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ENERGY OF ACTIVATION OF THE
DECOMPOSITION OF CELLULOSE NITRATE
BY AN EFFUSION PROCESS

JOHN F. HIGGINS

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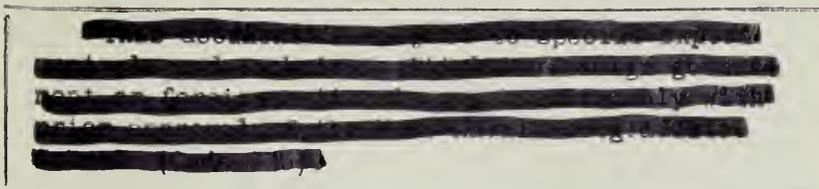
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John F. Higgins



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by

John F. Higgins

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Lieutenant, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE

United States Naval Postgraduate School
Monterey, California

1962

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This work is accepted as fulfilling
the thesis requirements for the degree of
MASTER OF SCIENCE

from the

United States Naval Postgraduate School

ABSTRACT

The energy of activation of the decomposition of cellulose nitrate was determined by extending the effusion technique to the study of decomposition. This technique was also used to measure the vapor pressure of picric acid over a temperature range just below its melting point, and the heat of sublimation of picric acid was computed.

The writer wishes to express his appreciation for the assistance and encouragement given him by Professor Carl A. Hering of the U. S. Naval Postgraduate School, and to Lieutenant Minoru Tanaka, Japanese Maritime Self Defense Force, for the translation of reports used in the research of this investigation.

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1. Introduction

The effusion process of measuring vapor pressure, as developed by Knudsen(8), has had wide application in the determination of vapor pressure of crystalline organic compounds in the pressure range of one micron to 200 microns. The effusion method is based upon the mass flow rate of gas through a small orifice. Organic crystals are placed in a capsule in which is drilled a small orifice. When the capsule is placed in an evacuated space, the crystals will sublime at a temperature below the melting point and the vapors effuse through the orifice. Measurement of the weight lost by the crystals over a period of time and knowledge of the orifice dimensions, along with several other parameters, allows determination of the vapor pressure of the compound at a particular temperature. Application of the Clausius - Clapeyron equation to the vapor pressure-temperature data, over a narrow range of temperatures, permits determination of the heat of sublimation of the compound.

The purpose of this undertaking was to evaluate the applicability of the process to those compounds which slowly decompose, rather than sublime. The compound selected for study was cellulose nitrate. The specific problem was to determine if the pressure exerted by the gaseous products of decomposition of this explosive may be considered proportional to the rate of decomposition of the compound, and the energy of activation of decomposition determined by using the Arrhenius equation. This value has been determined by other methods (9) (16) with fairly consistent results.

2,4,6, trinitrophenol (picric acid) was originally considered as a suitable material for testing and calibration of the apparatus, and refinement of technique because its vapor pressure approximated the

predicted pressure of the decomposition gases of cellulose nitrate. Some investigation revealed, however, that very little reliable information was available on the vapor pressure of picric acid. It was therefore decided to make additional determinations on picric acid over a range of temperatures so that the heat of sublimation might be calculated.

The author's general interest in this field is due to the work done at the U. S. Naval Postgraduate School by Kirschke on 2, 4, 6, trinitrotoluene and 2, 4, 6 trinitroanisole (6). This report represents an attempt to extend that work to the study of decomposition of complex polymers at low pressures.

2. Theory

The flow of gases at high pressure through large openings is an example of fluid flow and is explained by the laws of fluid mechanics. At very low pressures, through openings whose linear dimensions are large compared to the mean free path of the molecules, flow is in the Knudsen regime and its study is greatly simplified. This regime of free-molecule flow is defined by the Knudsen number: the ratio of mean free path to the orifice linear dimension. When this ratio is greater than ten (13), free-molecule flow is in effect.

Consider two closed chambers separated by a wall of negligible thickness in which is drilled a small orifice. If one chamber is evacuated, and the diameter of the orifice is less than the mean free path of the gaseous molecules in the other chamber, the rate at which these molecules pass through the orifice is equal to the rate at which they strike unit area of the wall. The number of molecules of a gas that strike unit area in unit time is

$$\dot{V} = \frac{nv}{4} \quad (1)$$

where n is the number of molecules per unit volume and v is the arithmetic average velocity. The number of molecules per cubic centimeter may be expressed as

$$n = \frac{1}{k} \frac{P}{T} \quad (2)$$

where k is the Boltzmann constant, T is the absolute temperature and P is the pressure. Assuming a Maxwellian distribution of velocities, the arithmetic average velocity is

$$v = \left[\frac{8R}{\pi M} T \right]^{\frac{1}{2}} \quad (3)$$

where M is the molecular weight and R is the universal gas constant.

By use of equations (2) and (3), equation (1) may be written

$$\dot{V} = \frac{3.51 \times 10^{25} p}{(MT)^{\frac{1}{2}}} \quad (4)$$

where pressure is in microns and the temperature is in degrees Kelvin.

The mass of a single molecule is

$$m = \frac{M}{N_A} \quad (5)$$

where N_A is Avogadro's number. The product of (4) and (5) represents the mass in grams of the vapor striking unit area per unit time:

$$w = 58.3 p \left(\frac{M}{T} \right)^{\frac{1}{2}} \quad (6)$$

The pressure on the high pressure side of the orifice is then

$$p = \frac{1.71 \times 10^4}{A t} W \left(\frac{T}{M} \right)^{\frac{1}{2}} \text{ microns} \quad (7)$$

where A is the area of the orifice in square centimeters, t is the time in seconds, and W is the mass in grams of the gases which have effused through the orifice in time t.

