UNIVERSITY OF SOUTHAMPTON

Department of Chemistry

STUDIES OF THE ELECTRICAL CONDUCTIVITY OF MOLTEN METAL ALKANOATES

A Thesis submitted for the Degree of

Master of Philosophy

by

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ABSTRACT

FACULTY OF SCIENCE

CHEMISTRY

Master of Philosophy

STUDIES OF THE ELECTRICAL CONDUCTIVITY OF MOLTEN METAL ALKANOATES.

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The electrical conductivity of molten alkali metal acetates and formates was measured under nitrogen, at pressures of up to approximately 1 kbar. Log conductivity showed a linear decrease with increasing pressure, and gradients were found to be similar to those of the alkali metal nitrates and nitrites. This behaviour was entirely consistent with that which would be expected from fully ionised salts.

Some preliminary work was also carried out on longer chain alkali and zinc carboxylates.

Acknowledgements

My main thanks are due to my supervisor Dr. B. Cleaver for his skilful guidance and well-judged advice. Thanks are also due to Mr. M Caplin and the other glass-blowers for making the cells and other non-standard glassware, to Dr. D. Adams for advice on molecular dynamics simulations, and to Mr. P. Francis for making the multiplexer.

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CONTENTS

1. Introduction

1. INTRODUCTION

Aim of the present work

Some work has been carried out at high pressure on inorganic molten salts, phase behaviour and electrical conductivity having been studied for various compounds(2). However no work had previously been carried out at high pressure on salts with organic ions. This is a very large and potentially valuable field of study. Organic ions cover a wider range of size than inorganic ions, giving a wider variety of behaviour. For example some long chain ions show a liquid crystal phase, which might usefully be studied. In addition some compounds are only partially dissociated and consequently have very low conductivity. The aim of this project was to begin the investigation of this large class of compounds, starting with conductivity measurements on the simplest organic salts, namely the alkali acetates and formates, and exploring ways in which research on organic molten salts might be furthered.

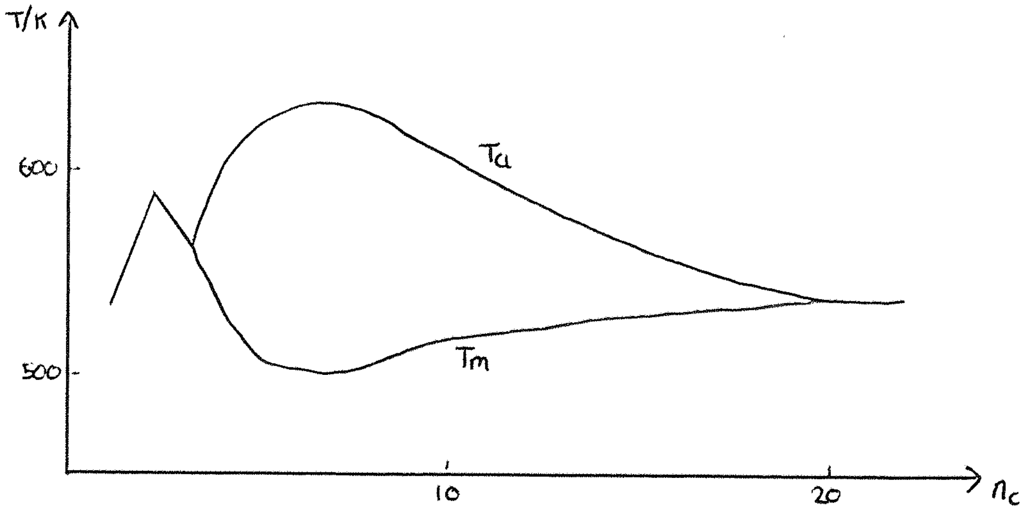
Carboxylates

Carboxylates is the name given to the group of compounds of formula $M^{m+}(C_nH_{2n+1}CO_2^-)_m$. Being the simplest and most readily available group of salts containing organic anions they have been very widely studied(3).

Extensive studies have been carried out in the molten state, and phase transition temperatures and transport properties have been measured. The longer chain alkali carboxylates ($n \geq 4$ for Na salts) are somewhat unusual amongst molten salts in that they show an anisotropic phase between the solid and isotropic liquid phases. In addition the very long chain homologues may contain plastic phases between the crystalline solid and the anisotropic liquid phases.

Values of the solid to mesophase transition temperature (melting temperature, T_m), and the mesophase to isotropic liquid transition temperature (clearing temperature, T_{cl}) have been obtained for many salts, and these may be plotted on a diagram, for example:

T_m and T_{cl} vs. chain length for sodium carboxylates(4)



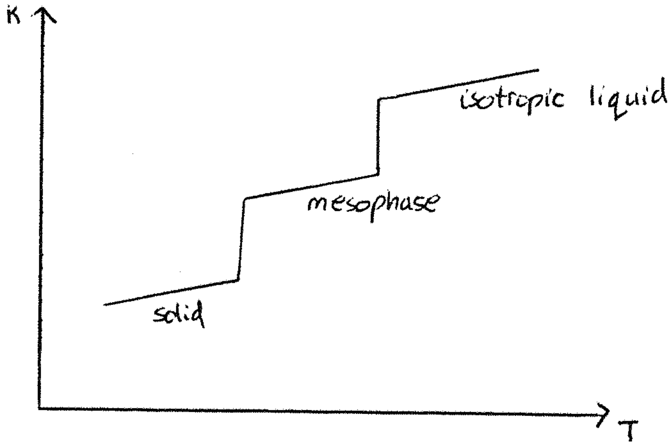
The carbon chains of the anions show a mutual affinity and will tend to align, which, when added to the mutual attraction of anion and cation, results in a tendency for layer structures in the mesophase(5,6,). The temperature range of existence of mesophases also increases substantially on replacing the sodium ion with a potassium ion(4). The mesophases differ in several respects from liquid crystals which include chiefly rod shaped molecules with long rigid parts. In particular, the anions of Na salts with $n < 6$ are quasiglobular and considerably smaller than any neutral molecule forming a liquid crystal phase(7). In the case of these small ions rotation is thought to be hindered and long range electrostatic forces impose long range ordering in the mesophase over 10^4 molecules.

The conductivity of some of the alkali acetates and formates has been measured (see chapter 5), as has the conductivity of the long chain zinc and lead carboxylates(8), some of which also form mesophases(8, 9). The conductivity κ of the acetates and formates, which are purely ionic, is slightly lower than that of a classical molten salt, for which $\kappa \sim 1 \mathrm{S cm^{-1}}$. The conductivity of the long chain carboxylates is several orders of magnitude lower.

This lower conductivity may be attributed to the very low degree of dissociation in the salt, or to the low mobility of ions within the melt. The principal charge carrier is thought to be the cation(10), complicated by the presence of micellar aggregates in both the mesophase and isotropic liquid(9, 11, 12).

Dissociation is accompanied by a volume decrease and so is favoured by pressure. Increasing pressure will therefore increase the degree of dissociation, and hence the number of free ions in the melt. Electrical conductivity will correspondingly increase.

The electrical conductivity of a mesophase is typically intermediate between that of the solid and that of the isotropic liquid thus(7, 13, 14):



Thermal stability of carboxylates

Organic ionic melts are far less stable than the crystals from which they originate. A high melting point means that the liquid state can only be investigated at temperatures where sufficient energy for numerous decomposition reactions is available. Furthermore, the free volume necessary to allow the volume increase accompanying activation is readily available in a melt, but not in a crystal lattice.

Chemical stability of the melt is greatly increased by the suppression of OH^- and the elimination of molecular oxygen, water, and transition metal ions(7,15,16). The limiting temperature for stability is about 350°C; above this temperature the anion undergoes spontaneous rupture into fragments, thermal energy being sufficient for bond breakage, e.g.:

$$RCH_2COO^- \longrightarrow OH^- + RCH{=}CO$$

(autocatalytic)

Electrical conductivity

When an electric field is impressed on a liquid the resulting ionic current(I) is defined as the rate of flow of charge, i.e:

$I=dq/dt$ (1)

where dq is the charge that passes through cross sectional area A in time dt. The current density(J), or net flux of charge is given by:

$J=I/A$ (2)

and the conductivity(κ) is defined by:

$\kappa=J/E$ (3)

and

$\rho=1/\kappa$ (4)

E is the electric field, $-d\phi/dx$. ρ is the resistivity. If ρ is independent of E then the conductor obeys Ohm's law. Under such circumstances the resistance is a measurable quantity defined by:

$R = dV/I$ (5)

where dV is the p.d. between the extremities of the conducting path of length L. dV is related to E by:

$$V = \int_0^L E.dL = EL \quad (6)$$

therefore from (6), (3) and (2):

$V = IL/\kappa A$ (7)

and from (7), (4) and (5):

$\rho = R(A/L)$ (8)

and

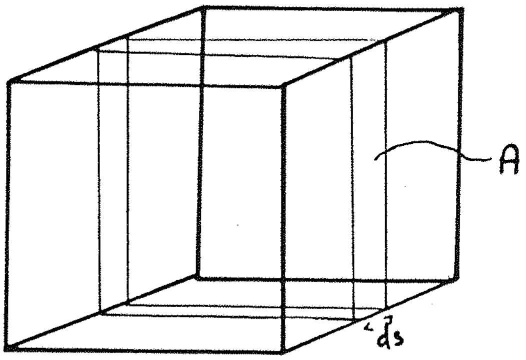
$\kappa = \sigma(L/A)$ (9)

Where σ is the conductance 1/R.

The ratio L/A is known as the cell constant and remains invariant at constant T and P. It may be determined by measuring L and A directly or, more conveniently, by calibration with an electrolyte of known conductivity.

If it is considered that conductance arises from the movement of ions in the electrolyte and that the total current is the sum of the currents carried by individual ions then an expression may be derived for the conductivity in terms of ionic mobilities and transport numbers. The former refers to the velocities of the ions and the latter to the proportion of the charge carried by each type of ion. If an ion i has charge $z_i e$ then under the influence of an electric field E it will give rise to an electric current density J_i.

Consider a conduction path of cross sectional area A:



In time dt ions with drift velocity (terminal velocity) v_i will travel distance ds, so all ions in volume ds.A will pass through the cross section. From (1) and (2):

$J=dq/dt.1/A$

dq=amount of charge passing through cross sectional area A in time dt

=no. of ions in volume A.ds x charge on ion

=A.ds x no. per unit volume x charge on ion

$=z_i eAv_i\, dt\ c_i N_A$ (c_i = molar concentration of ion i
N_A is Avagadro's number)

so:

$J_i=z_i eAv_i dtc_i N_A/dtA$ (10)

If all velocities are considered positive then::

$J_i=|z_i|Fv_i c_i$ (11)

where F is the Faraday constant=$N_A e$

Therefore total current density due to all ions is:

$J=\sum_i |z_i| Fc_i v$ (12)

and since $J=\kappa E$:

$$\kappa = \sum_i |z_i| F c_i (v_i/E) \qquad (13)$$

At low field strengths κ is independent of E. This implies that for a fixed concentration of ion i, the ratio of (v_i/E) must be constant and characteristic of ion i. This ratio is called the electrical mobility u_i. The terminal velocity of an ion is therefore proportional to the applied field E, and the proportionality constant is the ionic mobility. When mobilities are included in the expression for κ, eqn13 becomes:

$$\kappa = \sum_i |z_i| F u_i c_i \qquad (14)$$

The transport number t_i for ion i is defined as the fraction of the total current carried by that ion:

$$t_i = J_i/J \qquad (15)$$

From expressions 3,8,11, and given $u_i = v_i/E$:

$$t_i = |z_i| F c_i u_i/\kappa \qquad (16)$$

Thus the transport number of ion i can be calculated from its mobility. The sum of transport numbers over all ionic species is unity.

$$\Sigma t_i = 1 \qquad (17)$$

Experimental observations have shown that κ is a function of several variables, most notably temperature and pressure.

The temperature dependence of κ may be described by the Arrhenius equations:

$$\left(\frac{\partial \ln \kappa}{\partial (1/T)}\right)_V = \frac{-(E_\kappa)_V}{R} \qquad (18)$$

$$\left(\frac{\partial \ln \kappa}{\partial (1/T)}\right)_p = \frac{-(E_\kappa)_p}{R} \qquad (19)$$

Studies of pressure dependence in the range up to approximately 1 kbar have shown that $\ln\kappa$ varies linearly with P for a purely ionic compound, and it is convenient to represent results in the form of activation volumes, defined empirically by:

$$\Delta V_{\kappa} = -RT\left(\frac{\partial \ln \kappa}{\partial P}\right)_T \qquad (20)$$

Activation volumes are related to activation energies by:

$$(E_{\kappa})_{P} = (E_{\kappa})_{V} + \gamma_{V} T \Delta V_{\kappa} \qquad (21)$$

Where γ_V is $(\partial P/\partial T)_V$.

It should be noted that the use of the terms activation energy and activation volume does not imply the validity of a model for conduction based on singly activated ions or sites. The linear Arrhenius type relationships do however indicate that the process is dependent on generalised thermal activation of the bulk liquid.

If measurements of the variation in conductivity with pressure are being carried out it is necessary that temperature be controlled to within better than +/- 0.5K.

From (19):

$\kappa = A\exp(-E/RT)$

so:

$d\kappa/dT = A\exp(-E/RT).E/RT^2$

so:

$d\kappa/dT = \kappa.E/RT^2$

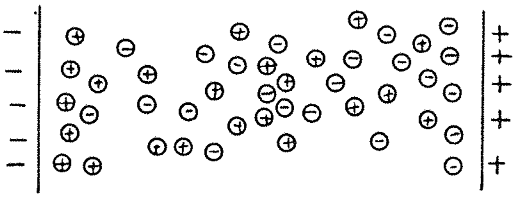
so:

$d\kappa/\kappa = dT.E/RT^2$

E will be typically 12000$Jmol^{-1}$, T will be of the order of 600K, so if dT=0.5K $d\kappa/\kappa=0.002$. So a temperature change of 0.5 °C produces a change in κ of 0.2%, which is significant in comparison with the size of the changes due to pressure over the range being measured.

AC impedance

Conductance at the electrode surfaces is due to the formation of electrical double layers which may be represented schematically thus:



In an ideal conductivity experiment, no charge transfer takes place between ions and electrodes. In practice it is usual to measure AC impedance to avoid electrode polarisation effects, which would cause d.c. conductance to fall rapidly to zero.

Impedance may be represented as a complex quantity having the following properties:

i)impedances combine like resistances, that is impedances in series add, while if in parallel their reciprocals add.

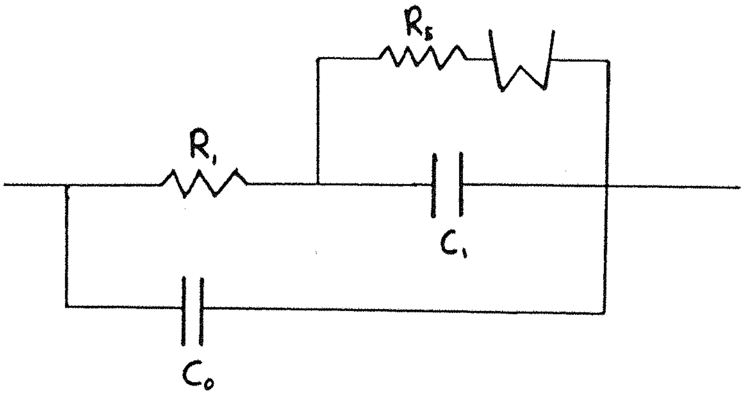
ii) a pure resistance R has an impedance Z=R which is a real quantity.

iii) a perfect capacitor of capacity c has impedence $z=1/j\omega C$ where ω is angular frequency and j is an operator having the mathematical properties of i, which represents a $\pi/2$ phase displacement between current and potential.

iv) a pure inductance L has impedence $Z=j\omega L$.

The object of measurements is to determine the pure ohmic resistance of the salt between the electrodes. In practice there are other sources of impedance, and the cell may be represented schematically by diagram 1.1. Effects associated with the relaxation of ionic atmospheres do not become appreciable until the MHz range.

Diagram 1.1: Network electrically equivalent to the conductance cell (17)



R_1 =ohmic resistance

C_0 =lead capacitance

C_1 =double layer capacitance at the electrode surfaces, minimized by making ω high (2KHz)

R_5 and W are due to electrolysis and should be negligible.

W is the Warburg impedance

2. EXPERIMENTAL METHODS

Experimental methods for measuring conductance

Bridge balancing methods may be used to measure the AC impedance of a molten salt. These are accurate, straightforward, and the necessary apparatus is readily available.

A transformer ratio arm bridge allows a wide range of conductivities to be measured. A simplified circuit diagram of this type of bridge is shown in diagram 2.1. A voltage from the source is applied to both arms of the bridge, inducing opposing fluxes in the primary coil of T2. When the flux in the primary of T2 between A and NP is equal and opposite to that between B and NP the induced voltage in the secondary of T2 will be zero. This balance point will be indicated by the detector connected to the secondary coil of the current transformer T2. In this condition:

$na.ia = nb.ib$

so:

$na.va/(zu+za)=nb.vb/(zs+zb)$

zu= unknown impedance
zs=standard impedance
na=no. of turns between NP and A
nb=no. of turns between NP and B
ia=current in coil between NP and A
ib=current in coil between NP and B
za=impedance of coil between NP and A
zb=impedance of coil between NP and B

va and vb are the potentials between C and NP over the arm containing the unknown and standard impedances respectively

From this it can be seen that the bridge may be balanced in three ways:

i) Adjusting the value of the standard impedance.

ii) Applying different potentials to the two arms of the bridge.

iii) Feeding the currents they pass through unequal numbers of turns on the primary of T2.

A selection of taps on the primary of T2 and the secondary of T1 allow a large range of unknown values to be measured.

Over the last few years accurate Digital Volt Meters have become available at relatively low cost and it is now often easier to measure AC impedence by simply measuring the AC potential across the unknown and a standard impedance.

Pressure experimental techniques

For pressures up to about 2kbar, gas, usually oxygen free nitrogen, is the most suitable medium for applying pressure. The sample is held in a container strong enough to withstand the necessary pressures, and gas admitted from a compressor via a valve.

The yield pressure is given by:

$$P_y = \frac{\sigma_y}{\sqrt{3}} \frac{K^2-1}{K^2}$$

The bursting pressure is given by: $P_b = 2\sigma_u \frac{K-1}{K+1}$

$K=r_o/r_i$

σ_y=yield stress of material

σ_u=ultimate tensile strength of material

r_o =outer diameter of vessel

r_i =inner diameter of vessel

Methods for detecting phase transitions

Several methods may be used to detect phase transitions, but not all are suitable for every case. For example, a transition involving a small volume change might escape dilatometric investigation but might be detected by microscopic observation using crossed polaroids. The experimental methods which have been most widely and productively used are:

i) T vs t curves, usually allowing the sample to cool slowly.

ii) Differential Thermal Analysis.

