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STABLE PRESSURE TRANSDUCER

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Interim Report

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ABSTRACT

This report describes recent work on the development of the solid-dielectric capacitive pressure transducer. The performance of the system with an invar sample holder is described. This device minimizes adiabatic heating effects so as to shorten thermal equilibration times and simplify thermostating. The temperature and pressure dependences of several new materials are reported. The potential of one of these, bismuth germanium oxide, as a transducer material in conjunction with As_2S_3 is presented. The possible use of doped-crystals for minimizing the temperature dependence of the capacitors is discussed.

INTRODUCTION

In our search for a stable pressure transducer we are continuing with the development of a capacitance gauge which uses hydrostatically pressurized solid dielectric capacitors. To circumvent the inherent temperature dependence of individual capacitors we are experimenting with a device where two different capacitors, placed in opposite arms of the Wheatstone bridge measuring circuit, are both within the pressure vessel. The resulting bridge balance gives the ratio of the two capacitances,

$$R = C_1/C_2 \tag{1}$$

The observed change of the ratio measurement with temperature and pressure is

$$\frac{1}{R} \frac{dR}{dT} = \frac{1}{C_1} \frac{dC_1}{dT} - \frac{1}{C_2} \frac{dC_2}{dT} \tag{2}$$

and

$$\frac{1}{R} \frac{dR}{dP} = \frac{1}{C_1} \frac{dC}{dP} - \frac{1}{C_2} \frac{dC_2}{dP} \; . \tag{3}$$

The appropriate capacitors for the pressure transducer are therefore, ones having nearly identical temperature dependences but widely differing pressure dependences. Capacitor pairs made from parallel and perpendicular cuts of calcite ($CaCO_3$) meet our basic requirements reasonably well so we have been proceeding with the development and testing of a device using this material. The calcite pair does have drawbacks so that the temperature and pressure dependences of capacitors made from other materials are continuing to be measured in the hope of finding a better combination. The current status of this work is presented.

INVAR SAMPLE HOLDER

The invar sample holder for the pressure transducer has been tested and found to be basically satisfactory. A picture of the partially disassembled sample holder is shown with the pressure vessel in Fig. 1. The purpose of this device is to minimize the time required for thermal equilibration after pressure changes and to simplify the thermostating as much as possible. Whenever a pressure vessel is pressurized, the contents of the vessel are compressed and their temperature increases while the vessel itself is stretched and cools. The idea behind the invar sample holder is to equate these heating and cooling effects so that the temperature of the system will return to its original value after thermal equilibrium is reestablished following a pressure change. The amount of heating that occurs in a piece of material under compressive or tensile stress is given by

$$Q = T \bar{V} \bar{\beta} \Delta P, \tag{1}$$

where $\bar{\beta}$ is the average thermal expansion coefficient of the material for the range of the pressure change, ΔP, and $\bar{V}$ is the average volume. Calculations indicate that for simple geometries the cooling that occurs when a vessel is internally pressurized would be equal in magnitude to the heating that would occur upon externally pressurizing a piece of the same material having a volume equal to the internal volume of the vessel. Since it is necessary to use oil, which has a very large expansivity, as the pressurizing fluid, the majority of the internal volume of the vessel has been filled with invar, which has a particularly small expansivity. By limiting the amount of oil to 7% or 12 cm^3 of the internal volume of the vessel and filling most of the remaining space with invar, we calculated that the average expansivity should equal that of the

steel vessel. Our experiments indicate that these ideas are basically correct.
In Fig. 2 we show the actual temperature change observed with the system
upon changing the pressure. The pressure vessel was effectively isolated from
the surroundings in an insulated container with a thermometer attached to the
outer surface of the pressure vessel. At the center of the figure is shown
the effect of depressurizing the vessel over about a 1 minute period from
140 MPa (20,000 psi) to zero. The outer surface of the vessel first warms
but as the vessel thermally equilibrates with the material inside, it cools,
stopping at a temperature 4 mK below the initial temperature. To the right
is seen the reverse effect when the system was repressurized. The slope of the
base line in the figure is due to small loss of heat to the surroundings. We
calculate that each cm^3 of oil in the system that is displaced by invar will
produce a 3 mK difference in the temperature change observed with a 140 MPa
pressure change. The results in Fig. 2 indicate that 1 1/3 cm^3 more oil needs
to be displaced from the system to exactly balance the heating and cooling
effects. To get to this point it was necessary to displace much more oil than
predicted by the calculation. In Fig. 3 we have plotted the temperature changes
observed with three different quantities of oil in the system and find that
the temperature changes are varying as predicted but are displaced from the
calculated curve by nearly 8 cm^3 of oil. Although it is not easy to determine
the exact amount of oil in the system, (considering screw slots, counter sinks,
oil equivalent of the O-ring seal, etc.) we do not think we are in error by
this amount. The volume differences between the plotted points in Fig. 3 are
accurately known, however, for they were determined by the volume of the invar
pieces used to displace successive quantities of oil. The most likely cause
of the discrepancy is our failure to properly account for the heating effects
of the threaded vessel closure. Our calculation assumed that the vessel has
spherical ends which when pressurized would be under a net tensile stress.

