ORGANIC CHEMICALS DIVISION

RESEARCH *Report*

REPORT NO.- 2961 JOB NO.- 4374 - Part I

FINAL REPORT

ON

THERMINOL FLUID VAPOR PRESSURE
AND THERMAL STABILITY INSTRUMENT

DATE - July 6, 1963 WRITTEN BY - W. N. Trump
C. E. Vogler

Monsanto

ST. LOUIS, MO.

0692699

MONSANTO CHEMICAL COMPANY
Organic Chemicals Division
St. Louis Research Department

St. Louis Research Report No. 2961

Final Report
on
Therminol Fluid Vapor Pressure and Thermal Stability Instrument

Job No. 4374 - Part I

July 6, 1963

Written by: W. N. Trump
C. E. Vogler

Work done by: W. N. Trump
C. E. Vogler
H. W. Luebke
L. Fowler
W. E. Koerner
A. J. Bindbeutel
A. L. Manno

0692700

DISTRIBUTION FOR REPORT NO. 2961

1. File
2. K. L. McHugh
3. W. R. Richard, Jr.
4. Duplicate File
5. Technical Reports Library
6. C. E. Vogler
7. W. N. Trump
8. L. Fowler
9. W. E. Koerner
10. R. Davis - Org. Sts.
11. W. B. Hewitt - J. F. Q.
12. Extra
13. Extra
14. Extra
15. Extra
16. Extra

TABLE OF CONTENTS

INTRODUCTION

An instrument was wanted for control use at Anniston which could be used to screen various lots of Aroclor production for designation as Therminol fluids. Desirable in this instrument was the ability to detect low-boilers and material which would decompose appreciably at operating temperatures. It was anticipated that specifications for the Therminol fluids could be based on this instrument. Another requirement of the instrument was that it would require a minimum of operator attention. An instrument which was considered to best fit the above requirements was one based on vapor pressure. This report concerns itself with the design, fabrication, operation and performance testing of such an instrument herein referred to as the Vapor Pressure and Thermal Stability Instrument.

SUMMARY

An instrument was designed and built which would measure the vapor pressure of materials which are liquid at ambient temperatures.

This instrument was tested for functionality, reproducibility and reliability with various lots of the Therminols and with pure substances of known vapor pressure.

The effect of possible contaminants upon the vapor pressure and thermal stability of the Therminols was determined.

An operating procedure for using the instrument was developed.

CONCLUSIONS

The Vapor Pressure Instrument adequately records the vapor pressure of the Therminols and other liquids as a function of temperature.

Unstable impurities in the Therminols which decompose at 200-300°C. can be readily detected from the vapor pressure trace at the 500 ppm chloride level. Low-boilers such as benzene are detectable at the 0.1% level but levels of biphenyl lower than 2% are not detectable from the instrument record.

Degassing of the inner sample cell surface requires temperatures in excess of 250°C. with the system under vacuum and is necessary to avoid any contribution to the system pressure in excess of the vapor pressure of the sample during a run. Dissolved gases in the sample also must be removed by applying vacuum to the sample prior to run.

RECOMMENDATIONS

It is recommended that vapor pressure specifications for the Therminol fluids be established based on a large number of measurements made at Anniston.

PATENT STATUS

A preliminary disclosure of invention has been filed. No reference to a similar device was found reported in the literature.

EXPERIMENTAL WORK AND DISCUSSION

A. Development of Operating Procedure

A detailed operating procedure is given in the instruction manual which is included in the appendix of this report. In this section the experimental work and observations which led to the operating procedure are discussed.

1. Early Work

The instrument with the original cell design shown in Figure 1 was tested with substances of known vapor pressure, namely, water and dodecane and also with samples of the Therminols whose vapor pressures had been determined with an isoteniscope by Dr. K. L. McHugh's group. Fairly reproducible plots of pressure vs. temperature were obtained but the data deviated widely from the known vapor pressure curves. The instrument records for the Therminols were somewhat "S" shaped exhibiting a hump in the curve at about 200°C. This was believed to result from temperature gradients in the cell. The considerable lag time between the furnace response and the sensing thermocouple also caused uneven programming of temperature and prompted the redesigning of the cell and improving the heat transfer from the furnace to the cell. The equipment modifications are described in detail under Design Considerations (Section B).

Dodecane was the first material tested in the modified instrument with the redesigned sample cell shown in Figure 9 of the Instruction Manual. The pressure vs. temperature plot was in excellent agreement with the known vapor pressures for dodecane and the programming of temperature was uniform. In the subsequent series of measurements with the Therminol fluids, the first test gave a reasonably straight line plot and the next showed slight S-shape curvature. The vapor pressure plots from the runs which followed became progressively more S-shaped and deviated more from the known vapor pressures. A recheck with dodecane agreed well with literature values but further tests with the Therminol fluids

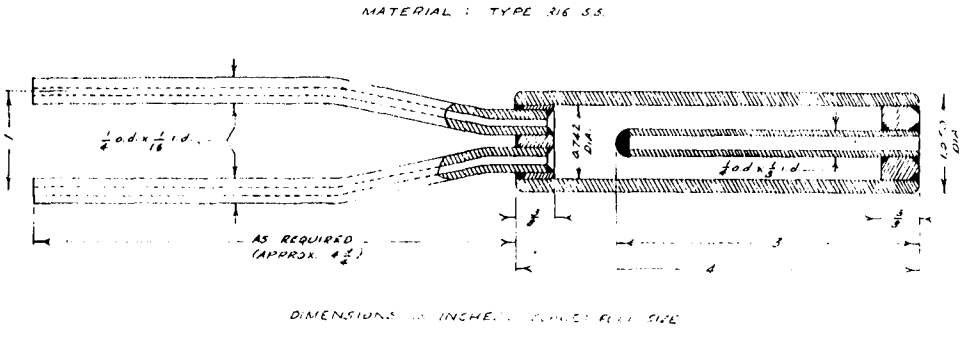


Figure 1. Sample Cell
(First Design)

again showed the hump in the curve. At this point it was thought that the hump in the vapor pressure curve might be characteristic of the Therminols possibly resulting from low-boilers in the samples. An attempt was made to verify this by running a sample of Therminol-FR-2 from which the lower boiling constituents had been removed by distillation. The vapor pressure curve still showed the characteristic hump. Another test was made to insure that the gases in the cell were composed entirely of Therminol vapor. A run was interrupted after attainment of a temperature of 220°C. The apparatus was turned upside down and the gases were evaquated without removing the liquid phase from the cell. The apparatus was then placed right side up and the remaining liquid phase allowed to equilibrate with its vapor. The run was resumed at this point. The instrument record after the outgassing followed a straight line agreeing fairly closely with the vapor pressures obtained by isoteniscope. Further tests of this type showed that the vapor pressure curve following outgassing of the vapor space could be shifted depending upon the temperature at which the outgassing was done. These observations still pointed to low-boilers in the sample as being suspect for the poor reproducibility and lack of agreement with the known vapor pressures.

Because up to this time it had been impossible to demonstrate the reliability of the instrument, the instrument was tested independent of the sample. The temperature and pressure recording systems were tested independently of each other by using a motor driven variac to program heat to the sensing thermocouple and by controlled bleeding of nitrogen into the system to simulate vapor pressure increase with temperature. These tests revealed inadequate thermostatting of components in the logarithmic converters and premature failure of mercury batteries in the bridge circuits as causes for variations in the vapor pressure-temperature traces. The correction of these difficulties is described in Section B, Design Considerations. Malfunction of the strain gage and fluctuations in line voltage were eliminated as possible causes for variation in the instrument. The mode of heating, either by instrument programming system or instrument-independent motor driven variac, was found to have little effect on the recorded vapor pressures.

Another possible explanation for the observed hump in the vapor pressure curve of the Aroclors was system leakage. One observation indicated that the pressure relief valve leaked slowly when the system was under vacuum and thus the valve was removed from the system. (It was later replaced.) Subsequent leak tests under vacuum at room temperature indicated a tight system. However, upon heating the evacuated system to 150°C., the pressure indication was similar to the development of a large leak (0.5 psi per minute). The cell was re-evacuated to minimum pressure at this temperature and the valves closed. The pressure increase was much slower than before. The system was then heated to 250°C. under vacuum. There was a slight increase in pressure at first but after about ten

minutes under vacuum at this temperature, the system appeared to hold vacuum; that is, there was no increase in pressure in ten minutes time. The system held vacuum upon cooling to room temperature and it was concluded that the observed pressure increases upon heating were not due to leakage but to the release of absorbed gases on the inner cell surface. Subsequent tests have shown that the cell surface is completely degassed when heated to 250°C. and evacuated for ten minutes. As a standard operating procedure degassing at the maximum temperature encountered in a run is recommended. A run made with Therminol-FR-2 following the degassing procedure, Figure 2, gave a vapor pressure curve of the expected shape and which agreed well with the isoteniscope measurements. Subsequent runs showed that outgassing the cell at temperatures of 250°C. or higher was an essential preliminary step for obtaining accurate vapor pressure curves.

In the early work, pumping the cell down to about 3 mm Hg at room temperature was thought to suffice since the pressure remained stable at this level when the cell was closed off. The problem of completely outgassing the cell before filling it with sample was not suspected nor evident from the vapor pressure curves and was the cause of much bewilderment in the early experimental work. The solving of this problem proved to be the critical one in developing an operating procedure for the instrument.

2. Selection of Sample Size

Theoretically the size of the sample should not affect its vapor pressure in a closed system as long as there is vapor space remaining and sufficient liquid phase to allow accurate measurement of its temperature. However, the vapor pressure exerted in a closed system by a sample which is a mixture of substances of varying volatility is dependent upon the volume of sample in the sample cell. A minor component of high volatility relative to the bulk of the sample would contribute considerably more to the system pressure when the liquid to vapor volume ratio is high than when the ratio is minimum. In a practical sense, for accurate measurement of temperature the cell would need to be filled at least one-fifth full and to avoid complete filling of the cell, the sample size would not exceed 90% of the total system volume. Between the extremes of 20% to 90% filling of the cell with a mixture whose components' volatilities vary over a relatively narrow range such as the Therminol fluids, the effect of sample size on the observed vapor pressure would be slight.

Errors arising from poor evacuation of the system before sample introduction or slight leakage in the system will be greater the larger the size of sample. On the other hand, sensitivity to measurement of decomposition is improved with larger sample size. Thus in choosing the sample size a balance of these factors must be sought depending on the demands made of the instrument.

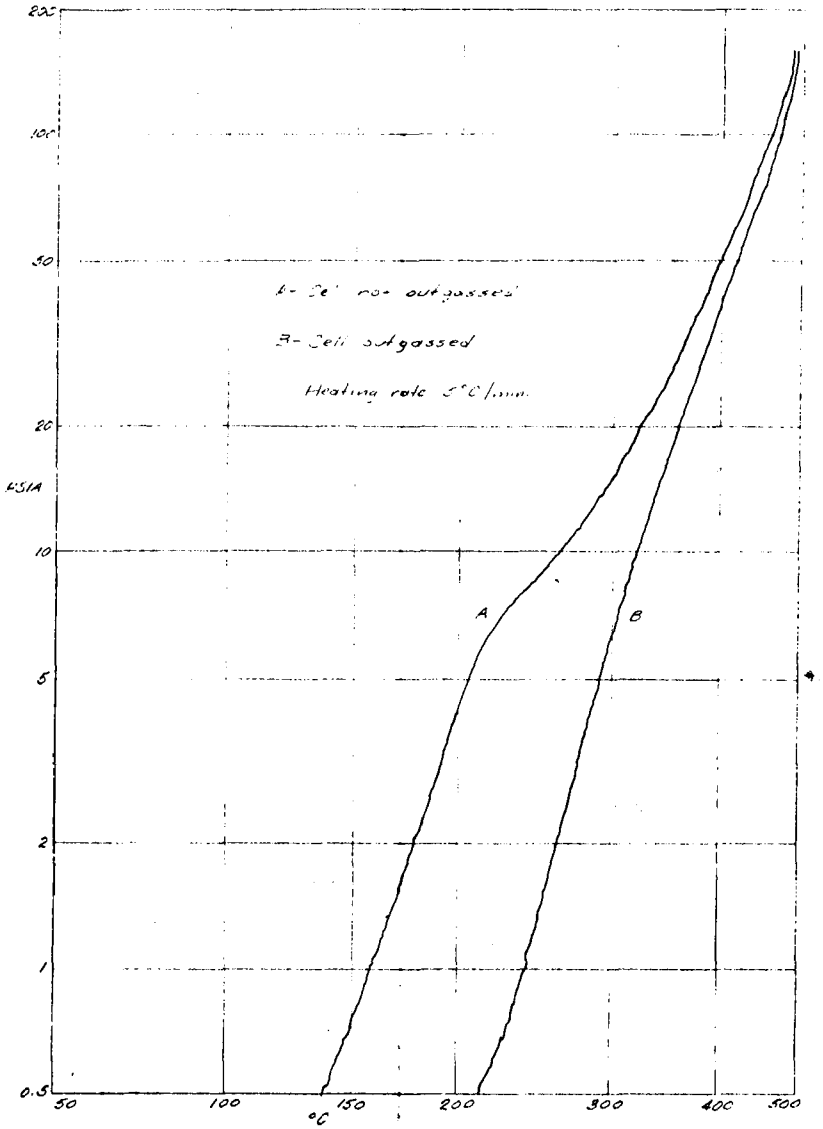


Figure 2. Effect of outgassing cell

0692708

In some of the early experimental work, the sample volume was varied to give about 1/4 to 3/4 filling of the cell with no evident effect on the vapor pressure record. In later work, filling the cell about 1/3 full gave satisfactory results both from the standpoint of temperature measurement (and hence, programming of temperature) and from being able to detect low-boilers and decomposition in the sample. The procedure was adopted to use 12 cc of sample (pressure relief valve in place, 10 cc with relief valve removed) in a system of 24 cc total volume. This amounts to having about 7 cc of sample in a 18.7 cc sample cell, the balance of the volume being in the piping and the valve and strain gage cavities.

In using the instrument for control purposes the exact amount of sample used isn't nearly as important as using the same amount of sample time after time. In other words, repeatability is the most essential demand of the instrument.

3. Selection of Heating Rate

Heating rates of 3-1/3°C./min and 10°C./min gave identical vapor pressure records (Figure 3) for a sample of Therminol-FR-2. Extremely rapid heating rates, i.e., 25°C./min, caused an appreciable shift in the pressure-temperature record due to the lag in response between the thermocouple and the sample which was equivalent to about 20°C. At a heating rate of 10°C./min or less this lag is not appreciable. At heating rates less than 5°C./min, cycling of the temperature with time became significant. These factors bracket the range of usable heating rates between 5 and 10°C./min which appear reasonable also from the standpoint of elapsed time per determination.

Another consideration in choosing the heating rate is the rate of decomposition of sample. Prolonging the run would accentuate the effect of decomposition gases on the pressure of the system and make the vapor pressure record more sensitive in detecting unstable material in the sample. Unstable Aroclor, however, was found to decompose rapidly enough to not be a limiting factor at a heating rate of 5°C./min.

In the early experimental work 5°C./min was chosen as a reasonable heating rate and most of the work was done at this heating rate. The observations made later merely confirmed that the choice had been a proper one. The operating manual specifies 5°C./min as the heating rate to be used with the Therminol fluids.

4. Detection of low-boilers

The chlorinated biphenyls usually contain dissolved gases which if not removed from a sample add to the system pressure during a run giving a pressure-temperature record higher than the vapor pressure of the material. The effect of degassing a sample prior to a run is shown in Figure 4. The same effect is observed

when a sample is admitted into a poorly evacuated system where the fixed gas left in the system is compressed when sample is admitted and increases in pressure with increase of temperature during the run. Evacuation of the sample to about 5 mm Hg at room temperature was found to adequately degas the samples and was adopted as a standard operating procedure. For the more viscous materials such as Therminol-FR-3, the degassing was facilitated by warming the sample to about 50°C. but care must be taken to avoid distilling out the low-boilers when degassing sample at elevated temperatures.

It is essential that the contributions to the system pressure from dissolved gases in the sample and residual gases in the evacuated cell be minimal when the instrument is used to detect low-boilers in the sample.

Nearly all of the Therminol samples studied with the instrument contained some low-boilers. Figure 5 shows the effect of removing the more volatile components from a sample of Therminol-FR-2, the difference in the vapor pressure curves being more evident at the low pressures because of the logarithmic scale of the instrument record. The presence of low-boilers in the Therminol samples imparts more curvature to the vapor pressure plots at the low pressure extremity of the instrument record. The presence of low-boilers in the Therminol samples was confirmed by Dr. K. L. McHugh's group by making the isoteniscopic measurements on samples where the low-boilers were removed and on those where they were retained. This effect is shown in Figure 6.

Tests to determine the sensitivity of the instrument to low-boilers in the Therminols were made, using benzene and biphenyl as representative of possible contaminants. In Figure 7 is shown the effect of a relatively large amount of low-boiler in Therminol-FR-1, i.e., 1.6% benzene. Here the slope of the instrument record is much less steep than for the uncontaminated sample. Lower concentrations of benzene do not alter the slope as drastically but levels as low as 0.2% benzene are readily detected from the instrument record and it is estimated that a level of 0.1% benzene would also be detectable from the vapor pressure curves. Biphenyl at a 5% level in Therminol-FR-1 did not appear to alter the slope of the vapor pressure curve (Figure 8), but did shift the curve toward higher vapor pressures the difference being equivalent to about 20°C. on the temperature scale. Judging from these results, a 1% level of biphenyl in FR-1 would not be discernible from the vapor pressure curve and a 2% level would be questionable because of the slight variances in instrument calibration. Using the change in slope at the low pressures as a guide post to contamination rather than the shift in the vapor pressure curve has considerable merit. For instance, the contamination of Therminol-FR-1 with biphenyl could not be distinguished from a somewhat lesser chlorinated biphenyl (intermediate between Aroclor 1232 and Aroclor 1242) containing no unchlorinated biphenyl but exhibiting approximately the same vapor pressure.