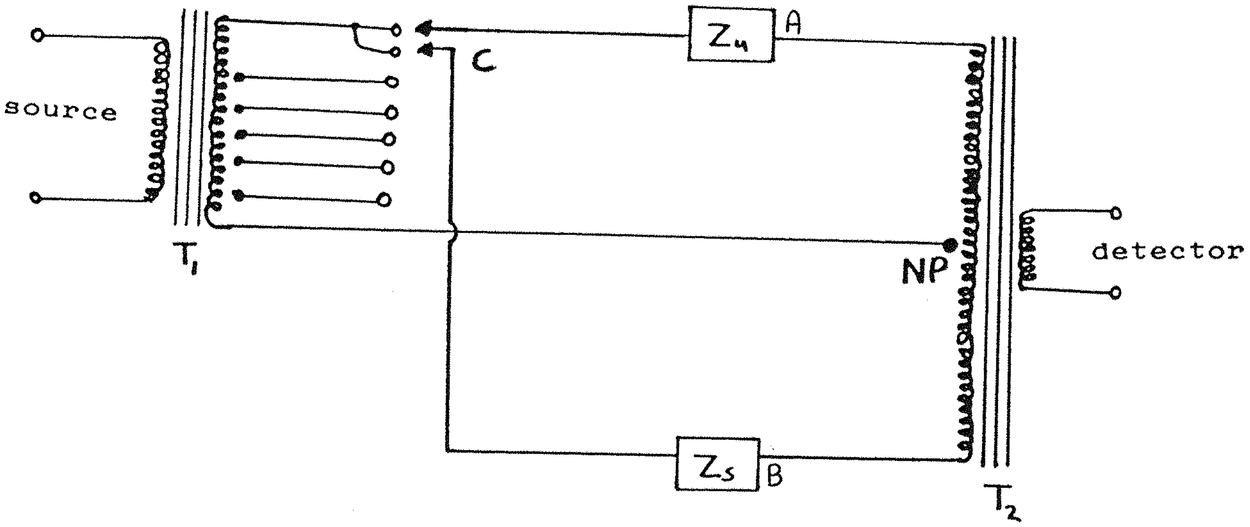
iii) Differential Scanning Calorimetry

iv)Photometric recording of light transmission during heating and cooling.

In both DTA and DSC a small sample and an inert reference material are heated and cooled at the same programmed rate. In DTA equal amounts of energy are supplied to each sample and ΔT vs T is measured. In DSC the energy supplied is enough to keep the samples at the same temperature during heating or cooling and $\partial \Delta q/\partial T$ is recorded, with first order transitions showing as peaks and higher order transitions showing as steps. DTA studies have been carried out at high pressure(18).

Other methods which have been used to study phase transitions include X-ray, NMR, and dielectric permittivity measurements. Alkali metal carboxylate phases have been characterised by birefringence and X-ray diffraction, the former being especially useful for identifying liquid crystal phases(4).

Diagram 2.1. Simplified circuit diagram of transformer ratio arm bridge.



3. EXPERIMENTAL WORK

The electrical conductivity of sodium formate, sodium acetate, potassium formate, potassium acetate and caesium acetate was determined as a function of pressure over the range 0-1kbar. Longer chain sodium carboxylates were tried but were found to undergo decomposition on fusion.

The design of cell used in the experiments is shown in fig.3.1. Another design was tried (fig.3.2) but was found to be difficult to fill and very susceptible to breakage. The cells were made of Pyrex. The cell was assembled and filled with acetone. The inner elements, b and c, were then removed and the level of the acetone marked(m).The cell was then emptied and dried.

The sodium salts were not appreciably hygroscopic and were transferred to the cell outer casing, a, in powdered form in air, after being dried under a pressure of 10^{-2} Torr for several hours at a temperature of 150°C. They were then melted in situ and more salt added until the melt filled the casing up to the mark, m. The cell inner elements b and c were then inserted, and the salt level rose to fill the cell. Caesium acetate was hygroscopic and was fused under vacuum, then pipetted into the cell under air, filling the cell to the mark m. Inner elements b and c were then inserted. The potassium salts were markedly hygroscopic and the fused salts decomposed rapidly on contact with air. The cell was filled using the apparatus shown in fig 3.3. The salt was fused under vacuum in chamber C, and the apparatus tilted to allow salt to run into the cell.

The cell was mounted on the lower flange of the vessel and the electrodes connected to the bridge via insulated cones and wires which passed through the lower flange(fig.3.4). The flange was then raised into the pressure vessel (fig.3.5), which was at a temperature about 10K above the melting point of the salt. The cell was usually inserted with the salt in solid form, but on the occasions when this was found to result in frequent cell breakage the salt was melted with a hot air blower before insertion.

Initially, the a.c. conductivity of a salt was measured using the arrangement shown in fig.3.6, which has been fully described elsewhere(19,20). The pressure was increased, then decreased in successive intervals of between 50 and 200 bar, waiting after each adiabatic pressure change for the temperature to return to its previous level. After the temperature had stabilised, conductivity, pressure and temperature were recorded.

This procedure was found to be tedious and time consuming so a system was developed to perform the experiment automatically. The design for the system is shown in fig.3.7.

The DVM was controlled via the IEEE interface, which was connected to the 1MHz Bus on the BBC. The required input could be selected by switching the multiplex to the appropriate channel. All cables were screened. Tests showed crosstalk and induced emfs to be negligible. The DVM could then be instructed to take a reading, and the value transferred into the computer for storage and later use. Four programs were used to control the system:

i)The experimental program.

The four inputs to be measured - thermocouple emf, transducer emf, pd across the cell, and pd across the standard resistor at each pressure - were each fed into a channel of the multiplex. The program selected the appropriate channel, and instructed the DMM to measure the requisite quantity, which was then transferred into the computer memory via the IEEE interface. The program then changed the pressure.

ii)The data processing program.

This read the unprocessed data from the disc file, calculated pressure, temperature, conductance and log conductance from the e.m.fs and p.d.s., then stored the processed data in new files.

iii)The least squares program.

This fitted the best straight line to the log conductance vs pressure data.

iv) The graphical program.

This plotted the graph of log conductance vs pressure.

In addition there was a program which enabled individual points to be disregarded, and a new fit obtained. Programs were stored on drive 0 and data from the experiment on drive

1. The programs are listed and described in detail in Appendix 1. In practice the automatic pressure valves proved faulty so it was necessary to change the pressure manually when prompted by the program, though all data logging and data processing was carried out automatically. The conductivity of potassium formate was measured using the computer system, all other results were obtained using bridge methods.

A frequency dispersion plot was obtained by measuring the conductivity at frequencies from 1kHz to 20 kHz, and the difference in the values obtained was found to be negligible.

The cell was calibrated using 0.1D KCl at 25°C. Calculations have shown that the difference between this value and the value at 30°C is negligible(21).

FIG 3.1 CELL DESIGN

Appoximately actual size

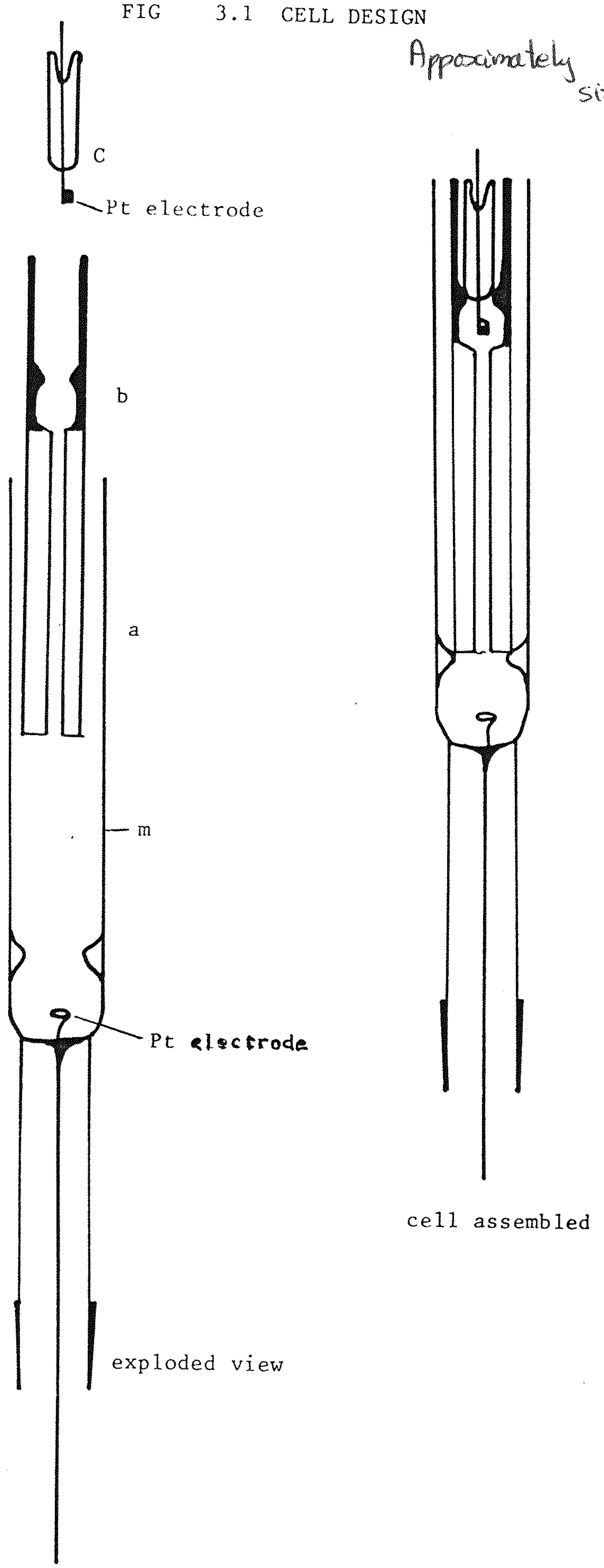


FIG 3.2 EARLIER CELL DESIGN

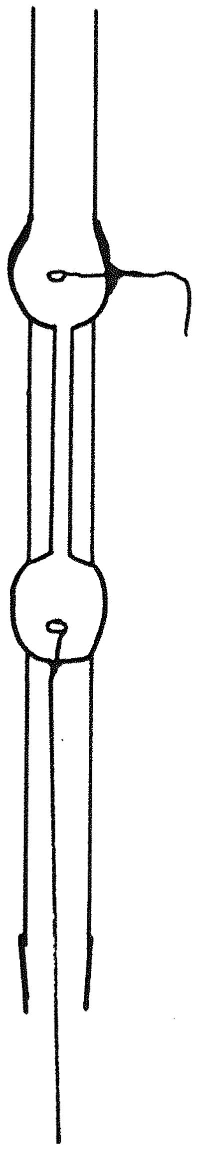


FIG 3.3 CELL FILLING APPARATUS

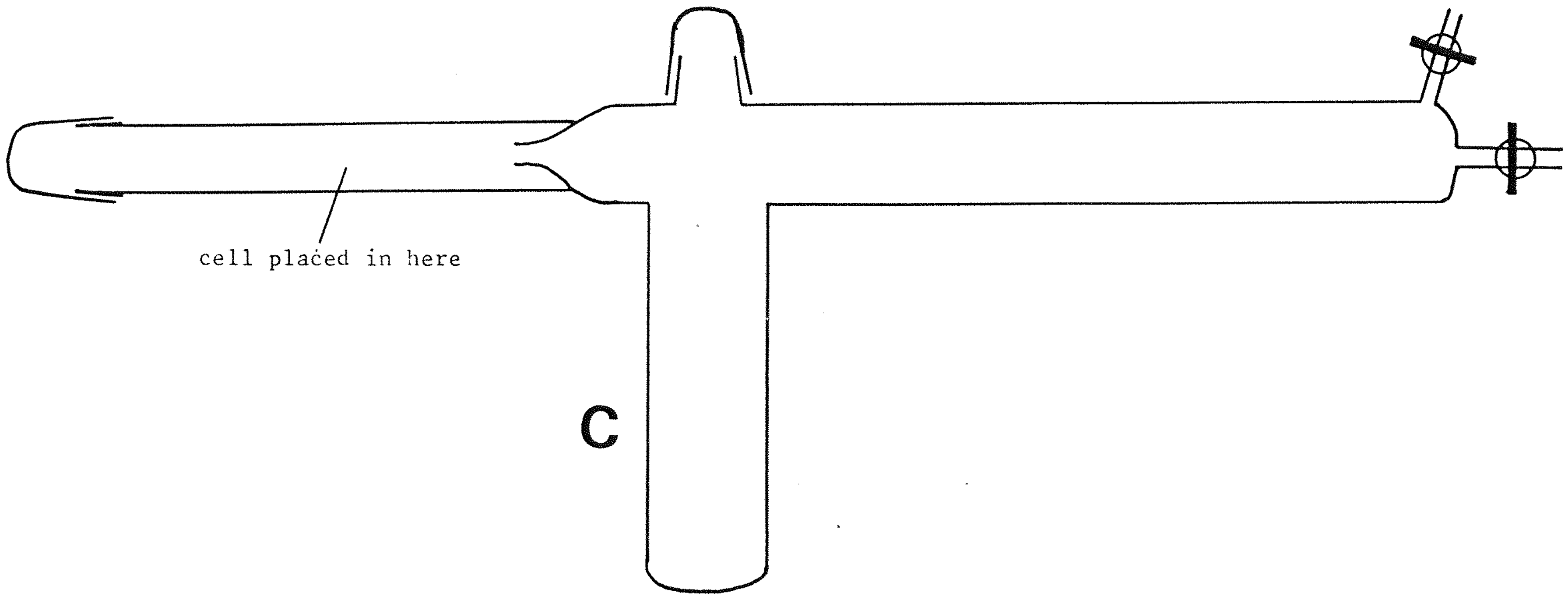
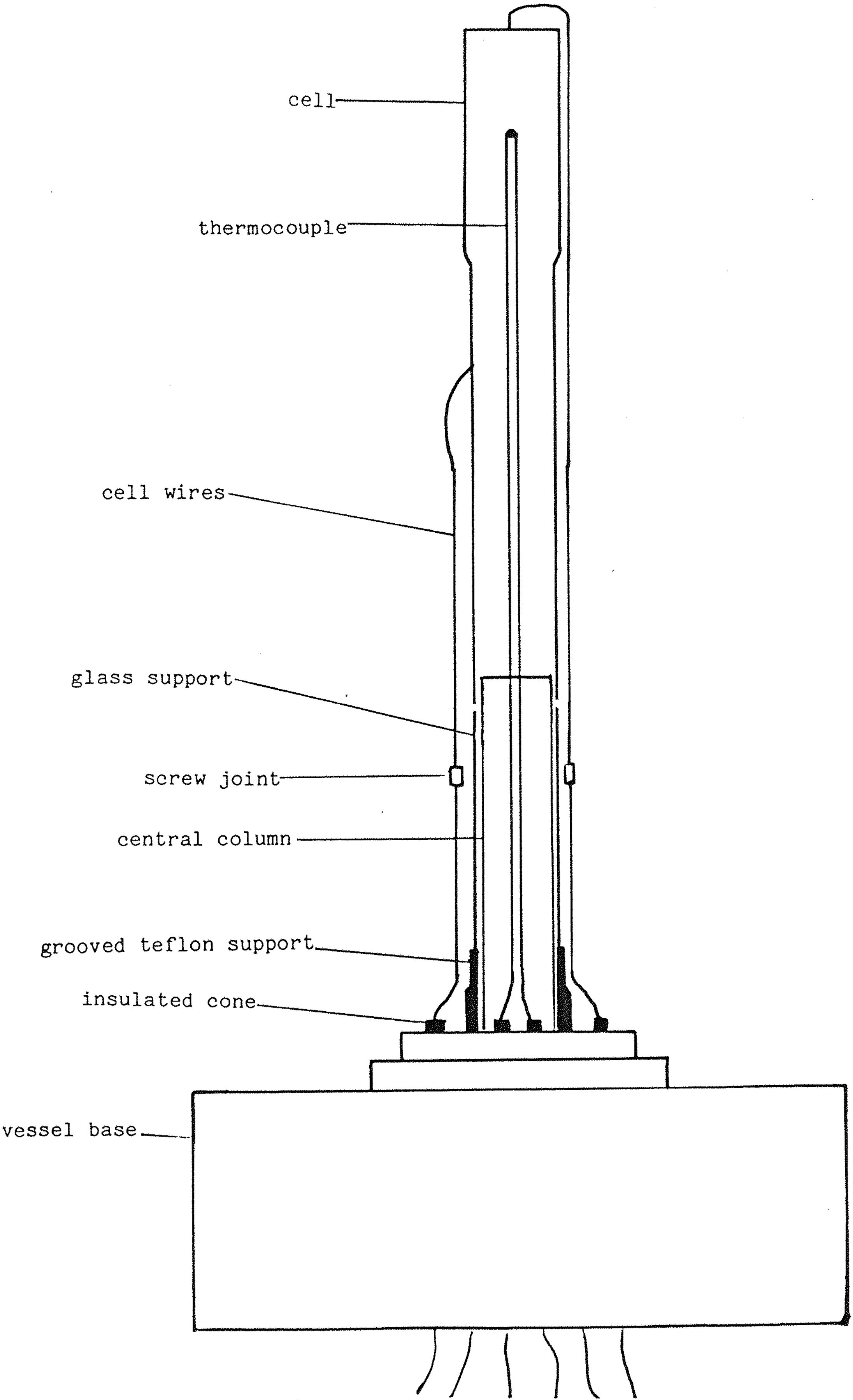


FIG 3.4

CELL AND THERMOCOUPLE ON PRESSURE VESSEL BASE

not to scale



wires from cell and thermocouple

FIG 3.5 PRESSURE VESSEL CONTAINING CELL (NOT TO SCALE)

