

SELECTED THERMODYNAMIC FUNCTIONS
OF
ETHYL CHLORIDE

A Thesis
Presented to
the Faculty of the Graduate School
University of Houston

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

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by

Eugene Gregory Suklars, B. S.

August, 1952

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**SELECTED THERMODYNAMIC FUNCTIONS
OF
THIONYL CHLORIDE**

**An Abstract of a Thesis
Presented to
the Faculty of the Graduate School
University of Houston**

**In Partial Fulfillment
of the Requirements for the Degree
Master of Science**

**by
Eugene Gregory Szklarz, B. S.
August, 1952**

The compound thionyl chloride when heated above the region of 500°K will undergo dissociation to a measurable degree. The reaction



is presumed to take place.

In this investigation a carefully purified sample of thionyl chloride was prepared and was found to boil at 76.5°C.

Samples of the thionyl chloride were heated in an all Pyrex apparatus and their pressures were measured with the aid of a Bourdon type sickle gauge. From these pressures it was possible to calculate the equilibrium constant at several temperatures. The equilibrium constant in turn made the calculation of ΔF° possible. The enthalpy change was determined by plotting the van't Hoff equation and measuring the slope of the line.

TABLE OF CONTENTS

TABLE OF CONTENTS

Part I

Introduction and Statement of the Problem	1
---	---

Part II

Description of Apparatus.....	5
-------------------------------	---

Part III

Preparation and Purification of Compound.....	14
---	----

Part IV

Experimental.....	15
-------------------	----

Part V

Summary and Conclusions.....	30
------------------------------	----

Part VI

Bibliography.....	32
-------------------	----

PART I
INTRODUCTION
AND
STATEMENT OF THE PROBLEM

This investigation deals with the determination of the dissociation constant of the substance thionyl chloride. The ΔF^0 is calculated from the constant and the change in entropy is derived from the value of the constant at different temperatures.

The molal free energy of a gas approaches an infinite negative value as the pressure approaches zero. In order to have a manageable function, G. N. Lewis invented another measure of escaping tendency, which is called the fugacity (1). We may partially define the fugacity, f , in terms of the molal free energy, F , through the equation

$$F = RT \ln f + B(T), \quad (I)$$

where $B(T)$ is a function of temperature alone and therefore a constant at a single temperature.

Between two isothermal states, the equation becomes

$$F_B - F_A = RT \ln \frac{f_B}{f_A}. \quad (II)$$

G. N. Lewis introduced another useful term, the activity (2). The activity, a , being the ratio between the fugacity f of a substance in some given state, and its fugacity f^0 in some standard state. The activity in any state is given by the equations

$$a = \frac{f}{f^0}; \quad F - F^0 = RT \ln a; \quad (III)$$

Consider a general reaction in which m mols of substance M and n mols of substance N , etc., give q mols of substance Q etc., as represented by the equation



Let ΔF be the free energy change in this reaction when the substances are in any given states,

$$\Delta F = (cF_c + rF_r + \dots) - (mF_M + nF_N + \dots), \quad (\text{IV})$$

and let ΔF^0 be the free energy change when each substance is in its standard state,

$$\Delta F^0 = (cF_c^0 + rF_r^0 + \dots) - (mF_M^0 + nF_N^0 + \dots). \quad (\text{V})$$

If a_M , a_N , etc., represent the activities in the non-standard states, then we have

$$m(E_M - E_M^0) = RT \ln a_M^m \quad (\text{VI})$$

and so on.

Combining the several equations we find

$$\Delta F - \Delta F^0 = RT \ln \frac{a_c^c a_r^r \dots}{a_M^m a_N^n \dots} \quad (\text{VII})$$

Whenever we meet with equilibrium we have important information, namely, that the free energy is equal to zero. Hence at equilibrium, equation (VII) becomes

$$\Delta F^0 = -RT \ln \frac{a_c^c a_r^r \dots}{a_M^m a_N^n \dots} \quad (\text{VIII})$$

At a given temperature ΔF^0 is a constant; it follows that the activity quotient also is a constant and may be designated as K .

The great majority of equilibrium measurements have been made at moderate pressures and dilute aqueous solutions. In such cases it is frequently possible, with adequate accuracy, to replace the activities with pressures in the case of gases

and molalities in the case of solutions. Expressed in this manner the "mass law" is evidenced in the form which we owe to Guldberg and Waage(3) and to van't Hoff(4). The well known equation of van't Hoff,

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad (\text{IX})$$

or in another form,

$$\frac{4.5757 d \log K}{d(1/T)} = - \Delta H, \quad (\text{X})$$

allows us to calculate the ΔH of the reaction should we plot $-R \ln K$ against $1/T$ and measure the slope of the curve.

