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STABLE PRESSURE TRANSDUCER

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ABSTRACT

This report describes recent work on the solid-dielectric
capacitive pressure transducer. Capacitance measurements on parallel
and perpendicular cut calcite crystals and CaF_2 crystals have been
determined at several temperatures against pressures determined by a
piston gauge. The results are used in an extensive discussion of the
effectiveness of various possible devices. Design parameters for
minimizing compressive heating in the pressure vessel are presented.
Data on several new materials are reported as well as the progress on
the automatic capacitance bridge to be use with the transducer.

INTRODUCTION

Since it was first demonstrated that solid dilectric capacitors could be used as highly stable pressure transducers, ways have been sought to reduce the pronounced temperature dependence of these devices. The search for a material that would have a small temperature dependence of capacitance and still retain a sizable pressure dependence has not been abandoned, but more effort is now being directed toward other ways of circumventing the problem. The current program in this laboratory is an attempt to use two capacitors inside the pressure vessel with one in each side of the bridge measuring circuit so that the bridge balance is a measure of the ratio of the two capacitors,

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

The temperature dependence of the ratio measurement 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 similarly, the pressure dependence is

$$\frac{1}{R}\frac{dR}{dP} = \frac{1}{C_1}\frac{dC_1}{dP} - \frac{1}{C_2}\frac{dC_2}{dP} \ . \tag{3}$$

By finding a pair of materials where the difference in Eq. 2 is sufficiently small relative to the difference in Eq. 3 we can produce a pressure transducer with tractable temperature effects. Note that it is the fractional change in capacitance that is of concern in Eqs. 2 and 3, this is a property of the material and does not depend on the magnitude of the individual capacitances.

To date, parallel-and perpendicular-cut calcite ($CaCO_3$) crystals are the
only pair tested that approach our requirements. In the present report we
begin by presenting recent data on calcite which is used to critically
evaluate the transducer performance that can be achieved with this material.
The possibility of using one of the calcite crystals in combination with
either KCl or KBr is explored. In this evaluation we also consider the
measurement method being tested at Redstone Arsenal which utilizes two
capacitors of the same material with one inside the pressure vessel and one
at ambient pressure.

Temperature and Pressure Dependence of Calcite and CaF_2 Capacitors

Detailed capacitance determinations as a function of temperature and pressure were carried out on a parallel and perpendicular cut pair of calcite samples which were measured both separately and in opposition to each other. Data were simultaneously collected on CaF_2, the material which has been used as a benchmark for comparisons throughout this work. Pressures were precisely determined by a Ruska type 2415, 0-20,000 psi piston gauge, rather than the Heise Gauge used for all previous measurements in this laboratory. The precise pressure measurements permitted a detailed analysis of the temperature and pressure dependence of these samples. Pressure determinations were carried out at four different temperatures so the cross derivatives of the capacitance could be determined. The data were assumed to have the usual functional form

$$C = C° (1 + AP + BP^2) \qquad\qquad (4)$$

which rearranges to

$$\frac{\Delta C}{PC°} = A + BP . \qquad\qquad (5)$$

Accordingly, with the data plotted as $\Delta C/PC°$ versus P as shown in Figs. 1-3 the quantities A and B are determined, respectively, by the intercept and slope of the lines. From these data dA/dT can be derived which is required to determine the temperature dependence of the pressure equation and also determines how the temperature dependence of the capacitance varies with pressure

Throughout the determination of these data we were experiencing difficulties with the reproducibility of the capacitance measurements. There were random shifts in the values amounting to several parts-per-million. After completion of the measurements it was discovered that shifts of the same magnitude in the capacitance measurement could be obtained by shifting the relay rack containing the capacitance bridge from side to side. The bridge problem is apparently due to ground loops which have now been partially corrected We are assuming that all our irreproducibility in the data was due to this cause for if the shifts were in the capacitor themselves they would indicate pressure uncertainties up to about 20,000 Pa (several psi). These arbitrary shifts in the capacitance show up as scatter in the data of Figs. 1-4 which is much larger than the expected imprecision of the measurements. The data at 20°C were take in two separate sets some two weeks apart and are distinguished by open and closed symbols. The systematic shift between these two sets of data is obvious.