Equation (7) is only valid when the low pressure side of the wall is effectively at zero pressure. Equation (1) considers molecules striking the wall, or passing through the orifice, from only one direction. In actual practice, however, the pressure in the evacuated chamber may be significant compared to the high pressure side and in this case the net transfer of gases must be considered. Equation (1) may be expressed as

$$\dot{V} = \frac{v}{4} (n_1 - n_2) \quad (1a)$$

where n_2 is the number of molecules per unit volume on the low pressure side of the wall. Carrying this factor through the above derivation, equation (7) is modified to

$$p = \frac{1.71 \times 10^{14} W}{A \times t} \left(\frac{T}{M} \right)^{\frac{1}{2}} + p_s \quad (7a)$$

where p_s is the pressure on the evacuated side of the wall.

This theory is directly applicable to the measurement of vapor pressures of organic crystals that sublime. The compound whose vapor pressure is to be measured is placed in the capsule, and the capsule placed into a chamber which is then evacuated. Within a short period of time the pressure in the capsule will be the equilibrium vapor pressure of the compound at that temperature. The gaseous molecules effuse through the orifice, resulting in a net loss of weight of the compound. Determination of the weight loss and knowledge of the other parameters of equation (7a) allow the determination of the vapor pressure of the compound. Repeating this procedure over a narrow range of temperatures allows determination of the vapor pressure at each temperature. Assuming that the Clausius-Clapeyron equation is applicable, and that the heat of sublimation is constant over the range of temperatures investigated, there is a straight line relationship between the log of the vapor pressure and the reciprocal absolute temperature. The slope of this line is directly proportional to the heat of sublimation of the compound.

Application of this theory to the study of cellulose nitrate, and other compounds which decompose rather than sublime, is not a straightforward problem. The effusion process has been used in the study of lithium hydroxide (4) and other such compounds where the dissociation is a simple process and only one gas is evolved. In the case of cellulose

nitrate, however, the molecules which effuse through the orifice are not molecules of cellulose nitrate, but are the gases of decomposition of this complex molecule. The hypothesis tested was that the average molecular weight of these gases could be used in equation (7a) to determine the decomposition pressure of the compound. It was assumed that this pressure is proportional to the rate of decomposition. If a straight line relationship exists between the \ln of decomposition pressure and the reciprocal of the absolute temperature, the slope of this line would be tested to determine if it would give the energy of activation for decomposition by application of the Arrhenius equation. Although the mechanism of decomposition has been studied extensively, uncertainty exists as to its true nature: the definitive quantitative determination of the composition of the gases of decomposition remains to be done, but was considered beyond the scope of this investigation.

It is generally agreed that the initial step in the decomposition is a homolytic cleavage of the O-N bond of the nitrate group with the formation of nitrogen dioxide and an alkoxy radical (1) (11) (17). Robertson and Napper determined that the decomposition of cellulose nitrate is accelerated if oxides of nitrogen are left in contact with the decomposing material (10). In the presence of air or oxygen, nitric oxide which is evolved combines with the oxygen of the air to form nitrogen dioxide which catalyzes the decomposition (3). The amounts of nitric oxide, and of nitrogen dioxide, depend on the mass of the sample. The catalysis of the decomposition of cellulose nitrate depends both upon the concentration of the gases and upon the surface area of the material undergoing attack. Robertson and Napper determined that 25% of the nitrogen evolved was in the form of nitrogen dioxide and they suggested

that the balance was nitric oxide, with a trace of nitrogen probably present. Koehler and Marqueyrol, in a more complete study, investigated the decomposition at various temperatures over an extended period (7). Their results indicate a definite shift in the composition with temperature. At 100°C they reported a composition of 51.9% nitric oxide, 24.1% carbon dioxide, and about 15% carbon monoxide. The remainder was nitrous oxide, nitrogen and a trace of hydrocarbons.

An average molecular weight of the gases of decomposition may be calculated from the data of Koehler and Marqueyrol. Although immediate objections may be raised on the grounds that there is a shift in composition with temperature, and the average molecular weight may not be considered constant over the range of temperatures studied, this shift is not so marked as to be of great significance. A second point worth consideration is that the catalytic effect of some of the gases upon the mechanism of decomposition, and therefore upon the composition of the effusing gases, is not completely known. Fortunately, however, the ultimate effect of these factors is minimized. All the proposed gases of decomposition vary in molecular weight from 28 to 46: therefore, fairly significant errors in the actual proportions of the effusing gases will tend to be masked, particularly since only the square root of the molecular weight appears in equation (7a).

3. Apparatus

The theory previously discussed indicates that the basic or minimum equipment required in vapor pressure determinations by the effusion process is a box or capsule with an orifice of known size, a closed vacuum system, and a means of maintaining a constant temperature. Practical considerations, however, dictate an assemblage similar to that of figure 1.

The capsules used were machined from brass and designed with a very fine thread to ensure a tight seal (figure 2). The orifice was drilled into a 0.001 inch brass shim and the shim was soldered over the hole in the box.

The flask was fabricated from two sections of standard three inch flanged Pyrex pipe. The bottom pipe was closed at a depth of about four inches to provide the base; the top was necked down at a height of about eight inches to accommodate the ground glass joint for connection to the vacuum system. The flanges and bolts were of aluminum with hard rubber inserts. A number of gasket materials were tested; most satisfactory at the pressures and temperatures of test conditions was the Neoprene type R-2, produced by Corning Glass Works.

