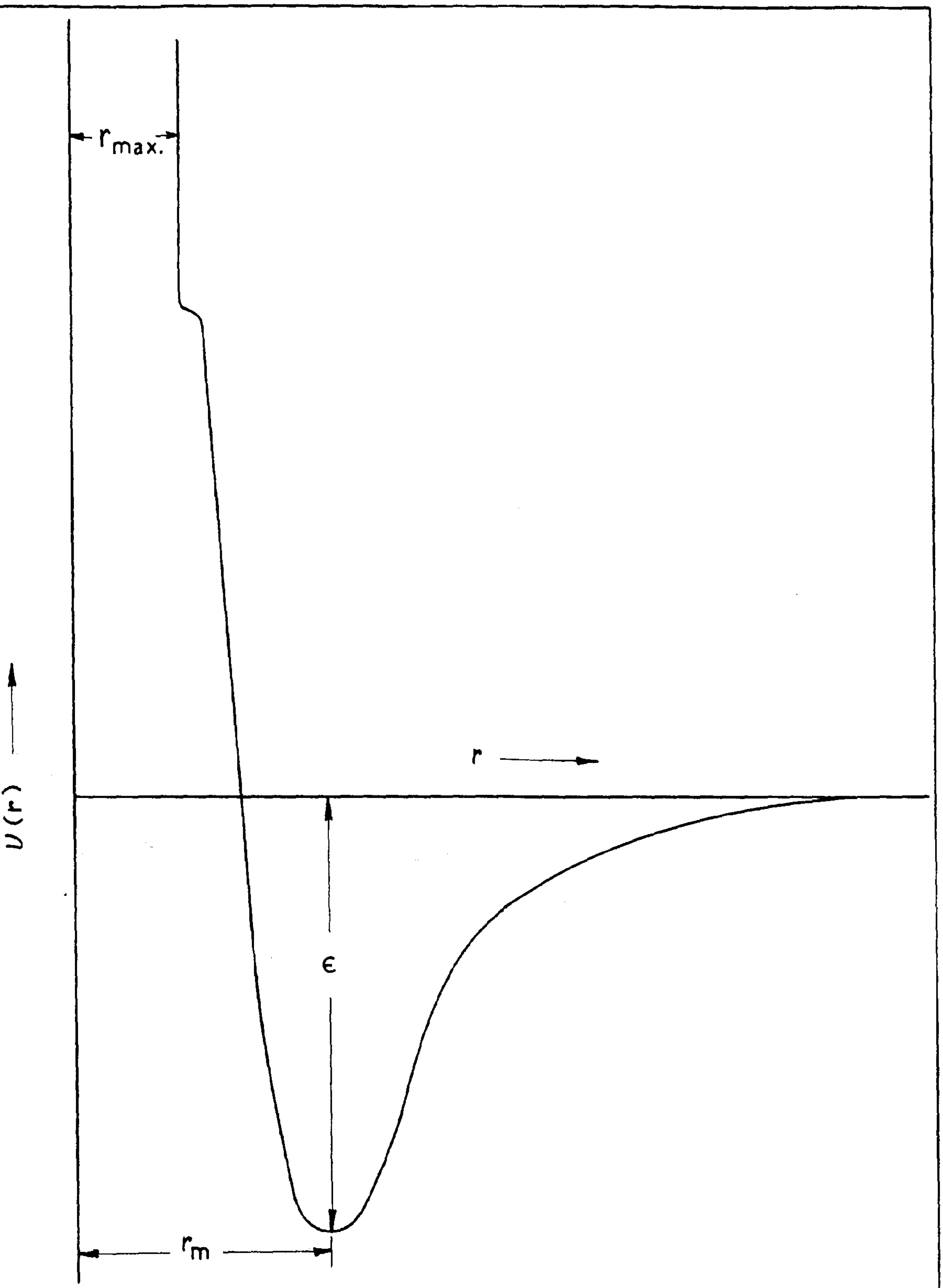


FIG. 9

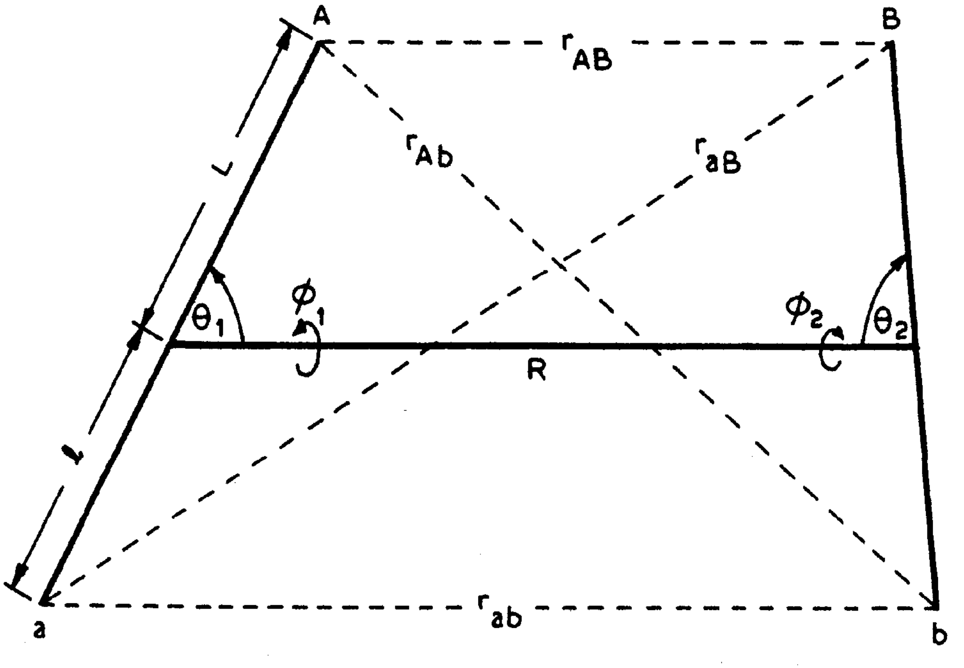


FIG. 10

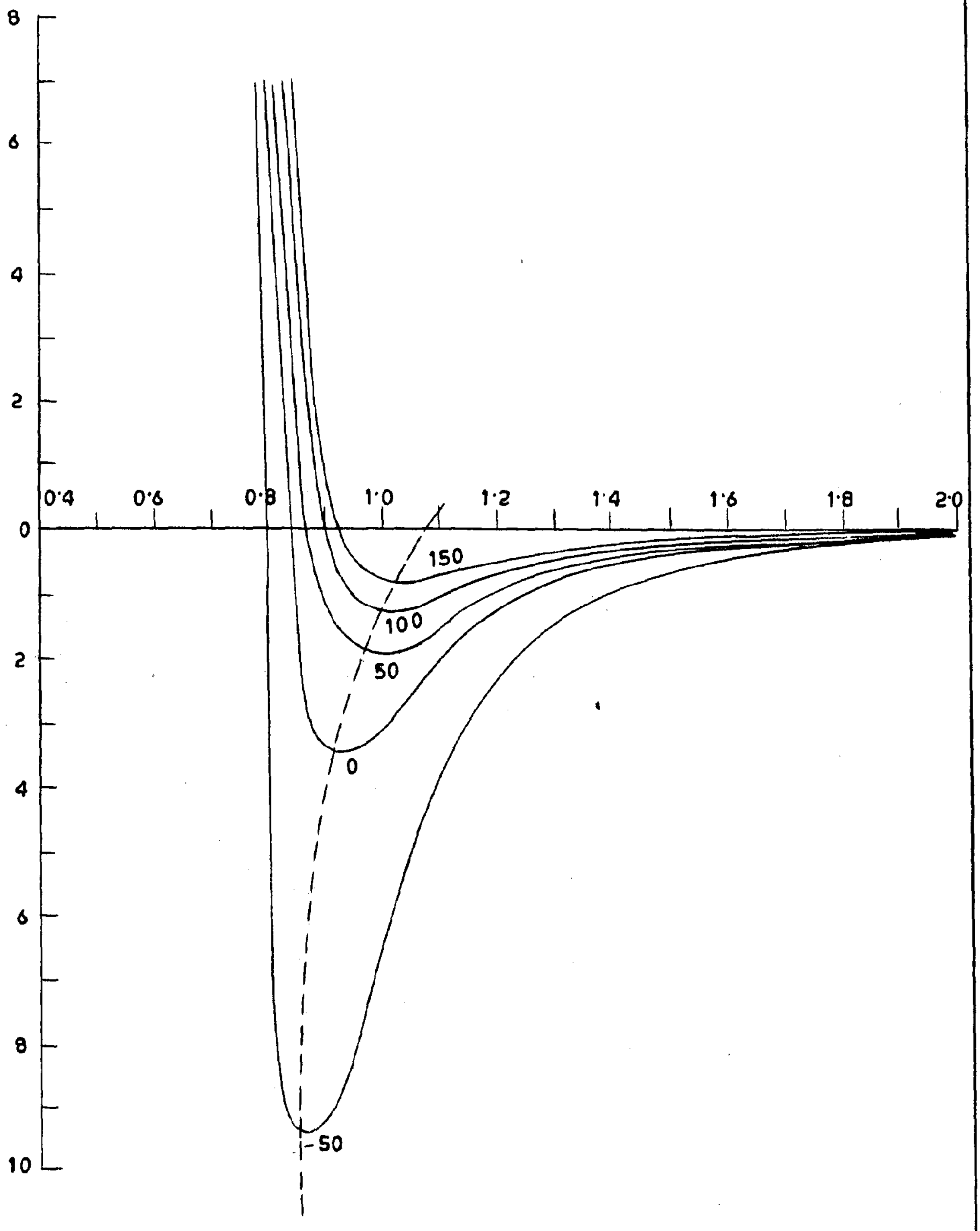


FIG. 11

CHAPTER II

A survey review of expressions for molecular potentials has already been given in Chapter one where it has been brought out that a temperature dependent potential may be [illegible] as a modification to the simple L-J potential form - a good possibility to which attention should be given In this Chapter we discuss this problem from an another point of view: starting from the experimental PVT - data for liquid water we shall see how it can throw light on an "effective" potential for liquid water.

EQUATION OF STATE FOR LIQUID WATER

The equation of state

$$PV = RT$$

for an ideal vapour makes the assumptions

(i) That the molecules are point masses, and

(ii) That they have no mutual interaction.

Van der Waal (73) in 1879 pointed out that at high pressures these assumptions are not valid and for a real gas the equation of state has to consider both the size of the molecules and the mutual interaction between them. So to allow for these two, he replaced V by $(V-b)$, and p by $(p+\frac{a}{V^2})$. He thus obtained the famous equation

$$\left(p + \frac{N^2a}{V^2}\right)(V - Nb) = RT \qquad (2.1)$$

which is known as the Van der Waal's equation. a and b are the Van der Waal's constants. When V is large, both b and a/V^2 become negligible, and equation (2.1) reduces to the simple gas equation, pV = RT.

The attractive force between molecules which give rise to the term (a/V^2) in Van der Waal's equation, is responsible not only for the deviations from the gas laws at high pressures but also for the condensation of gases to liquids. b is the excluded volume and is about four times the aggregate volume occupied by all the molecules in a gram. This equation is valid for gas under high pressures, though not so well for high densities (liquid).

The Eyring equation of state for liquids is a Van der Waal's type equation

$$\left(p + \frac{A(T)}{V^2}\right)\left(V - 0.7816\ b^{1/3}\ V^{2/3}\right) = RT \qquad (2.2)$$

where A is temperature dependent. The term $0.7816\ b^{1/3}\ V^{2/3}$ can be replaced to make it analogous to the Van der Waals equation, by a factor B = B(T) expecting it to be temperature dependent. So the equation of state for liquids becomes

$$\left(p + \frac{A(T)}{V^2}\right)(V - B(T)) = RT \qquad (2.3)$$

Here, in this equation A and B both are temperature dependent. We calculate first the actual values of A(T) and B(T) for the case of water from the known PVT- data (75) for liquid water. The values of A(T) and B(T) have been determined by solving the equation for known values of p, V, and T applying the Newton - Raphson method, see Appendix VI., using an electronic computer. The values of A(T) and B(T) so obtained are illustrated graphically in Figs (12) and (13). PVT behaviour of liquid water is illustrated in Fig. (14).

2.2 INTERPRETATION OF A(T) and B(T) FOR LIQUID WATER

To interpret A(T) and B(T) in terms of molecular structure we start from the statistical - mechanical derivation of the equation of state. The partition function for a real gas will be written as :

$$Z_N = \frac{1}{h^N}\frac{1}{N!}\iiint \cdots \int \exp\left[-\frac{(p_1^2 + p_2^2 + \ldots + p_N^2)}{2\,m\,k\,T} + \frac{\phi(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N)}{kT}\right] d\vec{p}_1 \cdot d\vec{p}_2 \ldots d\vec{p}_N \ldots d\vec{r}_1\, d\vec{r}_2 \ldots d\vec{r}_N \qquad (2.4)$$

where ϕ is the total interaction energy of the system which depends on the positions $\vec{r}_1$, $\vec{r}_2$, ... $\vec{r}_N$ of the molecules. Since ϕ depends only on position coordinates, we can write

$$Z_N = \frac{1}{h^N}\frac{1}{N!} \int \cdots \int \exp\left(-\frac{p_1^2 + p_2^2 + \ldots + p_N^2}{2mkT}\right) d\vec{p}_1\, d\vec{p}_2 \ldots d\vec{p}_N \, * \int \cdots \int \exp\left[-\frac{\phi(\vec{r}_1 . \vec{r}_2 \ldots \vec{r}_N)}{kT}\right] d\vec{r}_1\, d\vec{r}_2 \ldots d\vec{r}_N \qquad (2.5)$$

Then, evaluating the first integral and writing Q_N for the second we get

$$Z_N = \frac{1}{N!} \left(\frac{mkT}{h^2} \right)^{\frac{3N}{2}} Q_N \qquad (2.6)$$

Since Q_N is the only part of Z_N which depends on volume the formula for the pressure simplifies to

$$p = NkT \frac{\partial}{\partial v} (\ln Q_N) \qquad (2.7)$$

where,

$$Q_N = \iiint\limits_V \cdots \int \exp \left[- \frac{\phi(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N)}{kT} \right] d\vec{r}_1 \, d\vec{r}_2 \ldots d\vec{r}_N$$

$$= \prod_{i \neq j} \int \exp \left\{ - \frac{\Phi(r_{ij})}{kT} \right\} d\bar{r}_{ij}$$

or, because it has been reduced to two-particle potential, droping the subscripts, we write

$$Q_N = \prod \int \exp \left(- \frac{\phi(r)}{kT} \right) dr \qquad (2.8)$$

where r is the distance between two particles. To evaluate it, we introduce a new function

$$f(r) = \exp \left[- \frac{\Phi(r)}{kT} \right] - 1 .$$

So, we can write,

$$Q_N = \int \prod (1 + f_{ik}) \, dr_{ik}$$

or $Q_N = V^N + \frac{N^2}{2} \int d\vec{r}_1 \ldots d\vec{r}_{i-1} \; d\vec{r}_{i+1} \; d\vec{r}_{k-1} d\vec{r}_{k+1} \ldots d\vec{r}_N \int f_{ik} \; d\vec{r}_i \; d\vec{r}_k$

$$\therefore \quad Q_N = V^N + \frac{N^2}{2} V^{N-2} \int f_{ik} \; d\vec{r}_i \; d\vec{r}_k \qquad (2.10)$$

But, $f_{ik} d\vec{r}_i d\vec{r}_k = \int (e^{\frac{-\phi(r_{ik})}{kT}} - 1) \; d\vec{r}_i \; d\vec{r}_k$

$$\ldots\ldots = 4\pi V \int_0^\infty (e^{\frac{-\phi(r)}{kT}} - 1) r^2 dr$$

On placing the proper limits, and introducing

$\beta = 4\pi \int_0^\infty (e^{-\phi(r)/kT} - 1) \; r^2 dr$, the first irreducible integral.

Therefore from Equation (2.10), we get for configurational integral

$$\boxed{Q_N = V^N \left(1 + \frac{N^2}{2V} \beta\right)} \qquad (2.11)$$

$$Z_N = \frac{(2\pi mkT)^{3N/2}}{N! \, h^{3N}} V^N \left(1 + \frac{N^2}{2V} \beta\right)$$

And the equation of state as

$$p \cong \frac{NkT}{V} - \frac{N^2 kT}{2V^2} \beta \qquad (2.12)$$

Van der waal's equation of state, on the other hand is

$$p = \frac{NkT}{V - Nb} - \frac{N^2 a}{V^2}$$

$$\cong \frac{NkT}{V} + \frac{N^2 kTb}{V^2} - \frac{N^2 a}{V^2} \qquad (2.13)$$

Then, evaluating the first integral and writing Q_N for the second we get

$$Z_N = \frac{1}{N!} \left(\frac{mkT}{h^2} \right)^{\frac{3N}{2}} Q_N \qquad (2.6)$$

Since Q_N is the only part of Z_N which depends on volume the formula for the pressure simplifies to

$$p = NkT \frac{\partial}{\partial v} (\ln Q_N) \qquad (2.7)$$

where,

$$Q_N = \iiint_V \cdots \int \exp \left[- \frac{\phi (\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N)}{kT} \right] d\vec{r}_1 \, d\vec{r}_2 \, .. \, d\vec{r}_N$$

$$= \prod_{i \neq j} \int \exp \left\{ - \frac{\phi(r_{ij})}{kT} \right\} d\bar{r}_{ij}$$

or, because it has been reduced to two-particle potential, droping the subscripts, we write

$$Q_N = \prod \int \exp \left(- \frac{\phi(r)}{kT} \right) dr \qquad (2.8)$$

where r is the distance between two particles. To evaluate it, we introduce a new function

$$f(r) = \exp \left[- \frac{\phi(r)}{kT} \right] - 1 \quad .$$

So, we can write,

$$Q_N = \int \prod (1 + f_{ik}) \, dr_{ik}$$

or, on expanding the product

$$Q_N = \int (1 + \Sigma f_{ik} + \Sigma f_{ij} f_{k\ell} + \ldots) dr \qquad (2.9)$$

Now, if there is no interaction between the particles, $f(r)=0$ and the first term in the series (2.9) corresponds to the contribution in Q_N from separate non-interacting particles, as in an ideal gas. The terms of the first sum in the series (2.9) corresponds to the contribution from the interaction of all possible pairs one by one. The terms of the second sum in the series (2.9) describe the contributions in Q_N from the simultaneous interaction of two pairs of particles in the system, or the contributions from the interaction of triplets of particles. Analogously, the successive unwritten terms of the series (2.9) describe the interactions of triplets, quadruplets, ... etc. of particles.

In the case of a real gas, it is assumed that clusters of molecules of more than two are not likely, so that it is sufficient to consider only the first two terms in the expansion, equation (2.9). There will be $\frac{N(N-1)}{2} \cong \frac{N^2}{2}$ pairs of molecules. Furthermore, for a short-range potential $\Phi(r)$, the function $f(r)$ is appreciably different from zero only in the small region of influence of the intermolecular forces.

Therefore,

$$Q_N = \left(1 + \frac{N^2}{2} f_{ik}\right) \vec{dr_i} \ldots \vec{dr_N}$$

or $$Q_N = V^N + \frac{N^2}{2} \int \vec{dr}_1 \ldots \vec{dr}_{i-1} \; \vec{dr}_{i+1} \; \vec{dr}_{k-1} \vec{dr}_{k+1} \ldots \vec{dr}_N \int f_{ik} \, \vec{dr}_i \, \vec{dr}_k$$

$$\therefore \quad Q_N = V^N + \frac{N^2}{2} V^{N-2} \int f_{ik} \, \vec{dr}_i \, \vec{dr}_k \qquad (2.10)$$

But, $$f_{ik} \vec{dr}_i \vec{dr}_k = \int \left(e^{-\frac{\phi(r_{ik})}{kT}} - 1 \right) \vec{dr}_i \, \vec{dr}_k$$

$$\ldots\ldots = 4 \pi V \int_0^\infty \left(e^{-\frac{\phi(r)}{kT}} - 1 \right) r^2 dr$$

On placing the proper limits, and introducing

$\beta = 4 \pi \int_0^\infty \left(e^{-\phi(r)/kT} - 1 \right) r^2 dr$, the first irreducible integral.

Therefore from Equation (2.10), we get for configurational integral

$$\boxed{Q_N = V^N \left(1 + \frac{N^2}{2V} \beta \right)} \qquad (2.11)$$

$$Z_N = \frac{(2 \pi m k T)^{3N/2}}{N! \, h^{3N}} V^N \left(1 + \frac{N^2}{2V} \beta \right)$$

And the equation of state as

$$p \cong \frac{NkT}{V} - \frac{N^2 kT}{2V^2} \beta \qquad (2.12)$$

Van der waal's equation of state, on the other hand is

$$p = \frac{NkT}{V - Nb} - \frac{N^2 a}{V^2}$$

$$\cong \frac{NkT}{V} + \frac{N^2 kTb}{V^2} - \frac{N^2 a}{V^2} \qquad (2.13)$$

Comparing the equations (2.12) and (2.13) , we get,

$$\frac{\beta}{2} = \frac{a}{kT} - b \tag{2.14}$$

Now because ,

$$\beta = 4\pi \int_{0}^{\infty} (e^{-\phi/kT} -1) r^2 dr$$

$$= 4\pi \int_{0}^{\sigma} (e^{-\phi/kT} - 1) r^2 dr + \int_{\sigma}^{\infty} (e^{-\phi/kT} -1) r^2 dr$$

For a simple calculation of a and b in terms of the potential parameters, we take the simplified from of ϕ (r),

for $0 < r < \sigma$, $\phi(r) = \infty$, $e^{-\phi/kT} = 0$

$$\therefore \quad \beta = - 4\pi \int_{0}^{\sigma} r^2 dr + 4\pi \int_{\sigma}^{\infty} \left(- \frac{\phi(r)}{kT} + \frac{1}{2!} \left(\frac{\phi(r)}{kT}\right)^2 + .. \right) r^2 dr \tag{2.15}$$

Comparing equations (2.14) and (2.15), we get,

$$\left. \begin{aligned} b &= \frac{2\pi}{3} \sigma^3 \\ a &= 2\pi \int_{\sigma}^{\infty} |\phi(r)| \, r^2 \, dr \end{aligned} \right\} \tag{2.16}$$

The above derivation is fairly good for a real dilute gas, where clusters of more than two particles can be assumed non-existant. For liquids, however, this assumption is not correct. Since these constants in Eyring equation (2.3), on calculation turn out to be function of temperature, as in the previous section, therefore, for a liquid we can write

$$B = \frac{2}{3} \Sigma^3 \text{ and } A \mp 2 \int_{\Sigma}^{\infty} |\phi(r)| \, r^2 dr$$

logic does not suffer. Such a concept is not alien. A "flickering cluster model (76,77)" already exists for liquid state. In fact, the neutron scattering experiments do reveal a short range arrangement of molecules inside liquids.

Suppose g molecules, at a certain temperature, unite to form one drop on an average such that the liquid is treated to consist of $\frac{N}{g} = n$ drops now. The energy of clusterization of these particles

$$\varepsilon_{c\ell} = -\alpha g + \beta g^{2/3} + g kT \qquad (2.18)$$

where the first term is the condensation term which for a supersaturated vapour is given by $\alpha = \text{const.} * \ln S$ (S is the ratio of supersaturation), the second term is the surface tension and the third term is the vibrational energy of molecules inside the drop. Thus $\varepsilon_{c\ell}$ can be assumed constant for a certain temperature. If we denote by $\Phi(r_{ij})$ the interaction energy of two drops, and by p the momentum of the translatory motion of drop, then we can write for the energy of each drop as

$$E = \frac{p^2}{2M} + \varepsilon_{c\ell} + \Phi \qquad (2.19)$$

(Where M is the mass of the drop) and the partition function for the liquid will be, Comparing the equations (2.12) and (2.13) , we get,

$$\frac{\beta}{2} = \frac{a}{kT} - b \tag{2.14}$$

Now because ,

$$\beta = 4\pi \int_0^\infty \left(e^{-\phi/kT} - 1\right) r^2 dr$$

$$= 4\pi \int_0^\sigma \left(e^{-\phi/kT} - 1\right) r^2 dr + \int_\sigma^\infty \left(e^{-\phi/kT} - 1\right) r^2 dr$$

For a simple calculation of a and b in terms of the potential parameters, we take the simplified from of $\phi(r)$,

for $0 < r < \sigma$, $\phi(r) = \infty$, $e^{-\phi/kT} = 0$

$$\therefore \quad \beta = -4\pi \int_0^\sigma r^2 dr + 4\pi \int_\sigma^\infty \left(-\frac{\phi(r)}{kT} + \frac{1}{2!}\left(\frac{\phi(r)}{kT}\right)^2 + \ldots\right) r^2 dr \tag{2.15}$$

Comparing equations (2.14) and (2.15), we get,

$$\left.\begin{aligned} b &= \frac{2\pi}{3}\sigma^3 \\ a &= 2\pi \int_\sigma^\infty |\phi(r)|\, r^2\, dr \end{aligned}\right\} \tag{2.16}$$

The above derivation is fairly good for a real dilute gas, where clusters of more than two particles can be assumed non-existant. For liquids, however, this assumption is not correct. Since these constants in Eyring equation (2.3), on calculation turn out to be function of temperature, as in the previous section, therefore, for a liquid we can write

$$B = \frac{2}{3} \Sigma^3 \text{ and } A \doteqdot 2 \int_\Sigma^\infty |\phi(r)|\, r^2 dr$$

where Σ is the constant for liquid corresponding to σ for gas. Then, in so far as A and B are functions of temperature Σ and , ε , the depth of the potential $\Phi(r)$ appropriate for liquid should also be temperature dependent :

$$\Sigma = \Sigma(T) \; ; \quad \varepsilon = \varepsilon(T)$$

This would be the situation if cluster integrals in the expression of equation (2.9) could be neglected as in gas. But as we know they should not be: because of the large density the clusters are no less likely to be formed than the pairs. On the other hand, since a Van der waal form of equation of state, equation (2.9), describes the liquid very well, it should be possible to introduce some sort of a decoupling device (mathematico-physical) which will enable Q_N to be evaluated in a way analogous to the real gas case.

For this to do, let us imagine the liquid as a real gas of minute molecular "drops" of the liquid. These drops - the molecular aggregates - are assumed to play the same role in the liquid as the molecules in the gas. They have their internal energy of formation and they move inside the liquid as one identity. The 'drops' are not necessarily permanent structures, they may be transient to any degree. So long as such a situation prevails, that at any moment inside the liquid, on an average, if somewhere some 'drops' break-off an equal number of them form somewhere else, the logic does not suffer. Such a concept is not alien. A "flickering cluster model (76,77)" already exists for liquid state. In fact, the neutron scattering experiments do reveal a short range arrangement of molecules inside liquids.

Suppose g molecules, at a certain temperature, unite to form one drop on an average such that the liquid is treated to consist of $\frac{N}{g} = n$ drops now. The energy of clusterization of these particles

$$\varepsilon_{c\ell} = -\alpha g + \beta g^{2/3} + g kT \qquad (2.18)$$

where the first term is the condensation term which for a supersaturated vapour is given by $\alpha = \text{const.} * \ell n\, S$ (S is the ratio of supersaturation), the second term is the surface tension and the third term is the vibrational energy of molecules inside the drop. Thus $\varepsilon_{c\ell}$ can be assumed constant for a certain temperature. If we denote by $\Phi(r_{ij})$ the interaction energy of two drops, and by p the momentum of the translatory motion of drop, then we can write for the energy of each drop as

$$E = \frac{p^2}{2M} + \varepsilon_{c\ell} + \Phi \qquad (2.19)$$

(Where M is the mass of the drop) and the partition function for the liquid will be,

$$Z_{liq} = \frac{1}{h^n} \frac{1}{n!} \int \exp\left(-\frac{E}{kT}\right) \vec{dp}_1 \vec{dp}_2 \ldots \vec{dp}_n \cdot \vec{dq}_1 \vec{dq}_2 \ldots \vec{dq}_n \qquad (2.10).$$

Then, on writing $e^{-\frac{\varepsilon_d}{kT}} = C(T, g)$, a constant not depending on position or momentum of the drop, and evaluating the momentum integral, we get,

$$Z_{liq} = \frac{1}{n!} \left(\frac{MkT}{h}\right)^{\frac{3n}{2}} \left[C(T,g)\right]^n Q_{liq} \qquad (2.21)$$

where,

$$Q_{liq} = \int \exp\left(-\frac{\Phi(\vec{q}_1 \vec{q}_2 \ldots \vec{q}_n)}{kT}\right) \vec{dq}_1 \vec{dq}_2 \ldots \vec{dq}_n \qquad (2.22)$$

Now proceeding as in deriving equation (2.7) to (2.11) with the assumptions :

1. The drop-pair interaction potential is similar in nature to that of the molecules.

2. The likelyhood of three or more drops coming within the appreciable interaction range is negligible small, we get finally,

$$Q_{liq} = 4\pi V \int_0^{\infty} \left(e^{-\frac{\Phi}{kT}} - 1\right) q^2 \, dq$$

or

$$Q_{liq} = V^n \left(1 + \frac{n^2}{2V} \beta_{liq}\right) \qquad (2.23)$$

and

$$p = \frac{\partial}{\partial V} (\ln Q_{liq})$$

Such that $A(T) = 2\pi \int_0^{\infty} |\Phi(q)| \, q^2 dq = \frac{2\pi}{3} \alpha^3 \Sigma^3 \varepsilon$

$$B(T) = \frac{2\pi}{3} \Sigma^3$$

Where Σ is the radius of the drop and ε is the depth of the potential well in Φ, the drop-potential. It is clear, then that

$$\Sigma = \Sigma(T) \quad \text{and} \quad \varepsilon = \varepsilon(T)$$

Φ, it must be emphasized, is not a molecular potential, and in so far as it has been introduced as a decoupling device it is an " effective potential" involving the parameters $\Sigma(T)$ and $\varepsilon(T)$

We shall assume the nature of Φ to be the same as that of the L-J potential, only the parameters being different.

$$\Phi(r,tT) = \frac{\varepsilon}{\left(1 - \frac{m}{n}\right)} \left[\frac{m}{n} \left(\frac{\Sigma}{r} \right)^{n} - \left(\frac{\Sigma}{r} \right)^{m} \right] \tag{2.25}$$

where ε is the potential - well's depth and Σ is the radius of the drop as a hard-core. ε and Σ are then known from the values of $A(T)$ and $B(T)$.

Thus,

$$\varepsilon = \varepsilon(T) = \text{Const} \times \frac{A(T)}{B(T)}$$

$$\Sigma = \Sigma(T) = \left[\frac{3\pi}{2} B(T) \right]^{1/3}$$

With these values the liquid partition function (Equation(2.21)) is determined, except for g which must be fixed by comparing the property calculated with its experimental value.

The concept of effective pair potential is not entirely new. Recently Rowlinson et al (78) has also considered a effective pair potential which leads to correct distribution and correlation functions. These effective potentials depend on both density and temperature, but they do not have the free-energy character of some kinds of temperature dependent energy levels . They are to be regarded only as computational devices.

Rowlinson's treatment of the effective pair potential is although of general nature, is not easily amendble to experimental determination of the potential. In the present treatment the parameters of the effective drop potential are correctly known from the values of A(T) and B(T), which, in their turn have been obtained from the experimental PVT - data.