The threaded closure of the actual vessel, however, will be under largely compressive stresses. This oversight is unfortunate for in designing the sample holder we were overgenerous in the size of the openings allowed for various purposes and they will be difficult to modify.

Another, and potentially more serious problem is that in attempting to use the invar sample holder, we have repeatedly broken the calcite capacitors when changing the pressure in the system. The problem appears to be due to poor flow patterns for the oil in the system so that any pressure surge develops large pressure gradients across the crystals. The main path for the flow of oil in the system is the hole along the central axis of the sample holder. This hole communicates directly with the inner surface of the capacitors and probably results in a large pressure gradient across the capacitor. By blocking off this path and forcing the oil to enter the sample chambers at the edge of the capacitors we may be able to get around the problem. It is only the calcite crystals with the crystalline axis parallel to the faces that have been breaking. These crystals are particularly susceptible to any abuse because of the cleavage planes which lie normal to the faces of the discs. In trying to determine the cause of the breakage we exhausted our supply of these crystals and are just now getting back to the testing of the device.

NEW MATERIALS

The temperature and pressure dependences of capacitors made from several new dielectric materials are given in Table 1 and are plotted in Fig. 4 along with the values of materials measured earlier.

Table I

Material	Dielectric Constant	$\frac{1}{3}\frac{dC}{dP}$ x 10^{12}/Pa	$\frac{1}{C}\frac{dC}{dT}$ x 10^6/K
CaF_2-3%ER^{3+}	5.6	−50.4	182
$LiTaO_3$-X	54	−47.1	165.6
$LiTaO_3$-Z	44	−27.7	1302.5
BGO($Bi_{12}GeO_{20}$)	46	−102.5	72.0
Diamond	5.9	− 1.444	9.2
TeO_2(100)	23	+ 22.8	151.0
TeO_2(001)	27	− 38.0	255.5

The measurement of all but the erbium-doped CaF_2 sample was made possible by the development of techniques for handling samples smaller than the usual 1" discs. The $LiTaO_3$ and BGO (bismuth germanium oxide, $Bi_{12}GeO_{20}$) samples were 3/4" discs and the TeO_2 (paratellurite) samples were $\frac{6}{10}$" discs. The diamond sample was a triangular plate measuring approximately 3/8" by 1/2". Masking rings for the aluminum electrode coatings were 1/2" diameter for the 3/4" discs and 0.350" for the smaller samples. The diamond and doped CaF_2 samples were obtained from John Fontanella of the U.S. Naval Academy, the others were from commercial sources. Two of these new materials, BGO and the doped CaF_2, are of particular interest and are discussed in detail below.

Bismuth germanium oxide ($Bi_{12}Ge\ O_{20}$) is a pale yellow material that is commercially available as discs cut from optically clear single crystals. The sample used in our present measurements was of obviously poor quality; the highly polished disc of 0.024" thickness was not transparent. This is of importance since there was a drift in the capacitance which lasted for several hours following a temperature or pressure change. The total change during these periods of drift was small but amounted to an equivalent pressure change of the order of 10^5 Pa (tens of psi). Behavior of this type has been observed in two classes of materials, those that are impure and those that are either piezoelectric or pyroelectric such as quartz or $LiTaO_3$. BGO is piezoelectric so the observed drift may be associated with that property rather than the obvious poor quality of the present sample.