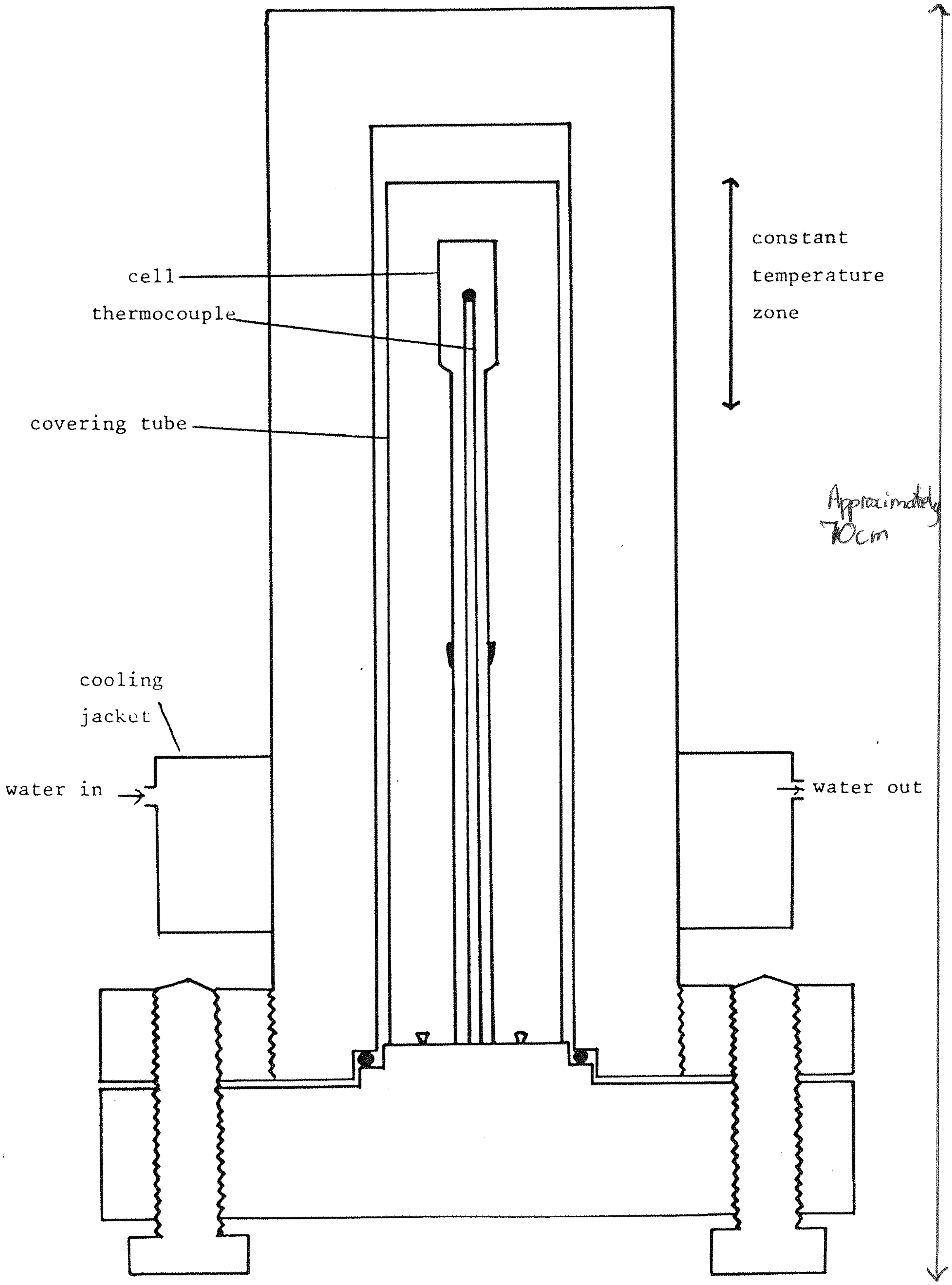


FIG 3.6
ARRANGEMENT FOR MEASURING AC CONDUCTANCE

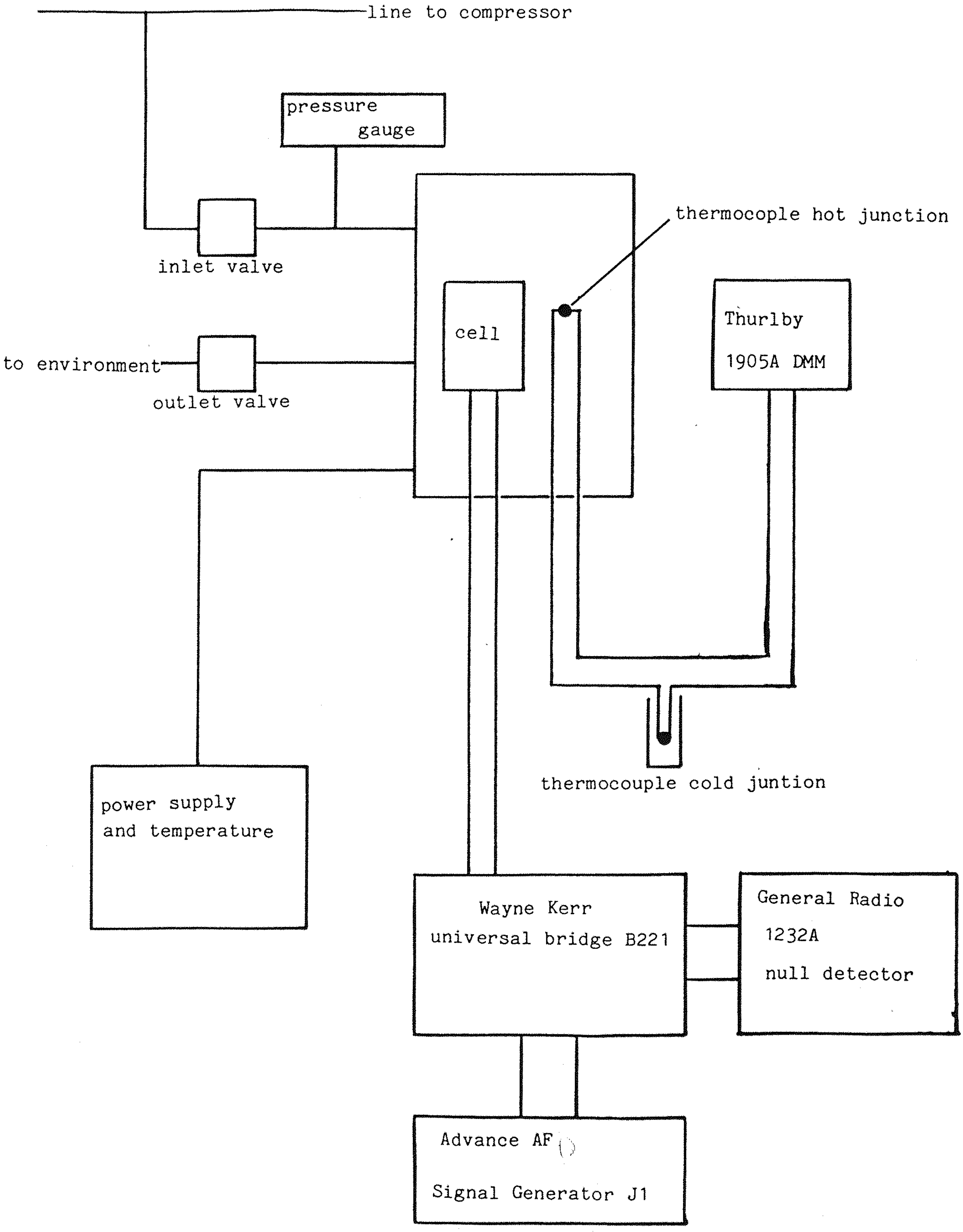
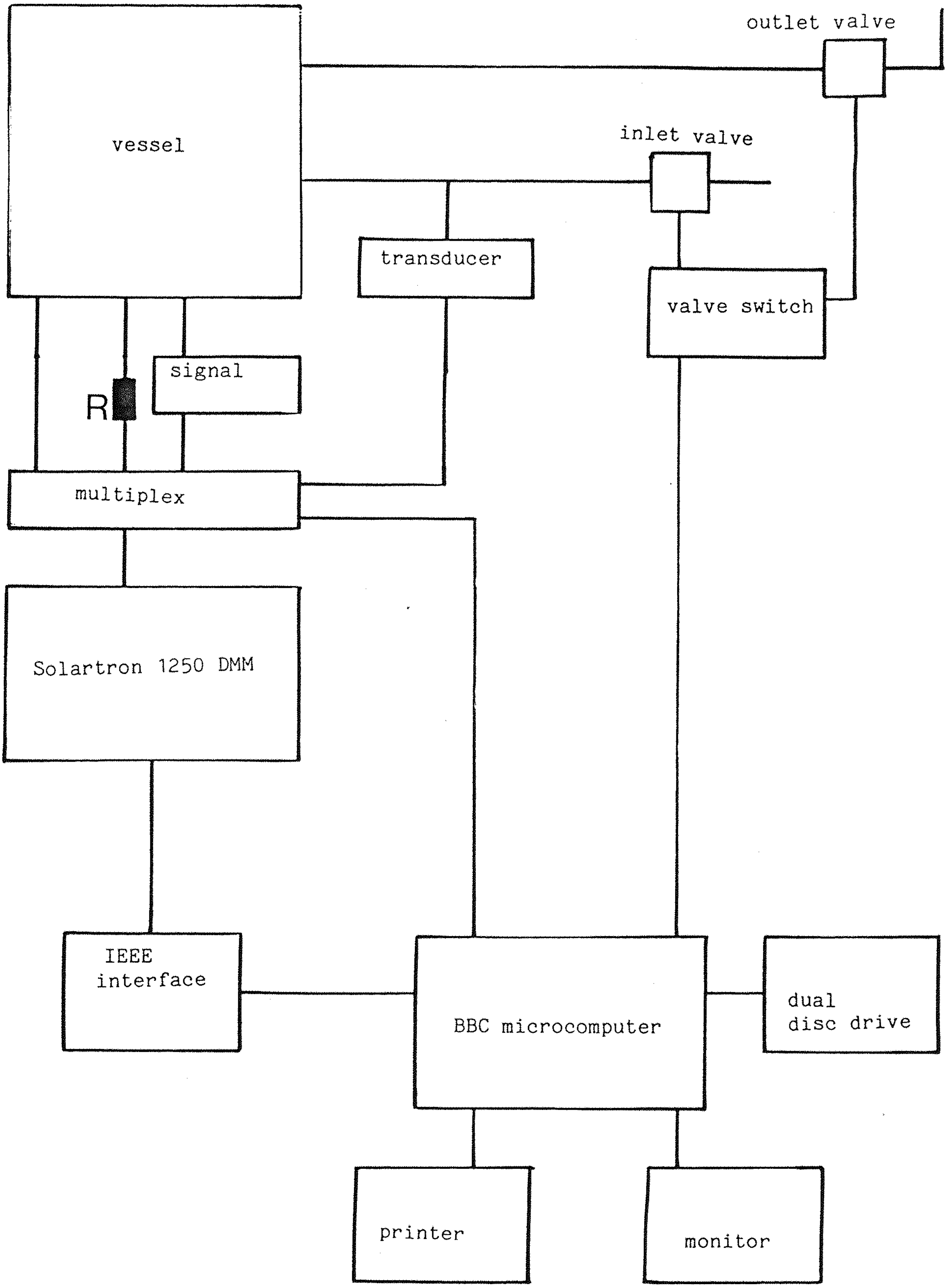


FIG 3.7
DESIGN FOR COMPUTER CONTROL SYSTEM



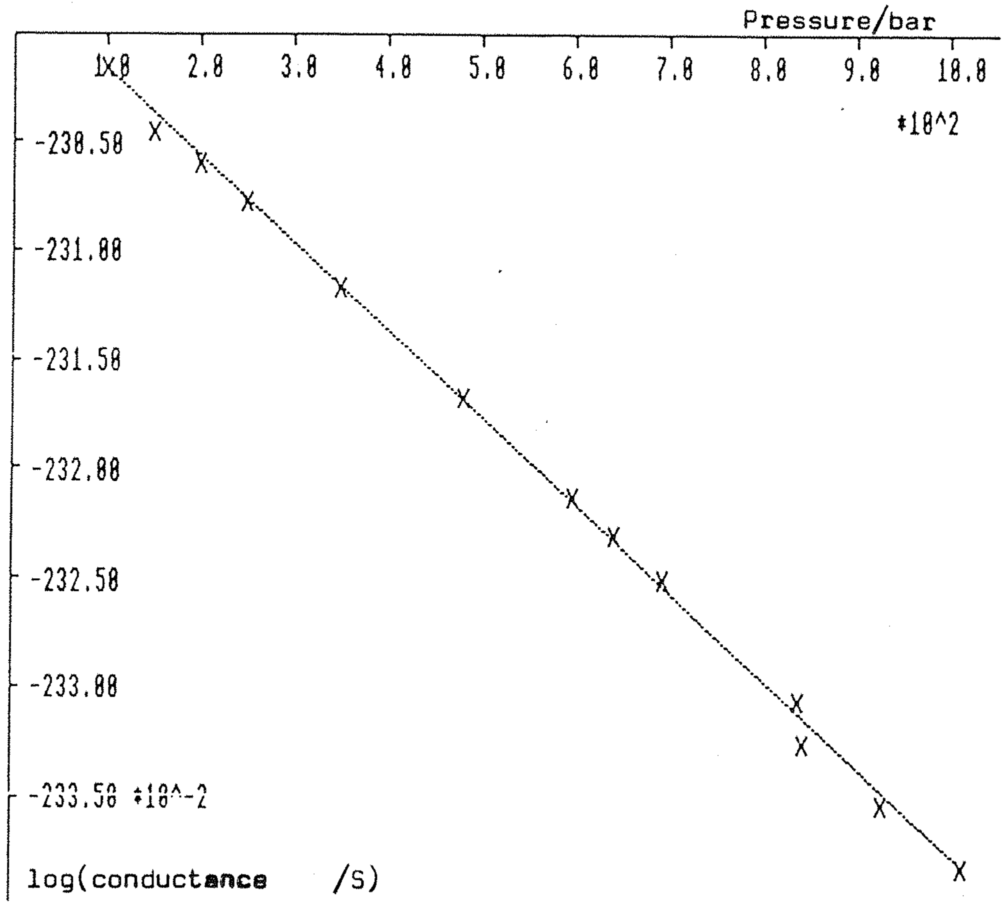
4. RESULTS

```
SODIUM FORMATE

CELL CONSTANT= 8.503E1
TEMP       PRESSURE SIGMA      LOGSIGMA
2.751E2   1.500E2   4.960E-3 -2.304E0
2.751E2   2.500E2   4.924E-3 -2.308E0
2.751E2   3.500E2   4.879E-3 -2.312E0
2.751E2   4.820E2   4.823E-3 -2.317E0
2.751E2   5.980E2   4.773E-3 -2.321E0
2.751E2   6.950E2   4.732E-3 -2.325E0
2.751E2   8.400E2   4.672E-3 -2.331E0
2.751E2   1.015E3   4.591E-3 -2.338E0
2.751E2   9.300E2   4.621E-3 -2.335E0
2.751E2   8.450E2   4.652E-3 -2.332E0
2.751E2   6.430E2   4.752E-3 -2.323E0
2.751E2   2.000E2   4.944E-3 -2.306E0
2.751E2   1.000E2   4.995E-3 -2.301E0

******************************************************************************

SLOPE (M)= -3.973902641E-5
SIGMA M= 4.472495566E-7
INTERCEPT B= -2.297794283
SIGMA B= 2.789945019E-4
STD DEV OF THE FIT= 4.864841794E-4
CORRELATION COEFF (R)= -0.9992306111
SIGMA AT OP= 5.037391637E-3
```



```
SODIUM FORMATE

CELL CONSTANT= 88.65
TEMP      PRESSURE SIGMA      LOGSIGMA
2.690E2   1.500E2  4.506E-3 -2.346E0
2.690E2   1.960E2  4.483E-3 -2.348E0
2.690E2   2.450E2  4.458E-3 -2.351E0
2.690E2   2.990E2  4.434E-3 -2.353E0
2.690E2   3.520E2  4.413E-3 -2.355E0
2.690E2   4.900E2  4.334E-3 -2.363E0
2.690E2   5.950E2  4.292E-3 -2.367E0
2.690E2   6.960E2  4.258E-3 -2.371E0
2.690E2   7.900E2  4.221E-3 -2.375E0
2.690E2   8.980E2  4.187E-3 -2.378E0

************************************************************************

SLOPE (M)= -4.353941628E-5
SIGMA M= 1.040742598E-6
INTERCEPT B= -2.340275523
SIGMA B= 5.549501666E-4
STD DEV OF THE FIT= 8.2208053E-4
CORRELATION COEFF (R)= -0.9974124569
SIGMA AT OP= 4.567982976E-3
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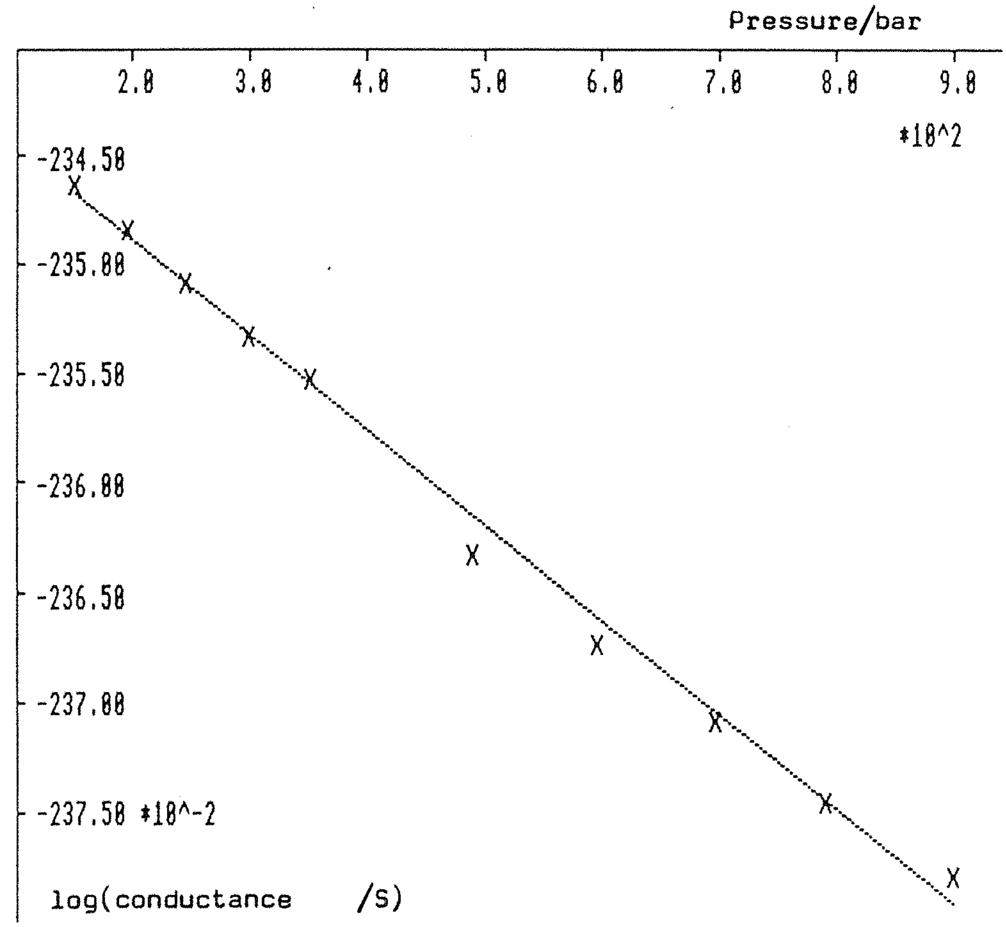
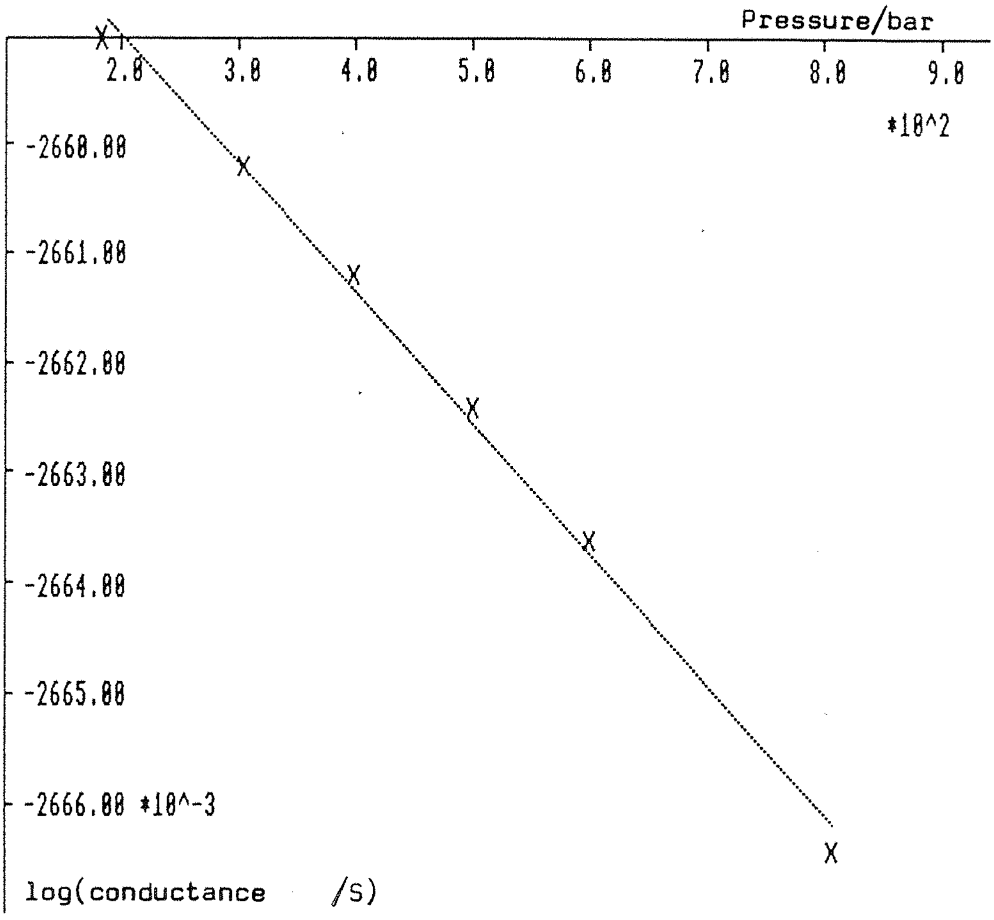


```
SODIUM ACETATE

CELL CONSTANT= 88.65
TEMP      PRESSURE SIGMA     LOGSIGMA
3.454E2   1.840E2  2.193E-3 -2.659E0
3.454E2   3.040E2  2.187E-3 -2.660E0
3.454E2   3.990E2  2.182E-3 -2.661E0
3.454E2   5.000E2  2.176E-3 -2.662E0
3.454E2   6.000E2  2.170E-3 -2.664E0
3.454E2   8.070E2  2.156E-3 -2.666E0