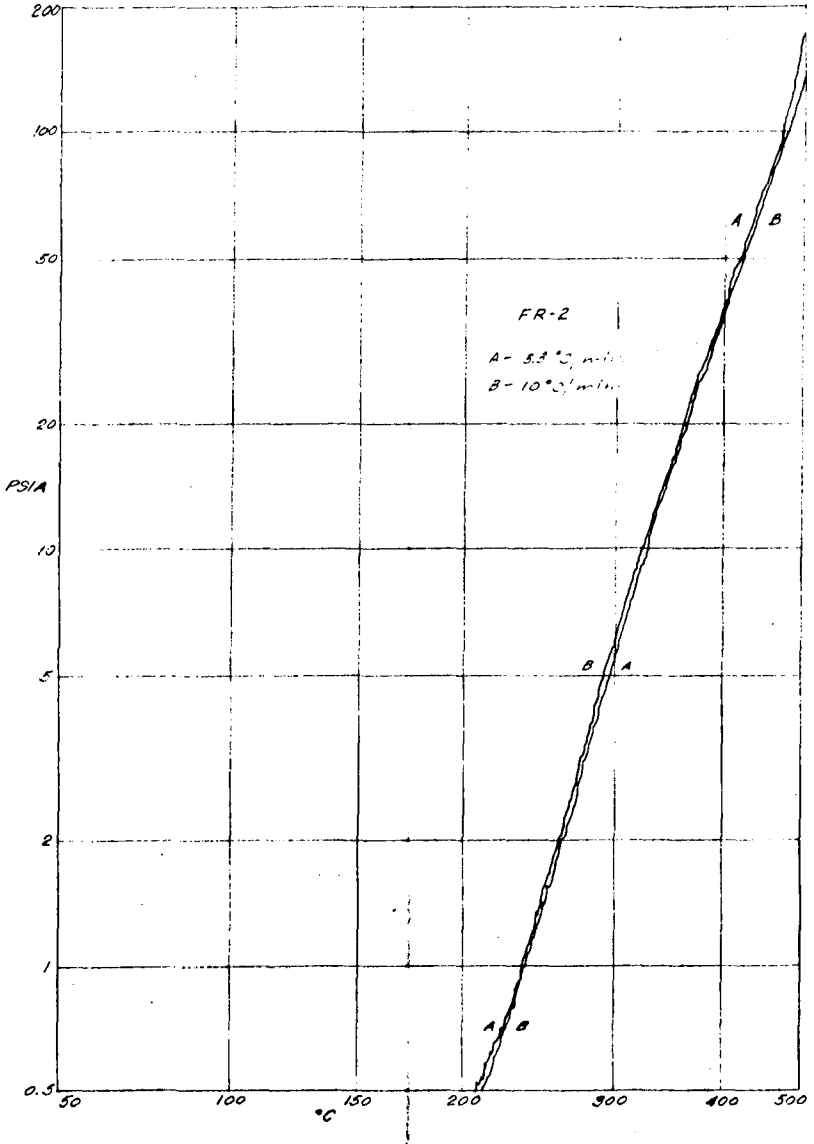


Figure 3. Effect of varying heating rate

0692711

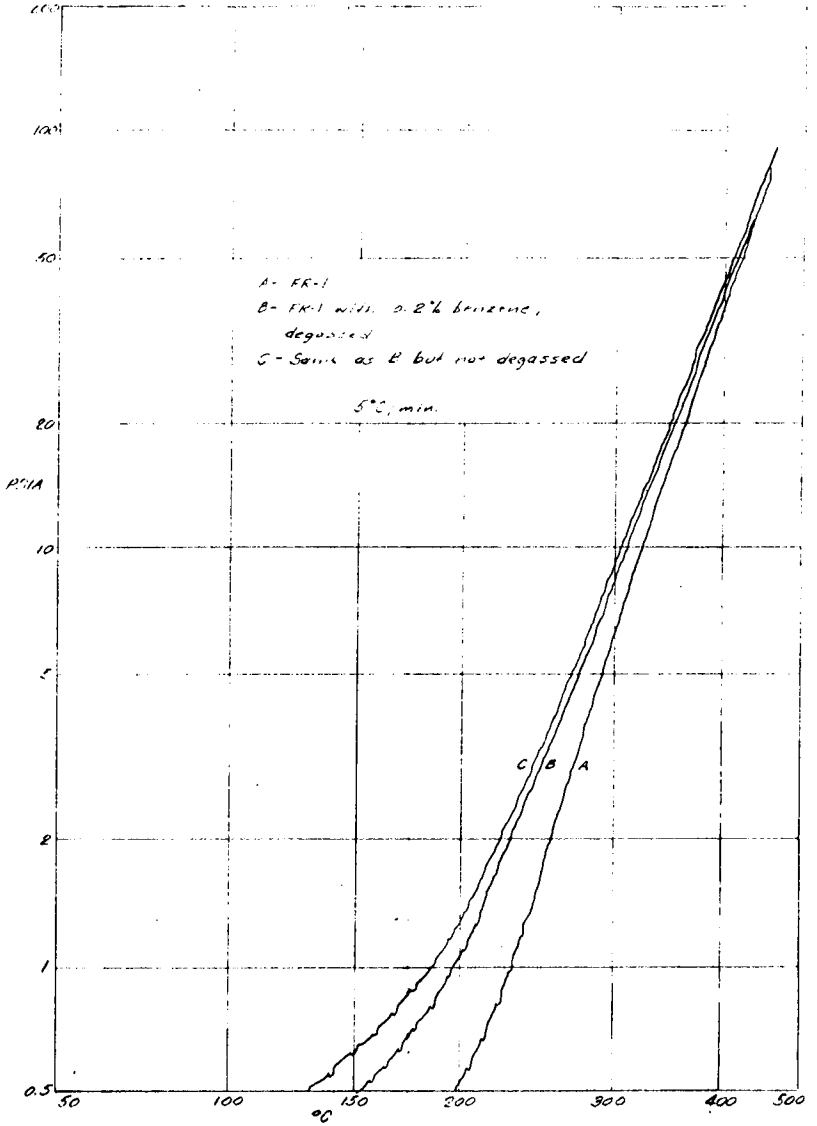


Figure 4. Effect of preliminary outgassing of sample

0692712

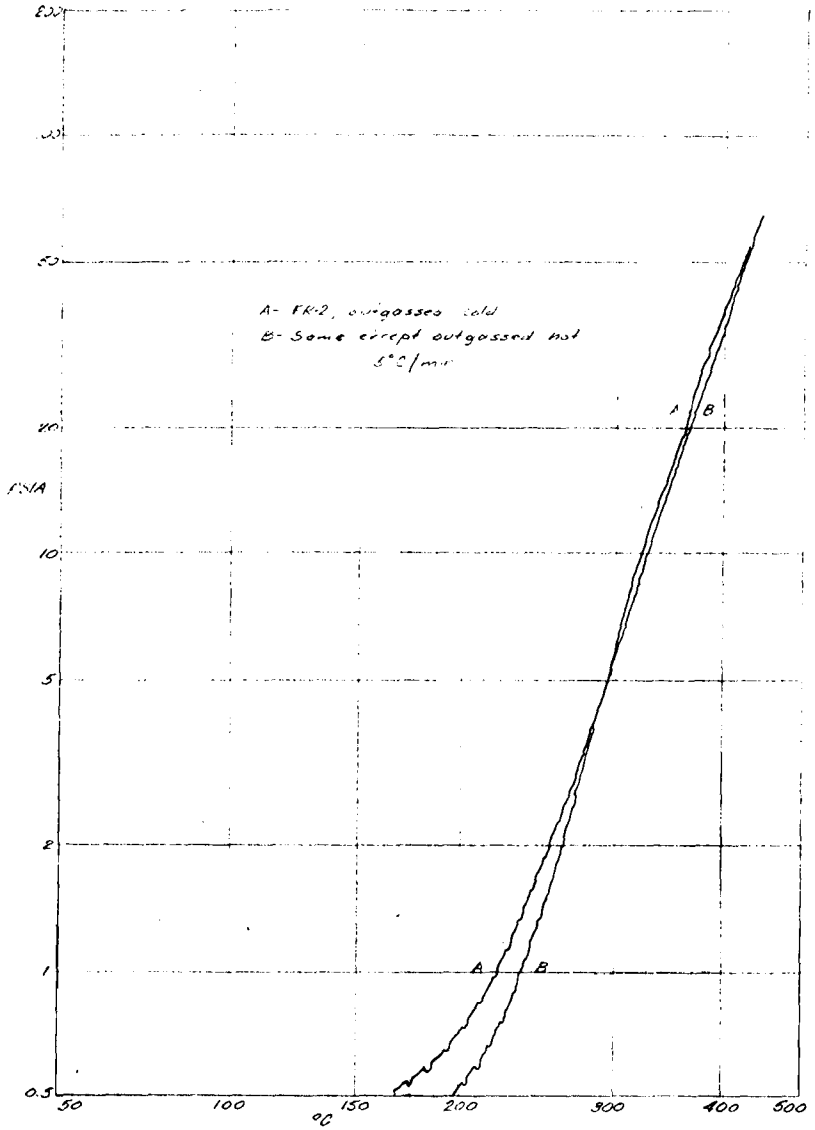


Figure 5. Removal of volatile components during outgassing of sample

0692713

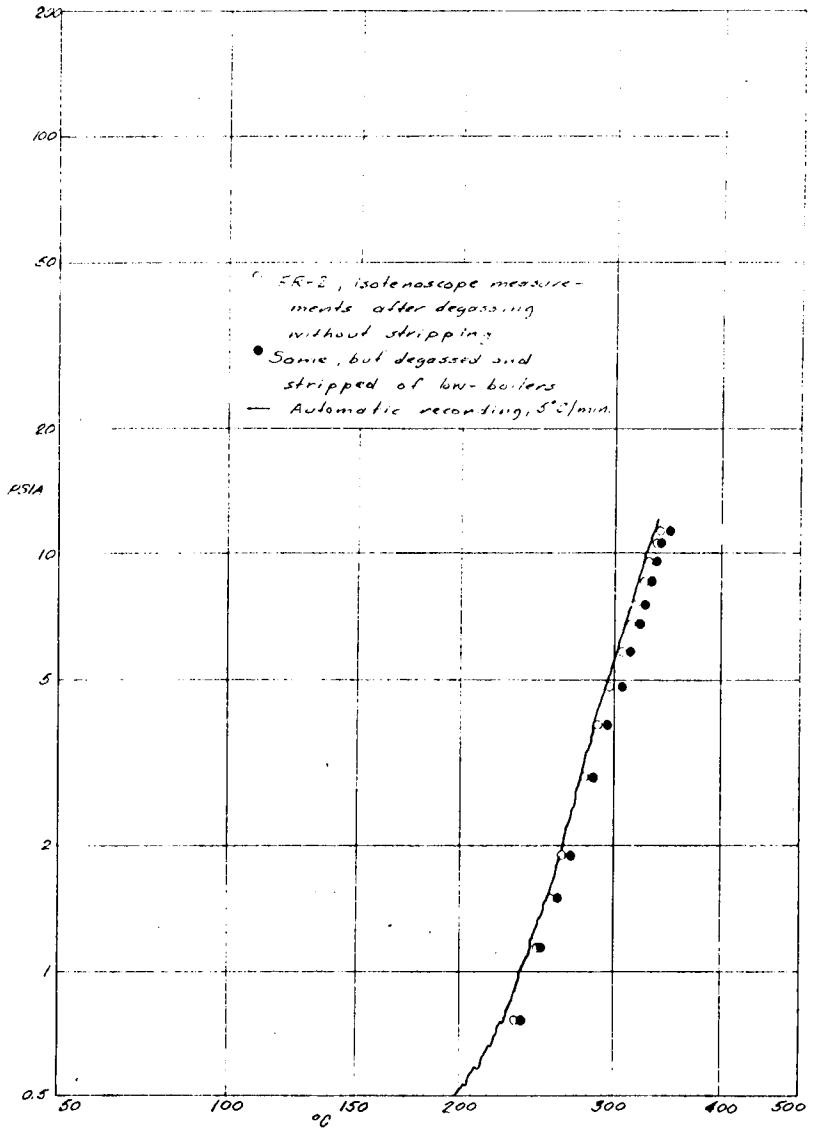


Figure 6. Comparison of vapor pressure recording with isotenoscope measurements

0692714

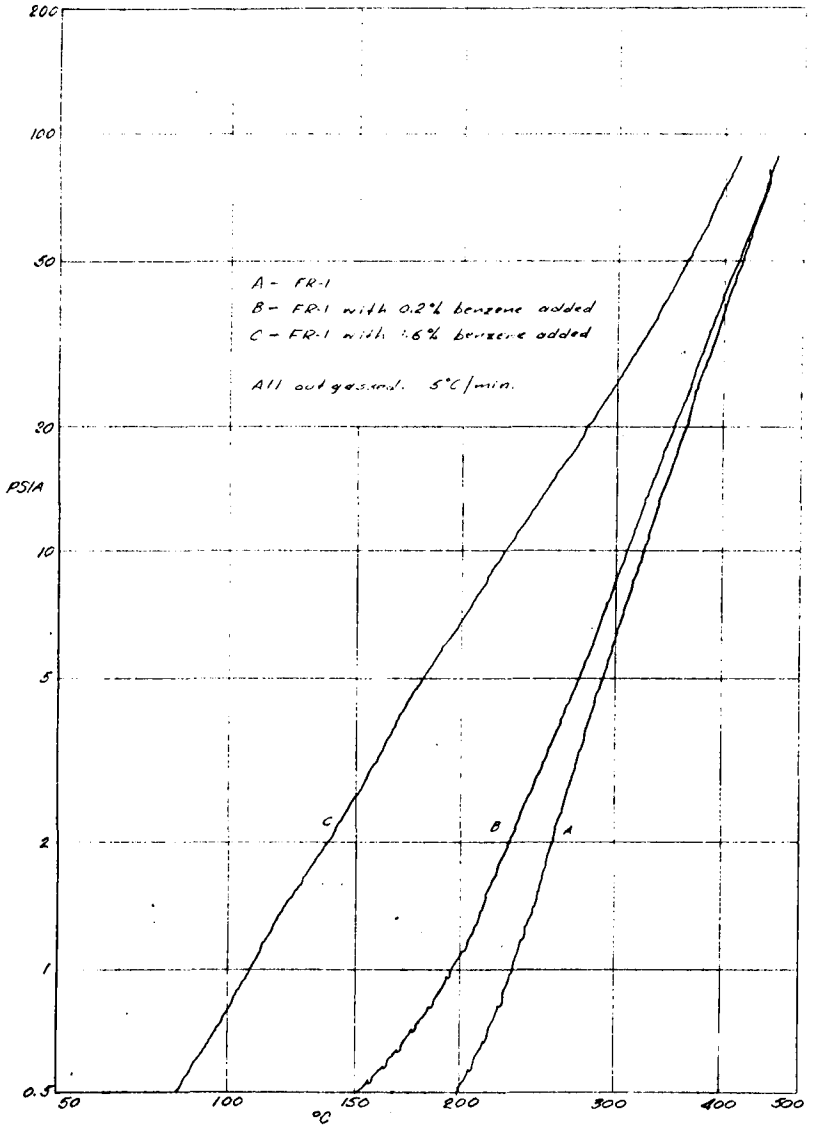


Figure 7. Detection of low-boiling impurity

0692715

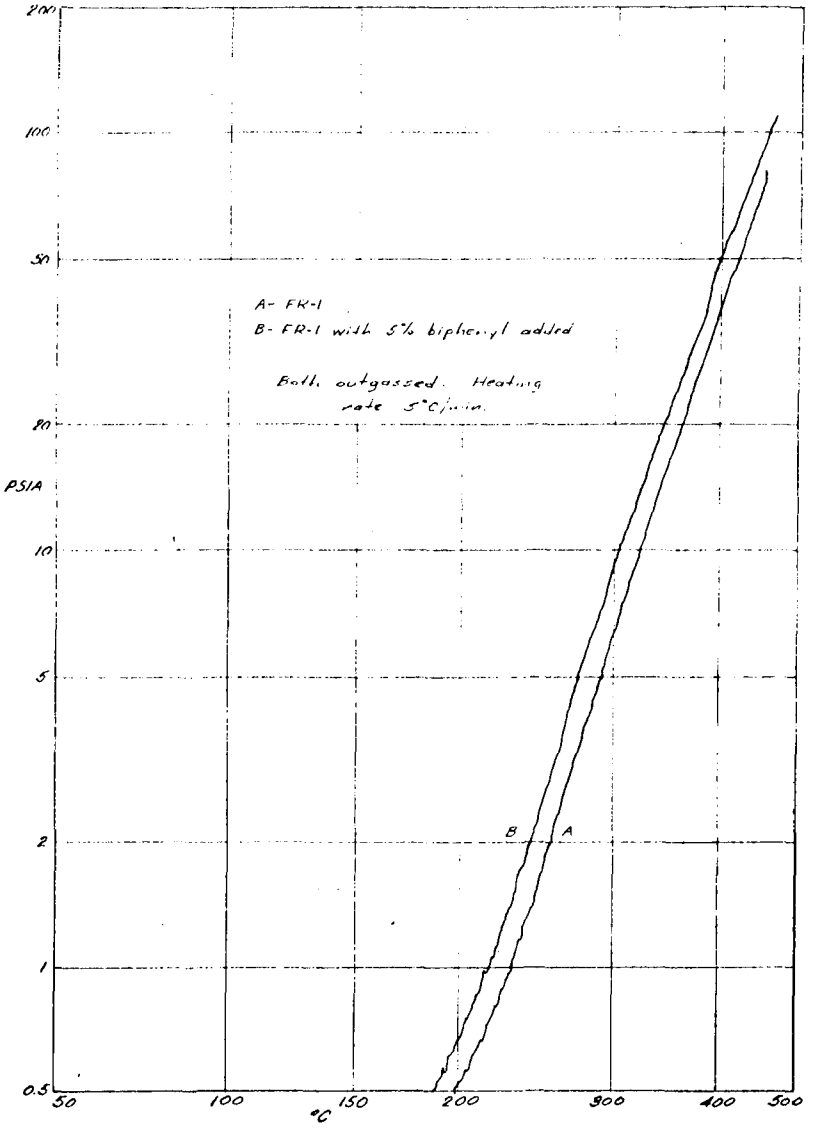


Figure 8. Detection of biphenyl

0692716

Contamination studies were considered necessary only with Therminol-FR-1 samples since the other members of the Therminols have lower vapor pressures and lower levels of contamination would be evident from the vapor pressure curves.

5. Vapor Pressure and Thermal Stability of the Therminols

Typical instrument records for runs with the Therminol fluids, FR-1, FR-2 and FR-3, and also Aroclor 1232 are shown in Figure 9. The vapor pressures agree well with those determined by isoteniscope for samples treated in similar manner. The isoteniscope measurements were made only at subatmospheric pressures and no reported vapor pressure data at higher pressures could be found for comparison. There appears to be a slight curvature in the vapor pressure-curves at the high pressures deviating to pressures lower than the expected straight line relationship. This curvature probably is quite real but it should be noted that the slight deviations of the temperature record from an exact reciprocal temperature scale could also cause some curvature in the instrument record.

All of the Therminols show evidence of considerable decomposition at temperatures beginning at about 440°C. The temperature at which decomposition began was evident by the increase in slope of the vapor pressure record. The decomposition which is evident at temperatures above 400°C. appears to be characteristic of the chlorinated biphenyls and is accompanied by an increase in color of the sample ranging from yellow to black depending on the degree of decomposition. This decomposition also leaves a carbonaceous layer on the walls of the cell which requires some effort for removal. It was concluded that the high temperature decomposition was unrelated to the quality of the Therminol fluids and could not be used as the basis for selecting Aroclor lots for use as Therminol fluids. Hence it is specified in the operating instructions for the run to be terminated at 400°C. to avoid the high temperature decomposition and hence to facilitate the cleaning of the cell. Another reason for avoiding the high temperature decomposition is that the carbonaceous layer on the cell walls contains trace amounts of metals from corrosion of the cell.

The instrument record of a sample of "unstable" Aroclor 1242 (Figure 10) in addition to the characteristic high temperature decomposition showed an appreciable pressure in excess of the vapor pressure at about 200°C. This sample contained 1480 ppm chloride (determined by alcoholic KOH treatment of the sample) which is equivalent to about 1 mole percent of the chlorinated biphenyl being the chlorine addition product instead of substitution product. The addition product upon thermal decompostion (or treatment with alcoholic KOH) loses HCl to produce the substituted biphenyl of one less chlorine. The liberation of HCl increased the system pressure in excess of the vapor pressure as temperature was increased until the unstable contaminant was depleted.

Beyond this point, the decomposition gas contributed to the system pressure as a fixed gas in accordance with the gas law. The resultant "hump" shape of the curve can be used to detect "unstable" Aroclor down to chloride levels of 500 ppm when 12 cc size samples are used. Larger size samples would make the instrument more sensitive since the vapor space in the cell would be decreased. With a sample volume of 22 cc (total system volume = 24 cc), it is estimated that 50 ppm chloride "unstable" material would be detectable. Monsanto's internal specification is less than 7 ppm Cl^- and even by using minimal free volume in the cell, it doesn't appear feasible that the vapor pressure curve could be used to detect unstable material at such low levels. This is not to imply that the instrument isn't utilizable as a control instrument since abnormal lots of chlorinated biphenyls containing high amounts of unstable or low-boiler contaminants could be readily detected with the instrument.

It is possible to use the instrument in a manner that would detect small amounts of decomposition. The gain in system pressure at room temperature after a run could be used as a measure of decomposition. It would be necessary to use the pressure offset, however, to get both pressure readings on the instrument record scale. In Figure 11 Therminol-FR-1 heated to 400°C. at the rate of 5°C./min and cooled rapidly to room temperature caused a pressure gain of 0.15 psi. This is equivalent to 0.006% decomposition during the run. The material spiked with "unstable" Aroclor to a chloride level of 250 ppm Cl^- showed a pressure increase of 0.75 psi. This difference is significant and measurable but only about one-fifth the pressure increase expected from 250 ppm chloride. This perhaps could be due to the solubility of hydrogen chloride in the chlorinated biphenyls.

Chlorodecane was originally believed to decompose similarly to the chlorine addition product of biphenyl and thus was used in an experiment to determine detectability limits. It appeared to decompose much more slowly and gave continued decomposition as the temperature was increased to 400°C., Figure 12. Evidently much higher temperatures are required for its decomposition rate to approach that of the chlorine addition product of biphenyl.

Since the main function of the instrument is to measure vapor pressure, it is possible that vapor pressure specifications for the Therminols could be based on measurements with this instrument. It is anticipated that such specifications would result from a large number of samples run at Anniston.

6. Vapor Pressures of Standards and Other Materials

Even though the vapor pressures of the Therminol samples were known up to atmospheric pressure, the fact that they weren't single component materials but mixtures made these samples unacceptable as standards for the instrument. Several organic

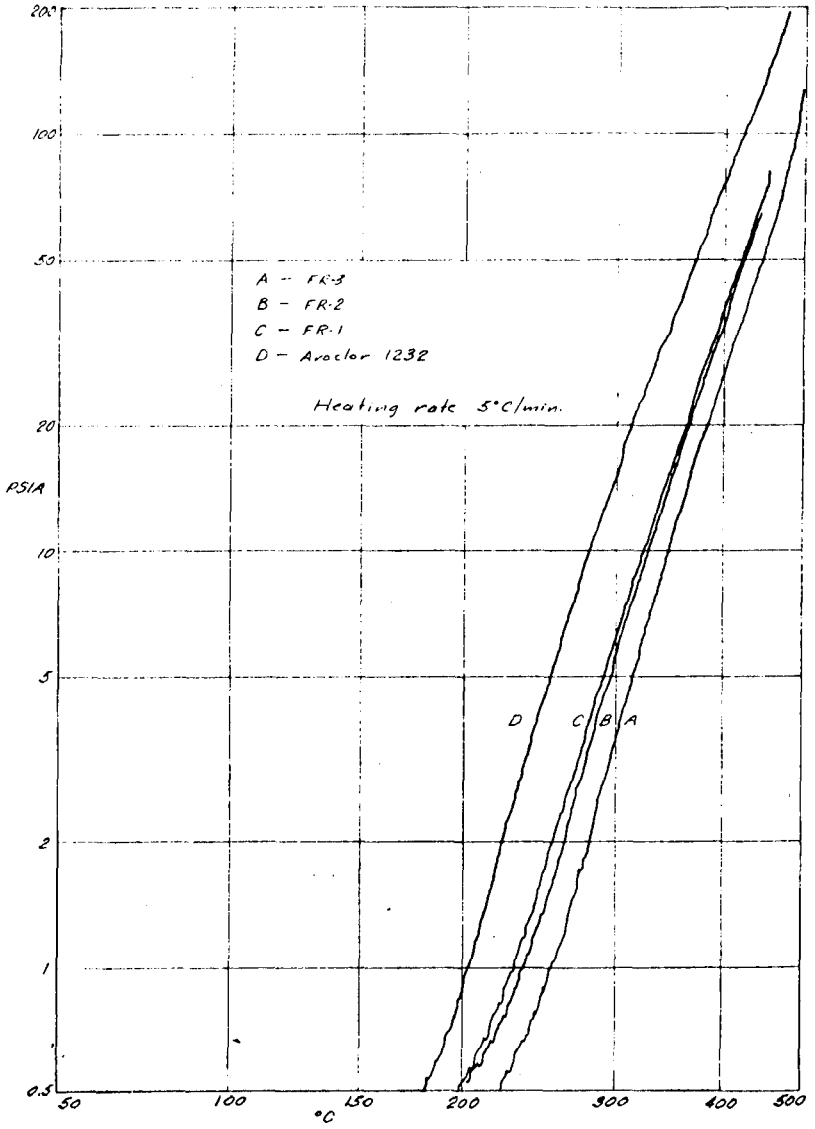


Figure 9. Vapor pressure curves

0692719

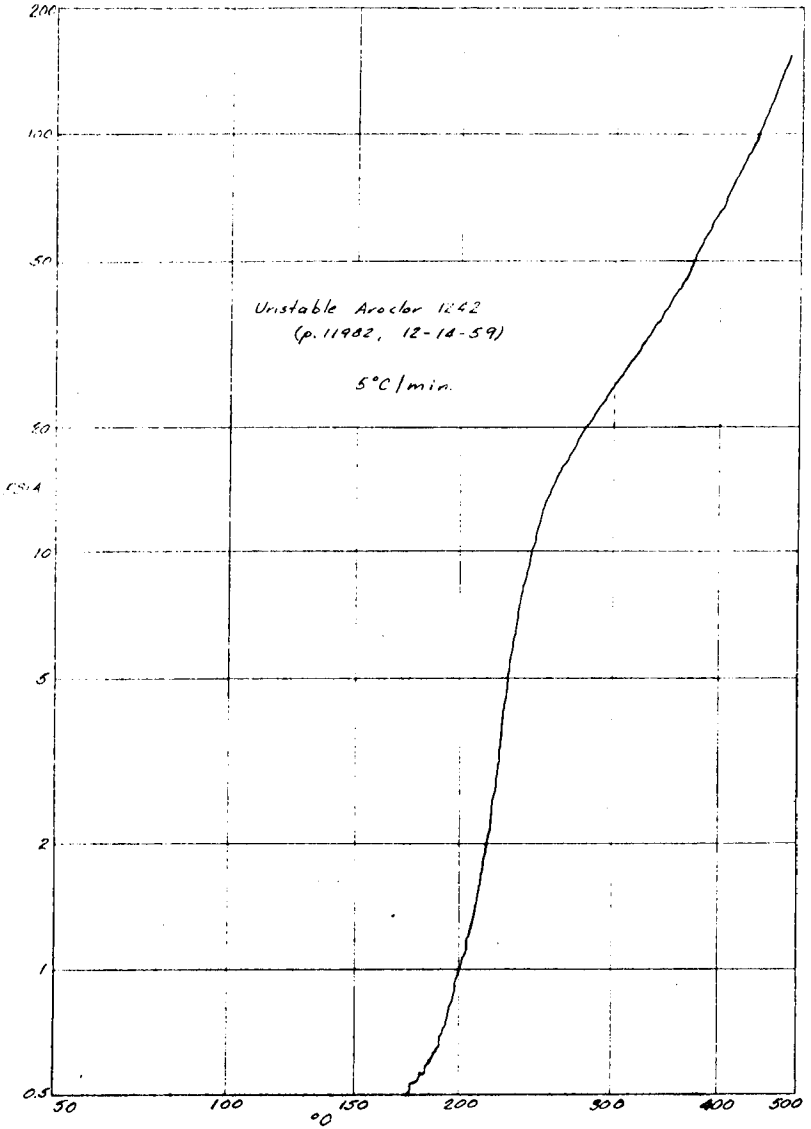


Figure 10. Vapor pressure recording of unstable Aroclor

0692720

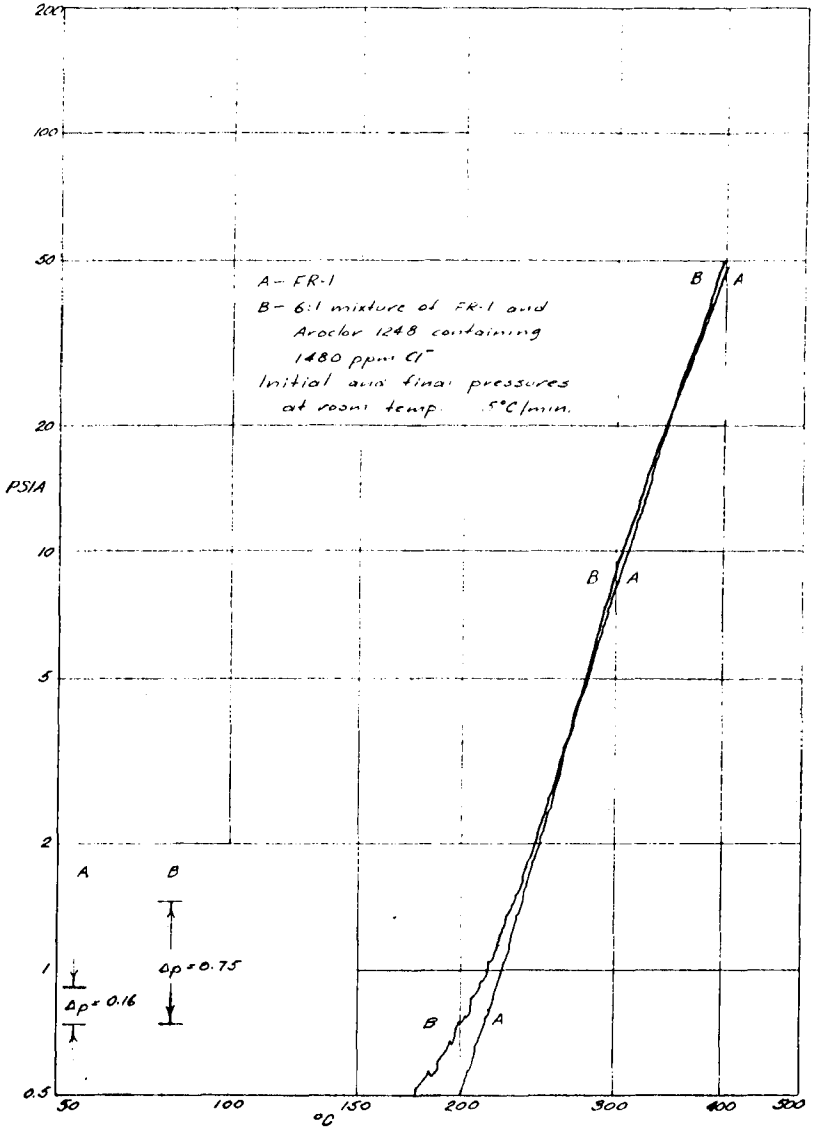


Figure 11. Vapor pressure curves and residual pressures of normal and high-chloride samples

0692721

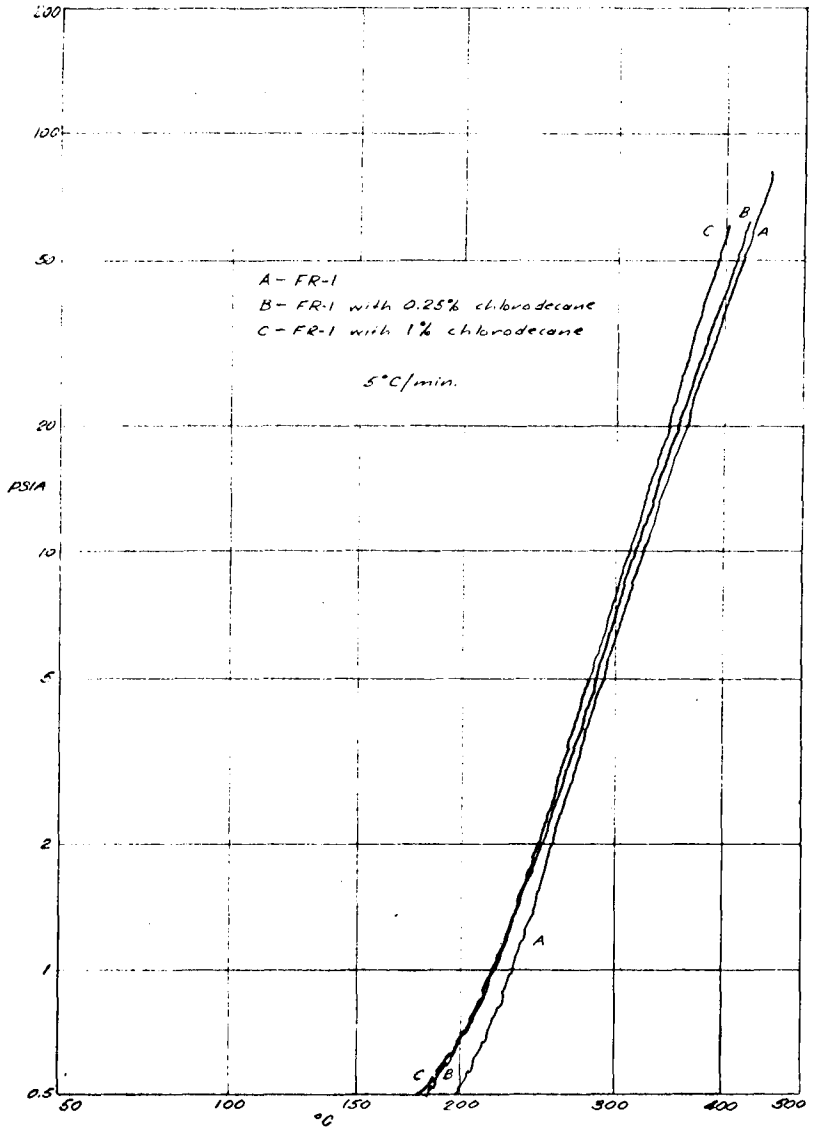


Figure 12. Effect of aliphatic chlorine compound

0692722

materials readily available in pure form and whose vapor pressure were accurately known were chosen as standards for the instrument. These included n-dodecane, o-xylene and o-dichlorobenzene. The instrument records for the runs with the standards are shown in Figures 13-15. Included for comparison are literature vapor pressure values. The agreement with the literature values is quite acceptable, the slight deviations in the 100-150°C. temperature range undoubtedly caused by error in the temperature scale which is discussed in Section B. One of the standards should be run in the instrument any time there is reason to suspect shifts in calibration or unreliability of the instrument. This would also serve to establish whether difficulties originated in the sample or in the instrument.

The vapor pressures of samples of Santowax OMP, 5% biphenyl - 95% Santowax OMP, and biphenyl were measured with the instrument and are shown in Figure 16. Since these materials are solid below 80°C., it was necessary to heat the lines and strain gage to about 100°C. to avoid blockage in the lines. The heating of the strain gage caused a small shift in the pressure axis calibration. No correction was made for this and it did not appear worthwhile to recalibrate the instrument for these samples when the instrument was to be used primarily with materials liquid at ambient temperature.

B. Design Considerations

This section includes a discussion of the factors involved in the detailed design of the Vapor Pressure and Thermal Stability Apparatus, especially those concerned with selection of components and circuits for the instrument.