The data for CaF_2 are plotted in Fig. 1. These results are in good agreement with the earlier data take by Andeen, Fontanella, and Schuele (Rev. Sci. Instr. 42, 495 (1971)) at 35°C; the 35°C curve drawn in Fig. 1 is the equation given in their paper. The value for dA/dT derived from the results in Fig. 1 is given in Table I.

In Fig. 4 are plotted the measured ratios of the calcite pair which are fitted to an equation of the same functional form as used for the individual capacitances,

$$R = R°(1 + A_r P + B_r P^2) \qquad (6)$$

TABLE I Temperature and Pressure Characteristics of Capacitors

Material	$\frac{1}{C°}\frac{dC°}{dT}\times10^6$/K	$\frac{1}{C°}\frac{dC°}{dP}=A\times10^{12}$/Pa	$\frac{dA}{dT}\times10^{12}$/(PaK)	$\frac{1}{A}\frac{dA}{dT}$ (K^{-1})	$B\times10^{20}$/Pa^2
CaF_2	262	-37.8	-0.025	0.00066	0.27
KBr	337	-147.7	-0.107	0.00072	5.6
$CaCO_3$ $\perp$	331.5	12.0	0.0149	0.00124	0.42
$CaCO_3$ $\parallel$	335	71.0	0.0169	0.00024	1.25
As_2S_3	65	116	0.05	0.0004	-1.36
BN	-52	126	0.05	0.0004	-6.9

Pair Combinations

Materials	$\frac{1}{R°}\frac{dR°}{dT}\times10^6$/K	$\frac{1}{R°}\frac{dR°}{dP}=A\times10^{12}$/Pa	$\frac{dA}{dT}\times10^{12}$/(PaK)	$\frac{1}{A}\frac{dA}{dT}$ (K^{-1})	$B\times10^{20}$/Pa^2
$CaCO_3$ Pair	3.6	59.0	0.0020	0.000034	0.76
$CaCO_3\parallel$-KBr	-2	219	0.124	0.00058	-1.10

The curves in Fig. 4, except for a small correction to the slopes, are the differences between the curves for corresponding temperatures in Figs. 2 and 3. Neglecting terms higher than quadratic in pressure, the correction is

$$\frac{\Delta R}{R^\circ P} = \frac{\Delta C_1}{C_1^\circ P} - \frac{\Delta C_2}{C_2^\circ P} - A_1(A_1 - A_2) \, P \tag{7}$$

To a good approximation the temperature dependence as a function of pressure for the individual capacitances can be written as

$$\frac{1}{C}\frac{dC}{dT} = \frac{1}{C^\circ}\frac{dC^\circ}{dT} + \frac{dA}{dT} \, P \tag{8}$$

It follows using Eqs. 2 and 6 that

$$\frac{1}{R}\frac{dR}{dT} = \frac{1}{C_1^\circ}\frac{dC_1^\circ}{dT} - \frac{1}{C_2^\circ}\frac{dC_2^\circ}{dT} + \left(\frac{dA_1}{dT} - \frac{dA_2}{dT}\right) P = \frac{1}{R^\circ}\frac{dR^\circ}{dT} + \frac{dA_r}{dT} \, P \;. \tag{9}$$

Values for the different parameters for the calcite crystals are given in Table I.

The data in Fig. 4 appear nonuniform when compared with those of Figs. 2 and 3, they are, however, consistant with all the above equations within the experimental uncertainty. This apparent inconsistency probably arises because we are looking at small differences between relatively large numbers (note that the scale on the ordinate of Fig. 4 is twice that of the other figures).

The zero-pressure temperature dependence of the parallel-cut calcite crystal increases linearly with temperature but that of the one cut perpendicularly varies somewhat from a linear behavior. As a result the temperature dependence of the ratio, in units of 10^{-6}/K, increases from 1.5 to 5 in the range 5 to 45°C but in the region 10 to 30°C it is essentially constant at 2.7. We have made measurements on a second calcite pair and again found the

temperature dependence very small but different from the first pair. The temperature dependence of the perpendicular cut crystal from this pair was nearly identical to the first. That of the parallel cut was smaller than the perpendicular cut at low temperatures but increased more rapidly so that the temperature dependence of the ratio actually passed through zero at about 35°C. It should be noted that the electrode gap on the low voltage side of the second parallel-cut crystal was initially shorted and was opened by physically scraping away some of the aluminum coating. The loss component for this sample was about five times larger than that for the other samples; this and the other deviate behavior observed with this sample may be due to the treatment it received. This result does point out, however, that considerable variation may be found in the ratio measurements of different pairs.

