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LOW TEMPERATURE HEAT CAPACITIES AND THERMODYNAMIC PROPERTIES
OF ANHYDROUS POTASSIUM FERROCYANIDE

PART - I

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NATIONAL CHEMICAL LABORATORY
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PART - II

TH-837

A THESIS SUBMITTED TO THE
UNIVERSITY OF BOMBAY FOR THE
DEGREE OF
MASTER OF SCIENCE

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BY

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MY LATE BELOVED PARENTS

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PART - II

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PART - I



CHAPTER - I

GENERAL INTRODUCTION

That the constituent particles take up equilibrium positions of minimum potential energy, where the forces of attraction and repulsion exactly balance each other, is applicable to any crystalline solid irrespective of the nature of the bonds between the units. The atoms or ions are not at rest, but vibrate about their equilibrium positions, even at the absolute zero, and as the temperature is raised the amplitude of vibration increases, and so also do the mean potential and kinetic energies. It is the rate of increase of the vibrational energy with temperature that determines the heat capacity of the solid.

If the total energy U of an assembly is a function of temperature, then one can define the specific heat C_x under a constraint 'x' as

$$C_x = \left. \frac{\partial U}{\partial T} \right|_x$$

The constraint 'x' may be either constant pressure or constant volume.

From the extraordinary wealth of information that can be obtained from cryogenic calorimetric determinations about substances, one is tempted to regard such investigations as of the most fundamental significance of all the methods of measurements. One may expect the variation of the specific heat

with temperature to throw light on the distribution of energy within the molecule and on the "structure", especially in the ranges where this variation represents the change of rate of energy absorption as the molecule passes from a state of little energy to the state in which one generally deals with it at room temperature. But the chief object of chemical cryogenic studies is to provide basic data for thermodynamic purposes. The heat capacity, besides being a sensitive and revealing parameter of the energetics of the substances and one of the most powerful tools available for the study of condensed phases, provides the raw material for chemical thermodynamic functions such as entropy, enthalpy and Gibbs free energy.

Anomalies in Thermal Properties

In the course of cryogenic measurements, phase transformations such as polymorphic transitions in crystals, fusion and vaporization are likely to be encountered. These have often been designated as first order transitions.

For example, hydrogen chloride⁽¹⁾ undergoes a transition at 98.36°K (entropy of transition = $2.89\text{ cal/mole.deg.}$), melts at 158.91°K (entropy of fusion = 3 cal/mole.deg.) and vaporizes at 188.07°K (entropy of vaporization = $20.52\text{ cal/mole.deg.}$).

Higher order transitions such as second order transitions also show a peak or hump in heat capacity vs temperature curve.

Magnetic Materials

Analysis of low temperature calorimetric data permits both the detection of magnetic transformations and the evaluation of the thermodynamic parameters associated with these phenomena. This calorimetric technique is relatively sensitive and precise, and compared to more direct magnetic measurements (e.g. susceptibility), less subject to being masked by traces of ferromagnetic impurities.

The heat capacity of zinc ferrite⁽²⁾ (ZnFe_2O_4) exhibits a cooperative thermal anomaly associated with antiferromagnetic ordering at 9.5°K and extending towards higher temperatures probably as a consequence of persisting short-range order.

Ferroelectric Substances

Since energy must be supplied to destroy the spontaneous polarization of a ferroelectric crystal, the heat capacity is expected to reveal a peak or hump in those regions where the spontaneous polarization is changing with the temperature.

There are two broad classes of ferroelectric substances:

(a) substances with high entropy of transition (order-disorder transformations) e.g., ammonium sulphate and potassium dihydrogen phosphate

and

(b) substances with very low entropy of transition e.g., thio-urea.

Matthias et. al.⁽³⁾ showed that ammonium sulphate has a ferroelectric Curie point at 223.7°K . The heat capacity determinations by Shomate⁽⁴⁾ exhibited a marked "hump" extending over a temperature of about 100° , the maximum occurring at 223.4°K , corresponding to the ferroelectric Curie temperature with an entropy of transition of about 4 cal./mole.deg.). Similarly ammonium chloride⁽⁵⁾ shows a peak at 242.8°K .

Two small lambda-type anomalies in the heat capacity curve of thio-urea⁽⁶⁾ were found at -106°C and -71°C , respectively, corresponding to the lowest and highest transition points with entropy changes of 0.018 and 0.006 cal./mol.deg. respectively. Goldsmith et al.⁽⁷⁾ associated the ferroelectric behaviour with relative displacements of entire molecules rather than in motion of ions within the crystal.

The electric properties of Rochelle salt, potassium dihydrogen phosphate and its isomers are very similar to the magnetic properties of ferromagnetic substances and exhibit anomalies in the heat capacities⁽⁸⁻¹⁶⁾ near the Curie points. The transition entropies of different KH_2PO_4 -type ferroelectrics do not differ substantially, though there are rather large differences in the transition temperatures. The most striking example in this respect is the pair KH_2PO_4 and KD_2PO_4 . According to Bantle⁽¹⁴⁾, both crystals have the same transition entropy, though the Curie temperatures differ almost by a factor of two. This factor and the order of magnitude of the transition entropy suggest that the transition is predominantly of the first class, namely order-disorder type. There is,

however, a big difference between this transition and the corresponding transition in alloys. The excess specific heat in the former case drops abruptly to zero above the transition point, indicating that the short-range order is destroyed simultaneously with the long-range order. In alloys, on the other hand, some excess specific heat is observed above the transition point due to persisting short-range order.

The following relation between spontaneous polarization P_s and excess specific heat ΔC_p was verified experimentally⁽¹⁷⁾

$$\Delta C_p = - \frac{T_0}{C} \cdot \frac{dP_s^2}{dT}$$

where C is the Curie constant and T_0 , the Curie temperature.

Schottky Effect

The quantum theories of specific heat are based on the assumption that all the atoms or molecules remain throughout in the lowest electronic level. If there is another possible level of the electronic energy higher by an amount ΔE than the lowest level, then at the absolute zero all the atoms or molecules will be in the lowest level but as the temperature rises, the upper state will also become populated. The number of atoms in the upper state at any temperature T is given by statistical theory as $n = n_0 e^{-\Delta E/kT}$ where ' n_0 ' is the number of atoms in the lowest state, so that at a temperature for which kT is very large compared with ΔE , there will be an equal number of atoms in each state. Some of the heat put into the body will go into raising some of the atoms from the ground state to the upper

state instead of increasing the translational energy of the atoms, and the apparent specific heat will consequently be greater than in the absence of higher electronic levels.

A Schottky-type anomaly occurs in the case of uranium tetrafluoride (UF_4) in the heat capacity⁽¹⁸⁾ at $6.4^\circ K$.

Molecular Disorder

Plastically crystalline substances are characterised by (a) entropy of fusion of less than 5 cal./mole.deg., (b) usually cubic or hexagonal-symmetry and (c) transparency and easy deformability.

Many tetrahedral molecules such as methane exhibit plastically crystalline behaviour. It was shown by Clusius *et al.*⁽¹⁹⁾ that the specific heat of solid methane begins to rise very rapidly in the neighbourhood of $20^\circ K$, reaches a maximum of more than 80 cal./mole.deg. at $20.4^\circ K$ and then falls rapidly to about 4.6 at $21.2^\circ K$. Like an order-disorder anomaly, this effect is a typical co-operative phenomenon. In these cases, owing to short interaction, the jumping of one atom or group of atoms to another energy state increases the possibility that another jump will occur. The effect is believed to be due to the methane molecule vibrating about some equilibrium position determined by the electrostatic field of the crystal lattice and periodically "flipping" to an equivalent position connected with the earlier one by some symmetry operation consistent with the type of lattice present. Above the ' λ -point' there is a random distribution of all equivalent positions, but below it an increasing degree of order persists.

The above discussion brings out in no small measure the importance of cryogenic calorimetric work. Hence in a programme to study the thermodynamic properties of ferroelectric and antiferromagnetic solids, an isothermal low temperature calorimeter has been constructed. An all-glass apparatus is also specially constructed for the calibration of copper-constantan thermocouples used for the measurements of temperatures.

The heat capacities of standard benzoic acid were determined at various temperatures in the range 78° - 300° K, to establish the reliability and accuracy of the measurements. These results have been described in Chapter (IV).

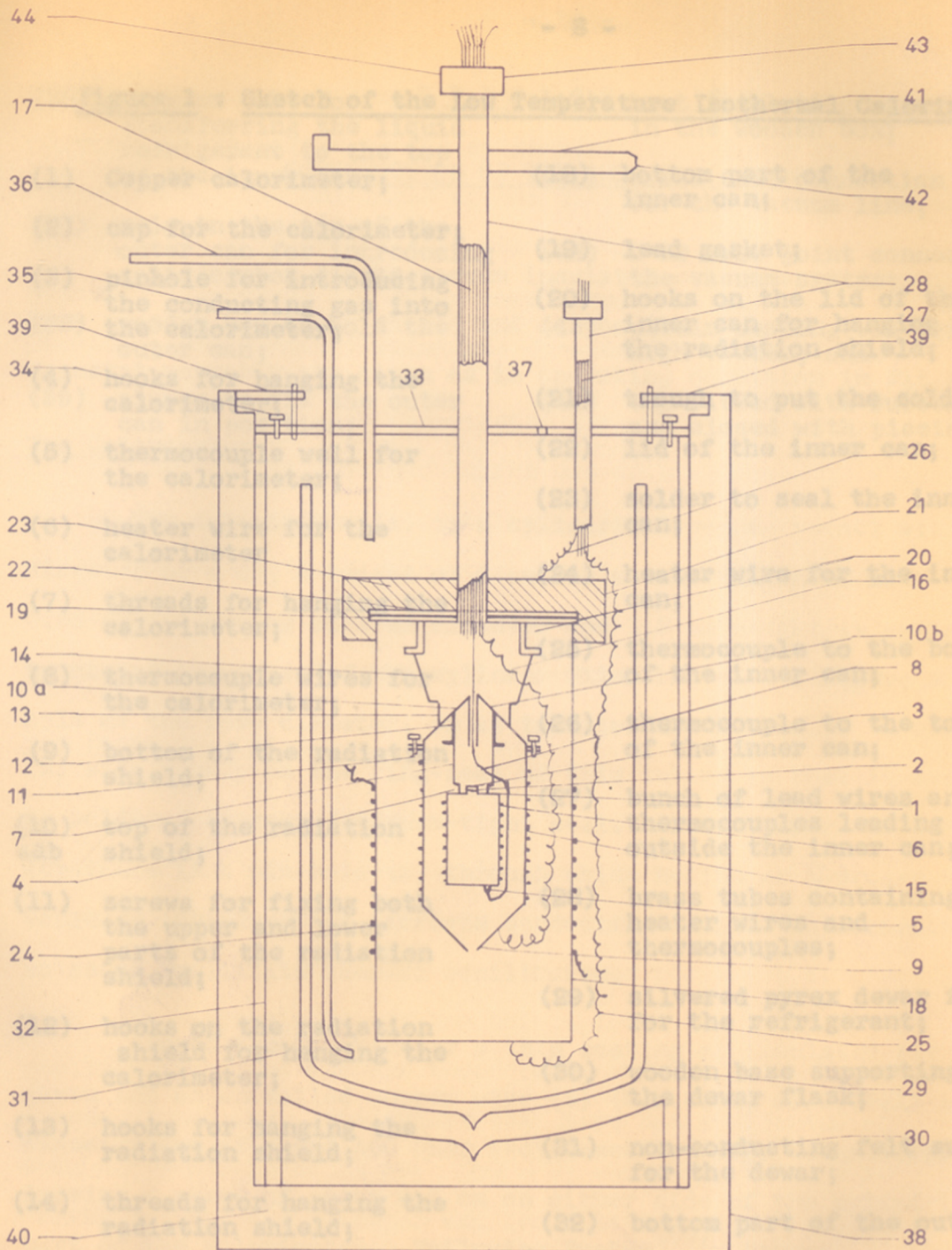


FIG.-1.

(1) innermost core;
 (2) surrounding layer;
 (3) radiation shield;
 (4) outer shell;
 (5) heater wire;
 (6) thermocouple wires;
 (7) thermocouple wires;
 (8) lead wires;
 (9) transfer tube;
 (10a) hooks for inner can;
 (10b) hooks for outer can;
 (11) threads for inner can;
 (12) threads for outer can;
 (13) screws for inner can;
 (14) threads for hanging the radiation shield;
 (15) heater wire for heating the radiation shield;
 (16) thermocouple wires for the radiation shield;
 (17) thermocouple wires for lead wires leading to inside the inner can;
 (18) transfer tube for transfer the liquid refrigerant to the bottom of the inner can;
 (19) lid of the water bath;
 (20) screws for fixing the bottom and top of the outer can in position;
 (21) bottom part of the outer can;
 (22) top part of the outer can;
 (23) water bath;
 (24) heater wire;
 (25) thermocouple wires;
 (26) transfer tube;
 (27) lid of the water bath;
 (28) screws for fixing the bottom and top of the outer can in position;
 (29) bottom part of the outer can;
 (30) top part of the outer can;
 (31) water bath;
 (32) heater wire;
 (33) lid of the water bath;
 (34) screws for fixing the bottom and top of the outer can in position;
 (35) transfer tube for transfer the liquid refrigerant to the bottom of the inner can;
 (36) top part of the outer can;
 (37) bottom part of the outer can;
 (38) water bath;
 (39) heater wire;
 (40) thermocouple wires;
 (41) transfer tube;
 (42) lid of the water bath;
 (43) top part of the outer can;
 (44) bottom part of the outer can;

Figure 1 : Sketch of the Low Temperature Isothermal Calorimeter

- | | |
|--|---|
| (1) Copper calorimeter; | (18) bottom part of the inner can; |
| (2) cap for the calorimeter; | (19) lead gasket; |
| (3) pinhole for introducing the conducting gas into the calorimeter; | (20) hooks on the lid of the inner can for hanging the radiation shield; |
| (4) hooks for hanging the calorimeter; | (21) trough to put the solder; |
| (5) thermocouple well for the calorimeter; | (22) lid of the inner can; |
| (6) heater wire for the calorimeter | (23) solder to seal the inner can; |
| (7) threads for hanging the calorimeter; | (24) heater wire for the inner can; |
| (8) thermocouple wires for the calorimeter; | (25) thermocouple to the bottom of the inner can; |
| (9) bottom of the radiation shield; | (26) thermocouple to the top of the inner can; |
| (10) top of the radiation shield;
a&b | (27) bunch of lead wires and thermocouples leading to outside the inner can; |
| (11) screws for fixing both the upper and lower parts of the radiation shield; | (28) brass tubes containing heater wires and thermocouples; |
| (12) hooks on the radiation shield for hanging the calorimeter; | (29) silvered pyrex dewar flask for the refrigerant; |
| (13) hooks for hanging the radiation shield; | (30) wooden base supporting the dewar flask; |
| (14) threads for hanging the radiation shield; | (31) non-conducting felt support for the dewar; |
| (15) heater wire for heating the radiation shield; | (32) bottom part of the outer can |
| (16) thermocouple wires for the radiation shield; | (33) lid of the outer can; |
| (17) thermocouple wires and lead wires leading to inside the inner can; | (34) screws for fixing the bottom and top of the outer can in position; |
| | (35) transfer tube for transferring the liquid refrigerant to the bottom of the inner can |

- (36) transfer tube for transferring the liquid refrigerant to the top of the inner can;
- (37) hole in the top of the outer can for introducing solid carbon dioxide;
- (38) wooden box to hold the outer can;
- (39) clamps to fix the outer can in position;
- (40) heat insulating material in the wooden box;
- (41) brass tube connection for the vacuum line;
- (42) B-19 male joint connecting the vacuum system;
- (43) picein sealing wax for high vacuum; and
- (44) cup fitted with rubber cork and closed with picein.

C H A P T E R - II

CONSTRUCTION OF THE CRYOSTAT ASSEMBLY

The details of the vacuum insulated calorimeter surrounded by a massive radiation shield and of the other parts of the cryostat assembly are given as in operating condition in Fig.1.

The Calorimeter

The calorimeter (1) is a cylindrical copper vessel with a diameter of 4 cm, a height of 6 cm and a wall thickness of 0.05 cm. A tubing of 1 cm diameter and 1.5 cm height is soldered to one of the faces of the cylinder which has at its centre a hole of the same diameter, so as to introduce a sample. A cap (2) sits firmly on the ring-seal of this tubing so that it can be soldered to make a vacuum-tight seal. On the centre of the cap there is a pin-hole (3) through which helium or hydrogen gas could be introduced to increase conduction of heat to a sample so as to facilitate thermal equilibrium.

Around the calorimeter a thin coating of insulated tar was given and an enamelled copper wire (6) (S.W.G.44) of 0.00813 cm diameter and of about 160 ohms resistance wound on it uniformly leaving a space of about 0.5 cm on either side of the cylindrical part of the calorimeter. Following Eucken (20), Nernst (21) and others (22), this copper wire was used as a combined resistance thermometer-heater for measuring temperature and energy. Since both the calorimeter and the thermometer-heater were made of the same material, strain due to temperature change was minimized (23).

After giving another coating of tar, first silver and then gold were vacuum deposited on the cylindrical surface of the calorimeter. The thickness of the plating was of the order of 10^4 \AA . Very thin gold foils were also attached to the cylindrical surface and since they have very negligible heat capacity, their contribution was considered as very small.

All joints in the calorimeter were silver soldered except the cap on the filling tube (which was soft soldered). Since copper has good thermal conductivity, the traditional use of vanes has been omitted without seriously lengthening the thermal relaxation time within the calorimeter. The weight of the empty calorimeter, including the thermometer-heater is 38.1 g.

The Radiation Shield

The radiation shield made out of a copper sheet and weighing about 650 g. (nearly 16 times heavier than the calorimeter) serves to maintain a good environment of constant temperature. It has two parts, the upper one which is shaped like a cone, consisting of two halves (10 a, b) fixed in position by screws and the lower part, a cylindrical one with a cone at one end. The cylindrical part has a diameter of 6 cm and a height of 14 cm. The cone ends have holes for taking out the thermocouple and lead wires. All these parts can be connected by brass screws (11). This arrangement has made the assembling and dismantling process easy. As in the case of the calorimeter an enamelled copper wire (15) (S.W.G. 40) of about 300 ohms resistance is wound on it and gold is vacuum deposited on the entire surface. A thermocouple (16)

is directly soldered to the bottom-cone part of the radiation shield (10b).

The Inner and Outer Cans

The inner can (18) is a heavy brass vessel with a diameter of 13 cm and a height of 23 cm. It has a flange that has a circular groove into which a lead-gasket (19) can be put and pressed against the lid (22) to prevent the solder from entering the inner can from the adjoining circular groove. A trough (21) at the top has a height of 3.5 cm and 10-12 lbs of soft solder (23) is required for filling it. Instead of this, generally heavy lead blocks are kept on the top of the inner can so as to stabilize the temperature of the latter. This large amount of solder is used with three purposes in view:-

- (1) the large quantity of the solder gives mechanical strength and partly relieves the strain produced while cooling the system;
- (2) the good height of 3.5 cm of the solder offers resistance against leakages while cooling to liquid nitrogen temperatures;
- (3) it stabilizes the temperature of the top of the can.