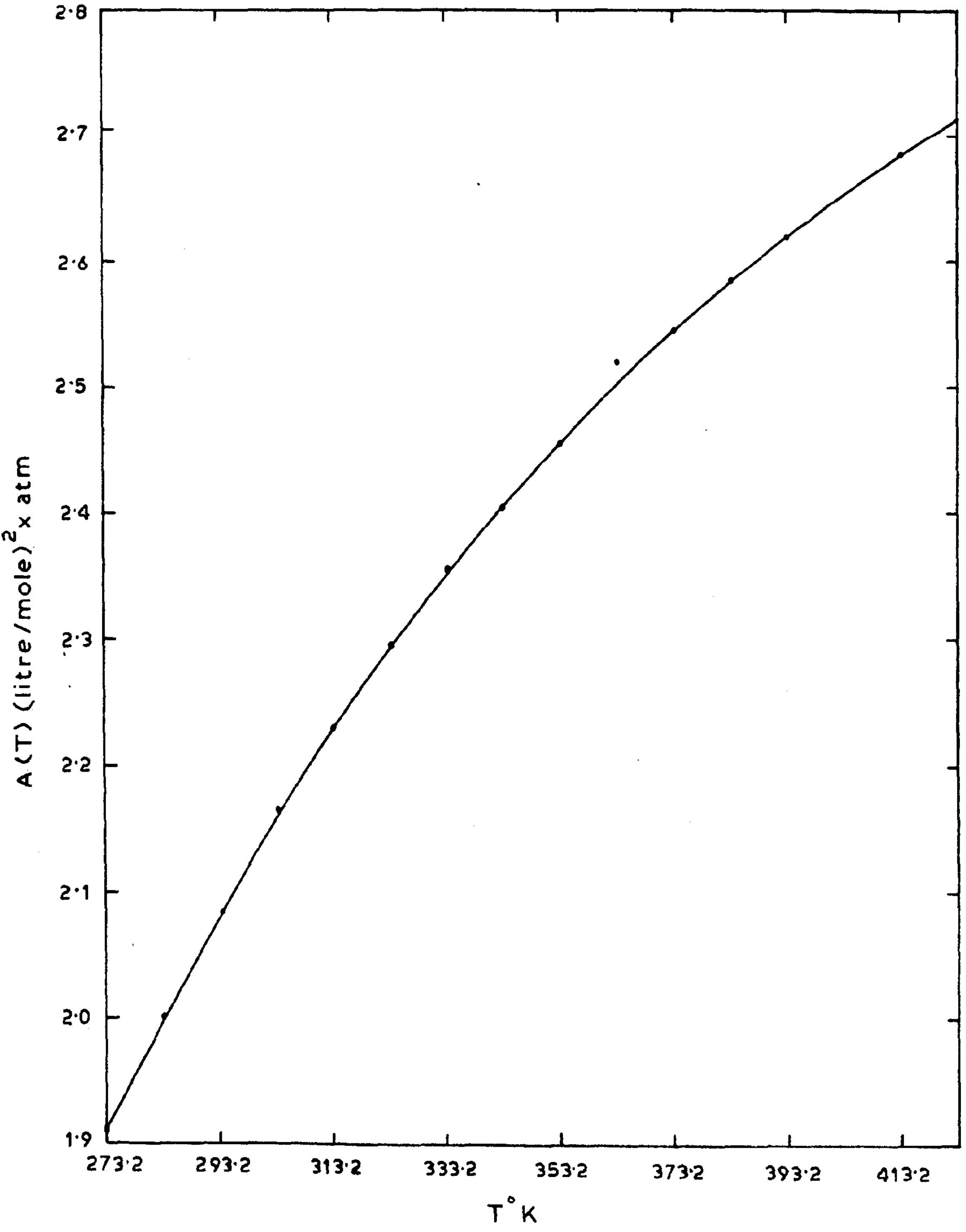

2·8
2·7
2·6
2·5
2·4
2·3
2·2
2·1
2·0
1·9
A (T) (litre/mole)^2 x atm
273·2
293·2
313·2
333·2
353·2
373·2
393·2
413·2
T°K

FIG. 12

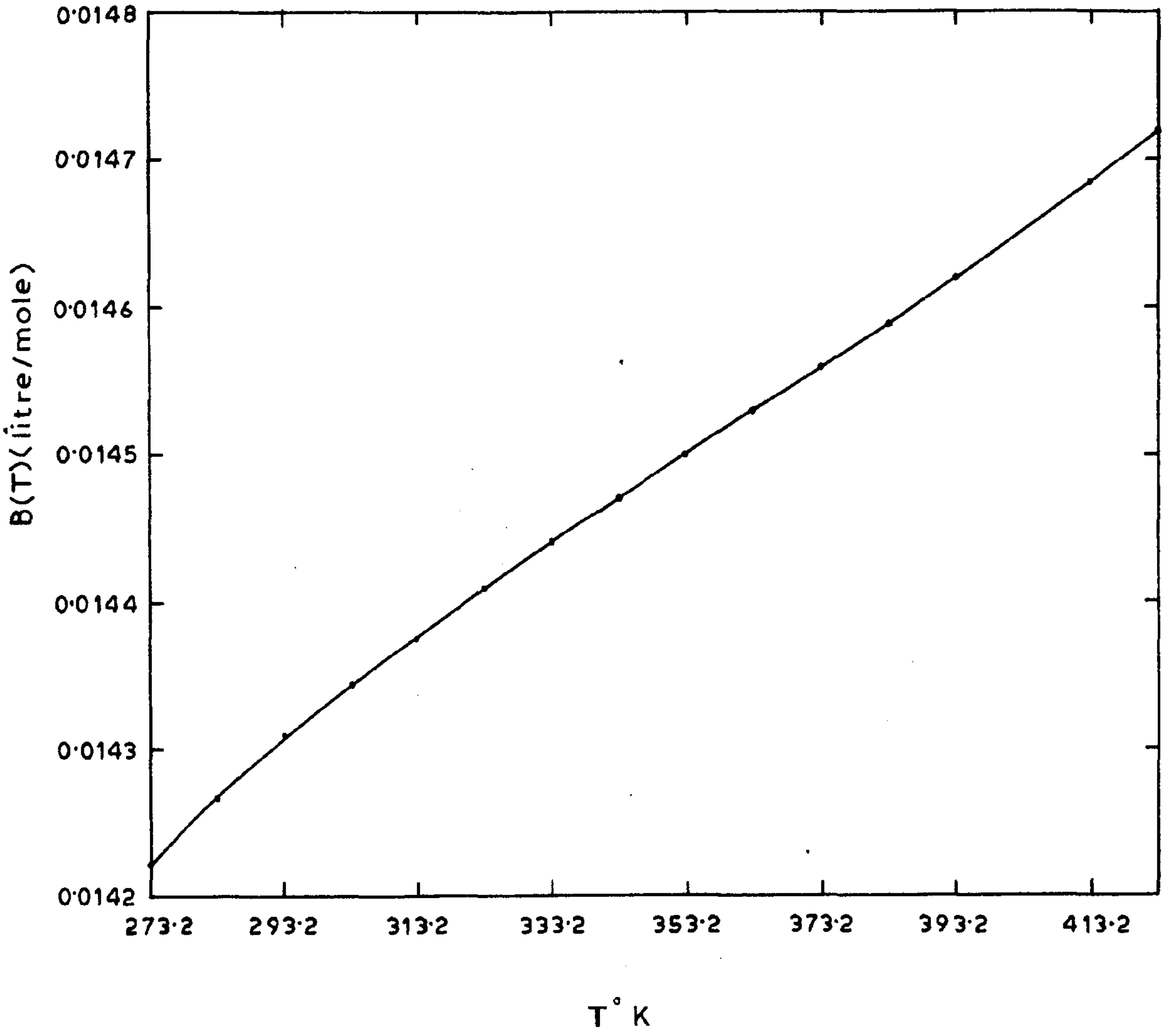

B(T) (litre/mole)
0·0148
0·0147
0·0146
0·0145
0·0144
0·0143
0·0142
273·2
293·2
313·2
333·2
353·2
373·2
393·2
413·2
T° K

FIG. 13

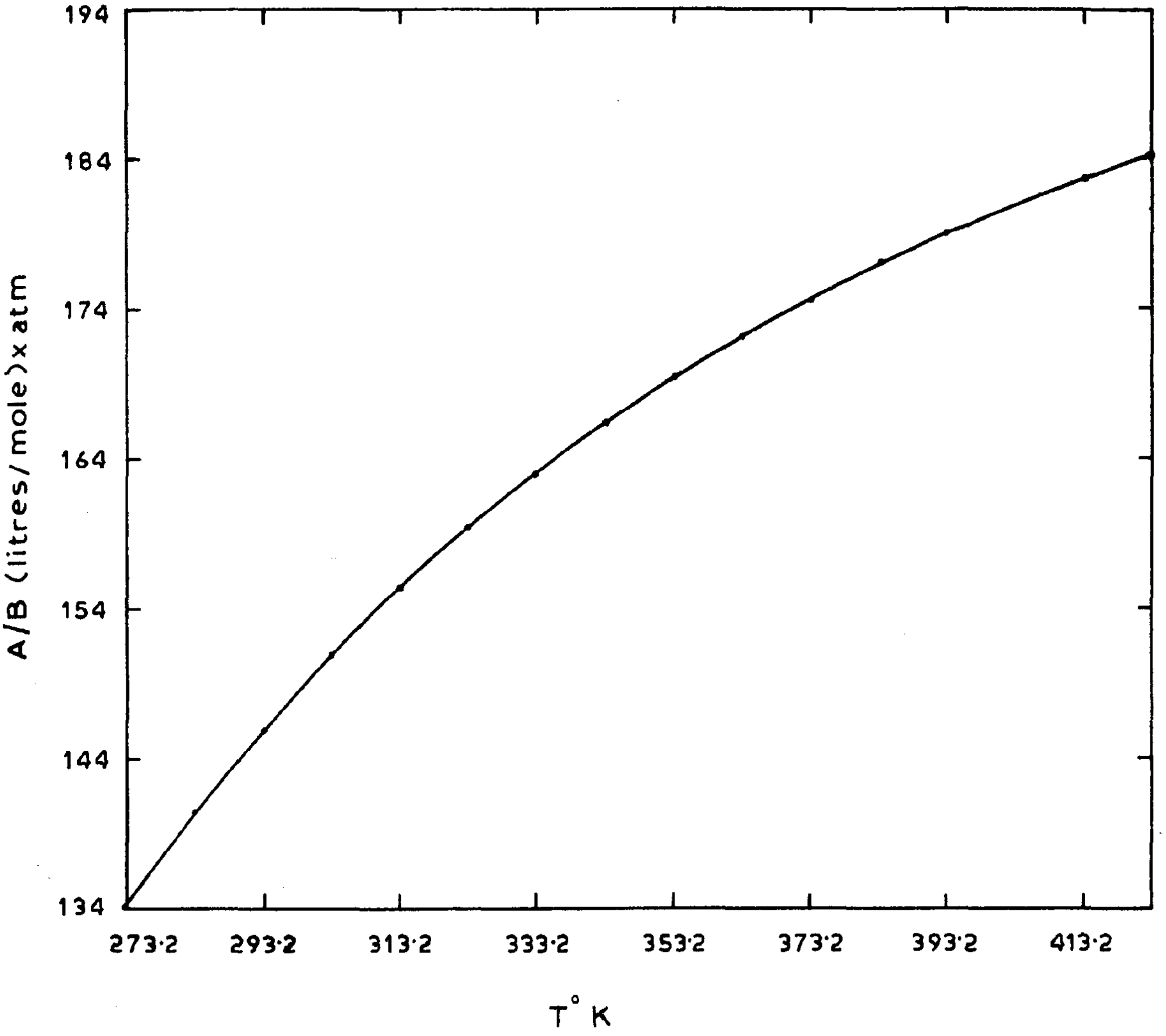

A/B (litres/mole) x atm
194
184
174
164
154
144
134
273·2
293·2
313·2
333·2
353·2
373·2
393·2
413·2
T° K

FIG. 14

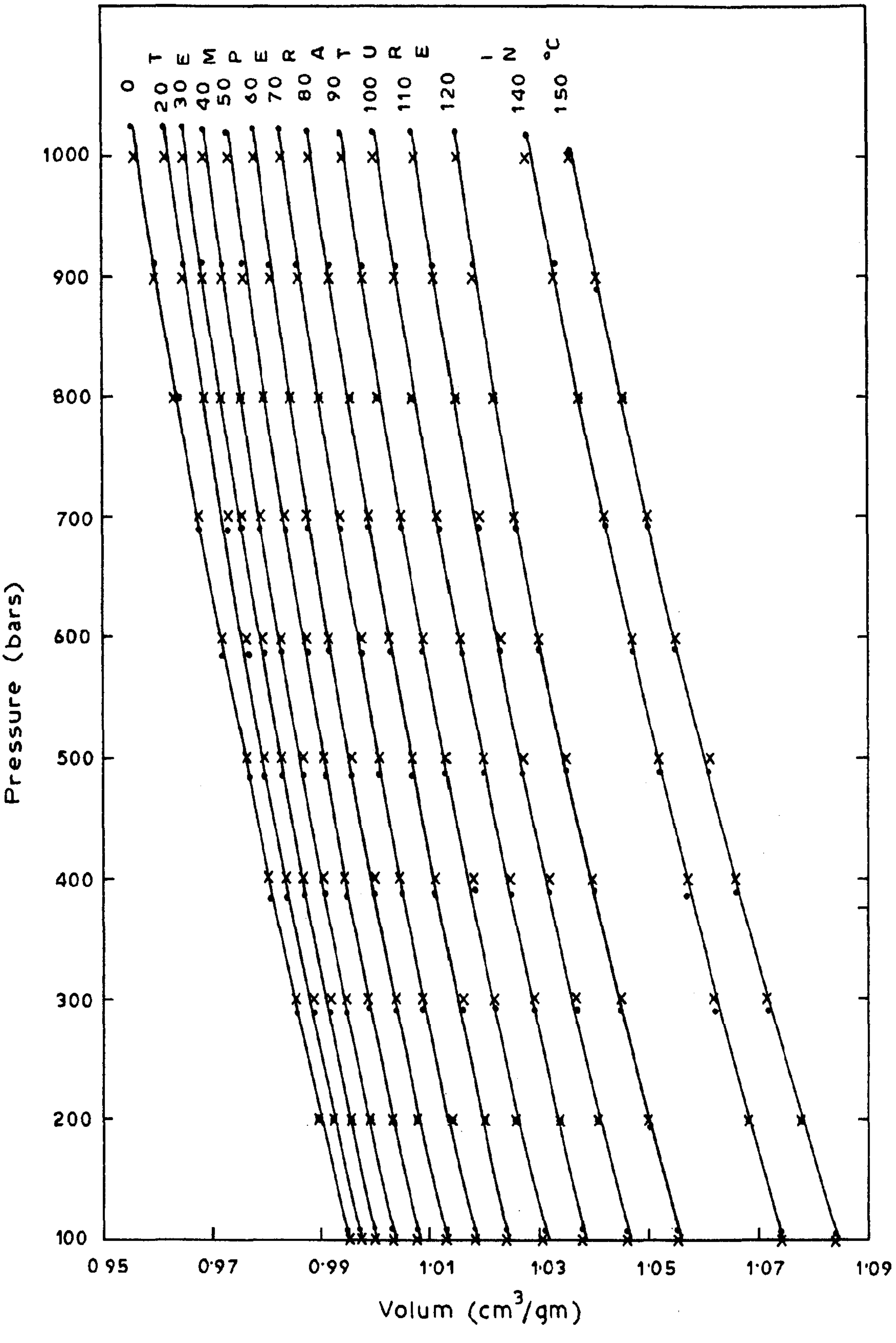

TEMPERATURE IN °C
0
20
30
40
50
60
70
80
90
100
110
120
140
150
Pressure (bars)
1000
900
800
700
600
500
400
300
200
100
0 95
0·97
0·99
1·01
1·03
1·05
1·07
1·09
Volum (cm³/gm)

FIG . 15

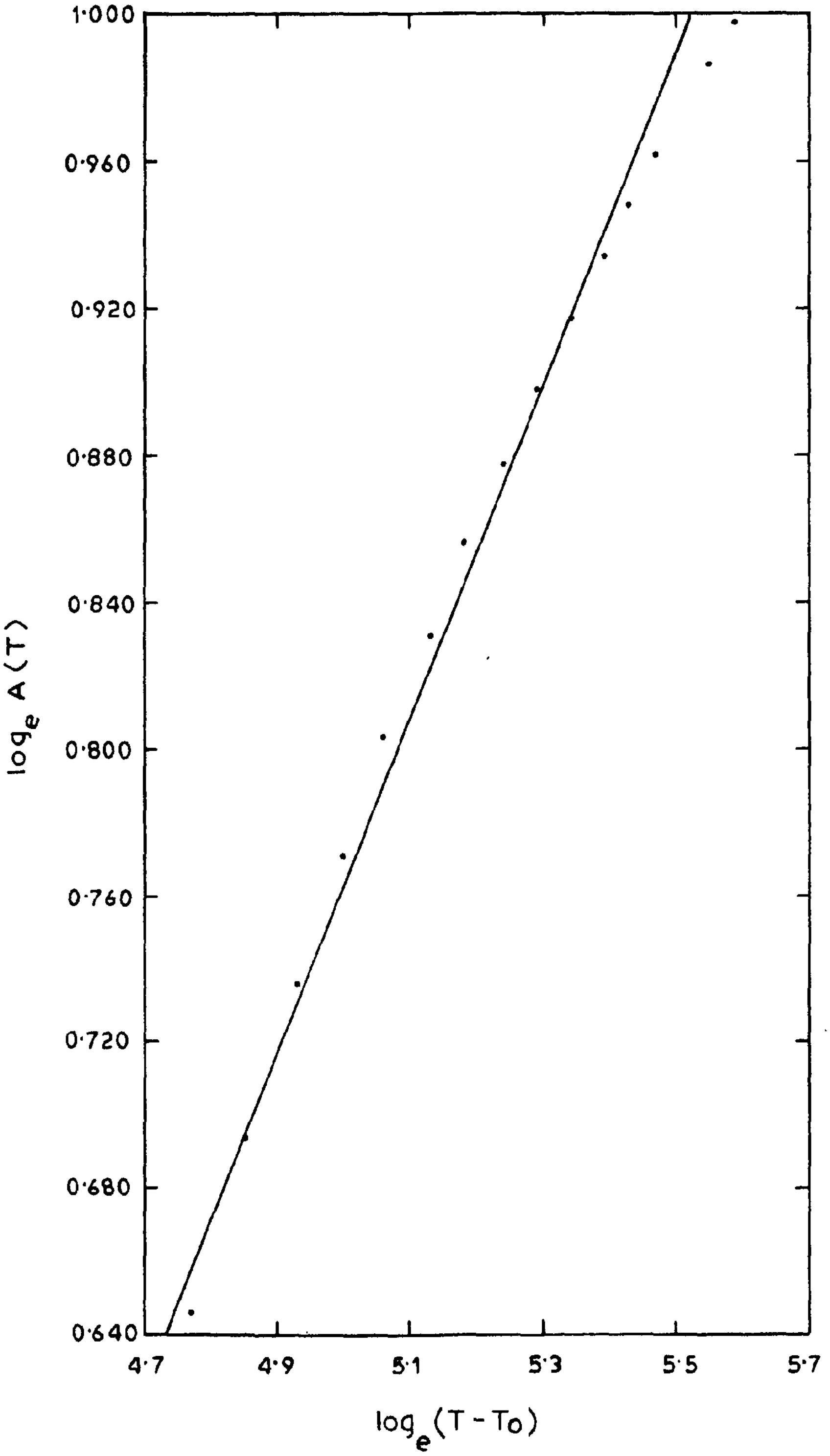

1·000
0·960
0·920
0·880
0·840
0·800
0·760
0·720
0·680
0·640
4·7
4·9
5·1
5·3
5·5
5·7
$\log_e A(T)$
$\log_e(T - To)$

FIG. 16

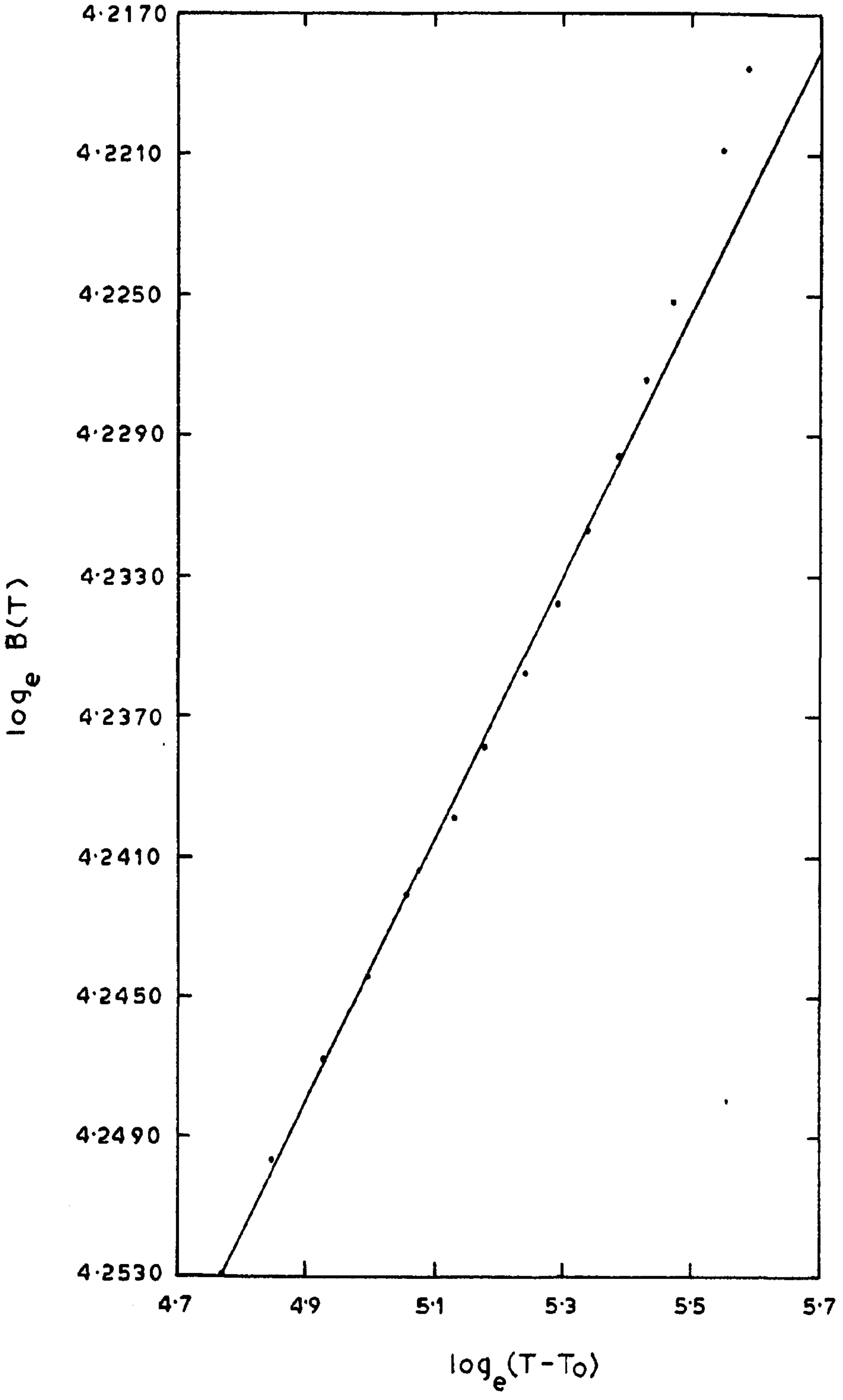

4·2170
4·2210
4·2250
4·2290
4·2330
4·2370
4·2410
4·2450
4·2490
4·2530
$\log_e$ B(T)
4·7
4·9
5·1
5·3
5·5
5·7
$\log_e(T-T_o)$

FIG. 17

CHAPTER III

A number of empirical and semi-empirical relations are available in the literature to study the temperature dependence of various properties of the liquid. But as for each property along there are many such empirical relations and not one gives a good fit with the experimental data in the whole range under study, the subject of studying the functional dependence of temperature of various properties of liquids becomes most unsatisfactory. As for example the temperature dependence of the viscosity of liquids has been studied by several authors over a long period of years, and a large number of relationships involving these variables has been compiled. A resume of a number of these expressions relating viscosity to temperature may be found in a Chapter by Arthur K. Doolittle in Allexander's Colloid Chemistry(79). Similarly a number of empirical or semi-empirical relations are available to study the temperature dependence of other properties also e.g. Surface tension (80-82) (though no direct relation giving temperature variation of surface tension is available in the literature), Dielectric constant (83-85) self-diffusion (86) , Sound velocity(87-89) Vapour pressure (90), Refractive index (91) etc.

From one point of view, according to which an empirical relation is a desirable first step towards explaining the property in terms of something basic about the liquid - say- the molecular structure or the molecular interaction - the present situation is certainly not satisfactory.

The Millers(92) expression for viscosity

$$\ln \eta = A + B / (T - T_0) \qquad (3.1)$$

prepares the way for a meaningful interpretation in terms of molecular structure. His expression (Equation (3.1)) holds good for liquid water. M iller (88() interprets his relation in context with the Doolittle's (93) free-volume equation for viscosity and Cohen and Turnbull's (94) temperature dependence of free-volume. He suggests that the term $(T-T_0)/B$ represents, f, the volume fraction of free-volume. This contention is further supported by the fact that the free-volume so obtained is also in agreement with an independent estimation of it according to the model of Némethy and Scherage (95).

Expressions of the type of Miller (Equation (3.1)) were later found to hold good for many more properties of water (96) and this leads to a dilemma, namely that the calculations for free-volume separately from each individual property are quite inconsistent among each other. This point has been discussed in detail in our earlier paper (96).

An alternative to free-volume could be the fractions of the open-packed or the close-packed species of the two-state theory. It should, however, be observed that just as the free-volume concept is only semi-empirical, so also the two-state theory of water, is in itself not fundamental, for, it should be possible to further reduce the assumptions of the theory - the dense- packed and open-packed constituents of liquid- in terms of molecular interactions.

The situation can be saved, however, if we write empirical relation in a modified form as

$$\ell nX = A_X + B_X \left(\frac{T_c - T}{T - T_0}\right) \qquad (3.2)$$

Here X represents the property, A_X and B_X are constants for that property, T_0 the same constant, reference temperature as in Equation (3.1) and T_c the critical temperature. In this form the volume fraction of free-volume should be expected to be represented by

$$f = \left(\frac{T - T_0}{T_c - T}\right) \qquad (3.3)$$

which will come out the same for any property. Here we have two reference temperatures, T_c and T_0, which almost coincides with the Debye temperature, has significance in the Cohen-

Turnbull derivation which state that the origin of the free volume in a liquid, as manifested by transport properties, is at this reference temperature T_o, and that the free-volume is proportional to temperature above T_o . The significance of T_c, the critical temperature, also becomes understandable in the same context. The liquid under all circumstances will become gas at and above the temperature T_c , and f can have meaning for temperature below T_c only.

Very recently, Singh, Dass and Varshneya (107,97) has shown that relation (3.2) holds good for almost all properties of water that we have tried, viz., surface tension (98) , viscosity (99), self-diffusion(100) , Dielectric-relaxation time (101), Spin-lattice relaxation time (100) Thermal conductivity (99), Mechanical-relaxation time(102) Ultrasonic absorption (102), Dielectric constant (98), Sound velocity (89), Density (103), Volume (98), Refractive Index (98), viscosity at high pressure (104), thermal conductivity at high pressures (105), Volume at high pressures(75), Magnetic susceptibility (106), of liquid water.

Computed results from Equation (3.2) for the properties under study at atmospheric pressure are given in Table 1, and for viscosity, thermal conductivity, volume , at high pressures are given in Tables II, III, IV, respectively. The agreement between present calculations and experimental data is found to be good. The results are also shown in graphical form at the end of this Chapter. The values of the constants A_X and B_X alongwith the range of study are reported in Appendices I, II, III, IV, respectively.

The activation energy of different properties of water can be calculated on differentiating the relation (3.2) with respect to temperature. The activation energies of viscous flow, Diffusion, thermal conductivity, and spin-lattice relaxation are calculated by the following relations :

$$E_{\eta} = - RT^2 \left(\frac{d\,\ln}{dT}\right)_P \qquad (3.4)$$

$$E_D = RT^2 \left(\frac{d\,\ln\,D}{dT}\right)_P \qquad (3.5)$$

$$E_{T_1} = RT^2 \left(\frac{d\,\ln T_1}{dT}\right)_P \qquad (3.6)$$

$$E_{\lambda_T} = RT^2 \left(\frac{d\,\ln\,\lambda_T}{dT}\right)_P \qquad (3.7)$$

are reported in Table V and graphically shown in Fig.(22).

In literature, we find that the activation-energy in case of water should be the same whether calculated from self-diffusion, viscosity, spin-lattice relaxation time, thermal conductivity . But the comparision of all the four activation energies i.e. E_{η} , E_D , E_{T_1} , E_{λ_T} shows that activation energies are different calculated from different properties.

The activation energy for thermal conductivity is less, roughly a factor 8 than that for other transport properties, i.e., the value of B_x is a factor 8 less. This result is not purprising due to the simple fact that in this region of 0^o to 100^oC the magnitude of all the transport properties (except thermal conductivity) varies 8 to 10 times, whereas the magnitude of thermal conductivity varies one and half times only.

The behaviour of transport properties of water could not be explained on the basis of transition state theory, according to which the activation process for viscous flow or self-diffusion etc. in a non associated liquid involves essentially the creation of a vacancy infront of the diffusing molecule for the latter to move into , because firstly, the molar volume of water is smaller than ice and secondly, at temperature not far away from 0^oC the viscosity of water decreases continually when the external pressure is increased from atmospheric pressure to about 1000 Kg/cm^2 and this picture of water behaviour is unlike that found for non-associated liquids. So, what can be concluded is that at ordinary temperatures, the water molecules are loosely -packed in their normal state so that enough vacancies exist to make the dissociation of water molecules from the semi-crystalline lattice.

Some more interesting points may be summarized as below :-

(i) Since the relation (3.2) expresses analytically the functional dependence of temperature of almost all the properties of water for the whole range of melting to boiling point. Therefore the relation (3.2) will also be useful (a) to have checks on the theoretical models, and (b) to calculate a number of parameters which cannot be obtained otherwise like activation energy of transport properties.

(ii) Because this relation gives the functional dependence of temperature of volume at different pressures, so it can be given the status of equation of state for water.

(iii) Recently, Krishnaji and Mansingh (108) have classified a number of liquids on the basis of the value of $\xi = E_\tau / E_\eta$ where E_τ is the activation energy of dielectric relaxation time and E_η is that of viscosity of a particular liquid. In case of water

$$\xi = \frac{E_\tau}{E_\eta} = 1.1$$

which suggests that dipole rotation is frozen in case of water at the freezing point.

(iv) The parameter T_0 is a constant quantity for a particular liquid but it is different for different liquids e.g. T_0 has the same value for all the properties of water under study. Therefore it appears that T_o is an important. parameter which is playing a very important role in the liquid state perhaps in the form of hydrogen bonding rather than a convenient reference temperature. This is in confirmation with the views of others (109).

(v) The value of $T_o = 155^oK$ for water is close to the Debye temperature, 135^oK found experimentally (110) by the slow r neutron diffraction technique as well as to the theoretical value obtained on the quasi-crystalline structure of water (111,112),.

(vi) If we collect the values of T_o for all other associated liquids, we find that except water all other liquids so far studied (107,113) on this approach , have negative value of T_o . We expect this due to the effect of hydrogen bonding being maximum in case of water and then comes methyle alcohol ($T_o = 0$) and so on. Further it may be used to classify the associated liquids into two categoreis (i) with positive value of T_o (ii) with (-ve) value of T_o.

(vii) In the literature, we find that T_o has been taken equivalent to the glass transition temperature at which the viscosity becomes of the order of 10^{13} poise. But except water all other liquids under study have (-ve) value of T_o. it therefore reflects that these liquids may be taken much below their melting point without solidifying i.e. liable to much supercooling (114).

(vii) It is also interesting to note from Appendix (III) that the values of B_x not only vary from property to property but even assumes the negative values in the case of some properties of water. The same conclusion becomes obvious while studying the pressure dependence of thermal conductivity because B_x increases upto 6000 Kg/cm^2 and afterwards decreases indicating that the free volume is increasing upto 6000 Kg/cm^2 whereas the value of B_x in case of viscosity decreases with pressure. They are in contrast to the experimental observations. This clearly indicates that the free volume conceived by Miller (92) is no more valid and something other than free volume is playing an important role.

DISCUSSION

What understanding does the above expression leads us into ? Firstly, we note, thatthe constant A_x corresponds to the value of the property at T_c, one of the two reference temperatures. At temperatures above T_c the matter cannot be expected to remain in liquid state, it would be gaseous, and there, from the Equation (3.2), since $T \gg T_o$, the second term would contribute little as it will also change sign. We may assume therefore that the factor $(T_c - T)/(T-T_o)$ is a temperature term characteristic of the liquid state. Secondly, the origin of this term must be sought in terms of something basic of the liquid. There may be two views :

(1) In terms of the two-state theory $(T_c - T) / (T - T_o)$ must have relation with the fraction of close-packed and open-packed species at a temperature, T, and (ii) in terms of molecular interaction, this term should find an appropriate place in relation to interaction energy. We consider these two views respectively in the following -

(i) TWO STATE THEORY

In the two-state theory(102) the fraction of the close-packed specy, X_c, in the liquid is obtained through involved and indirect methods. This is a function of temperature, and the values quoted by different authors have wide variability. In view of the foregoing discussion if we assume that X_c can be expressed as :

$$X_c = \frac{T - T_o}{T_c - T} \tag{3.8}$$

theh, the fraction of the open-packed specy, X_o will be

$$\begin{aligned} X_o = 1 - X_c &= 1 - \frac{T - T_o}{T_c - T} \\ &= \left(\frac{T_c - T_o - 2T}{T_c - T} \right) \end{aligned} \tag{3.9}$$

Although the assumptions (3.8) and (3.9) have not been proved here in any rigorous theoretical way(as a matter of fact, any theoretical expression to express X_c(or X_o) as a function of temperature would follow from the two-state theory where itself there is wide varaibility). Hence the fact that values obtained from (3.8) and (3.9) agree reasonably well with the two state calculation, should be regarded as, indirect proof, but it should be justified in view of the fact that the values of X_o so obtained lie at all temperatures of interest within the range of values quoted by various authors (95,115, 116,117). These assumptions (equation(3.8) & (3.9)) can be made use of to calculate some properties, say , the specific volume and refractive index of water, as we do here. The good agreement of these calculations with experimental results once again point to the justification of assumptions (3.8) and (3.9).

(a) Specific Volume -

The volume V , can be written as

$$V = X_o V_o + X_c V_c$$

Where V_o and V_c represents the specific volumes of the open-packed and close-packed species, respectively. The temperature dependence of these can further be expressed as

$$\left.\begin{aligned} V_o &= 19.657\,(1 + 1.55 * 10^{-4} t) \\ V_c &= V_c^o\,(1 + At + Bt^2) \end{aligned}\right\} \qquad (3.10)$$

Where V_o^o and V_c^o are the values at a reference temperature, A and B the coefficients and t the rise in temperature above the references temperature, then,

$$V = X_o * 19.657(1+1.55*10^{-4}t) + (X_c V_c^o\,(1+At+Bt^2)) \qquad (3.11)$$

Here X_o and X_c are known, V_c^o , A and B can be fixed from three known values of V. These are obtained to be

$$A = 3.6358 * 10^{-3} \; {}^{o}C^{-1}$$

$$B = -8.2859 * 10^{-6} \; {}^{o}C^{-1}$$

$$V_c^{\,o} = 0.802071 \; \text{c.c.}$$

The calculated values for V along with the experimental values are given in Table VI. The agreement is very good.

(b) Refractive Index :

Using equations (3.8) and (3.9) and the relation for refractive index of water given Mitra et al.(118) on two state approach,

$$(n-1)V = X_o K_o + X_c K_c$$

where n is the refractive index, V the specific volume and k_o, k_c some constants to be fixed empirically. They are obtained as $k_o = 0.3359$ and $k_c = 0.3311$. Then from experimentally known values of V, n can be calculated. These values alongwith the experimental are given in Table VI . The agreement is again very good.

MOLECULAR INTERACTION

As already remarked, the two-state theory of water is itself not fundamental, because it is further reducible in terms of molecular interactions. The close-packed and open-packed species, in as much as they represent two idealised classes of molecular groupings- not necessarily realistic - can also be expressed in terms of 'tight' and 'loose' molecular bindings. This may be hydrogen bonding or, in fact, any dipole and multipole binding. Then, to speak of temperature dependence of fractions of close-packed and open-packed species is equivalent to speaking of temperature dependence of molecular-interaction energy.

Quite at hand we know for dipole interactions that the energy depends upon the dipole moment, μ, the distance r, and relative orientation angles, Θ and ϕ, which certainly depend upon the temperature.

The above discussion, ffom which we learn that liquid water involves a term $\left| \frac{T_c - T}{T - T_o} \right|$ for the temperature dependence of its properties, we are led to conclude that the molecular interaction energy for liquid water must somehow or other involve this term as argument of a suitable function.