1. Sample system and furnace

The early plans for this instrument were based upon the use of a bomb type of cell. This was to have been a container similar to the Parr combustion bomb, with the addition of a glass liner so that there would be no contact of sample with the metal of the bomb, and with a tubing connection to the pressure transducer. However, the problem of finding materials of construction which would permit repeated assembly after exposure to a temperature of 500°C., and tight sealing at that temperature, seemed insuperable. Therefore the design was changed to a one-piece cell, to be permanently connected to a system of valves through which evacuation and filling would be accomplished. The cell shown in Figure 1 was built from type 316 stainless steel pipe. The furnace was constructed as described in the instruction manual, except that originally no blower was incorporated. It was thought at that time that stratification of the heated air within the furnace would not produce significant temperature gradients in the cell.

Experimental runs on water and on n-dodecane in the cell and furnace unit thus assembled gave apparent vapor pressures higher than the literature values at all temperatures, and this positive error persisted when the furnace was cooling as well as when it was being heated. The fact that the pressure deviation did not reverse upon reversal of the furnace heat input showed that is was not due to existence of a radial temperature gradient in the cell (although such a gradient undoubtedly was present). The explanation appeared to be that there was a vertical gradient of temperature along the length of the cell; the liquid-vapor interface was near the top of the cell, where the temperature was high, while the thermocouple rested in the well near the bottom of the cell in a region of low temperature.

Measurements with fine wire thermocouples attached to the outside of the cell showed a vertical temperature gradient of about 10° at low furnace temperatures and about 30° at the maximum temperature. When the control thermocouple was removed from the well and clamped to the outside of the cell temperature control was improved but the vertical temperature gradient was not much changed. In an attempt to increase the thermal diffusivity of the cell it was cut open, filled with 0.125 inch diameter stainless steel, balls, and rewelded. However, there resulted no significant change in the vertical temperature gradient, nor in the radial temperature gradient which was about 10° at a heating rate of 4° per minute. When a small air jet was introduced through the bottom of the furnace, directed upward (but off center, so that it did not strike the cell), the vertical temperature gradient disappeared while the radial gradient was not affected.

From these experiments it was concluded that 1) the cell should be constructed of material of high thermal diffusivity, in the thinnest possible layers, and so designed that the least possible thickness of liquid sample would be interposed in the direction of heat flow, and 2) mixing of the air in the furnace was essential to avoid vertical temperature gradients.

A new cell was built, of annular construction as shown in Figure 9 of the instruction manual. The dimensions were selected on the basis of availability of commercial tubing, and to give a volume of about 20 ml. The thermal diffusivities (ratios of thermal conductivities to heat capacities per unit volume) of some possible materials of construction and of a Therminol fluid are given below.

Material	Diffusivity, cm^2/sec
Silver	1.7
Gold	1.2
Copper	1.1
Aluminum	0.81
Flatinum	0.26

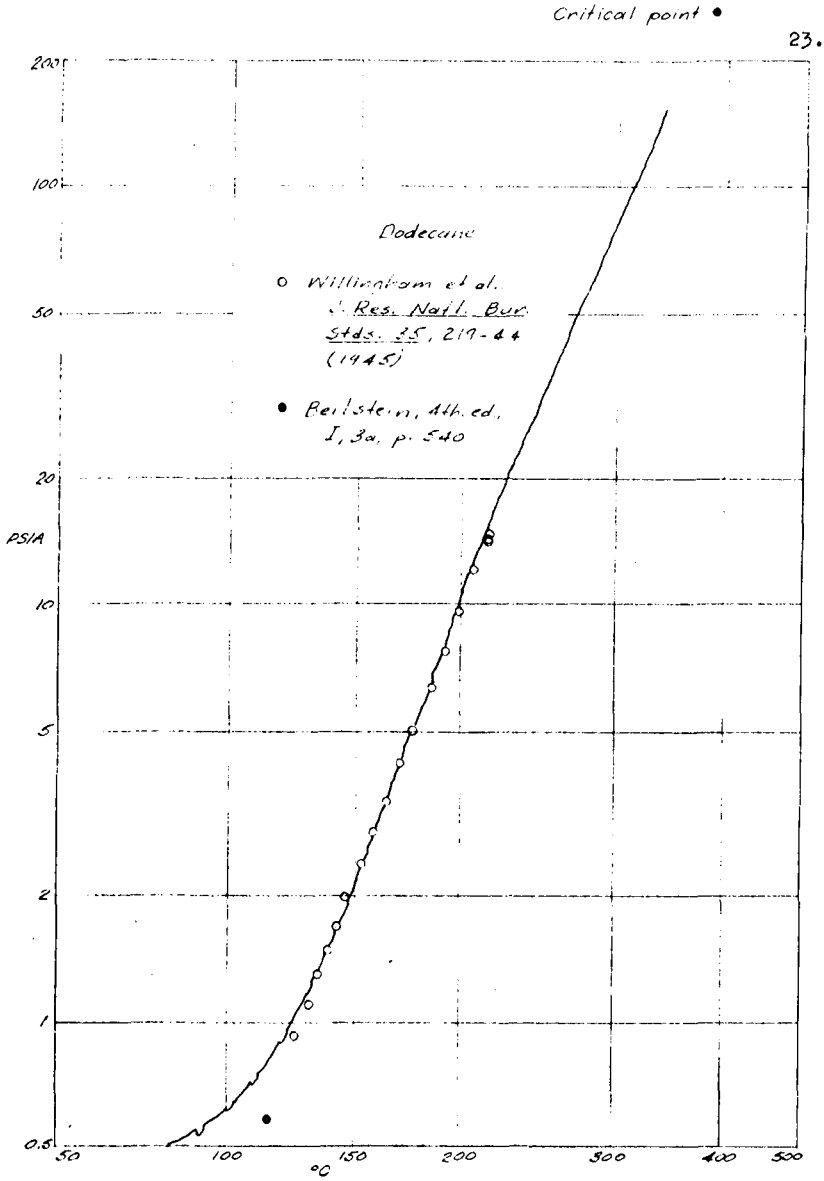


Figure 13. Dodecane standard

0692725

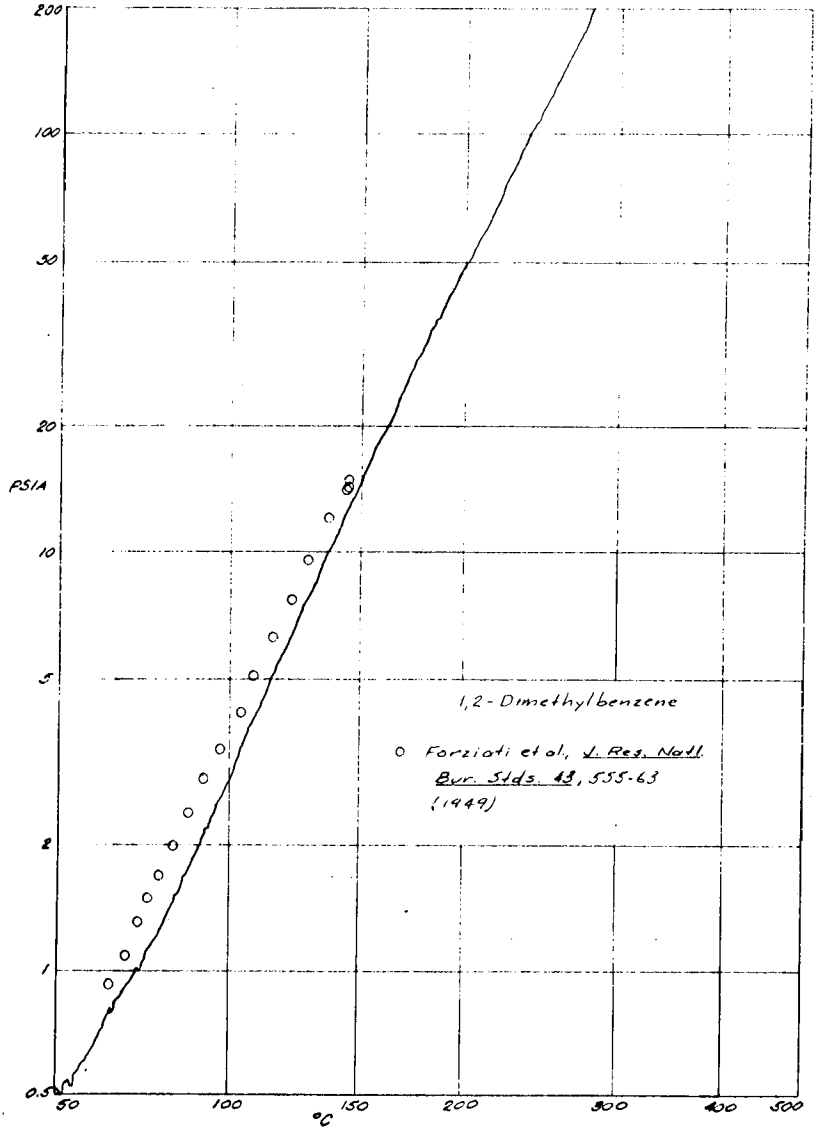


Figure 14. Xylene standard

0692726

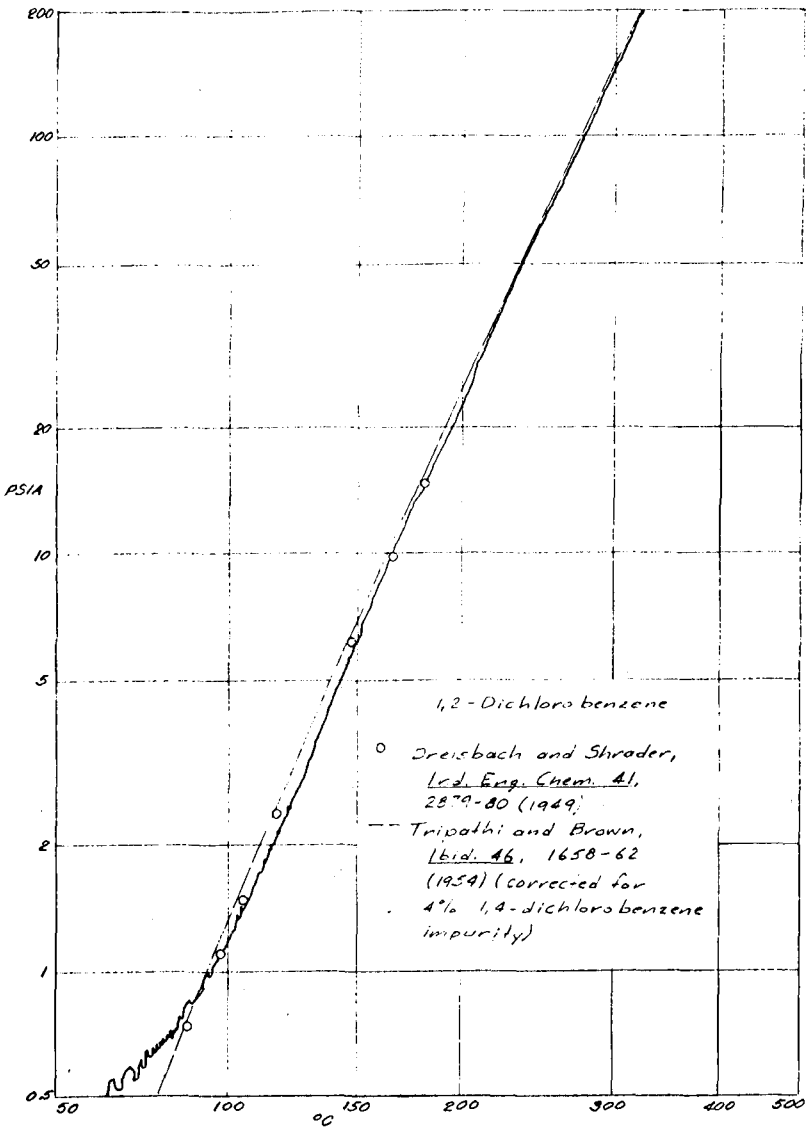


Figure 15. Dichlorobenzene standard

0692727

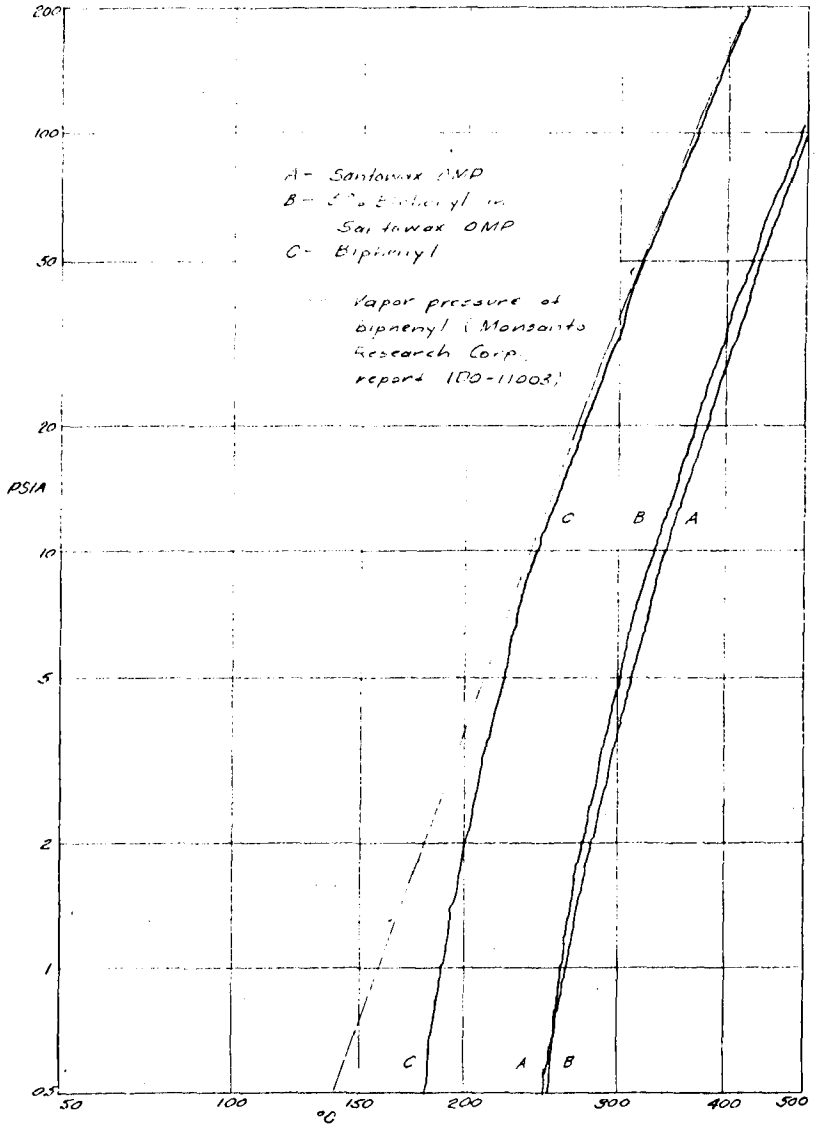


Figure 16. Samples solid at room temperature

0692728

Material	Diffusivity, cm^2/sec
Tantalum	0.22
Nickel	0.17
Stainless steel, type 304 or 316	0.053
K-Monel	0.042
Inconel	0.039
Hastelloy-C	0.036
Glass	0.007
Therminol FR-2	0.00063

Considerations of strength at high temperature, resistance to corrosion and commercial availability in a selection of tubing sizes limited the choice of material to type 304 stainless steel. This is an alloy of low thermal diffusivity, quite inferior (to the extent that this particular property is a suitable index of merit for this application) to such metals as nickel or platinum. However, comparison of the diffusivity value for type 304 stainless steel with that for Therminol FR-2 fluid shows that reduction of the thickness of liquid layer in the cell is a more important factor in heat transfer than would be an increase of the thermal diffusivity of the wall material.

The pressure which a cell constructed as shown in Figure 9 of the instruction manual could withstand was calculated from the tensile properties of the stainless steel. The tensile strength and yield point of type 304 stainless steel are:

Tensile strength (1)

25°C.	8.5×10^4 psi
500°C.	4.9×10^4

Yield strength (1)

25°C.	2.8×10^4 psi
500°C.	1.2×10^4

Tensile stress to rupture in 1000 hours (2)

500°C.	1.8×10^4 psi

(1) National Bureau of Standards, Circular C447, p. 257.

(2) Allegheny Ludlum Steel Corp., "Stainless Steel Handbook," 1951, pp. 2, 58.

The Barlow formula $P = 2S\ (t/d)$ gives the pressure corresponding to a given tensile stress S and ratio of wall thickness to outer diameter t/d for a cylindrical tube. For the dimensions used, $t/d = 0.028$, and the calculated pressures are:

Internal pressure to burst (S = tensile strength)

25°C.	4800 psi
500°C.	2700

Internal pressure to burst in 1000 hours
(S = 1000 hour rupture stress)

500°C.	1000 psi

Internal pressure to produce permanent set
(S = yield strength)

25°C.	1600 psi
500°C.	670

The cell pressure at which collapse of the inner wall would occur was estimated from curves given in "Metals Handbook," American Society for Metals, Inc., 1948, p. 134. For the inner tube, $t/d = 0.047$:

Cell pressure to collapse inner tube

25°C.	2600 psi
500°C.	1100

By these calculations, then, the cell should withstand more than three times the anticipated working pressure of 300 psia for 1000 hours at 500°C. Failure with increasing pressure would occur by collapse of the inner wall of the annulus at about 1100 psi at this temperature. Application of somewhat more than twice the working pressure would produce a permanent deformation of the outer wall.

The cell was tested hydrostatically at 2500 psi at room temperature. This pressure is about one-half of the calculated bursting pressure, but well above the deforming pressure, and it was noted that the cell exhibited a marked barrel shape after testing was completed. This was not considered to be deleterious to the safe use of the cell, which was mounted in the furnace unit. The design of this cell had been planned to include a tubular pocket for the thermocouple, welded to the outside wall of the cell at the middle. This feature, however, was omitted because of the possibility that welding on the thin tubing of the cell wall might weaken the wall excessively. Instead of using a pocket for the thermocouple, it was merely pressed against the cell by a band of thin sheet stainless steel wrapped tightly around cell and thermocouple.

The second desired modification of the furnace assembly, provision for circulation of air within the furnace, was obtained by installing a motor-driven blower. The driving motor was mounted on the underside of the furnace base, with an extension shaft to a blower wheel placed just above the bottom of the furnace. The blower consisted of a paddle wheel of 0.015 inch thick stainless steel, having 6 radial blades 0.88 inch high and 0.5 inch wide arranged inside a 2 inch diameter circle. Although the operating speed of 1675 rpm was relatively low for this small blower, smoke tests with a glass beaker substituted for the furnace cover showed that it produced rapid circulation and thorough mixing of the enclosed air.

The performance of the modified cell and furnace unit was tested by attaching fine wire thermocouples to the outside of the cell near the top and the bottom, and recording the cell temperatures, as well as the air and control thermocouple temperatures, during heating. Two heating rates, 5°C. and 20°C. per minute, were used. At neither rate was any systematic difference of temperature between the ends of the cell noted. At a heating rate of 20°C. per minute the air temperature was about 40° higher than the cell temperature; at the 5° rate the difference was about 15°. In both cases the control thermocouple, located at the center of the cell, was cooler than the end thermocouples. The difference was about 10° at the high rate and 3° at the low rate; it was ascribed to lag of response of the relatively massive, sheathed control thermocouple. As there would also be a lag of temperature of the liquid within the cell, behind the temperature of the outer wall, the actual error of temperature indication would be reduced.

The radiation shield surrounding the cell was not a part of the original design, but was added in an attempt to eliminate what appeared to be erroneously high vapor pressures in the low-temperature region. The experiments described in Section A1 showed, however, that the actual cause of the observed high pressures was not radiative heating of the cell but incomplete degassing before introduction of the sample. The shield was retained because of its possible utility in reducing radiative heat transfer to the outer wall of the cell, with consequent higher temperature there than at the inner wall.

2. Temperature recording and control system

In the design of a system to provide recording of temperature on a scale linear in reciprocal Kelvin temperature, the use of a platinum resistance thermometer element was first considered. Relatively simple circuits for obtaining linear rotation of a slidewire in terms of Celsius temperature have been developed. They use Wheatstone bridge measuring systems, and it would seem to be an obvious adaptation of such a system to produce a linear readout in reciprocal Kelvin temperature. The initial plans, however, called for the sensing element to be inserted in a well in the sample cell. For this use the most compact possible sensor was desired; in addition, it was necessary that the sensor have leads suitable protected for extension through the furnace at a temperature up to 500°C. No platinum resistance thermometer meeting these requirements was found. In addition, the rather high cost of resistance thermometers generally was also a deterrent to the use of this sensing element. For these reasons a thermocouple was selected instead for measurement of the cell temperature, and an electronic circuit was designed to obtain the desired linear scale of reciprocal absolute temperature from the thermocouple input.

The application of a thermocouple to recording of temperature on a scale linear in 1/°K. depends upon the observation that, for

an iron-constantan thermocouple, the function log (E + k) is very nearly linear with respect to reciprocal absolute temperature - E being the emf of the thermocouple referred to 0°C., and k an arbitrary constant. Figure 17 shows the fit obtained for two values of k. The curve most nearly conforms to a straight line, from room temperature to 500°C., for k = 3.0 mv. An exact fit can be obtained at 50°, 150° and 400°C. With three adjustments available - thermocouple offset voltage, recorder span and recorder zero - the recorder scale could be made to fit a scale of reciprocal absolute temperature at any three points. If the three temperatures listed were selected, the maximum temperature errors would be about -5° at 250°C., +10° at 500°C., +2° at 100°C. and -4° at 25°C. It was thought that these errors, representing at the higher temperatures 2% of the scale reading, would be acceptable, and the instrument was first set up in this way. The error at 25°C. was considered unimportant; however, a change was made to 50°, 200° and 400°C. as the calibration points in order to obtain a better fit in the 200°C. region. When the instrument was put into use, the temperature error in the region of 100°C. was found to be objectionably large, amounting to about +6°. The exact source of this error was not identified; possibly some non-linearity of the logarithmic compressor was present. Redrawing of the recorder chart with distortion of the temperature scale to produce the desired calibration was considered as a method of correcting this error, but it was decided that retention of the theoretical reciprocal absolute temperature axis was preferable to a change here. Instead, the temperature scale was corrected by the introduction of a non-linearity in the recorder function of voltage versus pen travel. In Figure 17, the curve for an offset of 2.0 mv shows a linear relation of log (E + k) to 1/°K at temperatures above 150°C.; at lower temperatures the thermocouple voltage drops more rapidly than is desired. This is also the shape of the curve of output voltage versus tap position of a resistive voltage divider the lower branch of which is shunted by a fixed resistance. Then by the introduction of such a shunt in the recorder potentiometer circuit it should be possible to match the log (E + k) curve. This was done experimentally: resistance values in the recorder circuit were manipulated, while varying the calibration adjustments already present, until a satisfactory fit of the temperature scale was secured. With this modification, the error of indicated temperature was reduced to +2° at 100°C. and -3° at 25°C. when the calibration was exact at 50°, 200° and 400°C.

The logarithmic compressor had a full-scale input of 100 volts. Therefore, an amplifier which would produce this voltage from the thermocouple output was required. Few of the large number of commercial d-c amplifiers have this output capability. Of those which do, the Philbrick UPA-2 amplifier was selected. This amplifier has adequate performance specifications with regard to gain and drift, and the cost is relatively low. The amplifier is supplied with a filament transformer, but without plate power supply because it is intended for use in analog computer applications where a common

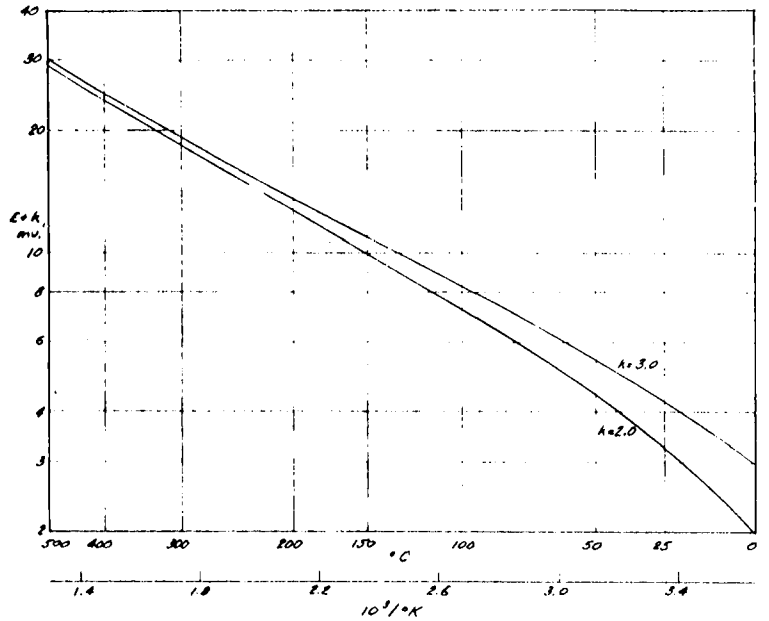


Figure 17. Thermocouple characteristic as a function of $1/^{o}K$

0692733

power supply serves several amplifiers. In the present application, however it seemed better to keep the temperature and pressure systems entirely separate and thus avoid having to rely on the electrical insulation of the thermocouple and pressure transducer. To obtain isolation, it was necessary to add a simple power supply to the amplifiers.

The Philbrick UPA-2 amplifier comprises a chopper-type d-c amplifier, followed by a direct-coupled amplifier. The circuit is shown in Figure 11 of the instruction manual. The chopper amplifier section, of two stages, is bypassed by an alternate signal path to the direct-coupled amplifier of two amplifying stages and a cathode follower. The bypass provides the signal path for amplification of signals above a few cycles per second in frequency. Although response to rapid variations of signal is not a requirement here, the high frequency response of the amplifier may assist in making it more stable when used in a feedback loop. No difficulty was found in applying this amplifier to feedback-stabilized amplification with the required gain of 3000. However, the relatively small amount of amplification in the chopper amplifier made the unit sensitive to line voltage changes, which were reflected as small variations of apparent input voltage. Presumably this effect arises in variation of the grid-cathode contact potential of the third stage as the heater voltage changes, and in variation of the fourth stage plate voltage as the supply voltage changes. Damping of the amplifier by addition of a capacitive feedback path, as shown schematically if Figure 12 of the instruction manual, reduced noise in the amplifier output appreciably but there were still some disturbances. The amplifiers in the temperature and pressure systems were first installed with their power supplies connected directly to the line; later, in an attempt to reduce noise, they were reconnected through a constant-voltage transformer. This transformer had only a small effect on the noise originating from random line voltage changes, but it did reduce greatly a previously-observed shift of temperature and pressure readings caused by line voltage drop when the furnace heater came on.

To convert the amplified thermocouple voltage to the desired logarithmic function, there appeared to be two possible mechanisms: use of a logarithmic recorder, and use of a linear recorder preceded by a passive logarithmic converter. The use of direct logarithmic recording would have several advantages. No separate logarithmic converter would be required; the recorder, unlike a logarithmic converter, would draw no power from the amplifier; and the logarithmic characteristic, being established by the recorder slidewire, would be perfectly stable. On the other hand, there is the disadvantage that no logarithmic x-y recorder is available, and that to convert a linear recorder to this use would involve much modification and experimentation. To avoid such modification, it was decided to apply a logarithmic converting element at the input of a standard linear x-y recorder.