An enamelled constantan wire (24) (S.W.G. 35) of about 300 ohms resistance is wound on the inner can for heating whenever necessary. A long brass tube (28) with a diameter of 2 cm is brazed at the centre of the lid of 14 cm diameter, which closes the inner can. At a height of 18 cm from this lid, another lid (33) of 26 cm diameter is welded to the brass tube for closing the outer can (32) simultaneously along with the

inner can. There are two thermocouples (25, 26) soldered to the top and bottom parts of the inner can to measure the temperatures and thus to give an indication of the extent of cooling caused by liquid nitrogen in the dewar (29) in which the can is kept.

The outer can is a large cylindrical brass vessel of 26 cm outer diameter and 60 cm height. It has a flange of 1.5 cm pointing inwards with an O-ring and a row of projected screws to press-tight the lid. The lid of the outer can has holes at corresponding positions so that the inner can^{can} can be put in a fixed position in the enclosed dewar (29). Two brass tubes (35, 36) of 0.5 cm diameter are welded through the top lid of the outer can. One of them goes to the bottom of the inner can and the other to the top. These are used for pumping the coolant liquid nitrogen into the dewar. There is also an opening (37) which can be closed at will, on the lid of the outer can through which solid carbon-di-oxide can be introduced, if required, to obtain the temperatures in the carbon-di-oxide range.

The outer can holds the glass dewar (29) that rests on felt pads supported by an wooden base (30). Non-conducting felt (31) prevents the dewar from coming into direct contact with the outer can. A double-walled wooden box (38) packed with heat insulating material (40) houses the entire cryostat in a stable fashion such that the whole brass system does not rock once locked inside the box with clamps (39). This is necessary as the side tube (41) of the inner can is directly connected to the rather fragile high vacuum glass system.

All the thermocouples and lead wires (17) of the calorimeter and the radiation shield with a few spare wires are drawn through a cup (44) at the end of the long tube and sealed with picein (43) for holding high vacuum. Similarly, the wires and thermocouples (27) of the inner can with a few spare wires are brought through a side tube (28) and sealed.

Figure 2 : Sketch of the Glass Apparatus used for Calibration of Thermocouples

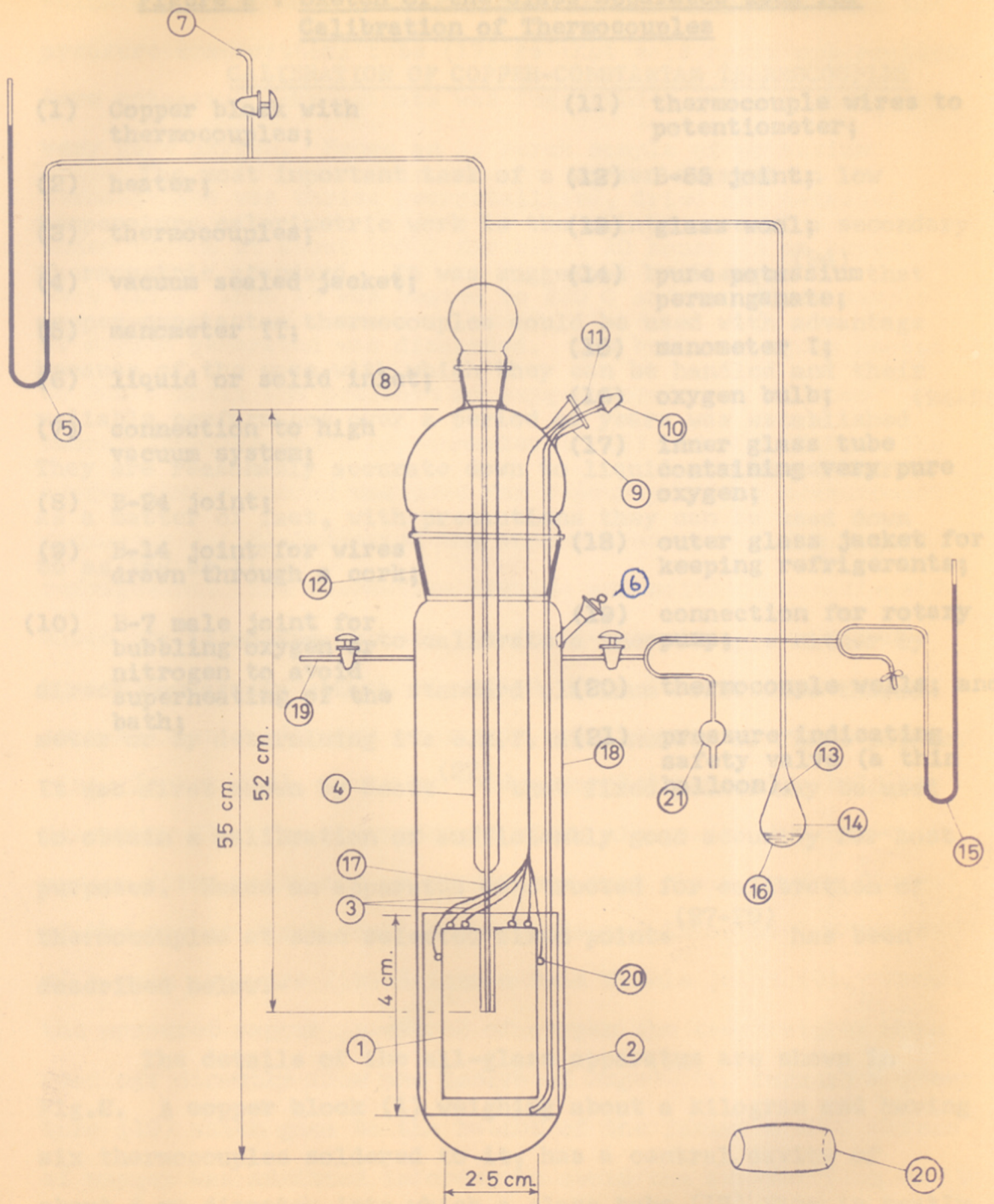


FIG. - 2 .

Figure 2 : Sketch of the Glass Apparatus used for Calibration of Thermocouples

- | | |
|--|---|
| (1) Copper block with thermocouples; | (11) thermocouple wires to potentiometer; |
| (2) heater; | (12) B-55 joint; |
| (3) thermocouples; | (13) glass wool; |
| (4) vacuum sealed jacket; | (14) pure potassium permanganate; |
| (5) manometer II; | (15) manometer I; |
| (6) liquid or solid inlet; | (16) oxygen bulb; |
| (7) connection to high vacuum system; | (17) inner glass tube containing very pure oxygen; |
| (8) B-24 joint; | (18) outer glass jacket for keeping refrigerants; |
| (9) B-14 joint for wires drawn through a cork; | (19) connection for rotary pump; |
| (10) B-7 male joint for bubbling oxygen or nitrogen to avoid superheating of the bath; | (20) thermocouple wells; and |
| | (21) pressure indicating safety valve (a thin balloon). |

CHAPTER - III

CALIBRATION OF COPPER-CONSTANTAN THERMOCOUPLES

The most important task of a worker engaged in low temperature calorimetric work is the maintenance of a secondary thermometric standard. It was suggested by Giauque⁽²⁴⁾ that copper-constantan thermocouples could be used with advantage because of the ease with which they can be handled and their reliable performance over a period of years was established⁽²⁴⁻²⁶⁾. They are reasonably accurate down to liquid air temperatures. As a matter of fact, with precautions they can be used down to as low as 11° K.

It is customary to calibrate a thermocouple either by direct comparison with a standard platinum resistance thermometer or by determining its e.m.f. at a number of fixed points. It was first shown by Scott⁽²⁷⁾ that fixed points may be used to obtain a calibration of sufficiently good accuracy for most purposes. Hence an apparatus constructed for calibration of thermocouples at some selected fixed points⁽²⁷⁻²⁹⁾ has been described below:-

The details of the all-glass apparatus are shown in Fig.2. A copper block (1) weighing about a kilogram and having six thermocouples soldered to it, has a central cavity of about 6 mm diameter into which a glass tube (17) fits in neatly. Around this glass tube which can be connected to a vacuum system as well as to pure oxygen source, is an evacuated jacket (4)

which keeps the bath from coming into direct contact with the pressure transmitting tube (17) so that cold spots are avoided. Pure potassium permanganate was suggested ⁽⁴²⁾⁽²³⁾ as the source of very pure oxygen. Hence an E. Merck sample of potassium permanganate was thrice recrystallized, dried and degassed under vacuum at about 150°C for about 10 hours in an oxygen bulb (16). Then it was heated to 220°C and the first sample of oxygen generated was discarded. The bulb was again heated to 220°C until the pressure of oxygen developed, at room temperature, as shown by Manometer II (5) was 900 mm Hg. The oxygen thus prepared was used for vapour pressure measurements. Manometer I (15) indicated the vapour pressure of the liquid refrigerant. The respective liquids and solid carbon-di-oxide could be introduced through the inlet-tube (6). The vapour pressure of oxygen which liquefied under its own pressure as soon as liquid nitrogen or oxygen was introduced into the outer glass jacket (18), could be read accurately with the help of Manometer II. The thermocouple wires along with two stout copper wires which act as supporters (not shown in the figure) of the copper block could be well clipped into the two halves of a cork and were fitted into a B-14 female joint (9). From the measured vapour pressures of oxygen the temperatures were read off directly from the tables of Hoge ⁽³⁰⁾. Through a glass tube (10) which goes to the bottom of the jacket a slow stream of oxygen was admitted in order to avoid the superheating of the bath. When the refrigerant was liquid nitrogen, gaseous nitrogen was bubbled instead of oxygen. The outer jacket (18) was kept in a big dewar vessel (not shown in the figure) and the

intermediate space between the dewar and the glass jacket was packed with thermocole and asbestos powder for heat insulation.

A specially-made constantan wire used for making thermocouples was purchased from Johnson, ~~and~~ ^{and} Matthey _k Co., London. The gauge of the wire is No.30 B and S. It has a resistance of 0.0866 ohm/cm and is diamel-coated for insulation. The composition of the wire is 56 copper to 44 nickel.

The accuracy with which copper-constantan thermocouples may be calibrated and used at low temperatures is usually limited by lack of homogeneity of the wires. That is, irregularities in the chemical composition or physical condition of the wires, in regions where temperature gradients exist, cause spurious e.m.f.s to appear, which change if the temperature gradient is shifted slightly along the wire. The constantan is usually the element responsible for most of the spurious e.m.f. the copper as a rule being relatively uniform. If several constantan wires are used in parallel with a single copper wire, effects of irregularities in the different wires are partially cancelled out. Hence three parallel constantan wires together with a single enamel-coated No.36 B and S copper wire constituted a thermocouple as suggested by Giauque et al. ⁽²⁴⁾. A dozen thermocouples were prepared and annealed by alternate heating to temperatures above 400° K and cooling to liquid nitrogen temperatures. Intercomparisons of these were made at the selected fixed points which showed reasonably good agreement and reproducibility of $\pm 1 \mu\text{V}$.

The following selected fixed points were used for calibration:-

(1) Liquid nitrogen	Vapour pressure	77.18° K
(2) Liquid oxygen	Vapour pressure	89.06° K
(3) Carbon-di-sulphide	Freezing point	161.56° K
(4) Toluene	Freezing point	178.06° K
(5) Solid carbon-di-oxide	Vapour pressure	193.92° K
(6) Carbon tetrachloride	Freezing point	250.26° K
(7) Ice	Melting point	273.15° K

Boiling points of Liquid Nitrogen and Oxygen

Liquid nitrogen and oxygen supplied by the Indian Oxygen Limited, Bombay, being commercial, were not pure and hence the temperatures of boiling points of these liquids were accurately determined by the oxygen vapour pressure thermometer previously described.

Freezing Point of Carbon-di-sulphide

The liquid carbon-di-sulphide was introduced into the glass jacket through the B-24 inlet and cooled with liquid air. The e.m.f. of the thermocouple went on increasing until the freezing point was reached, where it remained steady for some time. Then it was cooled to almost six degrees below the freezing point of the liquid. Then the dewar containing liquid air was taken out and the solid heated until some liquid carbon-di-sulphide was formed. As it was being heated, the e.m.f. went on decreasing and remained constant at the melting-point. The procedure was repeated thrice and the values noted.

Freezing Point of Toluene and Carbon-Tetrachloride

The same procedure as above was followed excepting that solid carbon-di-oxide was used to cool carbon-tetrachloride instead of liquid air.

Sublimation Point of Carbon-di-oxide

As solid carbon-di-oxide is usually handled it is seldom surrounded by an atmosphere of pure carbon-di-oxide vapour. Hence its temperature is considerably lower than the normal sublimation temperature. The temperature is that at which solid carbon-di-oxide has a vapour pressure equal to the partial pressure of the carbon-di-oxide vapour in atmosphere immediately surrounding the solid. If a dewar flask is filled with this solid carbon-di-oxide and diffusion of air into the flask is prevented by using a thick pad of cotton, the temperature will rise slowly with time, as the evaporated vapour washes out the air and eventually reach the temperature at which the vapour pressure of carbon-di-oxide is equal to the pressure of the atmosphere, in about 24 hours. But since the time taken for attaining equilibrium is comparatively large, the method suggested by Scott⁽²⁷⁾ was followed.

An enamelled copper wire (No.36 B and S) of about 40 ohms resistance was wound around a hollow thin copper cylinder open at both ends. This heater was embeded in the solid carbon-di-oxide. In the beginning heat input was maintained at about 30 watts for about 15 minutes. Then it was reduced to 10 watts so as to keep a stream of carbon-di-oxide vapour flowing out and thus preventing air from diffusion in.

The temperature of carbon-di-oxide was calculated from the equation⁽³¹⁾

$$\log_{10} p = 9.81137 - \frac{1349}{t + 273.15}$$

where "t" is the temperature in degrees centigrade and "p" the pressure in mm Hg.

Melting Point of Ice

Ice was prepared from freshly distilled water.

The respective chemicals used were carefully purified according to prescribed procedures and their purities are better than 99.5%. In all the above cases the ice-point was taken as the reference point (= 273.15^oK) as per the international scale. The e.m.f.s were measured in the conventional way with a vernier potentiometer (accuracy: $\pm 1 \mu\text{V}$) and a galvanometer (sensitivity = 8×10^{-8} A/mm and damping resistance = 30 ohms). A smooth curve is drawn through the points and a table of the rate of change of e.m.f. with temperature from 78^oK to 300^oK with a two-degree interval is prepared (see Table I).

The present apparatus can also be used for calibration of thermocouples at still lower temperatures e.g. triple points of nitrogen and oxygen. Thus the cork used for clipping thermocouples can be closed with sealing wax such as picein and also B-7 gas bubbler (10) can be closed. The liquid refrigerant is pumped through the wide-bore stop-cock (19) till it solidifies.

Table I : Thermo-e.m.f. E vs Temperature T

T°K	E Microvolts	dE/dT	T°K	E Microvolts	dE/dT
78	- 5510		124	- 4578	24
		17			24
80	- 5476		126	- 4530	24
		17			24
82	- 5442		128	- 4482	24
		17			24
84	- 5408		130	- 4434	24
		18			24
86	- 5372		132	- 4386	24
		18			24
88	- 5336		134	- 4338	24
		18			24
90	- 5300		136	- 4290	24
		18			24
92	- 5264		138	- 4242	24
		18			24
94	- 5228		140	- 4194	24
		18			24
96	- 5192		142	- 4146	24
		20			24
98	- 5152		144	- 4098	25
		20			25
100	- 5112		146	- 4048	25
		20			25
102	- 5072		148	- 3998	25
		20			25
104	- 5032		150	- 3948	26
		20			26
106	- 4992		152	- 3896	26
		21			26
108	- 4950		154	- 3844	26
		21			26
110	- 4908		156	- 3792	26
		23			26
112	- 4862		158	- 3740	26
		23			26
114	- 4816		160	- 3688	26
		23			26
116	- 4770		162	- 3636	27
		24			27
118	- 4722		164	- 3582	27
		24			27
120	- 4674		166	- 3528	28
		24			28
122	- 4626		168	- 3472	

$T^{\circ}K$	E Microvolts	dE/dT	$T^{\circ}K$	E Microvolts	dE/dT
170	- 3416	28	218	- 1976	32
172	- 3360	28	220	- 1912	32
174	- 3304	28	222	- 1848	32
176	- 3248	28	224	- 1784	34
178	- 3192	28	226	- 1716	34
180	- 3134	29	228	- 1648	34
182	- 3076	29	230	- 1580	35
184	- 3018	29	232	- 1510	35
186	- 2960	29	234	- 1440	35
188	- 2902	29	236	- 1370	35
190	- 2844	29	238	- 1300	35
192	- 2786	29	240	- 1230	35
194	- 2728	29	242	- 1160	35
196	- 2670	29	244	- 1090	35
198	- 2610	30	246	- 1020	36
200	- 2548	31	248	- 948	37
202	- 2486	31	250	- 874	37
204	- 2424	31	252	- 800	38
206	- 2360	32	254	- 724	38
208	- 2296	32	256	- 648	38
210	- 2232	32	258	- 572	38
212	- 2168	32	260	- 496	38
214	- 2104	32	262	- 420	38
216	- 2040	32	264	- 344	

contd..

$T^{\circ}K$	E Microvolts	dE/dT	$T^{\circ}K$	E Microvolts	dE/dT
266	- 268	38	284	+ 414	38.5
268	- 192	38	286	+ 492	39
270	- 116	38	288	+ 570	39
272	- 44	38	290	+ 648	39
274	+ 32	38	292	+ 727	39.5
276	+ 108	38	294	+ 806	39.5
278	+ 184	38	296	+ 886	40
280	+ 260	38	298	+ 967	40.5
282	+ 337	38.5	300	+ 1048	40.5

C H A P T E R - I V

OPERATION OF THE CALORIMETER.

Electrical Equipment

The operation of the calorimeter requires accurate measurement of initial temperature, energy (heat) input and final temperature. To determine the energy input, measurements should be made of (energy) current, voltage and heating time.

The calorimeter heater-wire (or thermometer-heater) is connected in series with a standard one ohm (PYE make) resistance. A resistance of about 10,000 ohms is kept in parallel to the above. A constant current (of the order of 500 microamperes) supplied from a bank of high capacity edison storage cells connected in series (designated as "Current Batteries") and discharging continuously through about 12,000 ohms resistance is passed through the calorimeter thermometer-heater wire. (This enables the measurement of resistance of the calorimeter heater wire). Another set of edison storage cells (designated as "Energy Batteries") provide a current which either passes through the calorimeter resistance or an equal dummy resistance thereby stabilizing the current, while energy is not being put into the calorimeter. (This enables to heat the calorimeter, whenever necessary). A weston standard cell is used as the standard of e.m.f. The e.m.f.s are measured with two vernier potentiometers (accuracy $\pm 1 \mu\text{V.}$) in conjunction with two box-type galvanometers with a sensitivity of 8×10^{-8} A/mm and damping resistance of 30 ohms.

The radiation shield heater wire in series with a rheostat (100 ohms) is connected to a set of direct current Exide acid batteries (connected in series) through a rotatory switch which enables to vary the voltage required to heat the radiation shield, whenever necessary. The rheostat helps to decrease or increase the current passing through the radiation shield heater wire, thereby regulating the rate of heating.

Experimental Procedure

A) Preliminaries

(1) Filling the calorimeter with the heat exchange gas

The calorimeter is kept in a glass enclosure. The system is evacuated, flushed with a heat exchange gas such as hydrogen or helium two or three times and then filled with the gas to one atmosphere. The pin-hole on the cap of the calorimeter is then closed with soft solder.

