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PART II

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THE RELATIONSHIP BETWEEN STRUCTURE AND THERMAL
STABILITY OF NEW HIGH TEMPERATURE POLYMERS

H. L. Friedman
General Electric Company

TECHNICAL REPORT ML-TDR-64-274, Part II

OCTOBER 1965

AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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PART II

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FOREWORD

This report was prepared by the General Electric Company under USAF Contract No. AF 33(657)-11300. This contract was initiated under Project 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, with Martin M. Tessler, 1/Lt., USAF, Project Engineer.

This work was performed in the Space Sciences Laboratory of the Valley Forge Space Technology Center, King of Prussia, Pennsylvania. The following personnel participated in this program: Dr. H. L. Friedman, Principal Investigator; Mr. J. E. Brown and Mr. G. A. Griffith, Technicians.

This report covers work accomplished from June 1964 to May 1965. The manuscript was released by the author in July 1965 for publication as an RTD technical report.

The author wishes to express his gratitude to John R. Mallin and Ara Shakarjian for their help with the design of the automatic data processing system.

This technical report has been reviewed and is approved.

William E. Gibbs

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ABSTRACT

Research aimed at obtaining quantitative relationships between structure and thermal stability of polymers was continued. Observation of further errors in vacuum thermogravimetry and further improvements in mass spectrometric analysis of pyrolysis gases caused the former to be dropped in favor of the latter. Mass spectrometric observations have been aided by providing better pumping, bake-out of the furnace tube in advance of pyrolysis, a horizontal furnace instead of vertical, and improved linear programming. Sample size was reduced from 10 mg. to 1 mg. for polybenzimidazoles. Methods of calibration were developed for both the very volatile and not so volatile products. An automatic data processing system was designed, and is nearly finished. Its inclusion in these experiments is expected to result in a vast increase in efficiency of converting the data to qualitative and quantitative analysis.

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INTRODUCTION

During the past few years, through a continuing research program of the Air Force Materials Laboratory and its contractors, many new classes of thermally stable polymers have been and are being synthesized. The thermal stability of most of these classes of materials has been investigated by thermogravimetry. This method has led to some qualitative relationships between chemical structure and behavior in the thermobalance. Quantitative relationships between these properties are not available.

In the first part of this program¹, an attempt was made to develop a vacuum microthermobalance to provide basic data for the evaluation of kinetic equations, which describe the chemistry of decomposition and serve as the quantitative measure of thermal stability. As research progressed, it was found that several errors influenced the results, and made them very difficult to interpret. Some research was started in connection with some of the sources of error. Time-of-flight mass spectrometric analysis of decomposition gases was originally used to identify chemical reactions which occurred in thermogravimetry. The resulting data proved to be of such high quality, that it was thought to have greater potential to provide quantitative measures of thermal stability than thermogravimetry, and methods were developed to obtain kinetic information from the data. Most of the research was carried out with polybenzimidazoles because of their good thermal stability and availability of a wide variety of chemical structures.

TECHNICAL DESCRIPTION

Thermogravimetry

During the first part of the program, samples of polytetrafluoroethylene coating both the top surface and bottom surface of the balance pan were heated in order to measure the effect of momentum transfer on vacuum thermobalance readings. It was clear, from the results of these experiments that molecular drag also played a part in these measurements. This conclusion was reinforced by noting a rather sizeable lift effect on an empty pan as a result of degradation of a polytetrafluoroethylene sample that was heated below it. During this part, an experiment was carried out where a polytetrafluoroethylene sample was decomposed as it was suspended just above the surface of the empty balance pan. The results of the last two experiments are shown in Figure 1.

It is clear that a smaller, but considerable lift effect occurred when the sample was heated above the pan. This shows that in the present apparatus, molecules migrate to regions below the balance pan and tend to lift it as they are pumped away in the direction of the support wire. Since the polytetrafluoroethylene samples used in these experiments weighed about 7 milligrams, it is clear that lift effects produce significant errors. It is likely that improved design could reduce such errors. Faster pumping could reduce the tendency of molecules to migrate below the pan. Increasing the space between the furnace tube and the pan could be helpful, as could concurrent fast pumping from the top and bottom of the furnace tube.

Analysis of the data and theoretical considerations showed that the simulation experiments could not possibly duplicate the drag effects which occurred during the two thermogravimetry experiments. Therefore, it must be concluded that these experiments could not be used to provide quantitative measurements of momentum transfer effects in thermogravimetry.

An article on errors in vacuum thermogravimetry was published in Analytical Chemistry².