The available methods of transforming from a voltage to a second voltage related to the logarithm of the first involve the use of either thermionic or semiconductor diodes. (A logarithmic servovoltmeter which is available commercially could not be considered because of the high cost.) Ranges as large as 7 logarithmic decades have been covered with thermionic diode converters. For the present problem a range of only 1 decade was required in the temperature system, and 3 decades in the pressure system. The Kane C-7A Logarithmic Compressor is a commercial semiconductor diode converter with a 3-decade range, which was selected for use here. The conververters were supplied in small cabinets with self-contained batteries. Except for two adjusting potentiometers, the circuit elements all were incorporated on a component board in each unit. The component boards were remounted in the recorder console of the vapor pressure instrument, with connections to a remote battery assembly. The original adjustments were replaced with fixed resistances, the need for adjustability having been eliminated by the use of stable mercury batteries and by the adjustments in the recorder. Originally the logarithmic compressor component boards were simply mounted on the panel of the instrument. It soon was apparent that large shifts of zero on both axes of the recorder were being produced by variations of temperature of the logarithmic compressors. The two transistors which comprise the output cathode follower of these units (see Figure 13a of the instruction manual) seemed to be extremely sensitive to variations of temperature. Although these transistors are of opposite type and therefore have opposite effects on the sign of output voltage variation with temperature, the cancellation of temperature effects was not complete. It was necessary to remount the component boards of the logarithmic compressors in a thermostatted box to suppress output voltage variations attributable to temperature changes. The box was made of aluminum with heaters dissipating 3.3 watts each, on each of the two larger opposite sides. A thermostat attached to the box near one of the heaters allowed a cycle of about 1.2°C. at that location, which produced a cycle of about 0.2°C. amplitude in the interior of the box. Instability of the thermostat was a problem in this application. The unit used, a Fenwal 32400-0, had an adjusting range of about 160°C. per revolution of the adjusting screw. With such a wide span, slight shifts of position produced by pressure on the thermostat body or terminals had a significant effect on the set temperature. It was found that to secure regulation at 40°C. with a stability of ±0.5°C. the insulation around the box had to be cut away to prevent exertion of any force on the thermostat. Use of a unit having a narrower span of adjustment, with correspondingly lower sensitivity to extraneous influences, would have been desirable.

The temperature control circuit was designed to utilize the amplified thermocouple voltage already present in the temperature recording system. Linear time programming of this voltage was considered sufficient. This does not quite correspond to a linear time increase of temperature, but the difference should be of no

concern in this application. With the specified amplifier gain of 3000, a temperature change of 1°C. at the cell corresponds to a voltage change of about 0.16 volt at the amplifier output. This change is not great enough to operate any simple relay directly, but with moderate further amplification a relay could be made to operate on temperature changes of 1°C. or less. Possible relays which were considered were semiconductor switches (silicon controlled rectifiers), gas tube switches (thyratrons), and mechanical relays.

The power requirement of the furnace heater was approximately 4.5 amp at 115 volts. This current is too large to be handled by a small thyratron but would not be excessive for either a mechanical relay or a silicon controlled rectifier. Use of the latter type of switching element was considered, but was rejected partly because of lack of familiarity with silicon controlled rectifiers and partly because such a circuit seemed more elaborate than was necessary for the degree of temperature control required. Therefore the mechanical relay was chosen: specifically, a mercury plunger relay in order to obtain durability and quiet operation.

The coil dissipation of a suitable mercury relay is in the range of 5 watts. Although hard-vacuum tubes are available which would readily supply this power, a simpler choice seemed to be the use of a thyratron operating directly from an a-c plate supply. The thyratron requires a control voltage swing of about 1 volt, which could be obtained from a single vacuum tube amplification stage. (The amplifier must invert, so that the thyratron is nonconducting when the signal voltage is high, if a normally-open relay is to be used.) The circuit shown in Figure 10 of the instruction manual was designed on the basis of these considerations. The amplifier stage was arranged for differential input, with the control signal coming to one grid of a twin triode and a reference signal to the other grid. By making the reference signal adjustable, provision for adjusting the set point of the controller was supplied. The active half of the difference amplifier was a simple direct-coupled stage, with a voltage divider in the output to reduce the voltage level to the cathode level of the thyratron.

The time programming was to be controlled by a voltage from the timer-driven potentiometer. Because the amplifier output voltage would vary over a range from about 10 to 90 volts, it did not appear to be feasible merely to apply the programming voltage to the reference grid of the difference amplifier. Instead, the signal and programming voltages were added, with inversion of the programming voltage, and the relay circuit was arranged to turn on when the voltage sum was positive or off when it was negative. The simple adding network used for this purpose incorporated a variable voltage ratio, so that the time rate of increase of the signal voltage, and therefore of cell temperature, could be varied.

The temperature programmer circuit was built originally without the 0.068 mfd capacitor in shunt with the amplifier load resistance. When the circuit was tested it exhibited a hysteresis of about 2°C.: that is, when the heater relay turned on, it was then necessary for the temperature to rise 2° before it would turn off, and conversely for rising temperature. The cause of this effect seemed to be some interaction between the thyratron plate circuit and the amplifier circuit. Whatever the cause was, the effect was eliminated by by-passing the amplifier load resistance.

A second later addition was the 100 mfd capacitor shunting the signal branch of the voltage adding circuit. The capacitor was incorporated to provide some anticipation of temperature changes, and thus improve the temperature control. It should have been possible to obtain the same result, and more effectively, by shunting with a capacitance the upper arm of the voltage divider between the difference amplifier plate and the thyratron grid; but when an attempt was made to do so, the thyratron conducted continuously at all signal voltages. This result is inexplicable from a superficial analysis of the circuit. As in the case of the plate load shunt, it probably arises by interaction between the output and input circuits of the controller. The added 100 mfd capacitor had a small effect on the cell temperature regulation obtained, a reduction in the amplitude of temperature cycling and increase of the frequency of the cycle being observed. The amplitude of temperature variation was about 4°C. and the frequency about 0.5 per minute.

As was mentioned at the beginning of this section on design, the original choice of a thermocouple as the temperature sensing element (and following from this, the selection of the circuit elements to obtain linear recording of reciprocal absolute temperature) was based upon the belief that a resistance thermometer would be unsuitable in physical form for use with the original cell. The cell design, however, was changed: placing the temperature sensor in a small well was no longer a requirement. Also, compact resistance thermometers designed to have both head and leads exposed to high temperature have become available. Thus if the design were to be done again a resistance thermometer might well be chosen as the temperature sensor. A surface unit, such as Winsco 2512, should be suitable. The higher cost of the resistance thermometer would be compensated by elimination of the amplifier and logarithmic compressor required for the thermocouple system, and the higher voltage level available from the resistance thermometer would appear to simplify the electronic design generally.

In section A1 there was mention of premature battery failures. These apparently resulted from the purchase of several batteries which had been stored too long by the distributor. Batteries from another distributor gave normal service. Use of line-operated power supplies instead of batteries was considered, but the 7 power supplies which would be required would have involved excessive bulk and expense.

The original design incorporated Mallory type TR-233 batteries for B3 and B5, which supply the output voltages of the logarithmic converters. These batteries exhibited a continuing decrease of voltage when in use. Replacement of the TR-233 batteries with the equivalent series arrangement of RM-3R cells gave a stable voltage. Although the TR-233 battery is physically composed of three RM-3 cells in series, there is apparently some difference in the manufacturing process for the cells which results in lower stability of voltage than that characteristic of individual RM-3R cells.

3. Pressure recording system

In order to detect both the effects of volatile impurities in a sample (producing an increase of pressure at low pressure) and the effects of unstable but non-volatile impurities (causing an increase of pressure at high temperature and therefore at high pressure) it was considered necessary for the pressure recording system to cover the widest possible span of pressure. However, hysteresis and zero shift of the pressure transducer, and zero drift of the amplifier, limit the minimum pressure which may be measured with a transducer of given upper pressure limit. The range of logarithmic conversion available with the Kane C-7A Logarithmic Compressor was 3 decades. Since the commercial pressure transducers usually are rated at 1% of full scale hysteresis error, it was thought that a 3-decade recording span would more than exhaust the ability of the transducer to measure low pressures. Experience however gave the opposite result. It was necessary to reduce the range of recording to 2.8 decades because of failure of the logarithmic compressor at the lowest voltages, a failure probably caused by operating the compressor at 40°C. in the thermostat instead of the nominal 25°C. Over this range the pressure transducer showed no significant lack of repeatability. Reproducibility of the zero point of the gauge was within 0.1 psi.

Preliminary calculations had indicated that an upper pressure recording limit of 500 psia would be required. A 500 psia range pressure transducer was obtained and installed, but the first tests of the instrument indicated that the transducer was defective. To save time, the 500 psia unit was exchanged for a 300 psia transducer which the manufacturer happened to have. Eventual replacement of the 500 psia transducer was planned, but the lower-range unit proved to be entirely satisfactory and was retained for permanent use.

4. Programming system

The features desired in the temperature programming system of the vapor pressure apparatus were production of an approximately linear temperature rise over the selected span, with a minimum of attention from the operator. Accurate linearity and exact reproducibility were not sought, since these factors should have only secondary effects on the vapor pressure versus temperature function. Operation of the heater from a variable transformer

provided with a time drive was first considered. In its most simple form, such a device would require resetting by the operator after each run, but automatic resetting could be provided. For example, the variable transformer might be driven by two motors through a differential, one motor driving forward during programming and the other driving backward rapidly for resetting when the program was completed. Variation of the rate of temperature rise could be obtained by feeding the motor-driven variable transformer from (or into) a second manually-set variable transformer which then would serve as the rate of rise control. Such a system is fundamentally simple, and has the advantage that the voltage applied to the furnace is continuous instead of intermittent as in on-off types of control. Disadvantages are the considerable weight and bulk of the variable transformers and the rather high cost of the mechanical components required if automatic resetting is to be incorporated. An additional disadvantage is that there would be no control of temperature as such, but only of voltage applied to the heater.

Because a temperature recording system was to be incorporated in the instrument, whatever type of temperature control was used, it seemed to be feasible and desirable to include an electronic temperature controller utilizing the components already present in the recording system. The programming element of such a controller would be a variable resistance, which would simplify the problems of time drive and of automatic resetting. Although schemes for electronic proportional control have been simplified by the introduction of controlled semiconductor rectifiers, it was thought that not even this degree of complication would be needed and that on-off control would suffice. A control circuit was designed as described in section 2C, to be actuated by differences of voltage between the amplified thermocouple output and a time-related reference voltage. The simplest method of obtaining the reference voltage appeared to be, to attach a potentiometer (supplied with a constant voltage from a regulated power supply) to a reset timer of which several are commercially available. The mechanical design of the different makes of timers apparently is similar: a motor drives the timer mechanism through a solenoid clutch, release of which at the end of the timing period permits the mechanism to be reset by a spring. An Eagle Signal Co. model HP2 timer was chosed for use here. The setting knob of the timer was removed, and a bushing was added for attaching the reference voltage potentiometer. The return spring of the timer provided only a small torque, so a potentiometer of low torque requirements was necessary; a Beckman model G unit was chosen. The potentiometer shaft was coupled to the timer indicator by a slotted tongue soldered to the potentiometer shaft and engaging a slot in the timer shaft. Initial trials of the assembly indicated that the torque of the timer spring was sufficient to rotate the potentiometer, but when the unit was installed in the vapor pressure recorder several instances of sticking were observed. The original timer spring was replaced with a heavier spring, which gave reliable resetting action. Probably the original spring would have

been adequate if a potentiometer of lower torque requirement, such as the Beckman model T, had been used.

The timer incorporated contacts operated by the clutch solenoid, which were utilized to obtain the desired self-holding function and to control the line power applied to the heater control relay. Design of the self-holding circuit, to be energized by the START button and reset by operation of the STOP button or by opening of any part of the limit switch circuit, was entirely conventional. The limit switches on the two axes of the recorder, and the limit thermostat in the furnace, were introduced as safety features. They are not expected to operate during a normal run, in which completion of the programming would be marked by completion of the selected time period with subsequent removal of power from the heater and automatic resetting of the timer. In case of some failure of the programmer or temperature controller, however, the temperature-axis limit switch would prevent a dangerous increase of furnace temperature. The occurrence of a pressure increase above 300 psia, at a temperature below the 500°C. limit, would trip the pressure-axis limit switch and thus avoid further heating. Finally, should heating somehow continue even after opening of either recorder limit switch, the furnace limit thermostat would open at about 600°C. to cut off the heater.

Programming of the temperature by the temperature control and programming sections of the apparatus seemed to be adequate for the intended use. A typical record of temperature versus time is shown in Figure 18. At the start of the program there was a rapid rise to about 65°C. After the initial rise the average temperature increased linearly to the maximum. The program had been set for 75 minutes at 5°C. per minute. Actually, the temperature increased 390°C. in 75 minutes, or 5.2° per minute. Both the initial rapid rise of temperature and the cyclic variation superimposed on the temperature curve are probably to be ascribed to the characteristics of the furnace, rather than to any property of the control and programming system. Presumably the lag of response of the thermocouple to heat input at the heater is the cause of both the initial overshoot and the cyclic fluctuation. For most of the materials for which this apparatus was designed, no measurable vapor pressure is found at temperatures up to about 70°C., and deviations of heating rate in this region are unimportant. The cyclic variation of temperature at the higher temperatures did produce a slight fluctuation of vapor pressure. The pressure variation was easily seen on a linear recording of the pressure on a separate recorder, but did not have any great effect on the pressure versus temperature recording. If the pressure and temperature variations were exactly in phase there should, of course, be no effect at all on the recording, but they might be expected to be out of phase in practice because of the temperature lag between thermocouple and sample.

5. Recorder

The use of an x-y recorder for plotting vapor pressure as a function of temperature seemed to be an obvious choice. Several makes of x-y recorders are available; the Houston Instrument Corp. model HR-92-1 was selected because of its low cost. Although this recorder was supplied in a case, it was considered preferable to remount it in the electronics console of the vapor pressure instrument in order to obtain a compact construction. Extensive circuit modifications would have been required in any event, so the original calibration controls were discarded, to be replaced by corresponding components in the console.

The original measuring circuits of the x-y recorder consisted of potentiometer bridges having output voltages equal to 6 times the maximum voltages to be measured on the two axes. The potentiometer voltages were then reduced by 6:1 voltage dividers in the recorder amplifiers for comparison with the voltages to be measured. This arrangement is satisfactory for the maximum measured voltage of 70 or 100 mv for which the recorder was designed, and has the advantage that spurious emf's in the potentiometer circuits are insignificant in comparison to the output voltage of 420 or 600 mv. In the present application, however, voltages up to nearly 400 mv were to be measured. With measured voltages of this magnitude, division of the potentiometer voltage is neither necessary to reduce interferences nor possible with a single cell power supply. Therefore the voltage-dividing networks were removed from the recorder amplifiers, converting them to direct comparison of potentiometer and measured voltages.

The recorder was intended to accept standard graph sheets having a 7" x 10" grid printed on 8.5" x 11" paper. Apparently there is no commercial stock of graph papers having reciprocal absolute temperature and logarithm of pressure as the scale arguments. For temporary use a master graph was drawn, to be copied by "Xerox" or similar process. It was thought that if use of the instrument continued for a long period, it would be desirable to have a supply of graph sheets produced by some more accurate printing process.

ACKNOWLEDGEMENT

The authors are appreciative of R. H. Munch's interest and helpful consultation in testing the instrument and to O. Hicks and G. M. Gasser for analytical work on the project.

APPENDIX

Instruction Manual.

W. N. Trump

C. E. Vogler

jm
8-20-63

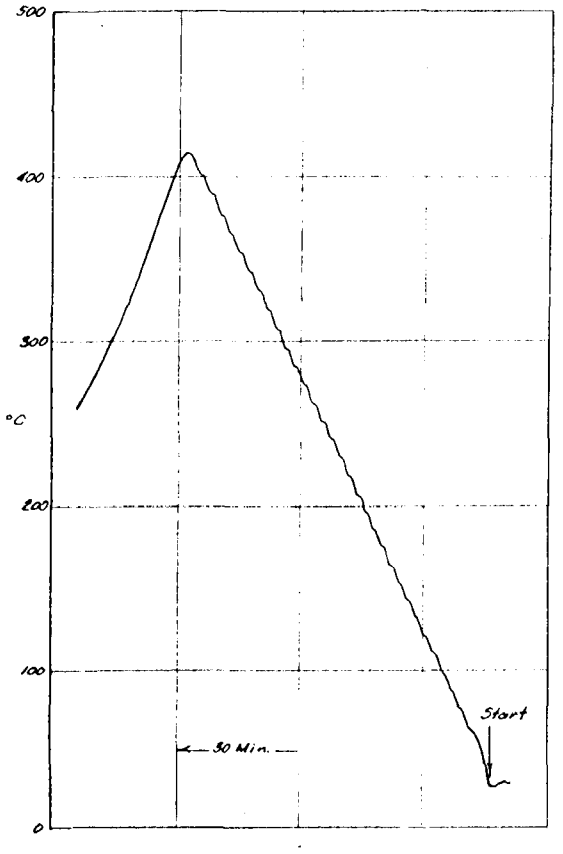


Figure 18. Temperature record

INSTRUCTIONS FOR

VAPOR PRESSURE AND THERMAL STABILITY APPARATUS

0692743

CONTENTS

Section 1. Introduction

A. General description and theory

If a solid or liquid substance is introduced into an evacuated, confined space, evaporation proceeds until the pressure in the space has risen to the equilibrium vapor pressure of the substance at the prevailing temperature. A famous equation, derived by Clapeyron, gives the temperature derivative of the resulting pressure in terms of the heat of vaporization of the substance and the volume expansion accompanying vaporization:

$$dP/dT = \Delta H/T\Delta V$$

If it is assumed that ΔH is independent of temperature, that the vapor is an ideal gas, and that the volume of condensed phase evaporated may be ignored in relation to the volume of vapor formed, this equation may be transformed to:

$$dP/dT = \Delta H/(RT^2/P)$$

which is integrated to:

$$\ln P = -\Delta H/RT + C$$

C being a constant of integration. Thus, for a substance meeting the specifications above, the logarithm of vapor pressure would be a linear function of reciprocal absolute temperature. Real substances do not have heats of vaporization which are invariant with temperature, their vapors do not conform to the law of ideal gases, and the expansion on vaporization is not so great that the volume of condensed phase dissipated in vaporization may be neglected. Nevertheless, most real substances show a variation of logarithm of vapor pressure which is nearly enough linear with respect to reciprocal of absolute temperature to make the plotting of these quantities a useful method of recording and interpolating vapor pressure data.

The vapor pressure and thermal stability apparatus, shown in Figures 1 and 2, is a laboratory instrument for recording automatically the curve of logarithm of vapor pressure as a function of reciprocal of absolute temperature. The sample may be any substance liquid at room temperature; the recording range extends from room temperature to 500°C., or to a pressure of 300 psia if this pressure occurs at a lower temperature. Rise of temperature is programmed automatically, at a rate adjustable from 1° to 25° per minute, for any time up to 150 minutes or to the maximum temperature of 500°C. Heating is terminated without operator attention at the end of the selected time; or if the recorder temperature reaches 500°C., or the pressure 300 psia, before that time; or if the furnace temperature reaches 600°C. regardless of sample temperature or pressure. Curves are plotted on a special

graph paper of 8.5 inch by 11 inch format. By comparing the recorded curve of a specific sample of Therminol or other fluid with a master curve prepared from material of known properties, the operator can detect the presence in the test sample of objectionable amounts of low-boiling impurities or of substances producing increased decomposition rate at high temperature.

Structurally the instrument consists of two units: a furnace assembly and a recorder console. The furnace unit contains the sample cell and associated filling and emptying connections, and the pressure and temperature transducers. It is connected by cables to the recorder unit which contains the electronic equipment and the x-y recorder for plotting the desired log P versus $1/T$ function.

B. Operating controls

Operation of the Vapor Pressure and Thermal Stability Apparatus requires both manipulations of the sample and operations of the electrical controls. Introduction and degassing of the sample involve the use of two stopcocks on the glass sample funnel, and three valves on the furnace base (see Figure 2). STOPCOCK A, STOPCOCK B and the INLET valve admit liquid from the sample funnel to the cell. The BYPASS valve connects the sample inlet directly to the outlet, for flushing and drying of the inlet connections. The OUTLET valve connects the sample cell to the outlet (which, in use, is connected to an evacuated trap).

Electrical controls which are operated routinely during recording of vapor pressure curves are located beside the recorder, as shown in Figure 3. The OFF-ON switch controls all power to the instrument. The LOAD-OPERATE switch, when in the LOAD position, causes the recorder pen to move to the upper right-hand corner of the platen so that a sheet of graph paper may be inserted or removed conveniently. In the OPERATE position, the recorder pen traces the pressure-temperature record. Pressing the START button initiates the automatic cycle of temperature programming; the associated pilot lamp shows that the program is running. Pressing the STOP button terminates any program which is in progress, and resets the programming timer. The pilot lamp beside the STOP button glows when the instrument is in standby condition (ready for the start of programming).

Two controls which are operated only to change program duration or rate of temperature rise are located on the front panel of the console, Figure 4. The TIMER is set for the desired program time. Heating begins when the START button is pressed, and continues for the selected time (unless the limit of temperature or pressure is reached before the time expires). The RATE OF RISE control is set for the desired rate of increase of temperature.

The maximum temperature attained during the run is equal to the product of cycle time (TIMER setting) by the temperature rise per minute (RATE OF RISE control setting) unless the product exceeds 500°C. As described in section 1A, heating is interrupted automatically at this temperature.

Other controls in the recorder console are used for calibration and adjustment. They are described in section 4D.

Section 2. Principles of operation

A. Introduction

This section of the Manual includes detailed descriptions of the elements of the Vapor Pressure and Thermal Stability Apparatus. The instrument consists of four, substantially independent systems:

Sample system and furnace
Temperature control and recording system
Pressure recording system
Programming system

The sample system consists of the sample cell and the associated components for handling the sample. The other three systems comprise the electrical mechanism for measuring and recording the vapor pressure curve of the sample.

The block diagram, Figure 5, shows the relationship of the systems and the locations of the major components within systems. The sample system and furnace section includes the thermocouple for measurement of sample temperature and the pressure transducer for measuring the pressure exerted by the sample. The thermocouple output passes through a reference-junction compensating circuit to an amplifier; the amplifier output is applied through a logarithmic conversion element to the temperature axis of the recorder. The circuitry is so arranged that the recorder indications are linear in reciprocal absolute temperature. The amplified thermocouple voltage also is applied to a comparison circuit in the temperature controller. The reference voltage of this circuit is controlled by the program timer. If the amplified thermocouple voltage is less than the reference voltage (indicating a temperature below the programmed temperature) the heater is turned on. If the voltage is greater than the reference voltage (indicating high temperature) the heater is turned off. Use of a logarithmic conversion for recording temperature on a linear scale of $1/^{\circ}K$. is described in the detailed discussion of the temperature system, section 2C.

The pressure exerted by the heated sample is detected by the pressure transducer, which is a strain-gauge unit energized by the power supply through the zero-adjusting circuit. The output

voltage of the pressure transducer is amplified, converted to a function of the logarithm of the amplified voltage, and recorded on a linear scale of log pressure.

Programming of the sample temperature is controlled by the timer, which runs until the selected time has expired unless operation is interrupted by action of the recorder limit switches or of the limit thermostat in the furnace.

B. Sample system and furnace

Figures 6 and 7 show the details of the sample system and furnace. The sample cell is supported centrally in the furnace, surrounded by the helical heater. Below the sample cell is a small blower wheel for circulation of air within the furnace. The high-temperature limit thermostat is mounted vertically between the heater and the cell, and the thermocouple, also protruding vertically through the bottom of the furnace, is clamped to the cell.

The furnace base supports all of the components associated with the furnace. The bottom of the furnace is mounted on the base on a "Transite" spacer, and is filled with glass wool insulation. The furnace cover consists of concentric shells, separated by a "Transite" ring and having the annular space filled with magnesia insulation.

The blower motor, pressure transducer, pressure relief valve and sample system plumbing are mounted under the furnace base.

Figure 8 shows schematically the arrangement of the sample system. The cell has two connections, so that through flow may be obtained for flushing and drying. Sample is introduced into a glass sample funnel, which is connected to the metal sample system through a semi-ball joint. Connections of the sample system outlet to the trap and vacuum pump also is made by such a joint. A chamber in the sample funnel permits preliminary outgassing of the sample, before it is introduced into the cell. The INLET valve admits sample to the cell; the OUTLET valve permits removal of the sample and cleaning of the cell; and the BYPASS valve makes it possible to remove unused sample from the inlet and sample funnel without disturbing the cell.

The pressure transducer is connected to one of the cell connections. To the other is attached a relief valve opening at 600 psig. The pressure transducer is rated for 300 psia range, with permissible overrange of twice this pressure.

Construction of the cell is shown in Figure 9. It is a thin-walled annular cylinder, made of types 304 and 316 stainless steel. This design provides rapid heat transfer both through the cell walls and through the liquid within the cell, from the air

which circulates downward around and through the cell. The cell is surrounded by a radiation shield to reduce heating by direct radiation from the heater. Cell temperature is measured by the thermocouple which is held against the outer cell wall by a band of thin stainless steel.

The heater, of the sheathed type with "Inconel" sheath, is rated for operation at 230 volts and 2 kw dissipation. Operated at 115 volts it dissipates about 0.5 kw, providing sufficient heat for the furnace with moderate heater temperature.

A limit thermostat is provided in the furnace to stop heating should the temperature in the furnace reach approximately 600°C. This is a safety control, operative in the event of failure of the temperature recording system.

C. Temperature control and recording system.

This system comprises those components of the instrument involved in the recording of sample cell temperature and in the regulating of that temperature in conformance with an established time schedule. The relationship of this system to the complete instrument is shown in the block diagram, Figure 5, in which the temperature recording and control system occupies approximately the lower half of the diagram. The sensing element is an iron-constantan thermocouple in a stainless steel sheath, which is clamped to the outer wall of the sample cell. The thermocouple output voltage is corrected for reference junction temperature by the compensating circuit and then is amplified by the amplifier which has a voltage gain of 3000. The amplifier output is applied to two circuit branches. In one branch the signal passes through a logarithmic compressor which converts it to a voltage proportional to the logarithm of the amplifier output voltage. The resultant logarithmic voltage is applied to the temperature axis of the recorder, in the reverse direction. Deflection of the horizontal recorder pen position which is linearly related to the reciprocal of the absolute temperature is thus obtained. In the other circuit branch, the amplified signal is compared with a reference voltage from a potentiometer driven by the timer. The reference voltage is proportional to the elapsed time of the recording program, while the amplifier output voltage is proportional to the thermocouple output and thus (approximately) to the temperature of the cell. The difference of these two voltages is used to operate a relay applying power to the furnace heater. If the reference voltage is the greater (indicating that the cell temperature is lower than the temperature required by the time program) the heater is turned on; if the amplifier voltage is the greater of the two (indicating a high cell temperature) the heater conversely is turned off. In this way the cell temperature is made to rise linearly with time.