(2) Cooling the calorimeter to liquid nitrogen temperature

After the apparatus has been assembled, high vacuum is obtained by using a mercury diffusion pump backed by a high capacity two-stage rotary pump, while the trap is cooled with liquid nitrogen. A considerable amount of water vapour and other condensible material (which generally enters the inner can while testing for leakages in the soldered part) collects in the trap. The sufficiently complete desorption of various substances takes at least 24 hours. The apparatus is warmed by passing a current through the heater wire of the inner can to facilitate desorption. A pressure of the order of 10^{-5} mm Hg

or less is then obtained. The pressures are measured with a McLeod gauge. The trap immersed in liquid nitrogen protects the apparatus from mercury vapour diffusing into it.

Liquid nitrogen is pumped into the dewar flask surrounding the inner can. The thermocouples at the top and bottom of the inner can indicate the extent of cooling of the apparatus. When both the thermocouples read the lowest temperature (about 78°K) the vacuum in the apparatus is broken with a heat exchange gas such as helium or hydrogen to facilitate the cooling of the calorimeter. When the calorimeter gets cooled to the liquid nitrogen temperature, high vacuum is obtained again. High vacuum around the calorimeter reduces errors due to conduction and convection of heat by air to a minimum. It also prevents the possible complications owing to the condensation of water vapour in the apparatus. A small current is then passed through the calorimeter heater-wire for a minute or two to remove "back-lash".

A series of heat capacity measurements could then be started.

B) Method of heat capacity measurements

The stabilization of voltage in "Energy" and "Current" batteries is achieved by commencing passing current through the respective closed circuits for a few hours before the start of the measurements.

The radiation shield is heated approximately $\frac{1}{2} \theta^{\circ} \text{K}$ (where θ° is the anticipated rise in temperature of the calorimeter after energy input) above that of the calorimeter. The energy is then put into the calorimeter for a definite time of 6, 8 or 10 minutes by passing a current of the order of 0.1 ampere. As the radiation shield is very massive, its temperature remains practically constant while that of the calorimeter becomes $\frac{1}{2} \theta^{\circ} \text{K}$ higher. Both the preheating as well as the cooling rate of the calorimeter are measured for 10 to 30 minutes depending upon the time taken for attaining equilibrium. In general, about 10 minutes are required for attaining the same. Temperatures are measured by thermocouples as well as the change in resistance of the calorimeter heater wire. The melting point of distilled water ice is taken as the reference point ($= 273.15^{\circ} \text{K}$) for thermocouple measurements. The resistance of the calorimeter is determined by comparing the potential drop across the heater-wire leads with that across the standard one ohm resistance. (A small current of the order of 500 microamperes from "Current Batteries" passing through the calorimeter heater wire enables the measurement of the potential drop.) Since a very high resistance of about 12,000 ohms is connected in series with the calorimeter heater wire, slight changes in thermometer-heater resistance due to heating produce negligible effect on the total resistance and the current remains practically constant. Thus two current readings, taken before and after putting energy into the calorimeter are sufficient in one heat capacity measurement.

The heating current input is calculated from the potential drop across the standard one ohm resistance (during energy input). The energy input is timed with an accurate stop-watch, with a precision of ± 0.2 sec. corresponding to an error of $\pm 0.03\%$ in a ten-minute heating period. The duration of a single heat capacity measurement ranges between 50-60 minutes.

The resistance of the thermometer heater is continuously checked and calibrated against the thermocouples as heat capacities are measured from 78° to 300°K . Also thermocouple readings to determine the temperatures of the various relevant parts such as the top and bottom of the radiation shield and inner can have been taken. If the inner can starts heating up very fast, it has to be cooled with liquid nitrogen and if liquid nitrogen pumped in becomes excessive, the inner can has to be heated by passing a current through the heater wire of the can.

Calculation of Heat Capacity

The method adopted for calculation of heat capacities is essentially the same as that given by Giaouque and co-workers^(1,22,32).

A) Heat interchange between the radiation shield & the calorimeter

Newton's law of cooling, which states that the heat transfer is proportional to the temperature difference, is used in calculating the heat interchange. This involves the knowledge of temperatures of both the calorimeter and the radiation shield at all times during a measurement.

The energy measurements furnish sufficient data for obtaining the external temperature of the calorimeter during the energy input. The temperature can be considered to increase linearly within the limits of necessary accuracy. This is due to two causes, first, the energy is put in rather slowly, and second, by using over 50 meters of wire in the calorimeter thermometer-heater, a very small amount of energy is developed per unit length which is almost instantaneously transferred and the current can be represented very accurately as delivered to the calorimeter. The radiation shield is a quadratic function of time, comparatively massive and hence only two readings during one heat capacity measurement are considered sufficient for calculations.

The correction for heat interchange is found to be of the order of 1-2% of energy input.

B) Determination of energy input

If H = Amount of energy input in calories

E = Voltage in volts

I = Current in amperes

t = time in seconds

then it is well known that

$$H = \frac{EIt}{4.184}$$

Here E and I refer to the average values of voltage and current respectively.

The applied voltage from "Energy Batteries" is practically constant and hence a single reading is sufficient for calculations.

The resistance of a combined thermometer-heater increases while energy is being introduced. This causes a continuous drop in current since the applied voltage is practically constant. In order to avoid a tedious graphical process of evaluation the method suggested by Gibson and Giauque⁽²²⁾ for obtaining the average value of the current has been followed.

The change of current with time is found to be nearly constant and the current can be represented very accurately as a quadratic function of time.

$$I = A + Bt + Ct^2$$

Let I_1 be the current after t_1 seconds; I_2 , the current after t_2 seconds; I_{av} , the average value of the current, and t_3 , the total time of energy input.

$$\text{Make } t_1 + t_2 = t_3 \text{ and } \frac{I_1 + I_2}{2} = I_{av}.$$

Then

$$I_{av} \cdot t_3 = \int_0^{t_3} I \cdot dt$$

$$= At_3 + \frac{1}{2}Bt_3^2 + \frac{1}{3}Ct_3^3$$

$$\therefore I_{av} = A + \frac{1}{2}Bt_3 + \frac{1}{3}Ct_3^2 \quad \dots (1)$$

$$\text{Also } I_{av} = \frac{I_1 + I_2}{2} \\ = A + \frac{1}{2}B(t_1 + t_2) + \frac{1}{2}C(t_1^2 + t_2^2) \quad \dots (2)$$

Comparing equations (1) and (2) we get,

$$\begin{aligned}\frac{t_3^2}{3} &= \frac{1}{3} (t_1^2 + t_2^2) \\ &= \frac{1}{3} \left\{ (t_3 - t_2)^2 + t_2^2 \right\} \quad (\because t_3 = t_1 + t_2) \\ &= \frac{1}{3} (t_3^2 - 2t_3t_2 + 2t_2^2)\end{aligned}$$

$$\therefore 6t_2^2 - 6t_3t_2 + t_3^2 = 0$$

$$\therefore t_2 = t_3 \left(\frac{1 \pm \sqrt{1/3}}{2} \right) = 0.79t_3 \text{ or } 0.21t_3$$

$$\text{and } t_1 = 0.21t_3 \text{ or } 0.79t_3.$$

Hence the arithmetic mean of the (energy) current readings taken at $0.21t_3$ and $0.79t_3$ minutes, where t_3 is the total predetermined period of energy input, as already stated above, gives the average value of the current. Frequent readings, in addition to these, are also taken, but only as a precautionary measure.

Heat Capacities of Standard Benzoic Acid

At its meeting on April 21, 1948, the Low Temperature Calorimetry Conference, which was organised for the purpose of promoting improved calorimetric techniques and setting up standards for testing and calibrating calorimeters of various designs, selected benzoic acid (C_6H_5COOH) as a standard for

the intercomparison of precision heat capacity calorimeters in the temperature ranges from 10° to 350° K. Hence the heat capacities of 31.3101 g. of Analar benzoic acid have been determined in the range 78° - 300° K. The material used was of high purity ($> 99.9\%$) and uniformity so that errors arising from these sources were well within the precision of experimental measurements. Since the measurements extend only upto 300° K, the possible complications due to the fusion of the material did not arise. The results obtained are converted to one mole of the substance and following the convention of N. B. S. (Washington, U.S.A.) publication⁽³³⁾, the heat capacities are given for each 5° rise from 80° to 300° K in Table II. The values are given in calories (1 calorie \equiv 4.184 abs. joules). The fraction of the heat capacity of the empty calorimeter to that of the filled calorimeter was 0.43 at 100° K, 0.38 at 200° K and 0.43 at 300° K. Percentage deviations from the N. B. S. values⁽³³⁾ are also given in Table II.

The precision of the present data is estimated by the scatter of the values from their own mean, the maximum deviation being $\pm 2\%$ for measurements between 80° and 300° K. It may be noted that the present results are scattered on either side of the N. B. S. values⁽³³⁾ around 200° K, whereas they are consistently greater at higher and lower temperatures, the maximum deviation being about 3% in the range 80° - 150° K, which gradually becomes less than 1% around the room temperature (300° K).

Table II : Comparison of the Heat Capacity (C_p) Values of Benzoic Acid (Mol. Wt. 122.13) determined with the Present Apparatus with NBS Data

Temperature °K	C_p cal./mole.deg.		Deviation from NBS values %
	Present expt.	NBS values ⁽³³⁾	
80	13.64	13.35	+ 2.25
85	14.17	13.90	1.94
90	14.70	14.37	2.30
95	15.18	14.83	2.39
100	15.66	15.28	2.48
105	16.14	15.73	2.61
110	16.60	16.17	2.65
115	17.04	16.63	2.46
120	17.48	17.09	2.28
125	17.93	17.54	2.22
130	18.40	17.99	2.28
135	18.83	18.45	2.06
140	19.33	18.90	2.28
145	19.77	19.36	2.12
150	20.30	19.82	2.42
155	20.70	20.27	2.12
160	21.13	20.73	1.93
165	21.60	21.20	1.89
170	22.04	21.68	1.66

Temperature °K	C _p cal./mole.deg.		Deviation from NBS values %
	Present expt.	NBS values ⁽³³⁾	
175	22.50	22.15	+ 1.58
180	22.92	22.63	1.28
185	23.42	23.12	1.30
190	23.85	23.60	1.06
195	24.29	24.08	0.87
200	24.65	24.59	0.24
205	25.03	25.09	- 0.24
210	25.56	25.60	- 0.16
215	26.18	26.11	+ 0.27
220	26.74	26.62	0.45
225	27.29	27.14	0.55
230	27.86	27.67	0.68
235	28.40	28.20	0.71
240	28.89	28.73	0.56
245	29.42	29.27	0.51
250	29.96	29.80	0.54
255	30.49	30.35	0.46
260	30.98	30.89	0.29
265	31.49	31.43	0.19
270	32.02	31.99	0.09
273.15	32.38	32.33	0.15

contd...

Temperature °K	C _p cal./mole.deg.		Deviation from NBS values %
	Present expt.	NBS values ⁽³³⁾	
275	32.60	32.53	+ 0.22
280	33.24	33.09	0.45
285	33.87	33.62	0.74
290	34.38	34.18	0.58
295	34.89	34.73	0.46
298.15	35.29	35.09	0.57
300	35.54	35.30	0.68

P A R T - I I

temperature and structure. CHAPTER - V is due to the crystal becoming ferroelectric in two and three directions simultaneously.

INTRODUCTION

(38,39)
The subject ferroelectricity has gained considerable importance in recent years due to the fact that it poses several intriguing problems in solid state physics and also because some of the ferroelectric crystals found industrial applications as a solid state device. The various excellent reviews (34-37) have discussed in detail the dielectric, X-ray, thermal, optical and domain configuration properties of ferroelectric crystals, as well as the theories of ferroelectricity that have been developed to explain this interesting phenomenon. Rochelle salt, $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, potassium dihydrogen phosphate, KH_2PO_4 and barium titanate, BaTiO_3 are the well-known ferroelectrics, each representing a family.

The rochelle salt-type has a range of temperatures in which it is ferroelectric with upper and lower Curie points that mark the separation between the ferroelectric region and the non-ferroelectric regions. Potassium dihydrogen phosphate, on the other hand, has a single Curie temperature. The crystal is ferroelectric from absolute zero up to a temperature of about 122°K , above which it becomes non-ferroelectric. Barium titanate is capable of becoming ferroelectric in any one of the three crystal axial directions. It has an upper Curie temperature at 393°K and has two transitions between this

temperature and absolute zero. These transitions are due to the crystal becoming ferroelectric in two and three directions, simultaneously.

Using a crystal structural data of rochelle salt^(38,39) a theory of the ferroelectric effect and the clamped dielectric constant of rochelle salt has been developed by Mason^(40,41). The ferroelectric effect is attributed to the motions of the hydrogen nuclei along hydrogen bonds between water molecules and oxygen ions.

Nature of Hydrogen Bond in KH_2PO_4 -type Ferroelectrics

It has been recognized that under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, instead of only one, so that it may be considered to be acting as a bond between them. This is called the hydrogen bond. The hydrogen atom, with only one stable orbital, can form only one covalent bond. The hydrogen bond is largely ionic in character and is formed only between the most electronegative atoms. Increase in the electronegativity of the two bonded atoms increases, in general, the strength of the bond. A brief but excellent review by Pauling⁽⁴²⁾, of the nature of the hydrogen bond, its effect on the physical properties of substances and the structure of crystals containing hydrogen bonds is available.

It had been known for several years^(16,43-46) that potassium dihydrogen phosphate, KH_2PO_4 , has a phase change of the second order at about 122°K , showing a dielectric analogue of ferromagnetism below this temperature. To account for the transition Slater⁽⁴⁷⁾ put forward a theory. Using statistical methods, he counted the number of arrangements of hydrogens consistent with each total polarization of the crystal and derived the free energy. The theory predicted a phase change of the first-order, with sudden transition from the polarized state at low temperature to the unpolarized state at high temperature, rather than the lambda-point transition or phase change of the second-order which was observed. However, the observed transition was confined to a very narrow temperature range compared to that predicted, for instance, by the Weiss theory, so that it seemed as if it might be merely a broadened transition of the first-order. Slater suggested that the broadening might result from the irregular shifts of transition temperatures of individual domains in the crystal on account of stresses resulting from the large piezoelectric effect and the resulting deformation of the crystal below the transition point.

The theory assumes that both above and below the Curie point each PO_4 group has two closest H atoms so that H_2PO_4 groups exist. Above the Curie point the two H's of an H_2PO_4 group are associated with any two of the four O's of a PO_4 tetrahedron (with the sole limitation that not more than one H

will lie between two oxygens of neighbouring PO_4 groups), so that the orientation of the H_2PO_4 groups is disordered. Below the Curie point ordering occurs in such a way that ferroelectric domain hydrogens are associated more closely with only the 'upper' oxygens of all the PO_4 groups, and in another domain only with the 'lower' oxygens. The H_2PO_4 dipoles, with their orientations parallel or antiparallel to the c axis, are then presumed to account for the spontaneous polarization.

Slater had based his theory on the crystal structure of KH_2PO_4 at room temperature determined by West⁽⁴⁸⁾; but no X-ray study had been made on the structure below the ferroelectric transition (Curie) temperature. Subsequent X-ray studies^(49,50) established a structural change at the Curie point. Further X-ray analysis of the structure of KH_2PO_4 was made by Frazer and Pepinsky⁽⁵¹⁾ at temperatures just above and just below the Curie point. Some measurable changes in inter-atomic distances were to be expected between the structure as determined by West⁽⁴⁸⁾ at room temperature and that just above the transition point and these could be expected to provide insight into the nature of the transition. The hydrogen bonds were found to contract from a room temperature distance of 2.53 \AA to 2.44 \AA at 126°K . and to expand in the transition to 2.51 \AA at 116°K . The following mechanism was suggested to explain the transition. As the crystal is cooled, the contraction of the hydrogen bonds causes the K to build up a preferred vibration parallel to c, which in turn induces a similar preferred vibration in the PO_4 groups.

Finally, a critical temperature is reached, the Curie point, at which the K's 'lock in' to a position displaced from their previous centres of oscillation. The displaced K's then exert a polarizing influence on the PO_4 groups and an electrostatic influence on the hydrogens. In this way the P's become displaced within their O_4 tetrahedra and the hydrogens become more ordered.

Neutron diffraction analyses were carried out⁽⁵²⁻⁵⁵⁾ to assess the position of the hydrogen ions. Bacon et al.⁽⁵⁵⁾ confirmed that the basis of Slater's theory⁽⁴⁷⁾, an ordering of the hydrogen positions, is correct and observed that there seemed little reason to assume the existence of the mechanism suggested by Frazer and Pepinsky⁽⁵¹⁾.

The discovery of ferroelectricity in guanidine aluminum sulphate hexahydrate, $(CN_3H_6).Al(SO_4)_2.6H_2O$, by Holden et al.⁽⁵⁶⁾ in methylammonium aluminum alum, $(CH_3NH_3).Al(SO_4)_2.12H_2O$, by Pepinsky et al.⁽⁵⁷⁾ in ammonium sulphate, $(NH_4)_2SO_4$, by Matthias et al.⁽³⁾ and in the isomorphous ammonium fluoberyllate, $(NH_4)_2BeF_4$, by Pepinsky and Jona⁽⁵⁸⁾ and in diammonium dicadmium sulphate, $(NH_4)_2Cd_2(SO_4)_3$, by Jona and Pepinsky⁽⁵⁹⁾, emphasised the significance of the role played by N-H...O bonds and the sulphate or related ions in the production of ferroelectricity in these types of compounds. Matthias et al.⁽⁶⁰⁾ discovered ferroelectricity in tri-glycine sulphate, $(CH_2NH_2COOH)_3.H_2SO_4$. While interpreting the crystal structure of the ferroelectric phase of tri-glycine sulphate, Prof. Pepinsky

and his collaborators⁽⁶¹⁾ stressed the importance of the O-H...O bond in the ferroelectric behaviour of the compound.

From a survey of the literature, as indicated above, it is apparent that hydrogen bonding has an important effect on ferroelectricity in a class of ferroelectric substances, even though the mechanism is not clearly understood. In order to provide basic data to elucidate the mechanism the present study on the low temperature thermodynamic properties of potassium ferrocyanide was undertaken.

Since potassium ferrocyanide trihydrate exhibits ferroelectric behaviour⁽⁶²⁾, it was considered worthwhile to investigate the role played by water molecules in the ferroelectricity of the compound. Hence the thermal studies of the anhydrous salt were undertaken and reported in this thesis. Apart from the above, this substance is important as it is often used for a variety of purposes viz. catalyst and laboratory reagent and also it has interesting structural characteristics.

Although the crystal structure of potassium ferrocyanide trihydrate at room temperature was worked out by Pospelov and Zdanov⁽⁶³⁾, the location of one water molecule out of three in the chemical formula had not been determined. In a recent X-ray structure analysis⁽⁶⁴⁾, the atomic coordinates of the unknown water oxygen were determined. In the crystal structure of potassium ferrocyanide trihydrate (space group $C_{2/c}$), there are double-layered group of octahedrally coordinated $[Fe(CN)_6]$

complex ions and surrounding K^+ ions. Between these double layers is inserted a layer of water molecules, in which O....O distances are 3.32 \AA . There are two kinds of water molecules in the room temperature structure; one kind consisting of two equivalent molecules and the other containing the remaining molecule. In the ferroelectric phase (space group Cc) a unit cell contains three kinds, the two equivalent water molecules becoming not equivalent.

C H A P T E R - VI

HEAT CAPACITIES AND THERMODYNAMIC PROPERTIES OF ANHYDROUS
POTASSIUM FERROCYANIDE

Preparation & Analysis

The sample for calorimetric investigation was prepared by the method employed by Loftfield et al.⁽⁶⁵⁾ with rigorous observation of the precautions prescribed by them.