TABLE - 1

Temperature	Surface Tension (dynes/cm)		Viscosity (cP)	
	Experimental	Calculated	Experimental	Calculated
0	75.64	75.64	1.7938	1.7938
5	74.92	73.98	1.5188	1.5236
10	74.22	72.48	1.3097	1.3107
15	73.49	71.12	1.1447	1.1404
20	72.75	69.88	1.0087	1.0022
25	71.97	68.74	0.8949	0.8888
30	71.18	67.70	0.8004	0.7946
35	70.38	66.74	0.7208	0.7156
40	69.56	65.86	0.6536	0.6487
45	68.74	65.04	0.5970	0.5917
50	67.91	64.28	0.5492	0.5426
55	67.05	63.57	0.5072	0.5001
60	66.18	62.90	0.4699	0.4630
65	-	62.28	0.4368	0.4305
70	64.42	61.70	0.4071	0.4018
75	-	61.15	0.3806	0.3764
80	62.61	60.64	0.3570	0.3537
85	-	60.15	0.3357	0.3334
90	60.75	59.69	0.3166	0.3152
95	-	59.26	0.2994	0.2988
100	58.85	58.85	0.2839	0.2839

TABLE 1 (Continued)

Temperature °C	Self-diffusion(10^{-5} cm^2/sec)		Dielectric constant	
	Experimental	Calculated	Experimental	Calculated
0	0.97	0.97	88.00	88.00
5	1.16	1.18	86.04	84.46
10	1.36	1.41	84.11	81.32
15	1.58	1.66	82.22	78.52
20	1.85	1.94	80.36	76.01
25	2.13	2.23	78.54	73.74
30	2.46	2.55	76.75	71.69
35	2.79	2.89	75.00	69.83
40	3.14	3.24	73.22	68.12
45	3.52	3.62	71.59	66.56
50	3.94	4.01	69.94	65.13
55	4.37	4.42	-	63.80
60	4.82	4.84	66.74	62.58
65	5.30	5.28	-	61.44
70	5.78	5.73	63.68	60.38
75	6.27	6.19	-	59.40
80	6.81	6.66	60.76	58.48
85	7.26	7.15	-	57.62
90	7.75	7.64	57.98	56.81
95	8.20	8.14	-	56.05
100	8.65	8.65	55.33	55.33

TABLE 1 (Continued)

Temperature °C	Thermal Conductivity (10^{-7} watt/cm °C)		Sound Velocity (Km/sec)	
	Experimental	Calculated	Experimental	Calculated
0	5.540	5.540	1.40274	1.40274
5	-	5.660	1.42650	1.41861
10	5.705	5.774	1.44759	1.43341
15	-	5.880	1.46625	1.44723
20	5.870	5.981	1.48266	1.46017
25	-	6.076	1.49700	1.47231
30	6.034	6.167	1.50944	1.48372
35	-	6.252	1.52012	1.49447
40	6.200	6.334	1.52918	1.50461
45	-	6.411	1.53672	1.51418
50	6.363	6.484	1.54287	1.52325
55	-	6.554	1.54770	1.53184
60	6.530	6.621	1.55130	1.53999
65	-	6.685	1.55376	1.54775
70	6.695	6.746	1.55512	1.55512
75	-	6.804	1.55545	1.56214
80	6.860	6.860	1.55481	1.56884
85	-	6.913	1.55325	1.57524
90	-	6.965	1.55079	1.58135
95	-	7.014	1.54750	1.58720
100	-	7.061	1.54341	1.59280

TABLE 1 (Continued)

Temperature °C	Refractive Index		Magnetic susceptibility	
	Experimental	Calculated	Experimental	Calculated
0	1.33433	1.33433	0.99717	0.99717
5	1.33427	1.33299	0.99789	0.99828
10	1.33408	1.33157	0.99860	0.99931
15	1.33377	1.33035	0.99931	1.00027
20	1.33335	1.32921	1.0000	1.00115
25	1.33287	1.32816	1.00068	1.00197
30	1.33228	1.32718	1.00136	1.00274
35	1.33157	1.32626	1.00202	1.00346
40	1.33087	1.3254	1.00268	1.00413
45	1.33011	1.32460	1.00333	1.00417
50	1.32930	1.32384	1.00396	1.00536
55	1.32846	1.32313	1.00459	1.00593
60	1.32754	1.32245	1.00521	1.00646
65	1.32652	1.32182	1.00582	1.00696
70	1.32547	1.32122	1.00642	1.00743
75	1.32434	1.32065	1.00701	1.00788
80	1.32323	1.32010	1.00759	1.00831
85	1.32208	1.31959	1.00817	1.00872
90	1.32086	1.31910	1.00873	1.00911
95	1.31959	1.31863	1.00928	1.00948
100	1.31819	1.31819	1.00983	1.00983

TABLE 1 (Continued)

Temperature °C	Spin-lattice relaxation (sec)		Dielectric relaxation time ($\tau_0 \times 10^{12}$ sec)	
	Experimental.	Calculated	Experimental	Calculated
0	1.59	1.59	18.7	18.7
5	1.88	1.89	-	15.5
10	2.20	2.23	13.6	13.0
15	2.55	2.59	-	11.1
20	2.95	2.97	10.1	9.5
25	3.37	3.38	-	8.3
30	3.82	3.82	7.5	7.3
35	4.30	4.27	-	6.5
40	4.76	4.75	5.9	5.8
45	5.27	5.24	-	5.2
50	5.77	5.75	4.7	4.7
55	6.78	6.28	-	4.3
60	6.81	6.82	-	3.9
65	7.36	7.38	-	3.6
70	7.91	7.95	-	3.3
75	8.49	8.53	-	3.1
80	9.10	9.12	-	2.9
85	9.70	9.71	-	2.7
90	10.30	10.32	-	2.5
95	10.95	10.93	-	2.4
100	11.55	11.55	-	2.2

TABLE 1 (Continued)

Temperature °C	Mechanical-relaxation time (* 10^{-12} sec)		Ultrasonic absorption (10^{-17} sec^2/cm)	
	Experimental	Calculated	Experimental	Calculated
0	4.05	4.05	79.6	79.6
5	3.37	3.36	61.4	64.99
10	2.86	2.83	49.5	53.91
15	-	2.42	-	45.35
20	2.14	2.09	34.3	38.63
25	-	1.82	-	33.28
30	1.64	1.60	25.9	28.96
35	-	1.42	-	25.43
40	1.30	1.27	19.5	22.51
45	-	1.15	-	20.08
50	1.08	1.04	16.0	18.03
55	-	0.95	-	16.29
60	0.89	0.87	13.8	14.81
65	-	0.80	-	13.53
70	0.75	0.74	11.5	12.42
75	-	0.69	-	11.45
80	0.64	0.64	10.6	10.60
85	-	0.60	-	9.85
90	-	0.56	-	9.19
95	-	0.53	-	8.60
100	-	0.50	-	8.07

TABLE 1 (Continued)

Temperature °C	Density (gm/cc)	
	Experimental	Calculated
0	0.99987	0.99987
5	0.99999	0.99612
10	0.99973	0.99268
15	0.99913	0.98951
20	0.99823	0.98658
25	0.99707	0.98386
30	0.99567	0.98133
35	0.99406	0.97897
40	0.99224	0.97676
45	0.99025	0.97470
50	0.98807	0.97275
55	0.98573	0.97093
60	0.98324	0.96922
65	0.98059	0.96760
70	0.97781	0.96606
75	0.97489	0.96461
80	0.97183	0.96324
85	0.96865	0.96193
90	0.96534	0.96069
95	0.96192	0.95951
100	0.95838	0.95838

TABLE 2

Pressure Atm. / Temp. oC	50		100		200		300	
	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
0	1.7810	1.7810	1.770	1.770	1.743	1.743	1.726	1.726
10	-	1.3054	-	1.303	-	1.293	-	1.288
20	1.001	1.0007	1.000	1.003	0.998	1.001	0.995	1.003
30	0.797	0.7952	0.798	0.800	0.798	0.802	0.800	0.807
40	0.653	0.6506	0.654	0.656	0.656	0.661	0.658	0.668
50	0.547	0.5451	0.549	0.551	0.552	0.558	0.555	0.565
60	-	0.4658	-	0.472	-	0.480	-	0.488
80	-	0.3568	-	0.363	-	0.371	-	0.379
100	0.287	0.2870	0.293	0.293	0.301	0.301	0.309	0.309

TABLE 3

Pressure Atm. / Temp. °C	1000		2500		4000		6000		8000	
	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
30	155.0	155.0	169.0	169.0	180.0	180.0	193.0	193.0	204.0	204.0
40	-	158.0	-	172.8	-	184.4	-	197.4	-	208.7
50	162.0	161.5	176.0	176.3	188.0	188.4	201.0	201.4	212.0	213.0
60	-	164.2	-	179.4	-	192.0	-	205.0	-	216.8
70	167.0	166.7	182.0	182.2	194.0	195.2	207.0	208.3	220.0	220.3
80	-	169.0	-	184.8	-	198.2	-	211.3	-	223.5
90	172.0	171.1	187.0	187.2	199.0	201.0	213.0	214.0	226.0	226.4
100	-	173.0	-	189.4	-	203.5	-	216.5	-	229.1
110	175.0	174.8	191.0	191.4	205.0	205.8	218.0	218.8	231.0	231.6
130	178.0	178.0	195.0	195.0	210.0	210.0	223.0	223.0	236.0	236.0

TABLE 4 (Continued)

Temp. °C / Pressure Atm.	30		40		50	
	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
50	1.002180	1.014318	1.005670	1.018505	1.009937	1.022208
100	0.999978	1.011873	1.003486	1.016071	1.007752	1.019784
150	0.997807	1.009468	1.001332	1.013677	1.005598	1.017400
200	0.995667	1.007102	0.999210	1.011323	1.003474	1.015056
250	0.993557	1.004775	0.997119	1.009006	1.00381	1.012750
300	0.991477	1.002484	0.995057	1.006727	0.999317	1.010480
350	0.989426	1.000231	0.993024	1.004485	0.997282	1.008248
400	0.987404	0.998014	0.991019	1.002279	0.995215	1.006052
450	0.985409	0.995832	0.989043	1.000107	0.993297	1.003889
500	0.983443	0.993685	0.987094	0.997971	0.991245	1.001762
550	0.981503	0.991570	0.985171	0.995866	0.989420	0.999667
600	0.979590	0.989489	0.983275	0.993796	0.987522	0.997605
650	0.977702	0.987440	0.981404	0.991756	0.985649	0.995574
700	0.975840	0.985423	0.979558	0.989748	0.983801	0.993574
750	0.974003	0.983436	0.977736	0.987770	0.981978	0.991605
800	0.972190	0.981478	0.975938	0.985821	0.980179	0.989664
850	0.970401	0.979549	0.974163	0.983901	0.978404	0.987751
900	0.968634	0.977649	0.972410	0.982008	0.976655	0.985866
950	0.966891	0.975775	0.970680	0.980143	0.974922	0.984007
1000	0.965169	0.973929	0.968970	0.978303	0.973214	0.982174

TABLE 4 (Continued)

Temp. °C / Preesure Atm.	60		70		80	
	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
50	1.014891	1.025506	1.020501	1.028463	1.026717	1.031129
100	1.012677	1.023092	1.018247	1.026057	1.024400	1.028730
150	1.010497	1.020717	1.016027	1.023691	1.022121	1.026372
200	1.008349	1.018382	1.013842	1.021364	1.019878	1.024052
250	1.006233	1.016085	1.011689	1.019074	1.017670	1.021770
300	1.004148	1.013824	1.009569	1.016822	1.015498	1.019525
350	1.002994	1.011600	1.007480	1.014606	1.013359	1.017316
400	1.000069	1.009413	1.005425	1.012426	1.011253	1.015144
450	0.998073	1.007259	1.003395	1.010280	1.009179	1.013204
500	0.996105	1.005140	1.001396	1.008169	1.007137	1.010900
550	0.994163	1.003053	0.999427	1.006089	1.005125	1.008827
600	0.992253	1.000999	0.997486	1.004043	1.003143	1.006787
650	0.990366	0.998977	0.995572	1.002027	1.001190	1.004777
700	0.988506	0.996984	0.993684	1.000041	0.999264	1.002798
750	0.986670	0.995022	0.991823	0.998086	0.997366	1.000848
800	0.984858	0.993088	0.989989	0.996158	0.995493	0.998926
850	0.983070	0.991181	0.988174	0.994258	0.993646	0.997032
900	0.981305	0.989030	0.986386	0.992085	0.991824	0.995164
950	0.979562	0.987450	0.984621	0.990537	0.990025	0.993321
1000	0.977841	0.985623	0.982879	0.988715	0.988249	0.991504

TABLE 4 (Continued)

Temperature °C / Pressure (Atm)	90		100	
	Experimental	Calculated	Experimental	Calculated
50	1.033545	1.033545	1.040972	1.035744
100	1.031153	1.031153	1.038486	1.033358
150	1.028801	1.028801	1.036045	1.031012
200	1.026488	1.026488	1.033645	1.028706
250	1.024213	1.024213	1.031287	1.026437
300	1.021974	1.021974	1.028969	1.024204
350	1.019772	1.019772	1.026691	1.022008
400	1.017606	1.017606	1.024451	1.019848
450	1.015473	1.015473	1.022248	1.017721
500	1.013375	1.013375	1.020081	1.015628
550	1.011308	1.011308	1.017949	1.013567
600	1.009274	1.009274	1.015851	1.011539
650	1.007270	1.007270	1.013786	1.009540
700	1.005296	1.005296	1.011752	1.007571
750	1.003352	1.003352	1.009749	1.005632
800	1.001435	1.001435	1.007776	1.003720
850	0.995546	0.995546	1.005832	1.001835
900	0.997683	0.997683	1.003915	0.999976
950	0.995845	0.995845	1.002024	0.998143
1000	0.994032	0.994032	1.000159	0.996333

TABLE 5

Temperature °C	E_{Λ}	E_D	E_{T_1}	$E_{\lambda T}$
0	5.04699	5.99028	5.42886	0.66433
5	4.81725	5.71760	5.18173	0.63409
10	4.61017	5.47182	4.95898	0.60684
15	4.42268	5.24929	4.75731	0.58216
20	4.25224	5.04699	4.57398	0.55972
25	4.09671	4.86239	4.40668	0.53925
30	3.95429	4.69335	4.25348	0.52050
35	3.82344	4.53804	4.11273	0.50328
40	3.70285	4.39493	3.98302	0.48741
45	3.59142	4.26266	3.86316	0.47274
50	3.48816	4.14011	3.75209	0.45915
55	3.39225	4.02626	3.64891	0.44652
60	3.30294	3.92027	3.55285	0.43477
65	3.21960	3.82135	3.46321	0.42380
70	3.14168	3.72886	3.37938	0.41354
75	3.06866	3.64220	3.30085	0.40393
80	3.00013	3.56086	3.22713	0.39491
85	2.93569	3.48437	3.15781	0.38642
90	2.87499	3.41233	3.09252	0.37843
95	2.81773	3.34437	3.03093	0.37090
100	2.76363	3.28016	2.97273	0.36378

TABLE 6

Temperature °C	X_c	X_o	Volume of water (cc)		Refractive Index	
			Experimental	Calculated	Experimental	Calculated
0	0.3160	0.6840	1.00013	0.99959	1.33433	1.3343
5	0.3339	0.6661	1.00001	0.99980	1.33427	1.3343
10	0.3522	0.6478	1.00027	1.00027	1.33408	1.3341
15	0.3710	0.6290	1.00087	1.00098	1.33377	1.3338
20	0.3904	0.6096	1.00177	1.00190	1.33335	1.3334
25	0.4103	0.5897	1.00294	1.00306	1.33287	1.3329
30	0.4308	0.5692	1.00435	1.00444	1.33228	1.3324
35	0.4519	0.5481	1.00598	1.00604	1.33157	1.3317
40	0.4736	0.5264	1.00782	1.00785	1.33087	1.3310
45	0.4960	0.5040	1.00985	1.00986	1.33011	1.3302
50	0.5191	0.4809	1.01207	1.01207	1.32930	1.3294
55	0.5429	0.4571	1.01448	1.01448	1.32846	1.3285
60	0.5675	0.4325	1.01705	1.01707	1.32754	1.3276
65	0.5929	0.4071	1.01979	1.01984	1.32652	1.3266
70	0.6191	0.3809	1.02270	1.02279	1.32547	1.3255
75	0.6461	0.3539	1.02576	1.02591	1.32434	1.3244
80	0.6741	0.3259	1.02899	1.02918	1.32323	1.3233
85	0.7024	0.2976	1.03237	1.03267	1.32208	1.3221
90	0.7324	0.2676	1.03590	1.03621	1.32086	1.3209
95	0.7641	0.2359	1.03959	1.03983	1.31959	1.3196
100	0.7963	0.2037	1.04363	1.04363	1.31819	1.3182

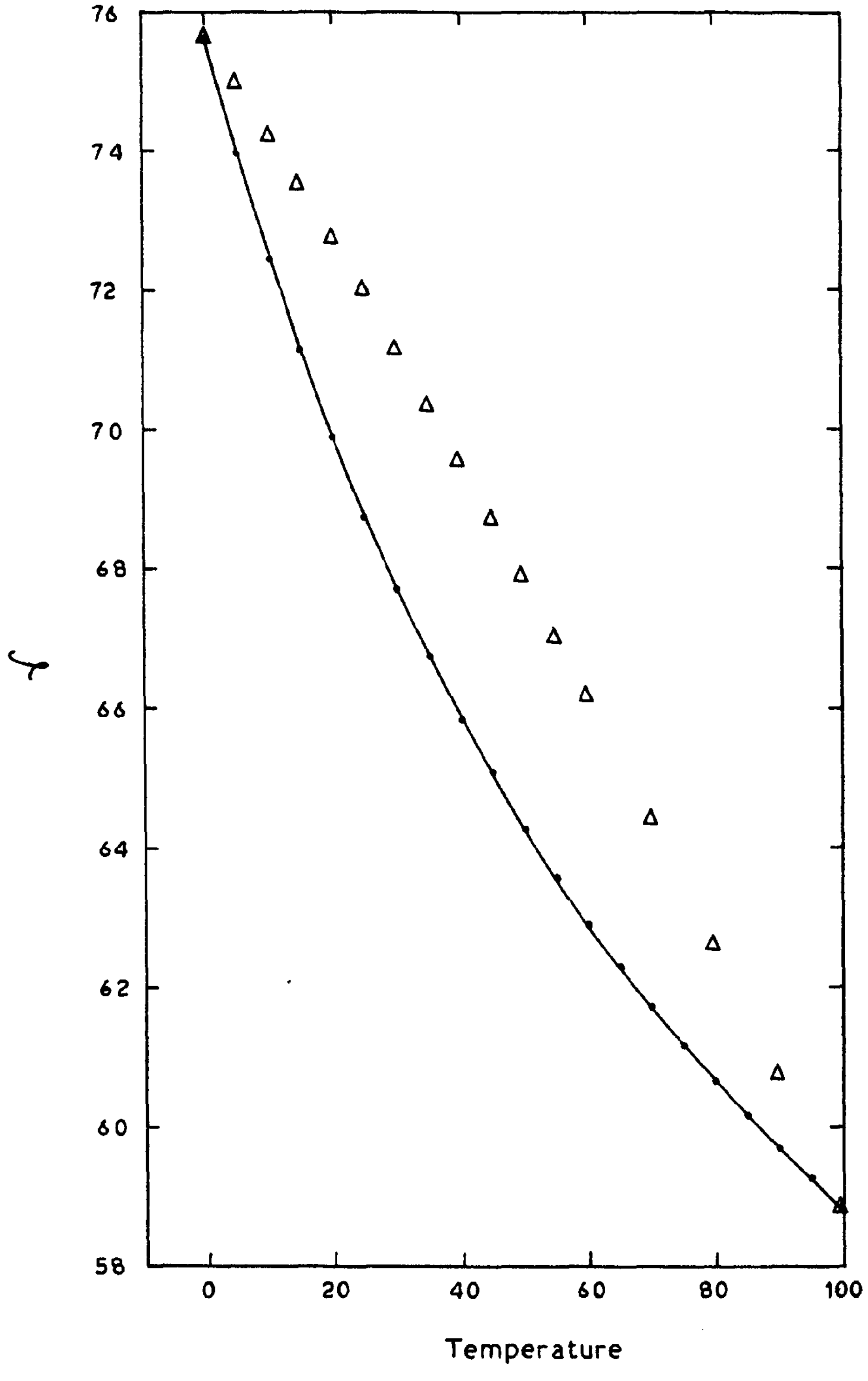


FIG. 18(a)

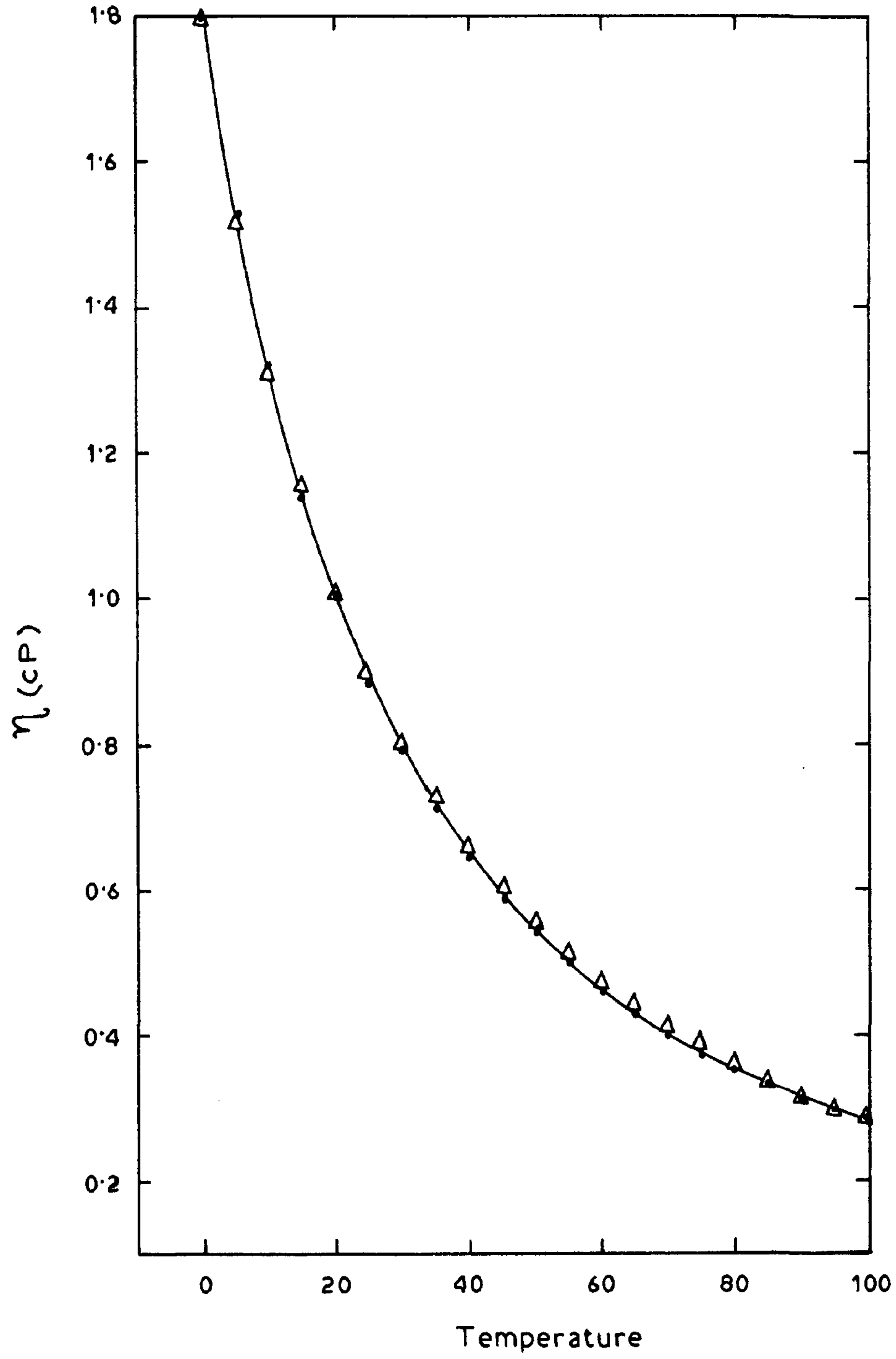


FIG.18(b)

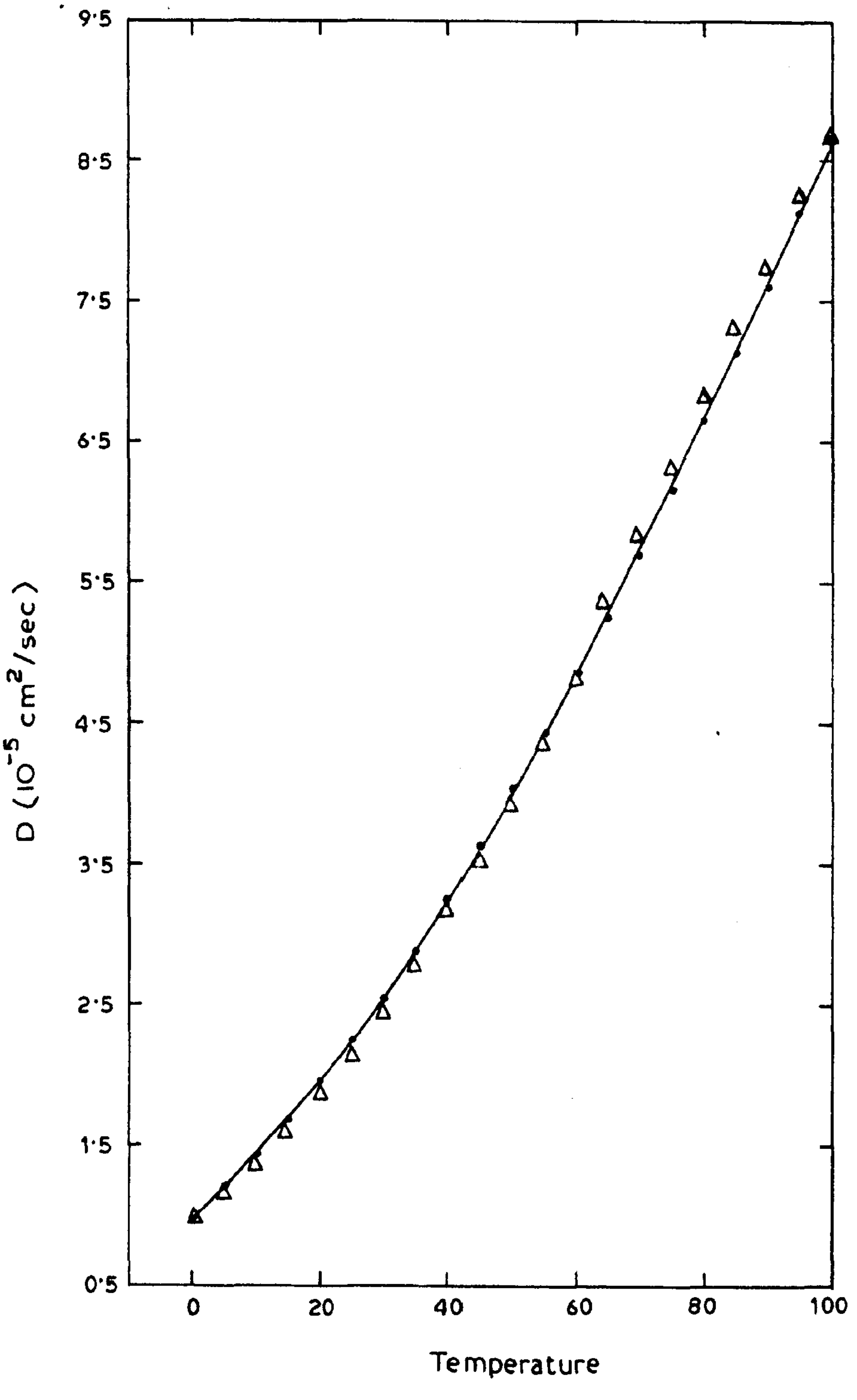

9·5
8·5
7·5
6·5
5·5
4·5
3·5
2·5
1·5
0·5
D (10^{-5} cm^{2}/sec)
0
20
40
60
80
100
Temperature

FIG. 18 (c)

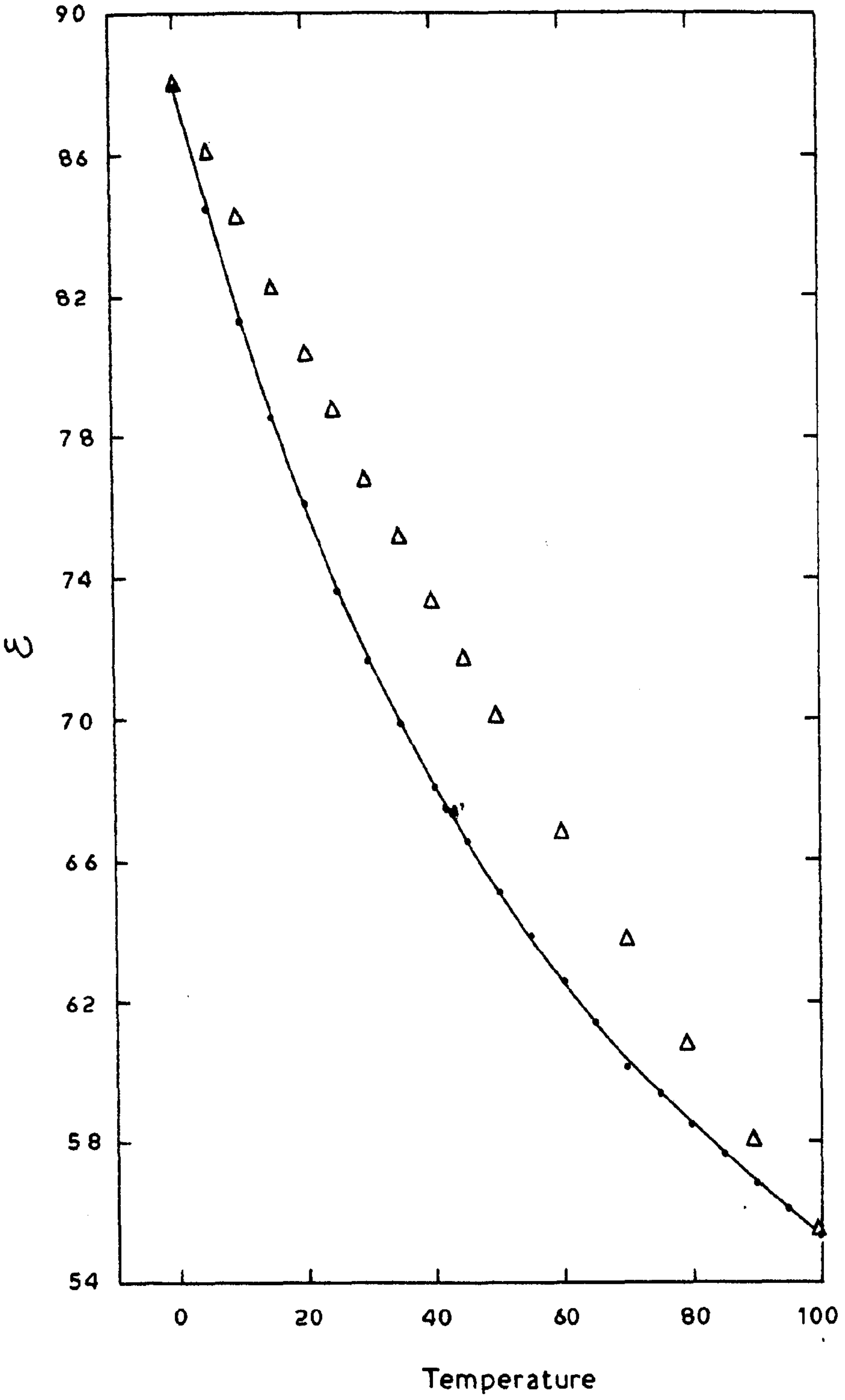
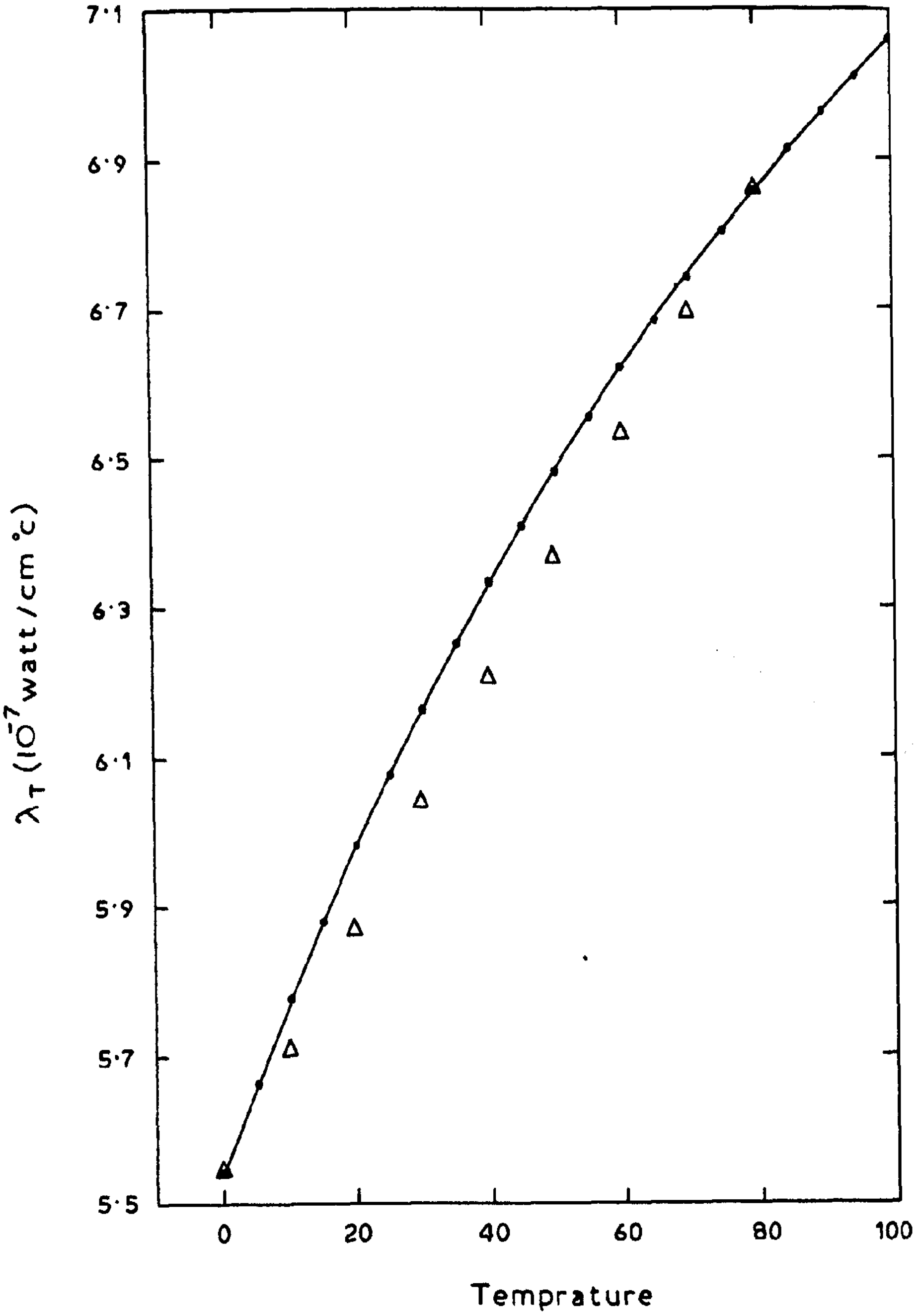


FIG. 18(d)



7·1
6·9
6·7
6·5
6·3
6·1
5·9
5·7
5·5
λ_T (10^{-7} watt/cm °c)
0
20
40
60
80
100
Temprature

FIG. 18(e)

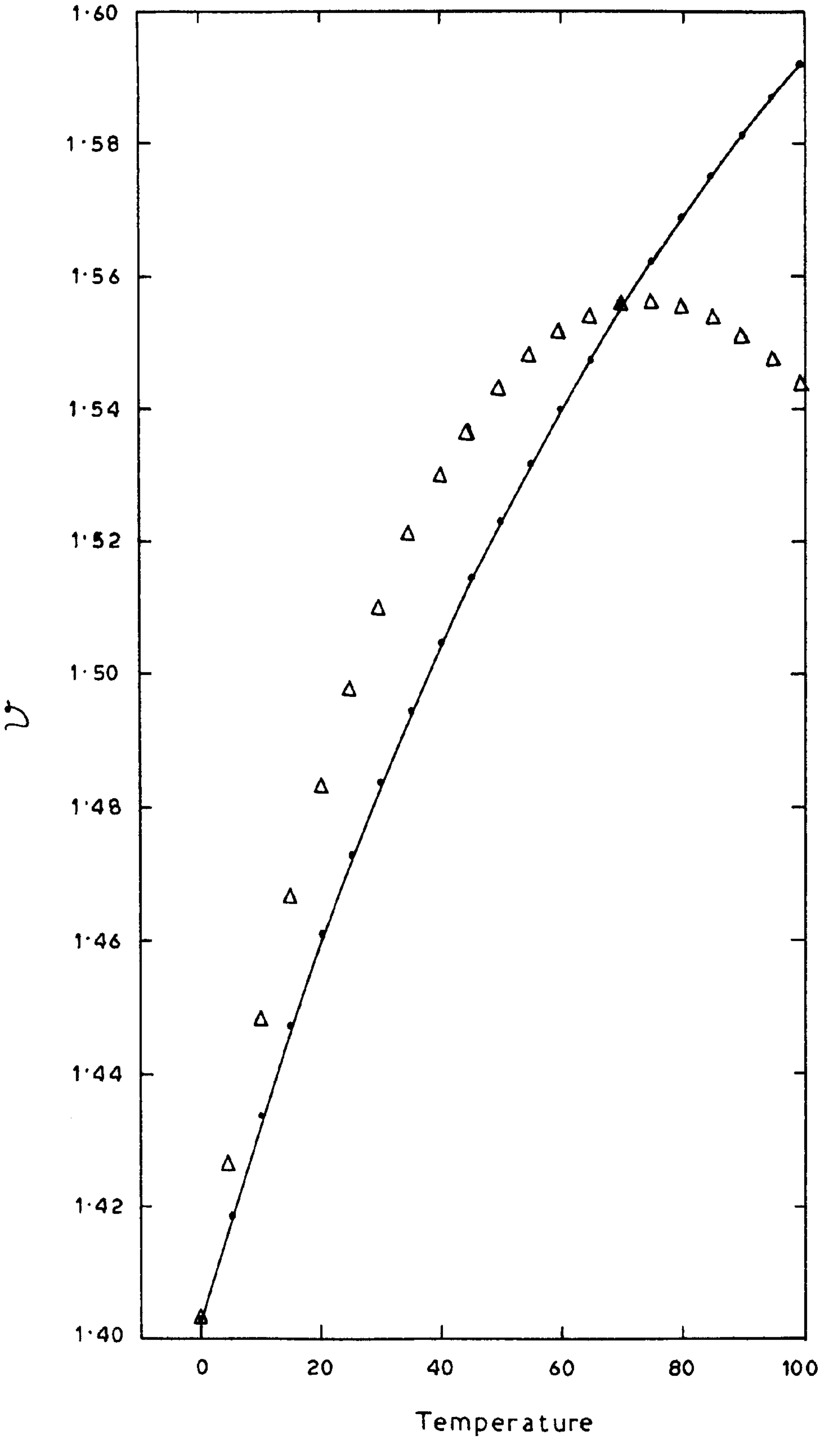

1·60
1·58
1·56
1·54
1·52
1·50
1·48
1·46
1·44
1·42
1·40
ν
0
20
40
60
80
100
Temperature

FIG. 18(f)