Use of a Calcite Crystal With KCl or KBr.

The temperature dependence of the two calcite crystals are very close
to the values for KCl and KBr so the there is the possibility of using one of
these combinations in the pressure transducer. The pressure dependence of
the alkali halides is negative whereas that of calcite is positive so that in
a ratio measurement their magnitudes will add. As a result the pressure
sensitivity of one of these combinations would be 2 1/2 to 3 1/2 times larger
than that of the calcite pair.

Values of the temperature and pressure dependencies of the four materials
at 35°C are plotted in Fig. 5. The arrows extending from the points indicate
the change in the two dependencies as the pressure is increased from zero to
138 MPa (20000 psi). The calcite values are taken from the present work using
Eq. 8 and the pressure derivative of Eq. 4. The pressure dependencies and
zero-pressure temperature dependence of the two potassium salts are from the
work of Fontanella, Andeen, and Schuele (Phys. Rev. $\underline{B6}$, 582 (1972) but unfortunate
they did not determine dA/dT for their samples. Smith and Riehl (J. Phys. Chem.
Solids $\underline{35}$, 1327 (1974)) have measured the pressure dependence of KBr at 211 K
and 295 K which, if we assume A is a linear function of T, gives us a value
for dA/dT (See Table 1). The magnitude of this value appears rather large but
the ratio (1/A) dA/dT is comparable to other values listed in Table 1 so there
is no reason to suspect it is in error. No data is available to determine dA/dT
for KCl but it is probably similar to the value for KBr. As can be seen from
Fig. 5, subtracting the temperature dependence of KBr from that of parallel-cut
calcite, the dependence of the combination will vary from -2 to + 15 x 10^{-6}/K
as the pressure is increased from zero to 138 MPa. The possible use of this
combination is discussed in the next section.

Resolution and Temperature Effects in the Pressure Transducer

It is now reasonable to expect accuracies from a ratio-transformer capacitance bridge of at least $1:10^7$. Using the data in Table 1 for individual capacitors we find that for CaF_2, $1:10^7$ accuracy in the capacitance corresponds to a pressure resolution of

$$\frac{1 \times 10^{-7}}{37.8 \times 10^{-12}} = 2600 \text{ Pa} = 0.4 \text{ psi}$$

With As_2S_3 or BN the resolution is improved to about 850 Pa = 0.12 psi. For the calcite pair the pressure resolution would be about 1700 Pa = 0.25 psi and for a $CaCO_3$ - KBr pair it would be 450 Pa = 0.07 psi. With these systems we can expect to achieve pressure resolution in the region of 700 Pa = 0.1 psi; what demand does this put on the temperature regulation of the system?

We will consider the two measurement methods that use the ratio of two capacitors, the pressurized pair described above and the pressurized and unpressurized combination of the same material. There are three ways that temperature effects can cause errors in the capacitance ratio measurements. The first, and most important, arises from the two capacitors being at a different temperature. The second way is for the temperature to be different during the reference determination, $R°$; and the pressure determination, R. The third possible error can arise from the absolute temperature of the device being different between calibration and use.

We will consider how large each of these temperature effects can be and still have pressure resolution of 700 Pa when using the two types of ratio measurements. The error arising from a temperature difference between the two capacitors depends on the temperature dependence of the individual capacitors relative to the pressure dependence of the combination. For CaF_2 in a pressurized-unpressurized combination, resolution of 700 Pa requires that the two capacitors be within

$$\frac{37.8 \times 10^{-12}/Pa \times 700 \ Pa}{262 \times 10^{-6}/K} = 0.10 \ mK \ .$$

With As_2S_3 or BN the requirements are less stringent, thermal equilibration of only 1.2 and 1.6 mK, respectively, is required. For the calcite pair we require the two capacitors to be within

$$\frac{59.0 \times 10^{-12}/Pa \times 700 \ Pa}{333 \times 10^{-6}/K} = 0.12 \ mK.$$

With the parallel-cut calcite-KBr combination the requirement drops to 0.46 mK.