Analar potassium ferrocyanide supplied by Merck & Co. Inc., Rahway, N.J. and containing maximum impurities of 0.03% was twice recrystallized from freshly distilled water. The recrystallized salt was thoroughly dried and the water of crystallization was determined. Three molecules of water per molecule of the compound were found to be present. The method, results and calculations are given below:-

Three samples, each weighing about 1-1.5 g were taken and heated at 90°C in a current of dry nitrogen gas for a few hours. They were then weighed after cooling in a vacuum desiccator. The process was repeated till constant weight.

(a) Weight of hydrated potassium ferrocyanide

- i) 1.22575 g
- ii) 1.47425 g and
- iii) 1.42550 g

(b) Weight of anhydrous potassium ferrocyanide

- i) 1.06860 g
- ii) 1.28530 g and

iii) 1.24070 g

$$\text{Let } \frac{\text{KFC} \cdot x\text{H}_2\text{O}}{\text{KFC}} = y$$

where $\text{KFC} \cdot x\text{H}_2\text{O} \equiv$ One mole of potassium ferrocyanide with 'x' moles of water of crystallization

and $\text{KFC} \equiv$ One mole of potassium ferrocyanide.

If y_1 , y_2 and y_3 represent the values of y for the first, second and third samples respectively, then,

$$y_1 = 1.147060,$$

$$y_2 = 1.147008 \quad \text{and}$$

$$y_3 = 1.148500.$$

Therefore, the weight of $\text{KFC} \cdot x\text{H}_2\text{O}$ corresponding to y_1 , y_2 and y_3 respectively is equal to

i) 422.4622 g

ii) 422.4430 g and

iii) 422.9930 g.

Therefore, the weight of 'x' moles of water present is

i) 54.1622 g

ii) 54.1430 g and

iii) 54.6930 g respectively.

Therefore, the number of moles of water present is

- 1) 3.0090
- ii) 3.0080 and
- iii) 3.0385 respectively.

∴ Average = 3

In addition to the above analysis, infrared absorption spectra in the NaCl-region were recorded. The results were in excellent agreement with those available in literature⁽⁶⁶⁾.

A known weight of potassium ferrocyanide trihydrate thus prepared was heated at about 90°C in a slow stream of nitrogen gas for several hours. Then nitrogen was removed with a water-pump and heating continued in vacuum for about two hours. The anhydrous salt formed was ultimately cooled in a slow stream of the gas. The completion of reaction was indicated by the constant weight of the anhydrous compound corresponding to the anticipated weight loss from the hydrated salt.

The following conditions were strictly observed:—

- 1) The temperature was never allowed to reach 100°C.
- 2) The dehydrated salt was kept out of contact with moisture before and during weighing.
- 3) The dehydrated salt was kept in the dark to prevent decomposition before filling into the calorimeter.

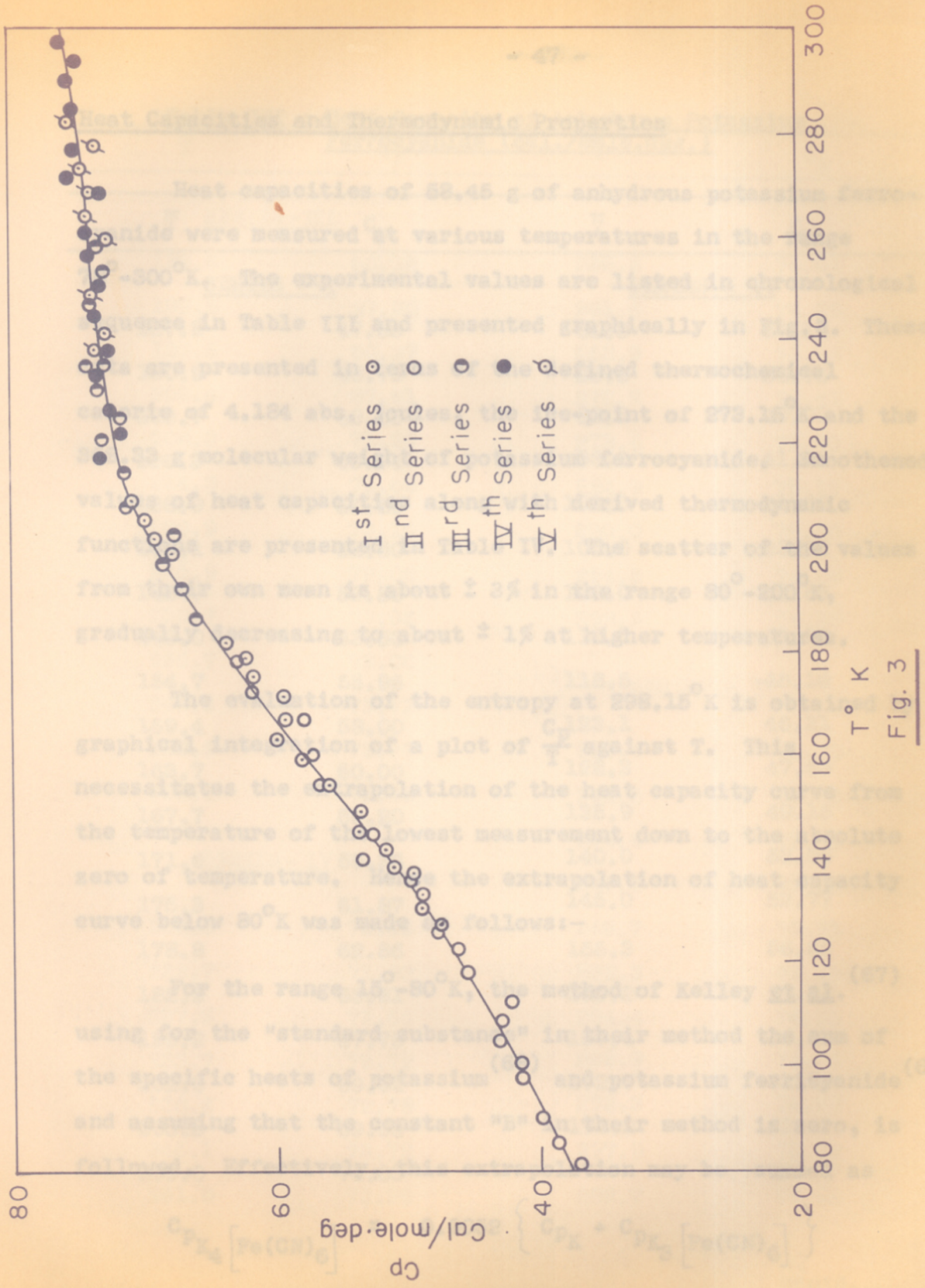


Fig. 3

Heat Capacities and Thermodynamic Properties

Heat capacities of 58.45 g of anhydrous potassium ferrocyanide were measured at various temperatures in the range 78°-300°K. The experimental values are listed in chronological sequence in Table III and presented graphically in Fig.3. These data are presented in terms of the defined thermochemical calorie of 4.184 abs. joules, the ice-point of 273.15°K and the 368.33 g molecular weight of potassium ferrocyanide. Smoothened values of heat capacities along with derived thermodynamic functions are presented in Table IV. The scatter of the values from their own mean is about ± 3% in the range 80°-200°K, gradually decreasing to about ± 1% at higher temperatures.

The evaluation of the entropy at 298.15°K is obtained by graphical integration of a plot of $\frac{C_p}{T}$ against T. This necessitates the extrapolation of the heat capacity curve from the temperature of the lowest measurement down to the absolute zero of temperature. Hence the extrapolation of heat capacity curve below 80°K was made as follows:-

For the range 15°-80°K, the method of Kelley et al. (67) using for the "standard substance" in their method the sum of the specific heats of potassium (68) and potassium ferricyanide (69) and assuming that the constant "B" in their method is zero, is followed. Effectively, this extrapolation may be summed as

$$C_{p_{K_4}}[\text{Fe}(\text{CN})_6] = 0.9052 \left\{ C_{p_K} + C_{p_{K_3}}[\text{Fe}(\text{CN})_6] \right\}$$

Table III : Heat Capacity of Anhydrous Potassium
Ferrocyanide (cal./mole.deg.)

\bar{T}	C_p	\bar{T}	C_p
<u>SERIES - I</u>		<u>SERIES - II</u>	
127.8	47.63	81.3	37.18
130.9	48.71	85.6	38.76
133.7	49.03	90.5	40.01
136.3	49.24	98.0	41.53
138.9	51.29	101.0	41.60
142.1	51.80	105.0	43.22
145.7	53.56	109.0	42.85
149.0	53.50	113.1	42.22
154.7	55.95	118.5	45.16
159.4	58.00	123.1	46.31
163.7	60.00	128.3	47.63
167.7	59.20	135.9	49.15
171.6	59.36	140.0	53.56
175.3	61.87	145.0	52.77
178.8	62.56	155.3	56.52
182.2	63.81	160.2	57.33
199.2	67.75	167.4	58.03
202.0	69.01	172.7	61.75
205.3	69.93	178.2	63.01
209.0	71.03	182.7	63.72
			75.61

contd...

Table IV : Thermodynamic Functions of Anhydrous Potassium Ferrocyanide

Temp. °K	C_p° cal./mole.deg.	$S^{\circ}-S_0^{\circ}$ cal./mole.deg.	$H^{\circ}-H_0^{\circ}$ cal./mole	$-(F^{\circ}-H_0^{\circ})/T$ cal./mole.deg.
80	38.31	(29.15)	(1428)	(11.30)
85	39.06	31.45	1622	12.40
90	40.01	33.71	1819	13.50
95	40.83	35.93	2021	14.68
100	41.65	38.08	2227	15.81
105	42.35	40.15	2435	16.95
110	43.16	42.15	2651	18.05
115	44.23	44.05	2869	19.05
120	45.11	45.95	3092	20.18
125	46.76	47.85	3321	21.25
130	48.52	49.75	3559	22.35
135	49.97	51.60	3805	23.40
140	51.68	53.45	4060	24.45
145	53.43	55.30	4324	25.50
150	54.94	57.10	4593	26.48
155	56.22	58.95	4871	27.55
160	57.84	60.75	5157	28.50
165	59.23	62.55	5449	29.55
170	60.80	64.35	5750	30.55
175	62.26	66.15	6057	31.55
180	63.63	67.95	6372	32.55
185	64.89	69.65	6694	33.45
190	66.42	71.40	7021	34.40

contd...

by means of

Temp. °K	C_p^0 cal./mole.deg.	$S^0 - S_0^0$ cal./mole.deg.	$H^0 - H_0^0$ cal./mole	$-(F^0 - H_0^0)/T$ cal./mole.deg
195	67.61	73.15	7356	35.45
200	68.87	74.90	7697	36.40
205	69.49	76.65	8044	37.40
210	70.42	78.35	8389	38.45
215	71.39	79.95	8744	39.30
220	72.01	81.65	9102	40.25
225	72.46	83.25	9469	41.15
230	72.78	84.90	9829	42.25
235	73.16	86.55	10192	43.15
240	73.41	88.05	10559	44.05
245	73.60	89.65	10927	45.00
250	73.72	91.15	11296	45.95
255	73.86	92.65	11658	46.90
260	74.04	93.95	12028	47.60
265	74.23	95.35	12398	48.55
270	74.42	96.65	12768	49.40
273.15	(74.54)	(97.60)	(13001)	(50.00)
275	74.61	98.15	13138	50.35
280	74.80	99.55	13528	51.20
285	74.98	100.75	13908	52.00
290	75.30	102.15	14268	53.00
295	75.61	103.40	14648	53.80
298.15	(76.01)	(104.19)	(14887)	(54.19)
300	76.25	104.65	15028	54.55

The extrapolation between 0° - 15° K was made by means of Debye functions. Table-V summarizes the entropy calculations. Contrary to earlier reports⁽⁶⁹⁾ the value of $S_{298.15}^{\circ}$ has been found to be more than that for potassium ferricyanide.

Table V : Molal Entropy at 298.15° K (cal./deg.)

$0^{\circ} - 15^{\circ}$ K	} extrapolated	5.50
$15^{\circ} - 80^{\circ}$ K		23.65
$80^{\circ} - 298.15^{\circ}$ K		75.04
$S_{298.15}^{\circ}$		104.19

Enthalpy and Gibbs free energy functions are evaluated from the well-known relations,

$$H^{\circ} - H_0^{\circ} = \int_0^T C_p \cdot dT \quad (\text{graphical integration})$$

$$\text{and } \frac{F^{\circ} - H_0^{\circ}}{T} = \frac{H^{\circ} - H_0^{\circ}}{T} - (S^{\circ} - S_0^{\circ}).$$

C H A P T E R - V I I

R E S U L T S A N D D I S C U S S I O N

It may be observed that the heat capacity increases regularly over the entire range of measurements. But the heat capacity⁽⁶⁾ of potassium ferrocyanide trihydrate reveals a "hump" at about -25°C , corresponding to the ferroelectric transition temperature. The absence of anomalous thermal behaviour in the anhydrous salt indicates that the ferroelectric properties vanish on loss of water molecules. This phenomenon is analogous to that exhibited by the rochelle salt even though the transitions are of different types.

The important role that hydrogen bonds and water molecules might play in the ferroelectric behaviour of rochelle salt was suspected long ago. From a detailed study of the Raman spectrum, it was shown⁽⁷⁰⁾ that vibrations of the C-H bond and the valence vibrations of the water molecules and O-H bonds were found in the high frequency spectrum (near 3000 cm^{-1}). The bands assigned to the water molecules and O-H bonds undergo measurable changes with varying temperature, indicating that these lattice constituents play an important role in the ferroelectric effect. In his theory of the ferroelectric effect of the rochelle salt Mason^(40,41) attributed ferroelectricity to the motions of the hydrogen nuclei along hydrogen bonds between water molecules and oxygen ions. Further the substitution of hydrogen by deuterium⁽⁷¹⁾ lowers the lower Curie point by 5°C and raises the

upper Curie point by about 11°C . But it is not possible to say whether the hydrogens of the OH groups on the tartrate molecule or hydrogens on the water molecules are responsible for these changes, since both kinds of hydrogens get substituted by deuterium. Even in the case of potassium ferrocyanide trihydrate, the substitution of hydrogen by deuterium shifts⁽⁷²⁾ the Curie point from -24.5°C to -18°C .

From proton magnetic resonance and infrared absorption studies of potassium ferrocyanide trihydrate, Blinc et al.⁽⁷³⁾ considered that the onset of ferroelectric behaviour is associated with a dynamical orientational ordering of the hydrogen-bonded water molecules.

Besides, the recent NMR and X-ray studies by Kiriyama et al.⁽⁶⁴⁾ indicate that some mode change of the rotational motion of the water molecules is closely connected with the ferroelectric transition. Their following observations and remarks about the behaviour of water molecules are worth noting:-

"The result of NMR study with single crystals of KFCT at room temperature shows no difference between two kinds of water molecules in their behaviour. They are rotating in the ferroelectric phase around two or more axes with frequencies higher than 10^5 cps.....the motion of water molecules occurring in a temperature range between -45°C and -140°C is considered as rotational oscillation or libration with fairly large amplitude.

Though precise atomic positions of the ferroelectric phase have not yet been available, there are some experimental evidences of no significant change in atomic arrangements of heavier atoms at the Curie point. First, even if the crystal is cooled down to a temperature of liquid nitrogen through T_c (transition temperature), it does not collapse. Secondly, the infrared absorptions reported by Blinc et al. (73) show no significant frequency shift between the high and low temperature phases, this result being also confirmed by us for the present sample. Thirdly, the values of enthalpy and entropy changes associated with the transition have been recently estimated as $\Delta H = 115$ cal./mole, $\Delta S = 0.46$ e.u. (6), and these values are smaller than those found in cupric formate tetrahydrate, $\text{Cu}(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$ (74) which contains layered water molecules in its crystal structure and exhibits a remarkable dielectric transition without any structural change.

It must be sure that some mode change of the rotational motion of the water molecules in KFCT is closely connected with the ferroelectric transition."

From the foregoing discussion it may reasonably be concluded that loss of water molecules destroys the ferroelectric properties of potassium ferrocyanide trihydrate.

potassium ferrocyanide are reported in this thesis. *

S U M M A R Y

Cryogenic calorimetric studies are very useful to elucidate both the first and second order transitions and also to provide basic data for chemical thermodynamic functions such as entropy, enthalpy and Gibbs free energy. In a programme of study on the thermodynamic properties of ferroelectric and ferromagnetic solids at low temperatures, an isothermal calorimeter has been constructed. An all-glass apparatus is also specially constructed for the calibration of copper-constantan thermocouples used for the measurements of temperatures.

The heat-capacities of standard benzoic acid were determined at various temperatures in the range 78° - 300° K and compared with the data from the National Bureau of Standards, to establish the reliability and accuracy of the measurements. The discrepancy was found to be about $\pm 3\%$ upto 100° K and $\pm 1\%$ around 300° K.

As potassium ferrocyanide trihydrate exhibits ferroelectric behaviour, it was thought worthwhile to study the role played by water molecules in the ferroelectricity of the compound. The results of thermal studies of anhydrous potassium ferrocyanide are reported in this thesis. No anomalous behaviour in the heat capacity was observed in the entire range of measurements (78° - 300° K). Thermodynamic properties such as entropy, enthalpy and Gibbs free energy were

evaluated. The extrapolation of heat capacity between 15° - 80° K was made in accordance with the well-known procedure adopted by Kelley, while that between 0° - 15° K was made by means of Debye functions.

Infrared absorption spectra of anhydrous and hydrated potassium ferrocyanide were recorded in the NaCl region to study the effect of dehydration on C-N stretching vibration (Appendix II). Other vibrations could not be studied for want of facilities.

Since the water molecules play an important role in the ferroelectricity of the trihydrate salt, thermo-gravimetric analysis in air upto 250° C was carried out to get some useful information about the dehydration process (Appendix III).

X-ray analysis of potassium ferrocyanide was also carried out (Appendix IV).

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A P P E N D I X - I

PUBLISHED WORK* OF THE AUTHOR NOT INCLUDED IN THIS THESIS

S.No.	Title of the publication	Reference
1.	Repulsion Constant of Polar Liquids	Z. Physik. Chem., <u>219</u> , 321-31 (1962)
2.	Vapour Pressure and Intermolecular Energy Constants of Liquids	Z. Physik. Chem., <u>220</u> , 71-8 (1962)
3.	The Heat Capacities of Potassium Manganese Trifluoride	Proc. Phys. Soc., (London), <u>81</u> , 191-2 (1963)
4.	Cohesive Energies of Alkali Halides	Ind. J. Phys., <u>37</u> , 238-40 (1963)
5.	Lattice Energy and other Properties of some Ionic Crystals	Z. Physik. Chem., <u>224</u> , 377-83 (1963)
6.	Imperfect Vapour Phase, Compressibility and Force Constants of Liquids	Ind. J. Chem., <u>2</u> , 27-8 (1964)
7.	A Finite Virial Expansion of Fluid State	Ind. J. Chem., <u>2</u> , 29-30 (1964)

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Repulsion Constant of Polar Liquids

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With 2 figures

(Received 4th July 1961)



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Repulsion Constant of Polar Liquids

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Abstract

A three constants potential function involving to account for the dipole-dipole interaction was used and the repulsion constant 'n' was evaluated by two methods; first by using the GRUNEISEN's constant and, second, by using $C_1 \equiv \frac{d(1/\beta)}{dP}$. The two calculated values agree fairly well; especially when considering the approximations made in deriving the equations. An equation analogous to that of solids derived by DEBYE was shown to hold for sub-cooled liquids at absolute zero where the thermodynamic relation $\left[\frac{\partial^2 U}{\partial V^2} \right]_{T=0} = \frac{1}{\beta V}$ is valid. Calculations were performed on methyl alcohol and the 'n' values computed by the two methods were found to be in good agreement.