*************************************************************************

SLOPE (M)= -1.192216868E-5
SIGMA M= 3.612515537E-7
INTERCEPT B= -2.656584014
SIGMA B= 1.83417272E-4
STD DEV OF THE FIT= 1.790471937E-4
CORRELATION COEFF (R)= -0.9974876908
SIGMA AT OP= 2.205037532E-3
```



```
PROGRAM TO DETERMINE THE VARIATION OF CONDUCTIVITY WITH PRESSURE

ENTER NAME OF COMPOUND:  POTASSIUM FORMATE

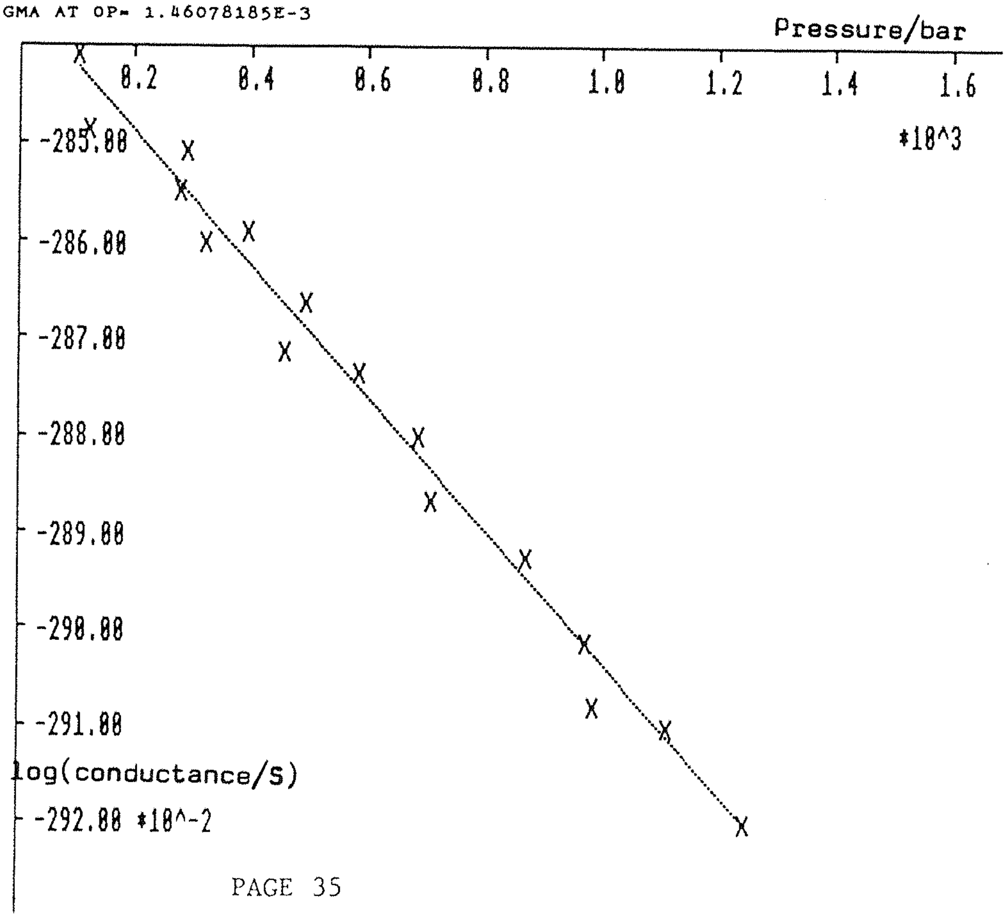
 UNPROCESSED DATA

 THERMOCOUPLE EMF TRANSDUCER EMF   V CELL              V STND RSTR    TIME
 +.0074150   V DC +.0053340   V DC +0.348330   V AC +0.488950   V AC 7MIN
 +.0074180   V DC +.0070450   V DC +0.353390   V AC +0.487000   V AC 15MIN
 +.0074210   V DC +.0086010   V DC +0.357630   V AC +0.484630   V AC 24MIN
 +.0074200   V DC +.0100590   V DC +0.360510   V AC +0.480490   V AC 41MIN
 +.0074230   V DC +.0117270   V DC +0.364120   V AC +0.478100   V AC 50MIN
 +.0074290   V DC +.0146720   V DC +0.370530   V AC +0.472500   V AC 58MIN
 +.0074250   V DC +.0162880   V DC +0.375220   V AC +0.469030   V AC 68MIN
 +.0074310   V DC +.0185410   V DC +0.380230   V AC +0.465740   V AC 77MIN
 +.0074280   V DC +.0206850   V DC +0.385320   V AC +0.461320   V AC 91MIN
 +.0074060   V DC +.0165210   V DC +0.376400   V AC +0.463590   V AC 105MIN
 +.0074180   V DC +.0148370   V DC +0.343560   V AC +0.466520   V AC 113MIN
 +.0074130   V DC +.0120580   V DC +0.362360   V AC +0.468720   V AC 121MIN
 +.0073980   V DC +.0080260   V DC +0.352530   V AC +0.472360   V AC 130MIN
 +.0074030   V DC +.0059020   V DC +0.345940   V AC +0.475670   V AC 138MIN
 +.0074130   V DC +.0051970   V DC +0.341960   V AC +0.475900   V AC 146MIN
 +.0073880   V DC +.0026580   V DC +0.338340   V AC +0.477380   V AC 154MIN
 +.0074130   V DC +.0023280   V DC +0.334040   V AC +0.479990   V AC 162MIN

 ******************************************************************

 PROCESSED DATA       Temperature= 182 C

            PRESSURE SIGMA     LOGSIGMA
            2.896E2  1.409E-3 -2.851E0
            3.964E2  1.384E-3 -2.859E0
            4.935E2  1.361E-3 -2.866E0
            5.845E2  1.338E-3 -2.874E0
            6.886E2  1.318E-3 -2.880E0
            8.724E2  1.280E-3 -2.893E0
            9.732E2  1.255E-3 -2.901E0
            1.114E3  1.230E-3 -2.910E0
            1.248E3  1.202E-3 -2.920E0
            9.878E2  1.236E-3 -2.908E0
            8.827E2  1.363E-3 -2.865E0 ———— erroneous point - disregarded
            7.092E2  1.299E-3 -2.887E0
            4.576E2  1.345E-3 -2.871E0
            3.251E2  1.381E-3 -2.860E0
            2.811E2  1.397E-3 -2.855E0
            1.226E2  1.417E-3 -2.849E0
            1.020E2  1.443E-3 -2.841E0
SLOPE (M)= -6.815431067E-5
SIGMA M= 2.214954422E-6
INTERCEPT B= -2.835414636
SIGMA B= 1.536956575E-3
STD DEV OF THE FIT= 3.044958144E-3
CORRELATION COEFF (R)= -0.9921744685
SIGMA AT OP= 1.46078185E-3
```



```
PROGRAM TO DETERMINE THE VARIATION OF CONDUCTIVITY WITH PRESSURE

ENTER NAME OF COMPOUND:  POTASSIUM  FORMATE
ENTER DATE:
 UNPROCESSED DATA

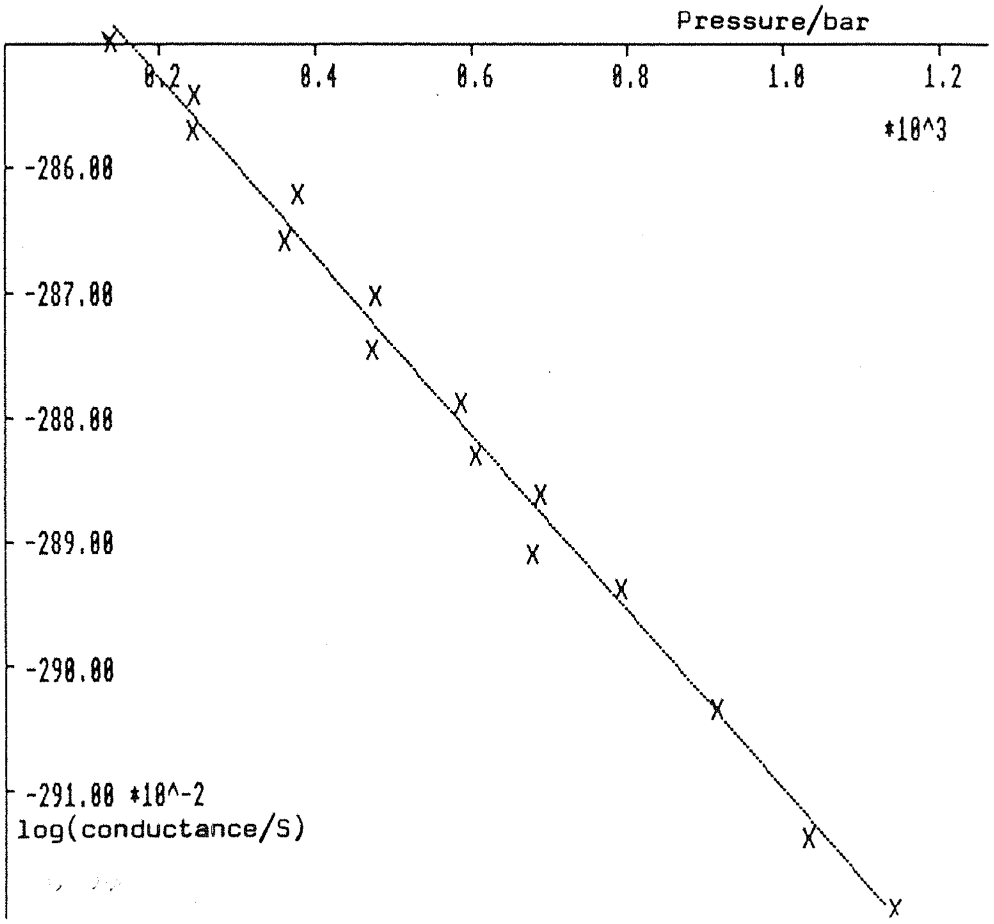
 THERMOCOUPLE EMF TRANSDUCER EMF  VCELL            V STND RSTR   TIME
 +.0074080  V DC +.0046210  V DC +0.479720  V AC +0.668410  V AC 9MIN
 +.0074120  V DC +.0067460  V DC +0.485770  V AC +0.664610  V AC 17MIN
 +.0074130  V DC +.0083210  V DC +0.492340  V AC +0.661250  V AC 25MIN
 +.0074130  V DC +.0100680  V DC +0.498250  V AC +0.656410  V AC 33MIN
 +.0074110  V DC +.0117230  V DC +0.504540  V AC +0.653500  V AC 42MIN
 +.0074110  V DC +.0133480  V DC +0.511050  V AC +0.650200  V AC 49MIN
 +.0074100  V DC +.0153320  V DC +0.518680  V AC +0.645390  V AC 58MIN
 +.0074130  V DC +.0190030  V DC +0.532260  V AC +0.638220  V AC 67MIN
 +.0074030  V DC +.0172220  V DC +0.527390  V AC +0.640820  V AC 75MIN
 +.0073900  V DC +.0115380  V DC +0.507830  V AC +0.650270  V AC 84MIN
 +.0074020  V DC +.0103680  V DC +0.500930  V AC +0.653190  V AC 93MIN
 +.0074040  V DC +.0082520  V DC +0.493130  V AC +0.656000  V AC 101MIN
 +.0074030  V DC +.0064660  V DC +0.486040  V AC +0.659330  V AC 110MIN
 +.0074050  V DC +.0045910  V DC +0.478460  V AC +0.662500  V AC 121MIN
 +.0073940  V DC +.0029110  V DC +0.473170  V AC +0.665940  V AC 130MIN

*************************************************************************

 PROCESSED DATA               Temperauture= 182 C
           PRESSURE  σ          log σ
         2.451E2  1.399E-3 -2.854E0
         3.777E2  1.374E-3 -2.862E0
         4.760E2  1.348E-3 -2.870E0
         5.850E2  1.323E-3 -2.879E0
         6.883E2  1.300E-3 -2.886E0
         7.897E2  1.277E-3 -2.894E0
         9.136E2  1.249E-3 -2.903E0
         1.143E3  1.204E-3 -2.919E0
         1.032E3  1.220E-3 -2.914E0
         6.768E2  1.286E-3 -2.891E0
         6.038E2  1.309E-3 -2.883E0
         4.717E2  1.336E-3 -2.874E0
         3.603E2  1.362E-3 -2.866E0
         2.432E2  1.390E-3 -2.857E0
         1.384E2  1.413E-3 -2.850E0

*************************************************************************

SLOPE (M)= -7.156887469E-5
SIGMA M= 1.854629411E-6
INTERCEPT B= -2.838424087
SIGMA B= 1.204476219E-3
STD DEV OF THE FIT= 2.056567168E-3
CORRELATION COEFF (R)= -0.9953392684
SIGMA AT OP= 1.45069433E-3
```



```
ENTER NAME OF COMPOUND:  POTASSIUM FORMATE

UNPROCESSED DATA

THERMOCOUPLE EMF  TRANSDUCER EMF   V ACROSS CELL   V STND RSTR         TIME
+.0073150   V DC +.0014180  V DC +0.491950  V AC +0.674970  V AC 6MIN
+.0073850   V DC +.0037400  V DC +0.487290  V AC +0.680420  V AC 20MIN
+.0074080   V DC +.0069340  V DC +0.496740  V AC +0.678040  V AC 29MIN
+.0074060   V DC +.0089960  V DC +0.470450  V AC +0.674550  V AC 38MIN
+.0074010   V DC +.0107090  V DC +0.512540  V AC +0.670020  V AC 46MIN
+.0073990   V DC +.0126670  V DC +0.519850  V AC +0.663990  V AC 54MIN
+.0074030   V DC +.0161690  V DC +0.532050  V AC +0.656070  V AC 62MIN
+.0074040   V DC +.0146960  V DC +0.526800  V AC +0.657590  V AC 70MIN
+.0073690   V DC +.0068250  V DC +0.501460  V AC +0.667710  V AC 79MIN
+.0073870   V DC +.0055580  V DC +0.492210  V AC +0.671810  V AC 87MIN

**********************************************************************

PROCESSED DATA
          PRESSURE    σ        log σ
        4.521E1   1.378E-3  -2.861E0 — erroneous point - disregarded
        1.901E2   1.402E-3  -2.853E0
        3.895E2   1.370E-3  -2.863E0
        5.181E2   1.440E-3  -2.842E0 — erroneous point - disregarded
        6.251E2   1.312E-3  -2.882E0
        7.472E2   1.282E-3  -2.892E0
        9.658E2   1.238E-3  -2.907E0
        8.739E2   1.253E-3  -2.902E0
        3.827E2   1.337E-3  -2.874E0
        3.036E2   1.370E-3  -2.863E0

**********************************************************************

SLOPE (M)= -6.817287169E-5

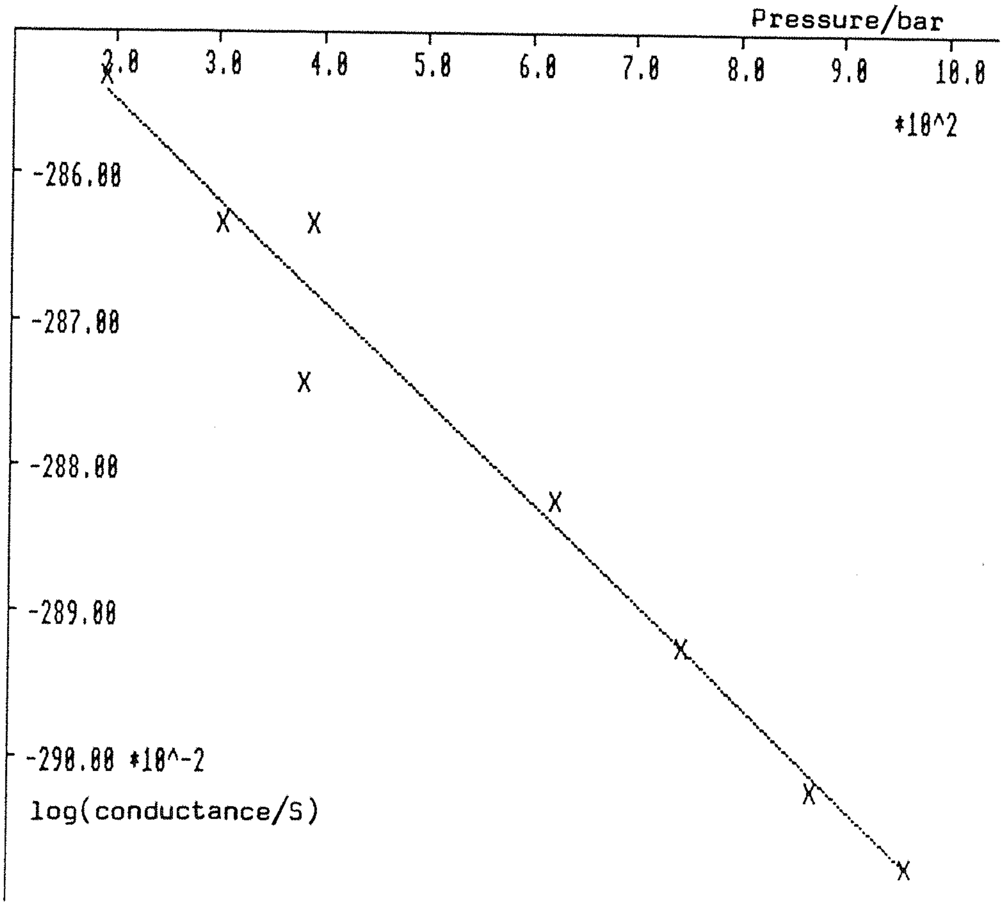
SIGMA M= 4.34741693E-6

INTERCEPT B= -2.841331713

SIGMA B= 2.694421465E-3

STD DEV OF THE FIT= 3.268641421E-3

CORRELATION COEFF (R)= -0.9860639554
```

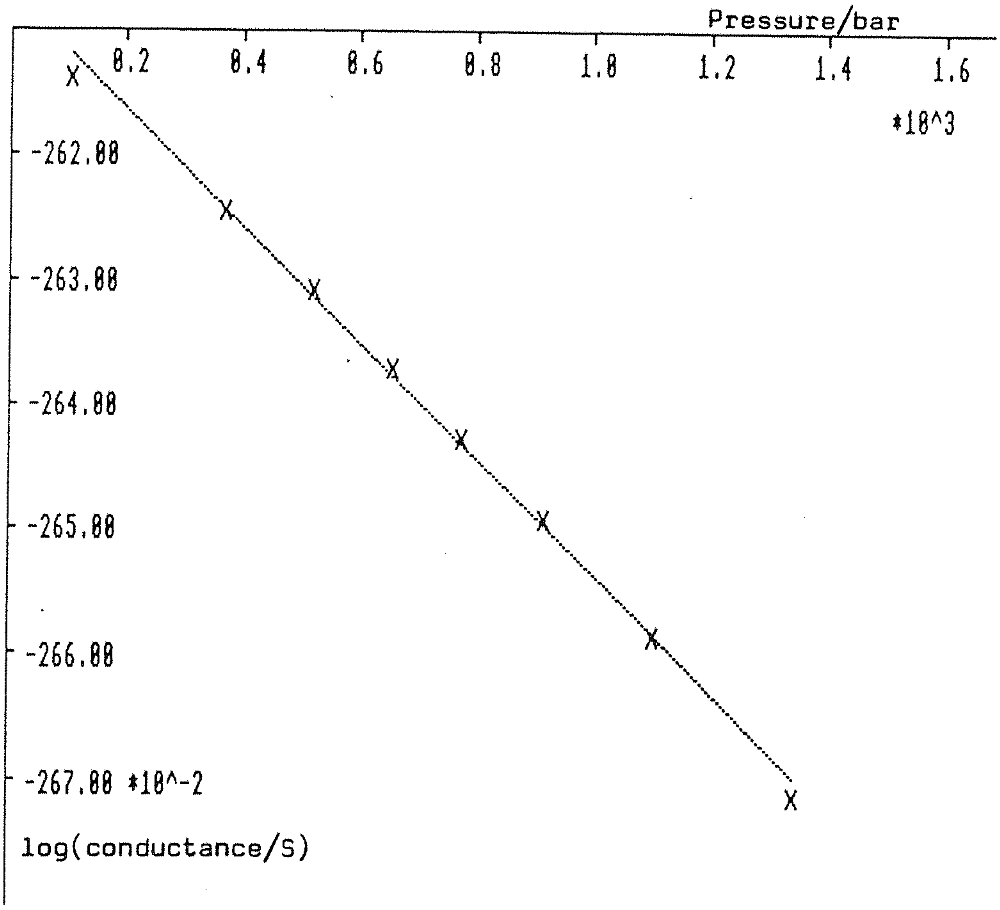