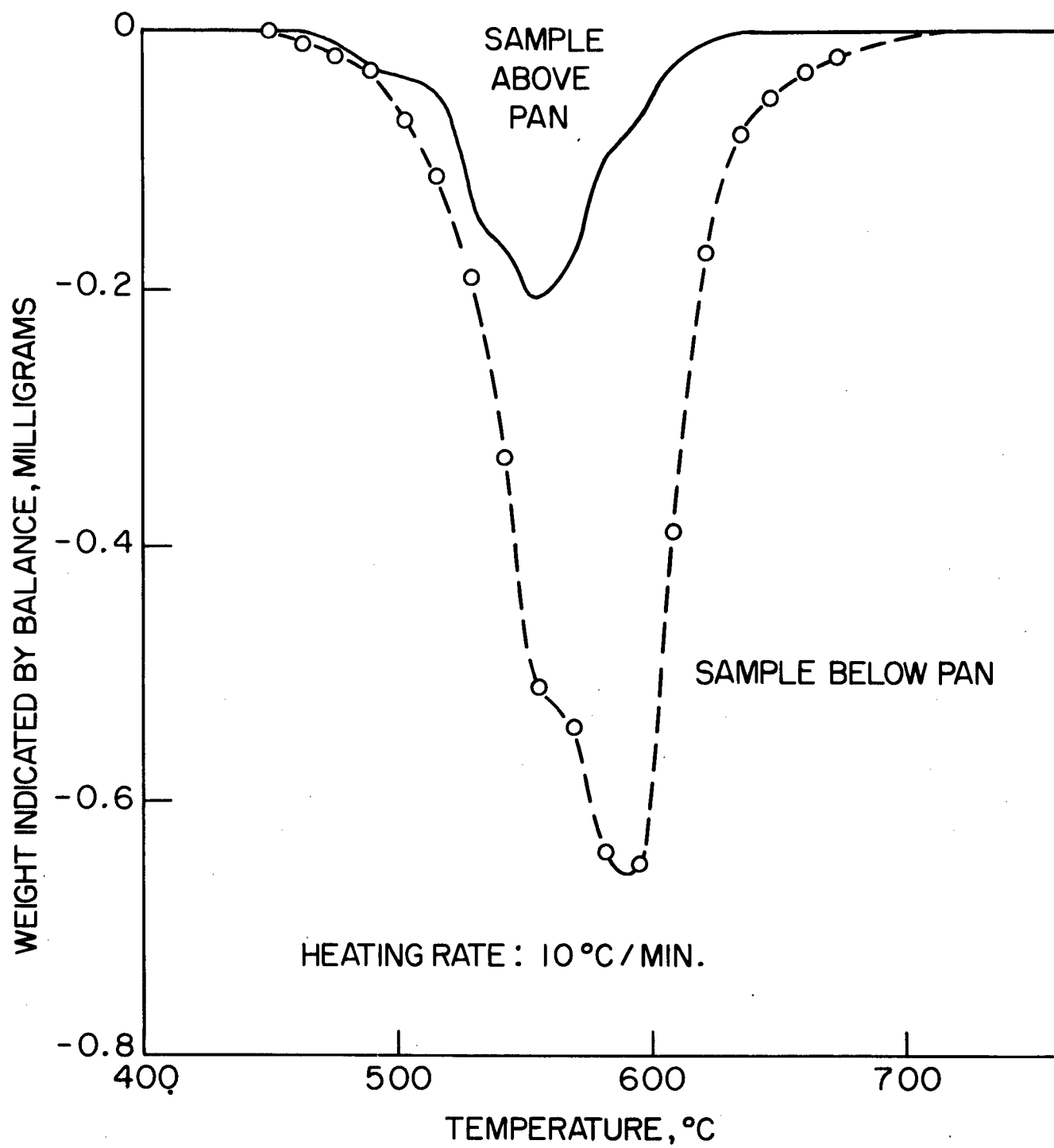


Figure 1. Effect of Polytetrafluoroethylene Gases on Empty Sample Pan.

Mass Spectrometry

Experimental

As experiments to calibrate the mass spectrometer to provide quantitative yields of decomposition products of the four polybenzimidazoles continued, the fact that operating conditions had been established that promoted mass spectrometer stability led to calibration data that were far more reproducible. It was then possible to observe that sources of impedance in the pyrolysis and calibration pumping lines limited the accuracy of relating pyrolysis to calibration data. A temporary glass system was built of large diameter tubing and with large bore stopcocks. Tests of this system showed the impedance effects to be eliminated. An entirely new permanent system was fabricated from components of suitable size.

During these experiments, it became necessary to clean and refill the mercury diffusion pump of the mass spectrometer. As a result of this and improved impedance in the sampling system, the background pressure was lowered by about an order of magnitude, with a similar reduction in the background signal. Improved pumping and impedance suggested that it would be possible to use sample which weigh as little as 100 micrograms initially, an improvement of two orders of magnitude in sample size. In addition, the geometry of the system was modified so that faster pumping allowed more rapid evacuation of the system, which resulted in more efficient use of the apparatus.

It was then clear that mass spectra of decomposition products of polybenzimidazoles would have to be measured again, but the new data were expected to be vast improvements over the old. The improvement in pumping was expected to sharpen up the yield peaks, and pumping corrections for the retention of product in the reaction chamber and pumping manifold would be minimized. Therefore, improvements in quantitative potential of the new data were anticipated.

Tests of the new sampling and pyrolysis vacuum system showed that it functioned as planned. The pumping speed was much faster

than before, and was close to that predicted by theory. The response of the micromanometer also showed that flow impedance had been much reduced. Therefore, 100 microgram samples of polybenzimidazoles were subjected to pyrolysis. Although the spectra appeared to have the general characteristics of those that were obtained for 10 milligram samples, they were much more noisy. In addition, the background spectra changed as pyrolysis progressed. Therefore three consecutive blank experiments were run without dismantling the system between heating cycles. The results of these showed that certain components, such as water were driven off continuously, and that their quantities were reduced from run to run. Others, such as nitrogen, were evolved most strongly at the higher temperatures, but their quantities were also reduced from run to run. Although the air background, as shown by m/e-32 was very steady throughout the experiment, a considerable scatter was found in the data, and a small burst of air appeared from time to time. The bursts were probably due to rupture of air pockets in stopcock grease or release from gasket spacing. They were of short duration, and so obvious that they will probably not be important. The scatter of the air background was of such a level as to influence the total spectrum at peaks where it occurs, and contributed to some of the noise in the product mass spectra. Some of the noise also appeared to be statistical, i.e. the number of ions formed during each cycle of mass spectrometer operation was small because of the small sample size. Therefore, the need for larger samples of this type of polymer was indicated. Calculations showed that 1 milligram samples would probably be adequate. It is important to note that the size of sample that can be used will depend on a number of factors, e.g. the quantities of gaseous products that are formed, their rates of evolution, the sensitivity of the mass spectrometer to the product and whether the peaks which represent the products coincide with background peaks.