It is customary to represent the potential of a pair of non-polar molecules by a bireciprocal function [1, 2, 3] of the type

$$\Phi(a) = \frac{A}{a^n} - \frac{B}{a^m}$$

where A , B , n and m are constants and a is the distance between a pair of molecules. The above type of equation has been extensively used by Lennard-Jones for a number of non-polar molecules. However, for polar molecules such a representation is not accurate. If there is a dipole moment then the attraction is not only due to dispersion forces but also due to dipole-dipole interactions. It was shown by London [4] that the dispersion energy is proportional to a^{-6} . The energy of interaction of two permanent dipoles can be obtained by simple electrostatic considerations [5, 6] as inversely proportional to a^3 . Thus if we neglect the interactions between dipole-quadrupole and quadrupole-quadrupole moments a simple and sufficiently accurate way to express the potential energy is

$$\Phi = Aa^{-n} - Ba^{-m} - Ca^{-p} \quad (1)$$

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This can be thought of as a two attractive potential function where the second term Ba^{-m} is due to VAN DER WAAL'S forces while the third term Ca^{-p} is due to dipole-dipole interactions. This extension may be of great physico-chemical interest [12a]. The values of A , B and C can be calculated from virial coefficients [2, 7]. Some of the calculations are involved and therefore we describe here some simpler means of determining intermolecular force fields using some common properties of liquids.

Compressibility and force constants

The exact form of potential energy curve is given in figure 1 where the potential energy is a minimum at $a = a_s$ and is equal to zero when $a = \sigma$.

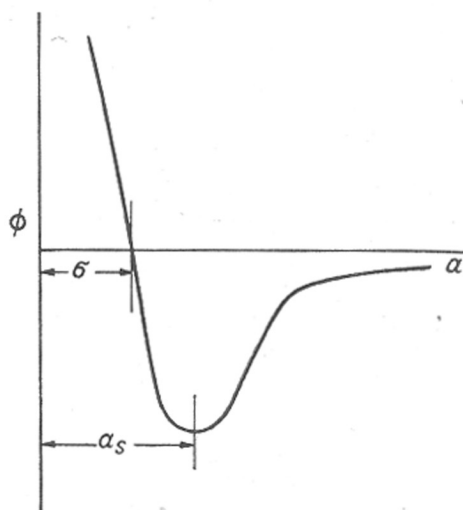


Fig. 1

Using equation (1) we can immediately write the following equations:

$$\Phi_s = Aa_s^{-n} - Ba_s^{-m} - Ca_s^{-p} \quad (2)$$

$$\left(\frac{d\Phi}{da}\right)_{a=a_s} = 0 = nAa_s^{-n} - mBa_s^{-m} - pCa_s^{-p} \quad (3)$$

$$0 = A\sigma^{-n} - B\sigma^{-m} - C\sigma^{-p} \quad (4)$$

$$A = \frac{\begin{vmatrix} \Phi_s - a_s^{-m} - a_s^{-p} \\ 0 - ma_s^{-m} - pa_s^{-p} \\ 0 - \sigma^{-m} - \sigma^{-p} \end{vmatrix}}{\Delta} \quad (5a)$$

and similar expressions can be written for B and C which we call (5b) and (5c). Here Δ is given by

$$\begin{vmatrix} a_s^{-n} & a_s^{-m} & a_s^{-p} \\ na_s^{-n} & ma_s^{-m} & pa_s^{-p} \\ \sigma^{-n} & \sigma^{-m} & \sigma^{-p} \end{vmatrix} \quad (6)$$

Thus on simplification A , B and C are given by

$$A = \frac{\Phi_s}{\Delta} \{ma_s^{-m}\sigma^{-p} - pa_s^{-p}\sigma^{-m}\} \quad (7)$$

$$B = \frac{\Phi_s}{\Delta} \{na_s^{-n}\sigma^{-p} - pa_s^{-p}\sigma^{-n}\} \quad (8)$$

$$C = \frac{\Phi_s}{\Delta} \{ma_s^{-m}\sigma^{-n} - na_s^{-n}\sigma^{-m}\} \quad (9)$$

For all systems at $T = 0$ all energy is potential, i. e. $E = U$, ignoring the small amount of zero point energy. BORN, LANDE and others [8, 9, 10] have shown both by thermodynamic arguments as well as statistical mechanical means that the same condition is very nearly true for condensed systems especially at sub-cooled temperatures. From the second law of thermodynamics we have the well-known relation

$$dU = TdS - PdV$$

$$\text{At } T = 0 \quad \therefore \left(\frac{dU}{dV}\right)_{T=0} = -P$$

and since

$$\beta = -\frac{1}{V} \left(\frac{dV}{dP}\right)_T$$

we have

$$\left(\frac{d^2U}{dV^2}\right)_{T=0} = \frac{1}{\beta V} \quad (10)$$

where U is the potential energy of one mole of the substance, β is the compressibility and V is the molar volume. Further we assume that

$$V = ka^3 \quad (11)$$

where k is a structural factor. Then it can be easily shown that

$$\frac{1}{\beta} = \frac{1}{9V} \left[a^2 \frac{d^2U}{da^2} - 2a \frac{dU}{da} \right] \quad (12)$$

From equations (1) and (12) one can easily derive that

$$\frac{1}{\beta} = \frac{1}{9V} [n(n+3)Aa^{-n} - m(m+3)Ba^{-m} - p(p+3)Ca^{-p}] \quad (13)$$

Now from equation (11) we have

$$C_1 \equiv \frac{d(1/\beta)}{dP} = \frac{d(1/\beta)}{dV} \frac{dV}{dP} = -\beta V \frac{d(1/\beta)}{dV} = -\frac{\beta a}{3} \frac{d(1/\beta)}{da} \quad (14)$$

Differentiating equation (13) with respect to 'a' we have,

$$\frac{d(1/\beta)}{da} = \frac{1}{9Va} [-n(n+3)^2 Aa^{-n} + m(m+3)^2 Ba^{-m} + p(p+3)^2 Ca^{-p}] \quad (15)$$

and hence from (14)

$$\frac{d(1/\beta)}{dP} = \frac{\beta}{27V} [n(n+3)^2 Aa^{-n} - m(m+3)^2 Ba^{-m} - p(p+3)^2 Ca^{-p}] \quad (16)$$

Using the relations (3) and (16) for values of 'a' not differing greatly from $a = a_s$ we have

$$\frac{d(1/\beta_s)}{dP} = \frac{1}{3} \left\{ \frac{my(n-m)(m+n+6) + pz(n-p)(n+p+6)}{my(n-m) + pz(n-p)} \right\} \quad (17)$$

where $x = Aa_s^{-n}$, $y = Ba_s^{-m}$ and $z = Ca_s^{-p}$.

From equations (8) and (9),

$$\begin{aligned} \frac{\Phi_s}{\Delta} &= \frac{B}{na_s^{-n}\sigma^{-p} - pa_s^{-p}\sigma^{-n}} = \frac{C}{ma_s^{-m}\sigma^{-n} - na_s^{-n}\sigma^{-m}} \\ \therefore \frac{B}{C} &= (na_s^{-n}\sigma^{-p} - pa_s^{-p}\sigma^{-n}) / (ma_s^{-m}\sigma^{-n} - na_s^{-n}\sigma^{-m}) \end{aligned}$$

Further

$$\frac{y}{z} = \frac{B}{C} a_s^{(p-m)} = (na_s^{p-m-n}\sigma^{-p} - pa_s^{-m}\sigma^{-n}) / (ma_s^{-m}\sigma^{-n} - na_s^{-n}\sigma^{-m}) \equiv R \quad (18)$$

$$y = zR \quad (19)$$

where for brevity the right-hand side of equation (18) is called R . From (17) and (19) we have the following important relation

$$\frac{d(1/\beta)}{dP} = \frac{1}{3} \left[\frac{Rm(n-m)(n+m+6) + p(n-p)(n+p+6)}{Rm(n-m) + p(n-p)} \right] \quad (20)$$

When $p = 0$, equation (20) reduces to the well-known equation [11]

$$\frac{d(1/\beta)}{dP} = \frac{1}{3} (n+m+6)$$

Equation (20) is very important. As in the case of non-polar liquids for polar liquids, too, the pressure change of the bulk modulus of rigidity is a constant for a given substance. A plot of $1/\beta$ against P for a number of polar liquids is

shown in figure 2 and it is found to be linear in every case. However, it may be pointed out that in this case $d(1/\beta)/dP$ is, a function not only of n , m and p but also of a_s and σ which are contained in R .

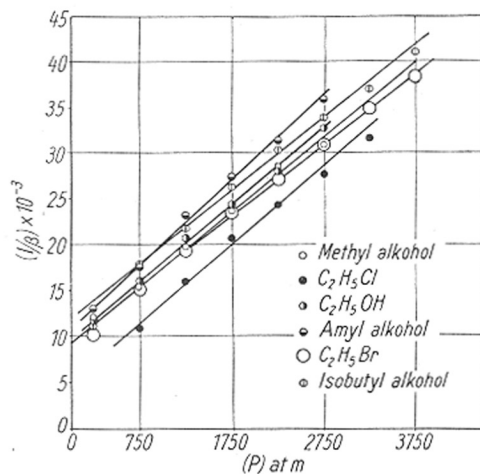


Fig. 2

Gruneisen's number and force constants

The HOOKE's law force constant for a small linear displacement from the average intermolecular separation can be shown [11, 12] to be given by

$$K = \frac{F}{3} \left(\frac{d^2\Phi}{da^2} + \frac{2}{a} \frac{d\Phi}{da} \right) \quad (21)$$

Further it is well known that the frequency ν is given by $\nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$ where μ is the reduced mass. But when F the number of nearest neighbours is large (generally 12 or so), μ can be taken as equal to the mass of one mole of the substance.

From equations (1) and (21) it can be easily shown that

$$K = \frac{2}{3} [n(n-1)Aa^{-(n+2)} - m(m-1)Ba^{-(m+2)} - p(p-1)Ca^{-(p+2)}] \quad (22)$$

and

$$\nu = \frac{1}{2\pi} \left[\frac{2}{3\mu} \{n(n-1)Aa^{-(n+2)} - m(m-1)Ba^{-(m+2)} - p(p-1)Ca^{-(p+2)}\} \right]^{1/2} \quad (23)$$

$$\ln \nu = \ln \left(\frac{1}{2\pi} \right) + \frac{1}{2} \ln \left(\frac{2}{3\mu} \right) + \frac{1}{2} \ln [n(n-1)Aa^{-(n+2)} - m(m-1)Ba^{-(m+2)} - p(p-1)Ca^{-(p+2)}] \quad (24)$$

Now in the model we present here we take the liquid molecule to be a three-dimensional harmonic oscillator of Planck-Einstein type. Hence the partition function is

$$f = \left[2 \sinh \frac{h\nu}{2kT} \right]^{-3} e^{-(U/RT)} \quad (25)$$

Also it is known that

$$\frac{\alpha}{\beta} = \left(\frac{dP}{dT} \right)_v ; \quad P = RT \left(\frac{d \ln f}{dV} \right)_T$$

$$\therefore \frac{\alpha}{\beta} = -3R \left(\frac{h\nu}{2kT} \operatorname{cosech} \frac{h\nu}{2kT} \right)^2 \frac{d \ln \nu}{dV}$$

But

$$C_v = \left[\frac{d}{dT} (RT^2 d \ln f / dT) \right]_v = 3R \left(\frac{h\nu}{2kT} \operatorname{cosech} \frac{h\nu}{2kT} \right)^2$$

$$\therefore -\frac{\alpha}{\beta} = C_v \frac{d \ln \nu}{dV}$$

$$-\frac{d \ln \nu}{d \ln V} = \frac{\alpha V}{\beta C_v} \quad (26)$$

Since

$$V = ka^3,$$

$$\frac{d \ln \nu}{d \ln V} = \frac{d \ln \nu}{3 d \ln a} \quad (27)$$

Using equations (23) and (27), we have, in the neighbourhood of a_s ,

$$-\frac{d \ln V_s}{d \ln V_s} = \frac{1}{2} \left[\frac{+n(n-1)(n+2)Aa_s^{-(n+2)} - m(m-1)(m+2)Ba_s^{-(m+2)} - p(p-1)(p+2)Ca_s^{-(p+2)}}{n(n-1)Aa_s^{-(n+2)} - m(m-1)Ba_s^{-(m+2)} - p(p-1)Ca_s^{-(p+2)}} \right] \quad (28)$$

Using equations (3), (18) and (27), equation (28) can be put in the following form:

$$\gamma \equiv \frac{\alpha V}{\beta C_v} = -\frac{d \ln \nu}{d \ln V} = \frac{1}{6} \left[\frac{Rm(n-m)(n+m+1) + p(n-p)(n+p+1)}{Rm(n-m) + p(n-p)} \right] \quad (29)$$

Here α is the volume coefficient of isobaric expansion, β the compressibility coefficient, V the molar volume, C_v the molar heat capacity, and ν is the well-known Gruneisen constant.

Equation (29) is very important and like $C_1 \equiv \frac{d(1/\beta)}{dP}$, v is also a function of n , m , p and R . Here again for non-polar liquids v is only a function of n and m while in the case of polar liquids it is also a function of σ and a_s . In the case of non-polar molecules, i.e., if there is no permanent dipole moment $p = 0$. Then equation (29) reduces to $v = \frac{1}{6}(n + m + 1)$, which is a well-known equation [11].

Compressibility and force constants

In the condensed systems of solids and sub-cooled liquids the greater part of the total potential energy of a molecule is due to interactions between nearest neighbours. Hence the average potential energy is given by

$$\Phi = \frac{1}{2} F \Phi^1 \quad (30)$$

where Φ^1 is the interaction energy of an isolated pair and F is the number of nearest neighbours. At the minimum potential energy of a molecule we have therefore

$$\Phi_s = \frac{1}{2} F \Phi_s \quad (31)$$

Using equations (5), (6) and (31), equation (1) can be written as

$$\Phi = \frac{\Phi_s}{\Delta} (L a_s^{-n} - M a_s^{-m} - N a_s^{-p}) \quad (32)$$

where

$$L \equiv m a_s^{-m} \sigma^{-p} - p a_s^{-p} \sigma^{-m} \quad (32a)$$

$$M \equiv n a_s^{-n} \sigma^{-p} - p a_s^{-p} \sigma^{-n} \quad (32b)$$

$$N \equiv m a_s^{-m} \sigma^{-n} - n a_s^{-n} \sigma^{-m} \quad (32c)$$

Using equations (12) and (32) we have, near the equilibrium,

$$\begin{aligned} \frac{1}{\beta_s} &= \frac{+U_s}{\Delta 9 V_s} \{n^2 L a_s^{-n} - m^2 M a_s^{-m} - p^2 N a_s^{-p}\} \\ &+ \frac{3U_s}{\Delta 9 V_s} \{n L a_s^{-n} - m M a_s^{-m} - p N a_s^{-p}\} \end{aligned} \quad (33)$$

Using equations (32a), (32b) and (32c) one can show that the expression in the second bracket is equal to zero. In the neighbourhood of equilibrium, we have

$$\frac{1}{\beta_s} = \frac{U_s}{\Delta 9 V_s} [n^2 L a_s^{-n} - m^2 M a_s^{-m} - p^2 N a_s^{-p}] \quad (34)$$

$$\therefore n L a_s^{-n} - m M a_s^{-m} - p N a_s^{-p} = 0 \quad (35)$$

then

$$n^2 L a_s^{-n} - m^2 M a_s^{-m} - p^2 N a_s^{-p} = m M a_s^{-m} (n - m) + p N a_s^{-p} (n - p) \quad (36)$$

From equations (5a) and (32a) we have

$$A = \frac{\Phi_s}{\Delta} L$$

and similarly

$$B = \frac{\Phi_s}{\Delta} M$$

$$C = \frac{\Phi_s}{\Delta} N$$

Using equation (18) we have

$$\frac{M}{N} = \frac{B}{C} = R a_s^{m-p} \quad (37)$$

Hence

$$n^2 L a_s^{-n} - m^2 M a_s^{-m} - p^2 N a_s^{-p} = N a_s^{-p} \{m R (n - m) + p (n - p)\}$$

Similarly it can be shown that

$$A = \frac{N a_s^{-p}}{n} [R(m - n) + (p - n)] \quad (38)$$

Hence

$$\frac{1}{\beta_s} = \frac{|-U_s|}{9 V_s} \left[\frac{n \{R m (n - m) + p (n - p)\}}{R (n - m) + (n - p)} \right] \quad (39)$$

Equation (39) is important as it can be used in determining molecular force constants.

Calculation of 'n' for methyl alcohol

As stated earlier it can be shown theoretically [4, 5, 6] that 'm' can be taken as 6 and p as 3. Further, if we define a dimensionless constant

$$z = \frac{9 V_s}{\beta_s |-U_s|} \quad (40)$$

and substitute the above values of 'm' and 'p' in equation (39). It can be shown that

$$R = \frac{(n - 3)(3n - z)}{(n - 6)(z - 6n)} \quad (41)$$

It can also be shown from equation (29) that

$$R = \frac{(n - 3)(n + 4 - 6v)}{2(n - 6)(6v - n - 7)} \quad (42)$$

From equations (41) and (42) we have

$$n = \frac{\kappa(10 - 6v)}{18 - \kappa} \quad (43)$$

Thus by putting the values of v and κ it is possible to calculate the value of the repulsion constant.

Now if we write $\frac{d(1/\beta)}{dP} \equiv C_1$ and use equation (20) with $m = 6$ and $p = 3$, R can be evaluated, which comes out to be

$$R = \frac{(n - 3)(n + 9 - 3C_1)}{2(n - 6)(3C_1 - n - 12)} \quad (44)$$

From equations (41) and (44) we have another important relation for 'n', viz.

$$n = \frac{3\kappa(C_1 - 5)}{\kappa - 18} \quad (45)$$

Thus it is possible to evaluate 'n' from different experimental data. In one case we require the Gruneisen constant and κ , and in the other we require the variation of the modulus of rigidity with pressure. Therefore this offers a good check in calculating 'n'.

The vapour pressure of methyl alcohol below 0 °C can be represented very well by the following equation [13]

$$\log_{10} p(mm) = 22.43 - 4.634 \log_{10} T - 2661/T \quad (46)$$

The molar heat of vapourisation, obtained from the CLAUSIUS-CLAPEYRON equation, is

$$L_1 = 6120R - 4.634RT \quad (47)$$

Hence using the relation [11] $U = -(L_1 + RT/2)$ we can evaluate L_1 at any temperature and hence U .

The best values of density below 0 °C are due to TINMERMANS [14] and are given by the following equation

$$d^t = 0.81015 - 0.001004t - 0.51802t^2 - 0.71657t^3 \quad (48)$$

From the above equations, both the thermal expansion coefficient and the volumes can be calculated as a function of temperature up to very near the solidification point and then extrapolated so as to find the sub-cooled values of the liquid at absolute zero.