```
POTASSIUM ACETATE

CELL CONSTANT= 90.22
TEMP      PRESSURE SIGMA     LOGSIGMA
3.224E2   1.059E2  2.433E-3 -2.614E0
3.224E2   3.715E2  2.375E-3 -2.624E0
3.224E2   5.225E2  2.341E-3 -2.631E0
3.224E2   6.564E2  2.308E-3 -2.637E0
3.224E2   7.763E2  2.278E-3 -2.643E0
3.224E2   9.159E2  2.243E-3 -2.649E0
3.224E2   1.104E3  2.194E-3 -2.659E0
3.224E2   1.343E3  2.133E-3 -2.671E0

************************************************************************

SLOPE (M)= -4.655210815E-5
SIGMA M= 9.618754371E-7
INTERCEPT B= -2.607144382
SIGMA B= 7.841533206E-4
STD DEV OF THE FIT= 1.017216624E-3
CORRELATION COEFF (R)= -0.9985113367
SIGMA AT OP= 2.470902553E-3
```

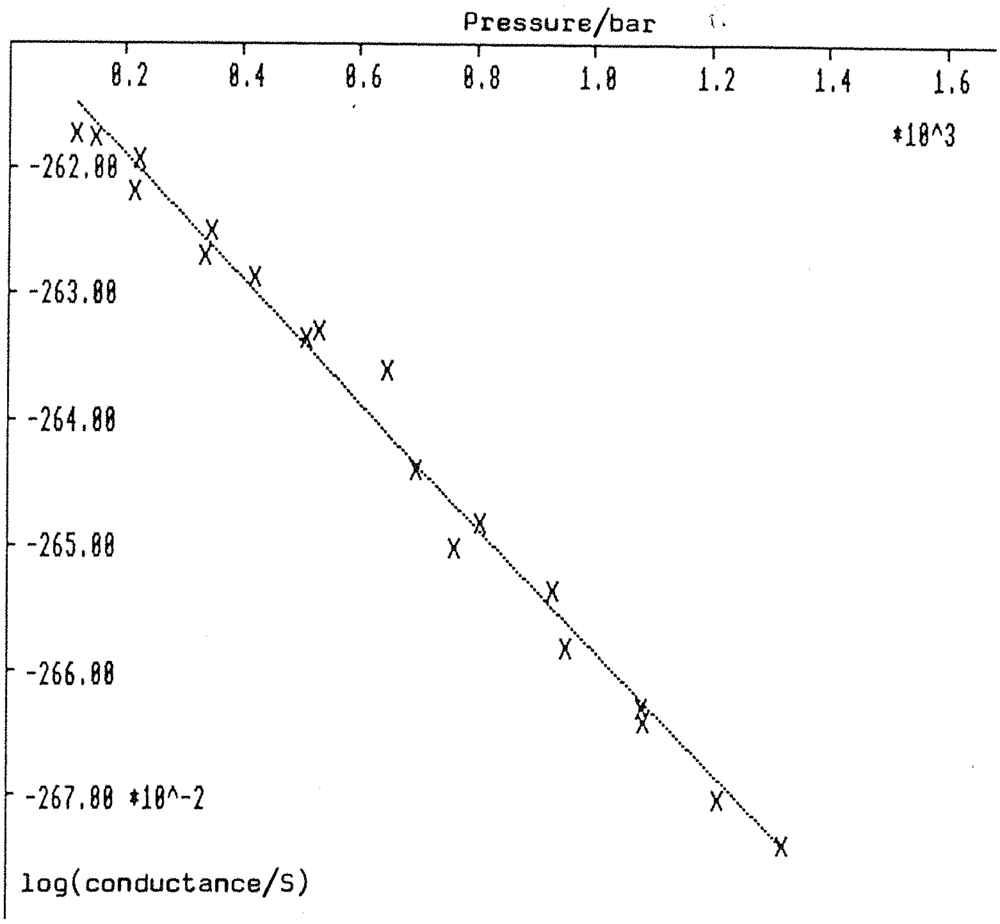


```
POTASSIUM ACETATE

CELL CONSTANT= 90.22
TEMP       PRESSURE SIGMA      LOGSIGMA
3.224E2    1.496E2  2.412E-3 -2.618E0
3.224E2    2.244E2  2.403E-3 -2.619E0
3.224E2    3.485E2  2.372E-3 -2.625E0
3.224E2    4.221E2  2.351E-3 -2.629E0
3.226E2    5.334E2  2.328E-3 -2.633E0
3.234E2    6.489E2  2.312E-3 -2.636E0
3.215E2    7.635E2  2.238E-3 -2.650E0
3.226E2    9.317E2  2.221E-3 -2.653E0
3.222E2    1.084E3  2.173E-3 -2.663E0
3.222E2    1.215E3  2.137E-3 -2.670E0
3.226E2    1.323E3  2.119E-3 -2.674E0
3.224E2    1.088E3  2.168E-3 -2.664E0
3.224E2    9.541E2  2.198E-3 -2.658E0
3.224E2    8.080E2  2.250E-3 -2.648E0
3.224E2    6.989E2  2.271E-3 -2.644E0
3.229E2    5.112E2  2.326E-3 -2.633E0
3.224E2    3.380E2  2.360E-3 -2.627E0
3.224E2    2.153E2  2.388E-3 -2.622E0
3.224E2    1.170E2  2.414E-3 -2.617E0

************************************************************************

SLOPE (M)= -4.91944909E-5
SIGMA M= 1.241693622E-6
INTERCEPT B= -2.609167933
SIGMA B= 9.274896161E-4
STD DEV OF THE FIT= 1.979595864E-3
CORRELATION COEFF (R)= -0.9943180652
SIGMA AT OP= 2.459416415E-3
```

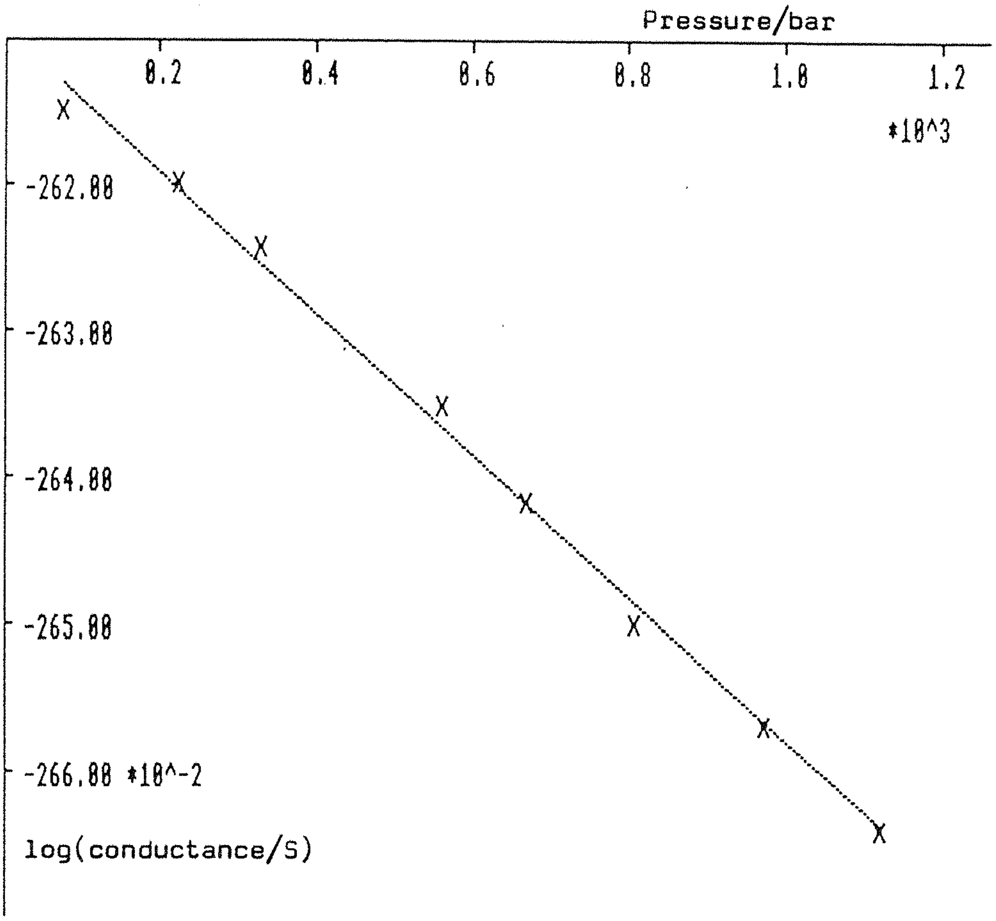


```
POTASSIUM ACETATE

CELL CONSTANT= 90.22
TEMP      PRESSURE SIGMA     LOGSIGMA
3.226E2   1.122E3  2.167E-3 -2.664E0
3.229E2   9.717E2  2.204E-3 -2.657E0
3.229E2   8.083E2  2.240E-3 -2.650E0
3.232E2   6.682E2  2.283E-3 -2.642E0
3.232E2   5.605E2  2.317E-3 -2.635E0
3.222E2   3.294E2  2.377E-3 -2.624E0
3.232E2   2.243E2  2.400E-3 -2.620E0
3.237E2   7.542E1  2.427E-3 -2.615E0

*************************************************************************

SLOPE (M)= -4.868797963E-5
SIGMA M= 1.195256576E-6
INTERCEPT B= -2.609260864
SIGMA B= 8.218024007E-4
STD DEV OF THE FIT= 1.164852743E-3
CORRELATION COEFF (R)= -0.9979006008
SIGMA AT OP= 2.458890202E-3
```



```
CAESIUM ACETATE

CELL CONSTANT= 88.65
TEMP      PRESSURE SIGMA     LOGSIGMA
2.056E2   2.010E2  8.022E-4  -3.096E0
2.058E2   2.560E2  7.929E-4  -3.101E0
2.061E2   3.070E2  7.879E-4  -3.104E0
2.063E2   3.960E2  7.735E-4  -3.112E0
2.062E2   5.010E2  7.557E-4  -3.122E0
2.061E2   5.980E2  7.390E-4  -3.131E0
2.062E2   6.910E2  7.226E-4  -3.141E0
2.061E2   7.990E2  7.033E-4  -3.153E0
2.062E2   8.970E2  6.890E-4  -3.162E0
2.062E2   1.019E3  6.679E-4  -3.175 E0
2.062E2   1.119E3  6.542E-4  -3.184E0
2.063E2   1.001E3  6.636E-4  -3.178E0
2.063E2   9.010E2  6.759E-4  -3.170E0
2.063E2   8.000E2  6.948E-4  -3.158E0
2.063E2   7.000E2  7.138E-4  -3.146E0
2.061E2   5.980E2  7.306E-4  -3.136E0
2.060E2   4.980E2  7.485E-4  -3.126E0
2.060E2   4.000E2  7.666E-4  -3.115E0
2.060E2   2.460E2  7.938E-4  -3.100E0
2.060E2   1.000E2  8.221E-4  -3.085E0

**********************************************************************
SLOPE (M)= -1.003638837E-4

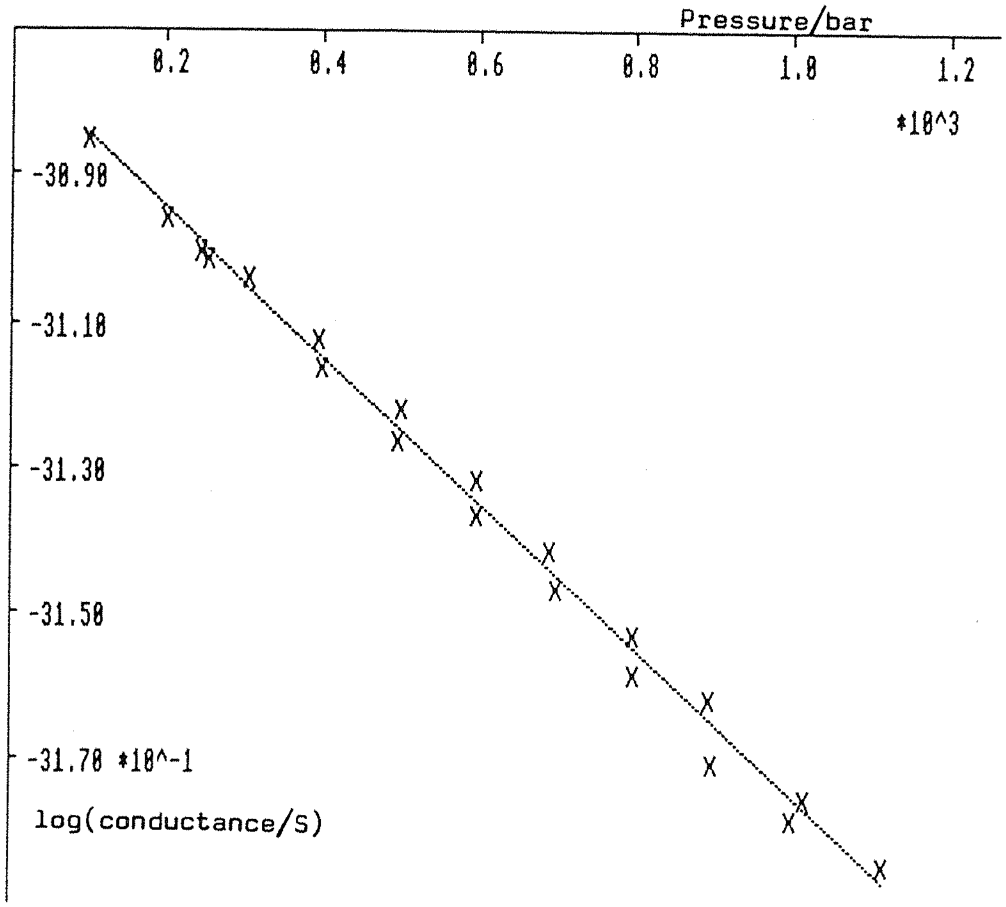
SIGMA M= 1.895299696E-6

INTERCEPT B= -3.074403571

SIGMA B= 1.268332659E-3

STD DEV OF THE FIT= 2.487761748E-3

CORRELATION COEFF (R)= -0.99662946
```

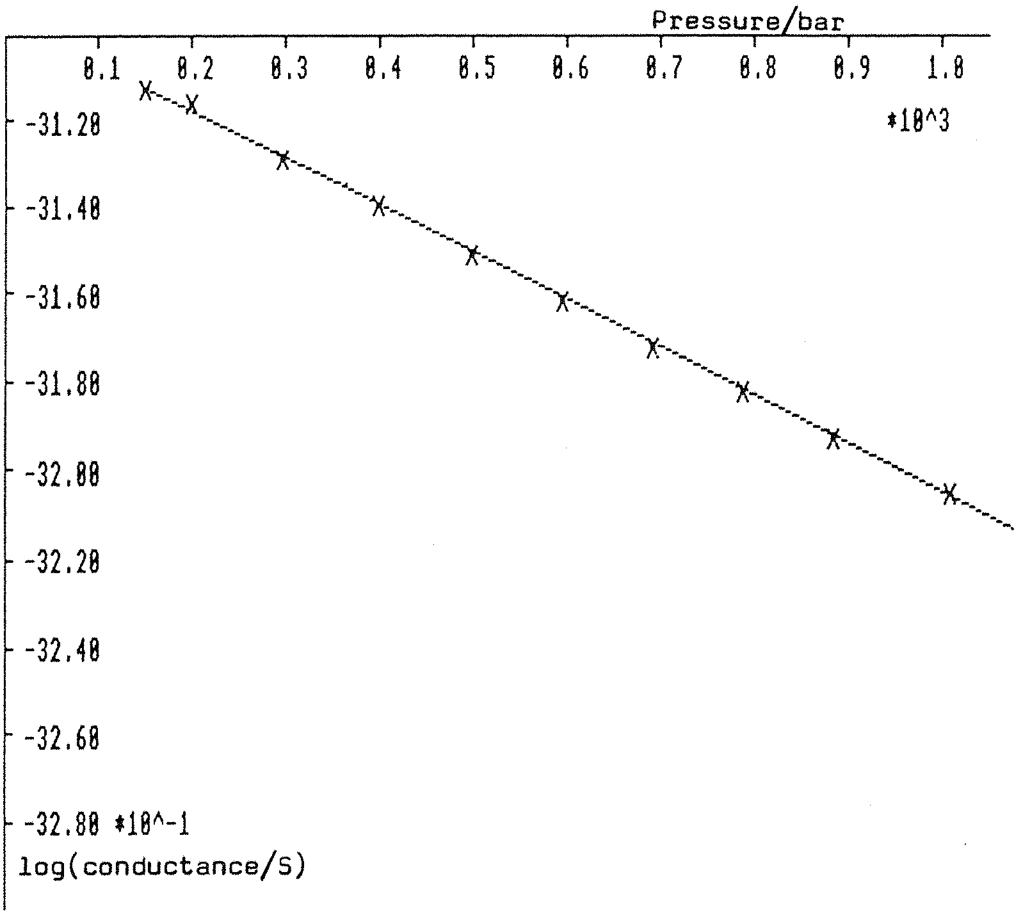


```
CAESIUM ACETATE

CELL CONSTANT= 88.65
TEMP      PRESSURE SIGMA     LOGSIGMA
2.001E2   1.500E2  7.718E-4  -3.112E0
2.001E2   2.000E2  7.657E-4  -3.116E0
2.001E2   2.980E2  7.429E-4  -3.129E0
2.002E2   3.990E2  7.247E-4  -3.140E0
2.002E2   4.990E2  7.071E-4  -3.151E0
2.002E2   5.960E2  6.897E-4  -3.161E0
2.002E2   6.920E2  6.736E-4  -3.172E0
2.002E2   7.880E2  6.581E-4  -3.182E0
2.002E2   8.840E2  6.421E-4  -3.192E0
2.003E2   1.008E3  6.244E-4  -3.205E0
2.003E2   1.107E3  6.107E-4  -3.214E0