The detailed circuit of the temperature recording and control section is shown in Figure 10. (In this figure the circuit elements and connections are complete, but the internal structure of the amplifier, logarithmic compressor and recorder is merely indicated schematically.) The thermocouple is connected through integral leads to terminals on the back of the recorder console. The junction between thermocouple wire and the copper part of the circuit is formed at this point. Compensation for the temperature at this junction is secured by a "Sensitor" silicon resistor mounted behind the panel carrying the thermocouple terminal board. The compensation circuit, energized by battery B1, is a Wheatstone bridge one arm of which is the THERMOCOUPLE OFFSET control. This control permits the introduction of an adjustable voltage in series with the thermocouple output, and is used in calibrating the temperature scale of the recorder to bring the low-temperature end of the scale to the correct reading. The other arm of the compensation circuit contains the temperature-sensitive resistor, with shunt and series resistances to give the required variation of 0.053 mv per degree temperature change for compensation of the cold junction emf of the thermocouple.

The compensated thermocouple output voltage is applied to the input of the amplifier. This is a feedback amplifier with a gain of 3000. It consists of a modified Philbrick UPA-2 amplifier, the modification being addition of an individual power supply and of the feedback circuit components. The basic amplifier is a chopper-stabilized amplifier mounted on the printed circuit board shown in Figure 11. The external connections to the circuit board are shown in Figure 12. The signal enters the amplifier at terminal 2 of the circuit board, is converted to alternating voltage, amplified, rectified and again amplified as direct voltage. The output appears at terminal 6 of the circuit board. A voltage divider consisting of 90 kilohm and 30 ohm resistors is connected across the output and common (number 1 and 4) terminals, and the junction of these resistors forms the return terminal for the input circuit. Therefore the fraction $30/9 \times 10^4$ of the output voltage is applied in opposition to the input (because the polarity of the output is inverse to that of the input), and the overall gain of the amplifier is very nearly the reciprocal of the feedback factor, or 3000. The series combination of 0.25 mfd capacitance and 10 kilohm resistance between output and input introduces additional feedback for varying signals, decreasing the overall gain for such signals and by this means reducing the response to line voltage transients and other disturbances.

The amplifier output voltage goes to the logarithmic compressor, the output of which is a linear function of the logarithm of the input amplitude. Basically the logarithmic compressor is a voltage divider containing a semiconductor diode in series with a resistance. With a suitable steady bias voltage applied to the diode, the voltage appearing across the diode is linearly related

to the logarithm of the voltage applied to the series combination of diode and resistance. The fundamental circuit is indicated in the logarithmic compressor box of the diagram, Figure 10, and the complete circuit is shown in Figure 13a. Two diodes are used, in opposition, because the unit is one which was intended to operate on alternating as well as direct current inputs. A bias voltage is established by battery B2 in series with the 150 ohm and 2-28 ohm resistors. The input signal is applied to the 200 kilohm resistance and the output appears at the junction of the diodes with this resistance. The output voltage, which is at a high impedance level, is transformed to a lower impedance level by the two transistors arranged as a two-stage, complementary emitter follower. The transistors are powered by battery B3.

The components of the logarithmic compressor are mounted on a circuit board, the arrangement of which is shown in Figure 13b. The transistors, especially, are extremely sensitive to changes of temperature. To reduce the effect of ambient temperature variations the component boards of both the temperature system and the pressure system logarithmic compressors are contained in a thermostatted box.

The signal from the logarithmic compressor is introduced into the temperature (horizontal) axis of the recorder. The recorder is a self-balancing potentiometer, which operates to keep the output voltage of the potentiometer circuit (at terminals 1 and 3 of the recorder amplifier) equal to the voltage from the logarithmic compressor (at terminals 1 and 2). The potentiometer circuit is of the Wheatstone bridge form, powered by battery B6 in series with the HORIZONTAL SPAN variable resistance. In one arm the HORIZONTAL ZERO adjusting potentiometer provides for shifting the zero point of the recorder scale. The slidewire, mechanically coupled to the servomotor and recorder pen, is in the other arm. The 2 kilohm shunting resistance across the lower part of the slidewire produces a slight non-linearity of balancing voltage versus pen travel. In combination with the emf-temperature characteristic of the thermocouple and the effect produced by logarithmic conversion, the recorder non-linearity gives a resulting pen motion which is nearly linear with respect to the reciprocal of the cell absolute temperature, over the range from 20°C. to 500°C.

The amplifier output is connected also to the input of the temperature control circuit. A resistance network composed of the 1 megohm RATE OF RISE potentiometer in series with 220 kilohm fixed resistors at each end is connected between the amplifier output and the slider of the TIMER potentiometer. The latter has applied to it a voltage which is negative with respect to the common terminal of the system. Thus, as the timer runs, the potentiometer output voltage becomes increasingly negative. The slider of the RATE OF RISE potentiometer is connected to one grid of a

twin-triode difference amplifier; the other grid is supplied with an adjustable reference voltage from the TEMPERATURE SET control. This control is adjusted so that the heater relay (controlled by the thyratron which in turn is controlled by the output of the difference amplifier) just operates when the RATE OF RISE voltage is zero. The action of the temperature control system, then, is to maintain zero voltage at the RATE OF RISE potentiometer tap by varying the cell temperature so that the amplifier output voltage balances the time-dependent reference voltage, and the ratio of these two voltages will be equal to the ratio of the resistances in the two branches of the circuit, measured from the RATE OF RISE potentiometer tap. When the slider is at the center point of the potentiometer, each 1 volt increase of TIMER potentiometer voltage requires 1 volt increase of amplifier output voltage, corresponding to a temperature increase of approximately 6°C. At the clockwise limit of the control the ratio is correspondingly 1.22/0.22 = 5.5 times as great; at the counterclockwise limit it is the inverse of this, or 0.18 times as great. The relationship between angular rotation of the timer per minute, and voltage applied to the TIMER potentiometer, is such that the potentiometer output voltage increases 0.72 volt per minute. At the midpoint of the RATE OF RISE potentiometer this is equivalent to a temperature change of 4.6°C. per minute; the extremes, corresponding to the counterclockwise and clockwise limits of the potentiometer rotation, are 0.8° and 25°C. per minute.

A 100 mfd capacitance connected between the thermocouple amplifier output and the clockwise end of the RATE OF RISE potentiometer introduces a certain amount of anticipation into the action of the temperature control circuit, to reduce the amplitude of cycling of the furnace temperature. The RATE OF RISE potentiometer and the resistors in series with it comprise a voltage divider between the amplifier output and the temperature control circuit input. Placing the capacitance in shunt with the upper arm of this voltage divider causes the transmission through it to increase with increasing rate of change of voltage. Thus the response of the control circuit to steady temperature is not affected, but changes of temperature are utilized to turn off the heater somewhat before the control point is reached when the temperature is rising or to turn it on in advance of the control point when the temperature is falling. The action may be regarded as a phase advance of the heater control relay action, compensating in part for the lag which exists between application of voltage to the heater and sensing of increased temperature by the thermocouple.

D. Pressure recording system

The pressure recording system is shown in the upper part of the block diagram, Figure 5. The pressure sensing element is a pressure transducer of the strain gauge type, operating from the power supply through a zero-adjusting circuit. The output of the

pressure transducer goes to an amplifier, thence to a logarithmic compressor and to the pressure (vertical) axis of the recorder. Pressure in the cell is recorded on a logarithmic scale, with a range of 0.5 to 300 psia.

The detailed circuit of the pressure recording system is shown in Figure 14. Power is supplied to the pressure transducer by an Elcor AT25-75 power supply. The ZERO ADJUST and ZERO CHECK ADJUST potentiometers are in series across the power supply. The pressure transducer is a Statham PA401TC-300-1700 unit. With the nominal 25 volts applied to its input, the output at the full scale pressure of 300 psia is 250 mv. The ZERO ADJUST control with associated 500 kilohm resistor provides a variable shunt on two adjacent arms of the pressure transducer bridge element to adjust the output at zero pressure. The ZERO CHECK ADJUST control provides an adjustable offset of the transducer zero when the ZERO CHECK button is pressed. This serves to bring the point of zero pressure on scale at the recorder for checking recorder calibration or for checking evacuation of the cell. Special provision for this is necessary because zero pressure does not appear on the logarithmic pressure scale of the recorder. The output of the pressure transducer is applied to an amplifier of gain = 400. The amplified signal passes to the logarithmic compressor and to the recorder. The amplifier, Philbrick UPA-2, and the logarithmic compressor, Kane C-7A, correspond to the descriptions of these units given in section 2C on the temperature system. In the amplifier, the feedback voltage divider consists of 80 kilohm and 200 ohm resistances to produce the necessary gain of 400. The logarithmic compressor is powered by batteries B4 for the bias and B5 for the output transistors. The recorder also is as described for the temperature system except that the potentiometer bridge network is entirely conventional, with a linear relationship between voltage and pen position. The bridge voltage is supplied by battery B7 in series with the VERTICAL SPAN adjustment and with the VERTICAL ZERO adjustment for shifting of the scale position. The recorder scale covers a span of 2.8 logarithmic decades, extending from 0.5 psia to the full-scale range of the pressure transducer, 300 psia.

E. Programming System

The duration of each automatic vapor pressure run and the termination of the run if excessive temperatures or pressures occur is the function of the programming system. As shown in Figure 5, this system consists of the timer in series with the recorder limit switches and the high temperature limit thermostat of the furnace. A detailed diagram of the circuit is given in Figure 15. The timer, Eagle Signal HF2746, contains a synchronous motor driving a cam through a solenoid clutch. The TIMER potentiometer is mounted on the front of the timer. The timer motor and the clutch coil are connected in parallel, so that whenever the motor is energized the clutch is engaged and the potentiometer shaft is

rotated. When the end of the selected time cycle is reached the motor-driven cam opens a switch to terminate the cycle: the motor is de-energized, the clutch releases, and a spring on the timer shaft returns the time indicator and TIMER potentiometer to the starting point. The clutch solenoid also operates two sets of contacts which control the locking and releasing functions of the START and STOP buttons.

Power is applied to the circuit at terminal 6 of the timer. With the instrument in the standby condition, the normally-closed solenoid contact applies power to terminal 7 to light the STOP pilot lamp. Pressing the START button makes connection from the line through the STOP button, the two recorder limit switches and the limit thermostat in series to terminal 5 of the timer, energizing the motor and solenoid. Action of the solenoid closes the circuit between terminals 6 and 8 of the timer, applying power to the heater relay for heating of the furnace. At the same time, the other set of solenoid contacts in series with the cam switch bypasses the START button contacts, holding the solenoid in and causing the timer to continue to run until the cam switch opens or there is some interruption of the limit switch circuit. The furnace circulating blower also runs during this time, as it is in effect connected in parallel with the timer motor.

Termination of a heating cycle normally is caused by opening of the cam switch when the preselected time has elapsed. This action removes the line voltage from terminal 1 of the timer, de-energizing the motor and solenoid through the limit switch circuit. Return of the solenoid to its inactive position removes the power from the heater relay and restores the entire circuit to the standby state.

The 0.47 mfd capacitor connected in shunt with the timer motor and solenoid (across terminals L1 and 5 of the timer) suppresses the voltage surge which occurs at the solenoid coil when it is de-energized. Without this capacitor the ending of the timer program is accompanied by a large transient deflection of the recorder.

The TIMER potentiometer is mounted on the front of the timer in such a way that its shaft rotates with the remaining-time hand of the timer, while its body moves with the cycle-time hand. At the start of a cycle the two indicators coincide, and the potentiometer is adjusted for minimum output voltage in this setting. As the timer runs the cycle-time hand is fixed while the remaining-time hand moves away from it toward zero time. The relative rotation of the two parts causes the potentiometer shaft to rotate, relative to the body, in the direction of increasing output voltage. This action programs the increase of furnace temperature as described in section 2C. At the end of the cycle, release of the timer solenoid clutch permits the remaining-time indicator to return to its starting position in coincidence with the cycle-time indication, simultaneously returning the TIMER potentiometer to its starting point.

Changing of the cycle-time setting of the timer does not affect the initial output of the TIMER potentiometer, because the two hands of the timer, and therefore the shaft and body of the potentiometer, rotate together. A change of cycle time changes the span of rotation of the potentiometer which is covered during the cycle, and hence the span of reference voltage applied to the temperature control circuit. Maximum cycle time of the timer is 150 minutes. The lowest rate of temperature rise with which the full temperature range may be covered is about 3.3°C. per minute. Lower rates of rise may be used with correspondingly shorter temperature spans; higher rates, up to the maximum RATE OF RISE control setting, may be used either by setting the timer for shorter times or by permitting the recorder temperature limit switch to terminate the program. The maximum useful rate of temperature rise is limited by thermal lag in the cell to about 15°C. per minute.

F. Recorder

The curves of vapor pressure as a function of temperature are recorded on a Houston Instruments HR-92 recorder, adapted for mounting in the top plate of the console. The recording pen is positioned by motion of two rods, which are driven by servomotors and also are coupled to balancing potentiometers. The servo amplifiers for the recorder are mounted on the back panel of the console. Measuring circuit components, other than the balancing potentiometers, are on the front panel.

The circuits of the two axes of the recorder are similar. Each receives the output of the respective logarithmic compressor. The servo systems operate by voltage comparison: motion of the pen, corresponding to rotation of the balancing potentiometer for the individual axis, varies the voltage output from the potentiometer circuit. If the difference of input and potentiometer voltages is not zero, the servomotor is driven in the direction necessary to reduce the difference to zero.

The potentiometer circuits are of conventional design. They are Wheatstone bridge networks having the balancing potentiometer and zero-adjusting potentiometer in adjacent arms. The output voltage of the potentiometer circuit appears between the taps of the two arms. As was mentioned in section 20 and shown in Figure 10, the horizontal axis circuit has a shunt on the balancing potentiometer to produce a desired non-linearity of voltage versus pen position along the temperature scale.

The servo amplifier circuit is shown in Figure 16. The amplifiers for the two axes are identical. Terminal 1 of the input plug P1 is the common terminal for both the measured and balancing voltages; it is grounded to the chassis of the amplifier, but the chassis is mounted on insulating bushings so that isolation of the temperature and pressure measuring circuits from each other and

from the physical ground (except at the thermocouple) is preserved. The voltage being recorded appears at terminal 2 of the amplifier, and is connected (through a filter to remove hum) to the grid of the first amplifying stage. The balancing voltage, at terminal 3, passes through a phase-advance network to the chopper which alternately connects it to and disconnects it from the input grid. If the two voltages are equal, action of the chopper causes no alternating component to appear at the input grid. If the voltages are not equal, the alternate opening and closing of the chopper contact produces an alternating voltage which is amplified through the 4 amplifier stages and is coupled to the servomotor control winding at terminals 2 and 4 of the output plug P3. Inductance coupling is used to bypass the d-c plate current of the output amplifier tube around the servomotor. The power winding of the servomotor is connected to the a-c line. Direction of rotation of the motor is determined by the phase of the control voltage relative to the line voltage, and this in turn is determined by the sign of the difference between the measured and balancing voltages at the amplifier input.

The LOAD - OPERATE switch substitutes line voltage for the amplifier output voltage at the servomotor control winding, to cause the pen to move to the upper right corner of the recorder platen and thus make easier the removal or insertion of chart paper.

An attenuator between the second and third amplifier stages adjusts the overall gain of the amplifier so that accurate positioning of the pen is obtained without oscillation. The phase advance network in series with the potentiometer voltage at the amplifier input also assists in this by partially compensating the overall phase lag of the recorder servosystem.

The paper for recording has a grid matching the 1/°K. and log pressure calibrations of the axes. Overall size of the paper is 8.5" x 11". Guides at the top and right edges of the platen control the position of the paper, which is held down also by clips at the left edge. Because the printed grid lines may not always be in exact relation to the edges of the paper, register marks are included on the paper for alignment with the guides. The ruling area of the chart is 7.0" wide by 9.26" high, located with the upper right corner 0.62" from the corner of the sheet in each direction. The register marks are 0.50" from the top and right boundaries of the ruling area, approximately aligned with the top left and right, and right top and bottom corners of the chart rulings. Table I gives the positions of the grid rulings for the temperature and pressure axes.

TABLE I

CHART RULINGS

A. Temperature (horizontal axis)

Distances measured from left edge of ruled area. Underlined temperatures are those marked on the axis. Designation of axis, TEMPERATURE - °C. The numerals under the heading Ruling show the relative line weights: 1 - light; 2 - medium; 3 - heavy.

Temperature °C.	Ruling	Position Inches	Temperature °C.	Ruling	Position Inches
20	3	0.00	180	1	3.98
25	1	0.19	190	1	4.14
30	2	0.37	200	3	4.29
35	1	0.55	210	1	4.43
40	2	0.72	220	1	4.57
45	1	0.89	230	1	4.70
50	3	1.05	240	1	4.83
55	1	1.20	250	2	4.96
60	2	1.35	260	1	5.07
65	1	1.50	270	1	5.19
70	2	1.64	280	1	5.30
75	1	1.78	290	1	5.40
80	2	1.92	300	3	5.51
85	1	2.05	320	1	5.70
90	2	2.17	340	1	5.88
95	1	2.29	360	1	6.05
100	3	2.42	380	1	6.21
110	1	2.65	400	3	6.36
120	1	2.87	420	1	6.50
130	1	3.07	440	1	6.64
140	1	3.27	460	1	6.76
150	3	3.46	480	1	6.88
160	1	3.64	500	3	7.00
170	1	3.81	Register mark	1	7.50

0692757

TABLE I (continued)

CHART RULINGS

B. Pressure (vertical) axis

Distances measured from bottom edge of ruled area. Designation of axis, PRESSURE - PSIA. Underlined pressures are those marked on the axis. The numerals under the heading Ruling show the relative line weights: 1 - light; 2 - medium; 3 - heavy.

Pressure Psia	Ruling	Position Inches	Pressure Psia	Ruling	Position Inches
0.5	3	0.00	16	1	5.01
0.6	1	0.26	18	1	5.18
0.7	1	0.49	20	3	5.34
0.8	1	0.68	25	1	5.67
0.9	1	0.85	30	2	5.92
1.0	3	1.00	35	1	6.15
1.2	1	1.26	40	2	6.34
1.4	1	1.49	45	1	6.51
1.6	1	1.68	50	3	6.67
1.8	1	1.85	60	1	6.93
2.0	3	2.01	70	1	7.16
2.5	1	2.33	80	1	7.45
3.0	2	2.59	90	1	7.52
3.5	1	2.82	100	3	7.67
4.0	2	3.01	120	1	7.93
4.5	1	3.18	140	1	8.16
5.0	3	3.33	160	1	8.35
6	1	3.60	180	1	8.52
7	1	3.82	200	3	8.68
8	1	4.01	220	1	8.81
9	1	4.18	240	1	8.93
10	3	4.33	260	1	9.05
12	1	4.59	280	1	9.16
14	1	4.82	300	3	9.26
			Register mark	1	9.76

Figure 17 shows the recorder chart. The original drawing for the chart is included with the instruction manual accompanying the instrument.

The recording pen is attached to a carriage resting on the intersecting pen drive bars of the recorder. A pivoted bracket for the pen tip permits the tip to be removed from the paper when no curve is being traced. The pen tip is a "Wrico" size 7 lettering pen point.

Section 3. Operating Procedures

A. Detailed Procedure

Preparation of Instrument for Operation

1. Turn on instrument - pilot light next to "stop" switch indicates that the instrument power is on. Allow at least one-half hour, preferrably two hours, for instrument warm-up.

2. With selector knob in "load" position, put recorder chart in place. Return the knob to "operate" position.

3. Degas the cell by heating to 400°C. under high vacuum (<0.05 psia). The instrument temperature program may be used at the maximum heating rate setting. Procedure for initiating the temperature program is given below in section C. Remove cover and allow cell to cool with both inlet and outlet valves closed.

Preparation of Sample for Measurement

1. Refer to Figures 2 and 8 for the locations of controls. Switch vacuum to sample funnel with stopcock A open and the by-pass valve closed. Allow several minutes for the lines to evacuate and then close stopcock A.

2. Fill upper chamber to mark with sample and open stopcock B to allow the sample to drip into the lower chamber. Close B when the upper chamber is emptied and continue degassing until bubbles no longer rise to surface. Relieve vacuum to the funnel and open stopcock A.

3. Adjust level of sample by opening the bypass valve until meniscus is even with one of the volume scale divisions.

4. Open inlet valve and admit 12 ml of sample into the cell. Close inlet valve.

Temperature Programming of Sample

1. Make heating rate settings with instrument in "stop" position. Indicator light next to stop button will be on. Timer setting should be such to provide the desired temperature interval at the chosen heating rate. For a heating rate of 5°/min and a terminal temperature of 400°C. (that is, 375° rise above room temperature), the timer setting would be 75 min.

2. Push "start" button to begin the temperature program. Lower recorder pen to recording position.

3. When run is terminated, remove cell cover and lift recorder pen.

Cleaning of Cell Following Completion of Measurement

1. When the sample has cooled to 200°C. or lower, discharge the sample by opening the outlet valve. Apply vacuum to the trap and open the inlet valve and also stopcock A to allow sample remaining in filling funnel to partially flush the cell. Evacuate the drained cell and close valves.

2. Put acetone in the sample funnel and open inlet valve to allow cell to fill with acetone.

3. Change to plant vacuum (or other aspirator type vacuum source), open outlet valve and flush cell with acetone finally allowing air to flow through the cell to remove excess acetone.

4. Change back to pump vacuum and evacuate cell. Close valves.

5. Repeat steps 2 - 4 as necessary to clean cell.

B. Discussion

Preparation of Instrument for Operation

After sufficient warm up the instrument should indicate close to room temperature and atmospheric pressure on the recorder. The pressure scale is corrected for the liquid sample head and when the cell is empty, the atmospheric pressure reading will be 14.4 psi. Under complete vacuum the pressure reading will be 0.5 psia when the ZERO CHECK button is depressed. These readings will indicate whether the instrument calibration has shifted appreciably and should always be made just prior to a run.

Failure to degas the inner surface of the cell before charging sample will result in degassing during the run which will increase the pressure in excess of the vapor pressure increase with temperature. The resultant pressure vs. temperature record will have an appearance similar to that from samples containing low-boilers or decomposable impurities or both. The chlorinated biphenyls when heated in excess of 400°C. produce a thin layer of carbonaceous matter on the cell surface which is only partially removed during the normal clean out. This carbonaceous material and the metal surface of the cell both could strongly adsorb low-boiling materials or air which would require stringent conditions for their removal. It appears that a temperature of 250°C. is sufficient to degas the cell, but to be on the safe side, heating to 400°C. under full vacuum is recommended as a standard procedure.

A good medium capacity vacuum pump should be used so that system pressures at least as low as 3 mm Hg can be achieved before the sample is introduced into the cell.

Occasionally the system should be tested for leakage. This may be done by measuring the pressure increase with time of the evacuated system following the degassing procedure. Leakage to the extent of 0.1 psi in one-half hour is permissible.

Preparation of Sample

Samples of chlorinated biphenyls usually contain dissolved gas which, if not removed, will add to the system pressure during a run. The effect will be the same as a poorly evacuated sample cell prior to the run. Evacuating the sample to several mm Hg at room temperature adequately degases Therminol FR-1 and FR-2 fluids. The degassing of more viscous fluids such as Therminol FR-3 is facilitated by warming the sample to 80-100°C. Heating of samples suspected of containing low-boilers should be avoided if the vapor pressure instrument is being used to detect the presence of low-boilers. Removal of the low-boilers by some heating during degassing however improves the ability to detect low levels of decomposable impurities such as the chlorine addition products with chlorinated biphenyls which decompose in the temperature range of 150-300°C.

Temperature Programming of Sample

Heating rates of 3° to 10°C./min may be used with little effect on the temperature-pressure record. Slower heating rates cause uneven programming of temperature and at rates higher than 10°C./min, temperature lag becomes significant. At heating rates less than 10°C./min, the instrument records quite close to the equilibrium vapor pressure of the sample vs. temperature.

Some difficulty has been experienced with slight changes or cycling in the instrument calibration during a run. Usually this is minor and does not appreciably change the P vs. T trace. Any shifts can usually be spotted and normally would not be confused with true pressure increases with temperature. These calibration shifts or cycles are due to inadequate thermostating of the logarithmic compressor units. The present thermostat has shifted about 1 degree from its original set point but currently appears to be maintaining fairly constant temperature with only slight cycling. If this problem worsens the thermostat should be replaced with a more reliable one.

A terminal temperature of 400°C. is recommended for runs with chlorinated biphenyl since the data beyond this temperature are not useful for screening purposes and the avoidance of the high temperature decomposition facilitates the cleaning of the cell.

Cleaning of Cell

Upon heating chlorinated biphenyl samples above 400°C., a carbonaceous deposit is formed on the cell surface. This thin film is loosened and partially flakes off during clean-out using fresh Aroclor, benzene, acetone, etc. as solvent. Acetone appears to

be the most satisfactory solvent, having fair solubility for chlorinated biphenyls and is easily removed from the system following the clean-out procedure. Successive evacuations, fillings, and dischargings of solvent are necessary to clean the strain gage and relief valve cavities. Three to four washings are adequate to clean the system.

C. Vapor Pressure of Therminol Fluids

Typical instrument records of the vapor pressure of the Therminols follow in Figures 17-22.

Included are curves which show the effect of failure to degas the cell prior to a run, the effect of unstable material, the effect of low-boiler contamination and the relative vapor pressures of the different Therminol fluids.

Section 4. Maintenance

A. Introduction

Maintenance procedures required for the Vapor Pressure and Thermal Stability Apparatus consist of:

1. Routine replacements of electronic tubes and batteries, and lubrication of mechanical parts;

2. Miscellaneous repairs or replacements not required on a routine basis;

3. Checking and adjusting instrument calibration, and adjusting operating controls to provide accurate recording of vapor pressure curves; and

4. Locating sources of trouble when an instrument failure occurs. These four types of maintenance procedures are described in the sections following.

B. Routine Maintenance

Routine, or preventive maintenance procedures for the instrument are quite simple. They comprise lubrication of moving parts in the recorder, and periodic replacement of tubes and batteries in the electronic circuits.

The recorder should be lubricated with a light instrument-grade oil, at 6-month intervals. Points to be lubricated are on the underside of the recorder chassis (Figure 22). One drop of oil should be applied at each point:

Motor intermediate gear shaft (2)
Motor output gear shaft (2)
Pen drive cable pulleys (8)

The timer presumably requires no lubrication, as the manufacturer of the unit supplies no instructions for this. Similarly, the furnace blower motor is sealed and is not intended to require routine lubrication.

All batteries should be replaced every 6 months, or every 1500 operating hours if this occurs sooner. The set of batteries includes 5-RM42R and 12-RM3R mercury cells. Positions of the batteries are shown in Figure 23, the batteries being held in clips on a sub-panel on the back of the console panel. The RM42R batteries are mounted individually; the RM3R batteries are held in groups of 6 in fiber sleeves. Recalibration as described in section 4D is required after replacement of batteries. The instrument should be run for 15 hours or longer after battery replacement, to stabilize the new batteries, before it is calibrated.

