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PROGRESS REPORT
ORGANIC CHEMICALS DIVISION
RESEARCH DEPT. - ST. LOUIS, MO.

REPORTED BY	FOR	DETAILS	REPORT NO.	PROJECT
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PROJECT TITLE

PHYSICAL CHEMICAL STUDIES

PROJECT OBJECTIVE

To provide physical properties data, thermal stability information, and fundamental physical chemical studies needed for the support of Research Department projects.

SUMMARY

1. Thermal Conductivity of Fusible Organic Solids

Minor modifications involving improvements in the methods of thermocouple and line source attachment in the non-steady state line source thermal conductivity apparatus have been completed. Measurements are now under way on a series of organic solids. Various factors such as variation between thermocouples, reproducibility of a single thermocouple, variation with power input, and effect of occluded air in the solid will be investigated more completely during this series.

2. Rapid High-Sensitivity Differential Thermal Analysis (DTA)

A series of sealed cell experiments at a rapid heating rate (8°C. per minute) involving comparison of stable materials of different specific heats and thermal conductivities has demonstrated the importance of a close matching of thermal properties of sample and reference in high speed analysis. Comparative experiments on Aroclor samples also indicated that convection is an extremely important mode of heat transfer for liquid samples where large cells are used to achieve high sensitivity, thus necessitating a close matching not only of thermal properties but of viscosity in high speed analysis. These results indicate the necessity for compromise between sensitivity and heating rate. Further work to define this area will be carried out.

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3. Therminol Fluid Vapor Pressure and Thermal Stability Instrument

Equipment modifications were made to provide more accurate recording of sample vapor pressure and temperature. Calibration drifts in the instrument which resulted from voltage changes in the mercury batteries in the logarithmic compressor units were eliminated by replacing the original mercury batteries with ones having superior voltage stability. Reproducible plots of pressure vs. temperature for the Therminol fluids and dodecane which agree well with published vapor pressure data have been obtained. Sample decomposition is discernible from the vapor pressure plots at heating rates of 5°C./min. Slower heating rates magnify the effect. The presence of low boilers in the Therminols is also discernible from the vapor pressure plots but their identification, if necessary, would require some other means of analysis. Work is under way to develop stability data with this instrument upon which specifications for the Therminols can be based.

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DETAILS

3. Therminol Fluid Vapor Pressure and Thermal Stability Instrument

In the course of testing the vapor pressure apparatus, several deficiencies of design were noted and were corrected. These concerned (1) the sample cell and furnace, and (2) certain components of the electronic recording and control assembly. The changes made to provide more accurate recording of the pressure-temperature curve of the sample are described below.

(1) Cell and Furnace Modifications

Tests of the original cell with thermocouples connected to an external recorder had shown that there were excessive temperature gradients both radially and vertically through the cell. Presence of a radial temperature gradient during the heating cycle was ascribed to the relatively great thickness of the cell walls and of the layer of sample within the cell; existence of a vertical temperature gradient was assumed to be caused by stratification of the air within the furnace. A new cell was made of annular cylindrical construction so that the liquid layer would be thin and with the least wall thickness consistent with a pressure test of 2500 psi at room temperature. In addition, a small motor-driven fan blade was placed in the bottom of the furnace compartment to provide continuous circulation of air in the furnace and hence convective rather than radiative heating. With these changes, temperature differences between different parts of the cell were reduced to about 2° at constant temperature, 5° at a heating rate of 5°/min., and 8° at a rate of 20°/min. Further improvements in minimizing temperature gradients and also in reducing the amplitude of the cycling of furnace temperature were made by placing an aluminum shield between the furnace and the cell. This was made at the suggestion of Dr. R. H. Munch to prevent radiative heating of the sensing thermocouple during the "on" portions of the furnace control cycle.