The blank experiments showed that bake-out is needed in advance of pyrolysis, so the pyrolysis system was modified so that this could be done effectively. The apparatus that is shown in Figures 2 and 3 was the most successful of several that were built for this purpose. The porcelain crucible which contains 1 milligram of sample is stored in the water cooled part of the chamber with a magnetizable push rod behind it. The furnace tube and thermocouple are baked-out at 1000°C while the mass spectrometer

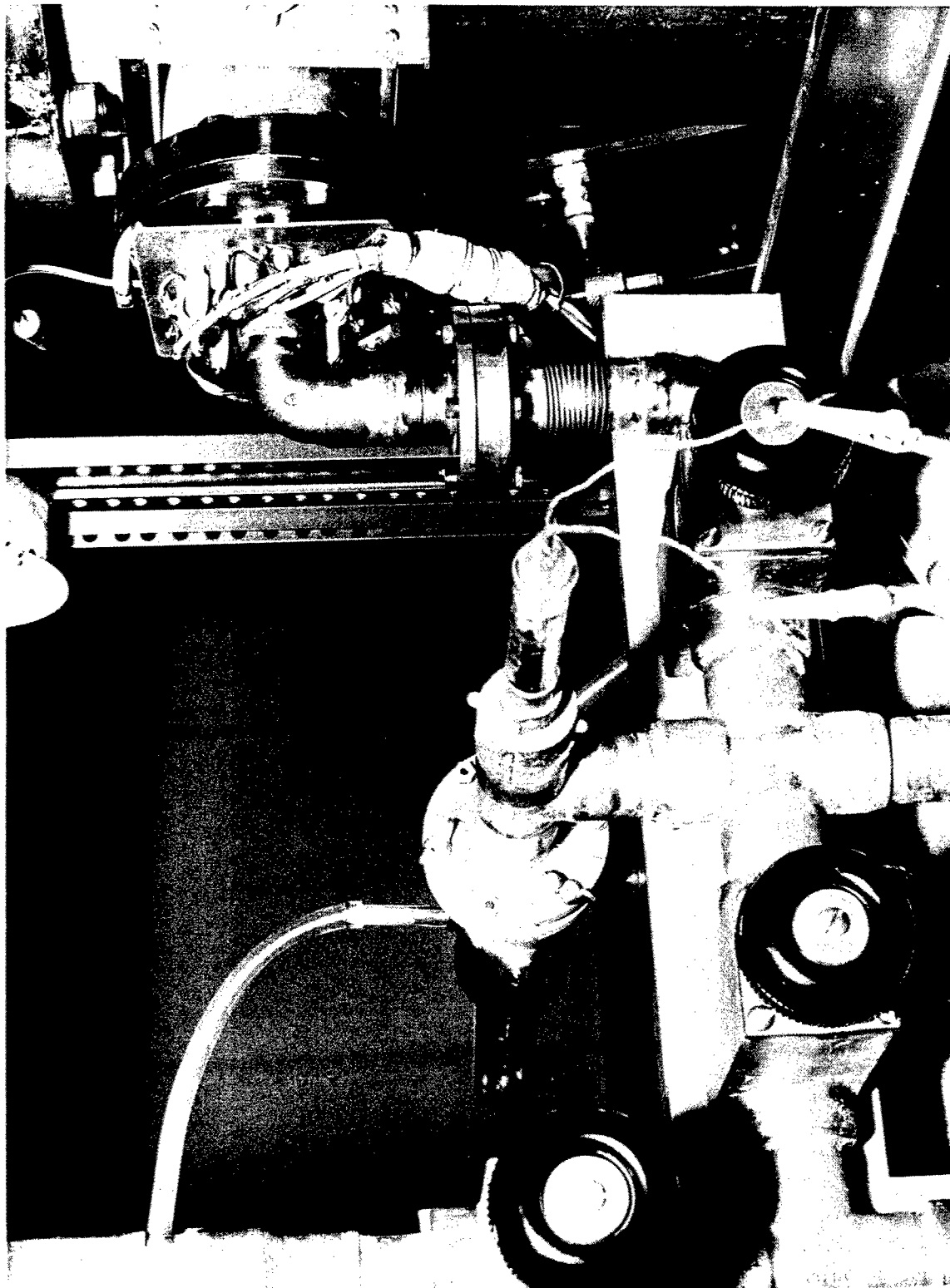


Figure 2. Sampling and Pyrolysis Vacuum System

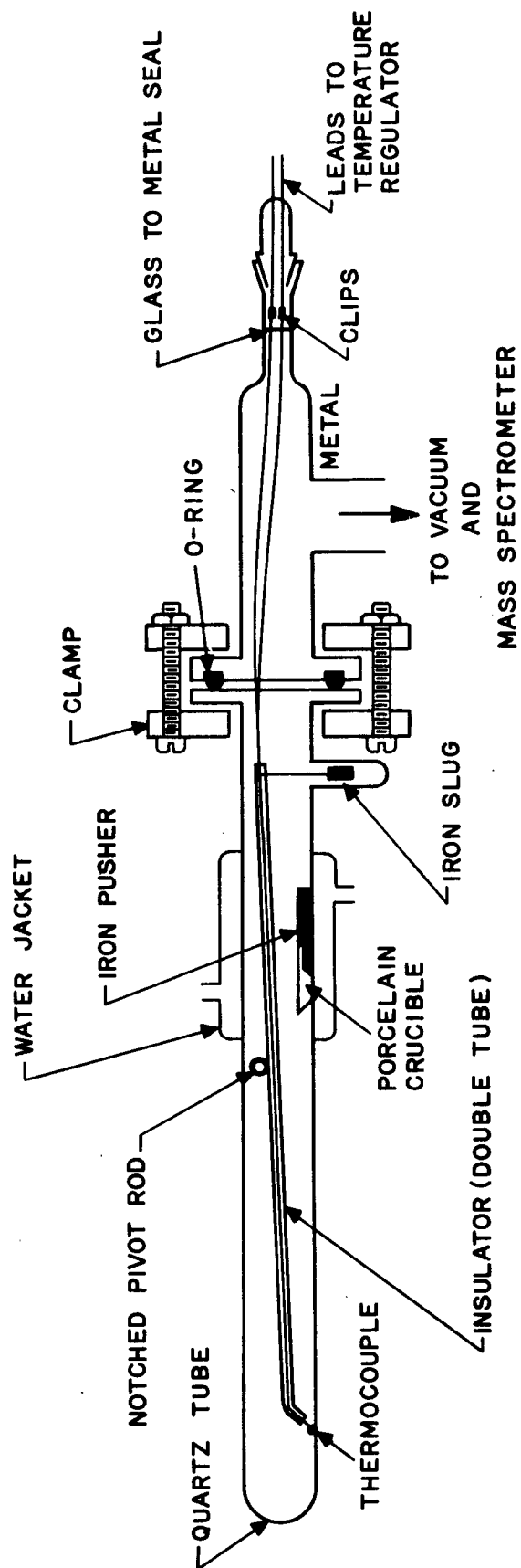


Figure 3. Details of Pyrolysis Vacuum System

is used to determine when bake-out can be terminated. The thermocouple tip is allowed to be suspended away from the walls of the tube during bake-out. The hot furnace is then removed, and the tube is allowed to cool to room temperature. The crucible is positioned with a magnet so that it is just below the thermocouple tip. The thermocouple tip is then lowered into the crucible. It sometimes takes several raisings and lowerings of the thermocouple tip, together with displacements of the crucible to achieve final placement, but the system has adequate flexibility to accomplish this in most cases. A second furnace is used for pyrolysis while the first furnace cools. The temperature regulator was originally designed for a 104 volt, 1500 watt furnace. Since it was not possible to dissipate so much power in the small furnace that was originally employed for mass spectrometric pyrolysis, it was necessary to use a load resistor in series with it. Nevertheless, programming was never quite so smooth as it was for the thermobalance. Since a horizontal furnace tube is used at present, and since a greater furnace tube length is also required, a furnace of the type that was used with the thermobalance was clearly desirable. The length of the Hevi-Duty Model 1012 S Furnace was too great to be used in the present system, so a smaller sized Model 70 T unit, which was available in the laboratory, was used. In order to make it fully compatible with the temperature regulator, 104 Volt coils and an appropriate saturable reactor were purchased and installed.

The proportional controller was adjusted to function properly with the new additions. While testing the apparatus, it was found to be excessively difficult to achieve linear temperature programming at the start of the experiment with the control system set for automatic operation. Because of initial slow heating, it was usual to get temperature overshoot, which was often followed by excessive reduction and a second overshoot. This has been corrected by starting in manual position, with the power set to deliver the proper rate of temperature rise as its maximum rate of rise. Once this rate is achieved, a process which takes only about 20°C, switching to automatic control produces a continued linear rate of temperature rise. The characteristics of the new furnace are such that a maximum temperature of about 940°C can be reached with a 10°C/min. rate of heating. 4°C/min. is the highest smooth rate that is available for linear heating to 1000°C. Since a more favorable signal to noise ratio results for