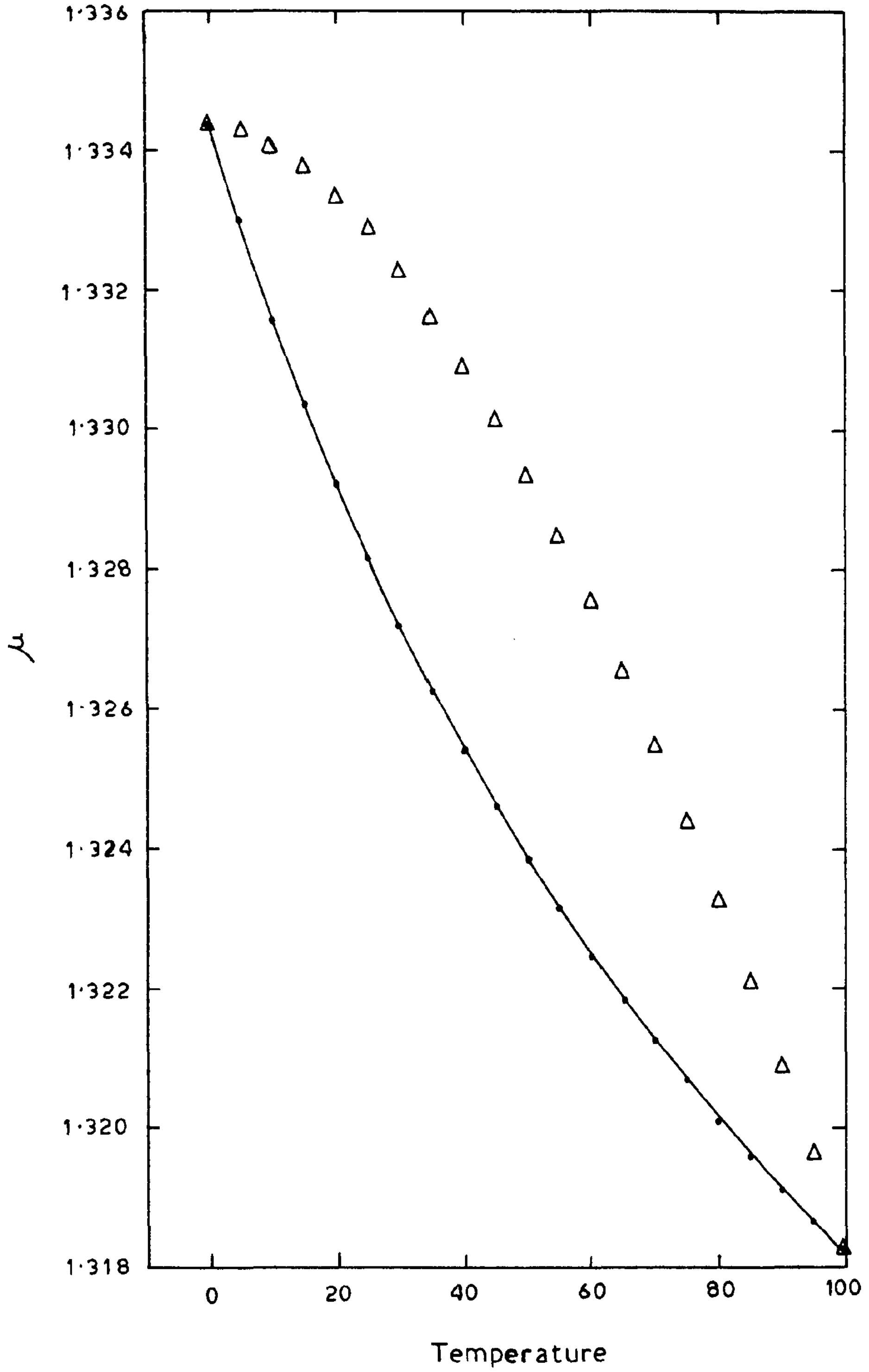

1·336
1·334
1·332
1·330
1·328
1·326
1·324
1·322
1·320
1·318
μ
0
20
40
60
80
100
Temperature

FIG. 18(g)

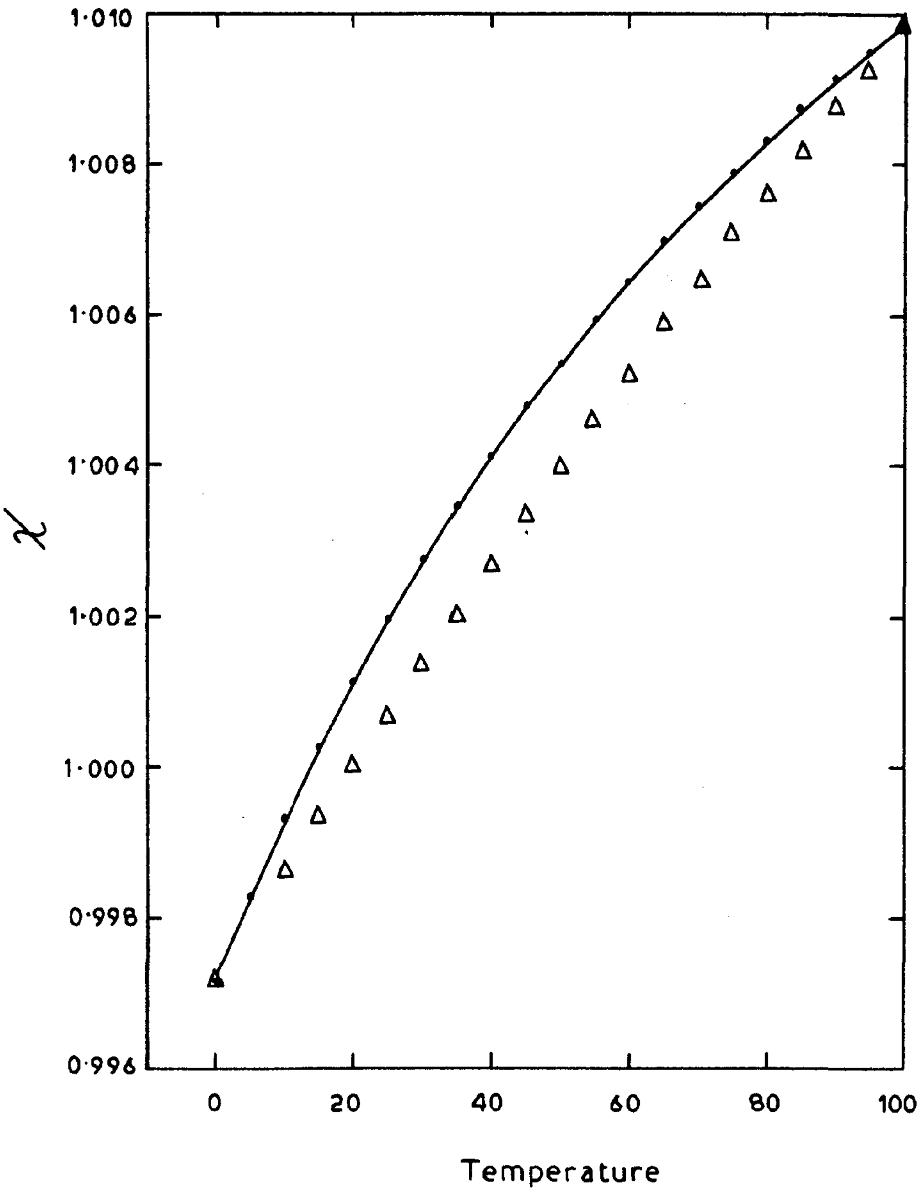

1·010
1·008
1·006
1·004
1·002
1·000
0·998
0·996
χ
0
20
40
60
80
100
Temperature

FIG.18(h)

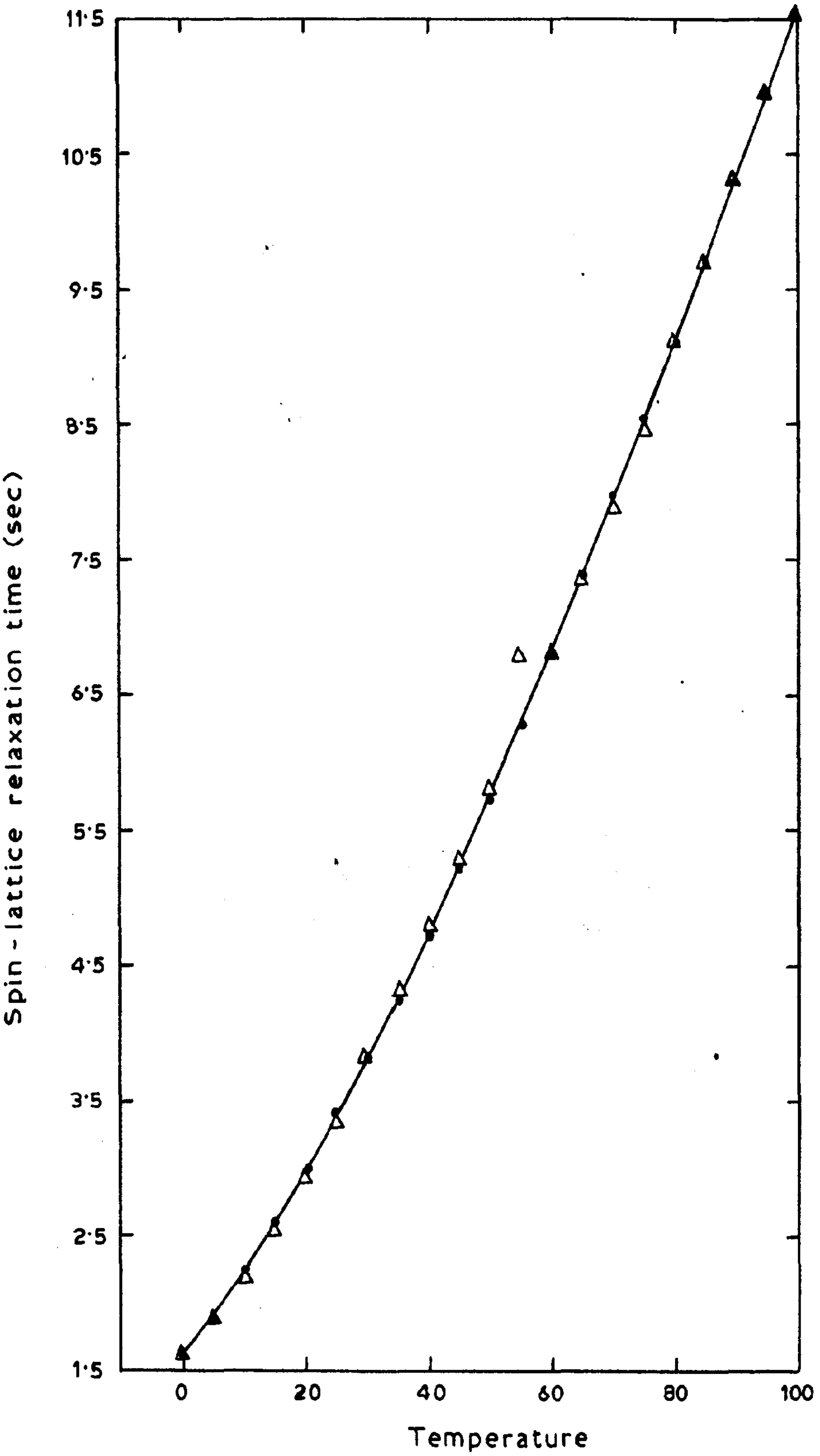

11·5
10·5
9·5
8·5
7·5
6·5
5·5
4·5
3·5
2·5
1·5
Spin - lattice relaxation time (sec)
0
20
40
60
80
100
Temperature

FIG. 18(i)

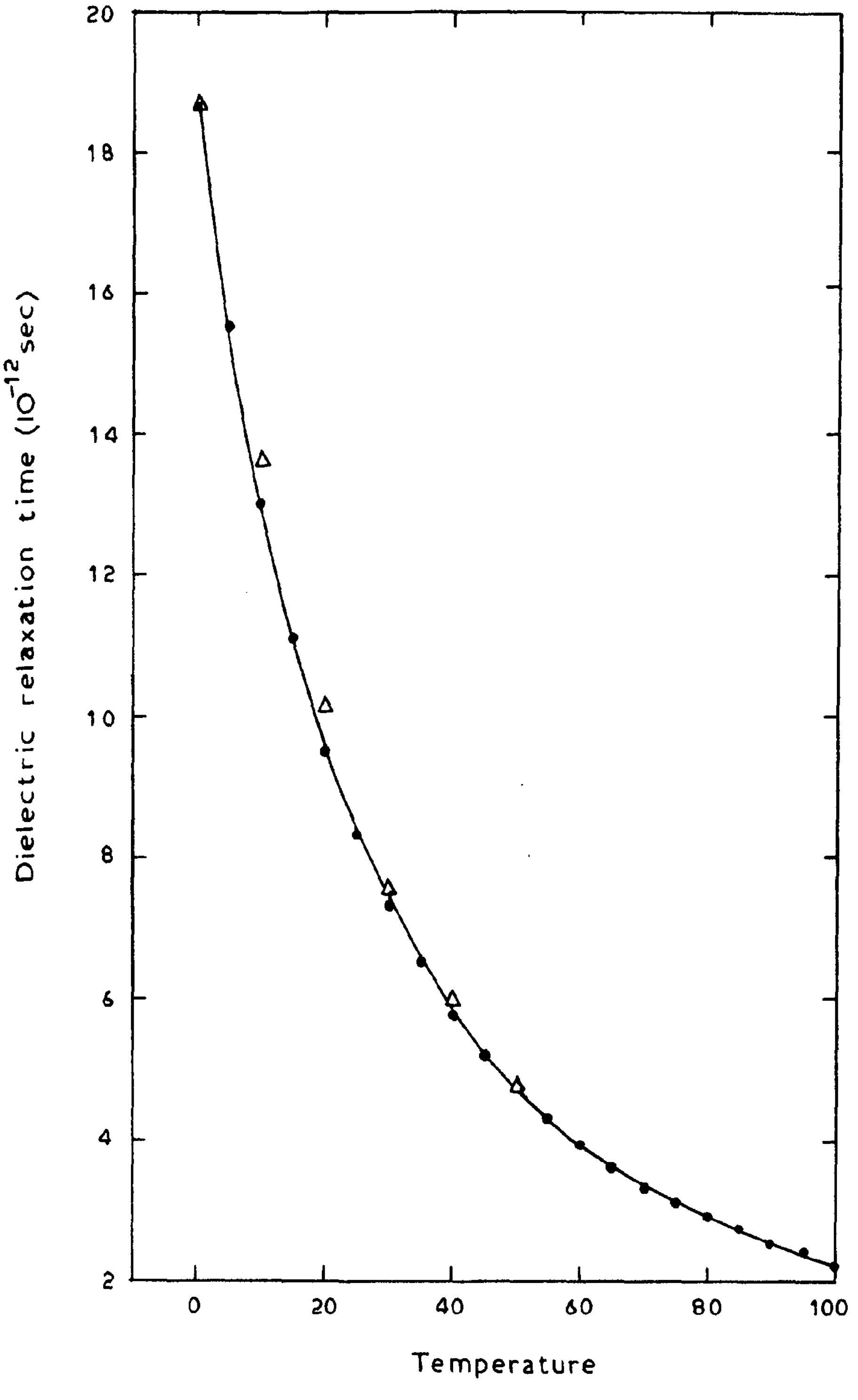

20
18
16
14
12
10
8
6
4
2
Dielectric relaxation time (10^{-12} sec)
0
20
40
60
80
100
Temperature

FIG.18(j)

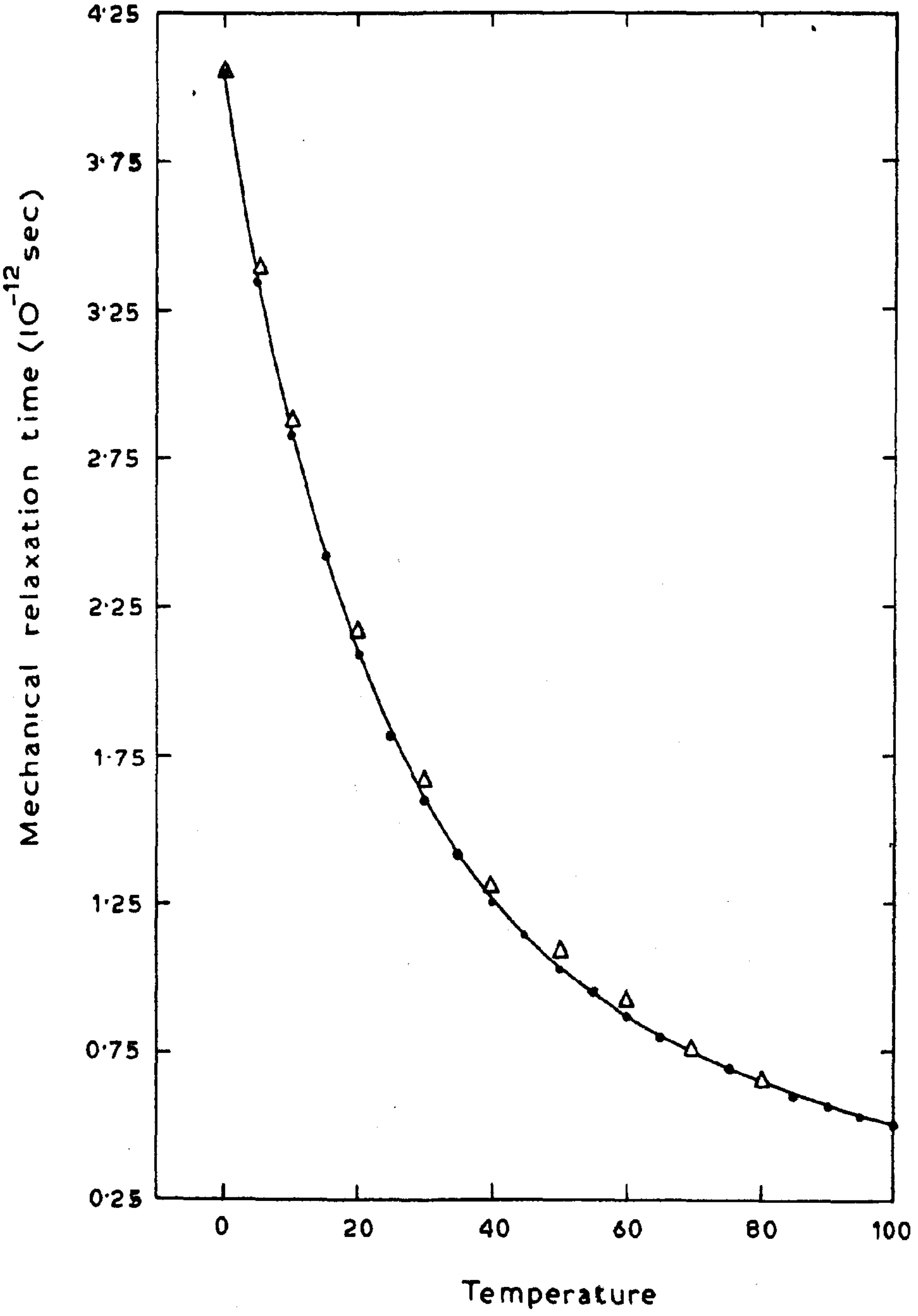

Mechanical relaxation time (10^{-12} sec)
4·25
3·75
3·25
2·75
2·25
1·75
1·25
0·75
0·25
0
20
40
60
80
100
Temperature

FIG. 18 (k)

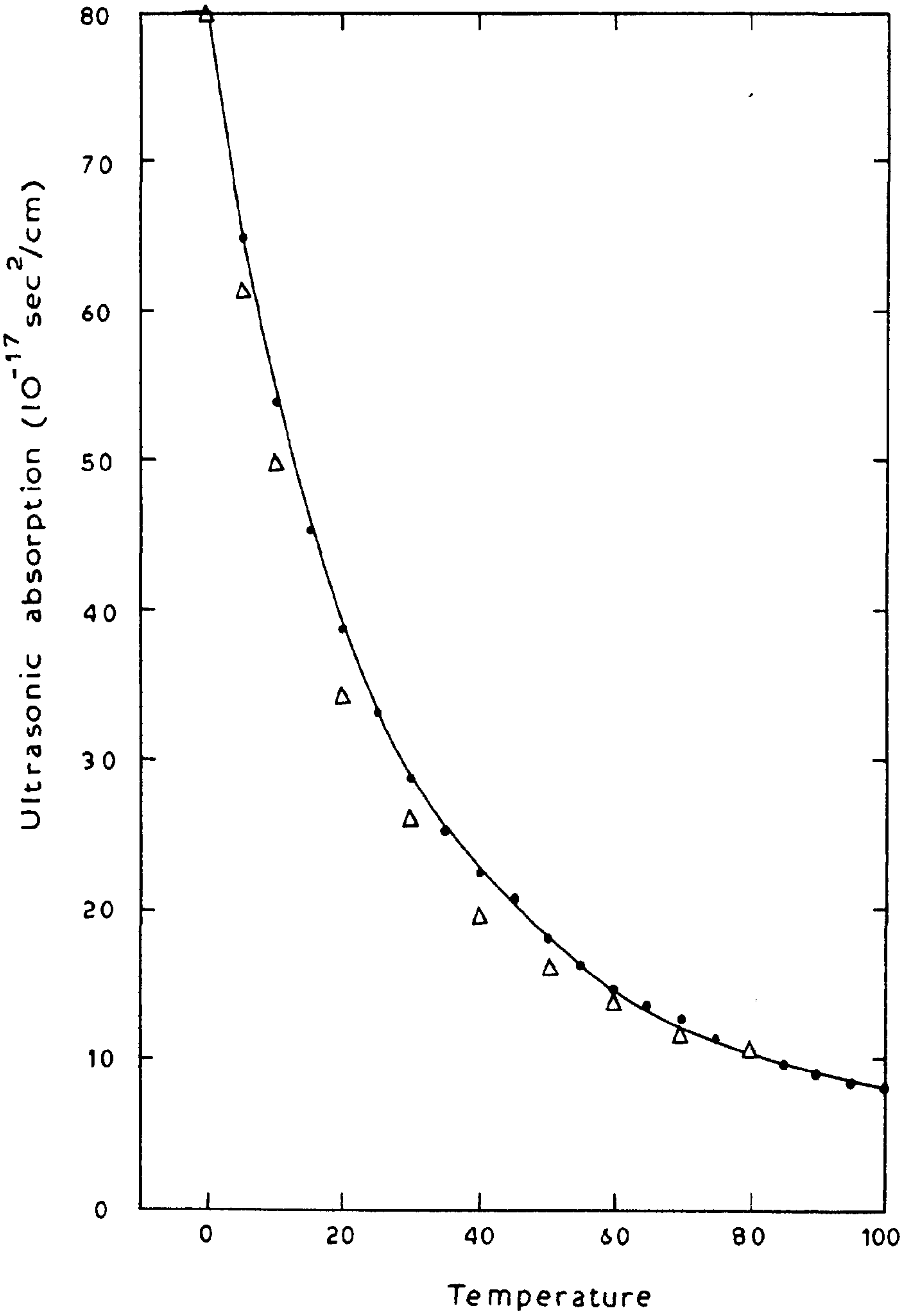

Ultrasonic absorption (10^{-17} sec^2/cm)
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
Temperature

FIG. 18(1)

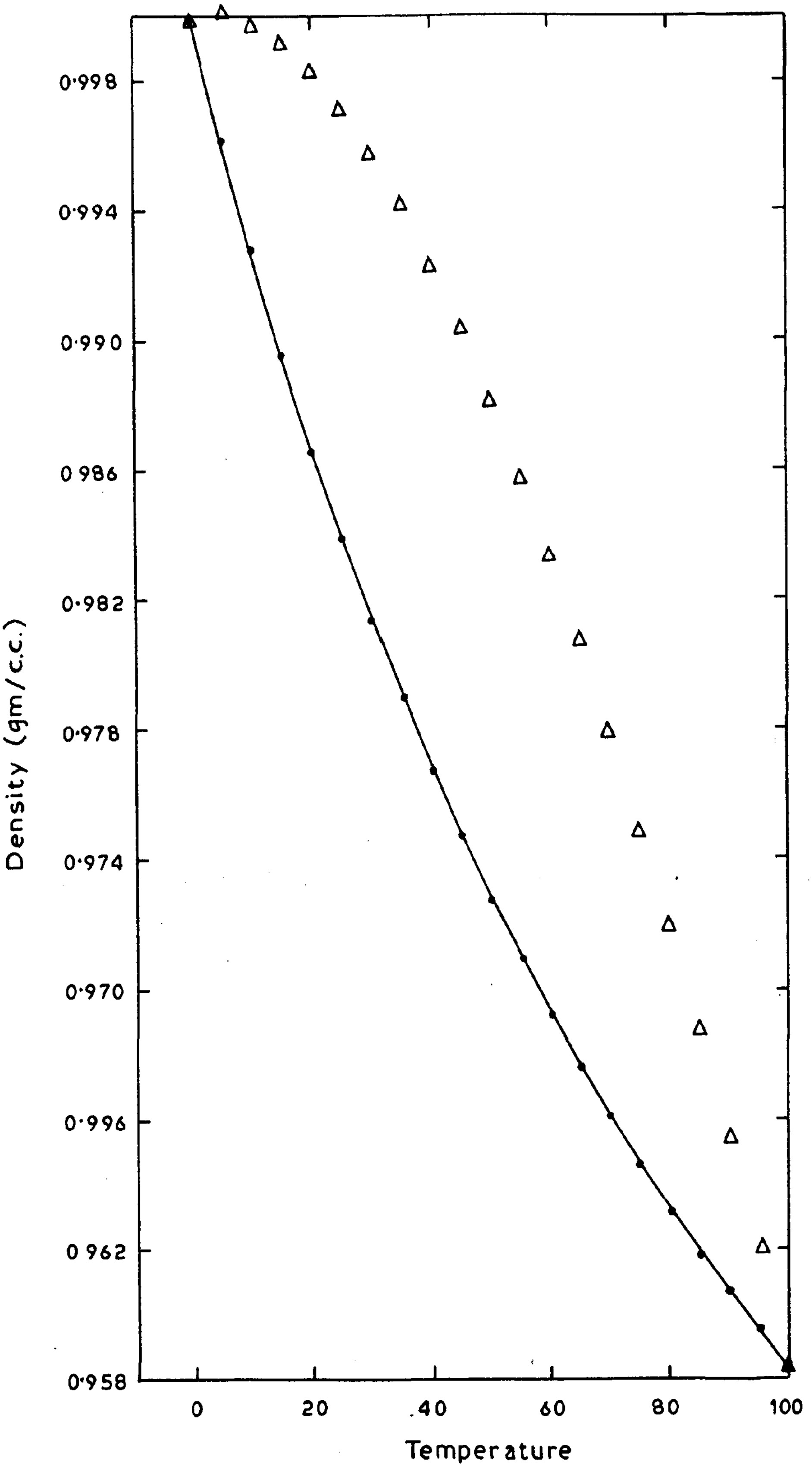

Density (gm/c.c.)
0·998
0·994
0·990
0 986
0·982
0·978
0·974
0·970
0·996
0 962
0·958
0
20
.40
60
80
100
Temperature

FIG. 18(m)

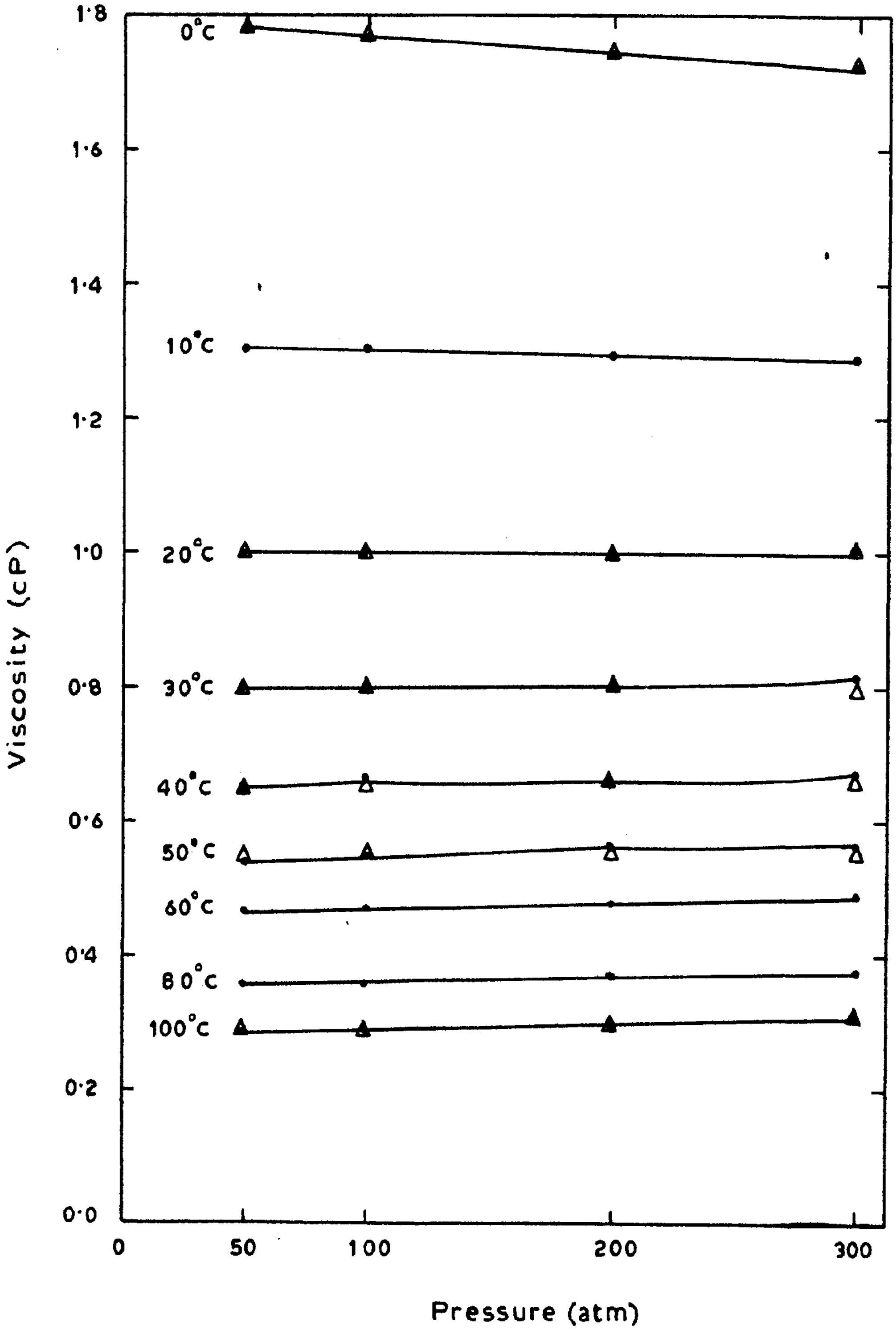

1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0·0
Viscosity (cP)
0°C
10°C
20°C
30°C
40°C
50°C
60°C
80°C
100°C
0
50
100
200
300
Pressure (atm)

FIG.19

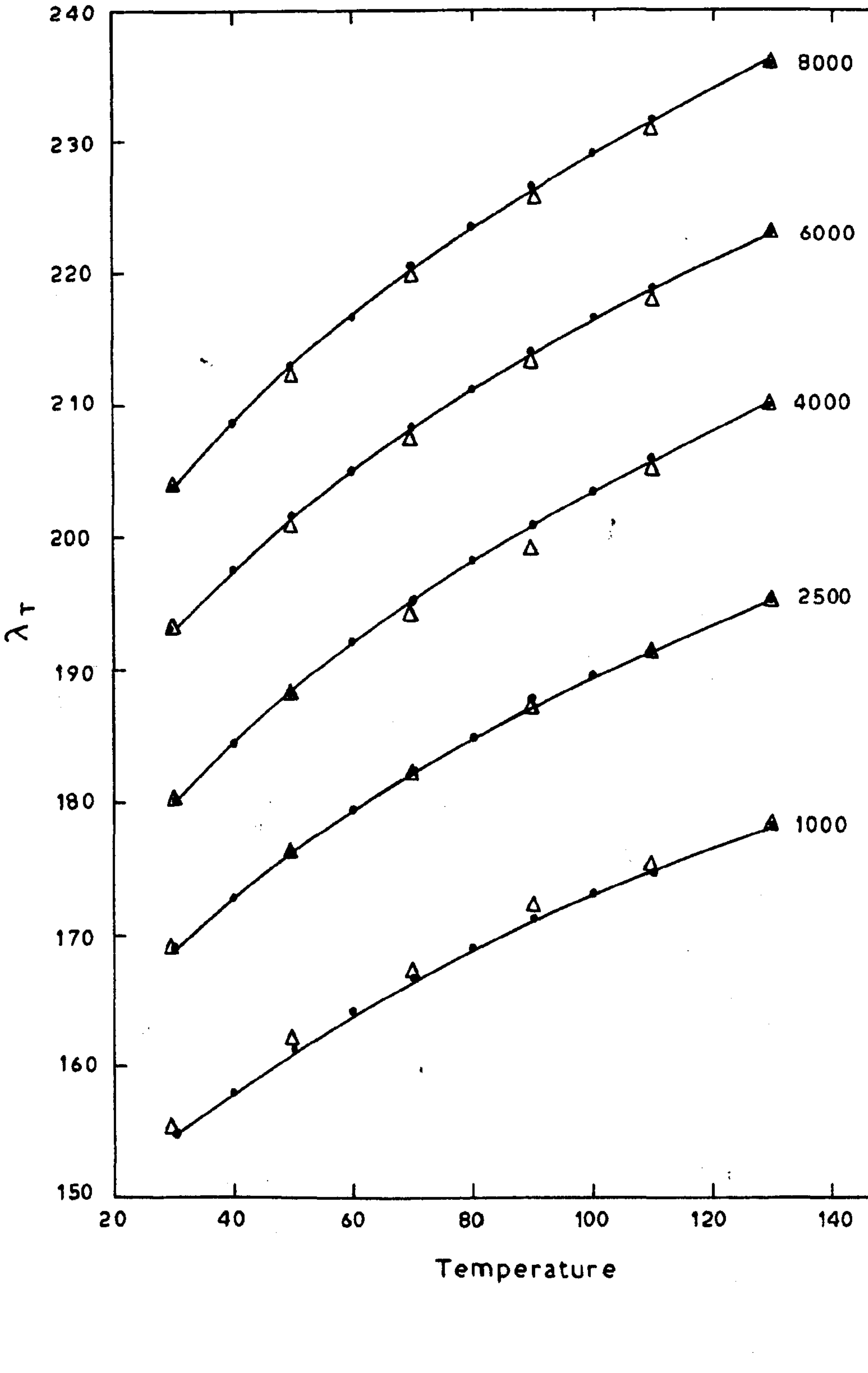

240
230
220
210
200
190
180
170
160
150
λ_T
20
40
60
80
100
120
140
Temperature
8000
6000
4000
2500
1000