(2) Electronics Modifications

The temperature and pressure recording systems of the instrument were tested independently of each other and of sample by using a motor-driven variac to program heat to the sensing thermocouple and by bleeding nitrogen into the system through a needle valve to simulate vapor pressure increase with temperature. 0547809
During these tests the outputs of the amplifiers were recorded separately. The deviations of the recorded vapor pressure curves from a smooth curve with respect to both temperature and pressure were cyclic with a period of about 2 minutes. These

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variations were found to originate in the logarithmic compressor units and to be synchronous with changes of temperature in these units. The logarithmic compressors had been placed in a thermally-insulated box provided with electrical heating under thermostatic control. The thermostat used apparently did not respond rapidly enough to give close control of the box temperature. As a temporary measure, a small heater was attached to the thermostat shell to produce anticipation of temperature changes. This change reduced the cycling of the logarithmic compressor output to an acceptable level. A type of thermostat better suited to this application was later obtained and may be installed as a permanent modification when the opportunity occurs.

Occasional slow changes of both pressure and temperature calibration also were observed, in addition to the cycling just mentioned. These slow changes also were traced to the logarithmic compressor units; specifically, to the batteries supplying current to the transistor amplifiers of these units. Changes of voltage here produced an apparent shift of zero of the temperature and pressure scales. Type TM-233 mercury batteries had been installed originally. Although each of these batteries is composed of RM-3 cells, the voltage stability of the assembled batteries seems to be inferior to that of individual RM-3R cells. Therefore, the TM-233 batteries were replaced by the equivalent stacks of RM-3R cells, with resulting elimination of the calibration drifts previously noted.

Some minor alterations were made in the temperature programming circuit in an attempt to reduce the amplitude of the cycling of furnace temperature. A small improvement was obtained with furnace temperature cycles of about 5° amplitude. This much variation of furnace temperature produced a detectable variation of vapor pressure. Further improvement of the temperature control probably would be desirable.

With the new design cell described above, vapor pressure-temperature plots in excellent agreement with known vapor pressures for dodecane were obtained. Therminol fluid samples which were thoroughly degassed and had the more volatile components removed gave a vapor pressure plot in good agreement with the isoteniscope measurements by Dr. K. L. McHugh's group. However, these runs were made before the major portion of electronic modifications were made and some doubt is cast upon their validity because of difficulties with instrument stability which followed. These difficulties appear to have been resolved and confidence in the reproducibility of the instrument has now been achieved. Recent runs with Therminol FR-2 check well with

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earlier runs made before the interim that difficulties with instrument stability were experienced. Attached to this report are the vapor pressure curves from several of the recent runs with Therminol FR-2. The traces between vapor pressures of about 5 up to 50 psia show nearly the straight line relationship which would be expected of a single component sample or a mixture of compounds with very similar boiling points and heats of vaporization. The lower portion of the curves appear to give some measure of the low boilers in the sample. In Run No. 44 some of the low boilers were removed during degassing and the resultant vapor pressures were discernibly lower than for Run No. 45 in which care was taken to retain the low boilers in the sample. The reliability of the curve below 3 psia is questionable because of high sensitivity in this region to upsets in the system and it is yet to be determined whether this portion of the curve will be useful in screening batches of Aroclor for designation as Therminols. If it becomes important to identify low boilers to determine if flammable components are present, analysis such as gas chromatography should also be utilized in screening the Therminol fluids.

The deviation of the upper part of the vapor pressure plots from an extension of the straight line portion is a measure of the decomposition and is readily discernible at a heating rate of 5°C./min. (plots No. 44 and 45). The deviation is greatly magnified at the slower heating rate of 1°C./min. as shown in plot No. 46. Optimum heating rates for control use of the instrument at Anniston appear to fall in this range (1-5°C./min.).

Experiments with Therminols contaminated with low boiler, e.g., benzene and decomposable impurities, e.g., alkyl chlorides are being made to help decide stability specifications for the Therminols based on this instrument.