Depending upon the temperature at which the run was made, either a water bath or a furnace was used to maintain constant temperature. The water bath was a Blue M Magni-Whirl Visibility Jar Bath, manufactured by the Blue M Electric Company. With its integral heater, controller and stirrer, it maintained temperatures within $\pm 0.1^{\circ}\text{C}$ at temperatures as high as 86°C . At temperatures in excess of this, an electric furnace was used. The cylindrical cavity of the furnace (figure 3) was about eleven inches deep and eight inches in diameter. This allowed almost complete immersion of the flask in the furnace. The flask was surrounded on all

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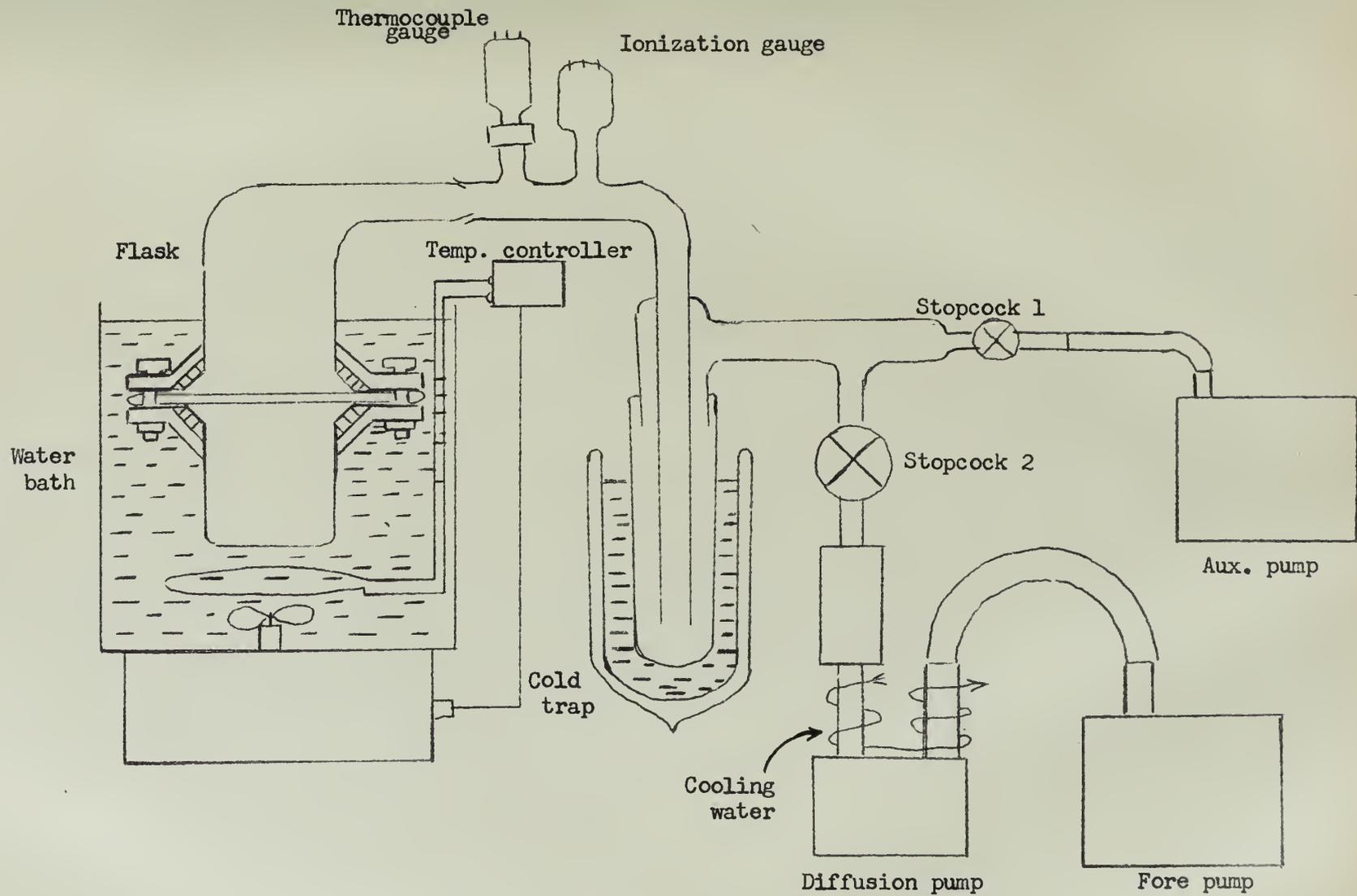


Figure 1. Schematic of System

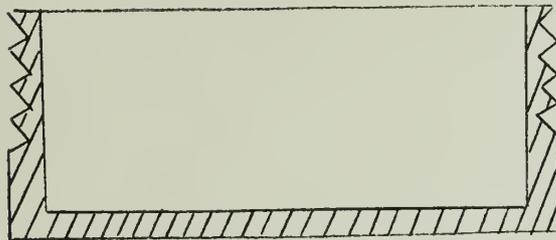
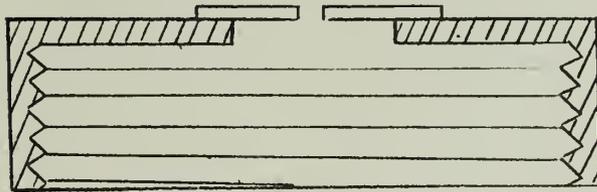
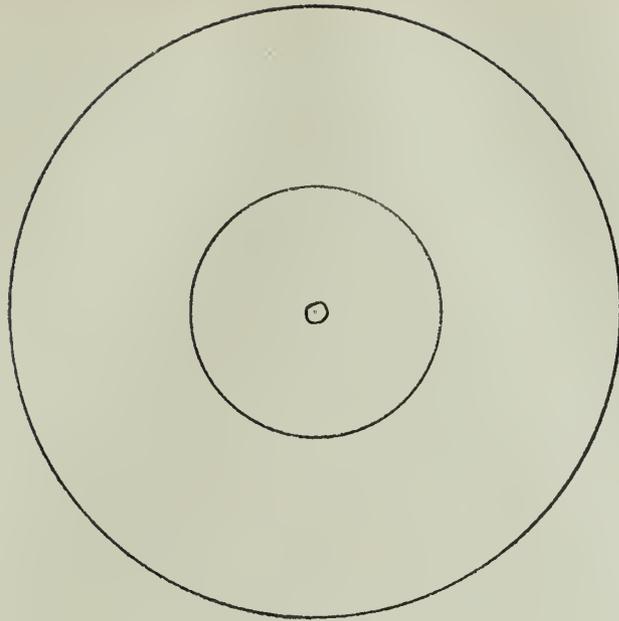