Thionyl chloride (sulfurous oxychloride) is a colorless liquid at room temperature and has a specific gravity of 1.638(5). The boiling point of thionyl chloride is frequently given to be 78.8°C (5)(6)(7). However, there is reason to believe that the boiling point is in the region of 76.5°C (8)(9).

Thionyl chloride may be prepared by several reactions. J. Persoz and N. Block(10) are credited to be the first to have prepared thionyl chloride from sulfur dioxide and phosphorus pentachloride according to the following reaction

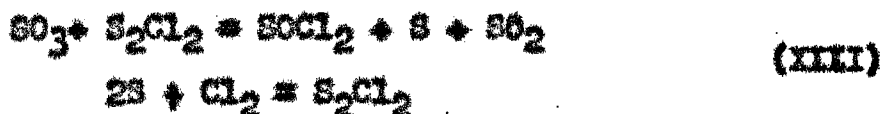


A preparation by the action of phosphorus pentachloride on the salts of sulfurous acid is analogous with the method for the preparation of organic acid chlorides,



One process consists in passing chlorine into a mixture of

SO_3 and S_2Cl_2 heated to $75^\circ - 80^\circ\text{C}$,



Sulfuryl chloride and phosphorus trichloride may also be the starting substances,



A more difficult reaction is one in which chlorine monoxide is passed into sulfur dissolved in sulfur monochloride. The solution is cooled to -12°C



Thionyl chloride decomposes when heated to a sufficiently high temperature according to the following(11)



Sulfur dioxide and chlorine will react to yield sulfuryl chloride; however, at 200°C or higher the reverse decomposition reaction is complete(12). The sulfur monochloride does not begin to dissociate below 300°C and the amount of dissociation is negligible appreciably above that temperature (13).

In this work a suitable apparatus was designed and constructed for the purpose of observing the dissociation constant of carefully prepared thionyl chloride samples. From the data obtained it was possible to arrive at the value of ΔH for the reaction. With the aid of this sort of data it is possible to obtain, by mere addition and subtraction, ΔF° and ΔH of other reactions with the use of standard thermodynamics methods.

PART II
DESCRIPTION
OF
APPARATUS

In Fig. 1 is shown an apparatus that was used in reacting sulfur dioxide and phosphorus pentachloride to obtain thionyl chloride and phosphorus oxychloride. The apparatus was constructed from 3 and 40 mm Pyrex tubing. Volume A had a capacity of approximately 25 cubic centimeters. The larger tube had 22 gage nichrome wire wound about it, followed by asbestos tape. The current input was regulated by means of a Variac.

Volume A was filled with phosphorus pentachloride and was heated by means of a predetermined setting of the Variac, so that the temperature was sufficiently high to distill the products. From a cylinder, SO_2 gas was passed into the apparatus at B. The products were collected in a bottle, protected from atmospheric moisture. The method of purification is discussed in a later section.

The pure thionyl chloride was transferred to a Pyrex manifold containing the sample capsules as shown in Fig. 2. Transfer of the purified material was made by evacuating the manifold to better than 10^{-5} millimeters of mercury and sealing off at A and breaking the sealed capillary in the purified thionyl chloride. The capillary was resealed. The sample capsules, containing the thionyl chloride, were removed with flame and sealed in the process of removal. A suitable length of capillary remained on the sample capsules.

The apparatus used in measuring the degree of dissociation of thionyl chloride is shown in Fig. 3. It con-

sisted mainly of a capsule well A, which was attached to a 1000ml flask B, whose pressure could be read with the use of a Bourdon type sickle gage. The ballast was made from a 500 ml Pyrex flask, its purpose was to facilitate the regulation of the manifold pressure.

A capsule was placed in the sample well followed by an iron bar sealed in glass. The tube was then sealed off at D after the system had been evacuated to better than 10^{-5} mm of mercury by means of a mercury diffusion pump. It is evident that the system thus sealed off allowed the sample to be in contact with no other material than Pyrex glass. The capillary on the capsule could then be broken with the glass sealed iron bar by the use of a magnet. The pressure that was developed caused the filament on the sickle gauge to deflect. The pressure in the manifold was increased by admitting air into it until the filament would return to its "rest position". The filament was sighted by a mounted cross-hair telescope. The pressure in the manifold was then measured with a mercury manometer.