Our interest in BGO stems from its temperature dependence being close to that of As_2S_3 while the pressure dependence of the two materials are large and of the opposite sign. The properties of these two materials are plotted in Fig. 4 where their relation to other materials can be seen and in Fig. 5 where their relation to each other is detailed. As_2S_3 samples from three different sourceswere measured and there is some variation between them as shown in the figures. In Table 2 the coefficients are tabulated for the fit of the experimental results to the equation,

$$C=C_0(1 + AP + BP^2) .\hspace{3cm}(5)$$

These are listed with a few other examples for comparison. $As_2S_3(B)$ values are used in the table. At the bottom of Table II are listed the coefficients that could be realized with an As_2S_3-BGO pair combination as well as those of a calcite pair.

Table II Temperature and Pressure Characteristics of Capacitors

Material	$\frac{1}{C°}\frac{dC°}{dT}$ x10^6/K	$\frac{1}{C°}\frac{dC°}{dP}$ = Ax10^{12}/Pa	$\frac{dA}{dT}$x10^{12}/PaK)	$\frac{1}{A}\frac{dA}{dT}$ (K^{-1})	Bx10^{20}/Pa^2
CaF$_2$	262	-37.8	-0.025	0.00066	0.27
CaCO$_3$ $\perp$	331.5	12.0	0.0149	0.00124	0.42
CaCO$_3$ $\parallel$	335	71.0	0.0169	0.00024	1.25
As$_2$S$_3$	67	116	0.047	0.00040	-1.36
BGO(Bi$_{12}$GeO$_{20}$)	72.0	-102	0.037	0.00036	1.8

Pair Combinations

Materials	$\frac{1}{R°}\frac{dR°}{dT}$ x10^6/K	$\frac{1}{R°}\frac{dR°}{dP}$=Ax10^{12}/Pa	$\frac{dA}{dT}$x10^{12}/(PaK)	$\frac{1}{A}\frac{dA}{dT}$(K^{-1})	Bx10^{20}/Pa^2
CaCO$_3$ Pair	3.6	59.0	0.0020	0.000034	0.76
As$_2$S$_3$-BGO	-5	218	0.004	0.000018	-3.4

The data for the pairs can be used to determine the thermostating requirements one would face in utilizing an As_2S_3-BGO pair compared to a calcite pair. There are three ways a capacitive pressure determination can be influenced by temperature effects. They are: (1) lack of thermal equilibrium between the two capacitors, (2) the capacitance measurement under pressure being made at a different temperature from that of the reference value at zero pressure (see Eqn. 5), and (3) the absolute temperature being in error since the coefficient of Eqn. 5 are temperature dependent. The equations for determining the effect of these errors were presented in the April, 1975 report on this project. A comparison of the allowable thermal variations for the two capacitor systems are presented in Table III. The considerable improvement achievable with the As_2S_3-BGO pair is evident.

Table III Thermal stability required to obtain 700 Pa (0.1 psi)
pressure resolution with calcite pair and As_2S_3-BGO
capacitor combinations.

Materials	Thermal equilibrium between capacitors	Short term temperature precision, 0 → 140 MPa	Long term temperature accur At 140 MPa
$CaCO_3$ pair	0.12 mK	11.5 → 10 mK	75 mK
As_2S_3-BGO	2.2 mK	30 → 39 mK	140 mK

We have ordered some high quality BGO samples and plan soon to test whether or not the drift behavior observed with our present sample is an intrinsic property of the material or due to impurities in our sample.