FIG. 20

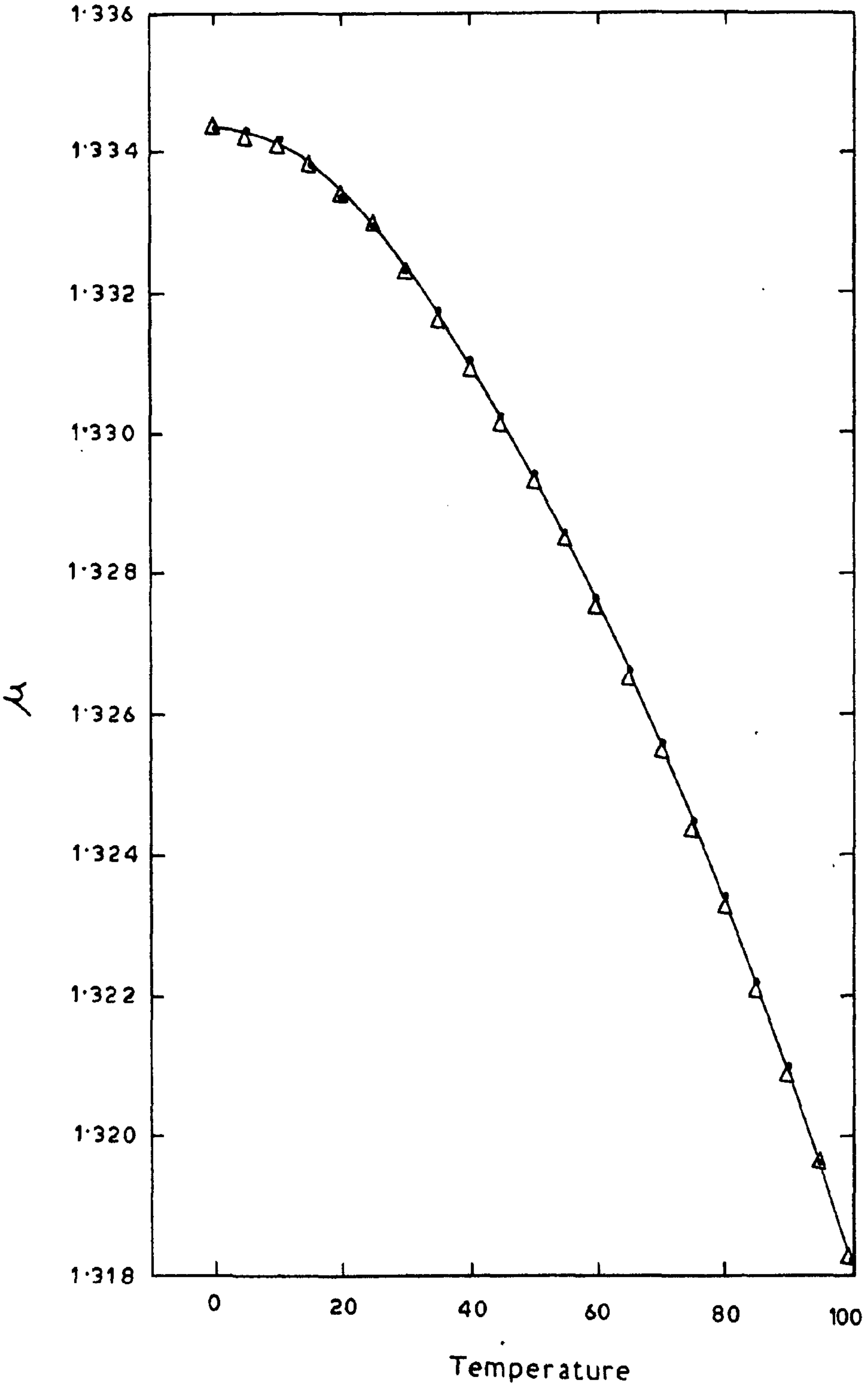

1·336
1·334
1·332
1·330
1·328
1·326
1·324
1·322
1·320
1·318
μ
0
20
40
60
80
100
Temperature

FIG. 25

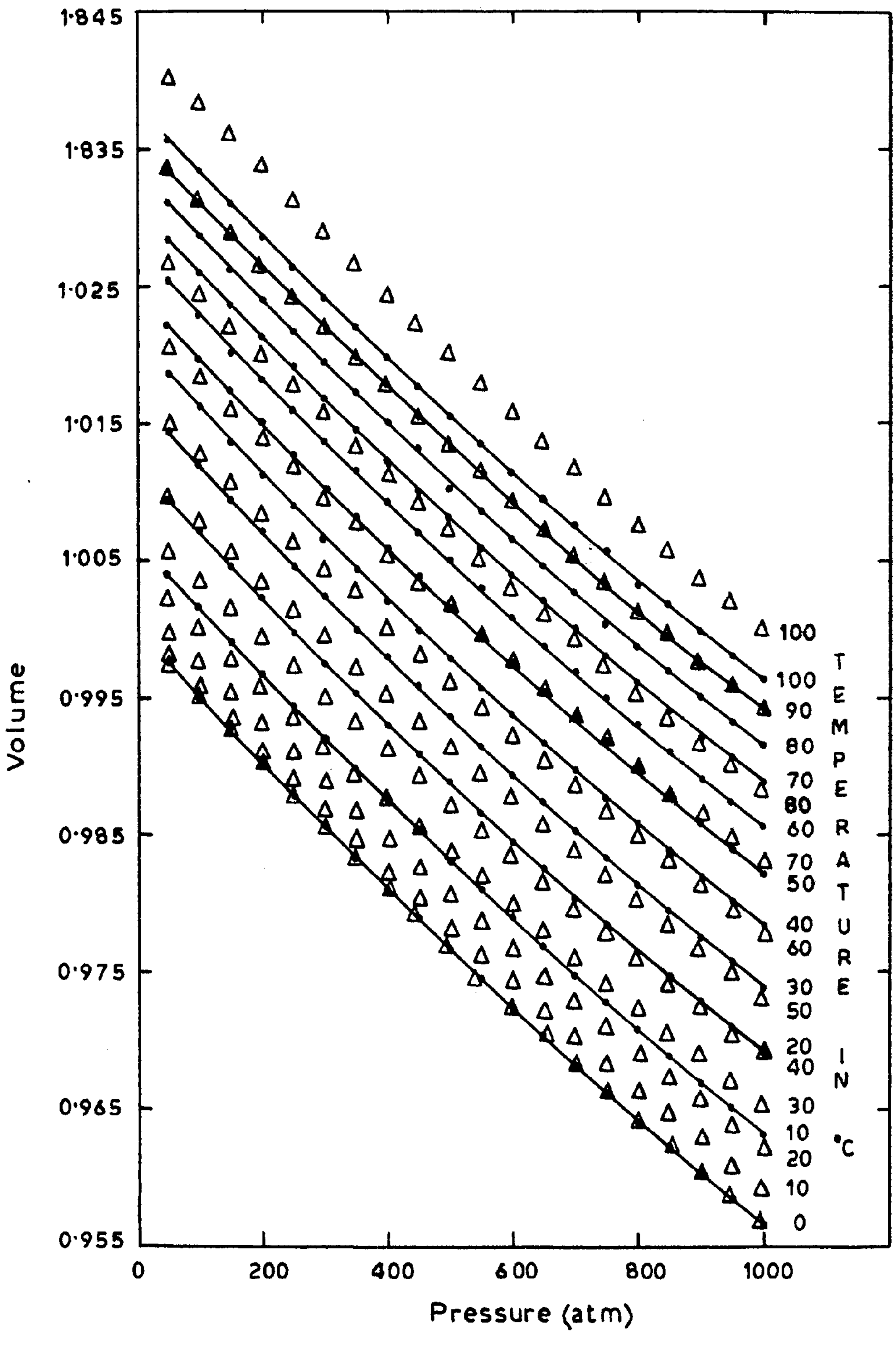

1·845
1·835
1·025
1·015
1·005
0·995
0·985
0·975
0·965
0·955
Volume
0
200
400
600
800
1000
Pressure (atm)
100
100
90
80
70
80
60
70
50
40
60
30
50
20
40
30
10
20
10
0
TEMPERATURE IN °C

FIG. 21

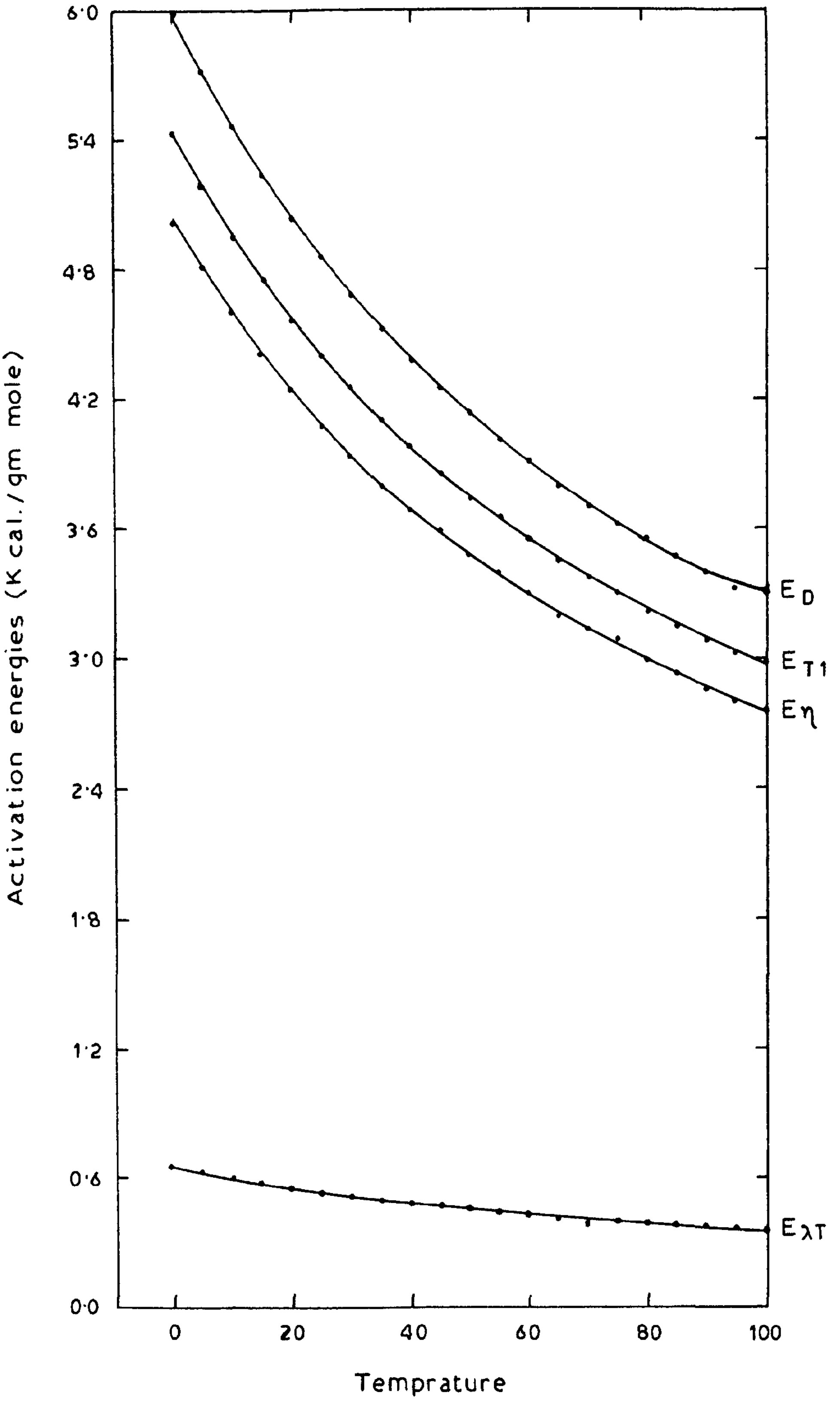

6·0
5·4
4·8
4·2
3·6
3·0
2·4
1·8
1·2
0·6
0·0
Activation energies (K cal./gm mole)
0
20
40
60
80
100
Temprature
E_D
E_{T1}
E_η
$E_{\lambda T}$

FIG. 22

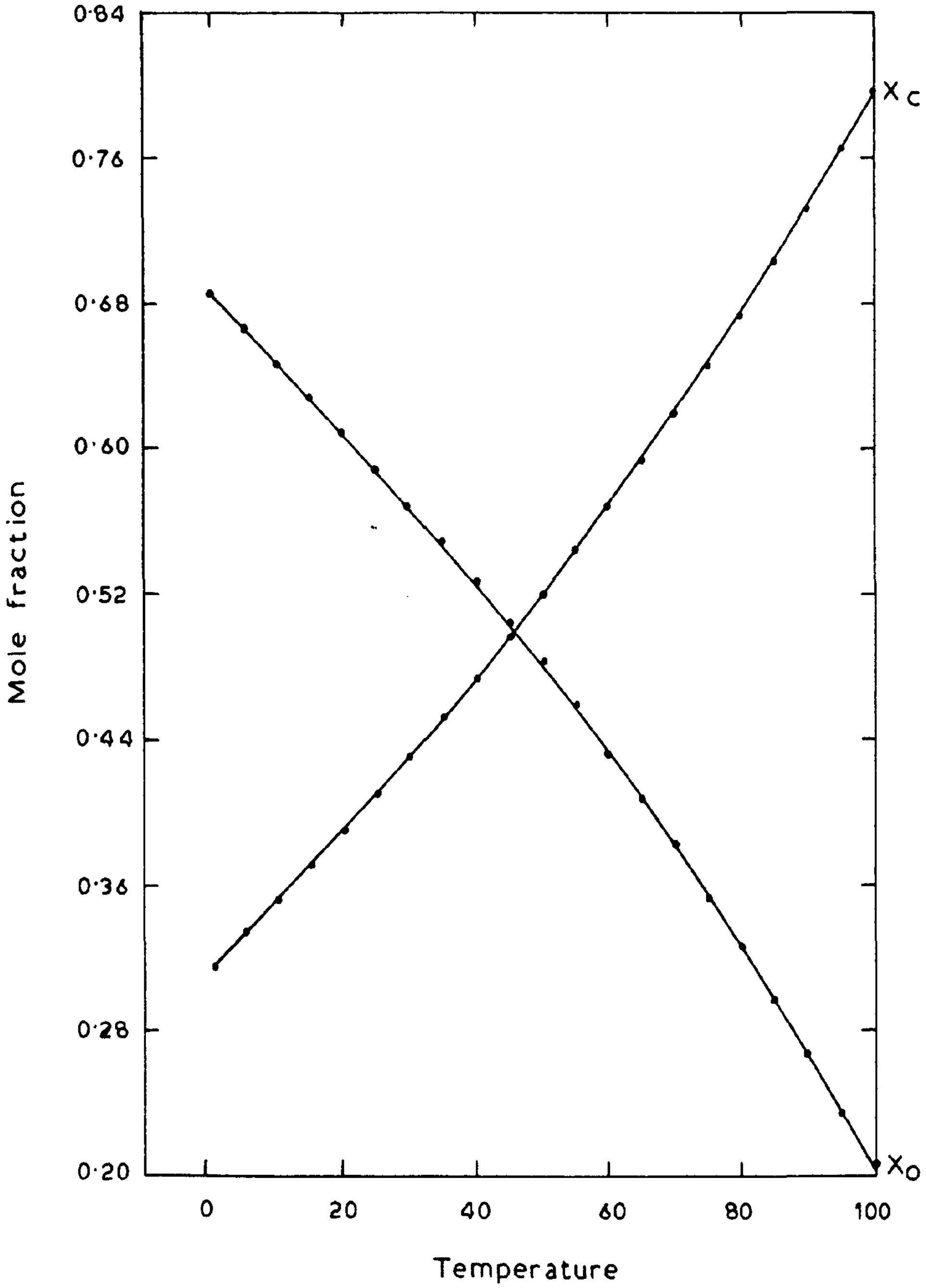

0·84
0·76
0·68
0·60
0·52
0·44
0·36
0·28
0·20
Mole fraction
0
20
40
60
80
100
Temperature
X_C
X_O

FIG. 23

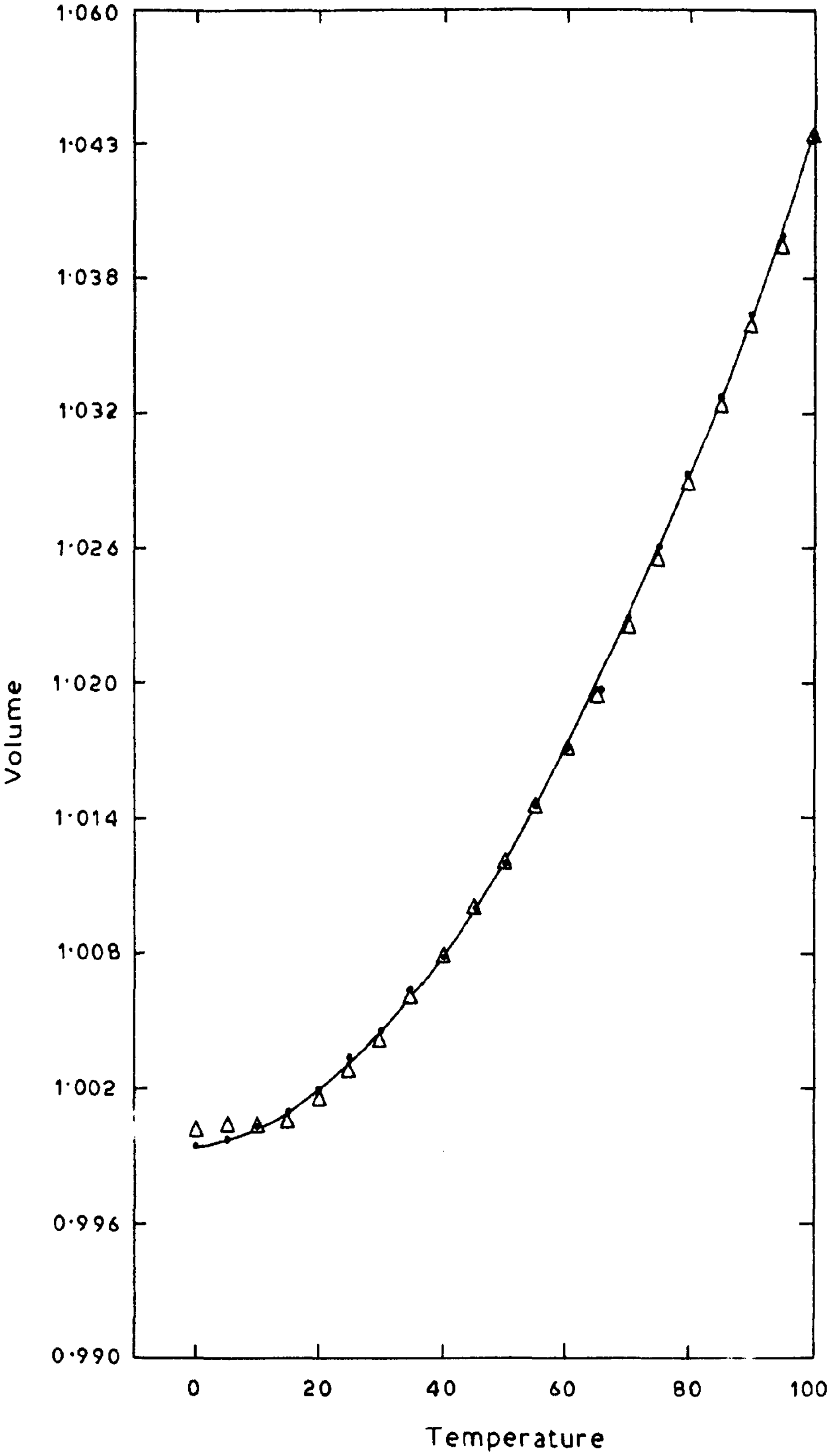

1·060
1·043
1·038
1·032
1·026
1·020
1·014
1·008
1·002
0·996
0·990
Volume
0
20
40
60
80
100
Temperature

FIG. 24

CHAPTER IV

From the works of Rowlinson et al.(78), Lester Haar et al.(119), "ZBH" (120) theory etc. and from our discussion in Chapter I and II, we conclude that a true pair potential especially for polar molecules should be temperature dependent and that the Lennard-Jones(6: n) potential could be modified such that its parameters σ and ϵ are temperature dependent.

4.1. AVERAGE POTENTIAL FOR POLAR GASES

The thermodynamic and transport properties of fluid can, in principle, be calculated by means of statistical mechanics once the intermolecular potential function is known. In the case of Polar gases the calculations in practice become complicated by the presence of the orientation dependent terms of the interaction. Monchick and Mason (121) have presented a solution for the transport properties based on a fixed orientation model using a set of simple assumptions :

(i) inelastic collisions have little effect on the trajectories.

(ii) in a given collision only one relative orientation is effective.

(iii) every possible orientation has equal weight.

their treatment has been extended to mixtures of polar gases (122) and to one component system of quadrupolar gases (123).

Recently Danon and Amdur (124) have proposed different method of calculation of transport properties based on the use of preaveraged free energy potentials (There are two different methods of averaging: The canonical averaging and the free-energy averaging. The canonical averaging by

$$\langle \phi\ (r,\ T) \rangle = \left[\int_\omega \phi(r,\omega) \exp(- \frac{\bar{\phi}(r,\omega)}{kT}) \Big/ \int_\omega \exp(\frac{-\phi(r,\omega)}{kT}) d\omega \right] \tag{4.1}$$

and the free-energy averaging by

$$\langle\langle \phi(r,tT) \rangle\rangle = - kT\,\ell n \left[\int_\omega \exp\ (- \frac{\phi(r,\omega)}{kT})\ d\omega \Big/ \int_\omega d\omega \right] \tag{4.2}$$

Both of these lead to different results). The procedure had previously been applied to the calculation of equilibrium thermodynamic properties of fluids by Cook and Rowlinson (125) and by Rowlinson (126) . Although there seems to be no similar theoretical basis for using the free-energy average potential in calculating non-equilibrium properties, the empirical evidences, however, indicates, this approach as a plausible and much simpler alternative to the more vigorous procedure of Monchick and Mason. It is found that if a procedure involving a preaveraged potential is used as an alternative to the method of Monchick and Mason, the free-energy average seems to be a better choice than the canonical average.

They assumed in their treatment that the stockmayer potential is a moderately realistic representation of the interaction between two dipolar molecules. The Stockmayer potential is

$$\phi\ (r,\omega)\ = 4\,\epsilon_0 \left[\left(\frac{\sigma_0}{r} \right)^n - \left(\frac{\sigma_0}{r} \right)^m \right] - \left(\frac{\mu^2}{r^3}\right) g(\omega) \qquad (4.3)$$

where μ is the dipole moment,

$$g(\omega) = 2\cos\theta_1 \operatorname{Cos}\theta_2 - \sin\theta_1 \operatorname{Sin}\theta_2 \operatorname{Cos}\phi$$

With θ_1 and θ_2 the angles between the axes of the molecular dipoles and the line joining the molecular centers, and ϕ the azimuthal angle in the plane perpendicular to this line. As $\mu \rightarrow 0$, $\phi(r,\omega) \longrightarrow \phi(r)$, the well known Lennard-Jones (6:12) potential with parameters σ_0 and ϵ_0 so defined that $\phi\ (\sigma_0) = 0$ and $\phi\ (r_{min}) = -\epsilon_0$. It has the additional ad-advantage of relating, after averaging according to either Equation (4.1) or Equation (4.2), reciprocal powers of r that may be written as r^{-3n}. As a result, to the second order of approximation, the orientation averaged potential has the same form as the Lennard-Jones potential, only the parameters are now temperature dependent. So, if the temperature dependent parameters of the average potentials are properly related to the temperature - independent parameters of the isotropic potential, it is possible to calculate the non-equilibrium (or equilibrium properties) by using collision integrals which are known for Lennard - Jones potential. Defining $\bar{\delta}_{max} = \frac{\mu^2}{2\,\epsilon_o\,\sigma_o^3}$ and $T_o^* = \frac{kT}{\epsilon_o}$, they show that free-energy average potential can be written as,

$$\langle\langle \phi\,(r,T)\rangle\rangle = 4\,\epsilon_o \left\{ \left(\frac{\sigma_o}{r}\right)^{12} - \left(\frac{\sigma_o}{r}\right)^{6} \left[1 + \left(\frac{\bar{\delta}^2_{max}}{3T_o^*} \right) \right] \right\} \tag{4.5}$$

Equation (4.5) can be written in the form of a Lennard-Jones potential applicable to dipolar molecules where ϵ_d and σ_d are new parameters which are temperature dependent and

$$\phi_d = 4\,\epsilon_d \left[\left(\frac{\sigma_d}{r}\right)^{12} - \left(\frac{\sigma_d}{r}\right)^{6} \right] \tag{4,6}$$

related to temperature - independent parameters, ϵ_o and σ_o by

$$\left.\begin{aligned} \epsilon_d &= \epsilon_o \left(1 + \frac{\bar{\delta}_{max}}{3T_o^*} \right)^2 \\ \sigma_d &= \sigma_o \left(\frac{\epsilon_o}{\epsilon_d} \right)^{1/2} \end{aligned}\right\} \tag{4.7}$$

From this emerges out clearly the following :

For polar molecules a true pair-potential can be a modified L-J potential with temperature dependent parameters. Some forms for polar gases have explicitly been obtained as in the work of Danon and Amdur discussed above.

4.2. TEMPERATURE DEPENDENT POTENTIAL AND THE LIQUID STATE

What form should be the temperature dependence of potential for a polar liquid, like water, is not obviously known so far. But the mere conclusion that molecular potential is temperature dependent leads to very interesting speculations regarding the treatment of liquid state suigenris, without referring to the gaseous or the solid state.

If we follow what happens to a solid on heating we can make the following picture. The solid is an ordered lattice arrangement, where the atoms or molecules are strongly bound to each other. On heating the solid whereas the kinetic energy of each molecule increases to dissociate them completely, ultimately leading to the gaseous state, the temperature dependence of the molecular force introduces a new element, namely, the molecular force, which changes with temperature in such a way that it balances the dissociation to the extent of forming minute molecular clusters in the average situation. There are thus three forces which keep a balance, (i) the molecular potential, (ii) the thermal energy and (iii) the surface energy of the molecular cluster.

This speculation is mentioned here by the way and cannot be worked out in detail unless the potential is precisely known.

In the following we shall make a heuristic attempt to search for a trial potential for liquid water.

4.3. TRIAL SEARCH FOR A TEMPERATURE DEPENDENT POTENTIAL

As a simple trial we take the potential (127),

$$\phi(r,T) = 4\,\epsilon_0 \left[\left(\frac{\sigma_0}{r}\right)^n - \left(\frac{\sigma_0}{r}\right)^6 (1 + \Omega) \right] \qquad (4.8)$$

Where Ω is a suitable function of temperature which should agree with the dipole-dipole interaction term of the stockmayer potential at different temperatures and has to be found out. We introduce the temperature function only in the attractive term of the L-J form, because the Stockmayer's modified (6 : n) potential has the addition of an extra attractive term which corresponds to direct and induced electrostatic dipole-dipole interaction. Since the dipole moment of molecules, their average distance and average relative orientations will largely be effected by temperature. We may, in a formal and empirical way, write for this potential the form of the type of equation (4.8) . Such a formal introduction of temperature in the potential is logical and should be consistent with the experimental data of gaseous properties, at least to the extent, the stockmayer potential is. This form of the potential can be written in the form (See Appendix VII)

$$\Phi(r,T) = 4\,\epsilon(T)\left[\left(\frac{\sigma(T)}{r}\right)^{n} - \left(\frac{\sigma(T)}{r}\right)^{m}\right] \qquad (4.9)$$

with $\epsilon(T)$ and $\sigma(T)$, related to temperature- independent parameters ϵ_0 and σ_0 by

$$\left.\begin{aligned} \epsilon(T) &= \epsilon_0(1+\Omega)^{n/n-m} \\ \sigma(T) &= \sigma_0(1+\Omega)^{1/m-n} \end{aligned}\right\} \qquad (4.10)$$

The function Ω must be a decreasing function of temperature and at a suitably high temperature it should become negligible small to reduce the equation (4.8) to the following form

$$\Phi(r) = 4\,\epsilon_0\left[\left(\frac{\sigma_0}{r}\right)^{n} - \left(\frac{\sigma_0}{r}\right)^{m}\right] \qquad (4.11)$$

which is the famous (m:n) Lennard-Jones potential, valid for high temperatures.

4.4. SOME PROPERTIES OF LIQUID WATER.THE FORM OF Ω

We now look for some clues for the function Ω Basing his arguments on the Némethy and Scheraga's (128) model for water and making use of the free-volume concept of Cohen and Turnbull (94) , Miller wrote an empirical relation for viscosity η of the form of

$$\ln\eta = A + \frac{B}{T - T_0} \qquad (4.12)$$

where A , B and T_0 are appropriate constants. Singh, Dass and Varshneya (97) later found that an empirical relation of the form,

$$\ln \chi = A + \frac{B\,(T_c - T)}{(T - T_0)} \qquad (4.13)$$

for any property χ is a good representation of experimental results, not only for viscosity but for many more properties of water including sound velocity and compressibility. Here A and B are appropriate constants (different for each property), T_c the critical temperature and T_0 having a value about 135°K. It is interesting to note that the Debye temperature of water also has this value. From this we guess for the liquid water a form for Ω :

$$\Omega = \left(\frac{T_c - T}{T - T_0}\right) \qquad (4.14)$$

In this form Ω is a decreasing function of temperature and is zero at $T = T_c$.

Since the potential given by Equation (4.9) should reduce to the L-J (6:n) potential at $T \sim T_c$ and since $\log A(T) \sim \log (T - T_0)$, as also $\log B(T) \sim \log (T - T_0)$ (Figs. (16) and (17)), the following form of the force parameters are justifiable

$$\left.\begin{aligned} \epsilon(T) &= \epsilon_0 \left(\frac{T_c - T_0}{T - T_0} \right)^{n/(n-m)} \\ \sigma(T) &= \sigma_0 \left(\frac{T_c - T_0}{T - T_0} \right)^{1/(m-n)} \end{aligned}\right\} \qquad (4.15)$$

Using these force parameters in equation (4.9), we now make use of the proposed potential to calculate the compressibility and sound velocity of water as in reference (129).

4.5. COMPRESSIBILITY AND SOUND VELOCITY OF LIQUID WATER

As is well known the sound velocity of liquids is a function of the compressibility K and the density ρ

$$v^2 = \frac{1}{K\rho} \qquad (4.16)$$

The temperature coefficient of v therefore is given by

$$\frac{1}{v}\frac{dv}{dT} = -\frac{1}{2}\left[\frac{1}{K}\frac{dK}{dT} + \frac{1}{\rho}\frac{d\rho}{dT}\right] \qquad (4.17)$$

In calculating the temperature coefficient of the compressibility it is supposed that the liquid contains N molecules per cm^3 which, under equilibrium conditions, are at a distance r_0 from each other, when applying an external pressure p, this value is reduced by an amount Δr . Assuming that the forces are harmonic in nature

$$p = N^{2/3} \; f_{r=r_0} \, \Delta r \cdot \qquad (4.18)$$

where $f_{r=r_o}$ = force constant. At this pressure the volume is reduced from $Nr_o^3 = 1\ \text{cm}^3$ to $V = N(r_o - \Delta r)^3$, so that K is given by

$$K = -\frac{d\,\ln V}{d\rho}$$

$$= -\frac{d}{d\rho}\left[3\ln N + 3\ln(r_o - \Delta r)\right]$$

$$K = \frac{3}{(r_o - \Delta r)}\ \frac{d\Delta r}{dp}$$

From equation (4.18)

$$\frac{d\Delta r}{d\rho} = \frac{1}{N^{2/3}\ f_{r=r_o}}$$

$$K \cong \frac{3}{(r_o - \Delta r)}\ \frac{1}{N^{2/3}\ f_{r=r_o}}$$

$$K = \frac{3r_o}{f} \qquad (4.19)$$

$$\frac{1}{K}\ \frac{dK}{dT} = \frac{1}{r_o}\ \frac{dr_o}{dT} - \frac{1}{f}\ \frac{df}{dT}$$

$$\therefore \left(\frac{1}{r_o}\ \frac{dr_o}{dT} = -\frac{1}{3\rho}\ \frac{d\rho}{dT}\right) \qquad (4.20)$$

Therefore the temperature coefficient of compressibility is given below

$$\frac{1}{K}\ \frac{dK}{dT} = -\frac{1}{3\rho}\ \frac{d\rho}{dT} - \frac{1}{f}\ \frac{df}{dT} \qquad (4.21)$$

Now the temperature coefficient of the force constant f can be calculated if the interaction energy between two molecules is known. Writing Equation (4.9) in an another form given below -

$$\Phi(r,T) = \frac{a}{r^n} - \frac{b}{r^m}\left(1 + \frac{T_c - T}{T - T_o} \right) \qquad (4.22)$$

$$\left(\frac{d\Phi}{dr}\right)_{r=r_o} = - \frac{n\ a}{r_o^{n+1}} + \frac{mb}{r_o^{m+1}} \left(1 + \frac{T_c - T}{T - T_o} \right)$$

$$b = \frac{na}{m} \left[\frac{T - T_o}{T_c - T_o} \right] r_o^{m-n} \qquad (4.23)$$

$$\left(\frac{d^2\Phi}{dr^2}\right) = \frac{n(n+1)a}{r^{n+2}} - \frac{m(m+1)b}{r^{m+2}} \left(1 + \frac{T_c - T}{T - T_o}\right)$$

$$f_{r=r_o} = \left(\frac{d^2\phi}{dr^2}\right)_{r=r_o} = \frac{n(n+1)a}{r_o^{n+2}} - \frac{m(m+1)b}{r_o^{m+2}} \left(\frac{T_c - T_o}{T - T_o} \right) \qquad (4.24)$$

Substituting the value of b from Equation (4.23) in Equation (4.24) , we get,

$$f_{r=r_o} = \left(\frac{d^2\phi}{dr^2}\right)_{r=r_o} = \frac{n\ (n+1)a}{r_o^{n+2}} - \frac{(m+1)na}{r_o^{m+2}}$$

$$f = \frac{n(n-m)a}{r_o^{n+2}} \qquad (4.25)$$

Now on differentiating Equation (4.24)

$$\frac{df}{dT} = \frac{d}{dT}\left(\frac{d^2\phi}{dr^2}\right)$$

$$= \left[\frac{-\ na(n+1)(n+2)}{r_o^{n+3}} \frac{dr_o}{dT} + \frac{m(m+1)(m+2)b}{r_o^{m+3}} \left(\frac{T_c - T_o}{T - T_o}\right) \frac{dr_o}{dT} + \frac{m(m+1)}{r_o^{m+2}}\ b.\left(\frac{T_c - T_o}{(T - T_o)^2} \right) \right] \qquad (4.26)$$

Now substituting the value of b in this equation, we get,

$$\frac{df}{dT} = \frac{na}{r_o^{n+2}} \left(- \frac{1}{r_o} \frac{dr_o}{dT} \right) \left[(n-m)(n+m+3) \right] + \frac{na(m+1)}{r_o^{n+2}} \frac{1}{(T-T_o)}$$

$$\therefore \frac{1}{f} \frac{df}{dT} = (n+m+3) \left(- \frac{1}{r_o} \frac{dr_o}{dT} \right) + \frac{m+1}{(n-m)} \cdot \frac{1}{(T-T_o)}$$

$$\because \left(\frac{1}{r_o} \frac{dr_o}{dT} = \frac{1}{3\rho} \frac{d\rho}{dT} \quad \text{from Equation (4.20)} \right)$$

$$\therefore \left(\frac{1}{f} \frac{df}{dT} \right)_{r=r_o} = \frac{n+m+3}{3\rho} \frac{d\rho}{dT} \qquad \frac{7}{(n-m)} \frac{1}{(T-T_o)} \qquad (4.27)$$

From Equations (4.21) and (4.27) , we get,

$$\frac{1}{K} \frac{dK}{dT} = - \left(\frac{n+m+4}{3\rho} \right) \frac{d\rho}{dT} - \frac{7}{(n-m)(T-T_o)} \qquad (4.28)$$

Now from Equations (4.17) and (4.28) , we get,

$$\frac{1}{v} \frac{dv}{dT} = \frac{n+m+1}{6\rho} \frac{d\rho}{dT} + \frac{7}{2(n-m)} \frac{1}{(T-T_o)} \qquad (4.29)$$

First of all, since we know that the sound velocity in water has a maximum at 76°C , we can use this condition in Equation (4.29) to fix n . Keeping $m = 6$ (theoretically justified) and $T_o = 135^\circ K$ we get $n \cong 14$. Now integrating Equation (4.28) , we get,

$$\ln K = -8 \ln \rho - \frac{7}{8} \ln (T-T_o) + \lambda_1 \qquad (4.30)$$

at an arbitrary reference temperature T_r,

$$\ln K_r = -8 \ln \rho_r - \frac{7}{8} \ln (T-T_0) + \lambda_1$$

$$\lambda_1 = \ln K_r + 8 \ln \rho_r + \frac{7}{8} \ln(T_r - T_0)$$

$$\therefore \ln K = 8 \ln \left(\frac{\rho_r \, K_r^{1/8}}{\rho} \right) - \frac{7}{8} \ln \left(\frac{T-T_0}{T_r-T_0} \right) \quad (4.31)$$

Now on integrating Equation (4.29) , we get,

$$\ln v = \frac{7}{2} \ln \rho + \frac{7}{16} \ln (T-T_0) + \lambda_2$$

At an arbitrary reference temperature T_r, we have

$$\lambda_2 = \ln V_r - \frac{7}{2} \ln \rho_r - \frac{7}{16} \ln (T_r-T_0)$$

$$\ln V = \frac{7}{2} \ln \left(\frac{\rho \, V_r^{2/7}}{\rho_r} \right) - \frac{7}{16} \ln \left(\frac{T-T_0}{T_r - T_0} \right) \quad (4.32)$$

Where K_r , ρ_r and V_r are experimental values at an arbitrary reference temperature T_r, of compressibility, density, and sound velocity respectively. It will be noticed that we get on expanding the logarithimic function for temperature upto the first term, approximate expressions for K and V similar to the one suggested by Varshneya et al(97) which has been found good empirically. We can calculate K and V using the values of $\frac{1}{\rho} \frac{d\rho}{dT}$ given in reference (98) . We see that these equations represents the experimental data (89, 98) very good as shown in Figs. (26) and (27).