the faster heating, the last 60°C of heating will be sacrificed for the 10°C/min. runs, which will be the backbone of future experiments. Another reason for doing so is that temperatures near 500°C are more important than the very highest temperatures for this study. Linearity may also be disturbed by a dirty temperature programmer slidewire. In order to assure cleanliness, temperature is recorded as a function of time during the bake-out period, since irregularities due to dirt will show up at that time. Thorough solvent cleaning will alleviate this problem. Prolonged cleanliness is promoted by keeping the case of the temperature regulator closed, except during the brief periods when it must be open to operate controls.

1 mg. samples of poly-2,6-(m-phenylene)-diimidazobenzene (I) and its p-phenylene analog (II) were subjected to pyrolysis at 10°C/min. Temperature programming was linear and smooth. Oscillograms were read for I and graphs were plotted. The results compared reasonably well with the earlier pyrolysis, which was carried out for a 10 mg. sample at 16 2/3°C/min., and the ion lens of the mass spectrometer was employed. Comparisons were made for the purpose of determining if sufficient ions were counted to provide smooth mass spectra when ion signal is plotted as a function of temperature for the various mass peaks. Smoothness was thought to be important for accurate kinetic analysis. Evaluation of the various parameters indicated that the rate of ion counting would be reduced by about a factor of 100. While this level was found to be sufficient for hydrogen cyanide at m/e-27, the strongest peak in the spectrum, more scatter than was desired was observed for the other spectra. Minor components, such as water and phenol, could not be observed. The graphs of ion signal vs. temperature were sharper and showed less of a tendency to tail-off, demonstrating the improvements in pumping. The levels of air and water background were very steady, and much reduced in comparison with the product spectra. This was attributed both to improved pumping and the bake-out procedure. It will be necessary to carry out blank experiments in order to determine the spectra that are characteristic of the system, and because the sample crucible will not be baked-out in advance of pyrolysis. Since use of the small sample is desirable, employment of the ion lens had to be considered.

Use of the ion lens had been avoided since counting of an excess of ions causes the multiplier to progressively lower its

output. Calibration of the mass spectrometer had been carried out with n-butane at pressures of about 10 microns, for accurate use of the micromanometer. The ion lens cannot be used at such high pressures, while accurate use of the micromanometer would not be possible at levels that permit use of the ion lens. Since extensive experimentation would be required to relate sensitivities for both modes of operation, a method was developed to calibrate with the ion lens. This technique requires measurement of a higher pressure in a known volume in advance of expansion to lower pressures for calibration, so that the initial pressure of the n-butane that enters the mass spectrometer may be calculated. Initial ion signal is determined by extrapolation of plots of log ion signal vs. time to zero time. The method was tested for higher pressures without the ion lens, and was found to be suitable. Tests with n-butane samples with pressures of about 1 micron showed that great stability was maintained with the ion lens in use, and that sensitivity increased by a factor of about five. Pyrolysis of a 1 mg. sample of polymer I with the ion lens showed the data to be very smooth, even for products of intermediate quantity.