Figure 2. Capsule and Orifice

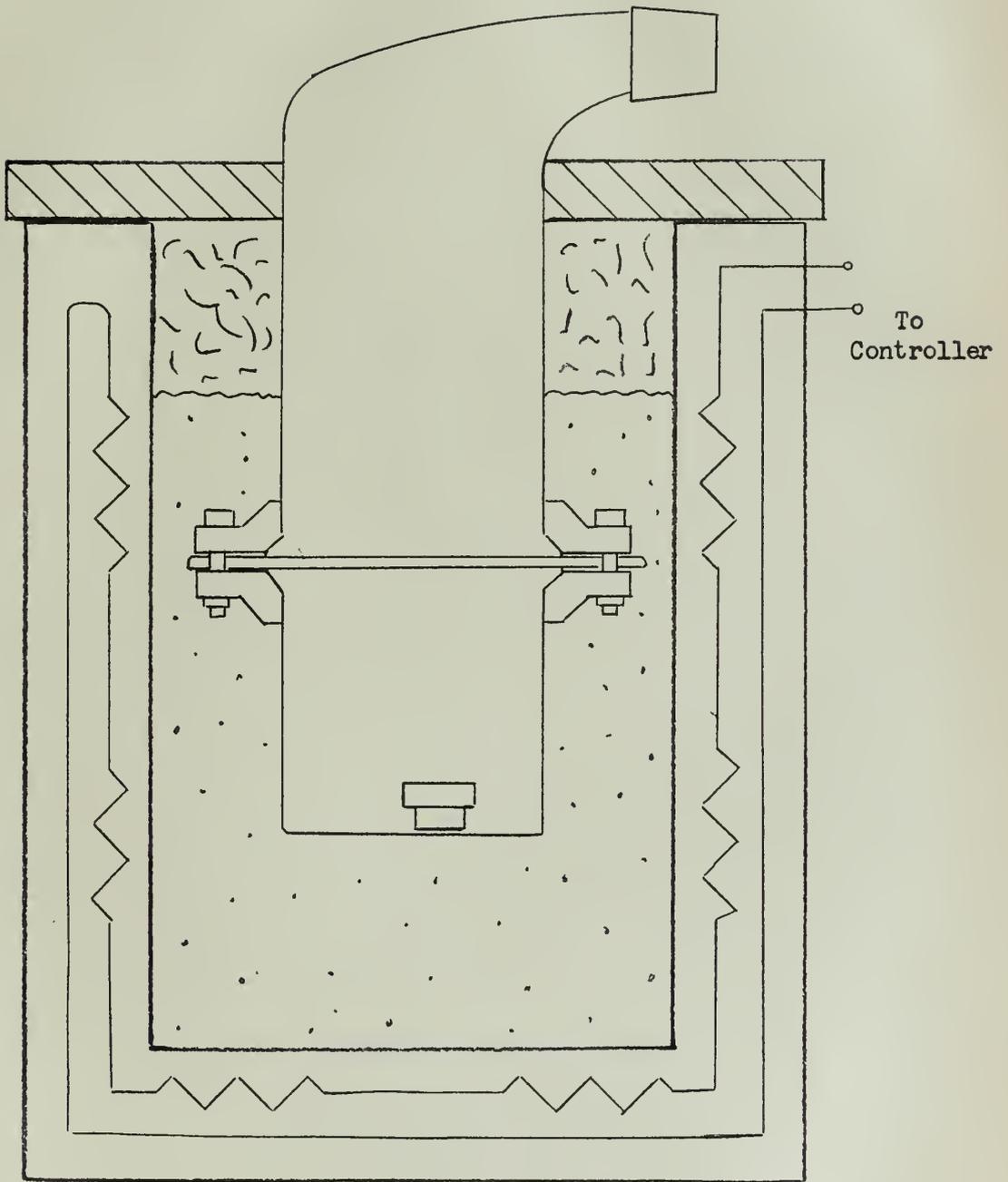


Figure 3. Furnace Assembly

sides, to within two inches of the top of the furnace, with sand to insure more uniform heat transfer. The top two inches were packed with insulation material. A cover of asbestos one inch thick, cut to the contour of the flask, sealed the furnace. Furnace temperature was controlled by a Leeds and Northrup Series 60 Control Unit and temperature was maintained within about $\pm 1.0^{\circ}\text{C}$.

The glassware used was that designed and fabricated by Kirschke. It is of relatively simple construction, has a minimum of glass to glass fittings, and is reasonably accessible for cleaning. Glass to glass joints and stopcocks were sealed with Apiezon N grease. This proved superior, from the viewpoint of ease of handling and cleaning, to other high vacuum greases.

In order to shorten, as much as possible, the period during which pressure is reduced from atmospheric to the ultimate operating pressure, mechanical pumps of considerable capacity are required. This is particularly true in the case of the auxiliary pump which must reduce pressure from atmospheric to below 100 microns in the minimum time, and which takes suction on the small passage through stopcock 1. For this purpose a Welch Duo-Seal 1405 two stage rotary mechanical pump, rated at 58.2 liters per minute, was used. A similar pump was coupled with the diffusion pump, a Distillation Products Company VFM 20-01 water cooled pump rated at twenty liters per second. The diffusion pump was connected to the system by a three inch section of heavy walled vacuum tubing. A similar piece of tubing was used to connect the diffusion pump to the fore pump.

The cold trap shown in figure 1 contained liquid nitrogen. It served to condense any condensable vapors in the system, allowing realization of a lower ultimate system pressure.

The thermocouple gauge was a National Research Corporation gauge type 501. It was connected to the system using the fitting designed by Kirschke and sealed by an "O" ring. An NRC ionization gauge type 507, of soft glass, was sealed to the system in the position indicated in figure 1, by a graded platinum seal. Used in conjunction with these gauges was an NRC Thermocouple and Emission Regulated Ion Gauge Control, Type 07 -1031-01.