It is difficult to assess the size of the temperature gradients one may expect in a system. They are certainly less likely to exist in the case where both samples are in close proximity within the pressure vessel than where the two are separated by a pressure bearing wall. Nevertheless, even if heat flows in the system were large enough to cause sizable temperature gradients, they would have to change significantly from those that existed during the gauge calibration before errors would result.

Temperature differences will be generated within the system when it is pressurized or depressurized and the time it takes to reestablish equilibrium between the two capacitors can be a major consideration. Again, having the two capacitors within the pressure vessel has a definite advantage, for the two capacitors will probably be in thermal equilibrium with each other long before equilibrium is established throughout the system. Whether this is an advantage or not will depend on the combination's response to the actual temperature changes which we now consider.

The effect of temperature changes on the two measurement methods using capacitance ratios is different and we have summarized the contributions for the two methods in Table II. In this table the quantities given are $R/R°$ where $R°$ is the value of the ratio measurement at zero pressure and temperature, T. Quadratic terms in the pressure dependence have been neglected.

For the pressurized-unpressurized combination in Table IIa, the observed ratio at P = 0 does not change with temperature since the two capacitors are of the same material and are affected identically. As a result, in changing the pressure from 0 to P, the same change will be observed when starting at a temperature T and ending at $T + \Delta T$ as when the whole process occurred at the temperature $T + \Delta T$. The magnitude of this change depends on the total pressure, and its fractional dependence, $(1/A)\, dA/dT$, is tabulated in Table I for the materials of interest to us here. At the maximum pressure we are considering, 138 MPa (20,000 psi), 700 Pa amounts to $5:10^6$(5ppm). The temperature change that would be equivalent to this pressure resolution with a combination of two CaF_2 capacitors would be

$$\frac{5 \times 10^{-6}}{0.00066/K} = 7.5 \text{ mK}$$

With As_2S_3 or BN this equivalent temperature change would be 12 to 15 mK. These temperature values will vary inversely as the total pressure for the fixed

TABLE II   Capacitance Ratios as a Function of Temperature and Pressure

(a) Pressurized-Unpressurized Combination

	0	P
T	1	$1 + AP$
T+ΔT	1	$1 + AP + \dfrac{dA}{dT} P \,\Delta T = 1 + AP \left(1 + \dfrac{1}{A} \dfrac{dA}{dT} \Delta T\right)$

(b) Pressurized Pair

	0	P
T	1	$1 + AP$
T+ΔT	$1 + \dfrac{1}{R^\circ} \dfrac{dR^\circ}{dT} \Delta T$	$1 + AP + \left(\dfrac{1}{R} \dfrac{dR}{dT} + \dfrac{dA}{dT} P\right)\Delta T = 1 + AP + \left(\dfrac{1}{R^\circ} \dfrac{dR^\circ}{dT} + 2 \dfrac{dA}{dT} P\right)$

resolution of 700 Pa.

Unless the temperature dependence of the two different capacitors in the pressurized pair arrangement are identical, the ratio measurement will not be completely independent of temperature as indicated in the first column of Table II b. Now when the system is pressurized there are two correction terms and as initially written in the table they are both pressure dependent. In rewriting the equation in the table, Eq. 9 is used to substitute for $(1/R)dR/dT$ so that we are left with one correction term which is dependent on pressure and one which is not. The equation for the temperature equivalent ΔT for a given pressure resolution ΔP is

$$\frac{\frac{1}{R}\frac{dR}{dP} \times \Delta P}{\frac{1}{R°}\frac{dR°}{dT} + 2\frac{dA}{dT}P} = \Delta T \tag{10}$$

For the calcite pair the temperature equivalent of $\Delta P = 700$ Pa at $P = 0$ is 11.5 mK while at the maximum pressure of 138 MPa it is 10.0 mK. These temperature changes are the permitted limits when the temperature at pressure is different than it was in the reference state of zero pressure. When the temperature remains at $T + \Delta T$, ie it is in error by ΔT, when the system is pressurized the term $(1/R°)\ dR°/dT$ drops out of the observed capacitance change and the temperature change at $P = 138$ MPa could be as large as 75 mK before it would be equivalent to 700 Pa.