To disassemble the apparatus, rubber tubing was connected from the bent tube above flask B to the stopcock on the extreme left hand side of the manifold as shown in Fig. 3. After the pressure in the manifold was regulated to be the same as the pressure in the sealed system, a capillary on the above mentioned bent tube was broken and the system allowed to come to atmospheric pressure.

These precautions were necessary to avoid large pressure differences across the sickle gauge, which necessarily must be fragile to be sensitive.

The method used in the construction of the sickle gauge will be explained with the aid of Fig. 5. A heavy walled test tube was shrunk with a sharp flame and blown to a bubble while it was gently drawn out. The resulting bubble was very thin walled, but was still rigid. With the use of a gentle flame a portion of it was callapsed until a sickle form was obtained. A sharp pointed flame was then directed on the sealed end of the sickled and a fine filament was drawn. The mouth of the test tube was then flared out to the dimensions of the tube it would be mounted in. It was then sealed in the tube in the same order as shown in the figure.

The part of the apparatus consisting of the 1000ml flask, sickle gauge and sample well were immersed in a cylindrical oven. The oven was constructed as shown in Fig. 4 from two cylindrical cans, insulated from one another by two inches of insulation. The smaller can had its inner surface coated with a quarter of an inch of plaster of Paris followed by a spiral of 22 gage nichrome wire which was covered by an eighth of an inch of plaster of Paris. The bottom of the oven had a nichrome wire helix stapled onto the underside of a one eighth inch asbestos sheet. The heating elements were regulated with two Variacs, The bottom element was used as a fine temperature control.

The temperatures were measured with a calibrated chromel
alumel thermocouple together with a Leeds Northrup potentio-
meter