Erbium doped CaF_2

John Fontanella and Carl Andeen have been conducting experiments on erbium doped calcium fluoride crystals. Their interest is primarily in the dipolar complexes formed by Er^{3+} doping, but the experimental results indicate that it may be possible to produce a capacitor having a low temperature dependence in this way. In Fig. 6 we have reproduced a figure from a paper they have recently submitted to Journal of Physics, C which shows the temperature variation of the dielectric constant of several CaF_2: Er^{3+} crystals. The lowest curve in the figure effectively represents the behavior of undoped CaF_2. The two highest curves at 1 and 3% Er^{3+} are the curves of interest, they show minima, i.e. zero temperature dependence, at temperatures of about 100 and 200 K, respectively. If by increasing the level of doping, the minimum could be raised to 300K the material would be well suited for a capacitive pressure transducer.
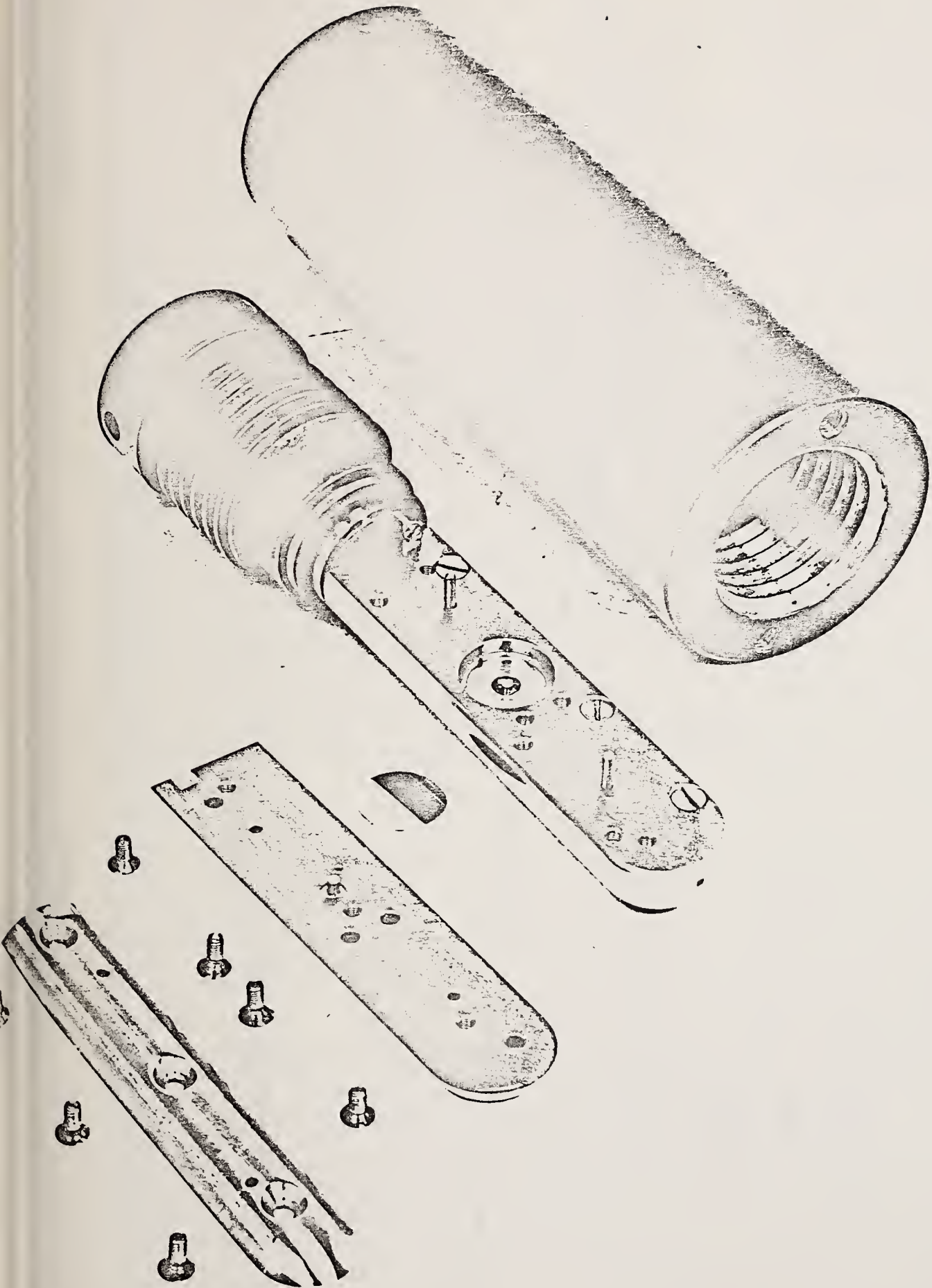
We have made capacitance measurements with the 3% Er^{3+} CaF_2 sample as a function of temperature and pressure and found the system well behaved. The loss component was up by about a factor of 50 over the pure material but was still at a tolerably low level. From the trend of the loss component with increasing Er^{3+} doping, however, one would predict that the loss may become too large at concentrations greater than 3% so that it may be necessary to use a different doped system to fully exploit this approach. These ideas will have to be verified by experiment.
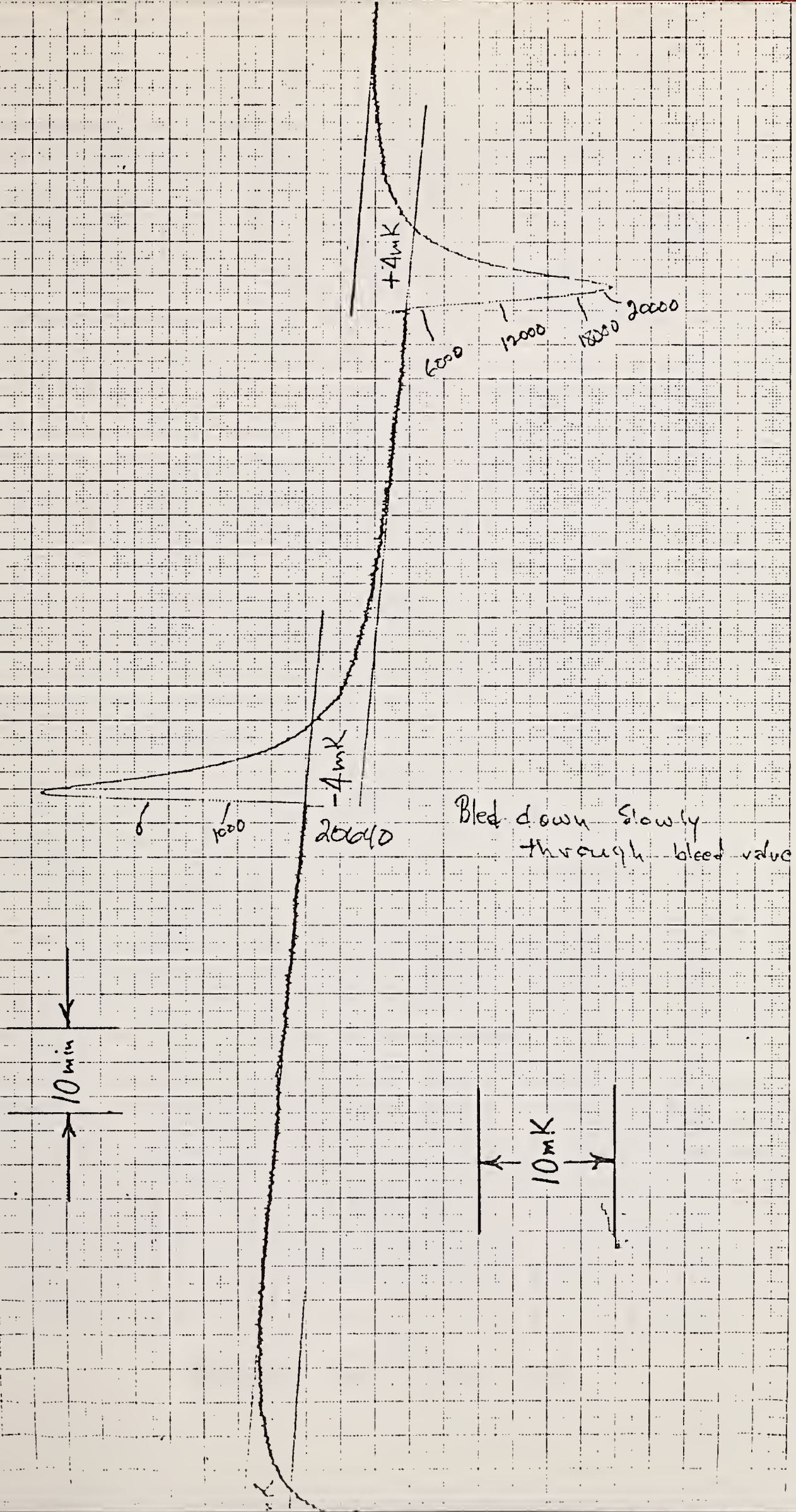
Capacitance Bridge