If a tube tester is available, the tubes should be tested at 6 month or 1500 hour intervals and any defective or doubtful tubes replaced. If a tester is not available, all tubes should be replaced at 12 month or 3000 hour intervals. Replacement of the 4 type 12AX7/ECC83 tubes in the Philbrick amplifiers with either this double-branded type or with type 5751 is recommended, instead of replacement with standard type 12AX7 tubes which may be excessively noisy for this application. Calibration of the temperature or pressure scales of the instrument should be checked after replacement of any tubes in the corresponding amplifiers, and adjustment of the TEMPERATURE SET control should be checked after replacement of any tubes in the temperature control circuit. Normally, however, tube replacements are expected to have negligible effects on calibration. Tube replacements in the recorder amplifiers may make it necessary to adjust the recorder gain controls for best recorder response.

C. Repairs and replacements

This section includes instructions for removal, repair or adjustment, and installation of various components of the instrument which are not expected to require attention routinely.

1. Recorder

If any extensive work is required on the recorder mechanism, it is convenient of obtain access to this part of the instrument by unsoldering the leads to the recorder balancing potentiometers (see Figure 22), removing the four screws at the corners of the top panel, and tilting the panel backward. Mounting of the motors and potentiometers is obvious. Replacement or adjustment of the pen drive cables is done as described below:

Each axis requires 11 feet of drive cable, which is General Cement type 88-100. Figure 24 shows the arrangement of the drive cord for the vertical drive, with the vertical pen drive bar in its uppermost position. The same illustration applies to the

horizontal drive when the horizontal pen drive bar is in its extreme left position, the drawing being turned 90° counterclockwise. Tie the drive cord to screw 1 and make 4 turns in a clockwise direction. Loop the cord counterclockwise around pulley 2; thence under motor pulley 3, which should be turned fully clockwise. Make 2 turns around 3, on the second turn looping through the slot and around the lug on the side of the pulley. Continue to potentiometer pulley 4, which should be about one-fourth turn clockwise. Make 3 turns clockwise around 4, then complete a fourth turn with a loop through the hole in the pulley and out to the stud on the side. Bring the cord on around 4, then clockwise around pulley 5 to stud 6. Make 4 turns clockwise around 6, pass the cord through the eye of the stud and then make 4 more turns counterclockwise. Loop the cord around pulley 7, then draw it across to pulley 8 so that it passes under the cord already in place. Loop around pulley 8 and thence back to the starting point at lug 1, at which point make 4 turns in a clockwise direction and tie the cord.

To adjust the cable tension, loosen the locknut on screw 6 and turn this screw until the cable near the center of the platen deflects 1/4 or 3/8 inch on slight pressure. To adjust the pen drive bar so that the pen moves parallel to the chart lines, rotate screw 1.

Proper operation of the recorder potentiometer circuits requires that the balancing potentiometers have the correct relation to the scale readings on the two axes. To check or adjust this condition, disconnect the recorder amplifier input plugs from the amplifiers and remove batteries B6 and B7 from their clips; then connect an ohmmeter to the CCW and S terminals of the horizontal balancing potentiometer (at the left side, when the recorder is viewed from the front). The resistance measured should be 450 ohms when the pen is at the left edge (20°C. mark) of the chart. If the resistance is not correct, adjust it by loosening the cable pulley set screw, slipping the pulley from the potentiometer shaft, and turning the shaft to give the correct resistance. For the vertical recorder axis, similarly, the resistance between CW and S terminals of the potentiometer should be 1100 ohms when the pen is at the bottom edge (0.5 psia mark) of the chart.

The recorder amplifiers are isolated from the cabinet by being mounted with insulating washers under the screw heads, and with rubber covers on the chassis edges. Care should be taken not to lose these parts if the amplifiers are removed for any reason. Mounting arrangement of the recorder amplifiers is shown in Figure 25.

2. Timer

The timer and attached timer potentiometer are shown in Figure 26. Removal or adjustment of the timer potentiometer can be done without disturbing the timer. To remove the setting knob, loosen the clamp screw (at left center in Figure 26) and slide the

knob off of the potentiometer body. To remove the potentiometer, loosen the set screw of the potentiometer bushing and slip the potentiometer assembly off the timer. The potentiometer is coupled to the timer by a tongue protruding into a slot in the screw which holds the timer pointer to its shaft. When replacing the potentiometer on the timer, line up the tongue and groove approximately and then work the two parts into contact by simultaneous rotation and forward motion. Pull the potentiometer backward slightly from the position of greatest insertion before tightening the set screw, to reduce friction at the potentiometer and timer shafts. For the method of adjusting the timer potentiometer electrically after it has been moved, see section 4D. The friction bushing in the face of the timer, on which the potentiometer is mounted, should be tightened enough to avoid chance movement but not so much as to prevent setting of the timer.

Access to the mechanism of the timer requires removing it from the panel. To do so, remove the potentiometer and then remove the four screws at the corners of the timer. Disconnect the wiring at the terminals on the rear of the timer, and slip the timer out forward through the panel hole. Removal of two screws through the back of the flange then permits the dial cover to come off. Remove the pointer screw, and the pointer and dial; remove four screws which were covered by the dial, and the flange will separate from the timer body to permit the cylindrical body cover to be removed. To replace the dial cover, turn the time-setting pointer to a position in which it is aligned with the remaining-time indicating pointer, and manipulate the dial cover until the pointers engage and the cover is seated on the timer flange.

Removal of the timer motor does not require removal of the timer from the panel. It is only necessary to disconnect the motor leads and to remove the two screws which hold the motor to the timer body.

3. Furnace

The cell, heater, thermocouple and blower motor are mounted on a split block under the center of the furnace base. The cell inlet and outlet tubes are clamped between the halves of the block; heater and thermocouple are held in holes through it by socket set screws; and the blower motor is supported below it on a U-shaped bracket. The limit thermostat is supported from the furnace base shell. The pressure transducer is supported by an angle bracket, and the relief valve is held in place by its outlet tube. Figure 7 shows the arrangement of components beneath the furnace base.

For removal of the heater or thermocouple, an Allen wrench long enough to extend through the slot at the back of the furnace base is useful. Removal of the connecting wires and terminal nuts from the heater permits it to be withdrawn vertically when the set-screws are loosened. The thermocouple is removable downward, after partial straightening of the bends in the furnace portion. If a

defective thermocouple is to be replaced, it can of course merely be cut off at a convenient point.

The blower motor may be removed by loosening the setscrew of the blower coupling, and removing the four screws which hold the motor mount to the split block.

The cell holding block is separable when the motor is removed, by loosening the two screws which hold the block together and the four screws which hold it to the furnace base plate. Removal of the intact cell was not contemplated in the design; it is necessary to cut the cell inlet and outlet tubes, conveniently just above the furnace shell base. To install a new cell, cut the inlet and outlet tubes to the required length as determined by trying the cell in place. Then the required right-angle bends below the furnace base can be made and the fittings installed before the cell holding block is put in place.

The pressure transducer is removable by disconnecting the tubes attached to it, removing the electrical connector and sliding the transducer out of the support bracket.

D. Adjustment and calibration

The temperature recording, temperature control and pressure recording sections of the instrument require adjustments to maintain satisfactory operation and accurate calibration. Location of the controls is shown in Figure 28.

1. Calibration of temperature recording system

To calibrate the temperature recording system it is necessary to have a potentiometer capable of supplying voltages which simulate the output of an iron-constantan thermocouple at temperatures from 20° to 500°C. Disconnect the leads from the furnace thermocouple at the terminal block on the back of the console, Figure 26, and connect the potentiometer to the terminal block with thermocouple wire. Measure the temperature at the potentiometer terminals, and set the reference-junction compensation of the potentiometer to the corresponding voltage. (This step is of course to be omitted if the potentiometer has automatic reference-junction compensation.)

Calibration of the temperature axis requires the setting of three adjustments: the THERMOCOUPLE OFFSET, HORIZONTAL ZERO and HORIZONTAL SPAN controls. The temperature scale is adjusted to register at three temperatures: 50°, 200° and 400°C. First set the potentiometer to 400°C. (21.85 mv), and adjust the HORIZONTAL SPAN control until the recorder reads this temperature. Change the potentiometer setting to 200°C. (10.78 mv), and adjust the HORIZONTAL ZERO control for this temperature. Repeat these adjustments in sequence until the scale is aligned at the two temperatures. Then set the potentiometer for 50°C., and adjust the

THERMOCOUPLE OFFSET control to produce agreement at this temperature. Finally repeat all three adjustments in sequence until the scale is in agreement at all three temperatures.

If the potentiometer is of the type which has both a step switch and a continuous slidewire, it is convenient to use the three voltages of 2.58, 12.58 and 22.58 mv. These correspond to 50°, 233° and 413°C., and the adjustments are made for these temperatures. Switching between the three points requires only the changing of the step dial of the potentiometer.

2. Adjustment of the temperature control system

The temperature control system must be adjusted to produce a temperature program of the correct rate of rise, beginning at room temperature. Mechanical alignment of the TIMER potentiometer and the RATE OF RISE dial, and electrical adjustment of the TEMPERATURE SET control are required. A volt-ohmmeter of the usual type is needed for making the adjustments.

Connect the meter, set for 100 volts range, to the top two terminals on the left side of the temperature control component board (lower left in Figure 23), the uppermost terminal being negative. With the cell at room temperature and the timer not running (it may be set for any time interval), loosen the TIMER potentiometer bushing setscrew and rotate the potentiometer. At one position the voltage will jump abruptly from near zero to about 100 volts. Turn the potentiometer counterclockwise a small amount from this position, so that a voltage of a few volts appears. Then turn the potentiometer clockwise until the voltage just stops decreasing (it will remain constant at a value which may be a few tenths of a volt either positive or negative). Tighten the setscrew in this position. Note the precaution in section 4C of allowing a small axial clearance between the tongue of the potentiometer shaft and the slot of the timer pointer screw.

Note the action of the heater relay while adjusting the TEMPERATURE SET control, with the RATE OF RISE control at approximately mid-range. Adjust the TEMPERATURE SET control until the relay plunger is just pulled down. Because of the delay of response of this circuit, it will be necessary to make the adjustment slowly, during an interval of about a minute.

Turn off the power to the instrument and connect the meter, as an ohmmeter on a 1-megohm range, between the center tap of the RATE OF RISE control and the two end terminals alternately. Rotate the knob of this control until the resistance readings for the two halves of the control are the same. Then loosen the knob, and reset it to the position representing 4.6° per minute rise.

3. Calibration of pressure recording system

The principle of calibration of the pressure recording system is the same as that for the temperature system: adjustment

so that the scale readings are correct at three points on the scale. The method of operation, however, is different because instead of applying standard voltages in place of the thermocouple output, standard pressures now must be applied to the pressure transducer. A source of gas pressure, such as a cylinder of nitrogen with a high-pressure regulator, and pressure gauges covering the range of 0.5 to 300 psia are required. A combination of gauges, such as a test gauge of 300 psia range with a manometer reading absolute pressure up to 1 atmosphere, is sufficient. These gauges should be connected through shut-off valves to a rudimentary manifold system attached to the cylinder pressure regulator (through a valve) and to the sample inlet fitting of the furnace unit. The vacuum pump normally used with the unit remains connected to the outlet fitting. Thus any pressure in the range of 0-300 psia may be applied to the pressure transducer in the furnace unit, and simultaneously measured by the reference gauges.

Before the pressure calibration is begun, the voltage applied to the pressure transducer should be checked. Connect a voltmeter of 25 volt range to the counterclockwise terminals of the ZERO ADJUST and ZERO CHECK ADJUST controls (the ZERO CHECK ADJUST control terminal being positive). If the voltage is not 25±0.5 volts, adjust to this value with the pressure transducer voltage adjustment on the power supply (Figure 23, upper right).

The calibration adjustments are made at 1.0 psia, atmospheric pressure, and 200 psia. However, the calibration is done with the cell empty, while in use the cell is half-filled with liquid and the pressure transducer therefore supports not only the gas pressure but in addition the pressure of the column of liquid between the transducer and the cell. The liquid column adds approximately 0.3 psi to the gas pressure in the cell, and the calibration pressures must therefore be increased by this amount -- that is, an actual pressure of 1.3 psia is used to calibrate at the 1.0 psia mark of the scale, and so on. This correction may be neglected at the higher pressures, 50 psia and above.

Apply 200 psia to the transducer and set the VERTICAL SPAN control for correct reading at this pressure. Release the pressure to atmospheric, and adjust the VERTICAL ZERO control until the scale reading is 0.3 psi less than atmospheric pressure. Repeat these two adjustments in sequence until both are correct. Then evacuate the cell to 1.3 psia (67.2 mm Hg) and adjust the ZERO ADJUST control for correct indication of 1.0 psia here. Finally repeat the entire sequence of adjustments to secure adequate alignment of the scale at all three pressures.

As the last step of adjusting the pressure recording system, the operation of the ZERO CHECK button must be set. Evacuate the cell, hold the ZERO CHECK button depressed and rotate the ZERO CHECK ADJUST control to give a reading of 0.5 psia on the chart.

4. Adjustment of recorder amplifier gain controls

The gain controls of the recorder amplifiers must be adjusted for best response as tubes age or after a change of tubes. Turn the gain controls (Figure 25) fully clockwise. If oscillation of the recorder pen occurs, turn the controls counterclockwise until the oscillation stops. Test the recorder response by moving the pen bars manually a short distance and releasing them; they should return to the balance position with a slight "bounce." If the action appears sluggish, increase the gain control setting; if there is a tendency to oscillation, decrease the setting.

The combination of narrower voltage span of the temperature axis of the recorder, and higher hum level in the temperature amplifier output, normally makes this axis of the recorder stable at full gain setting. If no oscillation occurs when the horizontal recorder amplifier gain is at its maximum setting, the control may be left in this position.

5. Adjustment of logarithmic compressor thermostat

The temperature of the box housing the logarithmic compressor units for both temperature and pressure axes is controlled by a thermostat mounted on the side of the inner compartment. Access to the thermostat is obtained by removing the outer box cover, which is the left side of the box as seen in the photograph (Figure 23, center). The thermostat adjusting screw is sealed with "Glyptal" cement. To loosen the cement, keep it wetted with acetone for a few minutes. It is not anticipated that adjustment will be required, but if the temperature in the inner box (measured by a thermocouple introduced in the interstices of the wire bundle entering the box) is not within the range of 36°-40°C. the thermostat should be readjusted to provide a temperature in this range. Change of temperature of the logarithmic compressors produces a change of calibration, which can be corrected by adjusting the HORIZONTAL ZERO and VERTICAL ZERO controls only, without change of the span, offset and transducer zero.

E. Trouble-shooting

Trouble-shooting of the vapor pressure apparatus depends upon first locating the section of the instrument in which a failure has occurred, and then locating and correcting the defect. Symptoms of trouble may be incorrect temperature or pressure readings at atmospheric pressure and room temperature; incorrect progression of temperature when programming; irregular (noisy) motion of the recorder pen; or failure of the pen to move along one or both axes.

It is helpful to remember that the temperature and pressure systems of the vapor pressure apparatus are independent except for receiving power from a common source, and having the

logarithmic compressors of the two systems in the same thermostat. Occurrence of the same malfunction in both systems therefore indicates a failure at one of the two common points. Conversely, a malfunction in one system alone eliminates the common units from consideration as points of failure. The first step in trouble-shooting, therefore, is to follow Chart I below. The appropriate chart of the other four may then be applied to location of the defect.

Trouble shooting chart I: preliminary

Indication	Proceed to chart
The same defect is shown on both temperature and pressure axes of the recorder	II
Defective operation is shown only on the temperature axis	III
Defective operation is shown only on the pressure axis	IV
No defect of recording either temperature or pressure is shown, but the furnace temperature is not being programmed correctly	V

Trouble-shooting chart II: Failures affecting both recorder axes

Indication	Probable cause of trouble	Verifying test
Recorder dead: pen may be positioned manually at any point on chart	No a-c power to recorder amplifiers	Check for lighted tubes
Recorder operating, but not giving correct readings		
a) Pen stays at lower left corner of chart	No a-c power to temperature and pressure amplifiers	Check for lighted tubes; check output voltage of Sola transformer
b) Low readings on both axes	High temperature in log compressor thermostat	Check thermostat temp.
c) Pen stays at upper right corner of chart	Defect of LOAD-OPERATE switch;knob not properly set on shaft	Check switch and try knob for correct position
d) High readings on both axes	Low temperature in log compressor thermostat	Check thermostat temp.
Noise in both temperature and pressure readings	Excessive a-c line noise; loose connection in line cord or internally in power circuit	Check line voltage; check wiring

Trouble-shooting chart III: Failures affecting the recorder temperature axis only

Indication	Probable cause of trouble	Verifying test
Dead: pen can be moved manually to any temperature reading	Inoperative horizontal-axis recorder amplifier (bad tubes; shorted capacitor across output; loose plugs)	Interchange with vertical amplifier by interchanging plugs
Noise in temperature indication	Defective tubes in temperature amplifier	Interchange tubes with pressure amplifier
Low reading at room temperature	Defective battery B1	Measure voltage: 1.35 volts normal
	Defective battery B3	Measure voltage: 8.1 volts normal
	Defect in temperature amplifier	Measure output voltage (between blue and black jacks, blue+): 8.2 volts normal at room temperature
Correct reading at room temperature, low reading at high temperature	Defective thermocouple	Measure thermocouple output at terminals on back panel, compare with auxiliary couple inserted in furnace
High reading at room temperature	Defective battery B2	Measure voltage: 1.35 volts normal
	Defective battery B6	Same
	Defect in temperature amplifier	Measure output voltage as above: 8.2 volts normal at room temp.

Trouble-shooting chart IV: Failures affecting the recorder pressure axis only

Indication	Probable cause of trouble	Verifying test
Dead: pen can be moved manually to any pressure reading	Inoperative recorder vertical-axis amplifier (bad tubes; shorted capacitor across output; loose plugs)	Interchange with horizontal amplifier by interchanging plugs
Noise in pressure indication	Defective tubes in pressure amplifier	Interchange tubes with temperature amplifier
Pen stays below lower chart margin at all pressures; or reads low at all pressures	No, or low, output voltage from transducer power supply	Measure power supply voltage: 25 volts normal
Low reading at atmospheric pressure	Defective battery B5	Measure voltage: 8.1 volts normal
	Defect in pressure amplifier	Measure output voltage (between blue and black jacks, blue+): 4.6 volts at atm. pressure, -0.1 volt evacuated
High reading at atmospheric pressure	Defective battery B4	Measure voltage: 1.35 volts normal
	Defective battery B7	Same
	Defect in pressure amplifier	Measure output voltage as above

Trouble-shooting chart V: Failures affecting the temperature program only

Indication	Probable cause of trouble	Verifying test
Program does not start	Recorder switch on LOAD position	Check switch position
	Defective recorder limit switch, or open circuit in limit control system; defective STOP switch	Check for presence of line voltage between timer terminals L1 and 5 when START switch is pressed
	Defective timer contact	Check for line voltage between L1 and 1 when START button is pressed
Heater does not go on	Timer motor not running	Observe motor
	Defective 2D21 tube	Change tube
Heater stays on continuously	Defective 12AX7 tube	Change tube
Rate of temperature rise not correct	Incorrect power supply voltage	Measure voltage across each OB2 tube: 105 volts normal
Program does not stop automatically	Timer motor not running	Observe motor
	Timer contact not opening at end of cycle	Check for absence of line voltage between L1 and 1 of timer when end of cycle is reached

F. Parts List

1. Sample system and furnace

a.	Valves	Whitey OVS2-A (2) Whitey OVS2 (1)
b.	Relief valve	Circle Seal 5120T-2MP-600
c.	Pressure transducer	Statham PA401TC-300-1700
d.	Heater	Electro-Therm 10-1452-26
e.	Blower motor	Bodine B8194E
f.	Limit thermostat	Fenwal 16050-0
g.	Thermocouple	ThermoElectric 5A2120F, 12" immersion, 60" leads

2. Recorder console

a.	Transformers	Sola 20-13-060 Triad R-4A (2) Triad R-73B
b.	Amplifiers	Philbrick UPA-2 (2)
c.	Log compressors	Kane C-7A (2)
d.	Power supply	Elcor AT25-75
e.	Relays	Ebert EM-1 Potter & Brumfield BS23D
f.	Choppers	Oak 660 (2) (equivalent: Airpax 172) James Electronics C1800 (2)
g.	Potentiometer (timer)	Helipot G, 10k, std. tol.
h.	Potentiometers (recorder)	Helipot C, 5k, std. tol. (2)
i.	Limit switches	Acro 1MD1-1A-A18M (2)
j.	Recorder chassis	Houston HR92-1
k.	Recorder motors	Barber-Colman EYAZ4456 (2)
l.	Temperature-compensating resistor	Texas Instruments TM-1/4 Sensitor, 500 ohm
m.	Log compressor thermostat	Fenwal 32400-0
m.	Recorder pen	Wrico No. 7
n.	Tubes	Standard makes 5-12AX7 4-12AX7/ECC83 or 5751 2-6X4 2-6U8 2-6S4 2-0B2 1-2D21
p.	Batteries	Mallory or equivalent 5-RM42R 12-RM3R
q.	Fuses	Buss AGC-10 amp. (2) Buss AGX-0.25 amp.

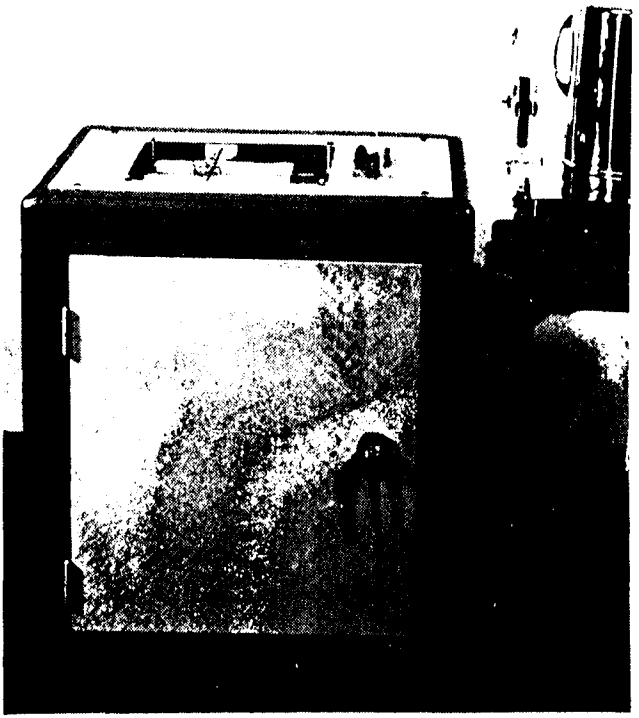


Figure 1. Console

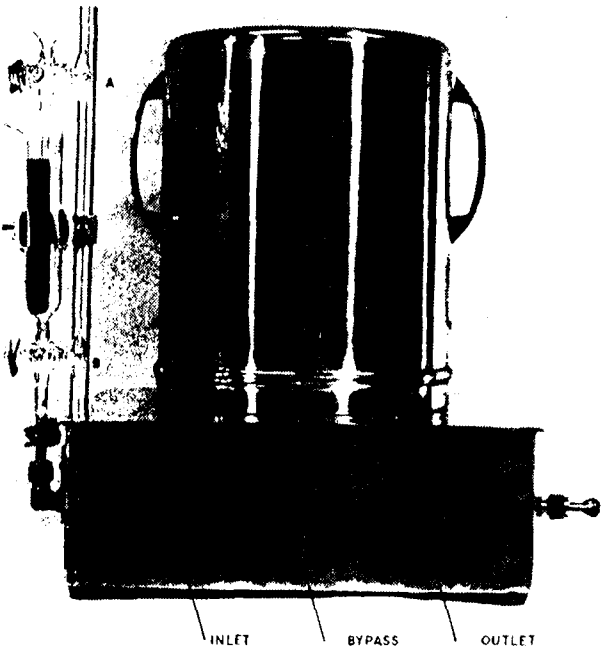


Figure 2. Furnace

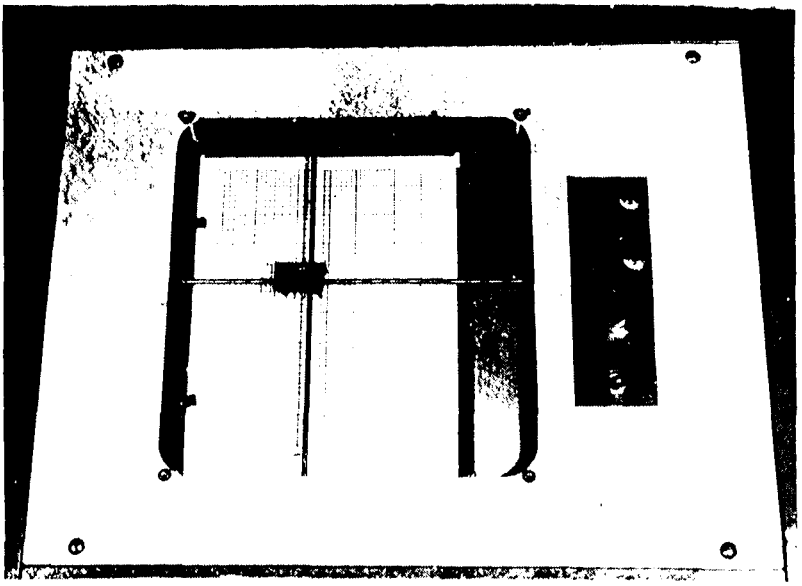


Figure 3. Operating controls

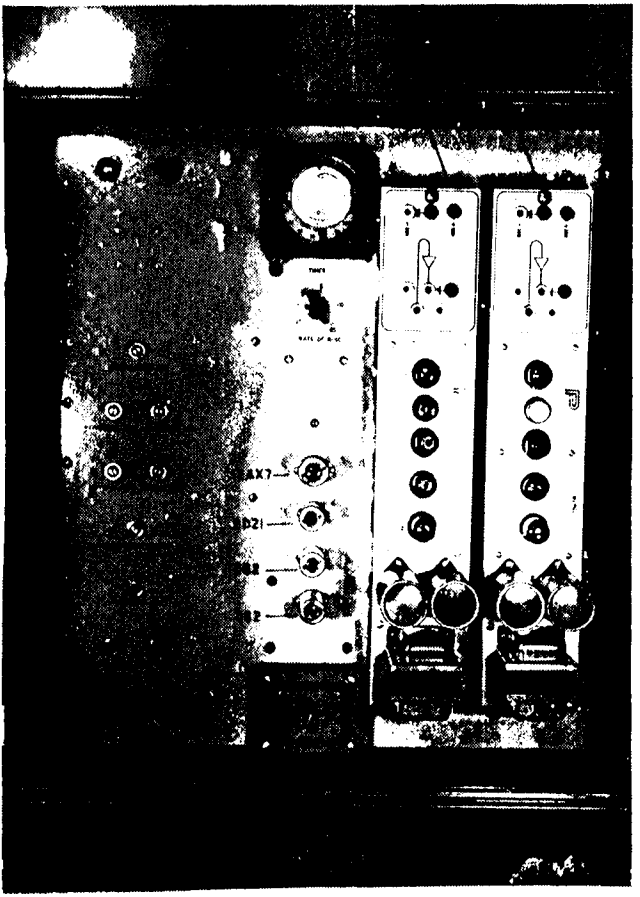


Figure 4. Panel (front)