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W. N. Trump

C. E. Vogler

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Atts. (3)

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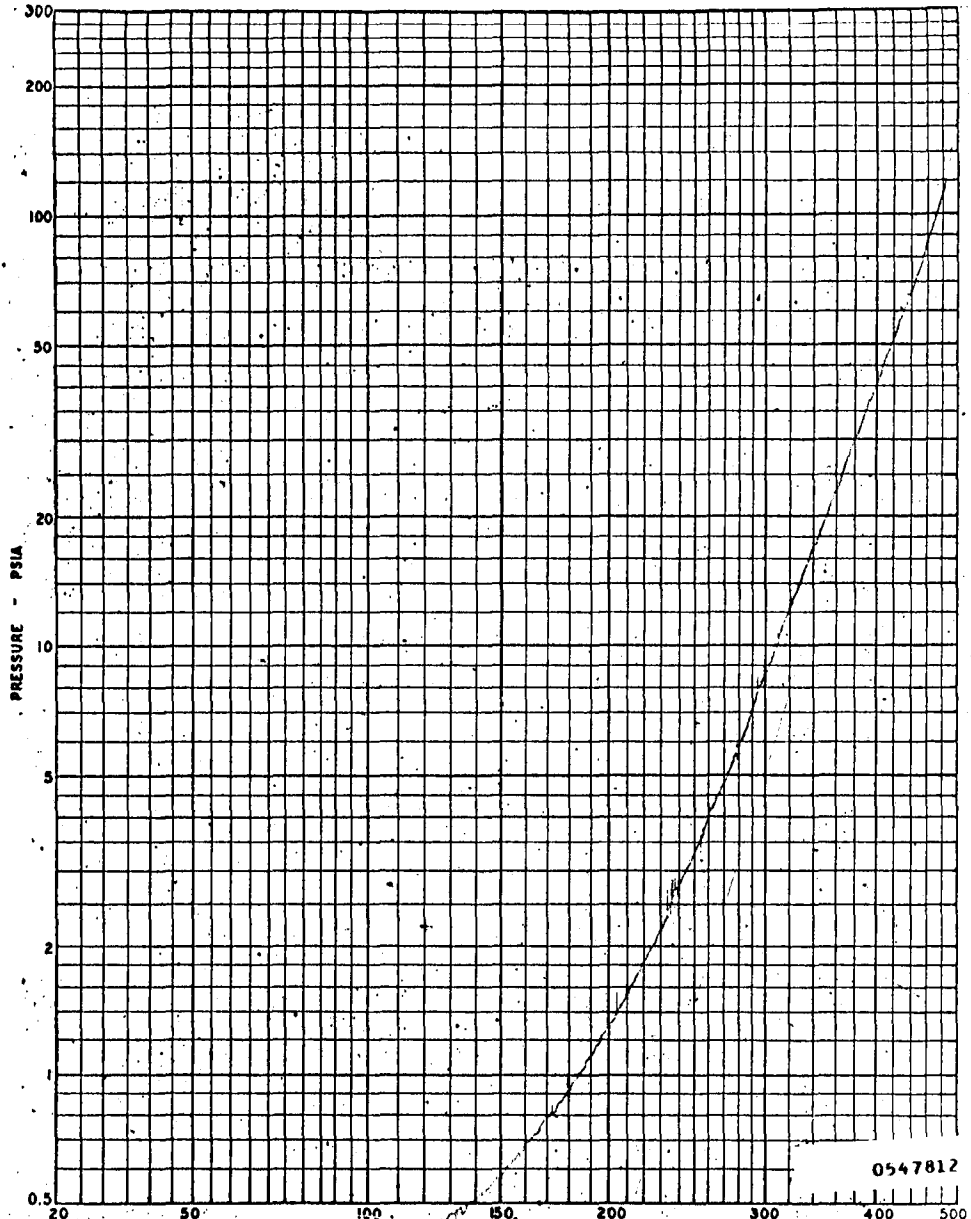
(44)