Because of its possible toxicity, the total yield of benzimidazole from pyrolysis of I was estimated. Conventional calibration techniques could not be used because of the low vapor pressure of this compound. About 20 micrograms of Eastman benzimidazole was put into a porcelain crucible, which was then put into the pyrolysis chamber. Mass spectra were recorded as a function of time. These showed that m/e-73 was the main ionic fragment, and that very little, if any, 118 results from this product. It seems likely, therefore, that the presence of 118 in the spectra indicates the presence of aminobenzonitrile as a decomposition product. Since other products make small contributions to the 73 peak, the use of this peak for the estimate should be considered to give a high value. Small quantities of other impurities, and some water were also observed in the benzimidazole spectra.

The results of pyrolysis of a 1.28 mg. sample of I were used as a basis for the computation. Equations (9) and (12) of Reference 1 were combined to give

$$\left(\frac{dn}{dt}\right)_p = \frac{\beta VI}{\gamma kT}$$

where n = molecules

t = time, sec.

$\beta = (kT/2 \pi m)^{1/2} A/V$

V = volume, cm^3

I = ion current

γ = sensitivity, ion current per unit pressure

k = Boltzmann constant

T = temperature, $^{\circ}\text{K}$

m = molecular mass, gm.

A = leak area, cm^2

p = subscript which represents pumping through the leak of the mass spectrometer

β was obtained from comparison with pumping characteristics during calibration experiments for n-butane. γ was gotten from the ratio of I to pressure, as measured by the micromanometer and corrected for water. dn/dt was converted to dw/dt (w = weight, gms.) by use of Aragadro's Number and molecular weight, and dw/dt was integrated graphically with respect to time. About 2.5 micrograms of benzimidazole were found in the products. Formation occurred between 600 and 750 $^{\circ}\text{C}$ at the heating rate of 10 $^{\circ}\text{C}/\text{min}$. Since about 30% of polymer volatilizes in heating to 1000 $^{\circ}\text{C}$, this product composes no more than 0.65% of the gases, and 0.2% of the total material. Because of the impurities in the benzimidazole, some of it has been purified by recrystallization, and will be employed for subsequent calibration.

Automatic Data Processing System

To review, as polymers are heated through linear rates of temperature rise, the decomposition gases are pumped through the leak of the mass spectrometer. Mass spectra are obtained

continually as the various peaks are integrated with the analog output system, starting at $m/e-0$ and scanning to the highest values, and then returning to 0 and starting over again. The speed of analog scan can be selected to provide a quantity of data that can be managed. Repeating of masses at 10°C intervals has been found to be reasonable. In heating to 1000°C , about 100 analog scans are needed. Since an average of about 50 peaks are produced per scan, it is necessary to determine mass number, temperature, and ion intensity for about 5000 peaks. The requirements of plotting graphs of intensity vs. temperature for the various peaks, and reduction of the data to qualitative and quantitative analysis, means that an enormous quantity of data must be processed for a single experiment. Machines do this type of operation more efficiently than humans, so an automatic data processing system has been designed and is being built. A diagram of the overall system, which is nearly completed, is shown in Figure 4.

Voltages which represent the three parameters will be read with an Electronics Associates Inc. (EAI) Model 5000 Digital Voltmeter (DVM). Temperature signals will be generated by the pyrolysis thermocouple, through the retransmitting slidewire of the Minneapolis-Honeywell Temperature Controller and Recorder. Ion intensity will be provided by the analog output of the mass spectrometer. The mass selector will provide 200 separate voltages to the analog gate (a variable time delay) in a stepwise fashion. It is composed of an accurate power supply, 200 reed switches, 200 potentiometers, and a 200 position stepping motor. The power supply is the Lambda Model 50 unit. A photograph of the Arthur Ansley Manufacturing Co. RS-200 Rotoreed Switch is shown in Figure 5. The reeds are activated by a permanent magnet that is mounted on a diametrical arm that is rotated by a Slo-Syn Model SS 25-1002 Bifilar Stepping Motor and Model ST 250B Translator. The potentiometers, which fix the position of the analog gate, will be the most critical part of the system. They will have to be set very precisely and must be stable because it will be important to measure the signal at the center of the peak. This will be most difficult for the high masses, for these peaks are comparatively close together, e.g. the centers of $m/e-200$ and 201 are about 0.25 per cent apart. The DVM is sensitive enough to make such measurements. In order to design the mass selector, two different model potentiometers were built. The first involved a group of separate