The KBr - $CaCO_3$ || pair is an interesting case, $(1/R°)\ dR°/dT$ and dA/dT are of opposite sign so that the denominator in Eq. 10 goes through zero at about 8 MPa (1200 psi). The temperature equivalents of a 700 Pa pressure change at various pressures are given as $\Delta T(1)$ in the following table.

| P | | ΔT(1) | ΔT(2) |
(MPa)	(psi)	(mK)	(mK)
0	0	77	∞
8	1200	∞	77
34	5000	24	18
69	10000	10	8.7
138	20000	4.5	4.3

The column headed ΔT(2) are the temperature equivalents for the case of
a pressure change with the temperature remaining at T + ΔT.

From these calculations it is evident that the KBr - $CaCO_3$ pair has less
stringent temperature requirements at pressures below 69 MPa and is only a
factor of two worse at 138 MPa when compared with a calcite pair. We saw
earlier that the thermal equilibrium requirement was a factor of 4 less
and the pressure resolution was a factor of 3.5 greater so on this basis
the KBr - $CaCO_3$ pair is superior in nearly every way.

In comparing the two pressurized pair combinationswith the performance
expected of either As_2S_3 or BN capacitor used in the pressurized-unpressurized
pair combination there is not a great contrast. In most of the cases the values
for the latter two combinations fall between the values for the former two.
Unless a material is found which would greatly enhance the performance of
one of the techniques the choice of which to use will rest on other
considerations.
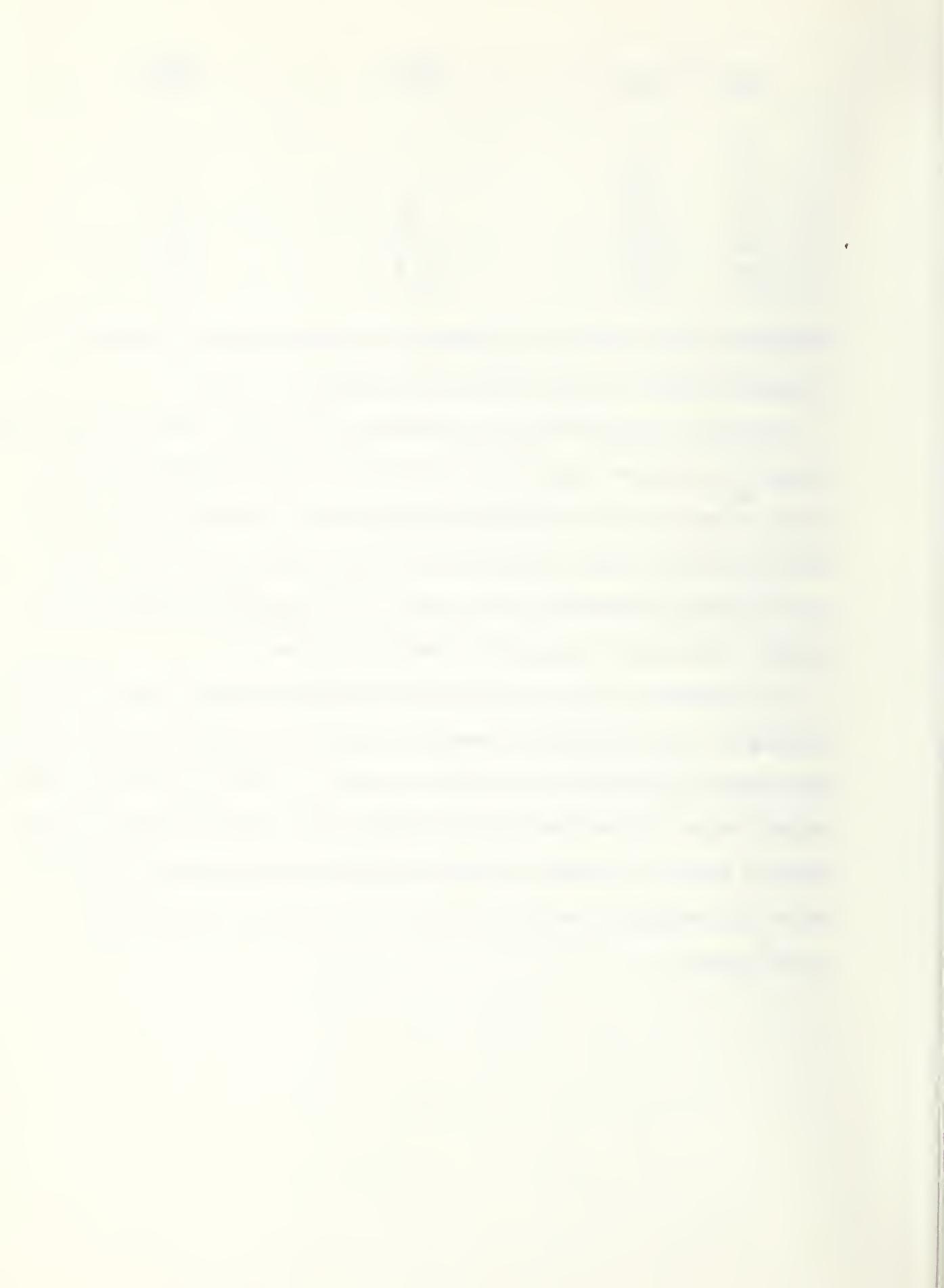
THERMOSTATING CONSIDERATIONS FOR THE PRESSURE TRANSDUCER