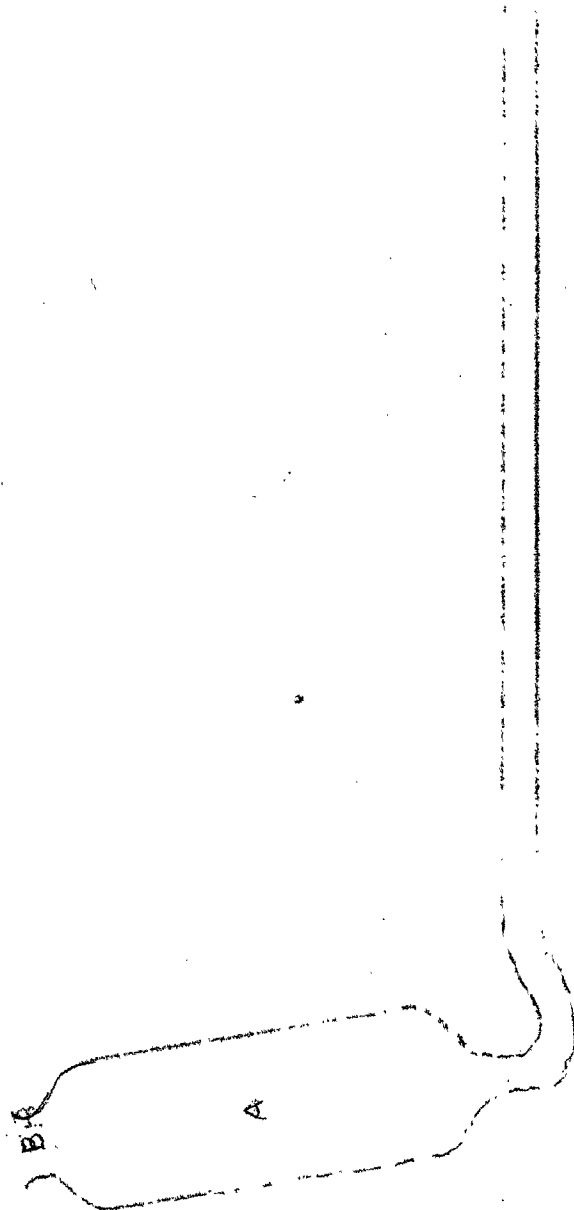


Fig. 1

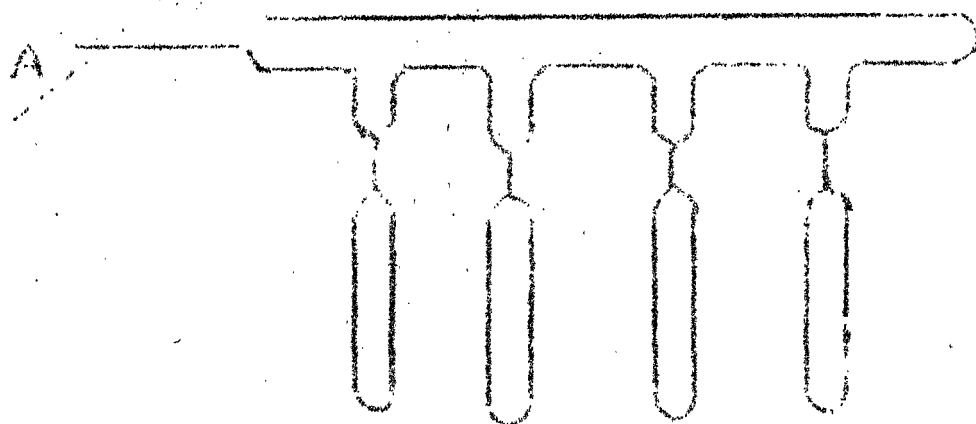


FIG. 2

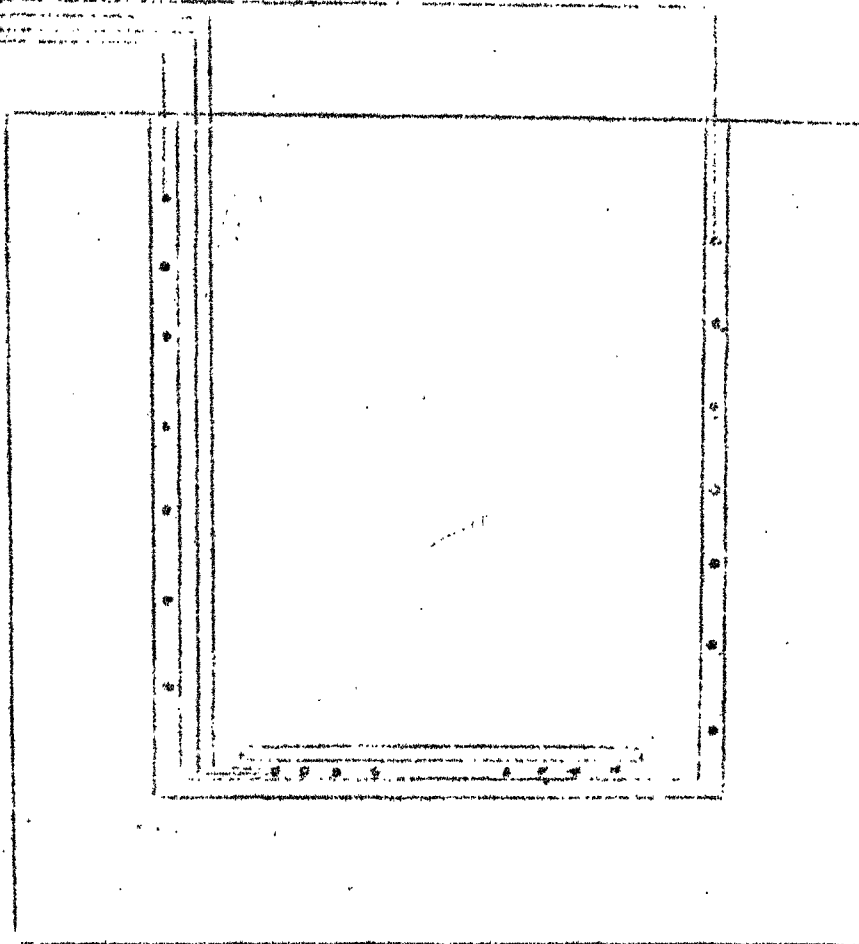


Fig. 4

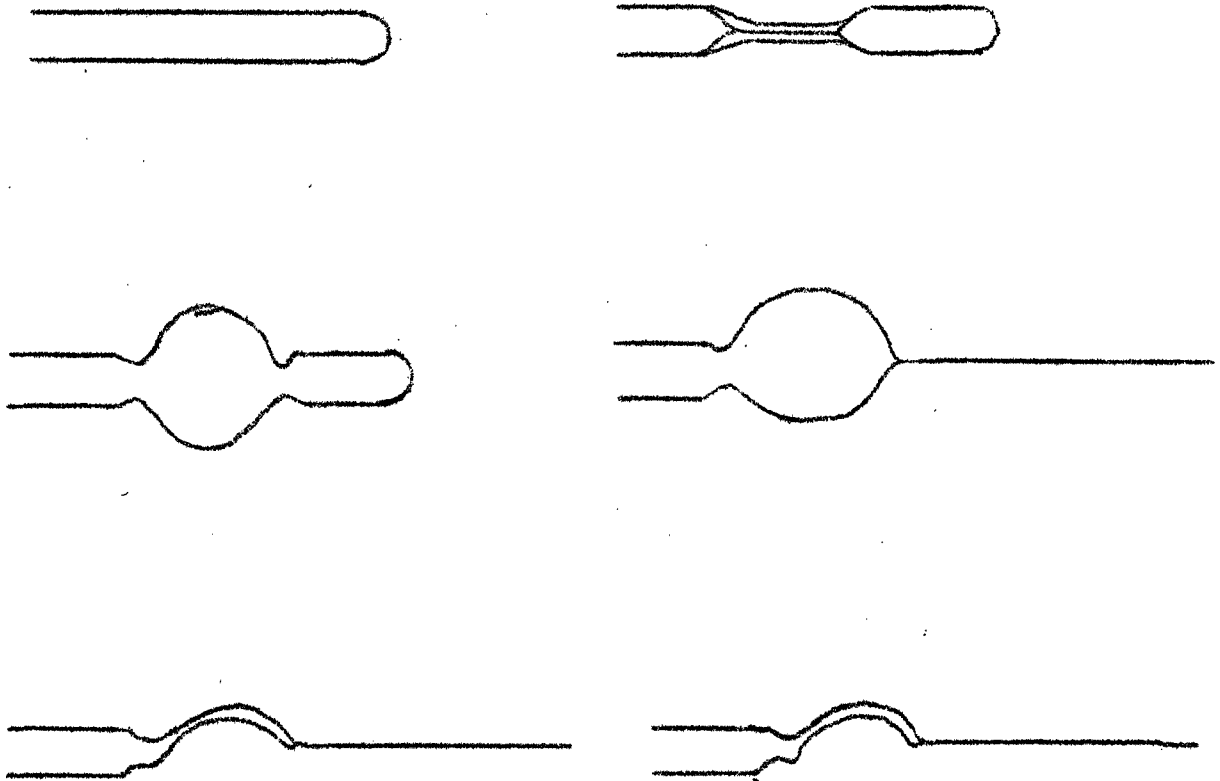


FIG. 5

PART XII
PREPARATION AND PURIFICATION
OF
COMPOUND

The mixture of thionyl chloride and phosphorus oxychloride that was prepared in the generator shown in Fig. 1 was partially purified with an ordinary laboratory still and was further purified with a Snyder fractionating column, according to the method described by D. L. Cottle(14). The fractionating system was equipped with an automatic take off head. The equipment was of all Pyrex construction and protected from atmospheric moisture.

There were taken 450 ml of product from the initial distillation together with 13 grams of flowers of sulfur and the mixture was refluxed for five hours. The mixture was then rapidly distilled through the Snyder Column. The product of distillation was straw colored. The distilled product was returned to the fractionating equipment, taking 14 hours to rid it of the colored forerun. The colorless product was then distilled over a very narrow range. The boiling point of the product was observed to be 76.5°C at a pressure of 760.3mm of mercury.

It is believed that any sulfuryl oxide present reacted with the sulfur during reflux to give sulfur dioxide and sulfur chlorides. The S_2Cl_2 which boils at 135.6°C was very likely left behind in the first distillation. The dichloride of sulfur was separated as the colored forerun, its boiling point being 69°C .

PART IV
EXPERIMENTAL

The sample capsules that were previously mentioned were weighed after they were detached from the manifold. The weighed sample capsule was then placed in the capsule well followed by the glass sealed iron bar. The apparatus was then evacuated and the Bourdon sickle gauge filament was indexed through the mounted cross hair telescope. The sample capsule capillary was broken after the apparatus had been sealed above it. An electromagnet and an Alnico magnet were used simultaneously to break the capillary. The electromagnet operated from an AC line therefore its field was pulsating. If the electromagnet and the permanent magnet were brought to the glass sealed iron bar, it would begin to chatter violently and with enough force to break the capillary. The manifold pressure was then regulated, with the aid of the sickle gauge to equal the pressure within the 1000 ml. flask. The pressure, P_n , of the manifold was read on the manometer by means of a meter stick. The oven temperature was read and as the oven temperature was permitted to rise, temperatures that were of importance were read together with barometric pressure, manifold pressure and time.