Sample - 10CC of FR-2 (AB-24) degassed
(part of low boilers removed)
Heating Rat - 5°/min (Instrument program)
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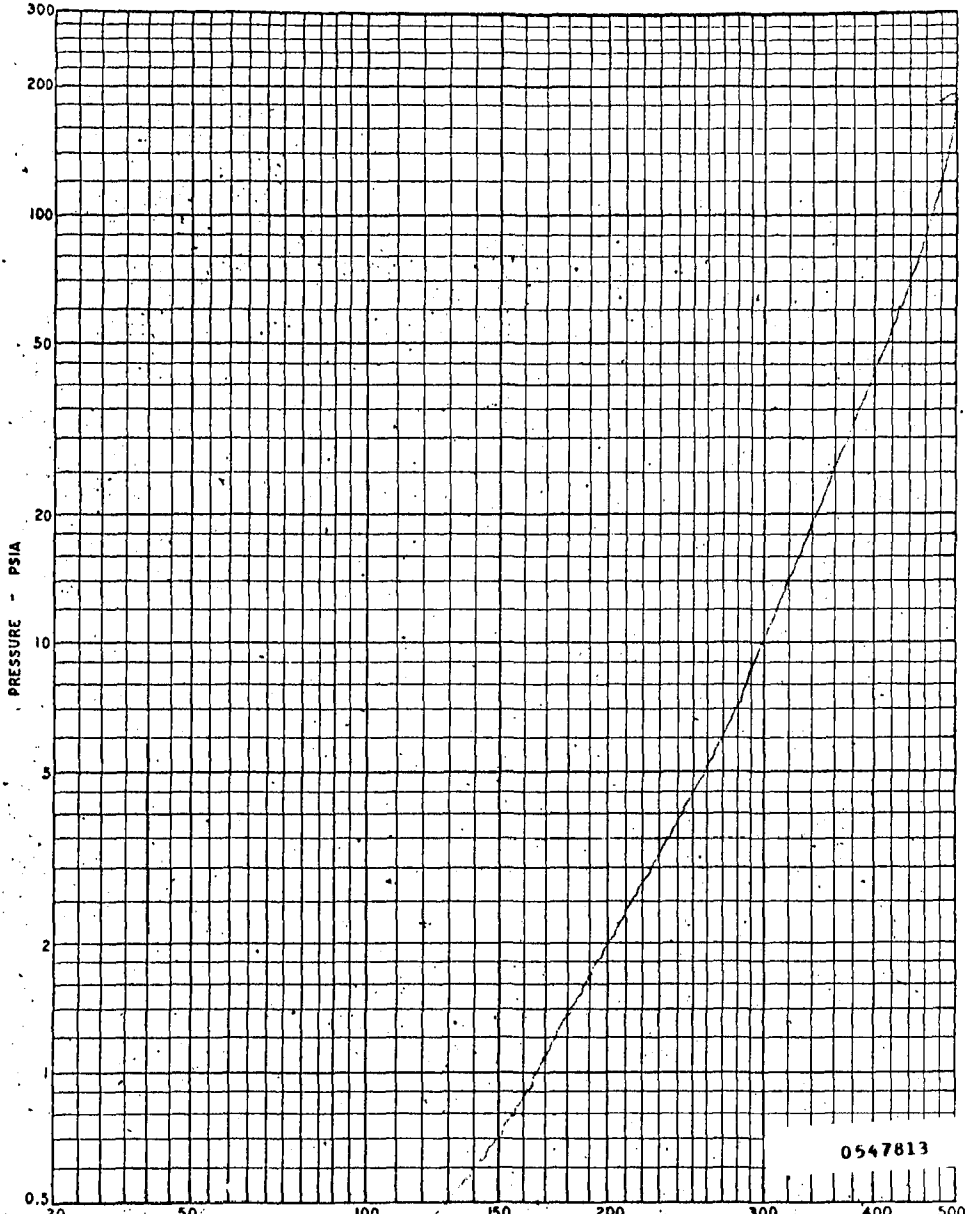
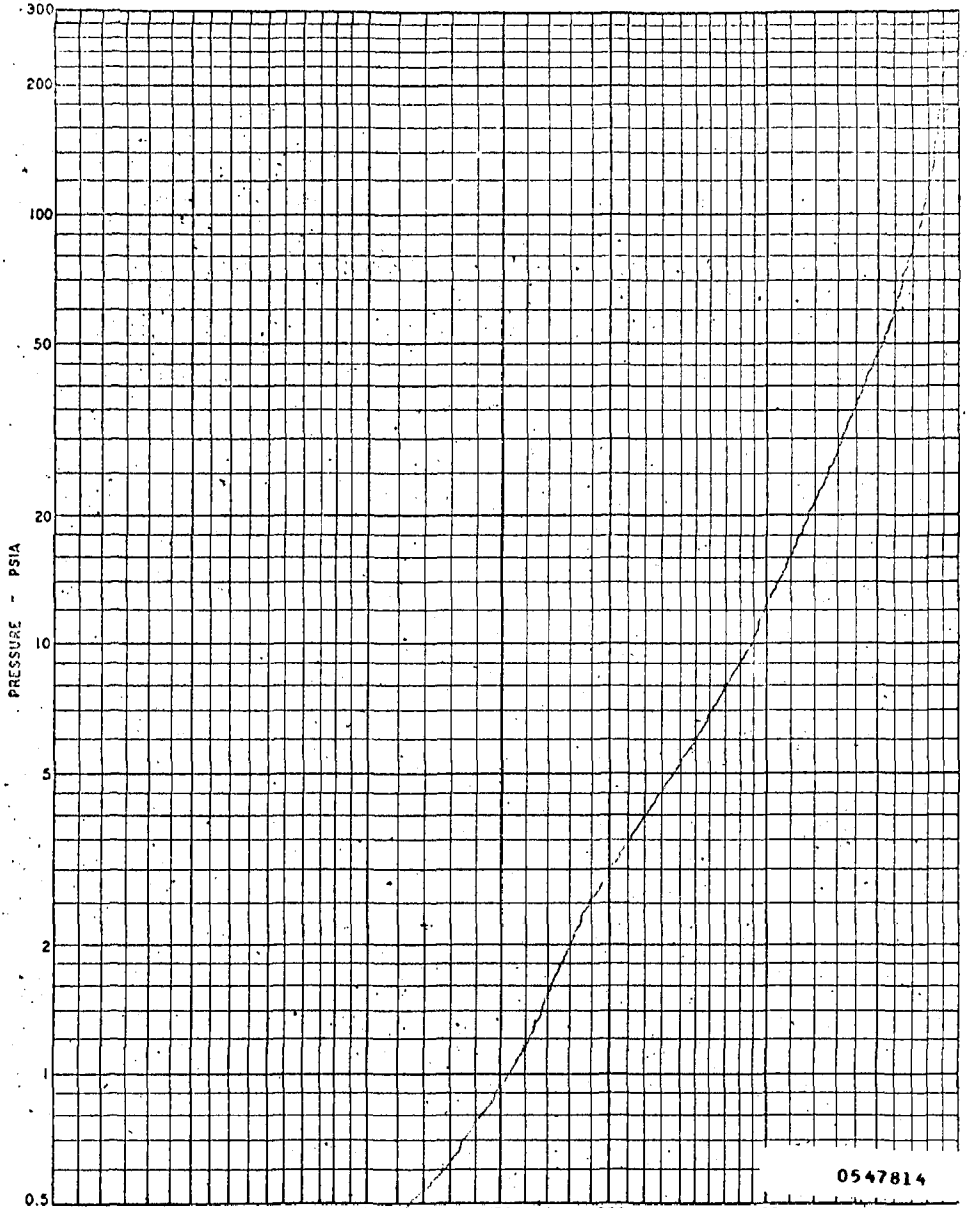


Sample - 10cc of FR-2 (AB-24) digested but all of low boilers retained

Heating Rate - 5°/min (Instrument programmed)

WNT 10-9-6

(46)



Sample - 10 cc FR-2 (AB-24) degassed
but all of low boilers retained
Heating Rate - 1°/min (Meter driven varies)

WNT 10-9-62

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