The best values of compressibility coefficients up to -100 °C are due to BRIDGMAN [15] from which the value of the compressibility coefficient at absolute zero was extrapolated. The sub-cooled value of heat capacity was chosen from the tables of LANDOLT-BORNSTEIN [16].

The following values were obtained for methyl alcohol sub-cooled to absolute zero:

$$\begin{aligned}\alpha &= 0.90 \times 10^{-3} \text{ deg.}^{-1} \\ c_v &= 13.5 \text{ Cal. deg.}^{-1} \text{ Mol}^{-1} \\ \beta &= 15 \times 10^{-6} \text{ atm.}^{-1} \\ d &= 1.03 \text{ gm/c.c.} \quad V = 31 \text{ c. c.} \\ U_s &= 12,118 \text{ Cal.} \\ C_1 &= 8.8\end{aligned}$$

$$\therefore v = \frac{\alpha V}{\beta C_v} = 3.32$$

and

$$\kappa \equiv \frac{9V_s}{\beta_s | -U_s |} = 37$$

Substituting these values of v and κ in equations (43) and (45) we obtain the value of 'n' as

$$\begin{aligned}n &= 19.5 \quad [\text{from equation (43)}] \\ n &= 22.2 \quad [\text{from equation (45)}] \\ n_{av} &= 20.85 \cong 21\end{aligned}$$

The value of 'n' obtained from equations (43) and (45) can be considered as good especially when we are dealing with the second differential coefficient of volume with pressure (as in the case of C_1) and the extrapolation of β and α to 0 °K. The sub-cooled values are hypothetical values and would be the real values only if the substance were to exist in the liquid state up to 0 °K. As a matter of fact the values of α and C_v tend to zero as T tends to zero, as required by the third law of thermodynamics.

Relation between C_1 and γ

A comparison of equations (20) and (29) or (43) and (45) shows that

$$C_1 = 2v + 5/3 \quad (49)$$

This equation is analogous to that derived by DEBYE [17].

On the other hand,

$$C_1 \equiv \frac{d(1/\beta)}{dP} = \frac{d}{dP} \left[-V \left(\frac{dP}{dV} \right)_T \right] = -1 - \frac{V \left(\frac{d^2P}{dV^2} \right)_T}{\left(\frac{dP}{dV} \right)_T}$$

Hence equation (49) becomes

$$v = -\frac{V}{2} \frac{\left(\frac{d^2 P}{dV^2}\right)_T}{\left(\frac{dP}{dV}\right)_T} - \frac{4}{3} \quad (50)$$

Thus the value of C_1 calculated from equation (49), viz. 8.3 compares favourably well with the experimental value, 8.8.

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Vapour Pressure and Intermolecular Energy Constants of Liquids

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With 1 figure and 1 table

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Abstract

From the idea of continuity of states a relation between the pressure change of the bulk modulus of rigidity, i.e. $\left[\frac{d(1/\beta)}{dP}\right]_T$, and vapour pressure has been formulated by using the well known virial equation. The relationship between $C_1 \equiv \left[\frac{d(1/\beta)}{dP}\right]_T$ and intermolecular energy force constants has been discussed. The derived equation has been applied to a number of liquids and was found to be very satisfactory especially when considering the simplicity of treatment of the fluid state.

The discovery by ANDREWS [1] of the critical phenomenon and the idea of corresponding states have greatly contributed to the realisation of the idea of continuity of states especially between a vapour and its liquid. KAMERLINGH, ONNES [2] and various others [3, 4] have extensively used the so-called virial equation to represent the behaviour of imperfect gases. From the idea of continuity of states one can extend the representation to liquid state as well. By such a representation and by using thermodynamic arguments important conclusions [5] can be arrived at. Therefore we write the equation of state for the fluids as

$$P = \frac{RT}{V} + \sum_{n=2}^m \frac{B_n}{V^n} \quad (1)$$

That is to say the pressure of a fluid can be adequately expressed as a polynomial of $1/V$. The B_n are the so-called virial coefficients which are functions of temperature and intermolecular forces only [6, 7].

At this point it may be remarked that equation (1) is not purely empirical because it was shown by MAYER and others [8, 9, 10, 11, 12, 13] with the help of statistical mechanics that P can be expressed as an inverse power of V .

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MAYER'S theory actually predicts the phenomenon of condensation and further it accounts for the constancy of pressure when the gas actually begins to liquify. However there is still much controversy about exactly how the change of state is associated with the singularities, even though it may be admitted that MAYER'S theory is a far greater advancement in formulating an equation of state. Further it is rather difficult to calculate the higher virial coefficients from the so-called cluster integrals [8]. But one can get greater satisfaction to-day from the fact that equation (1) is not purely empirical in nature.

For the process of actual vaporisation MAXWELL'S theorem states [14, 15] that

$$P(V_g - V_l) = \int_{V_l}^{V_g} P dV \quad (2)$$

where P is the vapour pressure of the liquid and V_g and V_l are the molal volumes of the gas and liquid phases respectively. Further, if the virial coefficients in equation (1) can be related to the derivatives $\left(\frac{dP}{dV}\right)_T$ for both liquid and gas the vapour pressure can be related to these derivatives which are properties of individual phases and are not related to equilibrium. Therefore through the idea of continuity of states, the equilibrium properties of the two phases can be predicted from the properties of the individual phases in question. However, because of the limitations of the available accurate data of compressibility, the practical realisation may not be as good as desired.

Relation between vapour pressure and pressure change of bulk modulus of rigidity

As a first approximation we make the assumption that $m = 5$ can represent the state of fluids adequately and hence equation (1) can be written for fluids as

$$P = \frac{RT}{V} + \frac{B_2}{V^2} + \frac{B_3}{V^3} + \frac{B_4}{V^4} + \frac{B_5}{V^5} \quad (3)$$

Hence for the volume of the gas and liquid we can write

$$P = \frac{RT}{V_g} + \frac{B_2}{V_g^2} + \frac{B_3}{V_g^3} + \frac{B_4}{V_g^4} + \frac{B_5}{V_g^5} \quad (4)$$

$$P = \frac{RT}{V_l} + \frac{B_2}{V_l^2} + \frac{B_3}{V_l^3} + \frac{B_4}{V_l^4} + \frac{B_5}{V_l^5} \quad (5)$$

By substituting equation (3) in equation (2) we get

$$P(V_g - V_l) = RT \ln \left(\frac{V_g}{V_l} \right) + B_2 \left(\frac{1}{V_l} - \frac{1}{V_g} \right) + \frac{1}{2} B_3 \left(\frac{1}{V_l^2} - \frac{1}{V_g^2} \right) + \frac{1}{3} B_4 \left(\frac{1}{V_l^3} - \frac{1}{V_g^3} \right) + \frac{1}{4} B_5 \left(\frac{1}{V_l^4} - \frac{1}{V_g^4} \right) \quad (6a)$$

Since compressibility is defined as $\beta = -1/V(dV/dP)_T$, we get from equation (5) for the compressibility of the liquid the following expression:

$$\frac{1}{\beta} = \frac{RT}{V_e} + \frac{2B_2}{V_e^2} + \frac{3B_3}{V_e^3} + \frac{4B_4}{V_e^4} + \frac{5B_5}{V_e^5} \quad (7)$$

Further, if the vapour pressure is not high, it is reasonable to assume that the vapour phase of the fluid obeys the ideal gas law. Therefore equation (4) becomes

$$0 = B_2 + \frac{B_3}{V_g} + \frac{B_4}{V_g^2} + \frac{B_5}{V_g^3} \quad (8)$$

Under ideal gas law conditions we also have $V_g \gg V_e$. Hence V_e can be neglected in comparison with V_g ; so that equation (6a) reduces to

$$RT - RT \ln \left(\frac{RT}{pV_e} \right) = \frac{B_2}{V_e} + \frac{B_3}{2V_e^2} + \frac{B_4}{3V_e^3} + \frac{B_5}{4V_e^4} \quad (6)$$

In the case of non-polar liquids, it was shown by MOELWYN-HUGHES [16] by thermodynamic arguments that the pressure change of bulk modulus of rigidity is a constant, i.e.

$$C_1 \equiv \left[\frac{d(1/\beta)}{dP} \right]_T = \text{constant}$$

Further he showed that [16]

$$C_1 = \frac{1}{3} (n + m + 6)$$

where n and m are the exponents for repulsion and attraction in the well known bireciprocal function of LENNARD-JONES [17, 18]. Even in the case of polar liquids a three constant potential function of the type [19]

$$\Phi = Aa^{-n} - Ba^{-m} - Ca^{-p}$$

adequately represents the potential of a polar molecule. Here A , B and C are constants and the first term is due to repulsion while the second and third terms are due to van der WAALS' forces and dipole-dipole interactions, respectively. It can be shown [20] that

$$C_1 \equiv \left[\frac{d(1/\beta)}{dP} \right]_T = \frac{1}{3} \left\{ \frac{Rm(n-m)(n+m+6) + p(n-p)(n+p+6)}{Rm(n-m) + p(n-p)} \right\} \\ = \text{constant}$$

and

$$R = \frac{(na_s^{p-m-n}\sigma^{-p} - pa_s^{-m}\sigma^{-n})}{(ma_s^{-m}\sigma^{-n} - na_s^{-n}\sigma^{-m})}$$

where a_s and σ are the equilibrium distance and collision diameter respectively. That is, in the case of liquids in general the pressure change of bulk modulus

of rigidity is a constant. Therefore from equation (7) we can easily evaluate C_1 which comes out to be

$$\frac{C_1}{\beta} = \frac{RT}{V_e} + \frac{4B_2}{V_e^2} + \frac{9B_3}{V_e^3} + \frac{16B_4}{V_e^4} + \frac{25B_5}{V_e^5} \quad (9)$$

Then from equations (5), (6), (7), (8) and (9) we can solve for C_1 and get

$$C_1 = \begin{vmatrix} 0 & 1 & 1/V_g & 1/V_g^2 & 1/V_g^3 \\ p - (RT/V_e) & 1/V_e^2 & 1/V_e^3 & 1/V_e^4 & 1/V_e^5 \\ RT - RT \ln x & 1/V_e & 1/2 V_e^2 & 1/3 V_e^3 & 1/4 V_e^4 \\ (1/\beta) - (RT/V_e) & 2/V_e^2 & 3/V_e^3 & 4/V_e^4 & 5/V_e^5 \\ RT/V_e & -4/V_e^2 & -9/V_e^3 & -16/V_e^4 & -25/V_e^5 \\ 0 & 1 & 1/V_g & 1/V_g^2 & 1/V_g^3 \\ 0 & 1/V_e^2 & 1/V_e^3 & 1/V_e^4 & 1/V_e^5 \\ 0 & 1/V_e & 1/2 V_e^2 & 1/3 V_e^3 & 1/4 V_e^4 \\ 0 & 2/V_e^2 & 3/V_e^3 & 4/V_e^4 & 5/V_e^5 \\ 1/\beta & -4/V_e^2 & -9/V_e^3 & -16/V_e^4 & -25/V_e^5 \end{vmatrix}$$

where $x = \frac{RT}{pV_e} = V_g/V_e$.

Neglecting V_e in comparison with V_g we can simplify the above determinant in a straightforward way and get

$$C_1 = -36\beta \left[p - \frac{25RT}{18V_e} - \frac{2RT \ln x}{3V_e} - \frac{11}{36\beta} \right] \quad (10)$$

If the vapour pressure is small, the first term is negligible in comparison with the remaining terms. Hence we have

$$\frac{11 - C_1}{\beta} = 2px(12 \ln x - 25) \quad (11)$$

Equation (11) is surprisingly simple and is convenient for evaluating C_1 and hence the intermolecular potential energy constants from single values of β and x .

In order to have an idea about the order of magnitude of the errors involved in neglecting V_e in comparison with V_g we can take the example of benzene. The vapour pressure of benzene at 20 °C is 74.8 mm Hg. At this vapour pressure and temperature, to a first approximation, one mole of benzene vapour occupies 22.4 litres and its molal volume in the liquid state at the same temperature is about 89 c.c. Therefore $V_g/V_e \cong 2500$ and hence

$V_g \gg V_l$. Further, in equation (10) p is neglected in comparison with the other terms because p is in general a fraction of unity while the other terms run into hundreds and thousands.

For example, again for benzene at 20 °C, $p = 0,099$ atm, while

$$\frac{25 RT}{18 V_e} = 375 \text{ atm}, \quad \frac{2 RT \ln x}{3 V_e} = 1425 \text{ atm} \quad \text{and} \quad \frac{11}{36 \beta} = 2900 \text{ atm}$$

Equation (11) has been applied to a number of liquids and the calculated values are given in Table I, column 6, while the experimental values [19, 21, 22, 23] are obtained from the slope of the graphs of $1/\beta$ vs. P and are given in column 7.

Table I

Liquid	Temp. °C	V ml	p mm 21, 23	[21, 22, 25]		[19, 21, 22]
				$\beta \cdot 10^6 \text{ atm}^{-1}$	$C_1(\text{cal.})$	$C_1(\text{Exp.})$
1. Hydrocarbons						
a) Pentane	20	112	183.7	176	6.74	—
b) Hexane	23	131	139.3	159	7.58	7.75
c) Heptane	20	147	41.4	144	7.65	—
d) Octane	23	163	12.5	121	7.96	8.5
e) Benzene	20	89	74.8	95	7.41	8.0
f) Toluene	20	106	22.2	92	7.56	8.0
2. Esters						
a) Methyl acetate	20	79.3	169.8	101	7.23	8.0
b) Ethyl acetate	20	98.0	72.8	105	7.44	8.0
c) Ethyl propionate	20	115.0	27.8	102	7.64	8.0
d) Methyl butrate	20	113.0	24.5	98	7.64	8.5
e) Ethyl butrate	20	132.0	11.3	101	7.61	8.5
3. Alcohols						
a) Methyl alcohol	0	40	30.0	90	2.0	8.8
b) Ethyl alcohol	0	57	12.2	100	3.4	5.4
c) Amyl alcohol	20	108	2.5	91	5.7	6.0
d) Isoamyl alcohol	20	109	2.3	99	6.2	8.7
e) n-butyl alcohol	20	92	4.3	97	5.7	9.0
f) Tertiary butyl alcohol	20	74.1	30.6	108	6.7	10.0
4. Miscellaneous						
a) Carbon tetrachloride	20	97	91.6	106	7.5	8.6
b) Mercury	0	14.8	$1.9 \cdot 10^{-4}$	3.9	8.1	6.8
c) Ethylene bromide	20	86.0	10.2	59	7.9	—
d) Carbon disulphide	20	60	298	87	7.0	7.5
e) Acetone	20	73	185	105	6.7	6.5
f) Chloroform	20	80	160	102	7.2	8.2

The agreement in most cases can be considered as very good especially when considering that we are dealing with the pressure change of bulk modulus of rigidity which contains the derivative of pressure with respect to volume. However, in the case of alcohols (especially those with low molecular weights) the calculated values of C_1 are in poor agreement with the experimental values, which is also the case even in the theoretical evaluation of compressibility coefficient [5]. The reason for this deviation is most probably due to the fact that higher order virial coefficients ($m > 5$) may have to be taken into account. That means the pressure of a fluid has to be represented by considering a greater number of virial coefficients in the polynomial expression (1). But this introduces a large number of unknowns which are to be eliminated in order to correlate the physical properties of the fluids.

In the case of non-polar liquids, C_1 is simply related to n and m , and by London's theory of dispersion [24] m can be taken as equal to 6 and hence n can be evaluated. In the case of polar liquids it is reasonable to take [20] $m = 6$ and $p = 3$, and in order to evaluate n one still requires a knowledge of the collision diameter σ and equilibrium distance a_s . At any rate equation (11) should be useful in checking the experimental value of C_1 i.e. the pressure change of bulk modulus of rigidity.

A General Correlation between Vapour Pressure and Intermolecular Energy Force Constants

It was shown [5] that

$$\beta p x (6 \ln x - 11) = 1 \quad (13)$$

where β , p and x have their usual significance, when the pressure of a fluid is expressed by

$$p = \frac{RT}{V} + \sum_{n=2}^4 \frac{B_n}{V^n}$$

This suggests that a plot of $\log x$ against $V_0/\beta T$ should be a straight line for all liquids at all temperatures. It is obvious that this is not the case. The reason probably is that the representation of the pressure of fluids as a polynomial of $1/V$ is inadequate, as has already been stated [5], and higher virial coefficients ought to be considered to get better agreement with experiment. Now, in the derivation of equation (11) it is assumed that $m = 5$, i.e. one more virial coefficient, namely B_5 , has been taken into account in expressing the pressure of fluids. Equation (11) can be put in the following form

$$\frac{V_0}{\beta T} = \frac{24 R \ln x}{11 - C_1} - \frac{50 R}{11 - C_1} \quad (14)$$

Equation (14) implies that a plot of $\log x$ against $V_0/\beta T$ should be a straight line at all temperatures for a particular liquid only, as shown in figure 1, in the region where the approximation holds, namely $V_g \gg V_0$, since the slope

of the graph contains C_1 which is a constant characteristic of a particular liquid and related to its intermolecular force constants, thus scoring definite edge over the inexplicable situation met with in the former case [vide equation (13)].

The authors are grateful to Dr. A. B. BISWAS, Assistant Director, for his interest in this work.

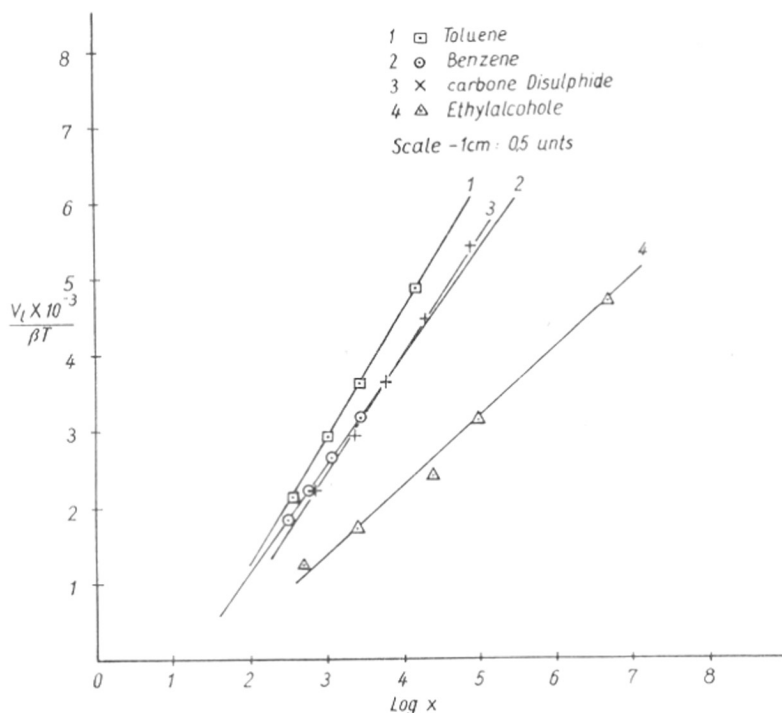


Fig. 1

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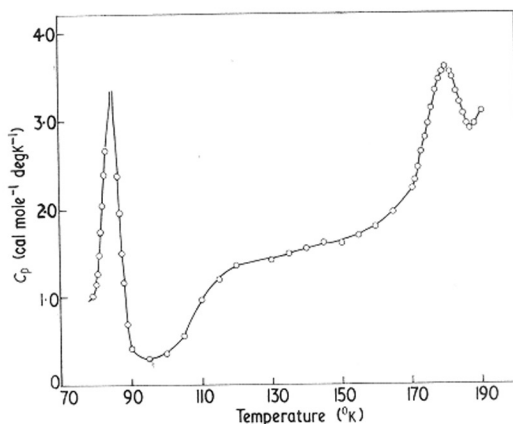
The Heat Capacities of Potassium Manganese Trifluoride

Recently the magnetic susceptibilities of a series of KMF_3 type of compounds (where M is Mn, Fe, Co, Ni or Cu) have been measured by Kinshiro Hirakawa *et al.* (1960) and these compounds show antiferromagnetic transitions above the liquid nitrogen temperature. Study of the variation of their specific-heat characteristics with temperature is under way in this laboratory. $KMnF_3$ has been prepared by a procedure given by Kinshiro Hirakawa *et al.* (1960). By x-ray diffraction the compound was found to be cubic with $a = 4.191 \text{ \AA}$ in good agreement with the value obtained by Okazaki *et al.* (1959).