In order to establish the certainty of equilibrium, the oven was cooled and a reading was taken at a lower temperature. A high enough temperature could always be reached so that upon cooling the pressures at the lower temperature were not in agreement with previously taken readings. Each run was discontinued when this temperature was reached,

since above this temperature the reaction was not reversible.

The apparatus was disassembled at D and E. The sample tube was removed and weighed. From the weight difference, the weight of the thionyl chloride was determined.

The apparatus was reassembled, care being exercised that the original volume be retained. It is estimated that the volume certainly did not vary by more than one milliliter. In a total volume of more than 1000 ml, this volume change was considered negligible. It was now possible to make a succeeding run with the apparatus.

As the thionyl chloride was heated its temperature-pressure curve plotted into a straight line, as was expected, until dissociation began to take place.

Plots for the three runs are shown in Figs. 6, 7 and 8 and their experimental data are tabulated in tables 1, 2 and 3. The dissociation takes place in the region of 560°K .

The extension of the above mentioned straight line was used as an index to determine ΔP , or the pressure over and above the pressure expected were the curve to continue in a straight line.

The equation for the reaction is assumed to be equation XVI.

If the fraction which has reacted to the right in equation XVI is α then the number of moles of each substance in equilibrium ($4 - 4\alpha$) of SOCl_2 ; 3α of Cl_2 ; 2α of SO_2 ; and α of S_2Cl_2 .

Total moles at equilibrium would then be $4 - 2\alpha$. The ratio of the observed pressure to the calculated or expected pressure would be $(4 - 2\alpha)/4$. is calculated from this fraction. It is possible to determine the partial pressures of thionyl chloride, chlorine, sulfur dioxide and sulfur monochloride from the calculation of α .

From the definition of the equilibrium constant from equation VIII it was possible to make the calculation of K from the partial pressures of the constituent gases. More explicitly,

$$K = \frac{(P_1)^3(P_2)^2(P_3)}{(P_4)^4}$$

where 1, 2, 3 and 4 are chlorine, sulfur dioxide, sulfur monochloride and thionyl chloride respectively. Further

$$P_1 = 3\alpha P / (4 - 2\alpha)$$

$$P_2 = 2\alpha P / (4 - 2\alpha)$$

$$P_3 = \alpha P / (4 - 2\alpha)$$

$$P_4 = (4P - 4\alpha P) / (4 - 2\alpha)$$

The equilibrium constants were calculated for the three runs at several temperatures and the results are tabulated in table 4.

With the use of equation VIII the ΔF° for the reaction was calculated from the values of the equilibrium constant and are given in table 4.

Employing the very usable form of the van't Hoff equation, namely, equation X of the introduction, it was possible to calculate the change of enthalpy for the reaction. If one

plots of $-4.58 \log K$ against $1/T$, the slope should yield the enthalpy. The enthalpies thus calculated are given in the summary and their respective plots are in Figs. 9, 10 and 11.

TABLE I

Weight of sample 1A: 0.6523

Toven	Pm	Tm	IP	IPt	IPo	Pmo	Pobs	TK
26	669.0	26.2	764.3	25.6	761.1	666.2	94.9	299
75	654.8	26.2	764.3	25.6	761.1	652.1	109.0	348
109	643.6	26.3	763.9	25.6	760.7	640.9	119.8	302
102	620.1	26.7	763.8	25.5	760.6	617.6	143.0	455
201	614.0	26.7	763.8	24.5	760.6	611.5	149.1	474
223	608.0	26.7	763.8	25.4	760.6	605.5	155.1	496
170	623.9	26.7	763.8	25.3	760.6	621.4	139.2	443
145	632.4	26.8	763.8	25.3	760.6	629.7	130.9	418
123	638.8	26.6	763.8	25.3	760.6	631.6	124.5	396
218	610.3	26.8	764.3	25.3	761.2	607.7	153.5	491
242	602.1	26.9	764.9	25.3	761.2	599.6	161.6	515
218	609.5	26.7	764.3	25.3	761.2	606.9	154.3	491
183	620.8	26.5	764.3	25.3	761.2	618.2	143.0	456
260	595.6	26.8	764.3	25.3	761.2	593.1	168.1	533
212	612.1	26.7	764.3	25.3	761.2	609.5	151.7	485
279	591.2	26.5	764.3	25.3	761.2	588.8	172.4	552
215	611.8	26.3	765.7	25.0	762.6	609.3	153.3	488
277	592.1	26.5	765.7	25.0	762.6	589.7	172.9	590
306	581.1	26.5	765.7	25.0	762.6	578.8	183.6	579
230	607.4	26.7	765.4	24.9	762.3	604.8	157.5	503
324	574.4	26.7	765.0	24.8	761.9	572.1	189.9	597
286	588.5	26.5	765.0	24.7	761.9	586.1	175.8	599