4.6 PRESSURE CHANGE OF BULK MODULUS

Differentiating Equation (4.30) with respect to pressure, we get,

$$\left(\frac{1}{K}\frac{dK}{dP}\right) = -\frac{8}{\rho}\left(\frac{d\rho}{dP}\right)_T + \left(\frac{\partial \lambda_1}{\partial P}\right)_T \qquad (4.33)$$

Now because isothermal compressibility is defined by

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

$$\text{or} \quad K = \frac{1}{\rho}\frac{d\rho}{dP} \qquad (4.34)$$

From Equations (4.33) and (4.34), we get,

$$\frac{1}{K}\frac{dK}{dP} = -8K + \left(\frac{\partial \lambda_1}{\partial p}\right)_T$$

Dividing both sides by $(-K)$, we get,

$$-\frac{1}{K^2}\frac{dK}{dP} = +8 - \frac{1}{K}\left(\frac{\partial \lambda_1}{\partial p}\right)_T$$

As a first approximation we assume that λ_1 is pressure independent (in fact it depends upon pressure slightly), then

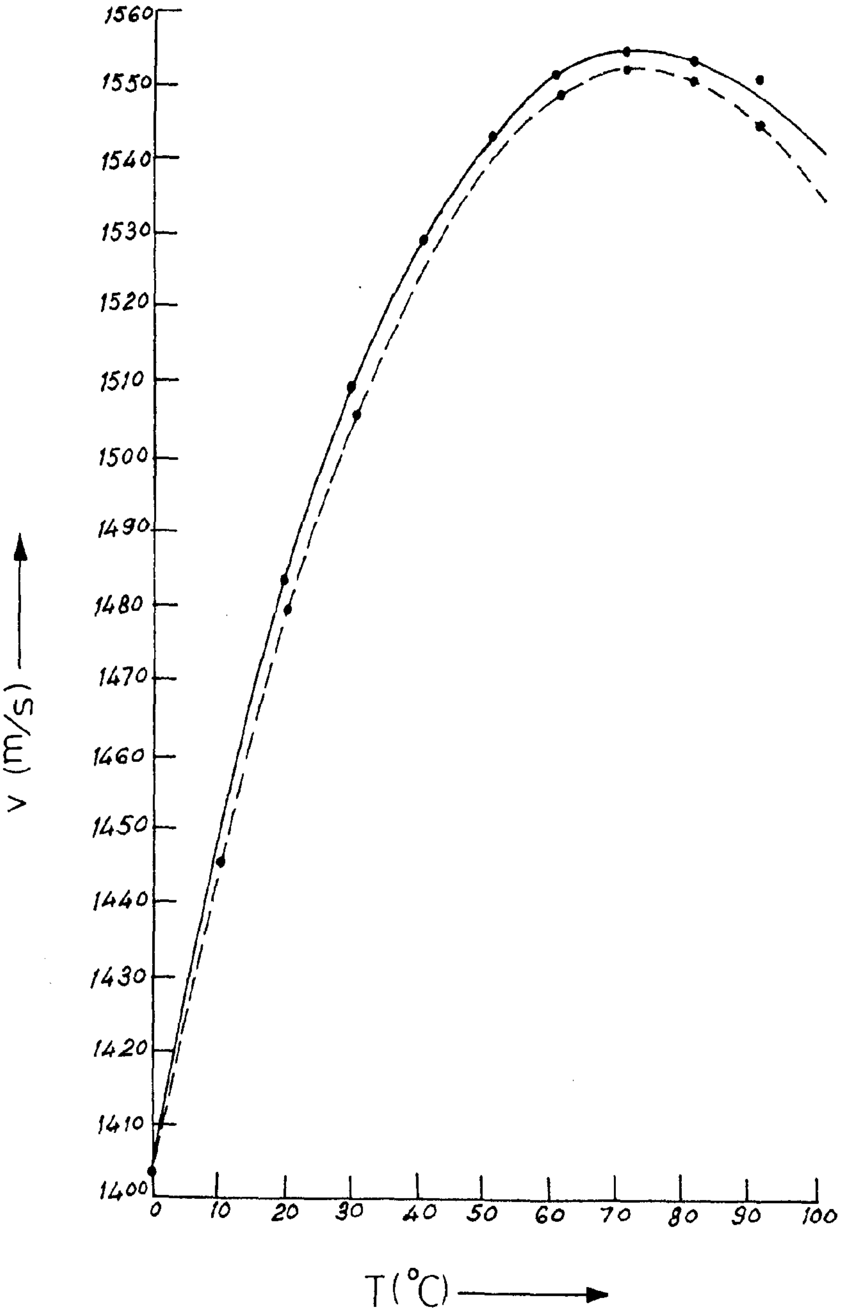
$$C_1 \equiv \left(\frac{d}{dP}(1/K)\right)_T = 8 \qquad (4.35)$$

In the case of non-polar liquids, it was shown by Moelwyn-Hughes (130) by thermodynamic arguments that the pressure change of bulk modulus of rigidity is a constant. Here in case of polar liquids (water) also we note from Equation (4.35) that the pressure change of bulk modulus of rigidity of water is also constant and has the value $C_1 = 8$, while the experimental value obtained from the slope of the graphs of $1/\beta$ Vs. P is 8.2, which is in good agreement with the calculated values,

4.7 CONCLUSION

In searching for a true pair potential which is both simple and workable, we thus see in the above that a temperature dependent potential of the form of Equation (4.9) is a promising one. There have been numerous attempts already in print which suggest variations of parameters of the Lennard-Jones (6:m) potential in some form or the other of adhoc nature to suit the experimental data. The suggested potential (4.9) gives a regular variation of the parameters of the L-J (6:n) potential in a consistent way and agrees with the data shown above.

Although a rigorous theoretical derivation of temperature dependence is yet to be attempted, the proposed potential may be found useful. To decide whether this is indeed the true pair potential, it would be most desirable to test this model against other equilibrium and non-equilibrium properties. This work presents an exploration of a possible potential function.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30
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70
80
90
100
T(°C)

FIG. 26

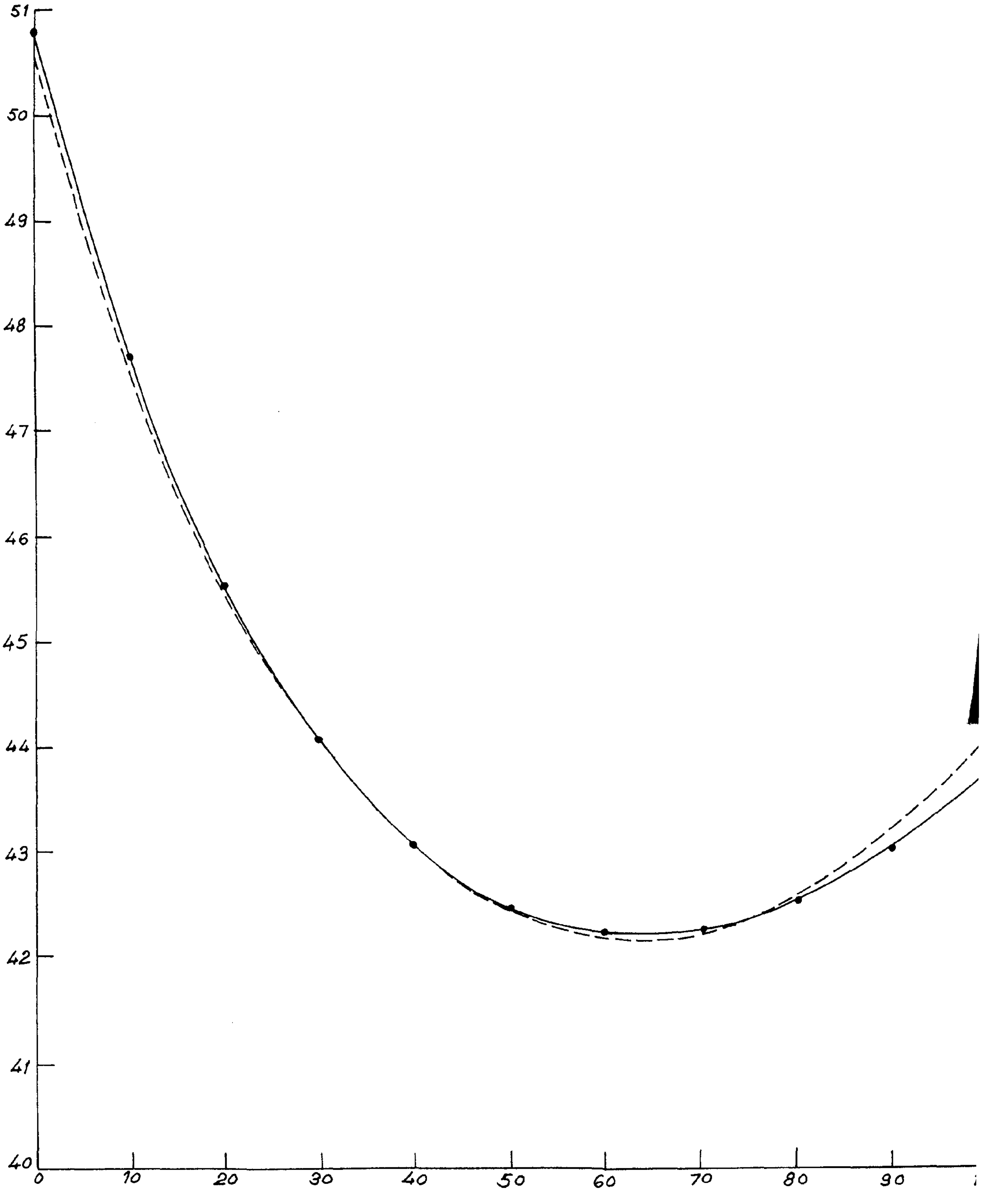


FIG. 27

CHAPTER V

There are many approaches prevalent to the liquid theories. Cell and hole theories appear to describe solids rather than liquids. The tunnel & 'worm' theories give good results for liquid densities and compressibilities but unsatisfactory results for entropy and critical constants. The Born-Green-Yvon, Percus-Yevick(131), and hypernetted chains theories and their extensions so far appear to be unsatisfactory in the presence of strong attractive forces (132). It appears that all theories based on density expansions meet a formidable barrier in their approaches to the liquid state, but there does not seem to be any such barrier in the ZBH theory (133) (Zwanzig theory modified by Barker and Henderson(120)).

Although the perturbation theories are in the process of developing into a consistent theory. But so far only it has been proven that they are physically satisfying approach to the theory of the equilibrium properties only and that is too for simple liquids not for non simple liquids like water.

Here below a brief discussion of some of the earlier theories is given.

5.1 CELL THEORY

The cell model (124) is based on the idea that each molecule in a liquid or compressed gas spends much of its time confined by its neighbours to a comparatively restricted region (cage or cell in which the central molecule moves). The number of cells is chosen to be equal to the number of molecules.

The simplest possible assumption is that the molecules move entirely independently of one another in their cells and when considering the motion of the central molecule, the neighbours which form the cage as fixed at the centres of their respective cells. Further all the cages are identical and that each contains just one molecule which imposes severe restrictions on fluctuations of density. Precisely speaking it restricts the configuration space available to the molecules to that fraction of the total configuration space in which every cell contains one molecule.

The regular lattice of cell centres brings back the very future of long-range order, thus it should not be surprising if the cell theory actually describes solids rather than fluids.

A simpler approach, developed by Eyring and Hirschfelder (135,136) is based on combining the expression for the configurational entropy with an empirical expression for the configurational energy. This uses the idea that the free volume and entropy are deterimined primarily by the repulsive forces and the energy primarily by the attractive forces. Strictly speaking such a separation effects cannot be rigorously justified, but however, it leads to a useful semi-empirical equation i.e. Eyring equation of state given below

$$(p + a(T)/\tilde{V}^2) \quad (\tilde{V} - 0.7816b^{1/3}\,\tilde{V}^{2/3}) \quad = \quad RT \qquad (5.1)$$

it is capable of giving a useful semiempirical description of the properties of liquids and gases (12).

The cell theory - abbreviated to "L-J-D" theory was first investigated in detail by Lennard-Jones and Devonshire. In their two papers (6,137) they calculated the thermodynamic properties based on the cell model for molecules interacting according to (6:12) potential and in later papers (4,5,138,139) they regarded the cell model as more precisely a model for solids, and they explained the differences between solids and liquids in terms of their order-disorder theory of melting.

In making comparisions with experiment they found that the L-J-D theory is in fact an excellent theory of solids in the temperature range where quantum effects are not important. This is not surprising since theory uses essentially the Einstein model with full correction for anharmonicity. One might have hoped that the theory would describe both solids and liquids in appropriate temperature ranges which is not the case because above the melting point the theory describes a solid phase which is metastable.

Inspite of this the theory is of fundamental importance in the theory of liquids, because effectively all progress towards a satisfactory lattice or structural theory of liquids has arisen from attempts to justify or improve the L-J-D theory. Furthermore the L-J-D theory may validly be regarded as an approximate theory of fluids Since from some points of view the thermodynamic differences between solids and fluids are small, particularly if the fluid and solid are considered at the same density.

5.2. THE VARIATIONAL THEORY AND CELL MODEL

Kirkwood (140) proposed a variation method based on the cell model. The method is closely analogous to the Hartree and Hartree-Fock self consistent field methods of quantum mechanics. Kirkwood proposed that the probability density function should be approximated by a simple product of identical cell distribution functions each depending on the coordinates of one molecule with respect to an origin at the centre of its cell. This corresponds to the assumption of independent motion in the L-J-D theory . It seemed likely that the variation method could be regarded both as a justification for the approximations of the L-J-D theory and as a method for calculating more accurate results than those given by the L-J-D theory. But later calculations due to Hirschfelder and his Colleagues (141,142) have proved that this is not the case. Comparision with experiment shows that the variational theory based on the cell model describes solids not liquids.

5.3. THE CELL-CLUSTER THEORY

The cell-cluster theory, developed by de Boer(143) provides an elegant and formally convergent method for taking account of correlation and multiple occupation effects which are ignored by the L-J-D theory. The basic idea is to devide the lattice of cells into clusters of cells and to express the total configuration integral as a sum of products of cell cluster configuration integrals. The simplest of these integrals is the L-J-D free volume, v_f , and the leading term in the sum of products is just the L-J-D result for the configuration integral. The remaining terms involve contributions from pairs or larger clusters of cells, and correct for correlation and multiple occupation effects. In practice the only clusters for which the integrals can be evaluated are pairs of cells. If only the contributions from these are induced then the cell-cluster theory suffers from roughly the same limitations as the L-J-D theory. However the cell cluster theory, with allowance for two cell clusters only, does not improve on the L-J-D theory as far as the pressure is concerned, although the entropy is certainly improved. To some extent it seems that what the cell cluster theory gains in simplicity and elegance it loses in flexibility. Of course if it becomes practicable to evaluate the integrals for larger clusters this situation will be changed-entirely. An advantage of the cell cluster theory is that it can easily be carried over into quantum mechanics, simply by replacing the classical cluster integrals by quantal . slater sums. Recently Dahler and Cohen (144) have generalized the cell cluster theory in such a way as to allow for the presence of holes or empty cells. The consequences of this modification are not yet known.

5.4. HOLE THEORIES OF LIQUIDS

Originally Eyring (145) introduced the idea of hole theory to decrease the coordination number of a molecule in the liquid by introducing into the cell theory the concept of empty cells or holes as was pointed out by de Boer (146) that the agreement of the L-J-D theory with experiment could be improved by choosing the number of nearest neighbours Z smaller than the value 12 corresponding to close packing. The presence of holes, and their more or less random distribution on the lattice, would explain at least part of the disorder in liquids which gives rise to the entropy increase on melting. Furthermore the presence of holes would give a basis for understanding the relative ease of diffusion and flow in liquids in terms of a vacancy. In fact hole theories give the correct value for the entropy of the perfect gas, so that the whole of the communal entropy is included in the low density limit. But at high densities the proportion of holes becomes very small and the predictions of the hole theories are very close to those of cell theories. In a hole theory the cell size remains constant (independent of the density and temperature) so that the whole of the thermal expansion is due to the increasing number of holes. Alternatively one could suppose that both the cell size and the number of holes vary.

Because in hole thoeries the number of cells exceeds the number of molecules and so there will be a number of empty cells or holes present even when no cell contains more than one molecule, which implies that the number of nearest neighbours is decreased below that of the solid in accordance with the experimental evidence.

These theories are based largely on this idea, that the cells can be chosen sufficiently small so that configurations with more than one molecule in any cell can be neglected entirely. There are some doubt as to the justification for the assumption that multiple occupation of cells can be neglected in the hole theories. Nevertheless this assumption has been made in existing hole theories.

The least satisfactory feature is that if the cell volume is determined to minimize the free energy then the cells are so large that multiple occupation cannot be neglected. Thus to develope a really satisfaftory hole theory, it would probably be necessary to allow for the effects of multiple occupation.

5.5 SIGNIFICANT STRUCTURES THEORY

Eyring and his associates (147,148) have proposed a model for the liquid state based on an arbitrary separation of the degrees of freedom of the system into 'solid like' and 'gas like' components. They suggest the following partition function for the liquid :

$$Z = \left[\frac{e^{E_s/RT}}{(1 - e^{-\Theta/T})^3} \left(1 + n_h e^{-a/n_h RT} \right) \right]^{\frac{Nv_s}{v}} \left[\frac{ev}{\Lambda^3} \right]^{\frac{N(v-v_s)}{V}} \qquad (5.2)$$

where,

E_s = the energy of sublimation

Θ = the Debye temperature of the solid

n_h = the fraction of molecules in the liquid which border holes.

a = a disposable parameter

v_s = molecular volume of the solid

v = molecular volume of the liquid

Λ = $(2\pi mkT)^{1/2} / h$ is proportional to the De De Broglie wave length.

with a suitable choice of a, this function does remarkably well in generating the thermodynamics.

This theory has been applied with the excellent degree of success to a tremendous range of liquids. Its usefulness cannot be doubted since the model can be applied to so many different liquids, can be used to calculate transport properties and surface tension, and can be used to compute the radial distribution function. The theory rests on a model of the liquid state which is reasonably successful. The model envisioned by Eyring et al is that which would be formed if all the volume increase upon fusion went to form holes of molecular size. Thus the immediate neighbour separations in the liquid are considered to be the same as in the solid, and melting decreases the average coordination number of a molecule by an amount proportional to the increase in volume fraction during fusion.

Any how the criticisms raised against the theory are as follows -

(i) It has a number of adjustable parameters.

(ii) It does not provide the reduce equation of state.

(iii) The agreement between calculated and observed heat capacity and Helmlioltz energy is not good as claimed by the authors.

5.6. MONTE CARLO METHOD

This method signifies a numerical calculation method in which specific probability elements are introduced in contradiction to the calculations made by classical techniques. The problem mainly consists in evaluating multiple integrals of the type of configurationals encountered in the Gibbs statistical physics by numerical integration over random sets of points instead of the usual method of integrating over a regular set of points. This method uses ensembles averaging and restricted to equilibrium phenomena but in this field is probably more satisfactory and is true for any law of interaction of particles, but depends only on the configurations of the particles, provided that the ergodicity condition is satisfied. This method was employed for the two dimensional case in one of the earliest works (149) . The still more interesting three-dimensional case has been dealt with by Rosenbluthe et al. (150) and Wood et al. (151).

Monte Carlo method is restricted by the fact that only a limited number of molecules can be connected, this limitation is imposed by computing speed rather than by information storage requirements. To minimize the effect of this restriction a periodic boundary condition is used. It is supposed that the whole of space is filled by repitition of a fundamental cell of volume V containing N molecules. As a consequence of this the Monte Carlo method is closely related to the simpler cell theories, The fundamental difference is that the cell is large and contains many molecules. Further differences lie in the treatment of the 'surface effects' which are of course much less important with a large cell, and in the fact that other cell theories permit approximate evaluation of the partition function. In the present state of the art of computing, the partition function, and therefore the entropy cannot be evaluated by this method. Any how with the rapid growth of the technical means and computational methods Monte Carlo method have bright prospects.

5.7. THE METHOD OF MOLECULAR DYNAMICS

Alder and Wain wright (152, 153) have used a fast electronic computer to study the behaviour of molecules moving randomly under specified attractive and repulsive forces at various densities corresponding to the solid, liquid, gaseous states.

The method is capable of dealing not only with equilibrium phenomena but also with relaxation and non-equilibrium phenomena. This method uses time averaging following the trajectories of the system. In this method the classical equations of motion for a system consisting of a very large number of particles are solved by a step-wise procedure. So far the calculations have been made only for rigid non-interacting spheres and square well potentials. The periodic boundary condition is used, so that a molecule leaving the fundamental cell through one face- re-enters it through the opposite face. In this way the number of molecules in the cell remain constant. In determining when and where the next collision will occur a convention analogous to the 'minimum image distance' rule is adopted. Initially, for each system, all the particles of the fundamental cell situated at the sites of the face-centred cubic lattice were uniformly distributed over the whole of the cell with equal speeds but random directions of motion. The velocity distribution tends rapidly to the Maxwell distribution. The total energy of course remains constant and determines the temperature.

The method of molecular dynamics show that even in fluid state the molecules appear to vibrate for considerable periods in localized regions.

Apart from the lack of a simple picture of the structure, the disadvantage common to both the Monte Carlo method and the method of molecular dynamics is the amount of computation required to obtain the results but with the rapid growth of technical means and computational methods, it seems that in the near future these methods (specially Monte Carlo method) will be great success in statistical physics.

5.8. THE TUNNEL THEORY

In 1960 Barker proposed a model (154, 155) for liquids - THE TUNNEL MODEL - according to which the whole system of molecules devided into sub-systems consisting of lines of molecules moving almost one-dimensionally in tunnels whose walls are formed by neighbouring lines. The advantage of this model over cell model and hole theories is basically that it permits a more extensive sampling of configuration space, in regions not necessarily 'close' to regular lattice configurations. Density fluctuations are permitted since the molecules may take up any position along the tunnel axis, and these include small fluctuations as well as the relatively gross fluctuations described in the hole theories by empty cells.

The tunnel theory has not yet been investigated as fully as the cell theory. This is developed only for rigid spherical molecules and for (6:12) molecules and predicts a radial distribution function for liquid argon in good agreement with experiment. It gives calculated values of pressure and energy which are in good agreement with experiment, but the calculated entropies are less satisfactory. At present this is perhaps the most promising of the lattice theories.

Any how the most serious objection to this theory is its anisotropic character.

5.9. TWO-STATE APPROACH

Due to its wide availability and unusual properties, water has always provided an interesting scientific challange. During the years a great number of qualitative and quantitative theories have been proposed to explain the properties of water and to elucidate its structure. A critical review of these theories reveals that a group out of these theories rely on two-state approach (102, 105,166-162). According to this theory water is considered to be as an equilibrium mixture of two classes of molecules. Class first is constituted by hydrogen bonded molecules(open structure or ice-like structure) and class II - is constituted by unbonded monomers (close-packed structure). Many authors have applied this approach with some degrees of success, to many properties of water, however, they do not agree on the values of the various two-state thermodynamic parameters.

For the first time, in 1948, Hall (102) presented a two-state theory of water, which was based on the assumption that liquid water was composed of two states. State 1 is characterized by large volume and lower free energy identifying it as more ice-like structure (open-packed structure) and state- 2 is characterized by smaller volume and higher free energy i.e. unbonded water molecules (close-packed structure), in order to explain the ultrasonic absorption data. Hall's theory succeeded in the interpretation of ultrasonic absorption data, but was pointed by Litovitz and Carnevale (161) to be unsatisfactory for the explanation of the pressure dependence of ultrasonic absorption. Since then the two state approach of liquid water has been developed in various ways by a number of authors (102, 105, 156-162) to investigate the effectiveness and limitations of the two-state approach. Some of them, the theory of Samoilov (163), Frank and Quist (159) etc. were found to emphasize the solid-like structure. On the other hand Frank and Wen (76) proposed a flickering cluster model based on the cooperative nature of hydrogen bonding formation, and pointed out the life time of the clusters to be as short as 10^{-10} or 10^{-11} sec. from the relaxation data. According to the suggestion of Frank and Wen (76,164), Némethy and Sheraga (128) have presented a refined statistical theory, in which water is assumed to be an equilibrium mixture of flickering clusters and unbonded molecules. The clusters are supposed to be composed of tetra-tri-di, and singly- hydrogen bonded water molecules, and therefore, Némethy and Scheraga's theory is also regarded as a five-state theory. The results from the Némethy and Scheraga model are in satisfactory agreement with the experimental values of entropy, free energy, and internal energy, but fail to predict the behaviour of the specific heat of water. In addition, the concentrations of the species derived by Nemethy and Scheraga do not show a satisfactory correlation with the experimental results of Buijs and Choppin (115) determined by infra-red techniques.

After the propostion of Némethy and Scheraga's theory several studies have been made along this line. Vand and Senior have recently presented a nine-state theory (165). The main feature of their approach was that the concept of descrete energy levels, corresponding to zero, one and two hydrogen bonds is abondoned and replaced by the concept of energy bonds without giving any theoretical explanation. This assumption means a continuous distribution of energy for water molecules and also means the introduction of a very large number of states since the energy changes continuously. Using a model of liquid water based on three species found experimentally by Buijs and Choppin and by introducing the above mentioned assumption they derived a partition function for the system. Using the experimental data of Buijs and Choppin and of Dorsey (104) (at 50°C), and introducing some other assumptions regarding the nature of the intermolecular forces, they evaluated the parameters needed in this partition function. Using the resulting partition function they found that their model successfully represents the thermodynamic properties of liquid water in the range of 0° to 100°C.

It is questionable that, when the life time of the hydrogen bonded region is known to be as short as 10^{-11}-10^{-10} sec, a number of different states within the hydrogen bonded region could be distinguished from each other, for a 'state' has to be regarded as corresponding to a structure. The assumption of the presence of a number of distinguishable states with as short a life time as 10^{-11} - 10^{-10} sec, may be doubtful, when the energy difference between the states is as small as the energy of the thermal motion. It may be generally said on constituting the theory, the number of states assumed is desirable to be as small as possible, so long as the increase in the number of states means the increase in the number of parameters.

Recently Davis and Litovitz (116) presented a two-state model of the structure of water and the evidence for the existence of two types of structures in water comes from the difference in the number of neighbors indicated by Raman spectra and X-ray diffraction which is consistent with the suggestion of Grjotheim and Krogh-Moe (157) that the first peak in the radial distribution curve is in reality two unresolved peaks corresponding to two different types of nearest neighbors in water. This model is based on two postulate - the first postulate is that in water there exist puckered hexagonal rings like those that make up the structure of ice (166). The presence of such rings in water is explained by the fact that the hydrogen bond is partially covalent leading to highly directional cooperative forces suggested by Frank which favor the formation of hydrogen bonds. The second postulate is that in water these rings occur in an equilibrium distribution of two structures, an open-packed structure as in ice while others are arranged in a more closely - packed nearly complete body centered cubic structure. Further they have pointed out that Hall's analysis requires modification. According to them the excess sound absorption is not completely an isothermal process but a large component of the excess loss results from the presence of a relaxational specific heat. When a liquid is subjected to variations in pressure or temperature, volume changes occur. These volume changes proceed by rapid changes in lattice spacing followed by slower structural (or relaxational) rearrangements (167). The lattice and relaxational components of the compressibility, expansivity and specific heat, $K_{T,\infty}$, $K_{T,r}$, α_r, $C_{P,\infty}$, $C_{P,r}$ respectively are related by the expressions

$$K_T = K_{T,\infty} + K_{T,r} \qquad (5.3)$$

$$\alpha = \alpha_{\infty} + \alpha_r \qquad (5.4)$$

$$C_P = C_{P,\infty} + C_{P,r} \qquad (5.5)$$

The molar volume of water on two-state approach is given by

$$V = V_o X_o + V_c X_c = X_o V' + V_c \qquad (5.6)$$

Where X_o, V_o and X_c, V_c are the mole - fractions and volume respectively, of the open-packed and close-packed structures respectively.

$$\left.\begin{aligned} V' &= V_o - V_c \\ \text{and} \quad X_c &= 1 - X_o \end{aligned}\right\}$$

Expression for expansivity is given by

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad (5.7)$$

From equations (5.6) and (5.7) we get,

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\frac{\partial}{\partial T}(X_o V' + V_c)$$

$$= \frac{V'}{V}\left(\frac{\partial X_o}{\partial T}\right)_P + \frac{X_o}{V}\left(\frac{\partial V'}{\partial T}\right)_P + \frac{1}{V}\left(\frac{\partial V_c}{\partial T}\right)_P \qquad (5.8)$$

Similarly, the compressibility of liquids is expressed as

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial}{\partial P}(V'X_o + V_c)\right)$$

$$\therefore \quad K_T = -\frac{V'}{V}\left(\frac{\partial V_o}{\partial P}\right)_T - \frac{X_o}{V}\left(\frac{\partial V'}{\partial P}\right)_T - \frac{1}{V}\left(\frac{\partial V_c}{\partial P}\right)_T \tag{5.9}$$

According to Davis and Litovitz

$$\alpha_r = \frac{V'}{V}\left(\frac{\partial X_o}{\partial T}\right)_P \tag{5.10}$$

$$\text{and } K_{T,r} = -\frac{V'}{V}\left(\frac{\partial X_o}{\partial P}\right)_T \tag{5.11}$$

Further in the equilibrium condition

$$\frac{X_o}{1 - X_o} = \exp\left(-\frac{G'}{RT}\right) \tag{5.12}$$

Using the thermodynamic relation

$$G' = F' + PV = H' - TS' \tag{5.13}$$

Where G' is the difference in the Gibbs free energy between two states, F' is the difference in the Helmholtz free energy, H' is the difference in the enthalpy, S' is the difference in the entropy, P is the pressure, R is the gas constant, and T is the absolute temperature.

From Equation (5.12)

$$\left(\frac{\partial X_0}{\partial T} \right)_P = \left(\frac{H'}{RT^2} \right) X_0(1-X_0) \qquad (5.14)$$

and

$$\left(\frac{\partial X_0}{\partial P} \right)_T = \left(\frac{V'}{RT} \right) X_0(1-X_0) \qquad (5.15)$$

Making the substitution of Equations (5.14) and (5.15) in Equations (5.10) and (5.11), we get,

$$\alpha_r = \left(\frac{V'H'}{V\,RT^2} \right) X_0(1-X_0) \qquad (5.16)$$

and

$$K_{T,r} = \left(\frac{(V')^2}{VRT} \right) X_0(1-X_0) \qquad (5.17)$$

The relaxation component of specific heat is obtained as

$$C_{P,r} = \left| \frac{(H')^2}{RT^2} \right| X_0(1-X_0) \qquad (5.18)$$

$$\alpha_\infty = \frac{1}{V} \left[\left(\frac{\partial V_c}{\partial T} \right)_P + X_0 \left(\frac{\partial V'}{\partial T} \right)_P \right] \qquad (5.19)$$

To determine the parameters X_0, V', G' and V_c , Davis and Litovitz solved equations (6.6) (5.12) , (5.16) and (5.19) in self consistent manner and then they have calculated various thermodynamic parameters.

Any how the main difficulty in the past has been in the determination of X_0. Actually there was no absolute method for the determination of X_0 and one have to set this parameter one or the other way. In the present work we have, by considering the structure of water and its properties, arrived at an expression to determine the fraction of hydrogen bonded molecules (X_o) and its functional dependence on temperature, and have ultimately discussed the effectiveness and limitations of the two state theory.

In a published work (97) we have proposed an empirical expression which represents the functional dependence of temperature of most of the properties of water. This expression is interpreted in terms of two state approach. In view of the forgoing discussion (Chapter III), if we assume that the fraction of the close packed specy, i.e.

$$X_c = \left(\frac{T-T_o}{T_c-T} \right) \qquad (5.20)$$

and then the fraction of the hydrogen bonded molecules (open-packed species), X_o will be

$$X_o = 1 - X_c$$

$$X_o = \left(\frac{T_c + T_o - 2T}{T_c - T} \right) \qquad (5.21)$$

Once we know the value of X_o, it becomes a simple matter to apply the two-state approach as by various investigators to obtain the volume and two-state thermodynamic parameters alongwith some other physical properties of water.

5.91 Specific Volume

The volume V, can be written as

$$V = X_o V_o + X_c V_c$$

Where V_o and V_c represents the specific volumes of the open-packed species and close-packed respectively. The temperature dependence of V_o and V_c can be expressed as

$$V_o = 19.657 (1 + 1.55 + 10^{-4} t) \qquad (5.22)$$

$$V_c = V_c^o (1 + At + Bt^2) \qquad (5.23)$$

and $$V' = V_o - V_c \qquad (5.24)$$

Where V_o^o (= 19.657) and V_c^o are the values at a reference temperature, A and B are the coefficients and t the rise in temperature above the reference temperature, then

$$V = X_o * 19.657 (1 + 1.55 * 10^{-4} t) + X_c V_c^o (1+At+Bt) \qquad (5.25)$$

Here X_o and X_c are known, V_c^o, A and B can be fixed from three known values of V. These are obtained

$$A = 3.6358 * 10^{-3} \, {}^oC^{-1}$$

$$B = - 8.2859 * 10^{-6} \, {}^oC^{-1}$$

$$V_c^o = 0.802071 \text{ c.c.}$$

The calculated values for V along with the experimental values are shown in Table 6 (Chapter III) . The agreement is found to be very good.

5.9.2. Refractive Index

Using again the values of X_o and X_c and the relation for refractive index of water given by Mitra et al. (118) on the two state approach,

$$(n-1)V = X_o k_o + X_o k_c \tag{5.26}$$

where n is the refractive index, V is the specific volume and k_o, k_c some constants to be fixed empirically. They are obtained as

$$K_o = 0.3359 \quad \text{and} \quad K_c = 0.3311$$

Then from experimentally known values of V, n can be calculated. These values along with experimental values are shown in Table 6 (Chapter III) . The agreement is found again very good.

5.9.3 Two-State Thermodynamic Parameters

Differentiating Equations (5.12) and (5.13) with respect to temperature yields.

$$\left(\frac{\partial G'}{\partial T}\right)_p = -S' = R \ln\left(\frac{1-X_o}{X_o}\right) - \left(\frac{RT}{X_o(1-X_o)}\right)\left(\frac{\partial X_o}{\partial T}\right)_p \tag{5.27}$$

and

$$\left(\frac{\partial^2 G'}{\partial T^2}\right)_P = -\frac{C'_P}{T} = -\frac{2R}{X_0(1-X_0)}\left(\frac{\partial X_0}{\partial T}\right)_P - \frac{RT}{X_0(1-X_0)}\left(\frac{\partial^2 X_0}{\partial T^2}\right)_P + \frac{RT\,(1-2X_0)}{(X_0(1-X_0))^2}\left(\frac{\partial X_0}{\partial T}\right)_P^2 \quad (5.28)$$

$$\because \quad H' = G' + TS'$$

or

$$H' = RT\,\ell n\left(\frac{1-X_0}{X_0}\right) - RT\,\ell n\left(\frac{1-X_0}{X_0}\right) + \frac{RT^2}{X_0(1-X_0)}\left(\frac{\partial X_0}{\partial T}\right)_P \quad (5.29)$$

Now from the forgoing discussion we know

$$X_0 = (T_c + T_0 - 2T) \,/\, (T_c - T)$$

$$\therefore \left(\frac{\partial X_0}{\partial T}\right)_P = -\left(\frac{T_c - T_0}{(T_c - T)^2}\right) \quad (5.30)$$

and

$$\left(\frac{\partial^2 X_0}{\partial T^2}\right)_P = -\frac{2\,(T_c - T_0)}{(T_c - T)^3} \quad (5.31)$$

Now it becomes very easy to compute the values of G', S', C'_P and H' using the above equations (Equations (5.13), (5.27), (5.28), (5.29), (5.21), (5.30), (5.31). Knowing these parameters on one hand, we can calculate Gibbs free -energy, enthalpy , entropy and specific heat for the individual state from the following relations, respectively,

$$\left.\begin{aligned} G &= X_o G' + G_c \\ G_c &= G - X_o G' \\ \text{and} \quad G_o &= G' + G_c \end{aligned}\right\} \qquad (5.32)$$

(as $G' = G_o - G_c$)

$$\left.\begin{aligned} H &= X_o H' + H_c \\ H_c &= H - X_o H' \\ \text{and} \quad H_o &= H' + H_c \end{aligned}\right\} \qquad (5.33)$$

(as $H' = H_o - H_c$)

$$\left.\begin{aligned} C_p &= X_o C'_p + C_{p_c} + C_{p,r} \\ C_{p_c} &= C_p - X_o C'_p - C_{p,r} \\ C_{p_o} &= C_{p_c} + C'_p \end{aligned}\right\} \qquad (5.34)$$

$$\left.\begin{aligned} S &= X_o S' + S_c - S_r \\ S_c &= S - X_o S' + S_r \\ \text{and} \quad S_o &= S' + S_c \end{aligned}\right\} \qquad (5.35)$$

The values so obtained of various two-state parameters are reported in Tables (7-15). In these tables the calculated values are also compared with the values obtained by various investigators.