0692779

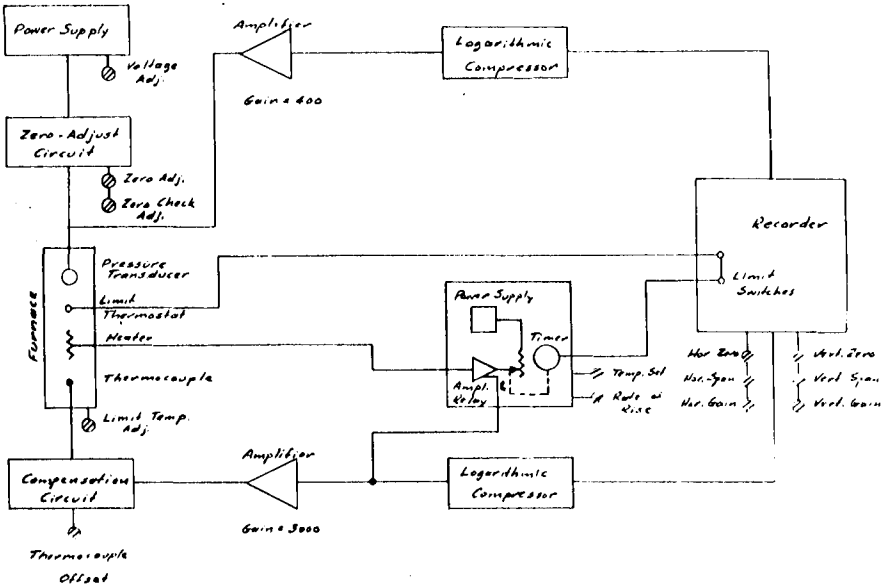


Figure 5. Block Diagram

0692780

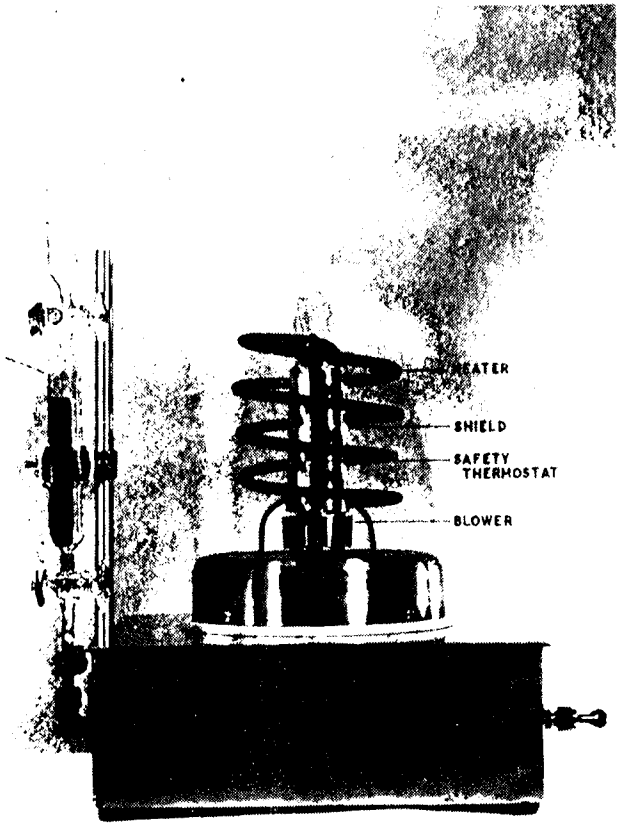


Figure 6. Furnace (cover removed)

0692781

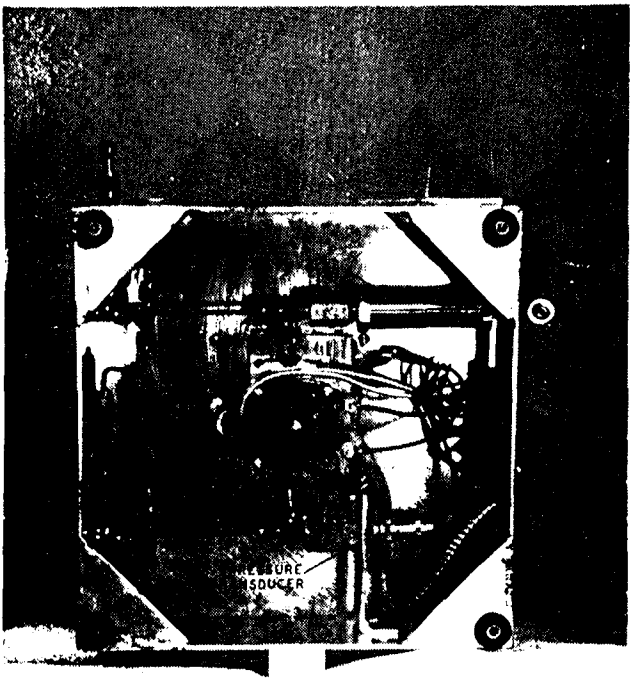


Figure 7. Pressure base

0692782

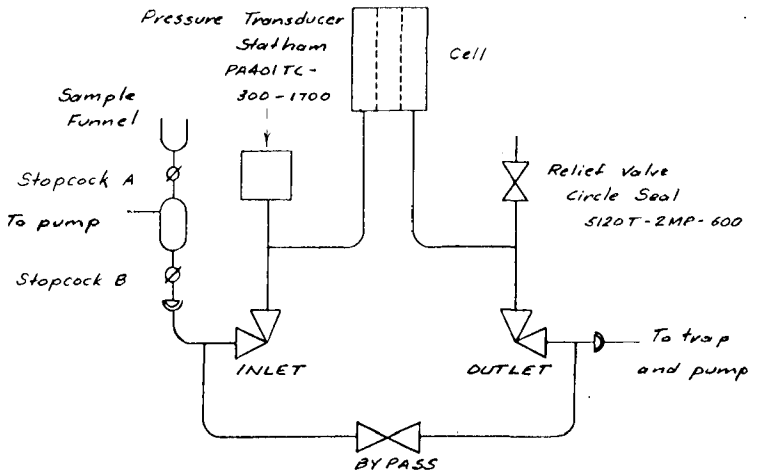


Figure 8. Sample System

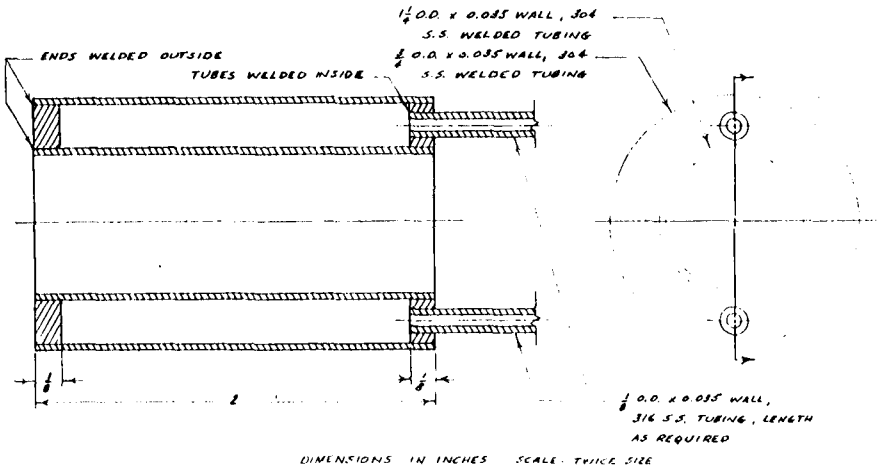


Figure 9. Sample Cell

0692784

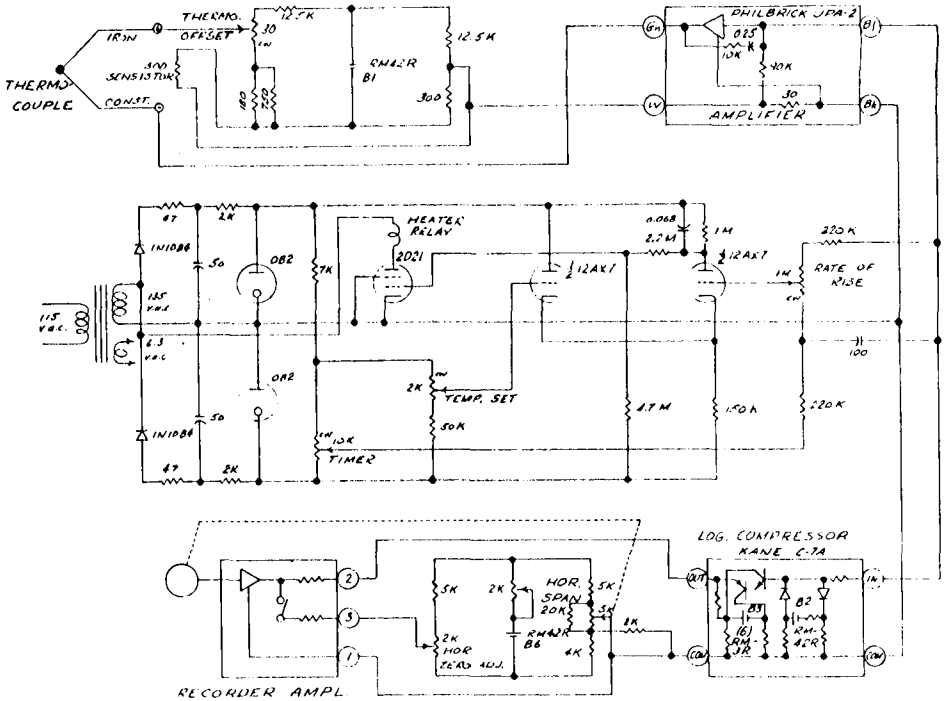
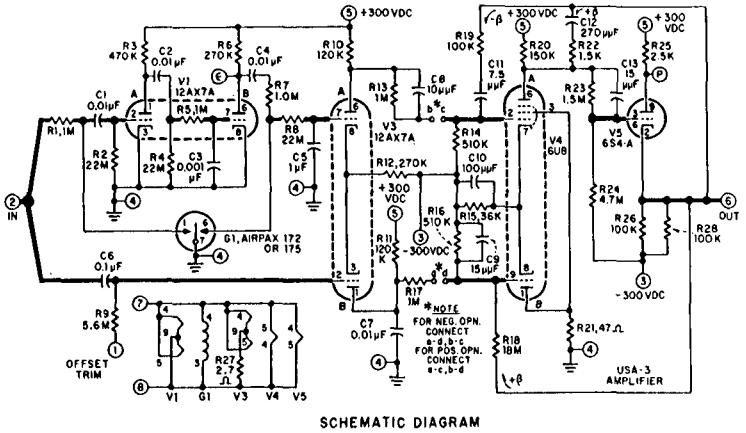


Fig. 10. Elementary Circuit Diagram (Temperature Recording and Control Section)

0692785



SCHEMATIC DIAGRAM

Figure 11. Philbrick Amplifier Component Boards

0692786

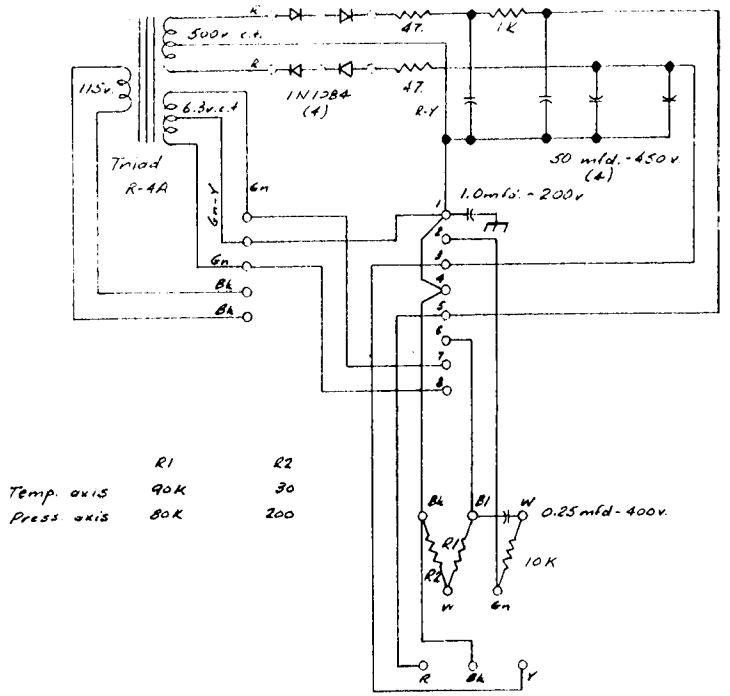


Figure 12. Philbrick Amplifier Chassis Wiring

0692787

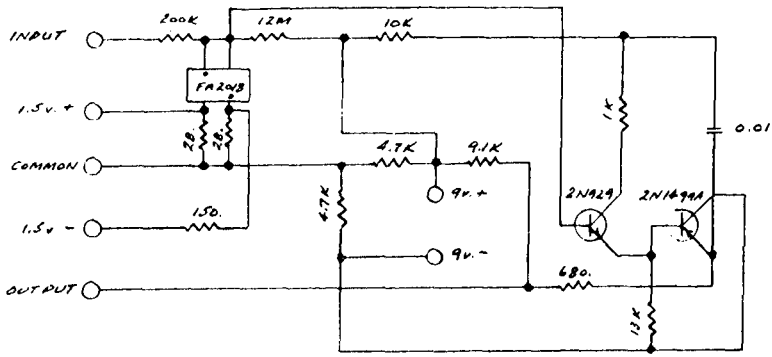


Fig. 13a. Logarithmic Compressor Schematic Diagram

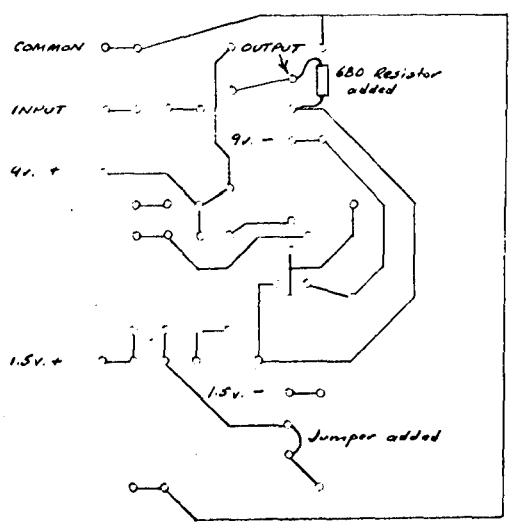


Fig. 13b. Logarithmic Compressor Circuit Board

0692788

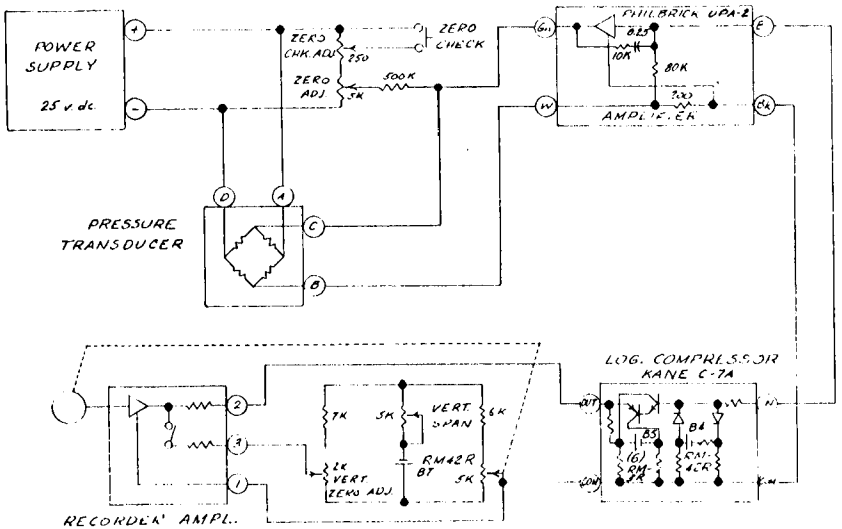


Figure 14. Elementary Circuit Diagram (Pressure Recording Section)

0692789

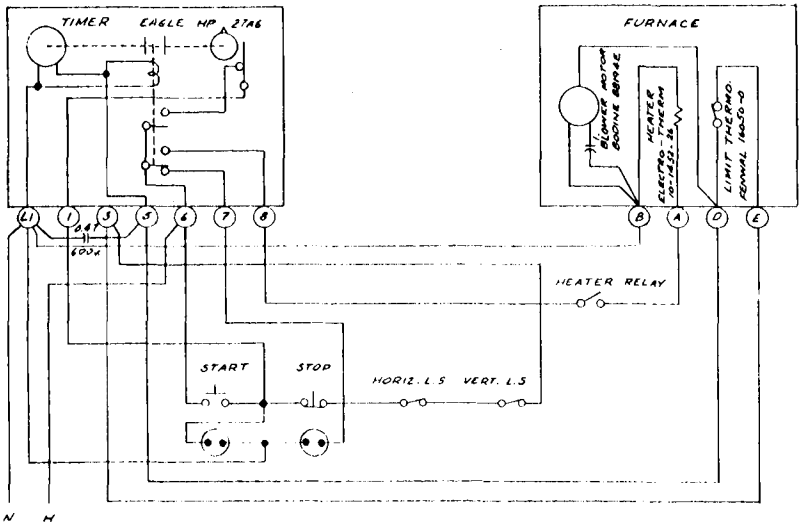


Figure 15. Elementary Circuit Diagram (Programming Section)

0692790

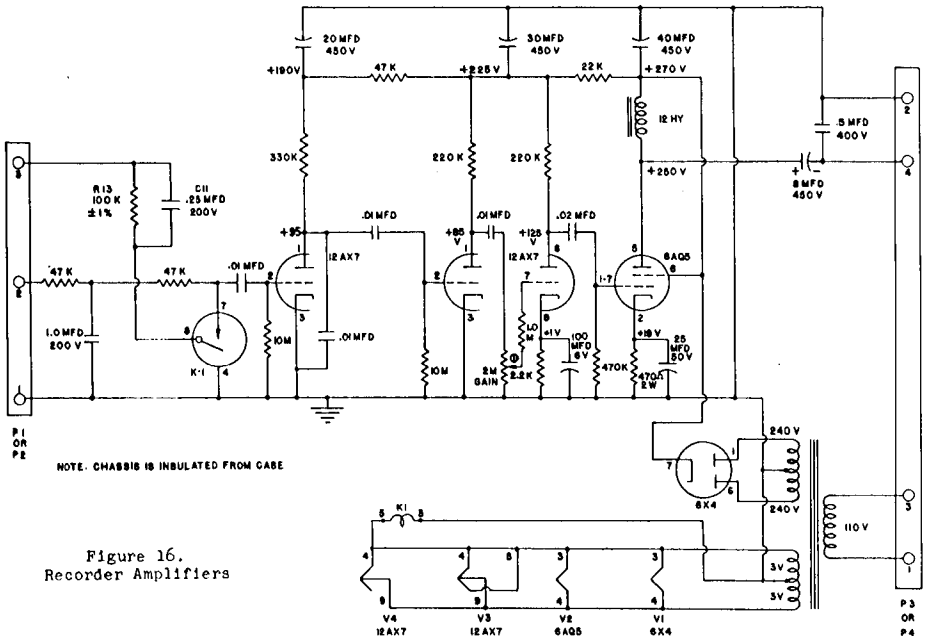


Figure 16.
Recorder Amplifiers

0692791

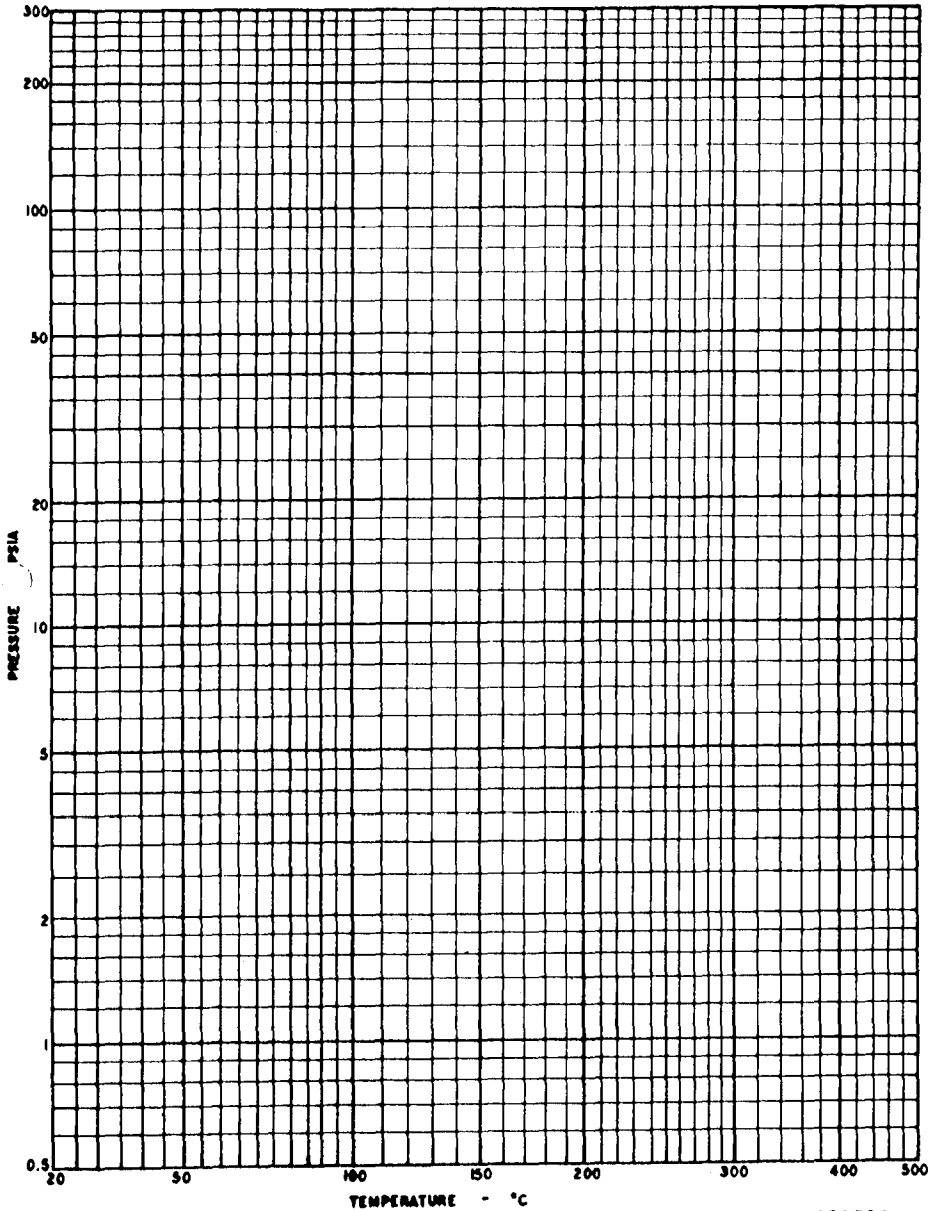
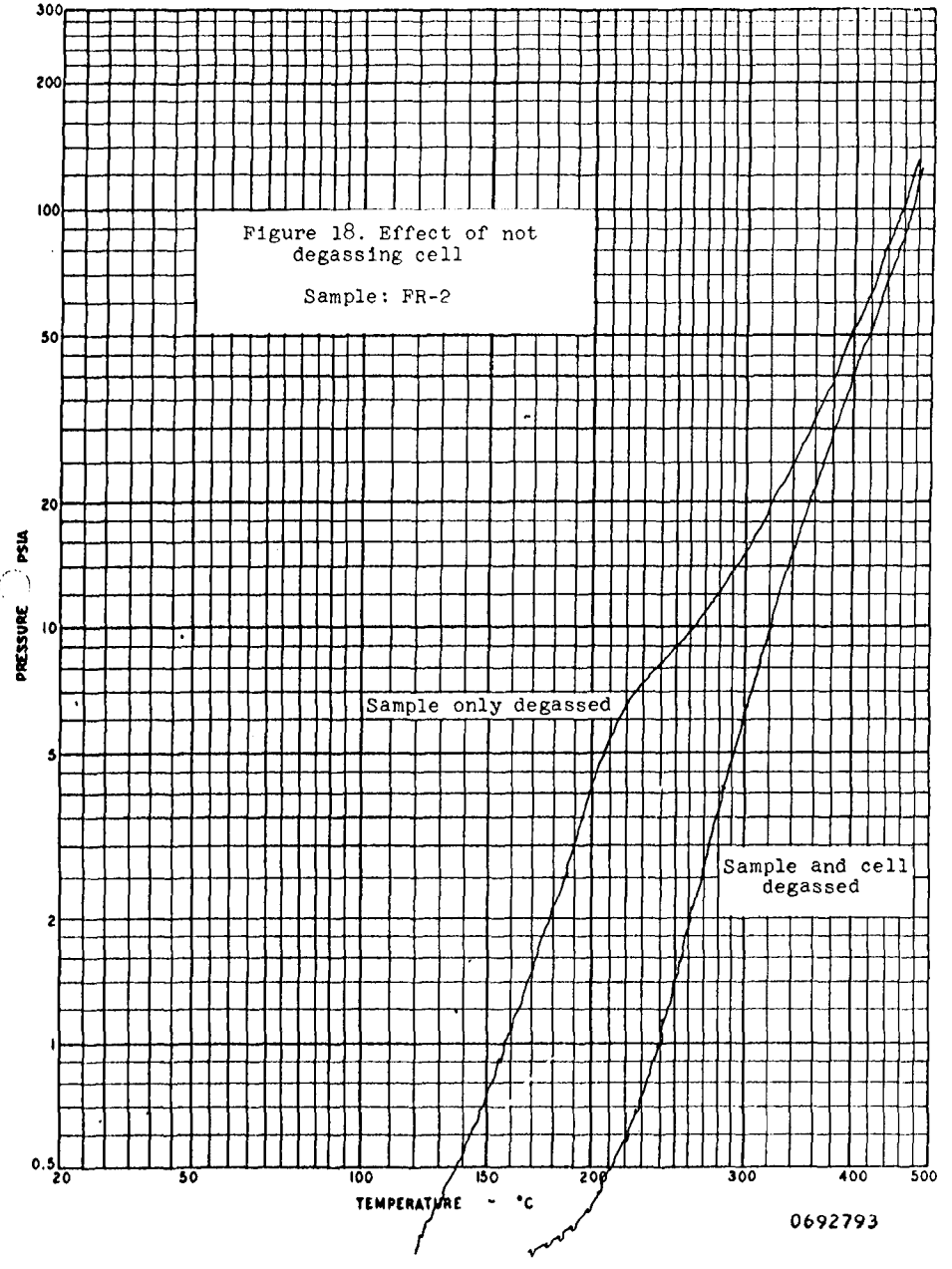