The simplest way to thermostat a system is to isolate it as well
as possible from its surroundings and to minimize any disturbances that
would tend to change its temperature. Utilizing this approach with the
pressure transducer is complicated to a large extent by the fact that the
pressurizing and depressurizing of the device results in considerable heating
and cooling of its component parts. We are starting the development of
system in which we believe the resultant heating effects can be made nearly
zero. This possibility exists because the material inside the pressure
vessel heats as the vessel is pressurized, while the vessel itself cools. If
these two opposing heating effects can be equated, a totally isolated system
will return to its original temperature when thermal equilibrium is
re-established after a pressure change.

The heating of a material under isothermal compression is given by
(see M. W. Zemansky, Heat and Thermodynamics, 5th Ed., p. 288)

$$Q = - T \int V\beta dP \qquad\qquad 11$$

where β is the volume thermal expansion. This can be usually written as

$$Q = T \bar{V}\bar{\beta}(P_f - P_i) \qquad\qquad 12$$

where $\bar{V}$ and $\bar{\beta}$ are average values as they are usually relatively independent
of pressure.

The cooling of the pressure vessel upon pressurization results from
the net tensile stress on the vessel. In the Appendix we show that for
pressure vessels of simple geometries the amount of cooling is given by an

equation identical in form (with opposite sign) to Eq. 11 or 12 but the volume, V, is the internal volume of the vessel. β is the thermal expansion of the pressure vessel material. Thus, to minimize the heating effects in the vessel, the amounts and thermal expansions of the materials used inside the vessel must average to the same thermal expansion as that of the vessel material.

The development is complicated by the requirement of using oil as a pressurizing fluid since all oils appear to have very large thermal expansion coefficients which are also very pressure dependent. The thermal expansion of the steel in the pressure vessel is about

$$\beta(steel) = 45 \times 10^{-6}/K$$

while that of most oils is in the range

$$\beta(oil) = (700 - 1000) \times 10^{-6}/K$$

The resolution of the problem appears to lie with the use of Invar, a high nickel steel which has a very small thermal expansion,

$$\beta(Invar) = 3.6 \times 10^{-6}/K.$$

By filling the internal volume of the pressure vessel primarily with invar and keeping the quantity of oil small the proper net expansion coefficient can be achieved.

We present here a calculated example using a commercial 20,000 psi (138 MPa) pressure vessel. The vessel has an internal diameter of 3.8 cm with a depth of 15 cm so that the internal volume is

$$V_i = 173 \text{ cm}^3$$

The vessel has a material volume of 1700 cm³, its mass is 14.8 kg and its heat capacity is 6.68 kJ/K.