**********************************************************************

SLOPE (M)= -1.076768208E-4
SIGMA M= 9.126269542E-7
INTERCEPT B= -3.096432555
SIGMA B= 6.175959443E-4
STD DEV OF THE FIT= 9.361697357E-4
CORRELATION COEFF (R)= -0.9996421859
SIGMA AT OP= 8.008799948E-4
```

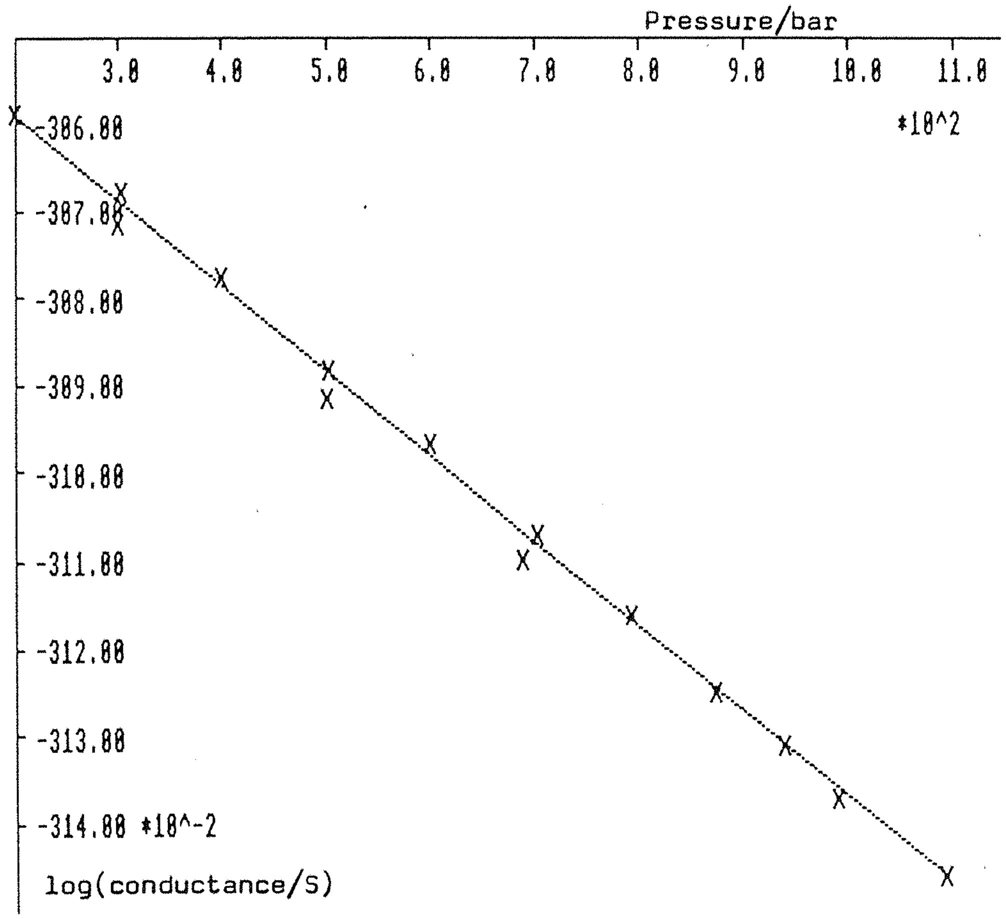


```
CAESIUM ACETATE

CELL CONSTANT= 88.65
TEMP       PRESSURE SIGMA     LOGSIGMA
2.030E2   2.010E2  8.732E-4 -3.059E0
2.030E2   3.030E2  8.555E-4 -3.068E0
2.030E2   4.000E2  8.368E-4 -3.077E0
2.030E2   5.010E2  8.167E-4 -3.088E0
2.030E2   5.990E2  8.003E-4 -3.097E0
2.030E2   7.020E2  7.819E-4 -3.107E0
2.030E2   7.920E2  7.657E-4 -3.116E0
2.030E2   8.720E2  7.501E-4 -3.125E0
2.030E2   9.880E2  7.290E-4 -3.137E0
2.030E2   1.090E3  7.139E-4 -3.146E0
2.030E2   9.380E2  7.392E-4 -3.131E0
2.030E2   6.880E2  7.767E-4 -3.110E0
2.030E2   5.000E2  8.101E-4 -3.091E0
2.030E2   3.000E2  8.486E-4 -3.071E0

*************************************************************************

SLOPE (M)= -9.798731446E-5
SIGMA M= 1.589440993E-6
INTERCEPT B= -3.039587376
SIGMA B= 1.094614081E-3
STD DEV OF THE FIT= 1.601355068E-3
CORRELATION COEFF (R)= -0.9983000434
SIGMA AT OP= 9.128777551E-4
```

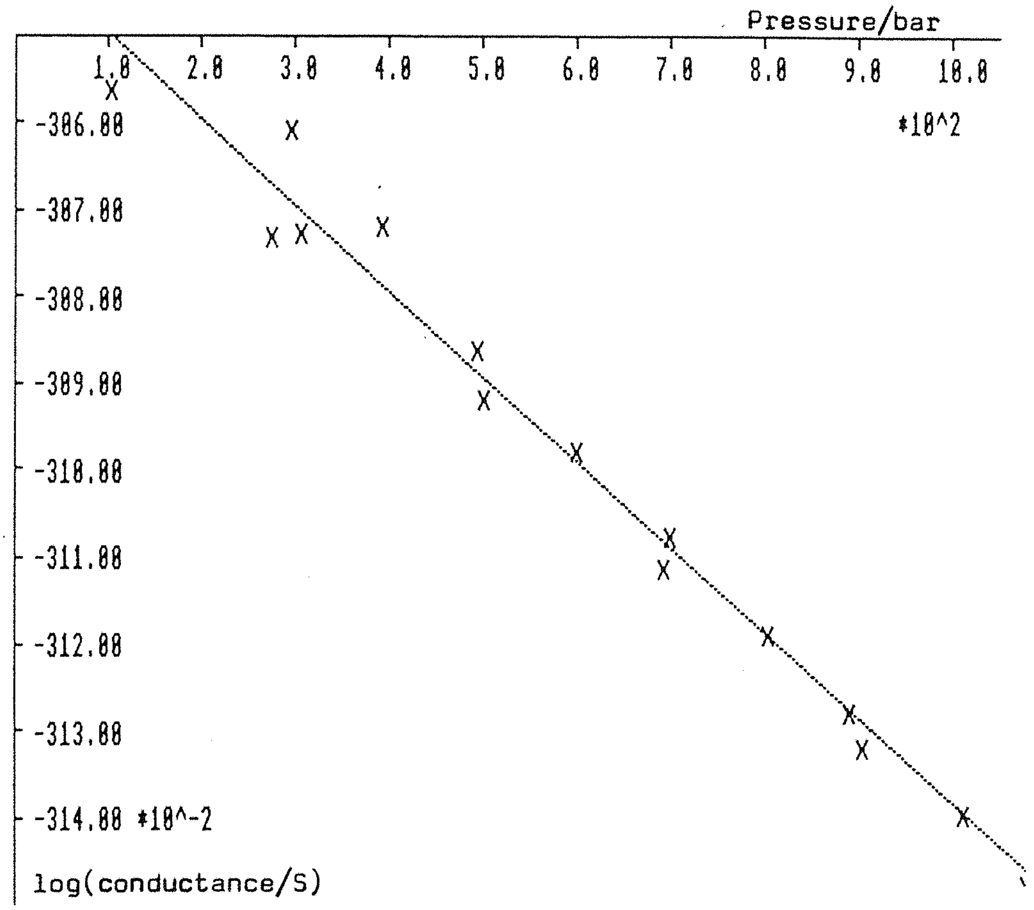


```
CAESIUM ACETATE

CELL CONSTANT= 88.65
TEMP      PRESSURE SIGMA     LOGSIGMA
2.030E2   2.980E2  8.696E-4 -3.061E0
2.030E2   3.930E2  8.476E-4 -3.072E0
2.030E2   4.960E2  8.202E-4 -3.086E0
2.030E2   6.000E2  7.983E-4 -3.098E0
2.030E2   7.000E2  7.804E-4 -3.108E0
2.030E2   8.040E2  7.603E-4 -3.119E0
2.030E2   8.890E2  7.448E-4 -3.128E0
2.030E2   1.010E3  7.246E-4 -3.140E0
2.030E2   1.090E3  7.112E-4 -3.148E0
2.030E2   9.040E2  7.379E-4 -3.132E0
2.030E2   6.940E2  7.741E-4 -3.111E0
2.030E2   5.020E2  8.097E-4 -3.092E0
2.030E2   3.070E2  8.463E-4 -3.072E0
2.030E2   2.770E2  8.455E-4 -3.073E0
2.030E2   1.040E2  8.786E-4 -3.056E0

************************************************************************

SLOPE (M)= -9.871959801E-5
SIGMA M= 3.628558834E-6
INTERCEPT B= -3.040017103
SIGMA B= 2.428127897E-3
STD DEV OF THE FIT= 4.032352199E-3
CORRELATION COEFF (R)= -0.9906706633
SIGMA AT OP= 9.119749245E-4
```



$K=\sigma(L/A)$ (9)

where L/A is the cell constant.

$$\Delta V_{\kappa}= -RT\left(\frac{\partial \ln \kappa}{\partial P}\right)_T \qquad (20)$$

1 bar $=10^5$ Pa.

Values of κ at zero pressure and ΔV_{κ} calculated from these expressions are:

T/°C	L/A/cm^{-1}	κ/Scm^{-1}	ΔV_{κ}/cm^3
sodium formate			
275.1	85.03	0.428	4.17
269.0	88.65	0.405	4.51
sodium acetate			
345.4	88.65	0.195	1.41
345		0.208(lit. value-ref.4)	
potassium formate			
181.4	90.22	0.130	5.93
181.8	90.22	0.131	6.23
181.9	90.22	0.132	5.93
potassium acetate			
322.6	90.22	0.222	5.56
322.4	90.22	0.222	5.61
322.4	90.22	0.223	5.31
323		0.224(lit. value-ref.4)	
caesium acetate			
200.1	88.65	7.10×10^{-2}	9.76
206.2	88.65	7.48×10^{-2}	9.21
203.0	88.65	8.09×10^{-2}	8.93
203.0	88.65	8.09×10^{-2}	9.00
203		7.2×10^{-2}(lit. value-ref.4)	

5. DISCUSSION

Findings

Values for κ at zero pressure/S cm^{-1}

	SODIUM	POTASSIUM	CAESIUM
FORMATE	0.42	0.13	
ACETATE	0.20	0.22	0.077

Values of ΔV_κ/cm^3

FORMATE	4.34	6.03	
ACETATE	1.41	5.49	9.23

For comparison the values of ΔV_κ obtained for the nitrites and nitrates are(2):

NITRITE	2.7	5.4	
NITRATE	2.7	4.4	6.7

Overall, the conductivity measurements have yielded data which conform well to eqn 20, with fair to good consistency, and approximate agreement with literature values, where these have been available for comparison. Consideration of consistency between runs, and comparison with literature values of conductivity suggests error limits of approximately ±3% for value of κ and ±5% for values of ΔV_κ.

Values for conductance were found to be stable during the period of the run, and also when the sample was left overnight, showing that decomposition of the salt was negligible and that diffusion of nitrogen into the conduction path had effectively been blocked by the cell design.

Values for cell constants were measured at 25°C. It has been shown(21) that the value for the cell constant obtained at this temperature is not significantly different from the true value of the cell constant under actual experimental conditions.

Discussion

The linear relationships observed and in particular the negative gradient of the $\log\sigma$ vs P plots indicate that the salts were completely ionised. The values obtained are similar to those of the alkali nitrites and nitrates, which would be expected in view of the similar structure of the anion.

The values for conductivity decrease from sodium to caesium, a trend also found in the nitrates. Molecular dynamics simulations(22) have shown that the conductivity of molten salts can be modelled effectively by simply adjusting the hard core potential. It therefore seems reasonable to attribute this trend to a size effect - the smaller sodium ion travels through the melt more easily than the larger caesium ion. Similarly the decrease in conductivity with pressure may be attributed to the fact that the ions become more densely packed as the pressure incresases, reducing the ease with which ions are able to move through the melt under the influence of an external electric field.

Numerous generalised theories of conduction have been proposed, based on models assuming discrete holes in the melt and energy barriers to single thermally activated 'jumps' by ions. However these theories have had limited success, and are fundamentally unrealistic.

Molecular dynamics simulations are potentially a much more revealing route to understanding molten salts, allowing a detailed picture of behaviour at a microscopic level to be built up, and allowing the effect of ion size and shape, and of intermolecular potentials to be understood.

6. Further Work

Having completed work on the acetates and formates it is natural to extend studies to the longer chain compounds. The longer chain compounds have two important characteristics which distinguish them from the acetates and formates. First, they are often only partially dissociated. Secondly, they can show a liquid crystal phase between the solid and isotropic phases.

It would be instructive to measure the conductivity, and its variation with pressure for a range of compounds. It should be possible to gain information about the extent of dissociation in the melt from both the absolute magnitude of the conductivity and its pressure gradient. Dissociation of a partially ionised molten salt is accompanied by a volume decrease, and is therefore favoured by increasing pressure. As a result the number of ions in the melt, and hence the conductivity, tends to increase with increasing pressure.

Liquid crystal phases, being more ordered than isotropic phases, tend to be favoured by pressure. It would be interesting to measure the conductivity of liquid crystal phases, and see if their behaviour could be interpreted in terms of the layer structures which have been proposed(5,6,23). In addition it might prove possible to induce mesophases at high pressure in those compounds which do not exhibit them at atmospheric pressure. Phase transitions might profitably be studied by methods such as DTA, though measurement of light transmission was found to have limitations as a method for studying the compounds under investigation (see Appendix 2).

Tests on the longer chain alkali carboxylates showed that they were unstable on melting and, though their melting points could be measured accurately they were not suitable for conductivity studies, which require the molten sample to be stable for at least an hour, and preferably longer. However conductivity and other properties of long chain zinc and lead carboxylates have been studied successfully in the molten state(11,24). The zinc salts do not have a liquid crystal phase at atmospheric pressure, though lead carboxylates do. Some work was carried out on zinc decanoate but problems were found in obtaining a consistent value for the very low conductivity (see Appendix 3).

To obtain a proper theoretical understanding of these systems it would be necessary to use computer simulation techniques. Molecular dynamics simulations would enable conductivity to be modelled and the effect of ion shape and intermolecular forces measured. Monte Carlo techniques might be used at a later stage to study phase behaviour.

APPENDIX 1. PROGRAMS

EXPERIMENTAL CONTROL PROGRAM "EXPTMP"

```
   10VDU2
   20PRINT "PROGRAM TO DETERMINE THE VARIATION OF CONDUCTIVITY WITH PRESSURE"
   30PRINT
   40REM ENTER INITIAL PARAMETERS
   50INPUT "ENTER NAME OF COMPOUND:  " N$
   60 INPUT "ENTER DATE:  ", L%
   70PRINT
   80INPUT "NUMBER OF STEPS", N%
   90VDU3
  100INPUT "ARE THESE DATA CORRECT", Y$
  110IFY$<>"Y" THEN50
  120INPUT "ENTER R WHEN READY TO START RUN" Y$
  130IF Y$<>"R" THEN 100
  140VDU2
  150PRINT
  160PRINT"**************************************************************"
  170PRINT
  180PRINT
  190REM CARRY OUT EXPERIMENT
  200TIME=0
  210DIMA$(N%,4)
  220PRINT"UNPROCESSED DATA"
  230PRINT
  240PRINT"THERMOCOUPLE EMF";" TRANSDUCER EMF ";" V ACRS CELL     ";" V STND RST
R   ";"TIME          "
  250*IEEE
  260C%=OPENIN("COMMAND")
  270D%=OPENIN("DATA")
  280PRINT£C%,"BBC DEVICE NO",0
  290PRINT£C%,"CLEAR"
  300V%=OPENIN("1")
  310PRINT£C%,"REMOTE ENABLE"
  320FOR N=1 TO N%
  330VDU3
  340SOUND1,-15,100,40
  350INPUT"CHANGE PRESSURE",Y$
  360 IFY$<>"R"THEN350
  370VDU2
  380PRINT£C%,"LISTEN",V%,"EXECUTE"
  390PRINT£D%,"M0R1"
  400PRINT£C%,"UNLISTEN"
  410PRINT£C%,"TALK",V%
  420PROCMON
  430PROCMEAS
  440NEXT
  450CLOSE£D%
  460CLOSE£C%
  470*DISC
  480*DRIVE1
  490UD$=STR$(L%)
  500UP=OPENOUT UD$
  510FORC=1TON%
  520FORD=0TO4
  530PRINT£UP,A$(C,D)
  540NEXT
  550NEXT
  560CLOSE£UP
  570*DRIVE0
  580PRINT
  590PRINT"**********************************************************************
***"
  600PRINT
  610VDU3
  620CHAIN"DATPROS"
  630END
  640DEFPROCMON
  650NOWTIME=TIME
  660?&FCC0=0
  670REPEAT
  680INPUT£D%,TE$
  690UNTIL TIME>(NOWTIME+40000)
  700ENDPROC
  710DEFPROCMEAS
  720?&FCC1=0
  730?&FCC0=0
  740INPUT£D%,A$(N,0)
  750?&FCC0=1
  760INPUT£D%,A$(N,1)
  770PRINT£C%,"UNTALK"
  780PRINT£C%,"LISTEN",V%,"EXECUTE"
  790PRINT£D%,"M1R2"
  800PRINT£C%,"UNLISTEN"
  810PRINT£C%,"TALK",V%
  820?&FCC0=2
  830INPUT£D%,A$(N,2)
  840?&FCC0=3
  850INPUT£D%,A$(N,3)
  860PRINT£C%,"UNTALK"
  870ETM=INT(TIME/6000)
  880A$(N,4)=STR$(ETM)+"MIN"
  890@%=&00000010
  900PRINTLEFT$(A$(N,0),15),LEFT$(A$(N,1),15),LEFT$(A$(N,2),15),LEFT$(A$(N,3),15
),LEFT$(A$(N,4),15)
  910ENDPROC
```

PROGRAM TO CONTROL EXPERIMENT

Lines 10 to 180 allow the parameters of the experiment to be entered and printed out.

Line 200 sets the clock to zero

Line 210 sets up an array to store data from the experiment

Lines 220 to 240 print out headings for the table of data from the experiment

Lines 250 to 310 set up the IEEE interface ready for use

Lines 320 to 440 are a loop to take readings at each of the N% pressures. Lines 330 to 370 give an audible signal and a pause to indicate that the pressure needs changing. When the operator has manually changed the pressure he presses "R <RETURN>" to proceed with the program. Lines 380 to 410 instruct the DVM to read DCmV. Line 420 calls the procedure to monitor the temperature for several minutes before taking readings. Line 430 calls the procedure to take readings.

Lines 450 and 460 close the channels of the IEEE interface.

Lines 470 to 560 select the Disc Filing System, and store the data in a file labeled by the date.

Lines 570 to 640 end the program and chain the data processing program

Lines 640 to 700 are the procedure for monitoring temperature before taking a reading. Line 650 notes the current elapsed time. Line 660 selects the thermocouple channel on the multiplex. Lines 670 to 690 take successive temperature readings, which will be displayed on the front panel of the DVM but not on the computer screen, until the elapsed time has increased by 40000 hundredths of a second (approx 7 minutes) from its initial value. This time may be – and often is – varied in the range 5 to 10 minutes as convenient.

Lines 710 to 910 take a set of readings. Line 720 selects the solid state inputs on the multiplex. Lines 730 and 740 select the thermocuple channel, channel 1 and store the value in an array. Lines 750 and 760 select the transducer channel on the multiplex and store the value of the input in the array. Lines 770 to 860 instruct the DVM to read AC volts, store the potentials across the cell (channel 3) and the standard resistor (channel 4) in the array. Lines 870 and 880 record the time at which the readings were taken in minutes since the start of the experiment. Lines 890 and 900 print out the four readings and the time.

LIST OF VARIABLES

N$=name of compound

L%=date

N%=number of pressure steps

C%,D%,V%=labels for use with IEEE interface

A$(C,0)=thermocouple emf for step C

A$(C,1)=transducer emf for step C

A$(C,2)=pd across cell for step C

A$(C,3)=pd across standard resistor for step C

A$(C,4)=elapsed time since begining of experiment

NOWTIME=variable to monitor time

ETM=time elapsed since start of experiment

UD$=string variable derived from the date used to label the data file on disc

DATA PROCESSING PROGRAM "DATPROS"