4. Procedure

a. Preparation of samples

Commercially pure picric acid was dissolved in hot water and filtered, and the filtrate cooled to precipitate the solid. The solid was washed with distilled water then placed in a vacuum oven to dry. Three small samples were removed for melting point determinations. Recrystallization was carried out a second and third time until a constant melting point was observed. The picric acid was dried at 105°C under a vacuum of about 20 inches of mercury and then placed in a dessicator until testing.

The cellulose nitrate was prepared from commercial spun cotton by standard laboratory methods, and was washed with distilled water at least four times. It was baked out in a vacuum oven at 105°C under a vacuum of twenty inches of mercury; the cellulose nitrate was then stored in a dessicator. The nitrogen content was 13.1%, determined by a standard nitrometer test.

b. The Experimental run

The sample to be tested was removed from the dessicator, and weighed in the brass capsule. The average sample mass was approximately forty milligrams in the case of picric acid, and 100 milligrams in the case of cellulose nitrate. The capsule was placed in the bottom half of the flask, and the gasket was added, and the two halves of the flask were bolted together. The flask was then placed in the water bath (or the furnace) and allowed to reach test temperature. This generally took about thirty minutes for the water bath and about two hours when the furnace was used.

Prior to connecting the flask to the system, both mechanical pumps and the diffusion pump were warmed up. Stopcocks 1 and 2 were both closed during this period. Meanwhile the gauge control was turned on and the thermocouple was placed on filament.

To begin the run, the flask was connected to the system, ensuring proper seating of the ground glass joint. Stopcock 1 was opened to allow the auxiliary pump to take suction on the system. As soon as the pressure began to drop, as indicated by the thermocouple gauge, the cold trap was filled with liquid nitrogen. Within a period of less than one minute, when a system pressure of less than 100 microns was indicated, stopcock 2 was opened, cutting in the diffusion pump. When the pressure had dropped to ten microns, about twenty seconds later, stopcock 1 was closed and the auxiliary pump was shut down. Simultaneously the ionization gauge was outgassed for a period of five minutes prior to being placed in the run position (20).

The first accurate pressure reading that could be made with the ionization gauge was between six and seven minutes after evacuation had been initiated. This first reading was usually in the range of 0.1 to 0.2 microns. From this point until the completion of the test the pressure dropped slowly, usually to the range of 0.04 to 0.005 microns after four hours. An average pressure was determined and used in the calculations. Pressure and temperature were recorded at regular intervals during each run. When using the water bath, it was possible to maintain the temperature within $\pm 0.1^{\circ}\text{C}$; when the electric furnace was used, it was possible to maintain the temperature within about $\pm 1.0^{\circ}\text{C}$.

Liquid nitrogen was added to the cold trap periodically to keep the level at about eight inches above the bottom of the trap to ensure that condensable vapors entered the trap before condensing, but yet did not reach the diffuser.

On the completion of the run the ionization gauge and gauge control were turned off. Stopcock 2 was closed and the diffusion pump was turned off (the fore pump was left running as was cooling water to the diffuser until the diffusion pump had cooled down). Vacuum was relieved by admitting air through a drying column which had been attached to the tubing from stopcock 1. The flask was removed from the system and disassembled. The capsule was then placed in a dessicator to cool prior to reweighing.

c. Orifice size and measurement

Orifice size should be small compared to the diameter of the flask: further, it must be small compared to the mean free path of gases effusing through the orifice.

The mean free path of gaseous molecule may be expressed as

$$L = \frac{1}{\sqrt{2} N S^2} \quad (8)$$

where S is the molecular diameter in centimeters and N is the number of molecules per cubic centimeter.

Molecular diameter is expressed as

$$S = \left[\frac{2.71 \times 10^{-21} \sqrt{MT}}{\eta} \right]^{\frac{1}{2}} \quad (9)$$

where η is the viscosity in poise. The main gaseous product of decomposition is nitric oxide: its diameter at an assumed temperature of 300°K is

$$S = \left[\frac{2.71 \times 10^{-21} \sqrt{30 \times 300}}{188 \times 10^{-6}} \right]^{\frac{1}{2}} = 3.71 \times 10^{-8} \text{ cm.}$$

From the standpoint of molecular structure, cellulose nitrate is similar to glyceryl trinitrate. Since the vapor pressure of glyceryl trinitrate is 0.8 microns at 300°K(18), we might expect the decomposition pressure of cellulose nitrate to be not greater than this value at that temperature.

Using the Ideal Gas Law,

$$\frac{n}{v} = \frac{p}{RT}$$

$$\frac{n}{v} = \frac{(0.8 \times 10^{-3})/760}{(82.057)(300)} = 4.28 \times 10^{-11} \frac{\text{moles}}{\text{cc}}$$

$$\begin{aligned} N &= 4.28 \times 10^{-11} \frac{\text{moles}}{\text{cc}} \times 6.02 \times 10^{23} \frac{\text{molecules}}{\text{mole}} \\ &= 25.8 \times 10^{12} \frac{\text{molecules}}{\text{cc}} \end{aligned}$$

Substituting this value in equation (8),

$$L = \frac{1}{\sqrt{2} \pi (25.8 \times 10^{12}) (3.7 \times 10^{-8})^2} = 63.5 \text{mm.}$$

Past investigators (5) (12) have reported that an orifice whose diameter is approximately one percent of the mean free path has proven satisfactory. Therefore a nominal orifice size of one millimeter was chosen. This corresponds to a Knudsen number of about 60.

Because of the difficulty in drilling through a shim 0.001 inches thick, microscopic examination revealed that the orifice was not perfectly circular, but was very slightly out of round. A Gaertner Scientific Company Comparator was used to determine orifice diameter. The diameter was measured every ten degrees and an average diameter was used to determine orifice area.

d. Cleaning the equipment

On the completion of each run, the cold trap and flask were rinsed with soap and water and then filled with acid dichromate cleaning solution, to remain overnight. On removing the cleaning solution, the flask and cold trap were washed with fresh water and laboratory detergent, triply rinsed with distilled water, and twice rinsed with acetone. These parts were then heated in an oven at 150°C for a period of at least two hours. The gasket was washed with laboratory detergent and fresh water and thoroughly rinsed with distilled water.