Figure 17. Recorder Chart



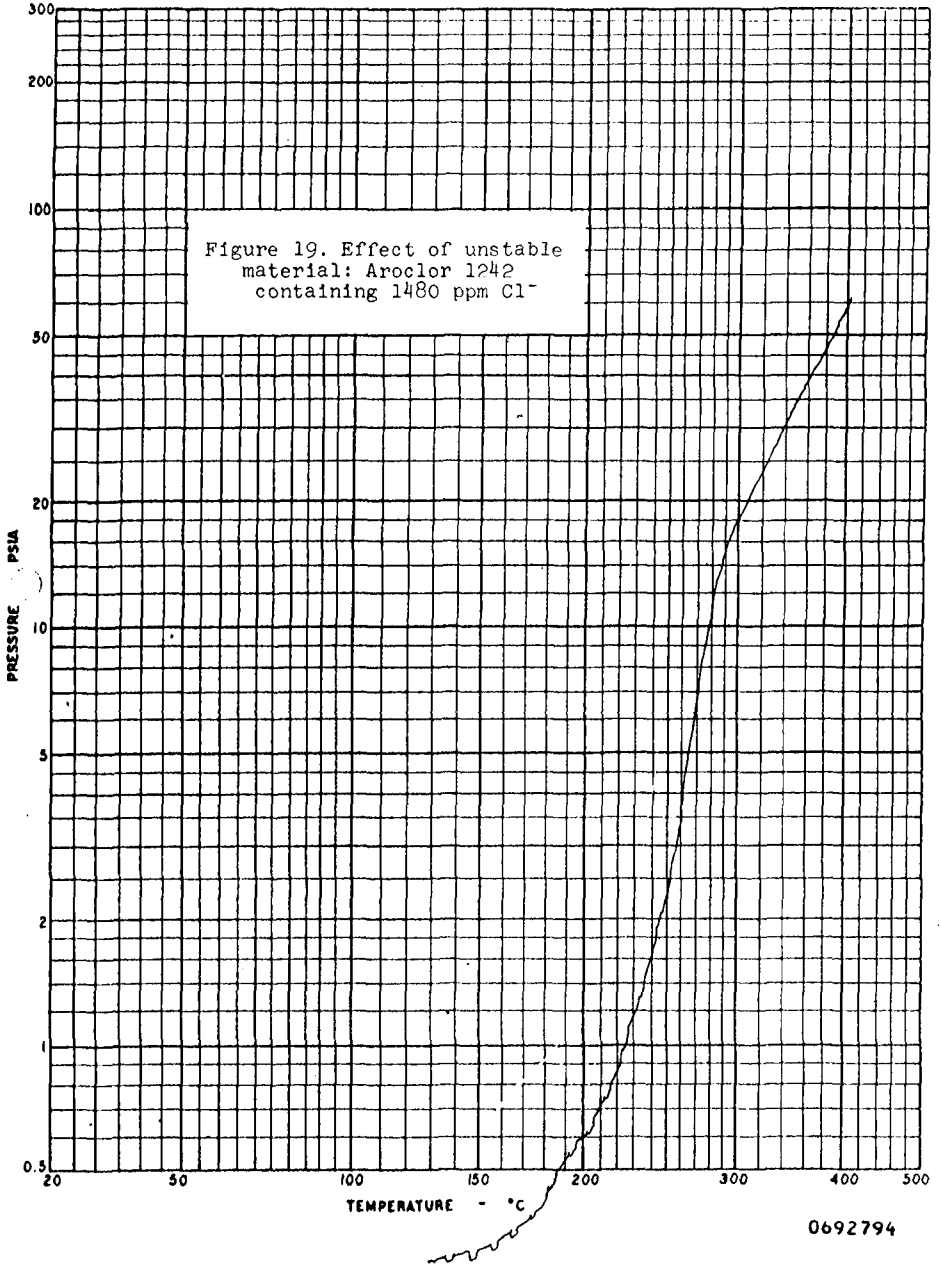
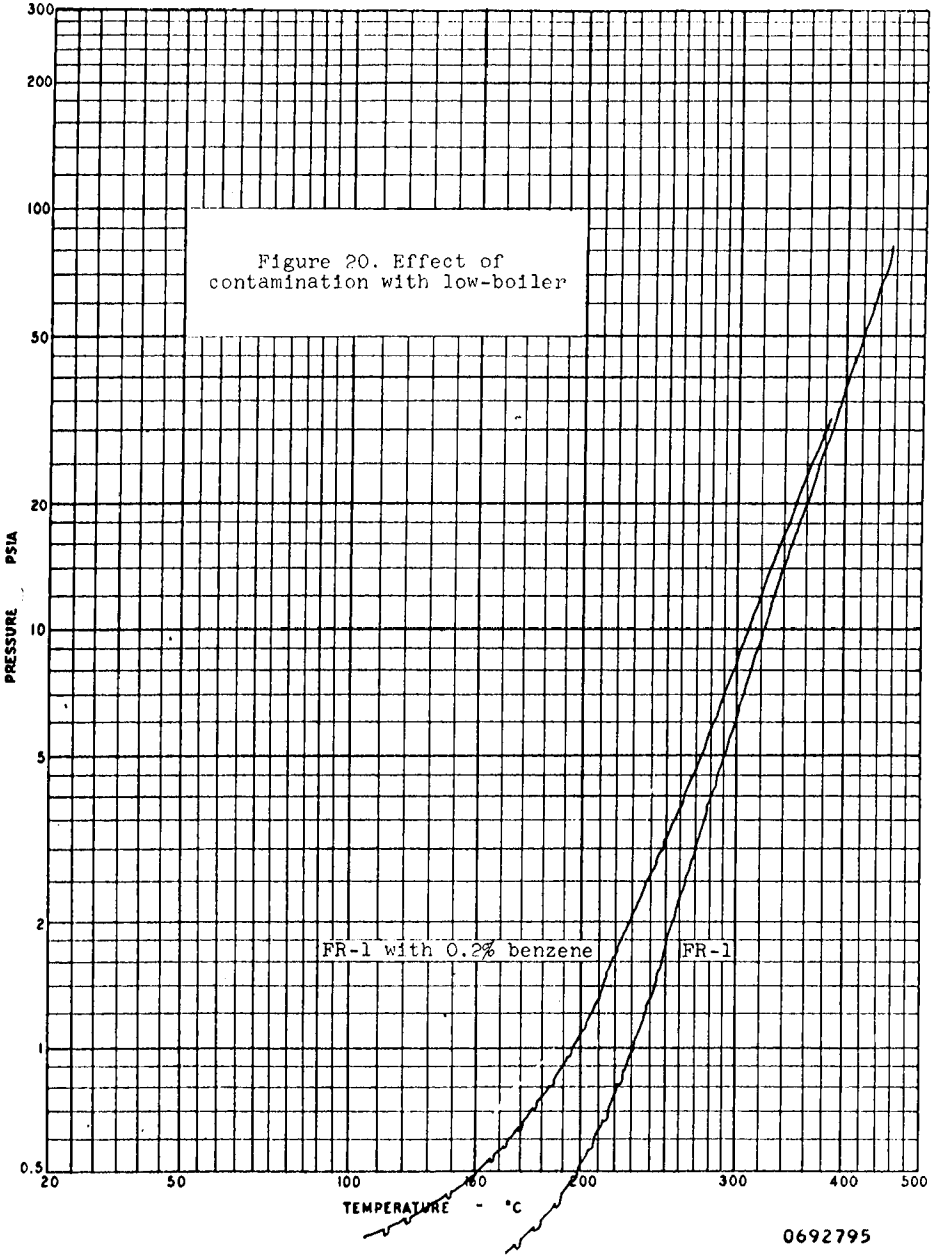


Figure 19. Effect of unstable material: Aroclor 1242 containing 1480 ppm Cl^-



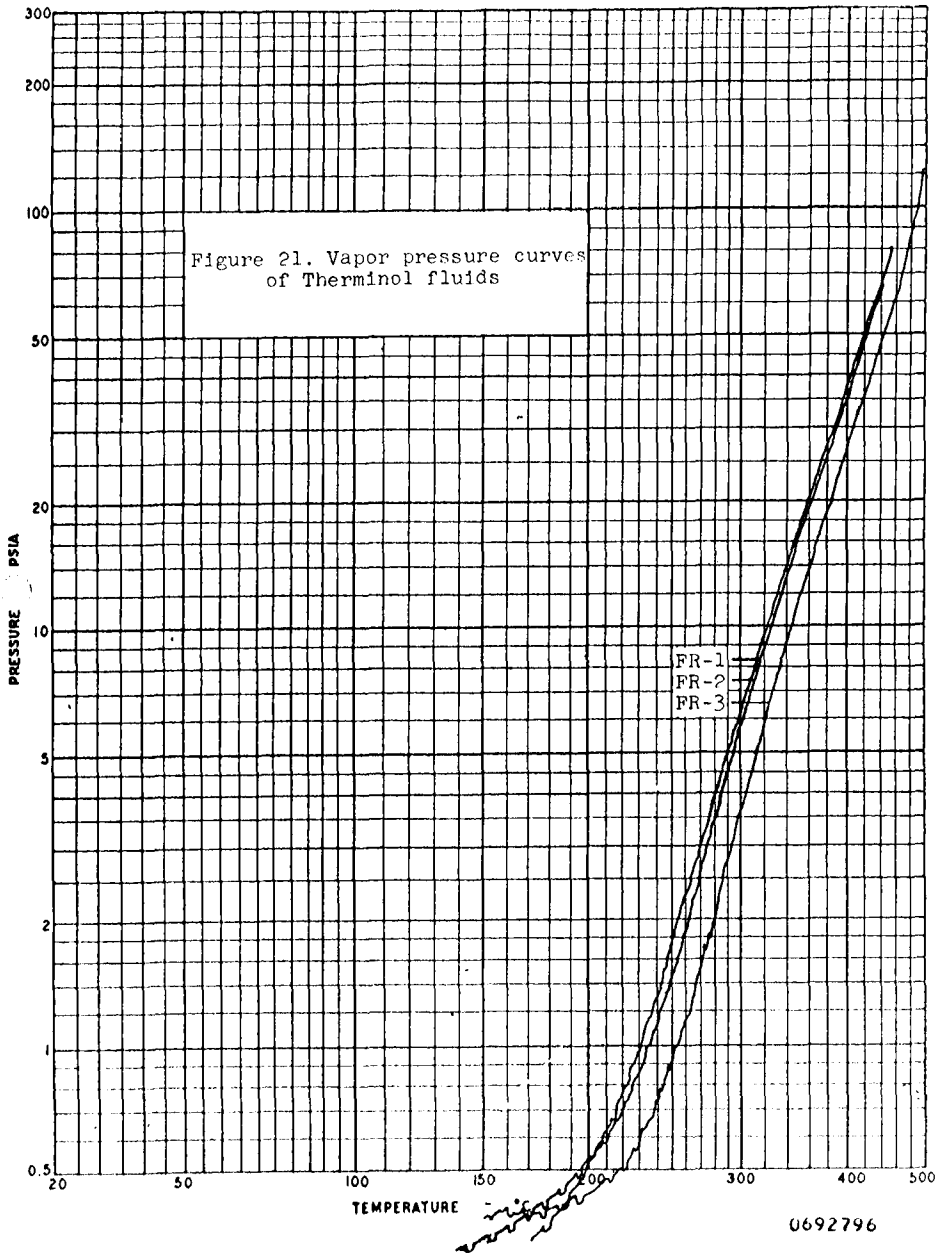
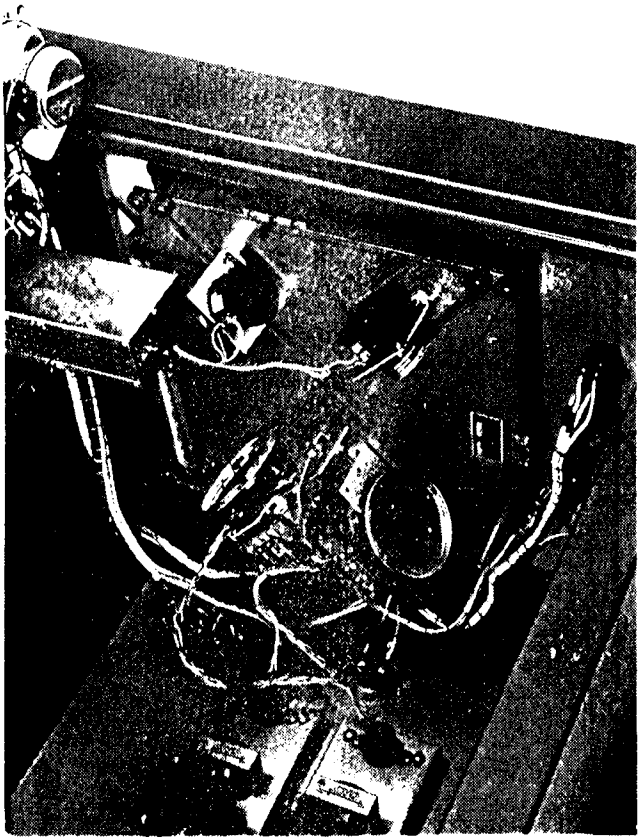


Figure 21. Vapor pressure curves of Therminol fluids



[illegible] Ejection Mechanism

0692797

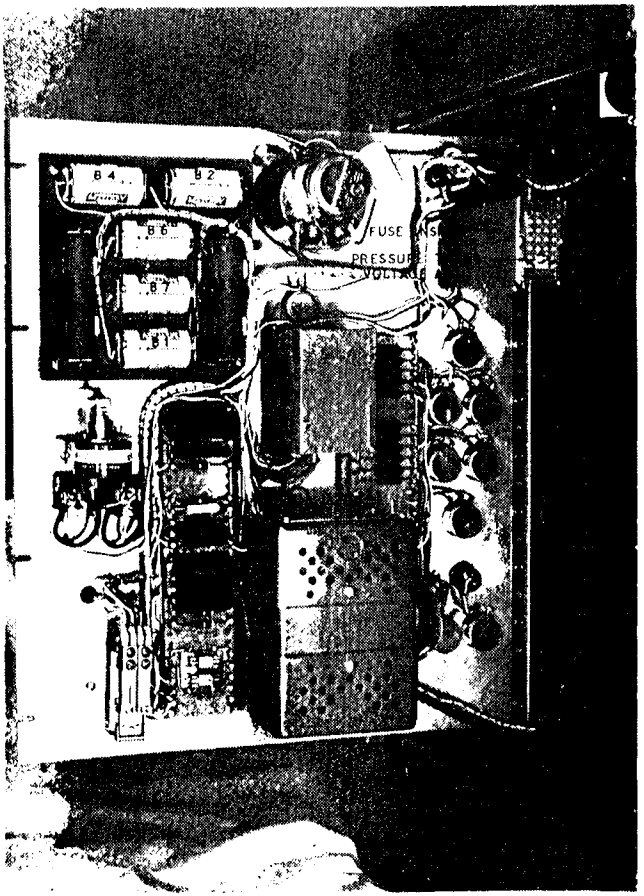


Figure 23. Panel (rear)

0692798

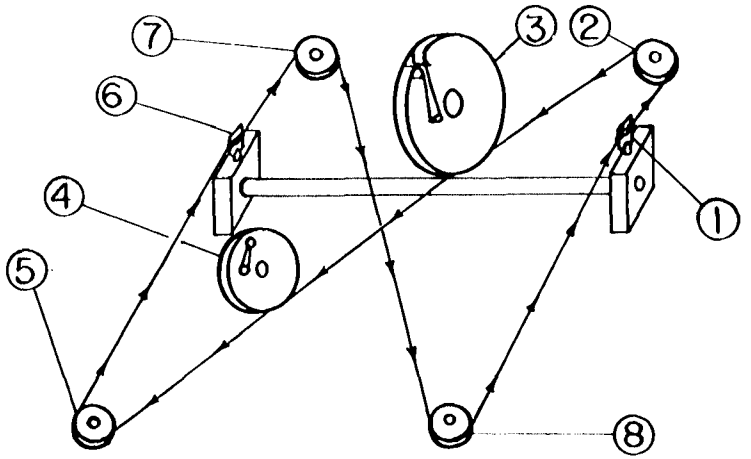


Figure 24. Recorder Drive Cable Stringing

0692799

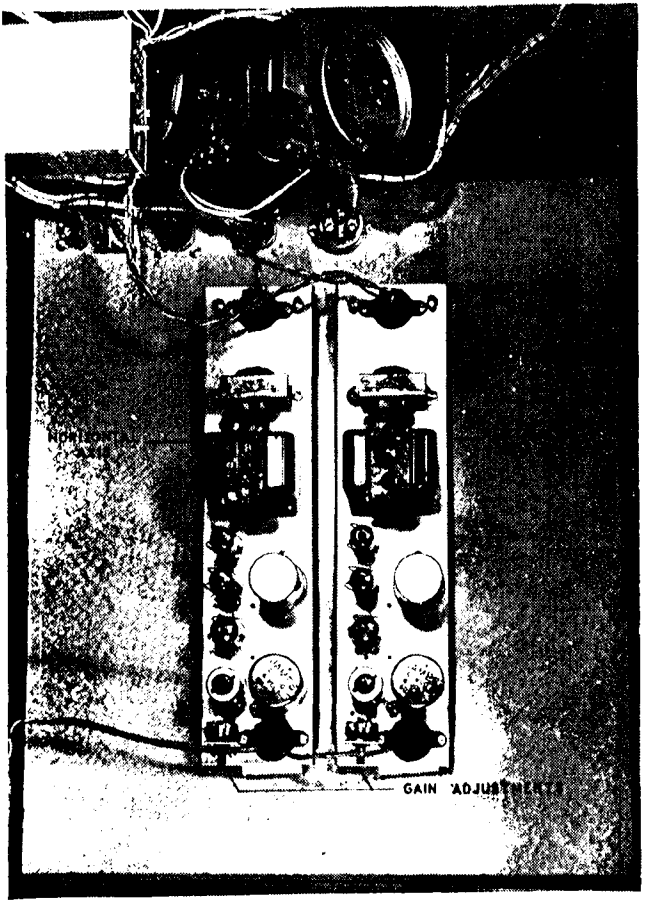


Figure 25. Recorder amplifiers

0692800

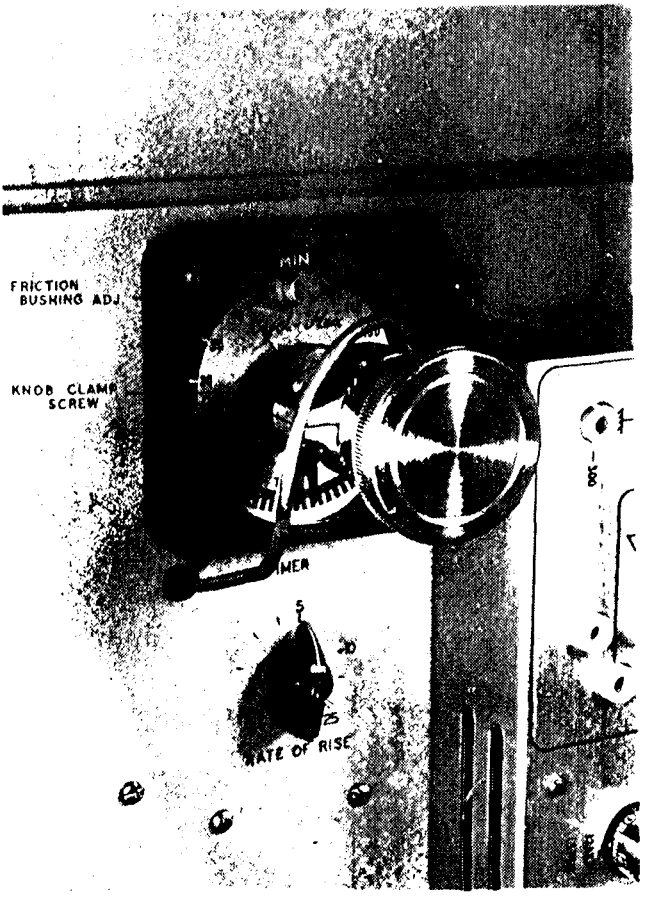


Figure 26. Timer

0692801

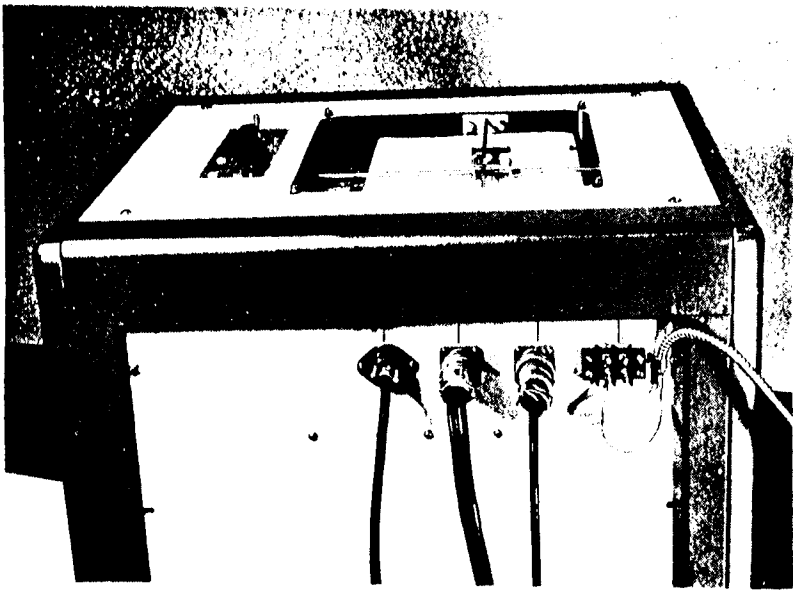


Figure 27. Cable connections

0692802

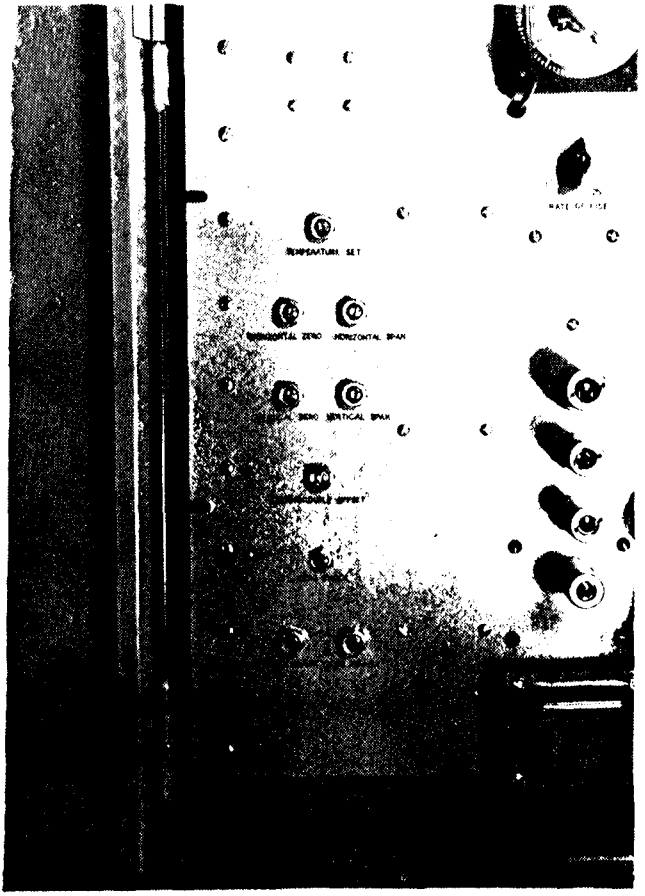


Figure 28. Calibration adjustments

0692803

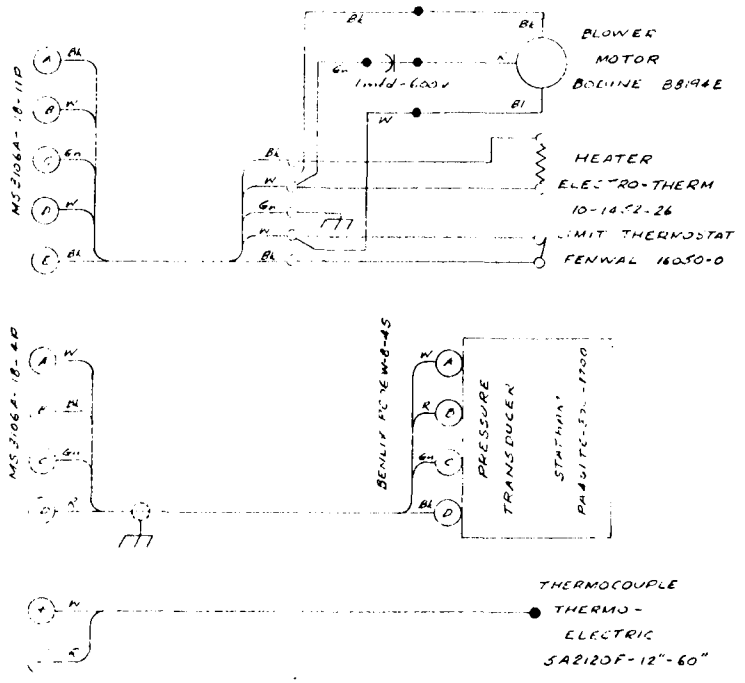
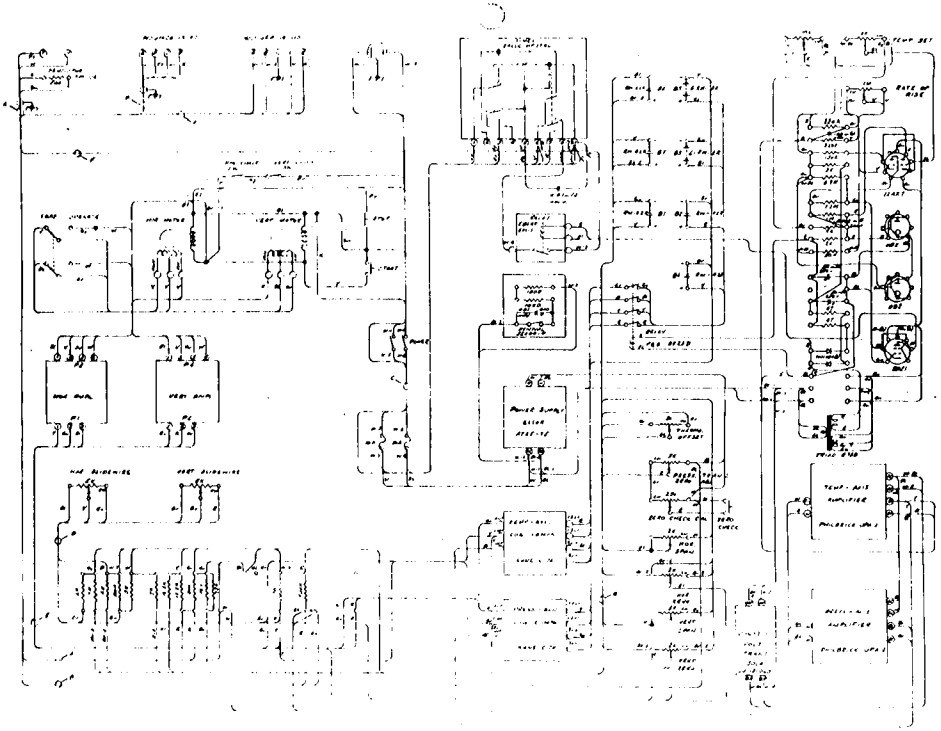


Figure 29. Furnace Wiring

0692804



0692805

4374

9

1961

0692806