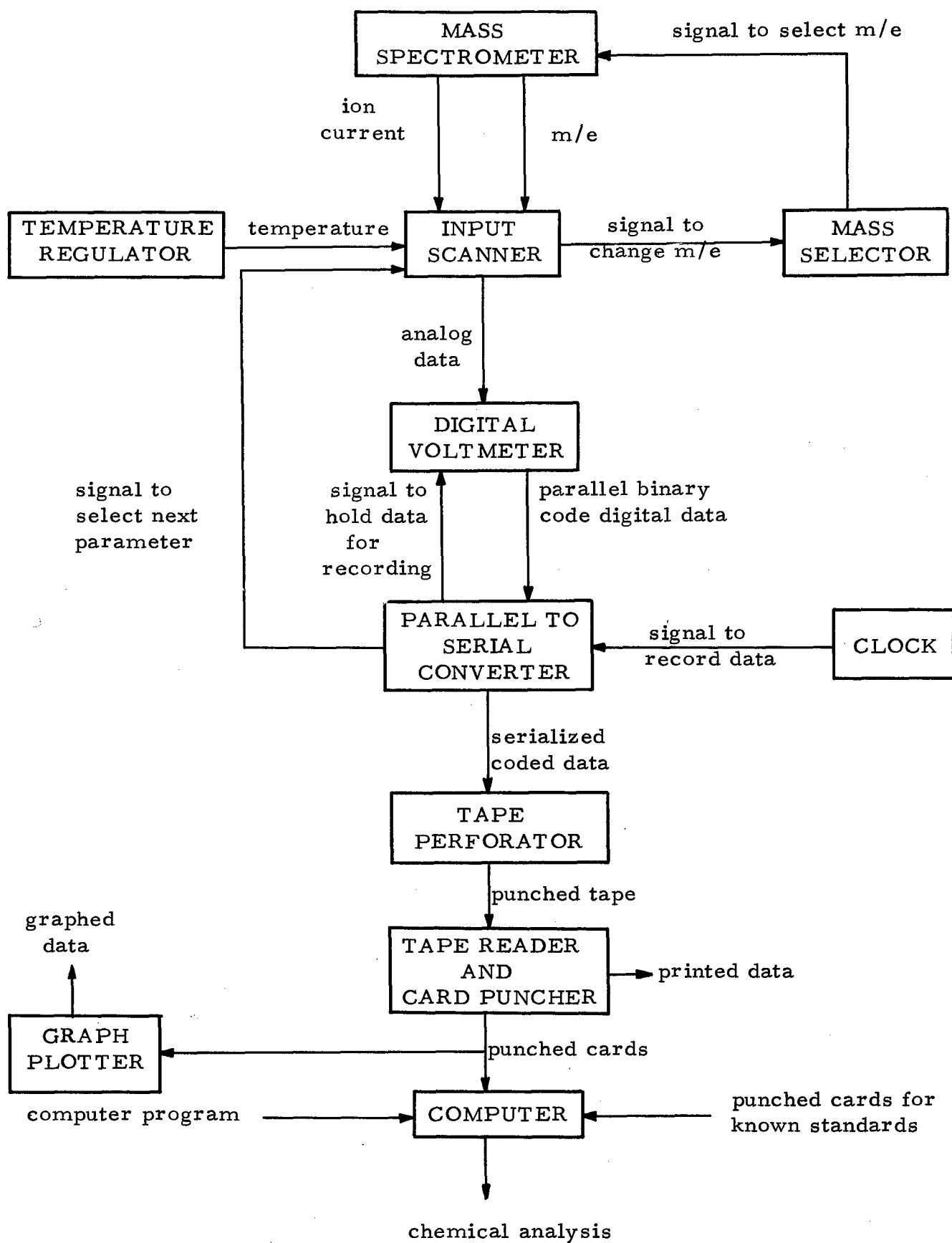


Figure 4. Automatic Data Processing System

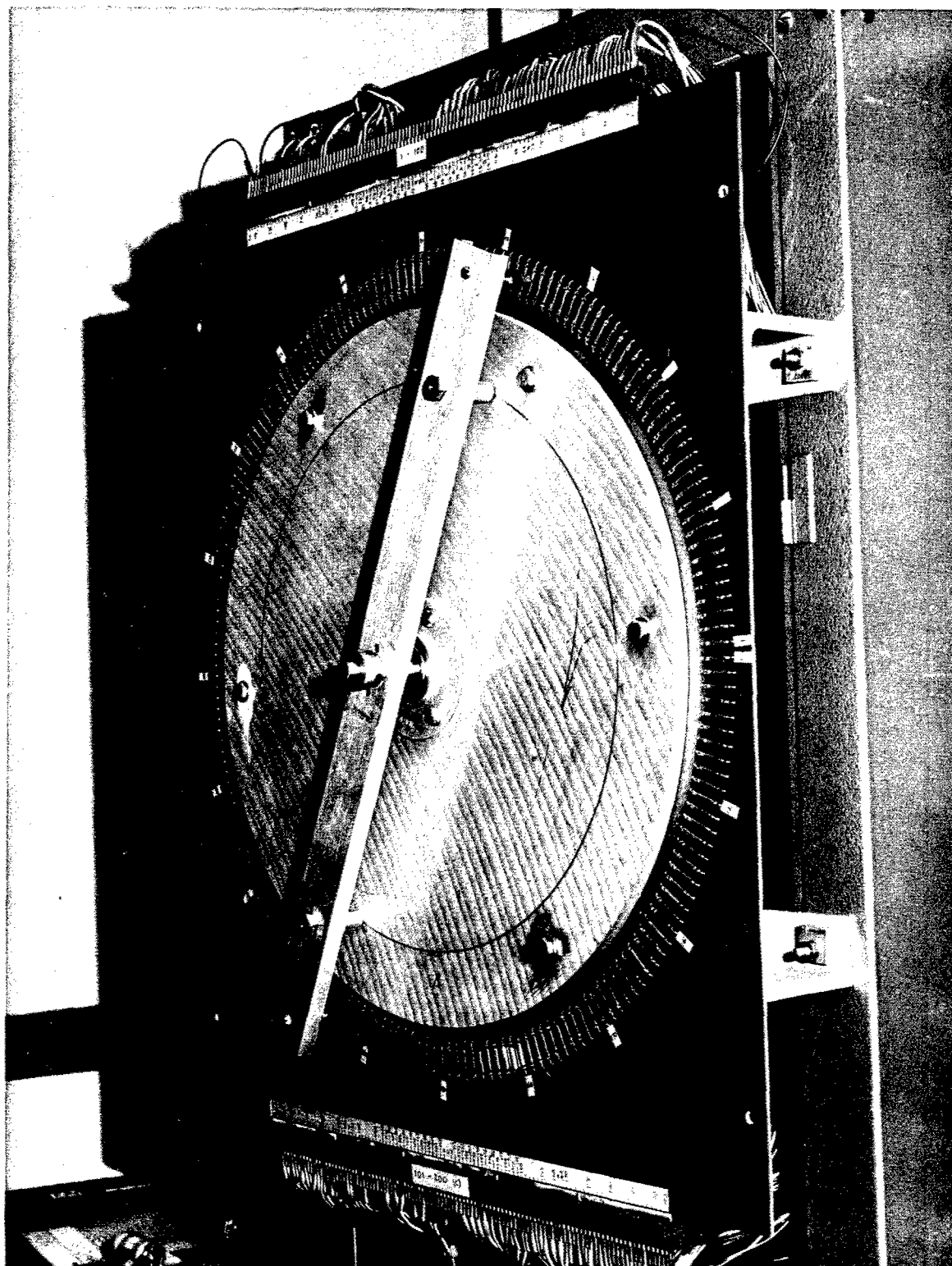


Figure 5. 200 Position Rotoreed Switch

potentiometers, where each one was adjusted for one peak. This type was unstable for the potential changed as each potentiometer warmed up. In order to use such a circuit effectively, one would need an auxilliary power supply and very complex switching. The second model consisted of a number of potentiometers wired in series, with taps between them. This model was found to be very stable following a short warm up period, presumably because the appropriate level of current flowed through all of the potentiometers continually. A further advantage of the second circuit was that it required only a single pole switch. Its main disadvantage is that the change of a single value of resistance will affect the whole system. 200 Bourns wire wound Trimpots were obtained, because these could be expected to have the greatest stability. They have been mounted, wired to plugs which connect to the Rotoreed Switch according to a color code, and installed as shown in Figure 6. Experiments were carried out to select a mass calibration standard and to determine how to set the potentiometers for peaks that must be interpolated and extrapolated. A pair of decade resistance boxes was used to provide an accurate potentiometer, and hexachloroethane was used as a standard for it provides very distinctive peaks up to $m/e-205$ at rather well placed intervals. The analog gate voltage provided by the potentiometers was found to