The remainder of the glassware was usually cleaned without disassembling. The branch holding the gauges and the inner wall of the cold trap were scrubbed with a long-handled test tube brush and a solution of laboratory detergent and hot water. Several rinsings with distilled water followed. Final cleaning was accomplished with laboratory tissues soaked in acetone.

After each test the metal capsule was washed with laboratory detergent and fresh water, rinsed several times with distilled water and finally, twice rinsed with acetone.

It was not found necessary to clean the remainder of the glassware and the rubber tubing after each run. Periodically, however, the main piece of glassware was cleaned following the same procedure as for the flask and cold trap. Care was taken to ensure that the dichromate cleaning solution did not come in contact with the metal parts of the pressure gauges. Rubber tubing was cleaned by immersion in a 0.1N solution of sodium hydroxide overnight, followed by repeated rinsings with distilled water.

e. Maintenance of vacuum and leak detection

Adherence to the cleaning procedures previously outlined would usually assure the attainment of satisfactory system pressures. Leak detection was accomplished in either of two ways; a spark coil leak detector, or an acetone spray. The leak detector can only be used on glassware. When leaks were suspected around grease-coated stopcocks or metal or rubber fittings, the area was sprayed with acetone and the gauge control unit was observed closely. Sudden changes in pressure indicated the presence of leaks. For a complete discussion of vacuum technique and leak detection, the reader is referred to Dushman (5).

Small leaks were temporarily stopped by using de Khotinsky cement. When properly cleaned and greased, ground glass joints and stopcocks did not leak. The heavy walled vacuum tubing between the glassware and the diffusion pump and between the diffuser and the fore pump proved perfectly satisfactory.

The part of the system most susceptible to leakage was the gasket between the top and bottom halves of the flask. The flange must be bolted securely to ensure good seating of the gasket. At temperatures in excess of about 90°C, and under this compression, most gasket materials tested softened after extended use, and developed holes. The Neoprene R-2 gasket, mentioned earlier, best withstood the high temperature and compression. However, it too had to be replaced after about 12 runs. Because of the metal flanges, the spark leak detector could not be used for leak detection in the area of the gaskets. Continued spraying of acetone on the gasket can weaken the gasket structurally: the usual procedure, therefore, was to investigate all other parts of the system for leaks first. If none were found, the flask was disassembled and the gasket inspected, cleaned and replaced if necessary.

5. Results

Tables 1 and 2 include the data and calculated values of pressure made on each of 23 runs conducted during this investigation; of these, 14 were on picric acid and nine on cellulose nitrate. Additional runs were made on naphthalene and 2, 4, 6 trinitrotoluene to check the operation of the equipment and to refine experimental technique. Data from these runs are not included.

The data for each compound were analyzed by the method of least squares, assuming the pressure - temperature relationship over the range of temperatures studied was of the form of the Antoine equation:

$$\ln p = A - B/T$$

The equation obtained for picric acid by this method is:

$$\ln p = 38.05 - \frac{13740}{T}$$

where p is in microns and T in degrees Kelvin. This equation is shown graphically in figure 4.

Assuming applicability of the Clausius - Clapeyron equation, and a constant heat of sublimation over the range of temperatures studied, gives a heat of sublimation of 27.3 Kcal per mole for picric acid. Using vapor pressure data from various sources (18) (19) and assuming a constant heat of sublimation over the very wide temperature range of 140 degrees, a value of 25.2 Kcal per mole was calculated in a similar manner. It is to be noted that while the vapor pressure at 100°C in (19) is reported as 2.6 microns, a value of 3.4 is indicated in figure 4.

<u>Temp.</u> °K	<u>Time</u> sec	<u>Wt. Loss</u> grams	<u>Orifice Area</u> cm ²	<u>Ps</u> microns	<u>p</u> microns
341.0	14,400	0.0098	0.0135	0.03	0.14
344.8	15,000	0.0010	"	0.05	0.15
345.2	14,400	0.0019	"	0.04	0.21
351.6	28,800	0.0059	"	0.02	0.34
351.8	14,400	0.0030	"	0.06	0.39
351.9	14,400	0.0026	"	0.02	0.30
352.5	28,800	0.0083	"	0.04	0.49
356.2	11,400	0.0024	"	0.03	0.36
357.7	13,080	0.0042	"	0.03	0.54
358.1	20,600	0.0091	"	0.04	0.74
369.2	14,300	0.0256	"	0.10	2.98
369.5	18,000	0.0208	"	0.04	1.90
369.9	12,700	0.0238	"	0.07	3.08
371.2	19,100	0.0283	"	0.07	3.69

Table 1 - Data and Calculated Values of Vapor Pressure
for Picric Acid

<u>Temp</u> °K	<u>Time</u> sec	<u>Wt. loss</u> grams	<u>Orifice Area</u> cm ²	<u>Ps</u> microns	<u>p</u> microns
362.0	14,400	0.0026	0.0155	0.03	1.01
369.2	14,100	0.0031	"	0.10	1.30
369.9	12,700	0.0018	"	0.07	0.84
371.2	12,600	0.0040	"	0.07	1.79
378.1	21,600	0.0054	"	0.07	1.45
378.8	17,700	0.0063	"	0.04	2.00
384.2	25,200	0.0116	"	0.07	2.63
386.5	11,300	0.0079	"	0.03	3.90
395.0	11,400	0.0080	"	0.10	4.02