An isothermal calorimeter has been constructed with a view to studying the phase transitions as well as obtaining thermodynamic data in the range of $78 \text{ }^\circ\text{K}$ to $300 \text{ }^\circ\text{K}$. The design of the cryostat and method of making measurements and calculations follow that of Giauque and his school (1923, 1929 and 1937) and Cole *et al.* (1960). For checking the performance and reliability, the heat capacities of benzoic acid were

measured and compared with those obtained by Furukawa *et al.* (1951). The agreement was satisfactory.

The heat capacity of potassium manganese trifluoride was measured in the range 78°–300 °K and it is found to give two maxima which correspond to two transitions in the heat capacity against temperature graph (see figure). The first peak was obtained



at 84.3 ± 0.2 °K and the second at 179.5 ± 0.2 °K. The first peak was identified with the antiferromagnetic transition for which the Néel temperature was reported to be 88 °K by Kinshiro Hirakawa *et al.* (1960). The second transition is attributed to a structural transition, as has already been observed from crystallographic studies by Beckman (1961), whereby an orthorhombic phase goes over to a cubic perovskite-like structure which is stable at room temperature.

The method of calibration of thermocouples and the detailed discussion of results regarding the standard substance and that of KMnF_3 will be published afterwards.

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COHESIVE ENERGIES OF ALKALI HALIDES

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The principal interactions in ionic lattices which are Coulomb interaction, van der Waals' interaction and overlap force, are two body forces. In the case of simple ions possessing spherical symmetry and rare gas structures, the cohesive energy can be represented as a function of their distance apart. For the ionic crystals a number of observable properties can be calculated using a bireciprocal Lennard-Jones potential function coupled with a coulombic term. Recently the cohesive energies of ionic crystals have been calculated (Sharma and Madan, 1961) using a (12 : 6) potential function. It was pointed out that the discrepancy with the experimental data was more pronounced for lighter alkali halides. Hence the authors presently aim to propose an appropriate (9:6) potential function for such alkali halides. This is reasonable in the light of the fact that the values of the repulsion constant 'n' obtained by Pauling's rules (1927, 1928) derived from a theoretical treatment of the interaction of closed shell electronic configurations, lie in the vicinity of 9 (Sherman, 1932).

Hence the energy per cell is represented by

$$\phi_{(r)} = -\frac{\alpha e^2}{r} + \frac{B}{r^9} - \frac{C}{r^6} + \epsilon_0 \quad \dots (1)$$

where α is the Madelung's constant, e is the electron charge, r is the distance between closest ion centres and ϵ_0 is the zero point energy. B and C are the coefficients for repulsive and van der Waals terms.

Here interactions between dipole-quadrupole and other than the nearest neighbours are neglected as their contribution is very small.

By the use of thermodynamic relations it can be easily shown that first and second derivatives of lattice energy can be expressed in terms of directly observable quantities. The equations are :

$$\frac{d\phi_{(r)}}{dr} = \frac{3vT}{r\beta} \left(\frac{1}{V} \cdot \frac{\partial V}{\partial T} \right)_P \quad \dots (2)$$

$$\frac{d^2\phi_{(r)}}{dr^2} = \frac{9v}{r^2\beta} \left[1 + \frac{T}{\beta} \left\{ \left(\frac{\partial \beta}{\partial T} \right)_P + \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \frac{1}{\beta} \left(\frac{\partial \beta}{\partial P} \right)_T \right\} + \frac{2T}{3V} \left(\frac{\partial V}{\partial T} \right)_P \right] \dots (3)$$

TABLE I
Cohesive energy in K. Cal/mole

Compound	Repulsion constant	Experimental	Calculated (present work)	Calculated (12 : 6)	c
LiF	6.0	246 ^a	264.6	273.1	246.8
NaF	7.0	218 ^a	227.3	236.6	218.7
LiCl	7.0	201.5 ^b	199.8	212.6	202.0
LiBr	7.5	191.5 ^b	189.9	200.0	190.7
NaCl	8.0	184.3 ^a	182.8	192.8	185.9
KF	8.0	193.0 ^a	195.8	205.8	194.4
LiI	8.5	180.0 ^a	174.8	184.3	176.8
NaBr	8.5	176.0 ^b	172.1	182.1	176.7
RbF	8.5	—	177.9	191.6	185.9
KCl	9.0	167.8 ^a	163.8	174.1	169.4
NaI	9.5	166.0 ^a	159.3	168.8	165.4
KBr	9.5	160.0 ^a	154.8	164.8	162.4
RbCl	9.5	162.0 ^a	155.8	166.8	164.0
RbBr	10.0	157.0 ^a	149.6	159.1	157.5
KI	10.5	152.0 ^a	145.0	155.0	153.0

a. Plendl (1961)

b. Born and Huang (1954)

c. Cubicciotti (1961)

Using Equation (3) the repulsive parameter B can be evaluated and hence the cohesive energy. The experimental data used have been taken from Huggins (1937), Seitz (1940) and Spangenberg (1956), Spangenberg *et. al.* 1957). The values of cohesive energy are compared with the observed values and also with other determinations. The values calculated with (12 : 6) potential function are also given. All values are listed in Table I.

In the case of lighter halides, the 'n' value is less than the assumed value of 9. Thus for the lightest one, namely LiF, the 'n' value is around 6 (Sherman, 1932) and hence cohesive energy is higher. Better agreement can be obtained using the value of 'n' as 7. As we go down the group of alkali halides the agreement becomes better. This is explicable since in all these cases, the 'n' values are either 9 or very near 9. For heavier crystals, the calculated values are lower and the discrepancy increases as we proceed towards still heavier compounds. Incidentally the 'n' value increases to 10.5 and (12 : 6) potential function becomes more appropriate.

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Lattice Energy and other Properties of some Ionic Crystals

By **C. D. Das, H. V. Keer and R. V. G. Rao**

With 2 Tables

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Lattice Energy and other Properties of some Ionic Crystals

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With 2 Tables

(Received 24 May 1963)

Abstract

Lattice energies of some ionic crystals at 0°K have been calculated using an inverse type of potential function with revised value of electronic charge. Compressibilities are evaluated and compared with experimental observations. An equation has been derived for thermal expansion coefficient with the potential function used and the room temperature values have been calculated.

Introduction

It is customary to represent the interaction energy of ions possessing spherical symmetry and rare gas structures as a function of their distance apart. Hence the authors presently aim to use an inverse type of potential function for calculating certain properties of some simple ionic crystals. In general the value of the repulsion constant for alkali halides and alkaline earth chalcogenides obtained by PAULING's rules [1] derived from a theoretical treatment of the interaction of the closed shell electronic configurations is about nine [2]. FOWLER [3] has actually calculated the lattice energies and compressibilities of some of these compounds using a constant value of nine for the repulsion constant. In his calculations he neglected the dipolequadrupole interaction and zero-point vibrational energy. Since then an important change has been made in the value of the electronic charge which not only affects the coulombic term directly but also changes the repulsive parameter indirectly [4, 5]. Hence it is felt necessary to recalculate the properties of these crystals using the revised value of the electronic charge and including the neglected terms with a uniform value of nine for the repulsion constant. The interactions between other than nearest neighbours have been neglected as their contribution is considered very small. The experimental data used have been taken from the available literature [5-8].

Lattice Energy

The lattice energy per cell in ergs can be written as

$$\varphi_{(r_0)} = -\frac{\alpha e^2 z^2}{\gamma_0} + \frac{B}{\gamma_0^9} - \frac{C}{\gamma_0^6} - \frac{D}{\gamma_0^8} + \epsilon_0 \quad (1)$$

The symbols in equation (1) have the usual significance.

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Table 1. Lattice Energies and Compressibility Coefficients

Com- pound	Lattice energy in Kcal/mole				Compressibility $\times 10^{12}$ cm ² /dynes		
	Calculated	Fowler [3]	Observed [10—12]	H & S [6]	Calculated	Observed [5, 6]	H & S [6]
LiF	253.3	—	245.9	—	0.65	1.43	—
Cl	200.8	—	201.5	—	2.35	3.17	—
Br	187.9	—	191.5	—	3.09	3.90	—
I	173.2	—	180.0	—	4.03	5.30	—
NaF	221.0	228.2	218.8	—	1.30	2.06	—
Cl	182.8	190.1	184.7	—	3.54	3.97	—
Br	173.0	181.4	175.9	—	4.41	4.75	—
I	160.2	170.8	166.3	—	5.90	6.21	—
KF	192.8	198.4	194.3	—	2.36	3.14	—
Cl	164.8	173.1	163.0	—	5.20	5.50	—
Br	157.5	166.3	160.0	—	6.35	6.45	—
I	147.2	158.8	151.0	—	8.23	8.07	—
RbF	184.6	187.1	186.3	—	4.40	3.66	—
Cl	158.2	165.7	159.0	—	6.78	6.16	—
Br	151.5	160.6	157.0	—	7.95	7.38	—
I	142.5	153.5	148.0	—	10.00	9.00	—
CsF	173.8	176.9	—	—	5.95	4.25	—
Cl	148.3	157.3	157.8	—	6.40	5.55	—
Br	142.8	153.5	152.3	—	7.35	6.28	—
I	134.6	147.7	141.0	—	8.71	7.83	—
BeO	1172.3	—	—	1082	0.17	0.27	0.37
S	917.7	—	—	893	0.44	—	0.66
Se	868.6	—	—	855	0.55	—	0.75
Te	793.4	—	—	795	0.79	—	0.94
MgO	979.1	976.0	—	938	0.27	0.42, 0.59	0.48
S	792.5	766.0	—	788	0.63	0.69	0.82
Se	755.9	743.0	—	757	0.76	0.75	0.91
Te	687.9	—	—	699	1.36	—	1.62
CaO	858.1	876	—	841	0.46	0.71, 0.88	0.69
S	725.9	714	—	726	0.89	0.98, 2.8	1.09
Se	697.3	700	—	701	1.05	1.04, 2.2	1.21
Te	650.3	648	—	662	1.39	2.40	1.46
SrO	801.4	829	—	792	0.60	0.83	0.84
S	686.6	688	—	692	1.11	3.80	1.28
Se	663.0	675	—	671	1.29	2.50	1.40
Te	621.2	626	—	635	1.67	2.10	1.68
BaO	747.0	780	—	746	0.79	1.74	1.00
S	648.1	662	—	659	1.41	2.90	1.50
Se	627.2	652	—	639	1.61	2.90	1.65
Te	591.2	609	—	608	2.03	3.30	1.96

Following HILDEBRAND's considerations [9] one finds that the first derivative with respect to γ of equation (1) becomes zero at 0 °K.

$$\gamma_0 \left[\frac{d\varphi}{d\gamma} \right]_{\gamma=\gamma_0} = 0 = \frac{\alpha e^2 z^2}{\gamma_0} - \frac{9B}{\gamma_0^9} + \frac{6C}{\gamma_0^6} + \frac{8D}{\gamma_0^8} \quad (2)$$

Using equations (1) and (2) repulsive parameter B and hence lattice energy are calculated. The values together with experimental and other determinations are given in Table 1.

The values are in better agreement with observed values than those of FOWLER [3].

Compressibility

From the second derivative of equation (1), we get

$$\beta = \frac{9K\gamma_0^3 \alpha}{\gamma_0^2 \left(\frac{d^2\varphi}{d\gamma^2} \right)_{\gamma=\gamma_0}} \quad (3)$$

where β is the compressibility coefficient,

K is a constant given by $V/N\gamma_0^3$,

V is the molar volume,

N is Avogadro's number

and

$$\alpha = 1 + \frac{T}{\beta} \left[\left(\frac{\partial \beta}{\partial P} \right)_T + \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \cdot \frac{1}{\beta} \left(\frac{\partial \beta}{\partial P} \right)_T \right] + \frac{2}{3} \frac{T}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

The calculated values of compressibility coefficients are given together with experimental and other determinations in Table 1. α is assumed to be unity for alkaline earth chalcogenides [6]. In the case of alkaline earth chalcogenides it was pointed out [13] that the observed values are unreliable and generally too high. Nevertheless it is gratifying to note that the values are in general in good agreement with those of HUGGINS and SAKAMOTO [6].

Thermal Expansion coefficient

Assuming that the oscillators vibrate independently of each other with the same frequency it was shown [14] that

$$\alpha' = - \frac{c_v}{2a\gamma_0} \cdot \frac{1}{\nu} \cdot \frac{d\nu}{d\gamma} \quad (4)$$

where α' is the linear thermal expansion coefficient,

c_v the specific heat at constant volume,

ν the frequency of vibration,

and

$$a = \frac{1}{2} \left(\frac{d^2 \varphi}{d\gamma^2} \right)_{\gamma=\gamma_0}$$

Now the frequency of vibration for linear harmonic oscillator is

$$\nu = \left[\left(\frac{d^2 \varphi}{d\gamma^2} \right)_{\gamma=\gamma_0} / 4\pi^2 m \right]^{\frac{1}{2}} \quad (5a)$$

where “ m ” is the reduced mass of the oscillating ions.

Near the equilibrium position

$$\frac{1}{\nu} \cdot \frac{d\nu}{d\gamma} = \frac{1}{4\pi^2 m^{\frac{1}{2}}} \left(\frac{d^2 \varphi}{d\gamma^2} \right)_{\gamma=\gamma_0}^{-\frac{1}{2}} \left(\frac{d^3 \varphi}{d\gamma^3} \right) \quad (5b)$$

Using equations (1), (4), (5a) and (5b) an expression has been derived which comes out to be

$$\alpha' = 2C_v \left[\frac{\left(\frac{26\alpha e^2 z^2}{\gamma_0} + \frac{81C}{\gamma_0^6} + \frac{40D}{\gamma_0^8} \right)}{\left(\frac{8\alpha e^2 z^2}{\gamma_0} + \frac{18C}{\gamma_0^6} + \frac{8D}{\gamma_0^8} \right)^2} \right] \quad (6)$$

Equation (6) gives α' in terms of C_v and potential energy constants. However, for solids generally C_p , the heat capacity at constant pressure, is available as a function of temperature. So in order to use the available C_p data we make the following readjustment.

It is well known from thermodynamics that

$$C_p - C_v = (3\alpha')^2 VT/\beta$$

Let

$$A = 2 \left[\left(\frac{26\alpha e^2 z^2}{\gamma_0} + \frac{81C}{\gamma_0^6} + \frac{40D}{\gamma_0^8} \right) / \left(\frac{8\alpha e^2 z^2}{\gamma_0} + \frac{18C}{\gamma_0^6} + \frac{8D}{\gamma_0^8} \right)^2 \right]$$

So from equation (6) we have $\alpha' = AC_v$

Hence

$$C_p = \frac{\alpha'}{A} + \frac{9(\alpha')^2 VT}{\beta} \quad (7)$$

Solving for α' from equation (7) and neglecting the negative root we have

$$\alpha' = \frac{\beta}{18VTA} \left[-1 + (1 + \delta)^{\frac{1}{2}} \right],$$

Table 2. Thermal Expansion Coefficient

Compound	Cp. Sp. heat at 298 °K Kcal deg. ⁻¹ mole ⁻¹ [15—18]	$\frac{1}{4} \delta = \frac{9 VTCpA^2}{\beta} \times 10^2$	Coefficient of Linear thermal expansion $\times 10^6$ at 298 °K/deg.	
			Calculated	Observed [6, 14]
LiF	10.04	3.65	27.80	34.0
Cl	12.20	6.07	39.80	44.0
Br	12.40	7.00	42.60	50.0
I	13.00	8.00	47.60	49.0
NaF	11.00	5.00	33.20	36.0
Cl	11.88	8.50	44.10	40.0
Br	12.50	8.50	46.00	43.0
I	13.00	9.80	49.10	48.3
KF	11.73	7.20	39.20	36.70
Cl	12.31	9.40	46.80	38.30
Br	12.82	10.55	50.20	40.00
I	13.16	12.00	54.00	45.00
RbF	12.20	10.70	40.60	
Cl	12.30	10.30	47.50	36.00
Br	12.68	11.00	51.00	38.00
I	12.50	12.20	52.60	43.00
CsCl	12.62	12.50	50.00	56.00
BeO	6.10	0.45	3.7	5.3
MgO	8.87	0.58	6.5	10.3
CaO	10.20	0.86	8.4	11.6
SrO	10.76	1.44	9.5	13.7
BaO	11.10	0.99	10.4	13.0
CaS	11.35	0.83	11.1	—

where

$$\delta = \frac{36VTCpA^2}{\beta}$$

The average value of δ for the alkali halides is 0.35 and that for the alkaline earth chalcogenides is 0.03. Hence expanding $(1 + \delta)^{\frac{1}{2}}$ and neglecting terms higher than the quadratic which causes an error of less than 1 per cent and simplifying we have

$$\alpha' = ACp \left(1 - \frac{1}{4} \delta \right) \quad (8)$$

Thus for alkali halides by using Cv instead of Cp one makes an error of 5–10 per cent and of 0.5–1.5 per cent for alkaline earth chalcogenides if thermal expansion

coefficients are calculated at room temperature. To avoid this the accurate equation (8) has been used for the calculation of α' . The calculated values together with experimental observations are given in Table 2.

To account for the polarization of ions KUMAR [14] used in his calculations certain empirical factors. It may however be noted that even though the authors have not resorted to any such empirical factors the agreement with observed values is satisfactory.

Gruneisen Constant

From equations (4), (5a) and (5b) we can write

$$\alpha' = -\frac{C_v}{2\gamma_0} \cdot \frac{(d^3\varphi/d\gamma^3)}{(d^2\varphi/d\gamma^2)^2}$$

It is well known that the Gruneisen constant is

$$\gamma = \frac{3\alpha'v}{c_v\beta}$$

Substituting the value of α' we get

$$\gamma = -\frac{3v}{2\beta\gamma_0} \cdot \frac{(d^3\varphi/d\gamma^3)}{(d^2\varphi/d\gamma^2)^2}$$

But $\beta = +\left(\frac{3v}{\gamma_0^2}\right) (d^2\varphi/d\gamma^2)^{-1}$ assuming κ to be unity in equation [3].

$$\gamma = -\frac{1}{6}\gamma_0 \frac{(d^3\varphi/d\gamma^3)}{(d^2\varphi/d\gamma^2)}$$

An identical relation was obtained by MEINCKE [19] from quantum mechanical considerations.

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Imperfect Vapour Phase, Compressibility & Force Constants of Liquids*

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Assuming the vapour phase of fluids to be imperfect, a relation between vapour pressure, compressibility coefficient and intermolecular energy constant (C_1) of liquids has been derived from the idea of continuity of states by using the virial equation. The derived relation has been applied to a number of liquids and the calculated values of C_1 are in good agreement with observed values.