vary smoothly and almost linearly with $\sqrt{m/e}$. Linear variation would be expected for an idealized instrument. Graphic or computerized extrapolation and interpolation seems feasible. Experiments are planned to determine the degree with which the presentation of the mass spectrum can be controlled. At worst, it is expected that the various potentiometers would have to be set precisely at each mass number for each run. It is more reasonable to expect, however, that a single setting will be suitable for a number of experiments, and perhaps for many months. There is considerable flexibility in selection of mass range.

The input scanner, which is an EAI Model 5700 Data Point Scanner is a 60 position Cunningham Type Crossbar Switch, has many functions. It will accept the three parameters and permit the selected one to be transmitted to the DVM. A signal from the serializer will cause the scanner to select each parameter, in sequence. At the appropriate time, a signal from the scanner will cause the stepping motor to move on to the next mass. The serializer, which is the EAI Model 5010 Parallel to Serial Converter has several other functions, the main one being to

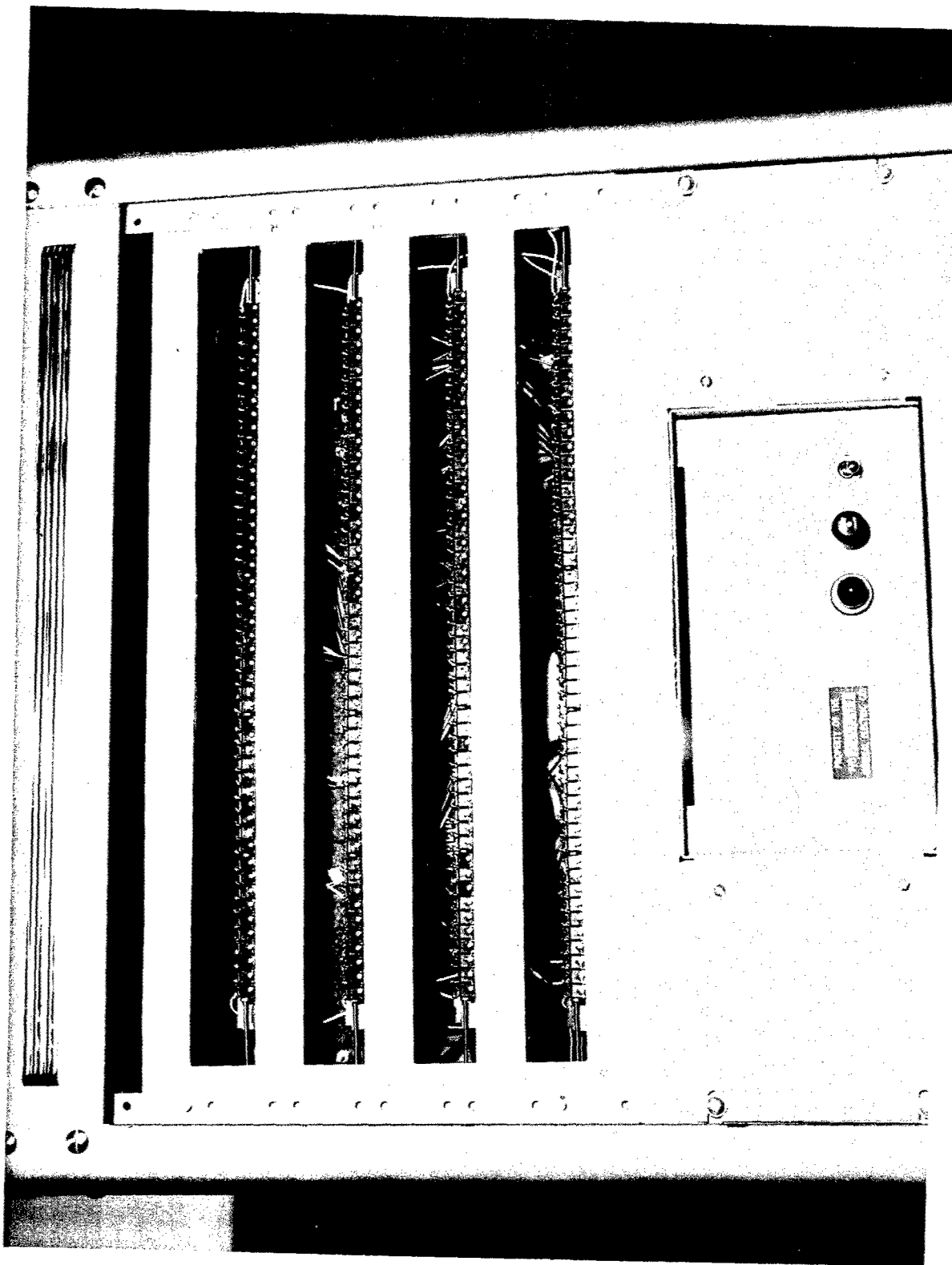


Figure 6. 200 Position Potentiometer

convert the DVM data to tape language, and to instruct the tape perforator to punch. The signal to punch will originate from a clock which has been designed for the system by J. R. Mallin of this Laboratory. The serializer will also instruct the DVM to hold its reading and release it for recording at the appropriate time.