TABLE I

T_{oven}	P_m	T_m	BP	BP _t	BP _o	P_{mo}	P_{obs}	T_k
341	568.0	26.7	764.7	25.0	761.6	565.7	195.9	614
288	586.8	26.8	764.7	24.8	761.6	584.5	177.1	561
323	574.5	26.8	764.7	24.8	761.6	572.1	188.7	596
366	566.2	26.8	764.7	24.8	761.6	554.0	204.6	639
292	580.7	26.5	764.7	24.8	761.6	578.4	183.2	565

TABLE II

Weight of sample 2A: 0.7242

Toven	Pm	Tm	IP	IP _g	IP _o	Pmo	Pobs	Tx
25	659.3	25.0	762.7	24.5	759.7	656.5	103.2	298
28	657.9	25.0	762.7	24.3	759.7	655.1	104.6	301
41	652.0	24.2	761.4	23.8	758.5	649.4	109.1	314
52	648.2	24.5	761.4	23.8	758.5	645.6	112.9	325
64	643.0	25.0	760.8	24.0	757.8	640.4	117.4	337
73	639.7	25.0	760.8	24.0	757.8	637.1	120.7	346
80	637.1	25.0	760.8	24.0	757.8	634.5	123.3	353
94	632.3	25.0	760.8	24.0	757.8	629.7	128.1	367
108	627.2	25.0	760.8	24.0	757.8	624.6	133.2	381
94	635.1	24.8	762.8	23.7	759.8	631.5	128.3	367
152	616.0	25.0	764.7	23.8	761.8	613.4	148.2	425
176	606.4	25.0	764.7	23.8	761.7	603.9	157.8	449
129	623.3	25.0	764.7	23.7	761.7	620.8	140.9	402
212	594.3	25.0	764.7	23.7	761.7	591.9	169.8	485
208	596.6	26.2	765.3	24.8	762.2	594.1	163.1	481
233	587.7	26.6	765.3	25.0	762.2	585.3	176.9	506
198	600.7	26.5	765.3	25.0	762.2	598.0	164.2	471
254	581.4	26.6	765.3	25.0	762.2	577.9	184.3	527
212	595.0	26.8	765.0	25.1	761.9	592.4	169.5	485
275	573.0	27.0	765.0	25.1	761.9	570.5	191.4	548
204	598.3	27.0	765.0	25.2	761.9	595.7	166.2	477

TABLE II

T_{oven}	P_m	T_m	BP	BP_t	BP_o	P_{mo}	P_{obs}	T_K
300	562.5	27.0	765.0	25.2	761.9	560.1	201.8	573
245	582.9	27.0	765.0	25.2	761.9	580.4	181.5	518
320	554.9	27.0	765.0	25.2	761.9	552.5	209.4	593
255	579.9	27.0	765.0	25.2	761.9	577.4	184.5	528
342	546.9	27.3	765.0	25.3	761.9	544.5	217.4	615
266	576.9	27.3	765.0	25.3	761.9	574.4	187.5	539

TABLE III

Toven	P _m	T _m	BP	BP _t	BP _o	P _{mo}	P _{obs}	T _K
51.0	679.5	23.8	764.8	23.0	761.9	696.8	65.1	324
100	688.9	24.0	764.8	23.0	761.9	686.2	75.7	373
138	681.9	24.0	764.3	23.0	761.4	679.3	82.1	411
213	663.9	25.3	763.1	24.0	760.1	661.2	98.9	486
262	652.9	25.5	763.0	24.0	760.0	650.2	109.8	535
282	648.4	25.7	763.0	24.0	760.0	646.1	113.9	555
300	644.9	25.8	762.8	24.0	760.5	642.2	117.6	573
318	639.2	25.8	762.8	24.0	758.8	636.5	122.3	591
327	637.2	25.7	762.7	24.0	758.8	634.5	124.3	600
343	633.4	25.7	762.7	24.0	758.8	630.7	128.1	616

Where P_m is the pressure read on the manometer;

T_m is the manometer temperature;

BP is the barometer reading

BP_t is the barometer temperature;

P_{mo} and BP_o are temperature corrected readings;

P_{obs} is the pressure in the manifold corrected.