A further test of the validity of the two state relaxational parameters can be made by calculating the ratio of the structural or volume viscosity to the shear viscosity in water, i.e. η_v / η_s . An expression for this ratio is obtained by rewriting Equation (100-6) in reference (167). Thus

$$\eta_v / \eta_s = \left[\frac{(V')^2}{R^2 T^2 K_s^2} \right] (1 - X_o) X_o^2 \quad (5.36)$$

Where K_s is the adiabatic compressibility. The results so obtained are compared with the other authors in Table(13). From the table it is clear that our model gives the better agreement with experimentally known values in comparison to others namely, Nemethy and Scheraga, Grjotheim and Krogh - Moe, Wada, Eucken, Davis and Litovitz. But at higher temperatures Davis and Litovitz model is better than others including ours. Here it appears that our model also may underestimate the amount of association at higher temperatures.

Further the sound absorption coefficient which is due to structural relaxation is computed using the following expression

$$\left(\frac{2 \alpha}{\nu^2} \right) = \frac{4 \pi^2}{v} K_{T,r} \frac{\tau_r}{K_T} \quad (5.37)$$

Where $$\tau_r = \frac{h}{kT} \frac{e^{E_\eta/RT}}{1 + e^{H'/RT}} \qquad (5.38)$$

where v is the sound velocity, $K_{T,r}$ is the relaxational part of the compressibility, E_η is the activation energy, h is the Plancks constant, N is the Avogadro's number.

5.9.4 Statistical Treatment

The formulation of the partition function, Z, for the mixture of NX_o molecules in Class I (constituted by hydrogen bonded molecules i.e. open structure or ice-like structure) and NX_c molecules in Class II (constituted by unbonded monomers i.e close-packed structure) is made as follows ,

$$Z = \frac{N!}{(NX_o)!\,(NX_c)!} (f_I)^{NX_o} (f_{II} e^{-\varepsilon/RT})^{NX_c} \qquad (5.39)$$

Where f_I and f_{II} are partition functions for each species. Now maximization of Z concerning x_o as a variable

$$\frac{\partial \ln Z}{\partial x_o} = 0 \qquad (5.40)$$

From Equations (5.39) and (5.40) and using Stirling's approximation we get the equilibrium value of x_o ,

$$x_o = \frac{f_I}{f_I + f_{II}\, e^{-\epsilon/RT}} \qquad (5.41)$$

and, introducing Equation (5.41) into Equation (5.39), the partition function, Z for the equilibrium mixture, is represented as follows, (See Appendix V). The partition function of each species, f_I and f_{II} are given in the following equations, Equations (5.42) and (5.43)

$$f_I = \prod_{i=1}^{6} \left(\frac{1}{1 - e^{h\nu_i/kT}} \right) \qquad (5.42)$$

$$f_{II} = \left\{ \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} v_f \right] \right\} \left\{ \left[\frac{(8\pi^2 kT)^{3/2} (\pi ABC)^{1/2}}{2h^3} \right] \right\} \qquad (5.43)$$

Where ν_i is the frequency of translational vibrations and liberations in state of class I, v_f is the free volume available to a molecule in the state of class II and A, B, and C are the principal moments of inertia of water molecule. The factor in the first bracket of f_{II} corresponds to the translational degrees of freedom and that in the second bracket to the rotational ones. The contribution from intramolecular vibrations into f_I and f_{II} is ignored, because it may be safely regarded as 1 at temperatures from 0°C to 100°C.

As for the frequencies which have been attributed to intermolecular vibrations a tentative assignment has been made referring to the data from the infrared and Raman spectroscopy : 210 cm^{-1} for three modes of translational vibrations(128,168,169) and 500 cm^{-1} for three modes of liberations on the average (168,170). The principal moments of inertia have been given to be the same as in the vapor state (171). The energy difference between two states, ϵ and the free volume, v_f , which is available to a molecule in the state of class II, are two main parameters used in this theory. It is impossible to determine the magnitude of ϵ and v_f precisely from theory at present. Any how here because we know X_0, so we can determine v_f as follows, from equations (5.43) and (5.41)

$$v_f = \frac{X_c \quad f_I}{\left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} * \frac{(8\pi^2 kT)^{3/2} \, (\pi ABC)^{1/2}}{2\,h^3} \right] X_0 e^{-\epsilon/RT}} \tag{5.44}$$

remaining is the parameter ϵ to be known, and ϵ has been treated as the adjustable parameters to give the best fit of calculated values to experimental data. The variation of this parameter was, of course, limited within the physically reasonable range. In the earlier treatment based on the two - state model the magnitude of ϵ has been estimated to be within the range of 2.5 -3.0 KCal/mol. Smith and Lawsen estimated the magnitude of ϵ to be 2.6 KCal/mol from their sound velocity data (160) and Lawson et al. estimated it to be 3 KCal/mol from their thermal conductivity data (105). Wada used the value of 2.51 KCal/mol in his treatment (158).

Taking account of the heat of fusion ice in addition to the estimation described above, we have taken the range of ϵ to be 2.75 - 3.15 KCal/mol and found that ϵ = 3 K Cal/mol gives the best fit of calculated values to experimental data.

5.9.5 Calculations of Thermodynamic Variables

Once we know the partition function, we can calculate the various thermodynamic properties of the system as follows :-

The Helmholtz energy, A is obtained from the following Equation (5.45)

$$A = - k T \ln Z$$

$$\text{or} \quad A = - N k T \ln (f_I + f_{II} e^{-\epsilon / RT}) \qquad (5.45)$$

and the energy and entropy can be calculated by Equations(5.46) and (5.47)

$$E = k\,T^2 \frac{\partial \ln Z}{\partial T}$$

$$= \frac{= NkT^2 \left(\frac{\partial f_I}{\partial T} + \frac{\partial f_{II}}{\partial T} e^{-\epsilon/RT} + \frac{\epsilon}{RT^2} e^{-\epsilon/RT} f_{II} \right)}{\left(f_I + f_{II}\, e^{-\epsilon/RT} \right)} \tag{5.46}$$

$$S = (E-A)/T \tag{5.47}$$

The specific heat is derived from the energy, E,

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V$$

$$C_V = \frac{RT^2}{\left(f_I + f_{II} e^{-\epsilon/RT} \right)^2} \left[\left(\frac{2\left(f_I + f_{II}\, e^{-\epsilon/RT} \right)}{T} - 1 \right) \left(\frac{\partial f_I}{\partial T} + \frac{\partial f_{II}}{\partial T} e^{-\epsilon/RT} \right. \right.$$

$$\left. + f_{II} \frac{\epsilon}{RT^2} e^{-\epsilon/RT} \right) + \left(f_I + f_{II}\, e^{-\epsilon/RT} \right) *$$

$$\left(\frac{\partial^2 f_I}{\partial T^2} + \frac{\partial^2 f_{II}}{\partial T^2} e^{-\epsilon/RT} + 2 \frac{\partial f_{II}}{\partial T} \frac{\epsilon\, e^{-\epsilon/RT}}{RT^2} - 2 f_{II} \frac{\epsilon\, e^{-\epsilon/RT}}{RT^3} \right.$$

$$\left. \left. + f_2 \left(\frac{\epsilon}{RT^2} \right)^2 e^{-\epsilon/RT} \right) \right] \tag{5.48}$$

where

$$\frac{\partial f_I}{\partial T} = \frac{3\,h\nu_1\,e^{-h\nu_1/kT}}{kT^2(1 - e^{-h\nu_1/kT})} * f_I + \frac{3\,h\nu_2\,e^{-h\nu_2/kT}}{kT^2(1 - e^{-h\nu_2/kT})} * f_I \tag{5.49}$$

and

$$\frac{\partial^2 f_I}{\partial T^2} = \left[f_I * \left\{ \left(\frac{3h\nu_1 e^{-h\nu_1/kT}}{kT^2(1-e^{-h\nu_1/kT})} \right) * \left(\frac{h\nu_1\ e^{-h\nu_1/kT}}{kT^2\,(1-e^{-h\nu_1/kT})} + \frac{h\nu_1}{kT^2} - \frac{2}{T} \right) \right.\right.$$

$$\left. + \left(\frac{3h\nu_2\ e^{-h\nu_2/kT}}{kT^2(1-e^{-h\nu_2/kT})} \right) \left(\frac{h\nu_2\ e^{-h\nu_2/kT}}{kT^2(1-e^{-h\nu_2/kT})} + \frac{h\nu_2}{kT^2} - \frac{2}{T} \right) \right\}$$

$$\left. + \frac{\partial f_I}{\partial T} \left\{ \left(\frac{3h\nu_1\ e^{-h\nu_1/kT}}{kT^2(1-e^{-h\nu_1/kT})} \right) \left(\frac{3\,h\nu_2\ e^{-h\nu_2/kT}}{kT^2(1-e^{-h\nu_2/kT})} \right) \right\} \right] \tag{5.50}$$

$$\frac{\partial f_{II}}{\partial T} = \left(\frac{2\pi\,mk}{h^2} \right)^{3/2} \frac{(8\pi^2 k)^{3/2}\ (\pi ABC)^{1/2}}{2h^3} \left\{ 3\,T^2\,v_f + T^3\,\frac{\partial v_f}{\partial T} \right\} \tag{5.51}$$

and

$$\frac{\partial^2 f_{II}}{\partial T^2} = \left(\frac{2\pi mk}{h^2} \right)^{3/2} \frac{(8\pi^2 k)^{3/2}(\pi ABC)^{1/2}}{2\,h^3} * T \left\{ 6v_f + 6T\,\frac{\partial v_f}{\partial T} + T^2\,\frac{\partial^2 v_f}{\partial T^2} \right\} \tag{5.52}$$

Using the values of the parameters as described above calculations of thermodynamic functions have been made over the temperature range from $0^{\circ}C$ to $100^{\circ}C$ at $10^{\circ}C$ intervals. The calculated values of the Helmholtz energy, A; the internal energy, E, the entropy, S and the specific heat at constant volume, C_v , are given in Table 16, . The results calculated are compared with the experimental data for water, which are taken from Dorsey (128, 104). The agreement is found to be better at higher temperatures than at lower temperatures for A, E and S. Further the agreement between the observed and calculated values of A, E, and S can be made better by choosing the new value of ϵ higher than 3 K Cal/mole. But the circumstances are different for the specific heat, C_v. The agreement between the observed and calculated values is very poor, for which the two-state approach has already been criticised.

TABLE 7

Investigators		x_o	V' (cc/mole)	$K_{T,r}*10^{12}$ (cm^2/dyne)	$\alpha_r * 10^3$ $(^oC)^{-1}$	H' (Cal/mol)	$H_o^{st}=x_cH'$ (cal/mol)	$C_{p,r}$ (cal/mol ^oC)	S' (eu)
Present authors		0.6840	5.20	14.30	-1.016	-2413	-762.508	8.49	-7.30
Davis and Litovitz	d_1	0.637	6.92	27.05	-1.666	-2782	-1010	12.07	-9.06
	d_2	0.593	7.24	30.90	-1.666	-2547	-1037	10.56	-9.57
Némethy and Scheraga		0.543	3.58	7.8	-0.72	-2640	-1246	9.64	-
Euken		0.30	1.90	11.6	-0.738	-3200	-3250	8.7	-11.7
Grjatheim and Krogh-Moe		0.44	2.90	5.2	-	-2600	-1456	11.2	-8.9
Wada		0.42	2.80	4.5	-	-2510	-1456	10.36	-9.79
Smith and Lawson		0.50	8.4	39.0	-1.46	-2600	-1300	14.77	-9.5
Hall		0.70	7.6-9.2	32.8-35.8	-	-	-	-	-
Litovitz and Carnevale		0.32	8.4	35.8	-	-870	-592	1.1	-1.4
Frank and Quist		0.82	-	22.8	-0.33	-2210	-	0.55	-12.43

TABLE 8

Temp. °C	X_c	$X_o = 1-X_c$	$\left[\left(\frac{\partial X_o}{\partial T}\right)_T * 10^2\right]$	$\left[\left(\frac{\partial^2 X_o}{\partial T^2}\right) * 10^{+4}\right]$
0	0.3160	0.6840	-0.351883	-0.188173
5	0.3339	0.6661	-0.361484	-0.195926
10	0.3522	0.6478	-0.371483	-0.204111
15	0.3710	0.6290	-0.381903	-0.212759
20	0.3904	0.6096	-0.392767	-0.221902
25	0.4103	0.5897	-0.404102	-0.231577
30	0.4308	0.5692	-0.41593	-0.241822
35	0.4519	0.5481	-0.428294	-0.252681
40	0.4736	0.5263	-0.441213	-0.264200
45	0.4960	0.5039	-0.454726	-0.276429
50	0.5191	0.4809	-0.468869	-0.28945
55	0.5429	0.4570	-0.483682	-0.303249
60	0.5675	0.4325	-0.499209	-0.317967
65	0.5929	0.4071	-0.515495	-0.333654
70	0.6191	0.3809	-0.532592	-0.350389
75	0.6461	0.3538	-0.550553	-0.368263
80	0.6741	0.3258	-0.569439	-0.387373
85	0.7031	0.2969	-0.589313	-0.407829
90	0.7331	0.2669	-0.610246	-0.429751
95	0.7641	0.2358	-0.632315	-0.453272
100	0.7963	0.2037	-0.655602	-0.478542

TABLE 9

Temperature °C	V_c (cc/mole)	V_o (cc/mole)	V' (cc/mole)
0	0.802071	1.090844	5.20
5	0.816485	1.091689	4.96
10	0.830568	1.092535	4.72
15	0.844318	1.093380	4.49
20	0.857735	1.094226	4.26
25	0.870821	1.095071	4.04
30	0.883574	1.095916	3.83
35	0.895995	1.096762	3.62
40	0.908083	1.097607	3.41
45	0.919840	1.098453	3.22
50	0.931263	1.099298	3.03
55	0.942355	1.100143	2.84
60	0.953115	1.100989	2.66
65	0.963542	1.101834	2.49
70	0.973636	1.102680	2.32
75	0.98340	1.103525	2.16
80	0.992829	1.104370	2.01
85	0.100193	1.105216	1.86
90	0.101069	1.106061	1.72
95	0.101913	1.106907	1.58
100.	0.102723	1.107752	1.45

TABLE 9 (Continued)

Temperature °C	X_o	G'	X_oG'	G (Kcal/mole	G_c	G_o
0	0.6840	-418.985	-286.586	1.20	913.414	494.429
10	0.6478	-342.738	-222.026	1.35	1127.974	785.236
20	0.6096	-259.489	-158.184	1.50	1341.815	1082.326
30	0.5692	-167.753	- 95.485	1.66	1564.515	1396.762
40	0.5264	- 65.746	- 34.609	1.83	1795.391	1729.645
50	0.4809	+ 49.063	23.594	2.00	2023.594	2072.657
60	0.4325	179.766	77.745	2.17	2247.749	2427.515
70	0.3809	331.071	126.105	2.36	2486.105	2817.176
80	0.3259	509.809	166.147	2.55	2716.147	3225.956
90	0.2676	726.244	194.343	2.74	2934.343	3660.587
100	0.2037	1010.465	205.832	2.94	3145.832	4156.297

TABLE 9 (Continued)

Temp-erature °C	C'_p	$X_o{*}C'_p$	C_p	C_{pr}	C_{p_c}	CP_o
0	-16.113	-11.022	1.007	8.492	20.683	4.569
10	-20.083	-13.010	1.001	9.634	21.419	1.336
20	-24.946	-15.207	0.999	11.067	22.139	-2.807
30	-31.163	-17.738	0.998	12.881	22.841	-8.321
40	-39.440	-20.761	0.998	15.212	23.534	-15.906
50	-50.959	-24.506	0.998	18.269	24.231	-26.729
60	-67.796	-29.322	0.999	22.387	24.944	-42.852
70	-93.968	-35.792	1.001	28.138	25.687	-68.281
80	-138.009	-44.977	1.002	36.568	26.470	-111.539
90	-220.417	-58.984	1.004	49.779	27.303	-193.113
100	-409.293	-83.373	1.007	73.295	28.223	-381.069

TABLE 9 (Continued)

Temperature °C	S'	X_oS'	S (Cal/deg mole)	$S_{c,r}$	S_c	S_o
0	-7.299	-4.993	14.5	1.474	20.967	13.668
10	-7.947	-5.148	15.1	1.273	21.521	13.574
20	-8.725	-5.319	15.7	1.019	22.038	13.313
30	-9.661	-5.499	16.3	0.698	22.496	12.836
40	-10.798	-5.684	16.9	0.290	22.874	12.076
50	-12.208	-5.871	17.5	-0.230	23.141	10.933
60	-13.998	-6.054	18.1	-0.890	23.257	9.258
70	-16.358	-6.231	18.6	-1.763	23.068	6.709
80	-19.625	-6.396	19.1	-2.903	22.593	2.968
90	-24.459	-6.545	19.6	-4.432	21.713	-2.745
100	-32.664	-6.654	20.0	-6.625	20.029	-12.635

TABLE 9 (Continued)

Temperature °K	$(\alpha_{\infty} * 10^3)$ $(°C)^{-1}$	$(K_{T,\infty} * 10^{12})$ $(Cm^2/dynes)$	$C_{p,\infty}$ (Cal/°C.mole)
273.2	0.957913	36.561	9.661
283.2	1.0600	35.804	8.409
293.2	1.132115	36.045	6.932
303.2	1.18178	36.881	5.103
313.2	1.214916	38.073	2.772
323.2	1.236066	39.481	-0.275
333.2	1.248526	41.041	-4.378
343.2	1.255218	42.711	-10.106
353.2	1.253164	44.492	-18.507
363.2	1.259213	46.396	-31.860
373.2	1.259553	48.462	-55.150

TABLE 9 (Continued)

Temperature ^{o}K	$(\alpha_r * 10^3)$ $(^{o}C)^{-1}$	$(K_{T,r} * 10^{-12})$ (cm^2/dyne)	$C_{P,r}$	η_v/η_s
273.2	-1.016013	-14.298	8.492	3.1407
283.2	-0.972901	-11.981	9.634	2.7269
293.2	-0.927215	- 9.823	11.067	2.2331
303.2	-0.879380	- 7.870	12.881	1.7306
313.2	-0.829716	-6.149	15.212	1.2710
323.2	-0.778466	-4.671	18.269	0.8820
333.2	-0.725826	-3.433	22.387	0.5751
343.2	-0.672019	-2.425	28.138	0.3489
353.2	-0.617264	-1.630	36.568	0.1936
363.2	-0.561813	-1.027	49.779	0.0957
373.2	-0.505853	-0.585	73.295	0.0394

TABLE 10

Temperature °C	α_{cal} (10^{-3}/°C) Present calc.	$\alpha_{meas.}$ (10^{-3}/°C)	α_{cal} (10^{-3} /°C) (Davis & Litovitz)
0	-0.0581	-0.031	-0.032
10	0.0871	0.094	0.084
20	0.2049	0.200	0.190
30	0.3024	0.295	0.287
40	0.3852	0.380	0.376
50	0.4576	0.457	0.458
60	0.5227	0.528	0.533
70	0.5832	0.596	0.602
80	0.6409	0.661	0.665
90	0.6974	0.724	0.724
100	0.7537	0.786	0.779

TABLE 11

Temp-erature °C	Present calc. 10^{-3}/°C	Davis & Litovitz 10^{-3}/°C	Eucken (10^{-3}/°C)	Némethy & Scheraga 10^{-3}/°C	Smith & Lawson 10^{-3}/°C	Frank & Quist 10^{-3}/°C
0	-1.016	-1.666	-0.738	-0.72	-1.46	-0.33
20	-0.927	-1.444	-0.515	-0.56	-	-
40	-0.830	-1.258	-0.320	-0.40	-	-
60	-0.726	-1.101	-0.186	-0.26	-	-
80	-0.617	-0.969	-0.101	-0.15	-	-
100	-0.506	-0.858	-0.053	-0.09	-	-

TABLE 13

Temperature °C	Present calculations	Measured	Davis & Litovitz		Némethy & Scheraga	Grjotheim & Krogh-Moe	Wada	Eucken
			d= 2.80 Å	d=2.82 Å				
0	3.14	2.33	3.97	4.23	0.98	0.53	0.44	0.80
10	2.73	2.18	3.75	4.06	0.86	-	0.39	-
20	2.23	2.10	3.48	3.83	0.73	0.40	0.32	0.34
30	1.73	2.10	3.20	3.56	0.59	-	-	-
40	1.27	2.01	2.92	3.27	0.46	0.23	-	0.11
50	0.88	2.01	2.64	3.00	-	-	-	-
60	0.57	2.04	2.37	2.72	0.26	0.14	-	0.03

TABLE 15

Temperature °C	Present calculations	Némethy & Scheraga	Davis & Litovitz		Eucken	Grjotheim & Krogh-Moe	Wada	Litovitz & Carnevale	Frank & Quist	Smith & Lawson
			d= 2.80 Å	d= 2.82 Å						
0	8.49	9.64	12.06	10.55	-	11.2	10.36	1.1	0.55	14.77
10	9.63	8.74	11.70	10.06	8.5	-	9.35	-	-	-
20	11.07	7.88	11.20	9.49	-	9.34	8.37	-	-	-
30	12.88	6.94	10.58	8.86	8.3	-	-	-	-	-
40	15.21	6.03	9.91	8.26	-	7.53	-	-	-	-
50	18.27	5.12	9.20	7.58	8.0	-	-	-	-	-
60	22.39	4.22	8.49	6.99	-	6.22	-	-	-	-
70	28.14	3.46	7.81	6.38	7.5	-	-	-	-	-
80	36.57	2.91	7.15	5.83	-	5.14	-	-	-	-
90	49.78	1.86	6.54	5.32	7.2	-	-	-	-	-
100	73.29	-	5.97	4.86	-	3.96	-	-	-	-

TABLE 16

Temperature °C	A(KCal/mole)		E(KCal/mol)		S(Cal/deg.mol)		C_v(Cal/deg.mol)	
	A_{obs}	$A_{cal.}$	E_{obs}	E_{cal}	S_{obs}	S_{cal}	$C_{v_{obs}}$	$C_{v_{cal}}$
0	-1.20	-0.98	2.75	2.29	14.5	12.01	18.1	24.83
10	-1.35	-1.09	2.93	2.50	15.1	12.69	18.0	24.25
20	-1.50	1.22	3.11	2.71	15.7	13.38	17.8	23.49
30	-1.66	-1.35	3.29	2.92	16.3	14.09	17.7	22.59
40	-1.83	-1.49	3.47	3.14	16.9	14.80	17.5	21.53
50	-2.00	-1.65	3.65	3.37	17.5	15.52	17.2	20.34
60	-2.17	-1.83	3.83	3.60	18.1	16.29	17.1	18.99
70	-2.36	-2.02	4.01	3.84	18.6	17.08	16.8	17.53
80	-2.55	-2.25	4.20	4.08	19.1	17.93	16.5	15.92
90	-2.74	-2.51	4.36	4.34	19.6	18.84	16.3	14.18
100	-2.94	-2.84	4.55	4.60	20.0	19.94	16.1	12.26

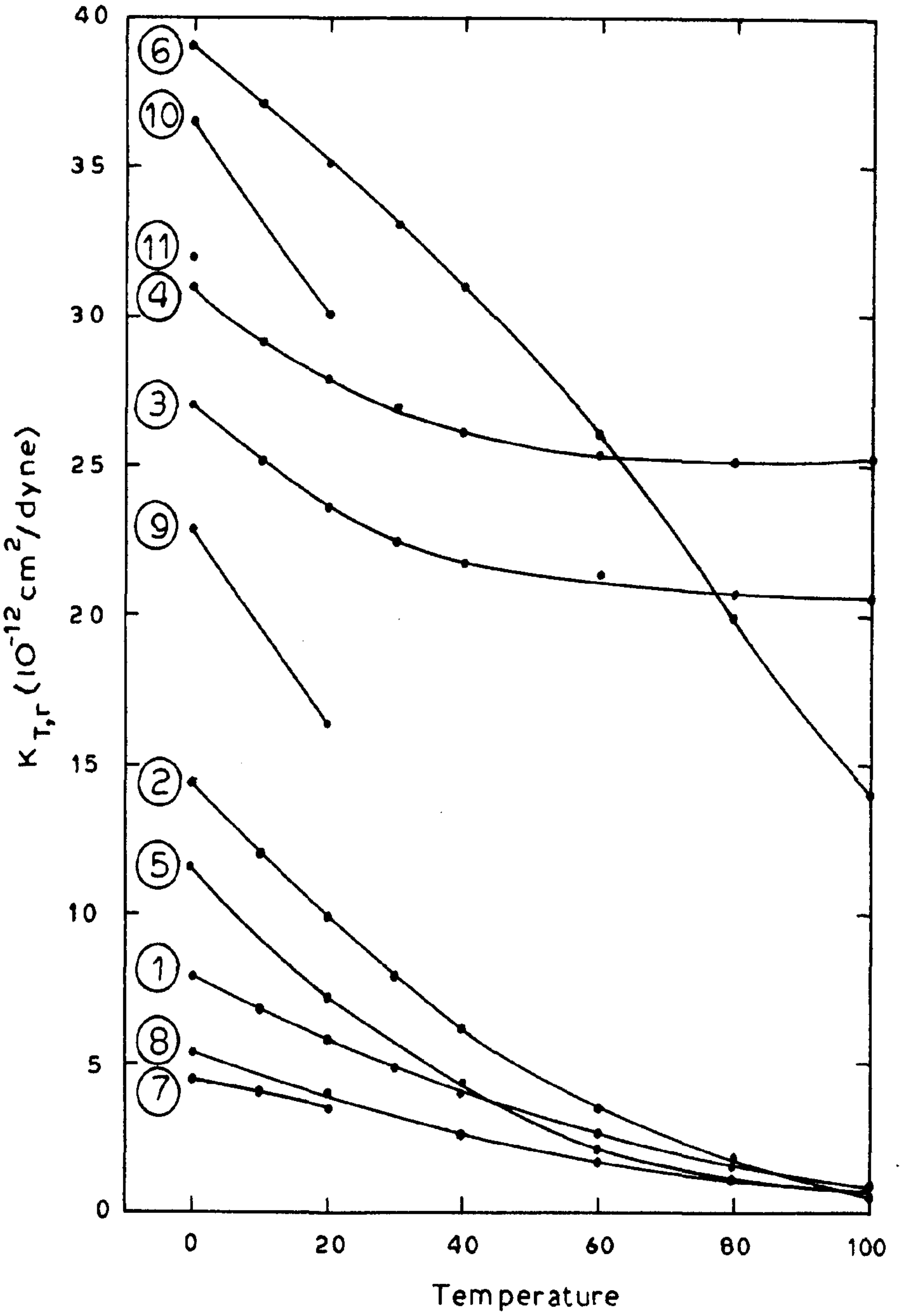
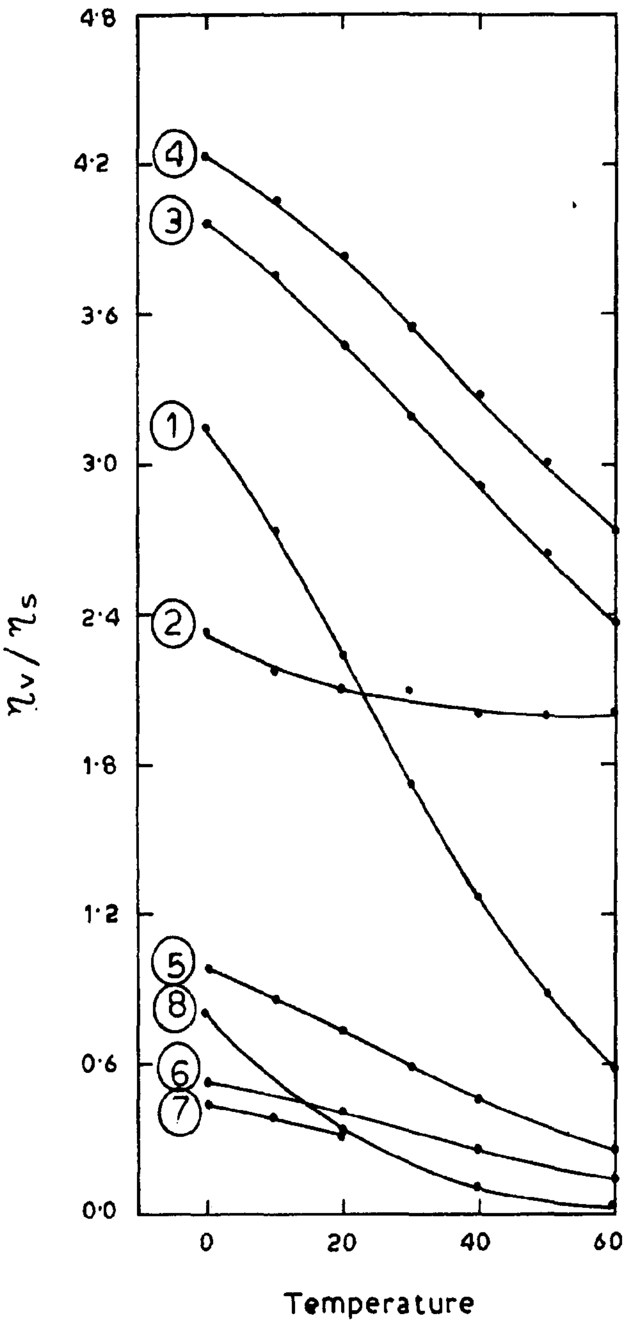

$K_{T,r}$ (10^{-12} cm^2/dyne)
40
35
30
25
20
15
10
5
0
0
20
40
60
80
100
Temperature
⑥
⑩
⑪
④
③
⑨
②
⑤
①
⑧
⑦

FIG. 28



4·8
4·2
3·6
3·0
2·4
1·8
1·2
0·6
0·0
η_v / η_s
0
20
40
60
Temperature
④
③
①
②
⑤
⑧
⑥
⑦

FIG. 29

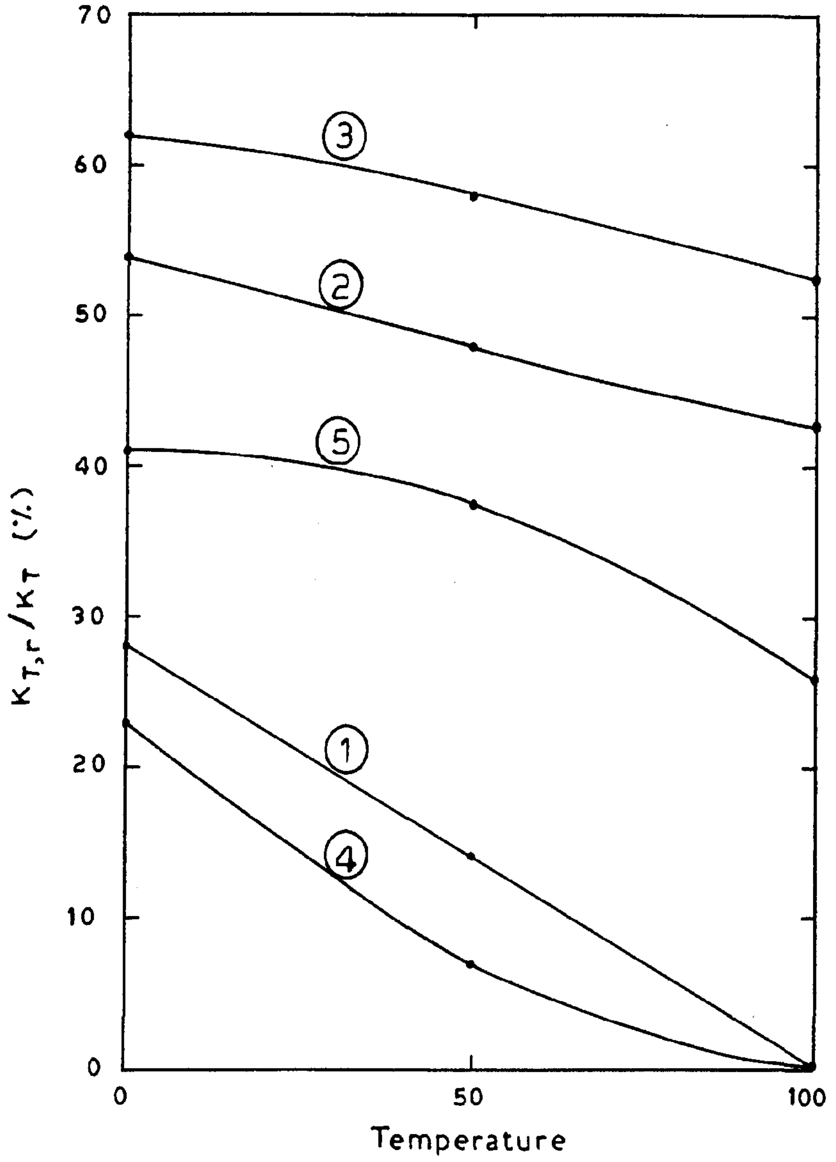


FIG. 30

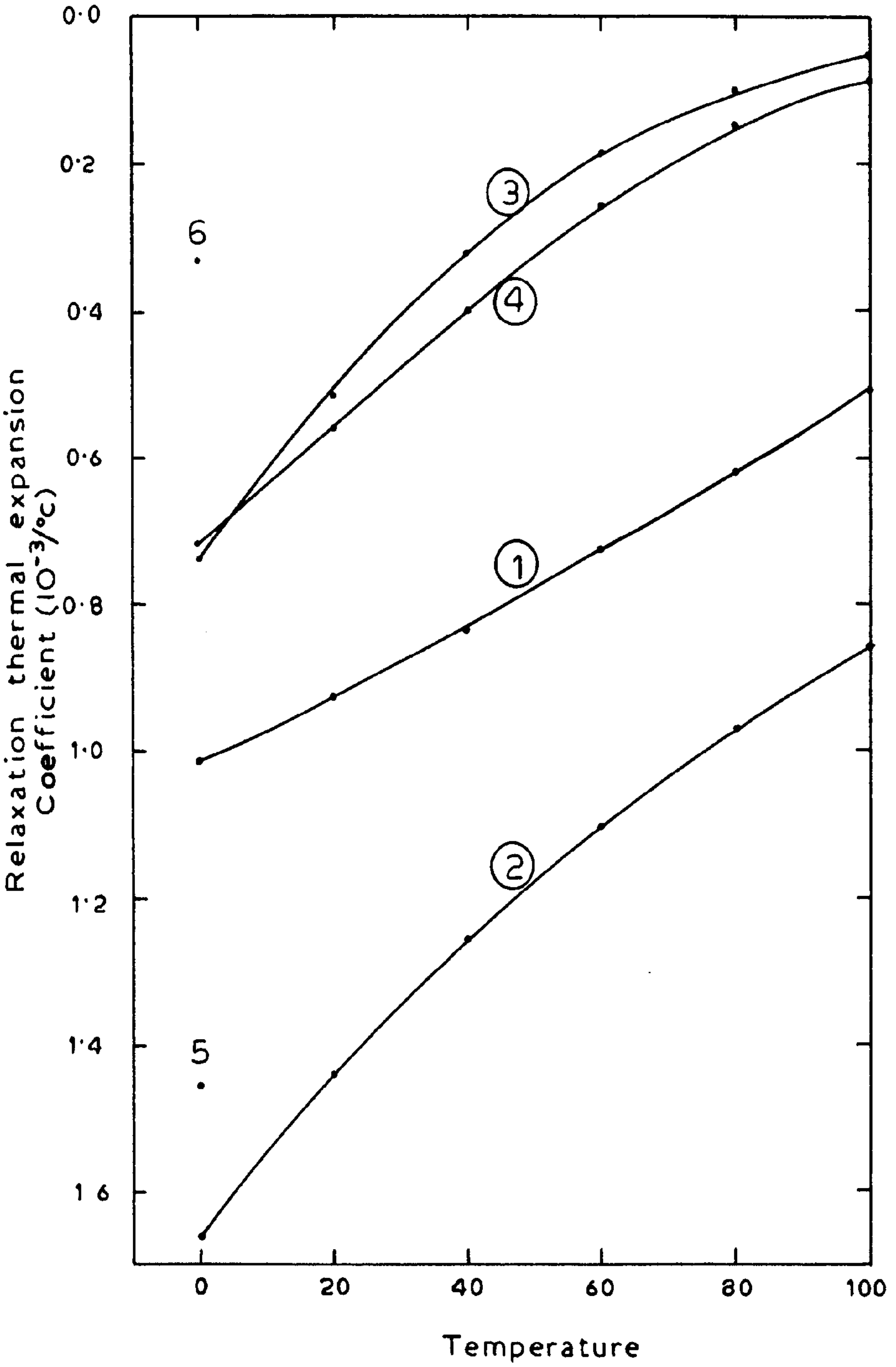

0·0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1 6
Relaxation thermal expansion
Coefficient (10^{-3}/°C)
0
20
40
60
80
100
Temperature
③
④
①
②
6
5