The heat taken up by the vessel when pressurized to 34.5 MPa (5000 psi) is

$$Q = T \bar{V} \beta (P_f - P_i)$$

$$= 308 \times 173 \times 45 \times 10^{-6} \times 34.5$$

$$= 82.7 \text{ MPa} \cdot \text{cm}^3 = 82.7 \text{ J}$$

If the vessel were pressurized adiabatically the cooling of the vessel would be

$$\Delta T = \frac{Q}{C} = \frac{165}{6.68} = 12 \text{ mK}$$

We have calculated the heating with the following amounts of material inside the pressure vessel.

Calcite samples	1 cm^3
Invar sample holder	160 cm^3
Paraffin Oil	12 cm^3

The heat evolved for a 34.5 MPa (5000 psi) pressure increase on the calcite and invar are:

Calcite

$$Q = - T \bar{V} \bar{\beta} \Delta P$$

$$= - 308 \times 1 \times 14 \times 10^{-6} \times 34.5$$

$$= - 0.14 \text{ J}$$

Invar

$$Q = - 308 \times 160 \times 3.6 \times 10^{-6} \times 34.5$$

$$= - 6.12 \text{ J}$$

Since the volume and thermal expansion of steel, invar, and calcite are relatively independent of pressure the net heating of these three components, 82.7 - 0.14 - 6.12 = 76.4 J, will be about the same for any 34.5 MPa pressure change. For the paraffin oil we have determined average values of the expansion coefficient for four different 34.5 MPa intervals from 0 to 138 MPa. The amount of heating of the oil on pressurizing gets smaller as the pressure gets higher. This reduction is compensated to a small extent by the small increase in the amount of oil in the system due to the expansion of the vessel and the compression of the internal components.

The heating due to the compression of the oil and the net heating and temperature change of the system for the four pressure ranges are given in the following table:

Pressure Change, MPa	Paraffin Oil $\bar{\beta} \times 10^6$	Q(oil) J	Q(oil) corrected	Q(net) System	ΔT(mK) System
0 - 34.5	680	-86.7	-86.9	-10.5	+1.4
34.5 - 69	605	-77.1	-77.5	- 1.1	+ .1
69 - 103.5	535	-68.2	-68.7	+ 7.7	-1.0
103.5 - 138	480	-61.2	-61.8	+14.6	-2.0

The temperature change for each 34.5 MPa interval was determined assuming a total heat capacity of 7.42 kJ/K.

For this example, increasing the pressure from 0 to 69 MPa will increase the temperature of the system by 1.5 mK but in continuing to increase the pressure to 138 MPa the temperature will drop to 1.5 mK below its initial value. In going from zero pressure to any value below 138 MPa the total temperature change will be no greater than 1.5 mK. The worst case would be to allow the system to stand for a long period at 69 MPa so as to equilibrate with the thermostat, pressurizing to 138 MPa would then cool the system to 3 mK below the thermostat temperature. These temperature changes are well below the temperature limits required by the calcite pair transducer. We are proceeding to check out these ideas in the laboratory.

Automatic Capacitance Bridge

The self-balancing capacitance bridge to be used with the pressure transducer should soon be operational. Initial testing turned up numerous wiring errors which are now being corrected. Two of the component amplifiers have malfunctioned and have had to be returned to the manufacturer which may delay resumption of testing.

New Materials Tested

A new sample of As_2S_3 has been obtained from Barnes Engineering and was found to have nearly the same temperature and pressure dependencies as found earlier for the Servo Corporation samples. The values are d $\ln C/dT$ x 10^6 = 66.2/K and d$\ln C/dP$ x 10^{12} = 114.4/Pa.

Magnesium aluminum spinel ($MgAl_2O_4$) was measured and found to have dependencies very similar to those of parallel cut sapphire. The values are d $\ln C/dT$ x 10^6 = 135.3/K and d $\ln C/dP$ x 10^{12} = 12.2/Pa.

Measurements have been made on $LiNbO_3$ which is a pyroelectric material, i.e. a polarized ferroelectric. The samples were poled, single-domain crystals cut parallel and perpendicular to the axis of polarization. The temperature dependence of both samples was rather large and the pressure dependence small so this material is not of particular interest to us. In addition both samples shows long term relaxation effects that amounted to tens of ppm in the capacitance. For the parallel cut sample d $\ln C/dT$ x 10^6 = 734/K and d $\ln C/dP$ x 10^{12} = 7.0/Pa and for the perpendicular cut d $\ln C/dT$ x 10^6 = 387/K and d $\ln C/dP$ x 10^{12} = 59/Pa. The loss component,

although about an order of magnitude larger than most of our samples, was still small tan $\phi = 0.0002$.