The limited-range automatic capacitance bridge being built for use with the pressure transducer has been essentially complete for several months but component failures have prevented us from testing it with the pressure transducer. The main problem has been with the voltage-to-frequency converters which failed, were repaired and failed again. The manufacturer could give no reason for the repeated failures and the components have been replaced with new models.
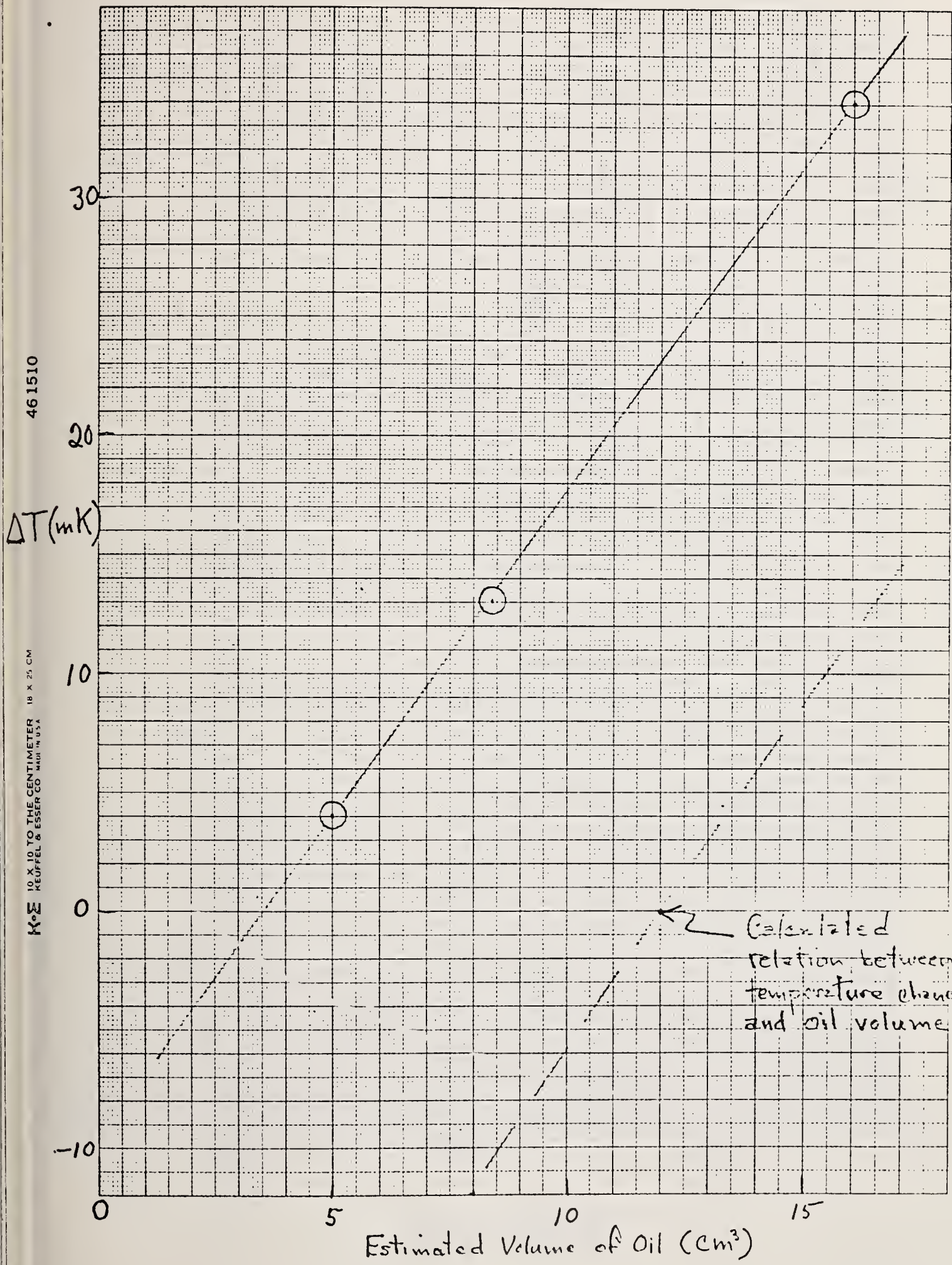
Figure Captions