FIG. 31

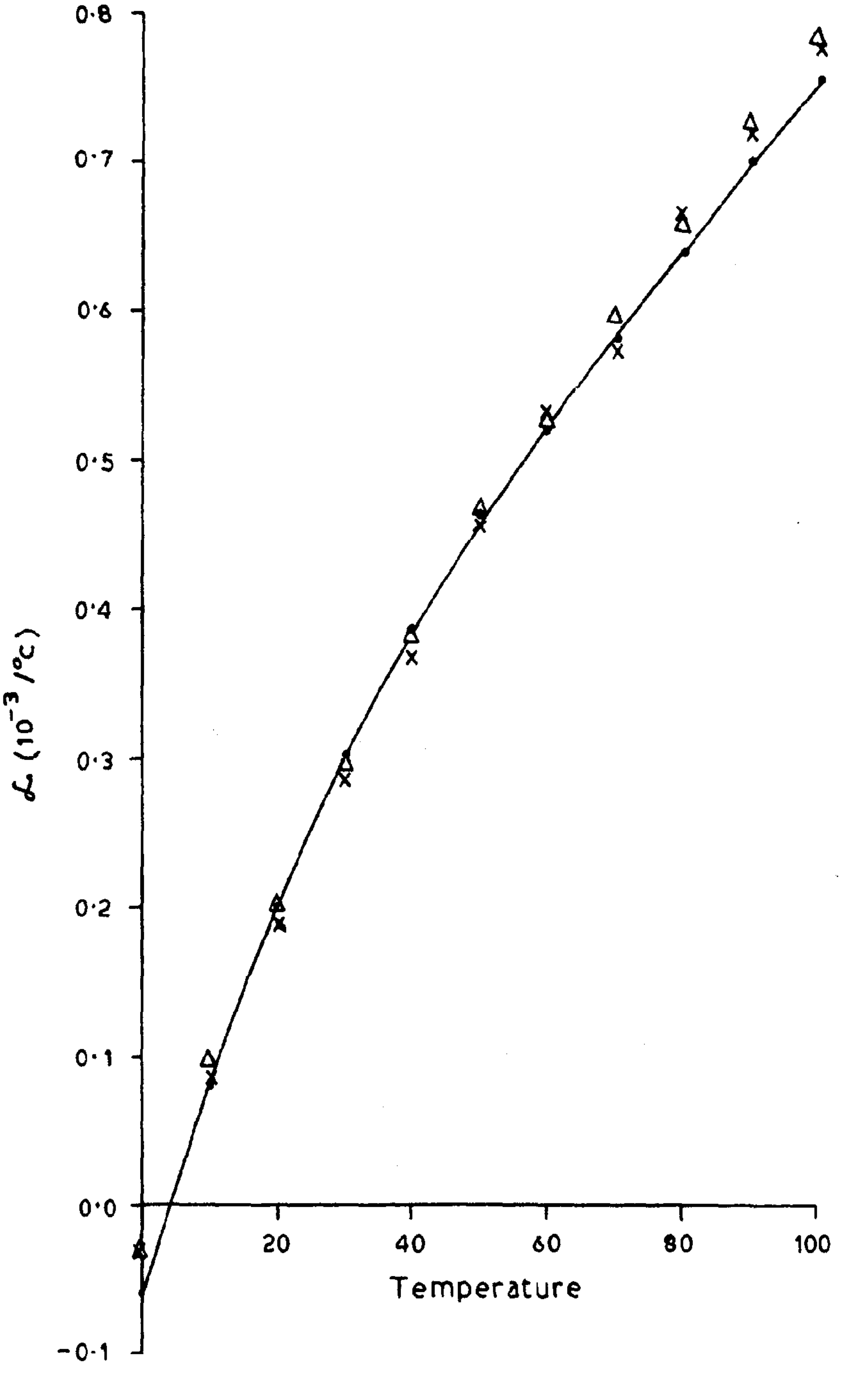

0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0
-0·1
$\mathcal{L}$ (10^{-3}/°C)
20
40
60
80
100
Temperature

FIG.32

REFERENCES

1. G.Mie, Ann.Phys., LpZ., 11, 657 (1903).
2. J.E. Lennard-Jones, Proc. Phys.Soc.43,461 (1931).
3. J.E. Lennard-Jones, Physica 4 , 941 (1937).
4. J.E.Lennard-Jones and A.F.Devonshire,Proc.Roy.Soc. (London) A169, 317(1939).
5. J.E.Lennard Jones and A.F. Devonshire, Proc. Roy.Soc. (London) A170, 464 (1939)
6. J.E.Lennard-Jones and A.F. Devonshire, Proc. Roy.Soc. (London) A163, 53 (1937)
7. J.E.Lennard-Jones and J. Corner, Trans. Faraday Soc. 36, 1156 (1940).
8. J.E.Lennard-Jones, Intermolecular forces, Indian Association for cultivation of Science Calcutta (1939).
9. J.E. Lennard-Jones and A.E. Ingham, Proc. Roy.Soc. (London)A107, 636 (1925).
10. J.E. Lennard-Jones, Proc. Roy.Soc. A106 , 463(1924).
11. F.London, Z.Phys.Chem. B11, 222(1930).
12. J.O.Hirschfelder, C.E. Curtiss and R.B.Bird, Molecular theory of Gases and Liquids (J. Wiley and Sons, New York) 1964.
13. E.A. Guggenheim, Rev. Pure Appl. Chem. 3 , 1 (1953)
14. T. Kihara, Adv. Chem. Phys. 1 , 268 (1958).
15. T.Kihara, Rev. Mod.Phys. 25 , 831 (1953).
16. T.Kihara, Rev. Mod. Phys. 27 , 412 (1955).
17. H.R.Hasse and W.R.Cook, Proc. Roy.Soc. A125, 196(1929).
18. E.M. Holleran and H.M. Hulburt, J. Chem.Phys. 19 ,232 (1951).

19. E. Whalley and W.G. Scheider , J. Chem. Phys. 23, 1644 (1955).

20. G.O.Jones, Z. Phys. Chem. (Frank furt) 16, 267 (1958)

21. J.Corner, Trans. Faraday Soc. 44, 914 (1948).

22. C.Domb and I.J. Zucker, Nature (London) 178, 484 (1956).

23. I.J. Zucker, J. Chem. Phys. 25, 915 (1956).

24. E.R.Dobbss, B.F. Figgins, G.O. Jones, D.C.Piercey and D.P. Riley, NATURE (London) 178, 483 (1956).

25. E.R.Dobbs and G.O. Jones, Rep. Progr. Phys.20, 516(1957).

26. R.B. Bird, E.L. Spotz and J.O. Hirschfelder, J. Chem. Phys. 18 , 1395 (1950).

27. T.Kihara, J. Phys. Soc. Zapan 3 , 265 (1948).

28. R.Bergeon, Compt. Rend. Acad. Sci. (Paris) 234, 1039 (1952).

29. J.S. Rowlinson, F.H. Summer and J.R. Sutton, Trans. Faraday Soc. 50, 1 (1954).

30. J.S. Rowlinson, Mol. Phys. 6, 75 (1963).

31. R.J. Munn, J. Chem. Phys. 42, 3032 (1965).

32. D.Henderson and L. Oden, Mol. Phys. 10 , 405 (1966).

33. S.Kim, D. Henderson and L. Oden, J. Chem. Phys. 45, 4030 (1966).

34. Pollack, Rev. Mod. Phys. 36, 748 (1964).

35. J.S. Rowlinson and Brown, Mol. Phys. 3, 35 (1960).

36. G. Boato and G. Casanova, Physica 27, 571 (1961).

37. Max Klein and M.S. Green, J. Chem. Phys. 39, 1367 (1963).

38. Disc. Faraday Soc. 15, 108 (1953).

39. J.A. Barker and P.J. Leonard, Phys. Letters. 13, 127 (1964).

40. R.D. Weir, I. Wynn Jones, J.S. Rowlinson and G.Saville, J. Chem. Phys. 63, 1320 (1967).

41. J.S. Rowlinson, Disc. Faraday Soc. 40, 19 (1965).

42. A.E. Sherwood and J.M. Prausnitz, J. Chem. Phys. 41, 413 (1964).

43. J.S. Rowlinson, Mol. Phys. 3, 265 (1960).

44. E.A. Guggenheim and M.L. McGlashan, Proc. Roy. Soc. A255, 456 (1960).

45. B.E.F. Fender and G.D. Halsey, J. Chem. Phys. 36, 1881, (1962).

46. I. Amdure and T.F. Schatzki, J. Chem. Phys. 27 , 1949 (1957).

47. I. Shavitt and S.F. Boys , Nature (London) 178, 1340 (1956).

48. J.H. Dymond, M.Rigby and E.B. Smith, J. Chem. Phys. 42, 2801 (1965).

49. J.A. Barker, W. Fock and F. Smith, Phys. Fluids 7, 897 (1964).

50. F.A. Guevara, B.B. McInter and Wagemann, cited by H.J.M. Handley and G.E. Childs, Science 159, 1114(1968)

51. M.Trautz and R. Zink, Ann. Physik 7 , 427 (1930).

52. V. Varilesco, Ann. Phys. (Paris) 20,292 (1945).

53. C.F. Bonilla, S.J. Wang and H. Weiner, Trans. ASME 78, 1285 (1956).

54. J.H. Dymond and B.J. Alder, J. Chem. Phys. 51, 309 (1969)

55. L.Z. Pollara and P.T. Funke, J. Chem. Phys. 31, 855 (1959).

56. S.D. Hamann and J.A. Lambert, Australian J. Chem. 7, 1 (1954).

57. R.Y. Koo and H.W. HSU, J. Chem. Phys. 52, 2392 (1970)

58. J.S. Rowlinson and J.R. Townley, Trans. Faraday Soc. 49, 20 (1953).

59. W.H. Stockmayer, J. Chem. Phys. 9, 398 (1941).

60. J.A. Pople, Proc. Roy. Soc.(London) A221 , 498, 508(1954)

61. A.D. Buckingham and J.A. Pople, Trans. Faraday Soc. 46, 1179 (1950).

62. A.D. Buckingham and J.A. Pople, Trans. Faraday Soc. 51, 1173 (1955).

63. A.D. Buckingham and J.A. Pople, Ibid., p. 1179.

64. J.H. Dymond and E.B. Smith, Trans. Faraday Soc. 60,1378(1964).

65. K.W. Suh and T.S. Storvick, J. Phys. Chem. 71,1450 (1967).

66. J.R. Sweet and W.A. Steele, J. Chem. Phys. 47, 3022 (1967).

67. J.R. Sweet and W.A. Steele, Ibid., p. 3029.

68. Y.D. Chen and W.A. Steele, J. Chem. Phys. 50, 1428 (1970).

69. Chang Lyoul Kong, J. Chem. Phys. 53, 1516 (1970).

70. Chang Lyoul Kong, Ibid.,p. 1522.

71. Lawley Sutton, Trans. Faraday Soc. 59, 2680 (1963).

72. Par Dominique Depeyre, Extrait du Journal de chimie Physique 66, 1956 (1969).

73. J.D. Van der Waals, Sr. Doctoral Dissertation (Leiden 1873).

74. O. Singh and N.C. Varshneya : to be published.

75. G.S. Kell and E. Whalley, Phil. Trans. Roy. Soc.(London) 258A, 565 (1965).

76. H.S. Frank and W-Y. Wen, Disc. Faraday Soc. 24, 133(1957).

77. H.S. Frank, Nat. Acad. Sci. - Nat. Res. Council Pub. 42, 141 (1963).

78. G. Casanova, R.J. Dulla, D.A. Jonah, J.S. Rowlinson and G. Saville, Mol. Phys. 18 , 589 (1970).

79. J. Alexander, Colloid Chemistry (Reinhold Pub. Co., New York, 1950), Vol. VII pp. 150-154.

80. S.S. Mitra and D.N.Chakravarti, J. Chem. Phys. 22, 1775 (1954).

81. S.T. Bowden, J. Chem. Phys. 23, 2454 (1955).

82. N.K. Sanyal and S.S. Mitra, J. Chem. Phys. 24 , 473 (1956).

83. E.W. Rusche and W.B. Good, J. Chem. Phys. 45, 4467 (1966).

84. C.G. Malmberg and A.A. Mary Cott, J. Res. Nat. Bur. Stand 56 , 1 (1966).

85. Akerlog and Oshry, J. Am. Chem. Soc. 72, 2844 (1950).

86. N. Dass and N.C. Varshneya, J. Phys. Soc. Japan 26, 873 (1969).

87. G.W. Willard, J. Acous. Soc. Am. 19, 235 (1947).

88. R.A. McConnel, and W.F. Mruk , J. Acous. Soc. Am. 27, 672 (1955).

89. M. Greenspan and E. Tschiegg, J. Acous. Soc. Am. 31, 75(1959).

90. J.A. Partington, An Advanced Treatise on Physical Chemistry, Longmans - Green and Co., Ltd., London, Vol. 2 (1951).

91. H. Eisenberg, J. Chem. Phys. 43, 3887 (1965).

92. A.A. Miller, J. Chem. Phys. 38 , 1568 (1963).

93. A.K. Doolittle, J. Appl. Phys. 22, 1031 (1951).

94. M.H. Cohen and D. Turnbull, J. Chem. Phys. 31, 1164 (1959).

95. G. Nemethy and H.A. Scheraga, J. Chem. Phys. 35, 1141(1961).

96. O. Singh and N. Dass, Indian J. Pure Appl. Phys. 9 , 92(1971).

97. O. Singh, N. Dass and N.C. Varshneya, Proceedings of the Nuclear and Solid Physic Symposium, India, 1972.

98. Hand book of Physics and Chemistry (Chemical Rubber Pub. Co. Cleveland, Ohio), 1960.

99. International Critical Tables (McGraw-Hill Book Co. Inc., New York), 1926.

100. J. H. Sympson and H.Y. Carr, Phys. Rev. 111, 1201 (1958).

101. J.A. Saxton, Proc. Roy. Soc. 213A, 473 (1952).

102. L. Hall, Phys. Rev. 73, 775 (1948).

103. T.L. Chang and L. H. Tung, Nature 163 , 737 (1949).

104. N.E. Dorsey, Properties of Ordinary Water substances (Reinhold Pub. Co. Inc., New York), 1940.

105. A.W. Lawson, R. Lowell and A.L. Jain, J. Chem. Phys. 30, 643 (1959).

106. R.Cini and M. Torrini, J. Chem. Phys. 49, 2826 (1968).

107. N. Dass and O. Singh, J. Phys. Soc. Japan 28, 806 (1970).

108. Krishnaji and A. Man Singh, J. Chem. Phys. 44, 1590 (1966).

109. A. Barlow, J. Lamb and A.J. Matheson, Proc. Roy. Soc. 292A, 322 (1966)

110. Thermal Neutron Scattering, edited by P.A. Eglestaff (Acad. Press Ltd., London), 1965.

111. S.K.Josh, J. Chem. Phys. 35, 1141 (1961).

112. S.C. Jain and R.C. Bhandari, J. Phys. Soc. Japan 23, 476 (1967).

113. O. Singh and N.Dass, Proceedings of the 58th Session of Indian Science Congress, 1971.

114. S.K.Mitra, N.Dass, O. Singh and N.C.Varshneya, Proceedings of the eleventh Symposium on Cosmicrays, elementary particles and astrophysics (1969).

115. K. Buijs and R. Choppin, J. Chem. Phys. 39, 2035 (1963).

116. C.M. Davis, Jr. and T.A. Litovitz, J. Chem. Phys. 42, 2563 (1965).

117. N.Das, Ph.D. Dissertation, Ch. VI, U.O.R., India (1970).

118. S.K. Mitra, N.Dass and N.C. Varshneya, J. Chem.Phys.(in press).

119. Lester Haar and Stephen H. Shanker, J. Chem. Phys.55, 4951 (1971).

120. J.A. Barker and D. Handerson, J. Chem. Phys. 47, 4714 (1967).

121. L. Monchick and E.A. Mason, J. Chem. Phys. 35, 1676 (1961).

122. E.A. Mason and L. Monchick, J. Chem. Phys. 36, 2746 (1962).

123. F.J. Smith, R.J. Munn, and E.A. Mason, ibid., 46, 317(1967).

124. F. Danon, and I. Amdur, ibid., 50, 4718 (1969).

125. D. Cook and J.S. Rowlinson, Proc. Roy. Soc.(London) A219, 405 (1953).

126. J.S. Rowlinson, Mol. Phys. 1, 414 (1958).

127. O. Singh and N.C. Varshneya, Model of Liquid Water, Proceedings of Nuclear Physics and Solid State Physics Symposium, 1972.

128. G. Němethy and H.A. Scheraga, J. Chem. Phys. 36, 3382 (1962).

129. J.Schuyer, J. Polymer Science XXXVI, 475 (1959).

130. E.A. Moelwyn - Hughes, Physical Chemistry, Pergamon Press, 324, 325 (1957).

131. Physics of Fluids, edited by H.W.V. Temperley, J.S. Rowlinson, and G.S. Rushbrooke, (North Holland, Amsterdam 1968), Chaps. 2,3 and 10.

132. D. Levesque, Physica 32 , 1985 (1966).

133. R.W. Zwanzig, J. Chem. Phys. 22 , 1420 (1954).

134. R.J. Buehler, R.H. Wentorf, J.O. Hirschfelder and C.F. Curtiss, J. Chem. Phys. 19, 61 (1951).

135. H. Eyring and J.O. Hirschfelder, J. Phys. Chem. 41, 249 (1937).

136. J.O. Hirschfelder, J. Chem. Educ. 16, 540 (1939).

137. J.E. Lennard-Jones and A.F. Devonshire, Proc. Roy.Soc. A165, 1 (1938).

138. A.F. Devonshire, Proc. Roy. Soc. A 174, 102 (1940).

139. J. Corner and J.E. Lennard-Jones, Proc. Roy.Soc.A178, 401 (1941).

140. J.G. Kirkwood, J. Chem. Phys. 18, 380 (1950).

141. J.S. Dahler, J.O. Hirshfelder and H.C. Thacher, J. Chem. Phys. 25, 249 (1956).

142. J.S. Dahler and J.O. Hirschfelder, J. Chem. Phys. 32, 330 (1960).

143. J.De Boer, Physica 20, 655 (1954).

144. J.S. Dahler and E.G.D. Cohen, Physica 26, 81(1960)

145. H.Eyring, J. Chem. Phys. 4, 283 (1936).

146. J.De Boer, Proc. Roy. Soc. A215, 4(1952).

147. H.Eyring, T. Ree and N. Hirai, Proc. Nat. Acad. Sci. 44, 683 (1958).

148. T.S. Ree, T. Ree and H. Eyring, Proc. Nat. Acad. Sci. 48, 501 (1962).

149. N.Metropolis, M. Rosenbluth, A. Rosenbluth, A Teler and E. Teller, J. Chem. Phys. 21, 1087 (1953).

150. M. Rosenbluth and A. Rosenbluth, J. Chem. Phys. 22, 881 (1954).

151. W.Wood and F. Parker, J. Chem. Phys. 27, 720 (1957).

152. B. Alder and T. Wainwright, J. Chem. Phys. 27, 1208 (1957).

153. T. Wain wright and B. Alder, Supl., V. IX Nuovo Cemento, No. 1, 116 (1958).

154. J.A. Barker, Aust. J. Chem., 13 , 187 (1960).

155. J. A. Barker, Proc. Roy. Soc. A259 , 442 (1961).

156. J. Bernal and R. Fowler, J. Chem. Phys. 1 , 515 (1933)

157. K. Grjotheim and J. Krogh- Moe, Act. Chem. Scand. 8, 1193 (1954).

158. G. Wada, Bull. Chem. Soc. Japan 34, 955 (1961).

159. H. Frank and A. Quist, J. Chem. Phys. 34 , 604 (1961).

160. A. Smith, and A. Lawson, J. Chem. Phys. 22 , 351 (1954).

161. T. Litovitz and E. Carnevale, J. Appl. Phys. 26, 816 (1955).

162. A Liebermann, J. Acoust. Soc. Am. 28, 1253 (1956).

163. O.Ya. Samoilov and T.A. Nosova, Zh. Strukt. Khim.6, 798 (1965).

164. H.S. Frank, Proc. Roy. Soc. A247, 481 (1958)

165. V. Vand and W.A. Senior, J. Chem. Phys. 43, 1869, 1873, 1878 (1965).

166. K. Lonsdale, Proc. Roy. Soc. (London) A247, 424 (1958).

167. K. Hertzberg and T. Litovitz, Absorption and Dispersion of ultrasonic waves (Acad. Press., Inc., New York, 1959)

168. P.A. Giguere and K.B. Harvey, Can. J. Chem. 34, 798 (1956).

169. P.C. Cross, J. Burnham and P.A. Leighton, J. Am.Chem. Soc. 59, 1134 (1937).

170. C.H. Cartwright, Phys. Rev. 49, 470 (1936).

171. R.P. Marchi and H. Eyring, J. Phys. Chem. 68, 221(1964).

APPENDIX I

Property	unit	Range of study °C	A_x	B_x
SURFACE TENSION	dynes/cm	0 to 100	0.39098381E+01	0.13152023
VISCOSITY	cP	0 to 100	-.24721381E+01	0.96597673
SELF-DIFFUSION	10^{-5} cm^2/sec	0 to 100	0.37371584E+01	-0.12579146E+01
DIELECTRIC RELAXATION TIME	10^{-12} sec	0 to 50	-0.60141840	0.11156128E+01
SPIN-RELAXATION TIME	Sec.	0 to 100	0.371492E+01	-.10390651E+01
THERMAL CONDUCTIVITY	10^{-7} watt/cm °C	0 to 100	0.21143176E+01	-.12715138
MECHANICAL RELAXATION TIME	10^{-12} sec	0 to 100	-0.20745722E+01	0.10977080E+01
ULTRASONIC ABSORPTION	10^{-17} sec^2/cm.	0 to 80	0.58151730	0.11995393E+01
DIELECTRIC CONSTANT	-	0 to 100	0.37079884E+01	0.24314699
SOUND VELOCITY	Km/sec	0 to 100	0.54910362	-0.66582701E-01
REFRACTIVE INDEX	-	0 to 100	0.26825220	0.63768605E-02
DENSITY	gm/c.c.	0 to 100	-.70396967E-01	0.22207242E-01
MAGNETIC SUSCEPTIBILITY	-	0 to 100	0.18083700E-01	-0.66109833E-02

APPENDIX II

Pressure (atm.)	A_x	B_x	Range of study(°C)
50	-2.4494197	0.95653348	0 to 100
100	-2.4110384	0.94244529	
200	-2.3562609	0.92027514	
300	-2.3063206	0.90139425	

APPENDIX III

Pressure (atm.)	A_x	B_x	Range of study ($^\circ C$)
1000	5.2834325	-0.10339864	30 to 130
2500	5.3781331	-0.10694290	
4000	5.4603588	-0.11520044	
6000	5.5133190	-0.10797428	
8000	5.5708826	-0.10889356	

APPENDIX IV

Pressure (atm.)	A_x	B_x	Range of study (°C)
50	0.59756407E-01	-0.19619117E-01	0 to 100
100	0.57577248E-01	-0.19720169E-01	
150	0.55430203E-01	-.19820277E-01	
200	0.53315581E-01	-0.19920108E-01	
250	0.51232753E-01	-0.20019716E-01	
300	0.49177572E-01	-0.20117379E-01	
350	0.47153262E-01	-0.20214654E-01	
400	0.45159525E-01	-0.20311762E-01	
450	0.43190884E-01	-0.20406815E-01	
500	0.41251383E-01	-0.20501090E-01	
550	0.39335553E-01	-0.20593365E-01	
600	0.37446984E-01	-0.20684806E-01	
650	0.35581490E-01	-0.20774248E-01	
700	0.33739067E-01	-0.20861690E-01	
750	0.31921783E-01	-0.20948354E-01	
800	0.30123356E-01	-0.21031907E-01	
850	0.28346707E-01	-0.21114126E-01	
900	0.26589549E-01	-0.21193624E-01	
950	0.24851614E-01	-0.21271233E-01	
1000	0.23131791E-01	-0.21346286E-01	

APPENDIX V

The partition function, Z, for the mixture of NX_0 molecules in class I and NX_c (or $N(1-X_0)$) molecules in class II, is given by

$$Z = \frac{N!}{(NX_0)!\,(N(1-X_0))!}\,(f_I)^{NX_0}\,(f_{II}e^{-\epsilon/RT})^{N(1-X_0)} \qquad \text{(a)}$$

Taking logarithm, we get

$$\log Z = \log N! - \log (NX_0)! - \log N(1-X_0)! + NX_0 \log f_I$$
$$+ N(1-X_0) \log (f_{II}e^{-\epsilon/RT})$$

Using Stirling approximation,

$$\log Z = N \log N - N - NX_0 \log N X_0 + NX_0 - N(1-X_0) \log N(1-X_0)$$
$$+ N(1-X_0) + NX_0 \log f_I + N(1-X_0) \log (f_{II}e^{-\epsilon/RT})$$

or

$$\log Z = N \log N - NX_0 \log NX_0 - N(1-X_0) \log N(1-X_0) + NX_0 \log f$$
$$+ N(1-X_0) \log (f_{II}\, e^{-\epsilon/RT}) \qquad \text{(b)}$$

Now maximizing equation (b), we get,

$$\frac{\partial \log Z}{\partial X_0} = 0 = N \log \left(\frac{1-X_0}{X_0}\right) + N \log \frac{f_I}{f_{II}\, e^{-\epsilon/RT}}$$

$$\therefore \quad \frac{X_0}{1-X_0} = \frac{f_I}{f_{II}\, e^{-\epsilon/RT}}$$

$$\text{or} \quad X_0 = \frac{f_I}{f_I + f_{II}\, e^{-\epsilon/RT}} \qquad \text{(c)}$$

or $$\log f_I - \log f_{II}\, e^{-\epsilon/RT} = \log \frac{X_0}{1 - X_0} \qquad (d)$$

Now equation (b) can be written as,

$$\begin{aligned}\log Z = {} & N \log N - NX_0 \left[\log N X_0 - \log N(1-X_0)\right] \\ & - N \log N\,(1-X_0) + NX_0\left[\log f_I - \log\left(f_{II} e^{-\epsilon/RT}\right)\right] \\ & + N \log f_I\, e^{-\epsilon/RT}\end{aligned}$$

Using equation (c), we get

$$\log Z = \log \left(\frac{f_{II}\, e^{-\epsilon/RT}}{1 - X_0}\right)^N \qquad (e)$$

Now from equations (c) and (e), we get finally,

$$\log Z = \log \left(f_I + f_{II}\, e^{-\epsilon/RT}\right)^N$$

$$\boxed{Z = \left(f_I + f_{II}\, e^{-\epsilon/RT}\right)^N}$$

APPENDIX VI

Let the given equations be

$$f(a,b) = 0 \qquad (1)$$

$$g(a,b) = 0 \qquad (2)$$

Now if a_0 , b_0 be approximate values of a pair of roots and δa , δb be the corrections, so that

$$a = a_0 + \delta a$$

$$b = b_0 + \delta b$$

Then equations (1) and (2) become

$$f(a_0 + \delta a\ ,\ b_0 + \delta b) = 0 \qquad (3)$$

$$g(a_0 + \delta a\ ,\ b_0 + \delta b) = 0 \qquad (4)$$

expanding equations (3) and (4) by Taylor's theorem for a function of two variables, we have,

$$f(a_0 + \delta a\ ,\ b_0 + \delta b) = f(a_0, b_0) + \delta a \left(\frac{\partial f}{\delta a} \right)_0 + \delta b \left(\frac{\partial f}{\partial b} \right)_0$$

$$+ \text{ terms in higher powers of } \delta a \ \& \ \delta b = 0 \qquad (5)$$

$$g(a_0 + \delta a\ ,\ b_0 + \delta b) = g(a_0, b_0) + \delta a \left(\frac{\partial g}{\partial a} \right)_0 + \delta b \left(\frac{\partial g}{\partial b} \right)_0$$

$$+ \text{ terms in higher powers of } \delta a \ \& \ \delta b = 0 \qquad (6)$$

Now since δa and δb are relatively small we neglect their squares, products and higher powers and then equations (5) & (6) become simply

$$f(a_0,b_0) + \delta a\left(\frac{\partial f}{\partial a}\right)_0 + \delta b\left(\frac{\partial f}{\partial b}\right)_0 = 0 \qquad (7)$$

$$g(a_0,b_0) + \delta a\left(\frac{\partial g}{\partial a}\right)_0 + \delta b\left(\frac{\partial g}{\partial b}\right)_0 = 0 \qquad (8)$$

Solving these equations by determinants, we find the first correction to be

$$\delta a = \frac{\begin{vmatrix} -f(a_0,b_0) & \left(\frac{\partial f}{\partial b}\right)_0 \\ -g(a_0,b_0) & \left(\frac{\partial g}{\partial b}\right)_0 \end{vmatrix}}{\Delta} \qquad (9)$$

$$\delta b = \frac{\begin{vmatrix} \left(\frac{\partial f}{\partial a}\right)_0 & -f(a_0,b_0) \\ \left(\frac{\partial g}{\partial a}\right)_0 & -g(a_0,b_0) \end{vmatrix}}{\Delta} \qquad (10)$$

where,

$$\Delta = \begin{vmatrix} \left(\frac{\partial f}{\partial a}\right)_0 & \left(\frac{\partial f}{\partial b}\right)_0 \\ \left(\frac{\partial g}{\partial a}\right)_0 & \left(\frac{\partial g}{\partial b}\right)_0 \end{vmatrix} \qquad (11)$$

The notation $\left(\frac{\partial f}{\partial a}\right)_0$ means the value of $\left(\frac{\partial f}{\partial a}\right)$ when a_0 and b_0 are substituted for a and b. Similarly $\left(\frac{\partial f}{\partial a}\right)_1$ means the value of $\left(\frac{\partial f}{\partial a}\right)$ when $a = a^{(1)}$, $b = b^{(1)}$; and so on.

I shall now apply this method to solve Van der waal's equation for a and b. The Van der waal's equation is

$$\left(p + \frac{a}{V^2} \right) \left(V - b \right) = RT \qquad (12)$$

Let

$$S = \sum_i \left[\left(p_i + \frac{a}{V_i^2}\right) \left(V_i - b\right) - RT \right]^2 \qquad (13)$$

$$f = \frac{\partial S}{\partial a} = b^2 \sum_i \frac{p_i}{V_i^2} + RTb \sum_i \frac{1}{V_i^2} - 2b \sum_i \frac{p_i}{V_i} + \sum_i p_i$$

$$- RT \sum_i \frac{1}{V_i} - a \left[2b \sum_i \frac{1}{V_i^3} - b^2 \sum_i \frac{1}{V_i^4} - \sum_i \frac{1}{V_i^2} \right] \qquad (14)$$

$$g = \frac{\partial s}{\partial b} = a^2 \sum_i \frac{1}{V_i^3} + 2\,a \sum_i \frac{p_i}{V_i} - a\,RT \sum_i \frac{1}{V_i^2} + \sum_i p_i^2\,V_i$$

$$- RT \sum_i p_i - b \left[\sum_i p_i^2 + 2\,a \sum_i \frac{p_i}{V_i^2} + a^2 \sum_i \frac{1}{V_i^4} \right] \qquad (15)$$

Therefore

$$\frac{\partial f}{\partial a} = - 2\,b \sum_i \frac{1}{V_i^3} + b^2 \sum_i \frac{1}{V_i^4} + \sum_i \frac{1}{V_i^2} \qquad (16)$$

$$\frac{\partial f}{\partial b} = 2b \sum_i \frac{p_i}{V_i^2} + RT \sum_i \frac{1}{V_i^2} - 2 \sum_i \frac{p_i}{V_i} - 2\,a \sum_i \frac{1}{V_i^3}$$

$$+ 2ab \sum_i \frac{1}{V_i^4} \qquad (17)$$

and

$$\frac{\partial g}{\partial a} = 2\,a \sum_i \frac{1}{V_i^3} + 2 \sum_i \frac{p_i}{V_i} - RT \sum_i \frac{1}{V_i^2} - b \left[2 \sum_i \frac{p_i}{V_i^2} + 2a \sum_i \frac{1}{V_i^4} \right] \qquad (18)$$

$$\frac{\partial g}{\partial b} = - \left[\sum_i p_i^2 + 2\,a \sum_i \frac{p_i}{V_i^2} + a^2 \sum_i \frac{1}{V_i^4} \right] \qquad (19)$$

Now the first correction is determined by substituting equations (14) to (19) in equations (9), (10) and (11)

Additional corrections can be found by repeated applications of these formulae with the improved values of a and b substituted at each step. The computed values of a and b this way are shown in Figures 12 & 13.

APPENDIX VII

The trial potential is

$$\phi\,(r,T) = 4\,\epsilon_0\left[\left(\frac{\sigma_0}{r}\right)^n - \left(\frac{\sigma_0}{r}\right)^m \quad (1+\Omega)\right] \qquad (1)$$

We can write for this equation

$$\phi\,(r,T) = 4\,\epsilon_0(1+\Omega)^{\alpha}\left[\left(\frac{\sigma_0\,(1+\Omega)^{\beta}}{r}\right)^n - \left(\frac{\sigma_0(1+\Omega)^{\beta}}{r}\right)^m\right] \qquad (2)$$

Comparing equations (1) and (2), we get for the powers,

$$\alpha + n\,\beta = 0 \qquad (3)$$

$$\alpha + m\,\beta = 1 \qquad (4)$$

Now subtracting equation (4) from equation (3), we get,

$$\beta = -\frac{1}{(n-m)} \qquad (5)$$

Substituting the value of β in equation (3), we get for α

$$\alpha = \frac{n}{(n-m)} \qquad (6)$$

Hence equation (2) becomes

$$\phi\,(r,T) = 4\,\epsilon\,(T)\left[\left(\frac{\sigma(T)}{r}\right)^n - \left(\frac{\sigma(T)}{r}\right)^m\right] \qquad (7)$$

$$\left.\begin{aligned} \text{where}\quad \epsilon(T) &= \epsilon_0\,(1+\Omega)^{\frac{n}{(n-m)}} \\ \sigma(T) &= \sigma_0(1+\Omega)^{-\frac{1}{n-m}} \end{aligned}\right\} \qquad (8)$$