IT is well known from statistical mechanical methods¹⁻⁶ that the pressure can be expressed as an inverse power of volume. Actually the pressure of a fluid as a polynomial of $1/V$ has been successfully used in correlating a number of physical properties of fluids by the present authors^{7,8}. In the previous paper⁸, assuming the vapour phase to

be ideal, an equation was derived for $C_1 \equiv \left[\frac{\partial(1/\beta)}{\partial P} \right]_T$

which has been proved to be a constant for non-polar as well as polar liquids and related to intermolecular energy constants^{9,10}. Although the agreement was excellent for non-polar liquids, the deviations for polar liquids were marked. In the present communication it is shown how a consideration of the imperfection of the vapour phase can improve the agreement in the case of polar liquids as well.

Assuming the polynomial to be of the 5th order, the following equations can be written:

$$P = \frac{RT}{V_g} + \frac{B_2}{V_g^2} + \frac{B_3}{V_g^3} + \frac{B_4}{V_g^4} + \frac{B_5}{V_g^5} \dots \dots \dots (1)$$

$$P = \frac{RT}{V_l} + \frac{B_2}{V_l^2} + \frac{B_3}{V_l^3} + \frac{B_4}{V_l^4} + \frac{B_5}{V_l^5} \dots \dots \dots (2)$$

$$P(V_g - V_l) = RT \ln \left(\frac{V_g}{V_l} \right) + B_2 \left(\frac{1}{V_l} - \frac{1}{V_g} \right) + \frac{B_3}{2} \left(\frac{1}{V_l^2} - \frac{1}{V_g^2} \right) + \frac{B_4}{3} \left(\frac{1}{V_l^3} - \frac{1}{V_g^3} \right) + \frac{B_5}{4} \left(\frac{1}{V_l^4} - \frac{1}{V_g^4} \right) \dots \dots (3)$$

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$$\frac{1}{\beta} = \frac{RT}{V_l} + \frac{2B_2}{V_l^2} + \frac{3B_3}{V_l^3} + \frac{4B_4}{V_l^4} + \frac{5B_5}{V_l^5} \dots \quad (4)$$

$$\frac{C_1}{\beta} = \frac{RT}{V_l} + \frac{4B_2}{V_l^2} + \frac{9B_3}{V_l^3} + \frac{16B_4}{V_l^4} + \frac{25B_5}{V_l^5} \dots \quad (5)$$

Assuming that the vapour phase of fluids does not obey the ideal gas law, it can be represented as

$$P = \frac{RT}{V_g} + \frac{B_2}{V_g^2}$$

Hence equation (1) reduces to

$$0 = B_3 + \frac{B_4}{V_g} + \frac{B_5}{V_g^2} \dots \quad (6)$$

and equation (3) to

$$(RT - PV_l) = RT \ln \left(\frac{V_g}{V_l} \right) + B_2 \left(\frac{1}{V_l} - \frac{2}{V_g} \right) + \frac{B_3}{2} \left(\frac{1}{V_l^2} - \frac{1}{V_g^2} \right) + \frac{B_4}{3} \left(\frac{1}{V_l^3} - \frac{1}{V_g^3} \right) + \frac{B_5}{4} \left(\frac{1}{V_l^4} - \frac{1}{V_g^4} \right)$$

Therefore, neglecting V_l in comparison with V_g , we get

$$RT - RT \ln \left(\frac{V_g}{V_l} \right) = \frac{B_2}{V_l} + \frac{B_3}{2V_l^2} + \frac{B_4}{3V_l^3} + \frac{B_5}{4V_l^4} \dots \quad (7)$$

Calculation of $\ln(V_g/V_l)$

$$\begin{aligned} \text{Since } P &= RT/V_g + B_2/V_g^2 \\ \therefore V_g &= \frac{1}{2} \left[\frac{RT}{P} + \sqrt{\left(\frac{RT}{P} \right)^2 + \frac{4B_2}{P}} \right]^* \\ &= \frac{1}{2} \left[\frac{RT}{P} + \frac{RT}{P} \left(1 + \frac{4B_2 P}{R^2 T^2} \right)^{\frac{1}{2}} \right] \end{aligned}$$

Since $4B_2 P/R^2 T^2 \ll 1$ by expanding and neglecting higher terms we have

$$\begin{aligned} V_g &= \frac{1}{2} \left[\frac{RT}{P} + \frac{RT}{P} \left(1 + \frac{2B_2 P}{R^2 T^2} \right) \right] \\ \frac{V_g}{V_l} &= \frac{RT}{PV_l} \left(1 + \frac{B_2 P}{R^2 T^2} \right) \\ \ln \left(\frac{V_g}{V_l} \right) &= \ln \left(\frac{RT}{PV_l} \right) + \ln \left(1 + \frac{B_2 P}{R^2 T^2} \right) \end{aligned}$$

Again expanding the last logarithmic term in the above equation and neglecting higher terms we get

$$\ln \left(\frac{V_g}{V_l} \right) = \ln \left(\frac{RT}{PV_l} \right) + \frac{B_2 P}{R^2 T^2} \dots \quad (8)$$

Substituting equation (8) in equation (7)

$$RT(1 - \ln x) = B_2 \left(\frac{1}{V_l} + \frac{P}{R^2 T^2} \right) + \frac{B_3}{2V_l^2} + \frac{B_4}{3V_l^3} + \frac{B_5}{4V_l^4} \dots \quad (9)$$

where $x = RT/PV_l$. Solving the determinant for C_1 from Eqs. (2), (4), (5), (6) and (9) and neglecting minor terms as in the previous case⁸, we get

$$(10 - C_1) = \beta P x (12 \ln x - 31) \dots \quad (10)$$

The above equation has been applied to both polar and non-polar liquids.

*The other root is not considered since it is negative which cannot be the case.

TABLE 1 — CALCULATED AND EXPERIMENTAL VALUES OF C_1 FOR DIFFERENT FLUIDS

Liquid	Present work	Exp.	Previous work
HYDROCARBONS			
Pentane	8.09	—	6.74
Hexane	8.47	7.75	7.58
Heptane	8.47	—	7.65
Octane	8.60	8.5	7.96
Benzene	8.36	8.0	7.40
Toluene	8.41	8.0	7.56
ETHERS			
Methyl acetate	8.30	8.0	7.23
Ethyl acetate	8.37	8.0	7.44
Ethyl propionate	8.44	8.0	7.64
Methyl butyrate	8.45	8.5	7.64
Ethyl butyrate	8.49	8.5	7.61
ALCOHOLS			
Water	3.70	4.6	2.3
Methyl alcohol	5.75	8.8	2.0
Ethyl alcohol	6.47	5.4	3.4
Amyl alcohol	7.93	6.0	5.7
Isoamyl alcohol	7.76	8.7	6.2
n-Butyl alcohol	7.52	9.0	5.7
tert-Butyl alcohol	7.30	10.0	6.7
MISCELLANEOUS			
Carbon tetrachloride	8.41	8.6	7.5
Mercury	9.88	6.8	8.1
Carbon disulphide	8.20	7.5	7.0
Chloroform	8.28	8.2	7.2
Valeric acid	7.54	9.5	—

The agreement between calculated and observed values of C_1 appears to have been improved considerably.

Further, it may be pointed out that Eq. (10) gives, in general, higher values while the previous equation with ideal gas assumption gave lower values⁸. Thus it appears that the assumption of non-ideality appears to give better agreement with experiment as expected because as is well known highly polar vapours are imperfect in the vapour phase even at lower pressures. The present calculated values, and the experimental and previous calculated values⁸ are given in Table 1.

The authors are thankful to Dr A. B. Biswas for his keen interest in this work.

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A Finite Virial Expansion of Fluid State*

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A method has been outlined to extend the virial equation so as to include a finite number of higher virial coefficients. An equation has been derived between

$$C_1 \equiv \left[\frac{\partial(1/\beta)}{\partial P} \right]_T$$

vapour pressure and compressibility coefficient using the virial equation up to the seventh virial coefficient. The equation has been applied to a number of polar liquids and the calculated values of C_1 are in good agreement with the observed values.

It is customary to represent the pressure (P) of a fluid as a polynomial of V^{-1} so as to correlate the various equilibrium properties of fluids^{1,2}. It is also known that the complete equation of fluids must be of odd degree in V , for the volume increases with diminishing pressure at both ends of the P - V curve. Further, the equation must be of at least third degree in volume since a certain pressure may correspond to more than one volume. Thus the famous van der Waals equation satisfying these conditions has been of great use in interpreting the relations of liquid and vapour. In the previous paper² the equation of the fifth degree in volume has been successfully used to obtain a relation between vapour pressure and intermolecular energy constants of liquids. In the present communication it is demonstrated how such a representation can be extended to use the higher powers of volume.

Thus by adopting the method previously described by the authors^{1,2} and extending it up to the seventh power, the following equations can be written:

$$P = \frac{RT}{V_g} + \frac{B_2}{V_g^2} + \frac{B_3}{V_g^3} + \frac{B_4}{V_g^4} + \frac{B_5}{V_g^5} + \frac{B_6}{V_g^6} + \frac{B_7}{V_g^7} \dots \dots \dots (1)$$

$$P = \frac{RT}{V_l} + \frac{B_2}{V_l^2} + \frac{B_3}{V_l^3} + \frac{B_4}{V_l^4} + \frac{B_5}{V_l^5} + \frac{B_6}{V_l^6} + \frac{B_7}{V_l^7} \dots \dots \dots (2)$$

$$RT(1 - \ln x) = \frac{B_2}{V_l} + \frac{B_3}{2V_l^2} + \frac{B_4}{3V_l^3} + \frac{B_5}{4V_l^4} + \frac{B_6}{5V_l^5} + \frac{B_7}{6V_l^6} \dots \dots \dots (3)$$

$$1/\beta = \frac{RT}{V_l} + \frac{2B_2}{V_l^2} + \frac{3B_3}{V_l^3} + \frac{4B_4}{V_l^4} + \frac{5B_5}{V_l^5} + \frac{6B_6}{V_l^6} + \frac{7B_7}{V_l^7} \dots \dots \dots (4)$$

$$\frac{C_1}{\beta} = \frac{RT}{V_l} + \frac{4B_2}{V_l^2} + \frac{9B_3}{V_l^3} + \frac{16B_4}{V_l^4} + \frac{25B_5}{V_l^5} + \frac{36B_6}{V_l^6} + \frac{49B_7}{V_l^7} \dots \dots \dots (5)$$

where R is universal gas constant; T , temperature in absolute degrees; V_g , volume of gas; V_l , volume of liquid; $B_2, B_3 \dots B_7$, the virial coefficients; β , the compressibility coefficient; $C_1 \equiv \left[\frac{\partial(1/\beta)}{\partial P} \right]_T$; and $x = RT/PV_l$.

It has been shown^{3,4} that both for non-polar as well as polar liquids, the pressure change of bulk modulus is constant and was related to intermolecular energy constants (C_1). Hence Eq. (5) can be differentiated and further equations can be obtained

TABLE 1 — EXPERIMENTAL AND CALCULATED VALUES OF C_1

Liquid	Temp. °C.	V_l ml.	P mm. (ref. 5, 6)	βX (10 ⁶ atm. ⁻¹) (ref. 5, 7, 8)	C_1	
					Calc.	Exp. (ref. 5, 7, 9)
Water	20	18.0	17.50	47.0	4.07	4.60
Methyl alcohol	0	40.0	30.00	90.0	6.40	8.80
Ethyl alcohol	0	57.0	12.20	100.0	7.80	5.40
Amyl alcohol	18	108.0	2.50	91.0	10.43	6.00
Isoamyl alcohol	20	109.0	2.30	99.0	10.18	8.70
<i>n</i> -Butyl alcohol	20	92.0	4.30	97.0	9.83	9.00
<i>tert</i> -Butyl alcohol	20	74.1	30.60	108.0	9.48	10.00
Ethyl chloride	0	70.0	485.00	135.0	8.70	10.14
Ethyl bromide	20	76.2	386.00	114.6	9.47	10.45
Isobutyl alcohol	20	92.5	8.70	105.3	9.90	12.60
<i>n</i> -Propyl alcohol	20	75.0	14.50	89.6	9.85	8.90
Ethyl iodide	20	80.6	108.50	98.8	10.76	9.60
Valeric acid	20	108.0	0.45	90.0	9.84	9.50

to solve for higher virial coefficients in any finite virial expansion.

Thus if we differentiate Eq. (5) twice we get the following two equations:

$$\frac{C_1^2}{\beta} = \frac{RT}{V_l} + \frac{8B_2}{V_l^2} + \frac{27B_3}{V_l^3} + \frac{64B_4}{V_l^4} + \frac{125B_5}{V_l^5} + \frac{216B_6}{V_l^6} + \frac{343B_7}{V_l^7} \dots \dots \dots (6)$$

$$\frac{C_1^3}{\beta} = \frac{RT}{V_l} + \frac{16B_2}{V_l^2} + \frac{81B_3}{V_l^3} + \frac{256B_4}{V_l^4} + \frac{625B_5}{V_l^5} + \frac{1296B_6}{V_l^6} + \frac{2401B_7}{V_l^7} \dots \dots \dots (7)$$

This procedure can be extended to include higher virial coefficients by differentiating Eq. (7) and so on.

From Eqs. (1) to (7) one can solve for $1/\beta$ in a straightforward way and get

$$C_1^3 - 24C_1^2 + 221C_1 - 954 = \frac{RT\beta}{V_l} (1764 - 720 \ln x) - 1800P\beta$$

In deriving the above relation it was assumed that the vapour behaves ideally and that the volume of liquid is negligible in comparison with that of vapour. In the above equation the term $1800P\beta$ is of the order of 10^{-3} whereas the other terms are very large and hence can be safely neglected. Therefore, the above equation reduces to

$$C_1^3 - 24C_1^2 + 221C_1 - 954 = \frac{RT\beta}{V_l} (1764 - 720 \ln x) \dots \dots \dots (8)$$

Thus Eq. (8) gives a relation between compressibility, vapour pressure and C_1 . Since the equation is cubic in C_1 , it has three possible values. The solution actually gives one real and two imaginary roots† and hence only the real value is considered.

Eq. (8) has been applied to a number of liquids and the calculated values of C_1 are found to be in

†A cubic equation of the type $y^3 + py^2 + qy + r = 0$ can be reduced to the form $X^3 + ax + b = 0$, with $y = x - p/3$, $a = 1/3(3q - p^2)$ and $b = 1/27(2p^3 - 9pq + 27r)$. So if $b^2/4 + a^3/27 > 0$ then there will be one real and two conjugate imaginary roots which is the case with Eq. (8).

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good agreement with the experimental values in the case of polar liquids (Table 1). It may be pointed out at this stage that even though a method has been outlined in this paper for using higher virial coefficients, the procedure may not give accurate results since successive differentiations of Eq. (5) make Eqs. (6) and (7) approximate as any slight inaccuracies in the experimental values will be exaggerated. Unfortunately Eq. (8) has been found to give higher values in the case of non-polar liquids. However, it is important to realize that in principle one can find a method of using higher virial coefficients for finding equilibrium properties provided accurate data of compressibility are available.

The authors are thankful to Dr A. B. Biswas for his keen interest in this work.

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A P P E N D I X - II

INFRARED ABSORPTION STUDIES OF POTASSIUM FERROCYANIDE

Since the water molecules play an important role in the ferroelectricity of potassium ferrocyanide trihydrate, the study of the effect of dehydration on the structure was necessary. Hence infrared absorption spectra were recorded in "Nujol Mulls" on a Perkin-Elmer Model 221, equipped with rock salt prism.

Results and Discussion

$K_4Fe(CN)_6 \cdot 3H_2O$	$K_4Fe(CN)_6 \cdot 11H_2O$	$K_4Fe(CN)_6$	Assignment
3571 ssh	3571 msh	-	$\nu \left\{ \begin{array}{l} H_2O \end{array} \right.$
3509 sb	3509 sb	-	
3367 sb	3367 sb	-	
2037 ss	2037 ss	2037 ss	C-N stretching
1637 msh	1637 msh	-	δ (O-H)
1613 ss	1613 msh	-	

The C-N stretching vibration remains undisturbed on dehydration of the hydrated salt. Other vibrations could not be studied for want of facilities.

The results for the hydrate, from which the anhydrous salt has been prepared, agree well with those available in literature (1).

Reference

- (1) F.A. Miller and C.H. Wilkins, Anal. Chem., 24, 1253-94 (1952).

A P P E N D I X - I I I

THERMOGRAVIMETRIC ANALYSIS OF POTASSIUM FERROCYANIDE TRIHYDRATE

Since ferroelectricity in potassium ferrocyanide trihydrate is attributed to some mode change of the rotational motion of the water molecules, it was considered worthwhile to carry out thermogravimetric analysis of potassium ferrocyanide trihydrate in air so that some useful information would be obtained about the dehydration process.

Experimental

A silica spring balance type apparatus designed and constructed in our laboratory was used for this purpose.

A known weight (approximately 25 mg) of finely powdered freshly crystallized potassium ferrocyanide was taken in an aluminium bucket and hung from a calibrated quartz spring balance, which had a sensitivity (elongation) of 40.67 cm/gm.

Temperature was raised by a resistance heating furnace at a constant linear rate of about $2^{\circ}\text{C}/\text{min}$. using a temperature regulator and a variac. Temperatures were calculated from the e.m.f. values of a calibrated chromel-alumel thermocouple which was kept in a close vicinity of the sample in the furnace.

A travelling microscope having least count of 0.001 cm was used to observe the change in length of the spring.

Results and Discussion

Potassium ferrocyanide trihydrate starts losing water molecules at about 60°C. One molecule of water gets completely lost between 60°-85°C. Another molecule is removed between 85°-92°C while the third one is expelled rather rapidly at 94°C.

It may be presumed that if the rate of heating had been slower, dehydration would have been complete at a slightly lesser temperature viz. 90°C vide preparation of anhydrous potassium ferrocyanide⁽¹⁾ and dehydration data available in literature⁽²⁾.

References

- (1) R.B. Loftfield and E. Swift, Jr., J. Am. Chem. Soc., 60, 3083-84 (1938).
- (2) K. Masuno and S. Waku, Nippon Kagaku Zasshi, 83, 116-7 (1962).

A P P E N D I X - I V

X-RAY ANALYSIS OF POTASSIUM FERROCYANIDE

Potassium ferrocyanide and its trihydrate were analysed by X-ray diffraction using a 14 cm Debye-Scherrer camera and Mo-K α ($\lambda = 0.709 \text{ \AA}$) radiation filtered through a zirconium foil. The 'd' values were calculated in the usual manner and were found to be in excellent agreement with the observed data⁽¹⁾. In the case of anhydrous potassium ferrocyanide the unit cell was determined by indexing the pattern with the help of the standard c/a vs log d chart for tetragonal symmetry. Comparison of the lattice constants thus obtained with the work of Pospelov et al.⁽²⁾ and Kiriyama et al.⁽³⁾ showed satisfactory agreement.

References

- (1) ASTM Index Cards for $K_4Fe(CN)_6$ and $K_4Fe(CN)_6 \cdot 3H_2O$.
- (2) V.A. Pospelov and G.S. Zdanov, Z. Fiz. khim. SSSR, 21, 405, 521, 879 (1947); Also Structure Report, AI, 421, 424.
- (3) R. Kiriyama, H. Kiriyama, T. Wada, N. Niizeki and H. Hirabayashi, J. Phys. Soc. Japan, 19, 540-49 (1964).

A C K N O W L E D G E M E N T

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