```
   10*DRIVE1
   20VDU2
   30REM READ IN UNPROCESSED DATA
   40UD$=STR$(L%)
   50UP=OPENIN UD$
   60DIMA$(N%,4)
   70DIMB(N%,3)
   80FOR C=1TON%
   90FOR R=0TO4
  100INPUT£UP,A$(C,R)
  110NEXTR
  120NEXTC
  130CLOSE£UP
  140 REM READ DATA FROM ARRAY AND CONVERT
  150FOR C=1 TO N%
  160B(C,0)=1000*VAL(A$(C,0))/0.04
  170B(C,1)=(1000*VAL(A$(C,1))-0.69356)/0.0160234
  180VC=VAL(A$(C,2))
  190VS=VAL(A$(C,3))
  200RS=997.5
  210RC=(VC*RS/VS)-1.1
  220B(C,2)=1/RC
  230B(C,3)=LOG(B(C,2))
  240NEXT
  250PD$=UD$+"A"
  260PP=OPENOUT PD$
  270REM PRINT PROCESSED DATA ONTO SCREEN AND INTO FILE
  280 D=OPENOUT "DATA"
  290PRINT"PROCESSED DATA"
  300PRINT
  310PRINT"STND RESISTOR= ";RS
  320@%=&00010409
  330PRINT"TEMP       ":"PRESSURE ":"SIGMA     ":"LOGSIGMA "
  340FORC=1TON%
  350PRINT B(C,0),B(C,1),B(C,2),B(C,3)
  360PRINT£PP,B(C,0)
  370PRINT£PP,B(C,1)
  380PRINT£PP,B(C,2)
  390PRINT£PP,B(C,3)
  400PRINT£D, B(C,1)
  410PRINT£D,B(C,3)
  420NEXT
  430CLOSE£PP
  440CLOSE£D
  450*DRIVE0
  460PRINT
  470PRINT"**********************************************************************
***"
  480PRINT
  490VDU3
  500CHAIN"LSQM"
```

DATA PROCESSING PROGRAM

Lines 10 to 130 set up arrays to store the processed and unprocessed data and reads the unprocessed data in from the file on drive 1

Lines 150 to 240 calulate the required physical quantities from the experimental data recorded. line 150 calculates the temperature from the thermocouple emf. Line 170 calculates the pressure from the transducer EMF. Lines 180 to 230 calculate the conductivity of the salt form the ratio of voltages across cell and standard resistor, allowing for 1.1 ohm lead resistance(line 210)

Lines 250 to 290 open out a file to store the processed data labelled by the date string with an extra A added, and a file labelled data to store the values of pressure and logsigma required for a least squares fit.

Lines 290 to 440 print out the calculated values for the physical quantities, store them disc files and close the files.

Lines 450 to 500 end the program and chain the least squares fit.

LIST OF VARIABLES

L%,N%= resident integer variables from experimental control program.

UD$=string used to label file of unprocessed data on disc

A$(C,D)=as for control program

B(C,0)=approximate temperature at step C

B(C,1)=pressure at step C

B(C,2)=conductance of cell

B(C,3)=log of conductance

VC=p.d. across cell

VS=p.d. across standard resistance

RS=standard resistance

RC=resistance of cell

PD$=label for file storing processed data

LEAST SQUARES FITTING PROGRAM "LSQM"

```
    10*DRIVE1
    20 DIM X(100),Y(100):DEF FNA(L)=INT(L*1E3+0.5)/1E3:REM ROUND TO 3 FIGS
    30F1=OPENIN "DATA"
    40 N=0
    50 REPEAT :N=N+1
    60 INPUT£F1,X(N),Y(N)
    70 UNTIL EOF£F1
    80 CLOSE£F1
    90 @%=&10:S1=0:S2=0:S3=0:S4=0:S5=0
   100 FOR I= 1 TO N
   110 S1=S1+X(I)*Y(I)
   120 S2=S2+X(I)
   130 S3=S3+Y(I)
   140 S4=S4+X(I)*X(I)
   150 S5=S5+Y(I)*Y(I)
   160 NEXT I
   170 Q=S1-(S2*S3)/N
   180 T=S4-(S2*S2)/N
   190 V=S5-S3*S3/N
   200 W=SQR(T*V)
   210 R=Q/W
   220 M=Q/T
   230 B1=(S3-(M*S2))/N
   240 S6=SQR((S4-S2*S2/N)/(N-1))
   250 S7=M*S6/R
   260 Y1=0
   270 FOR I=1 TO N:Y1=(Y(I)-M*X(I)-B1)^2+Y1:NEXT I
   280 S8=SQR(Y1/(N-1))
   290 S9=SQR(S8*S8/(S6*S6*(N-1)))
   300 Z1=S9*SQR(S4/N)
   310VDU2
   320 PRINT"SLOPE (M)= ";M
   330 PRINT"SIGMA M= ";S9
   340  PRINT"INTERCEPT B= ";B1
   350 PRINT"SIGMA B= ";Z1
   360 PRINT"STD DEV OF THE FIT= ";S8
   370 PRINT"CORRELATION COEFF (R)= ";R
   380SIG=10^B1
   390PRINT"SIGMA AT OP= ";SIG
   400 VDU3
   410 PROCresults
   420 A%=1:REM SET A%=1 FOR XY4 TO READ DATA FROM POINTS
   430*DRIVE0
   431INPUT"POSITION PAPER",Y$
   432IFY$<>"R"THEN 431
   440 CHAIN"PLOTMA"
   450 END
   460 DEFPROCresults
   470 X=OPENOUT("POINTS")
   480 FOR I=1 TO N:PRINT£X,X(I),Y(I):NEXT:CLOSE£X
   490 XMAX=-1E38:XMIN=1E38:YMAX=-1E38:YMIN=1E38
   500 FOR I= 1TO N
   510 IF X(I)>XMAX THEN XMAX=X(I)
   520 IF Y(I)>YMAX THEN YMAX=Y(I)
   530 IF X(I)<XMIN THEN XMIN=X(I)
   540 IF Y(I)<YMIN THEN YMIN=Y(I)
   550 NEXT
   560 X=OPENOUT("MAXMIN"):PRINT£X,XMAX,XMIN,YMAX,YMIN:CLOSE£X
   570 X=OPENOUT("LINE"):Y=XMAX*M+B1:PRINT£X,XMAX,Y:Y=XMIN*M+B1:PRINT£X,XMIN,Y:CL
 OSE£X
   580ENDPROC
```

```
  10 MODE 0
  30 VDU 23:8202;0;0;0:REM TRUN OFF FLASHING CURSOR
  40 X=OPENIN("MAXMIN"):INPUT£X,XMAX,XMIN,YMAX,YMIN:CLOSE£X
  50 PROCscale(XMAX,XMIN):X5=Y7:AX=V9 :X3=Y6
  60 XMIN=B:XMAX=XMIN+(X3*X5)*1.05:REM X5=DIV DIST :X3=No OF DIV
  70 PROCscale (YMAX,YMIN):Y5=Y7:Y9=V9 :Y3=Y6
  80 YMIN=B:YMAX=YMIN+(Y3*Y5)
  90 PROCaxis
 100 PROCplot
 110 PROCwindow
 120 VDU 12 :REM **** TEXT WIN TO DEF **
 160 CLS
 165 *FX6,10
 175*SCDUMP
 180PRINT "END OF EXPERIMENT"
 185*DRIVE0
 190 END
 200 REM *************************** END MAIN BODY OF PROG *********************
 210 REM **************************** SCALE AXIS ************************
 220 DEFPROCscale(V8,V7)
 230 GOSUB 420:A=V8:B=V7:ENDPROC
 240 REM SCALE FACTOR
 250  X6=ABS(V6):X7=0:X8=0:IF X6=0 THEN 400
 260 IF X6<1 THEN 290
 270 IF X6<= 10 THEN 310
 280 X6=X6/10:X7=X7+1:GOTO 260
 290 X6=X6*10
 300 X7=X7-1: GOTO 260
 310 X8=INT(X6+.95)
 320 IF X6<1.01 THEN 400
 330 IF X6>2.5 OR X6=0 OR X6>1.6 AND X6 <=2 THEN 400
 340 IF X6>2 THEN 370
 350 IF X6>1.2 THEN 390
 360 X8=1.2:GOTO 400
 370 X8=2.5
 380 GOTO 400
 390 X8 =1.6
 400 X9=10^X7*X8
 410 RETURN
 420 REM DIVISION DIST
 430 IF V7<=V8 THEN X6=V7 ELSE X6=V8
 440 IF V7>=V8 THEN V8=V7
 450 GOSUB 730:V6=V8-V7
 460 GOSUB 240:IF X8 =1.2 THEN 560
 470 IF X8=1.6 THEN 540
 480 IF X8=2.5 THEN 590 ELSE IF X8>5 THEN 500
 490 ON X8 GOTO 520,520,560,540,520
 500 Y6=X8
 510 GOTO 600
 520 Y6=10
 530 GOTO 600
 540 Y6=8
 550 GOTO 600
 560 Y6=6
 570 GOTO 600
 580 ON X8 GOTO 520,520,560,540,520
 590 Y6=5
 600 REM
 610 V9=X7:V6=V8:IF Y6=0 THEN 720
 620 Y7=ABS(X9/Y6):IF SGN(V7)=SGN(V8) THEN 670
 630 GOSUB 240 :V8 =Y7*INT(SGN(V8)*X9/Y7):V6=V7:GOSUB 240
 640 V7=Y7*INT(SGN(V7)*X9/Y7)
 650 IF ABS (V8-V7)<=Y7*Y6 THEN 720
 660 Y6=Y6+1:GOTO 640
 670 IF ABS(V7)<ABS(V8/10) THEN 700
 680 IF ABS(V8)>ABS(V7/10) THEN 720
 690 V8=0 :GOTO 720
 700 V7=0
 710 REM V7=MIN ,V8=MAX,Y7=DIV DIST,Y6 = NO DIV
 720 RETURN
 730 REM
 740 V7=X6:V6=V8-V7:Z0=0.99
 750 GOSUB 240
 760 V7=INT (V7/10^X7)*10^X7
 770 RETURN
 780 REM ******** DEF ORIGIN AND TEXT WINDOW POSn *******************
 790 DEFPROCorigin
 800 IF XMAX <=0 AND XMIN <0 THEN 810 ELSE 820
 810 OX=1249 :GOTO 850
 820 IF XMIN>=0 AND XMAX >0 THEN OX=30
 830 GOTO 850
 840 OX=1219*(ABS(XMIN)/(XMAX+ABS(XMIN)))+30
 850 IF YMAX<=0 AND YMIN<0 THEN 860 ELSE 870
 860 OY =1003:GOTO 900
 870 IF YMIN>=0 AND YMAX >0 THEN OY=20 ELSE 890
 880 GOTO 900
 890  OY=1003*(ABS(YMIN)/(YMAX+ABS(YMIN)))+20
 900 VDU 29,OX;OY;
 910 ENDPROC
 920 DEFPROCwindow
 930IF OX >=500 THEN 950 ELSE  940
 940G=43 :I=73:GOTO 960
 950 G=4:I=34
 960IF OY<= 515 THEN 980 ELSE 970
 970 H=31:J=31:GOTO990
 980 H=0:J=0
 990 VDU 28,G,H,I,J:REM **** TEXT WINDOW  ******
1000 ENDPROC
```

```
1010 REM  *************************** DRAW AXIS ********************************
1020 DEF PROCaxis
1030 @%=&01020103
1040 REM SET GRAPHICS WINDOW
1050 VDU 24 0:0:1279;1023;
1060 PROCorigin
1070 DEF FNA(L)=INT((L*1E3)+0.5)/1E3
1080 DEF FNB(L)=INT((L*1E2)+.05)/1E2
1090 VDU5
1100 REM ************************* X AXIS **********************************
1110 IF OY>900 THEN I=-1 ELSE I=1
1115 IF OY>900 THEN I1=-0.5 ELSE I1=1
1120 PROCscax(XMIN):MOVE XPT,0:PROCscax(XMAX):DRAW XPT,0
1130 X=XMIN:X4=0:REPEAT :X4=X4+1:PROCscax(X):IF XPT >-50 AND XPT <50 THEN 1170
1140 MOVE XPT,0:DRAW XPT,15*I:MOVE XPT-2,0:DRAW XPT-2,15*I:MOVE XPT-20,50*I1
1150 X=FNA(X):A1=X/10^AX:A1=FNB(A1)
1160 I$=STR$(A1):PRINTI$
1170 X=X+X5:UNTIL X4=X3+1
1180 @%=01020202
1190 IF XMAX<=0 THEN PROCscax(XMIN+X5/2)
1200 MOVE XPT-70,I*85:PRINT"*10^";AX
1210 REM ************************ YAXIS ****************************************
1220 @%=&01020203
1230 IF OX > 1200 THEN I=-1 ELSE I=1
1235 IF OX>1200 THEN I1=-4  ELSE I1=1
1240 PROCscay(YMIN):MOVE I*1.5,YPT:PROCscay(YMAX):DRAW I*1.5,YPT
1250 PROCscay(YMIN):MOVE 0,YPT:PROCscay(YMAX):DRAW 0,YPT
1260 IF YMAX<=0 THEN 1320
1270 Y=YMIN:Y4=0:REPEAT:Y4=Y4+1:PROCscay(Y)::IF YPT >-50 AND YPT <50 THEN 1290
1280 MOVE 0,YPT:DRAW I*15,YPT:MOVE I1*25,YPT+10:AY=Y/10^Y9:AY=FNB(AY):I$=STR$(A
Y):PRINTI$;
1290 Y=Y+Y5:UNTIL Y4=Y3+1
1300 @%=01020202
1310 IF I<0 THEN MOVE -200,YPT-30
1315 PRINT" *10^";Y9 :GOTO 1390
1320Y=YMAX:Y4=Y3:REPEAT:Y4=Y4-1:PROCscay(Y):IF YPT >-50 AND YPT <50 THEN 1340
1330MOVE 0,YPT:DRAW I*10,YPT:MOVE I1*25,YPT+10:AY=Y/10^Y9:AY=FNB(AY):I$=STR$(AY
):PRINTI$;
1340Y=Y-Y5:UNTIL Y4=0
1350 @%=01020202
1360 IF I<0 THEN PROCscay(YMIN+Y5) ELSE 1380
1370 MOVE I*80,YPT-50
1380 IF I<0 THEN MOVE -200,YPT-30:PRINT" *10^";Y9 :GOTO 1390
1387PRINT" *10^";Y9
1390 ENDPROC
1400 REM ******************** SCALE X TO GRAPHICS UNITS  *****************
1410 DEFPROCscax(XVAL)
1420 XPT=((XVAL-XMIN)/(XMAX-XMIN))*1219-OX+30
1430 ENDPROC
1440 REM ******************** SCALE Y TO GRAPHICS UNITS  *****************
1450 DEFPROCscay(YVAL)
1460 YPT=((YVAL-YMIN)/(YMAX-YMIN))*983-OY+20
1470ENDPROC
1480 REM *********** READ & DRAW POINTS & LINE ***********
1490 REM A%=1 WHEN CH. FROM LSQ1
1500 DEFPROCplot
1510VDU23,224,0,0,0,0,0,12,6,3 :A$=CHR$(224)
1520VDU23,226,192,96,48,0,0,0,0,0:A1$=CHR$(226)
1530VDU23,225,0,0,0,0,0,48,96,192:B$=CHR$(225)
1540VDU23,227,3,6,12,0,0,0,0,0:B1$=CHR$(227)
1550PNT$=A1$+CHR$(8)+CHR$(8)+B1$+CHR$(8)+CHR$(11)+A$+B$
1560 IF A%=1 THEN F$="POINTS"
1570 IF A%=2 THEN F$="PDATA1"
1580 F1=OPENIN(F$)
1590 REPEAT
1600 INPUT£F1,X,Y
1610 PROCscax(X)
1620 PROCscay(Y)
1630 MOVE XPT,YPT-4
1640 PRINTPNT$
1650 UNTIL EOF£F1
1660 CLOSE£F1
1670 VDU 4
1680 IF A%=1 THEN F$="LINE"
1690 IF A%=2 THEN F$="PDATA2"
1700 FX=OPENIN(F$)
1710 N=0
1720 REPEAT
1730 N=N+1
1740 INPUT£FX,X,Y
1750 IF N=1 THEN K=4 ELSE K=5
1760 PROCscax(X):PROCscay(Y):PLOT K,XPT,YPT
1770 UNTIL EOF£FX
1780 CLOSE£FX
1790 ENDPROC
1800 DEFPROCscreen
1810VDU 2
1820*FX6,10
1830 VDU1,34
1840 FOR L%=79 TO 0 STEP-1
1850 VDU 1,27,1,84 ,1,&30,1,&38
1860VDU 1,27,1,83,1,&30,1,&35,1,&31,1,&32
1870 FOR T%=0 TO 31
1880 FOR G%=0 TO 7
1890VDU 1,?(HIMEM+T%*640+G%+L%*8),1,?(HIMEM+T%*640+G%+L%*8)
1900NEXT G%,T%
1910VDU1,13,1,10
1920NEXT L%
1930VDU 1,27,1,65,1,&1B,1,&41
1940 VDU 3
1950 ENDPROC
```

DATA CORRECTION PROGRAM "DC"