FUTURE WORK

The idea of using a calcite capacitor in combination with a potassium halide capacitor will be checked out in the laboratory. Additional calcite crystals will be obtained and tested so that we will be in a position to proceed with the development of the transducer whichever combination appears to work best. An invar sample holder will be fabricated for use with a capacitor pair in a commercial pressure bomb. Assuming the temperature changes in the pressure vessel are within our estimated requirements we will proceed with the development of the actual thermostat for the transducer. If these various aspects of the project go well we should be in a position to begin evaluation tests of the transducer and its capacitance bridge early in the next fiscal year.

APPENDIX

Cooling of a Pressure Vessel upon Pressurization

The isothermal heating which occurs in a piece of material under compressive stress can be calculated by writing the formula

$$Q = - T \int V\beta \, dP \qquad (A1)$$

in a more general form as

$$Q = - T \iint \alpha \, dS \, dV. \qquad (A2)$$

$dS = \Sigma dS_i$ is the sum of the three components of the stress acting on the volume dV. $\alpha = 1/3 \, \beta$ is the linear thermal expansion coefficient. Shear stresses are neglected.

The individual stress components for uniformly shaped pressure vessels under internal pressure, P, can be calculated using standard formulae as given by R. J. Roark (Formulas for Stress and Strain, 4th Ed., p. 308).

As a practical example we consider a cylindrical vessel with spherical ends. The internal and external radii are a and b and the stresses at a point r in the vessel wall are given by:

Cylindrical Portion -
longitudinal stress
$$dS_1 = -\frac{a^2}{b^2-a^2} \, dP,$$

hoop stress
$$dS_2 = -\frac{a^2(b^2+r^2)}{r^2(b^2-a^2)} \, dP,$$

radial stress

$$dS_3 = + \frac{a^2(b^2-r^2)}{r^2(b^2-a^2)} \, dP \ ,$$

Spherical Ends -

hoop stresses

$$dS_1 = dS_2 = - \frac{a^3(b^3+2r^3)}{2r^3(b^3-a^3)} \, dP,$$

radial stress

$$dS_1 = + \frac{a^3(b^3-r^3)}{r^3(b^3-a^3)} \, dP \ .$$

The contributions of the individual stress components can be found by multiplying by the appropriate volume element, $2\pi r dr$ for cylindrical segments and $4\pi r^2 dr$ for spherical segments, and integrating over r from a to b.

The total contribution is, however, more easily found since the sum of the three components of both segments are independent of r,

$$dS_{cyl} = - 3\left(\frac{a^2}{b^2-a^2}\right) \, dP$$

and

$$dS_{sph} = - 3\left(\frac{a^3}{b^3-a^3}\right) \, dP$$

(A3)

The volume integrations of Eq. A2 can now be carried out separately giving

$$V_{cyl} = \pi \ell (b^2-a^2)$$

and

$$V_{sph} = 4/3 \, \pi (b^3-a^3)$$

(A4)

Multiplying the appropriate parts of Eqs. A3 and A4 and substituting in Eq. A2 we have

$$Q = T \int 3 \, \alpha (\pi a^2 \ell + 4/3\pi a^3) \, dP$$

The expression in parentheses is just the internal volume V_i of the vessel so we can write

$$Q = T \int \beta \, V_i \, dP$$

.This is just the expression for the compression heating by the pressure change dP of a volume V_i with thermal expansion β as given by Eq. 1A but with the sign changed.

FIGURE CAPTIONS

1. Pressure dependence of the CaF_2 capacitor as a function of temperature.

2. Pressure dependence of the parallel-cut calcite capacitor as a function of temperature.

3. Pressure dependence of the perpendicular-cut calcite capacitor as a function of temperature.

4. Pressure dependence of the calcite-pair capacitor combination as a function of temperature.

5. The temperature and pressure dependence of the capacitance of KCl, KBr and the two cuts of calcite. Circles indicate the zero-pressure values at 35°C and arrows indicate how the values change as the pressure is increased to 138 MPa (20,000 psi). Data are not available on the variation with pressure for KCl.