Table 2 - Data and Calculated Values of Decomposition

Pressure for Cellulose Nitrate

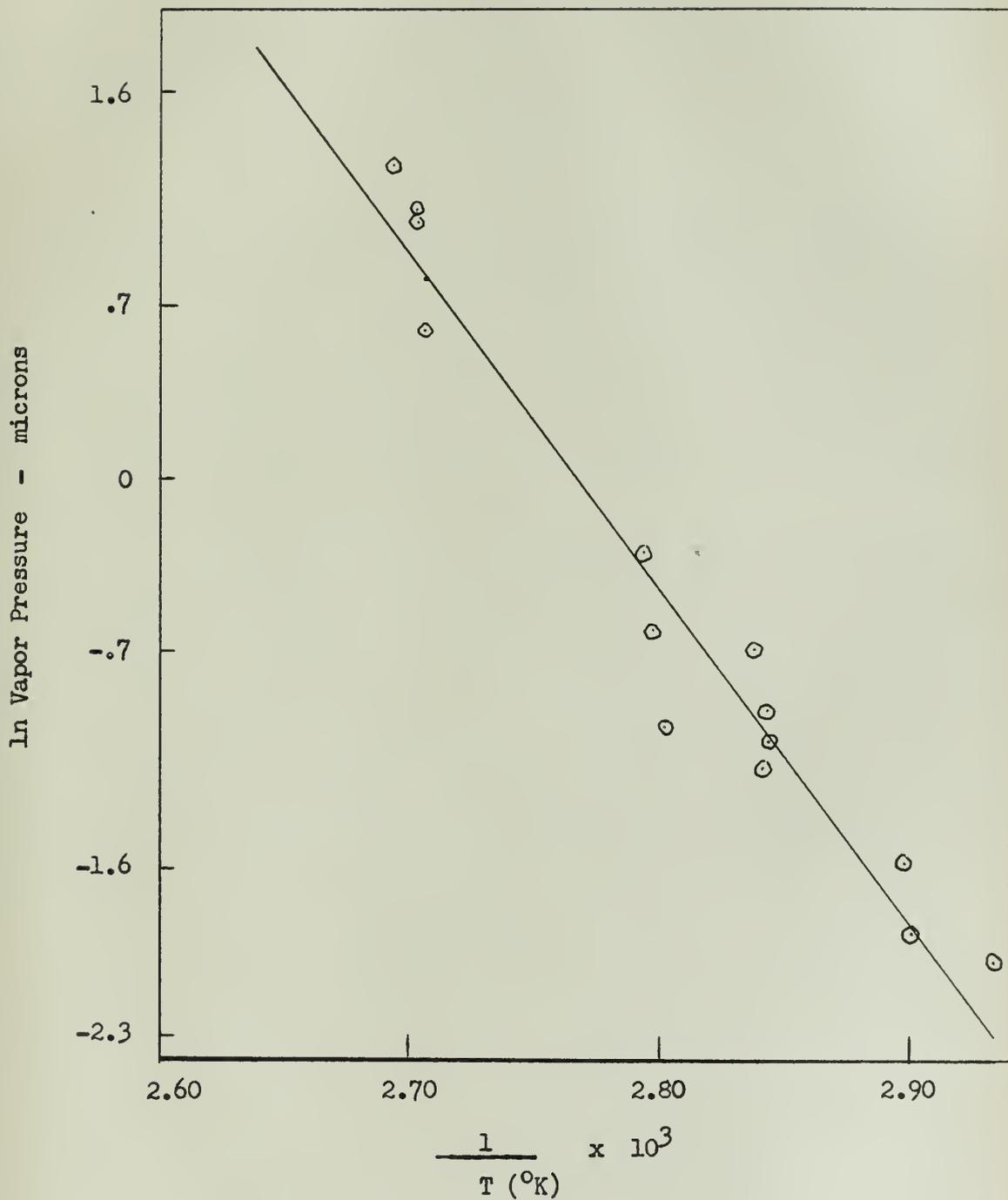


Figure 4. Picric acid

Figure 5 illustrates that for cellulose nitrate the relationship between temperature and decomposition pressure is similar to the temperature - vapor pressure relationship of compounds which sublime. Although experimental scatter is somewhat greater than is the case for picric acid, a least mean squares analysis gives the equation

$$\ln p = 18.37 - \frac{6700}{T} .$$

These data were calculated using an average molecular weight determined from the results of the investigation of Koehler and Marquoyrol. At 100°C, they reported the following percentages in the decomposition gases: NO, 62%; CO, 8.95%; N₂O, 3.51%; N₂, 6.32%; mixed hydrocarbons, .22%. The average molecular weight of these gases is 32.7 and this value was used in the calculations.

Testing the original hypothesis that the Arrhenius equation would in this case yield the energy of activation for the decomposition of cellulose nitrate, a value of 13.3 Kcal per mole is calculated. The significance of this figure, and the interpretation of its meaning, are more fully discussed in the following section. It is noted that a 20% change in the assumed average molecular weight used in the calculations changes the value of the slope by less than 10%.