```
 10MODE0
 20*DRIVE1
 30DIMM(N%,1)
 40D=OPENIN"DATA"
 50FORC=1TON%
 60INPUT£D,M(C,0)
 70INPUT£D,M(C,1)
 80PRINTC;M(C,0);M(C,1)
 90NEXT
100CLOSE£D
110N%=N
120INPUT"ARE THESE POINTS CORRECT",A$
130IF A$="Y" THEN 210
140N=N-1
150INPUT "NUMBER OF POINT YOU WISH TO CORRECT",L
160FORA=L TO N
170M(A,1)=M(A+1,1)
180M(A,0)=M(A+1,0)
190NEXT
200GOTO120
210DC=OPENOUT"DATA"
220FORC=1TON
230PRINT£DC,M(C,0)
240PRINT£DC,M(C,1)
250NEXT
260CLOSE£DC
270*DRIVE0
280END
```

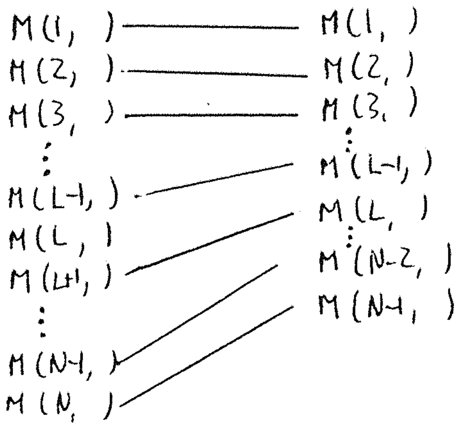
PROGRAM FOR REMOVING ERRONEOUS DATA POINTS FROM DATA FILE

Lines10 to 100 read in data from the file labelled DATA

Lines 120 and 130 branch the program. If the data are correct the program moves to line 210 and stores the corrected data, if not it proceeds directly to correct the data.

Lines 140 reduces the number of points by one

Lines 150 to 190 remove the incorrect data point thus:



incorrect point L is not retained

uncorrected data corrected data

Line 200 sends the program back to the branch at line 100

Lines 210 to 250 replace the old DATA file with a new one anD store the corrected data in the file and end the program.

LIST OF VARIABLES

N%=resident integer variable from experimental control program

M(C,0)=value of pressure for point C

M(C,1)=value of logsigma for point C

A$=string for holding answer to question

N=total number of data points left after removal of erroneous values

L=sequence number of incorrect point

APPENDIX 2. LIGHT TRANSMISSION

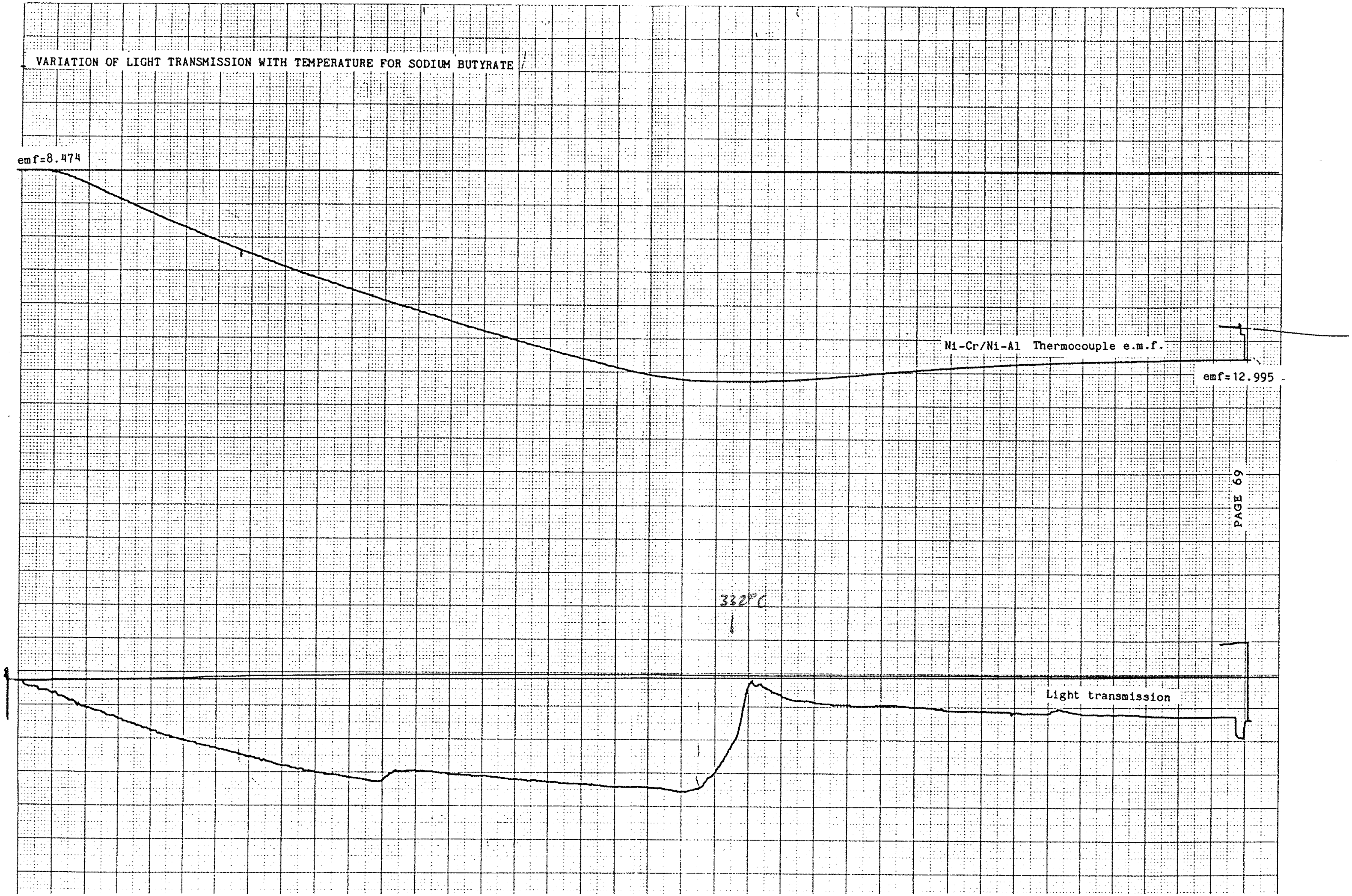
Some investigations were carried out to determine phase transition temperatures using variations in light transmission.

The light transmission of a sample could be recorded using the apparatus shown in fig.A2.1 and fig.A2.2. A solid sample of the salt was placed in the vessel and the temperature slowly raised to above T. The output from the photodiode and thermocouple was monitored as a chart recorder trace.

Traces showing variation of light transmission with temperature for sodium butyrate were obtained and examples are presented here. It can be seen that there is a large increase in light intensity at or just below a temperature of 332°C; followed by a fall off in intensity as the salt decomposed, turning brown and eventually black.

Sodium butyrate clears at a temperature of about 332 °C, and the step in intensity observed at about this temperature can be assigned with confidence to the anisotropic to isotropic liquid transition of the salt. It had been hoped that there would be an additional marked rise in transmission at a lower temperature, corresponding to the solid to smectic transition which sodium butyrate undergoes at about 256 °C(4). However, despite repeated attempts, this was not observed.

These experiments led to the conclusion that light transmission was not a fully effective method for studying the phase transitions in carboxylates, and that other more powerful and reliable methods should be used (e.g. DTA).



VARIATION OF LIGHT TRANSMISSION WITH TEMPERATURE FOR SODIUM BUTYRATE

VARIATION OF LIGHT TRANSMISSION WITH TEMPERATURE FOR SODIUM BUTYRATE

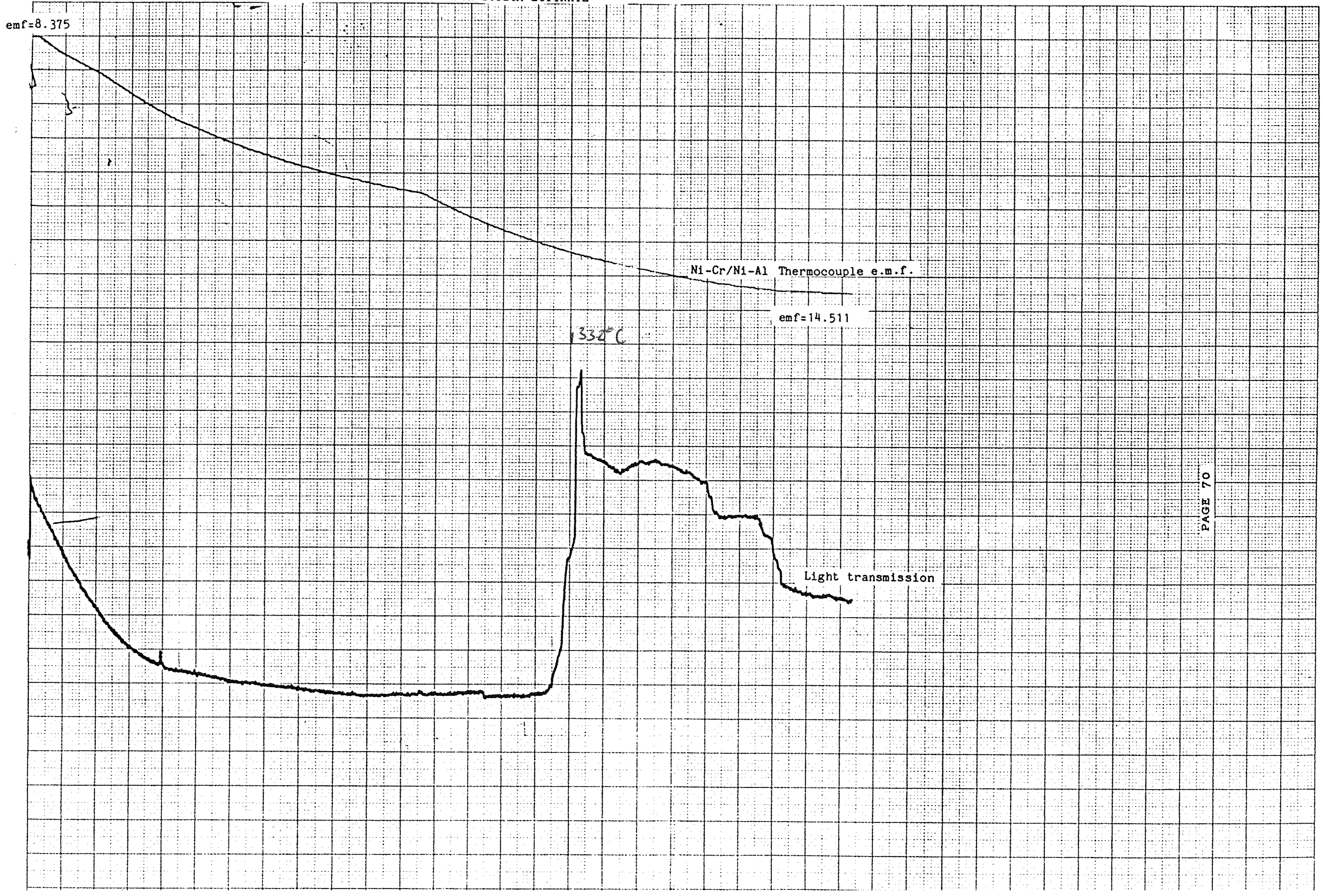


Fig A2.1

ARRANGEMENT FOR MEASURING LIGHT TRANSMISSION

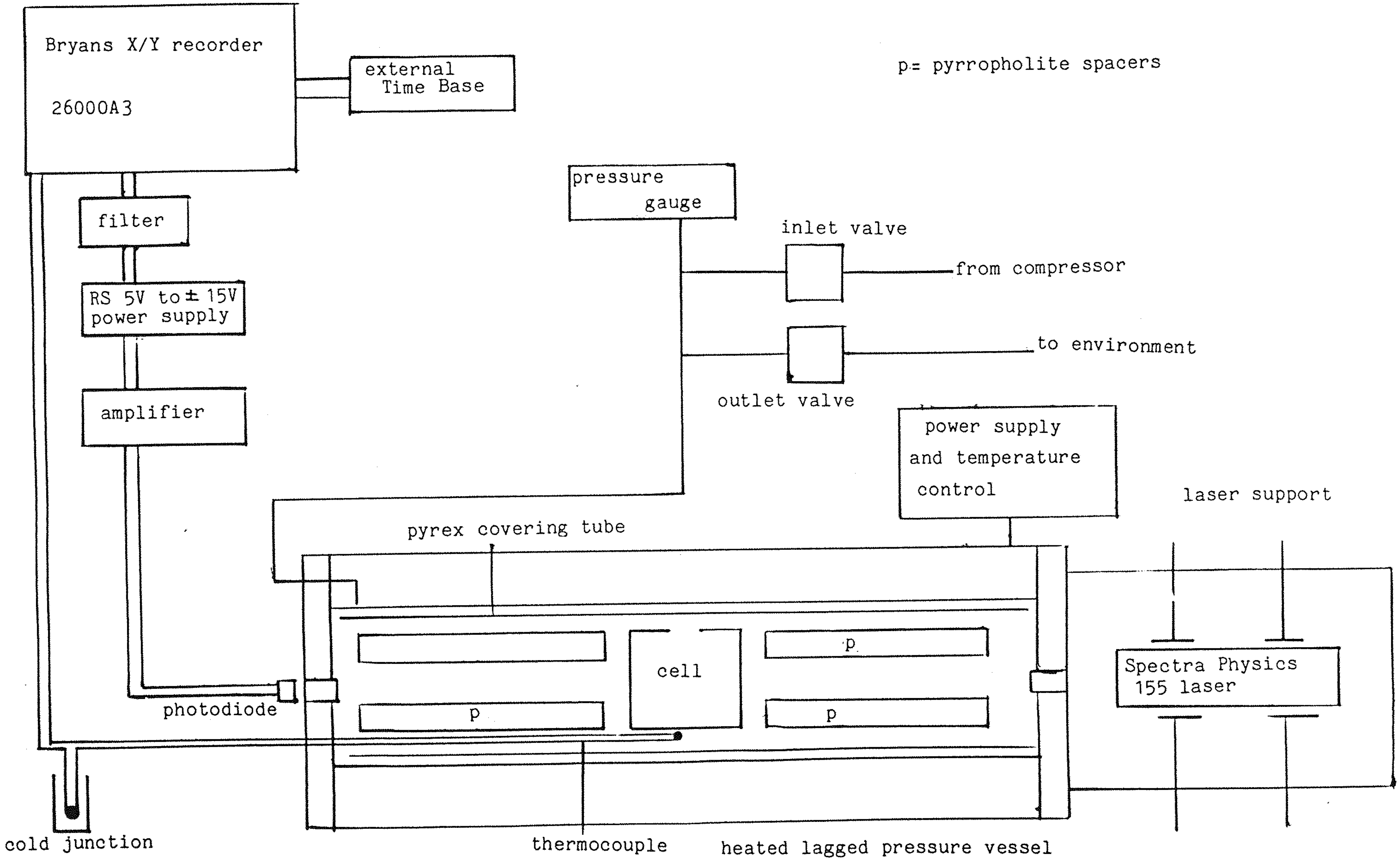
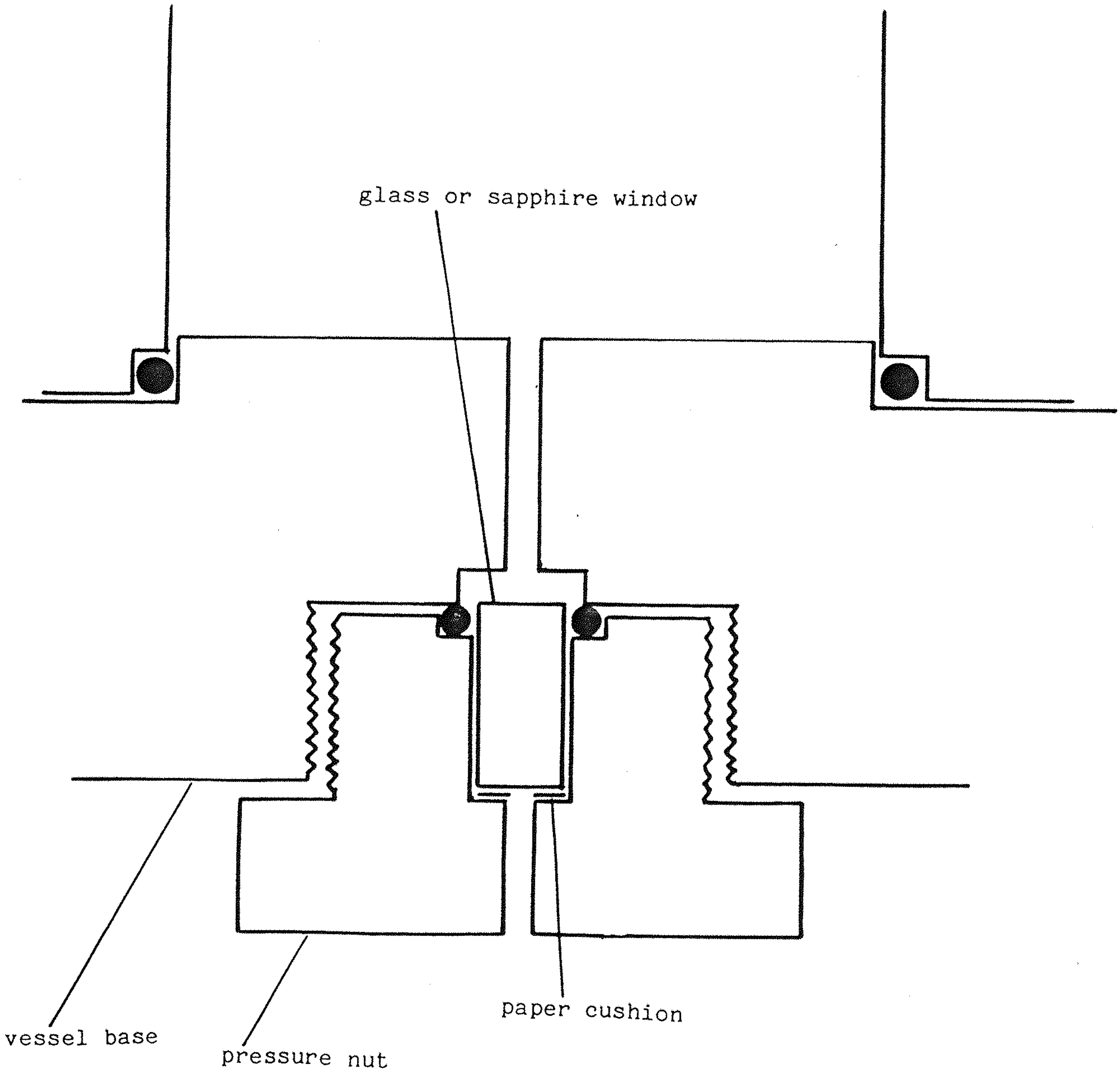


Fig A.2.2
DIAGRAM OF PRESSURE VESSEL ENDS WITH WINDOWS



APPENDIX 3.ZINC CARBOXYLATES

The zinc decanoate was prepared as follows. The acid was dissolved in hot ethanol and the stoichiometric amount of potassium hydroxide added to this solution. The stoichiometric amount of zinc sulphate dissolved in the minimum quantity of water was then added. This gave a white precipitate which was filtered and washed with water, ethanol and acetone, and then recrystallised from hot benzene.

The conductivity of zinc decanoate is very low ($K \sim 10^{-6}$ Scm^{-1}). To obtain conductances large enough to be measured with the apparatus available it was necessary to use a cell with a cell constant of about $1cm^{-1}$ (figA3.1), which was very much greater than that of the capillary types used previously. In addition it proved necessary to improve the electrical insulation on the leads into the vessel by using longer cones (fig.A3.2). The 'leakage conductance' between two of the old cones was about $2x10^{-6}S$ with no cell in place, presumably due to moisture on the cone surfaces. This resulted in negligible errors when the sample conductance was of the order of $10^{-3}S$, as in the case of the acetates and formates, but was significant when the conductance of the sample was about $10^{-6}S$, as in the case of decanoate. The new cones had a leakage conductance of $<10^{-9}$ S.

It has been suggested that the zinc carboxylates, of which zinc decanoate is typical, are dissociated to only a very small extent, and that conductivity is due almost entirely to the zinc ions (8, see introduction). Initial conductivity readings indicated that conductance tended to increase slightly with pressure (Table A3.1), which would be consistent with partial dissociation.

Studies indicated that the salts tended to give inconsistent readings (Table A3.2). Adding impurities to samples had no systematic effect on conductivity, and the reason for the discrepancies remained unclear. However this was clearly a serious problem and would obviously need to be investigated further.

Fig A3.1 CELL DESIGN FOR LONG CHAIN CARBOXYLATES

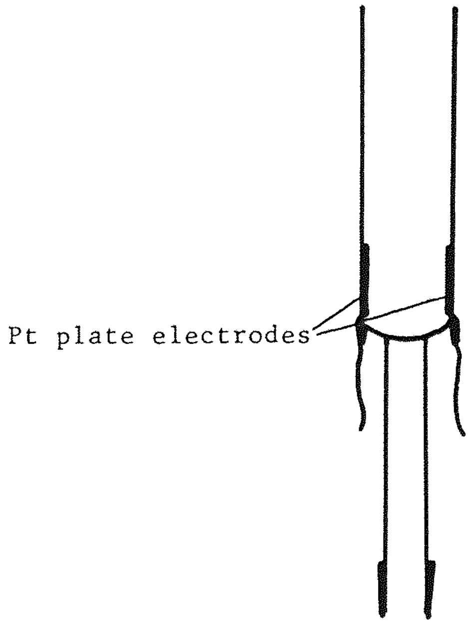


Fig A3.2 NEW CONE DESIGN

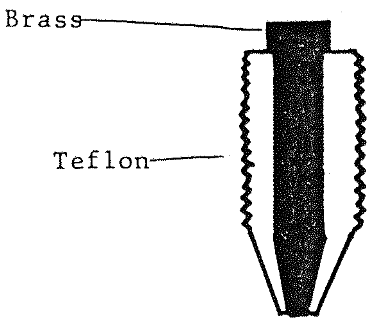


Table A3.1. Preliminary conductance readings for zinc carboxylates

Conductivity/μmho	Pressure/bar
1.178	303
1.192	640
1.211	820
1.198	557

Readings were carried out without accurate temperature measurement, and must therefore be regarded as unreliable.

Table A3.2. Conductivity values at zero pressure for separate samples of zinc decanoate.

Sample	Conductivity at 435K/μmho
1	1.54
2	3.8
3	1.02 and 1.14
4	3.47
5	1.46
literature	1.04 at 450K (11)

Measurements carried out by R. Jackson

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