1. Invar sample holder and pressure vessel.

2. Temperature changes at the outer surface of the isolated pressure vessel resulting from 140 MPa (20,000 psi) pressure changes. Vessel contains the invar sample holder and about 5 cm^3 of pressurizing oil. Central peak is for decreasing pressure to zero and peak at right is for repressurizing.

3. Net temperature changes in isolated transducer system containing different quantities of oil.

4. The pressure dependence of the capacitance of various materials as a function of their temperature dependence. The values given are for 35°C and atmospheric pressure. The lines joining samples of different crystalline orientation indicates values that could be achieved at intermediate angles.

5. The temperature and pressure dependence of BGO ($Bi_{12}Ge\ O_{20}$) and As_2S_3. Three different samples of As_2S_3 samples were measured: (A) Servo Corporation, (B) Barnes Engineering, and (C) an older Servo Corporation sample supplied by John Fontanella. Arrows indicate how the dependences change under a pressure of 140 MPa.

6. The real part of the dielectric constant of several Er^{3+} doped CaF_2 crystals as a function of temperature. Top curve is a 3% sample, the next is 1% and the lowest is 0.001%. The results were obtained by John Fontanella and Carl Andeen and are to be published in Journal of Physics, C.
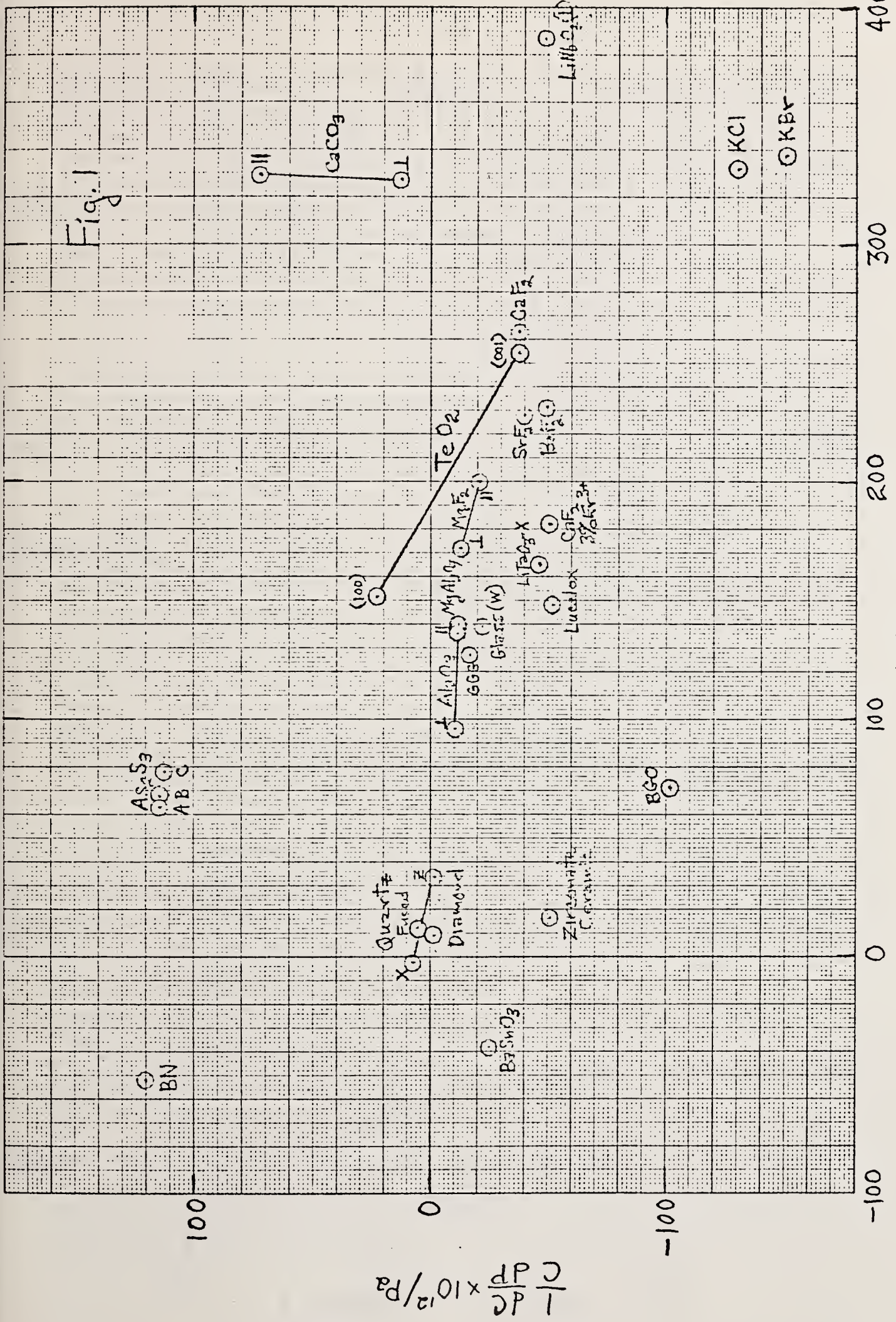
+4mK

6000   12000   18000   20000

-4mK

6   1000

20040

Bled down slowly
through bleed valve

10 min

10 mK.

Estimated Volume of Oil (cm³)

Calculated relation between temperature change and oil volume.

Fig. 1

CaF$_2$:Er

1000 Hz

ϵ'

8.46255

7.46255

6.46255

100   200   300   400

T(k)