A Tally Model 420 PR-48-10 Tape Perforator will be used to record the data. A rather crude 48 Volt power supply was used to trigger the perforator at first, but this was found to recover its power too slowly, so a Sorenson Power Supply was purchased to replace it. The tape perforator was then found to accurately and dependably record the information that was available from the digital voltmeter. A spark suppression network was fabricated to promote perforator dependability. The perforator writes at a maximum speed of 60 cps. Each parameter will require 5 perforations, so 15 perforations will be recorded for each mass peak. Therefore, up to 4 mass peaks can be handled every second, or as many as the full 200 in 50 seconds. It will be possible to vary the speed of the clock so that slower rates can be used, if necessary. Heating at the basic rate of about 10°C/min. will produce about 120 analog scans, or 24,000 mass peaks and 360,000 perforations. This requires 3,000 feet of recorder paper. Since the perforator is designed to handle 1,000 foot rolls, it will be modified to handle 3,000 foot rolls. It is likely, however, that slightly slower clock speeds will be used. The punched tape will be taken to an IBM Model 826 Document Writing System which is available, for converting the punched tape to punched cards. The Document Writing System can also be used to provide printed data, if it is necessary to examine this. The punched cards, together with cards that are prepared for known standards, will then be processed by one of the several types of computers that are available, in order to complete the chemical analysis. Qualitative analysis will be aided by using the punched cards to generate graphs of peak intensity vs. temperature for each mass number on graph plotters that are available.

CONCLUSIONS

The clear demonstration of molecular collision errors in

vacuum thermogravimetry, other errors and shortcomings of the method, plus vast improvements in mass spectrometric analysis of decomposition gases, led to the abandonment of thermogravimetry in favor of mass spectrometry. The problems of vacuum thermogravimetry can probably be solved, and offer interesting research possibilities, but even at its best thermogravimetry cannot compete with quantitative product analysis for understanding of the chemistry of decomposition.

Improvements in apparatus and the way of use have resulted in satisfactory experimental methods. The new pyrolysis and sampling vacuum system provides several advantages. Bake-out in advance of pyrolysis reduces the level of background signal. The horizontal furnace results in greater uniformity of sample temperature than the vertical furnace. Enlargement of the tubing and valves has produced a marked reduction in flow impedance, thus requiring smaller corrections for hold-up due to slow pumping in calculating rates of formation of the various products, and allowing the apparatus to be used more efficiently. Better control of linear programming and improved stability and reproducibility in operating the mass spectrometer have also helped the quality of the resulting mass spectra.

The smallest sample size for polybenzimidazoles with this apparatus is about 1 milligram, which is a reduction of a factor of 10 from before. In order to reduce sample size further, drastic changes would be necessary. Possible benefits could arise from continuous ionization. At present, the ionization pulse lasts for 1/4 microseconds with 100 microseconds between flight pulses. It is possible to extend ionization time to nearly the full 100 microseconds, with an increase from 200 to 300 times in sensitivity. This would mean that sample size would have to be reduced to about 5 micrograms with the ion lens and 25 micrograms without it. Experience indicates that the level of background signal would be too high for use of the present apparatus with such small samples. Therefore, major modifications in apparatus and sample techniques would be required to accomplish this. Since the results of present experiments appear to be quite satisfactory, it does not pay to divert efforts in developing such modifications for the present program. Thus the present apparatus will be used for the remainder of the research.

The better data are expected to result in better kinetic analysis for several reasons. Smaller sample size should permit reduction of diffusion controlled weight loss, and secondary reactions which result therefrom. Bake-out and reduced pumping impedance should provide more accurate rates of formation. Examination of the data shows that curves of more Gaussian-type shapes are to be expected.

Suitable calibration techniques have been developed for both the very volatile and not so volatile products. A great improvement in efficiency of converting the data to qualitative and quantitative analyses is expected to result from incorporating the automatic data processing system. The concept of the system has been examined thoroughly, and various aspects have been tested. It appears to be sound, and it is expected to be incorporated into the pyrolysis experiments in the very near future.

RECOMMENDATIONS FOR FUTURE WORK

Use existing apparatus and techniques which have been developed to carry out pyrolysis experiments for the four polybenzimidazoles, plus benzimidazole itself. Convert data to punched cards and process to provide quantitative yields of specific products, and carry out kinetic analysis for selected products, especially those that occur during early decomposition.

Complete and test the automatic data processing system, and incorporate it into the experiments when it is ready.

Extend studies to other polymer families.

Examine the resulting information and compare with existing knowledge to determine quantitative relationships on the overall influence of chemical structure on thermal stability which will cover wide varieties of new high temperature polymers.

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2. H. L. Friedman, Anal. Chem. 37, 768 (1965).

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		Nonmetallic Materials Division, Air Force Materials Laboratory, Research & Technology Div., Air Force Systems Command, WPAFB, Ohio
13. ABSTRACT		
Research aimed at obtaining quantitative relationships between structure and thermal stability of polymers was continued. Observation of further errors in vacuum thermogravimetry and further improvements in mass spectrometric analysis of pyrolysis gases caused the former to be dropped in favor of the latter. Mass spectrometric observations have been aided by providing better pumping, bake-out of the furnace tube in advance of pyrolysis, a horizontal furnace instead of vertical, and improved linear programming. Sample size was reduced from 10 mg. to 1 mg. for polybenzimidazoles. Methods of calibration were developed for both the very volatile and not so volatile products. An automatic data processing system was designed, and is nearly finished. Its inclusion in these experiments is expected to result in a vast increase in efficiency of converting the data to qualitative and quantitative analysis.		

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KEY WORDS

LINK A

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LINK C

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Polymer
Degradation
Mass Spectrometry
Polybenzimidazoles

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