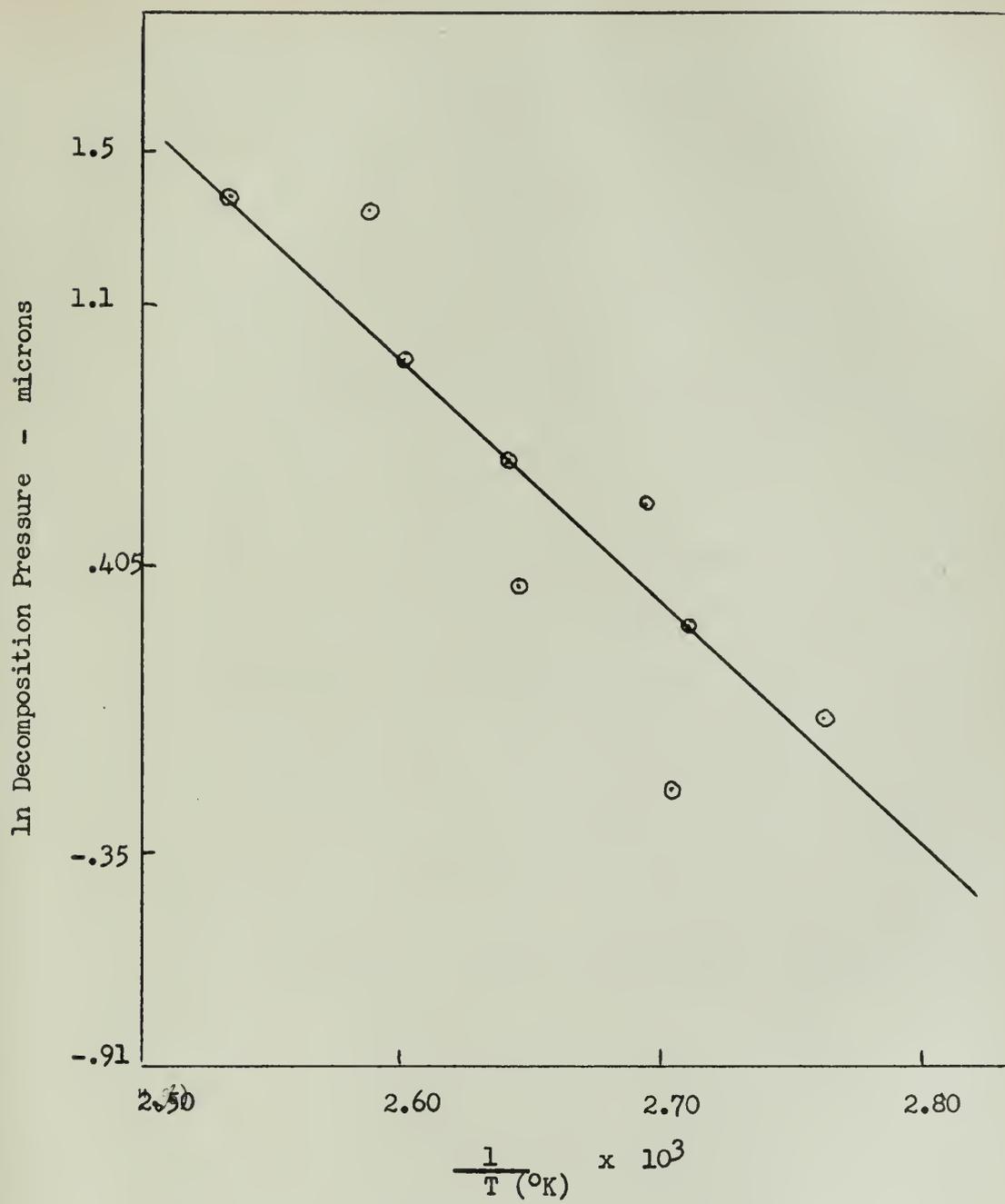


Figure 5: Cellulose nitrate

6. Discussion

The experimental scatter for the points in the investigation of picric acid indicates an acceptable degree of precision: the plot of figure 4 is, within close limits, collinear with the data from other sources (18) (19). Ordinarily, the effusion method is not considered applicable to measurement of vapor pressure less than one micron, below which value fall ten of the 14 points investigated. The effusion method has been extended to considerably lower vapor pressures by Balson (2), but the complexity of the additional equipment was considered prohibitive in this investigation.

The ultimate system pressure which can be attained with the pumping equipment used becomes an important factor at very low vapor pressures. Ideally, system pressure should be negligible to the number of significant figures to which the vapor pressure is measured. In measuring these low vapor pressures, the system pressure varied from 2% to 33% of the vapor pressure being determined. This may introduce some doubt as to the accuracy of the vapor pressure at these lower values and in the ultimate value of the heat of sublimation, since all points were weighted equally in the least mean squares analysis.

A great deal of care must be used in discussing and interpreting the data collected from the runs made on cellulose nitrate. Wilfong, Daniels, and Penner (17) determined the decomposition rate of cellulose nitrate by absorbing in sodium hydroxide the gases given off at 160°C and about one atmosphere. They analyzed for acidic decomposition products, which were mainly oxides of nitrogen, and concluded that the rate of decomposition of cellulose nitrate was proportional to the rate at

which acidic oxides of nitrogen were absorbed, as determined by analysis with potassium permanganate and sodium thiosulfate. The log of this rate was plotted against reciprocal absolute temperature: the slope of the straight line obtained was multiplied by the universal gas constant to give the energy of activation for decomposition. This value they reported as 46,700 calories per mole. Furthermore, they interpret the results of their experiment as relating to the single O-N bond of the nitrate group. Phillips, Orlick, and Steinberger (9) investigated the problem by study of weight loss and by infrared investigation of the residue of a decomposed sample of cellulose nitrate and reported a value similar to that of the earlier investigators, 45,000 calories per mole.

There is, however, a very real degree of ambiguity in the concept of a mole of a polymer. It may be inferred that the mole referred to is the repeating $(C_6H_7O_4N_3)$ unit. It would seem there is a greater precision of terminology in the value determined by Watanabe. In this latter case the energy of activation is reported as 27,000 calories per mole of $-ONO_2$ (14). Although Watanabe's method of reporting seems the more logical, there is no apparent quantitative correlation between his results and that of the earlier investigators, nor is there any apparent correlation between the value determined by the present investigation and either of those values. This suggests that not only does the composition of the gases of decomposition shift with temperature, but that there are competing mechanisms in the decomposition, one or another of which takes precedence at various temperatures. There is no concrete evidence to support this contention: it is offered as one possibility to explain the unusual spread in the values reported. It is worth noting here that not only has it been reported that decomposition is a complex function of nitration

time, but there is evidence to suggest that the primary nitrate groups decompose more readily than the secondary ones (15).

It may well be most precise therefore, to report the results of this experiment as 13,300 calories per mole of activated complex, ignoring the all too obvious fact that the activated complex has not been defined. It is difficult to draw any precise conclusions regarding the applicability of the effusion method to the study of the decomposition of complex polymers. It is not beyond the realm of possibility that, within limitations, all the different values reported are mutually correct. The key to the problem lies in a greater understanding of the mechanism of the decomposition. Not until this process is fully understood can an attempt be made to correlate, or to discount, the conflicting values reported.

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