FIG. 6

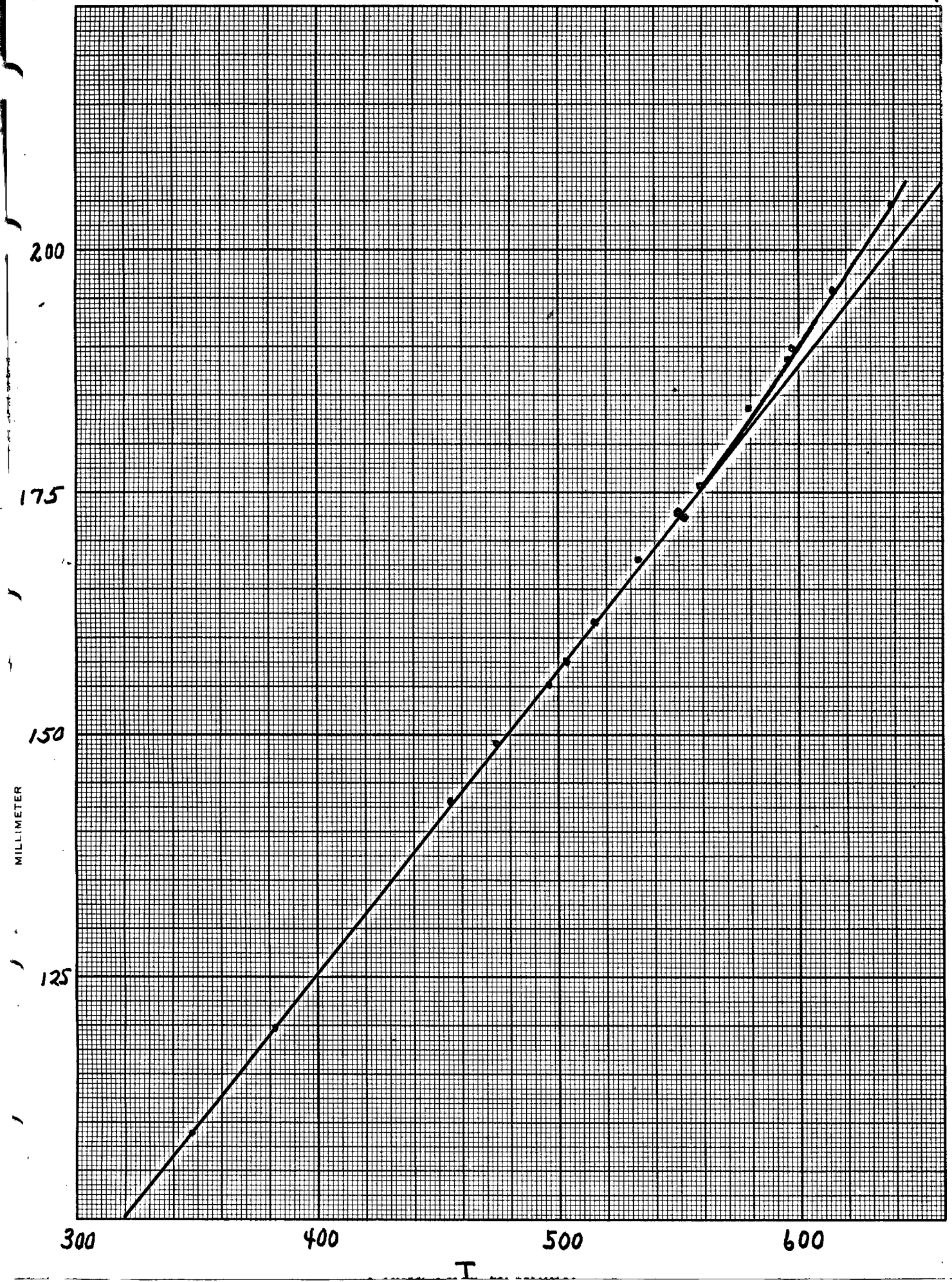


FIG. 7

29

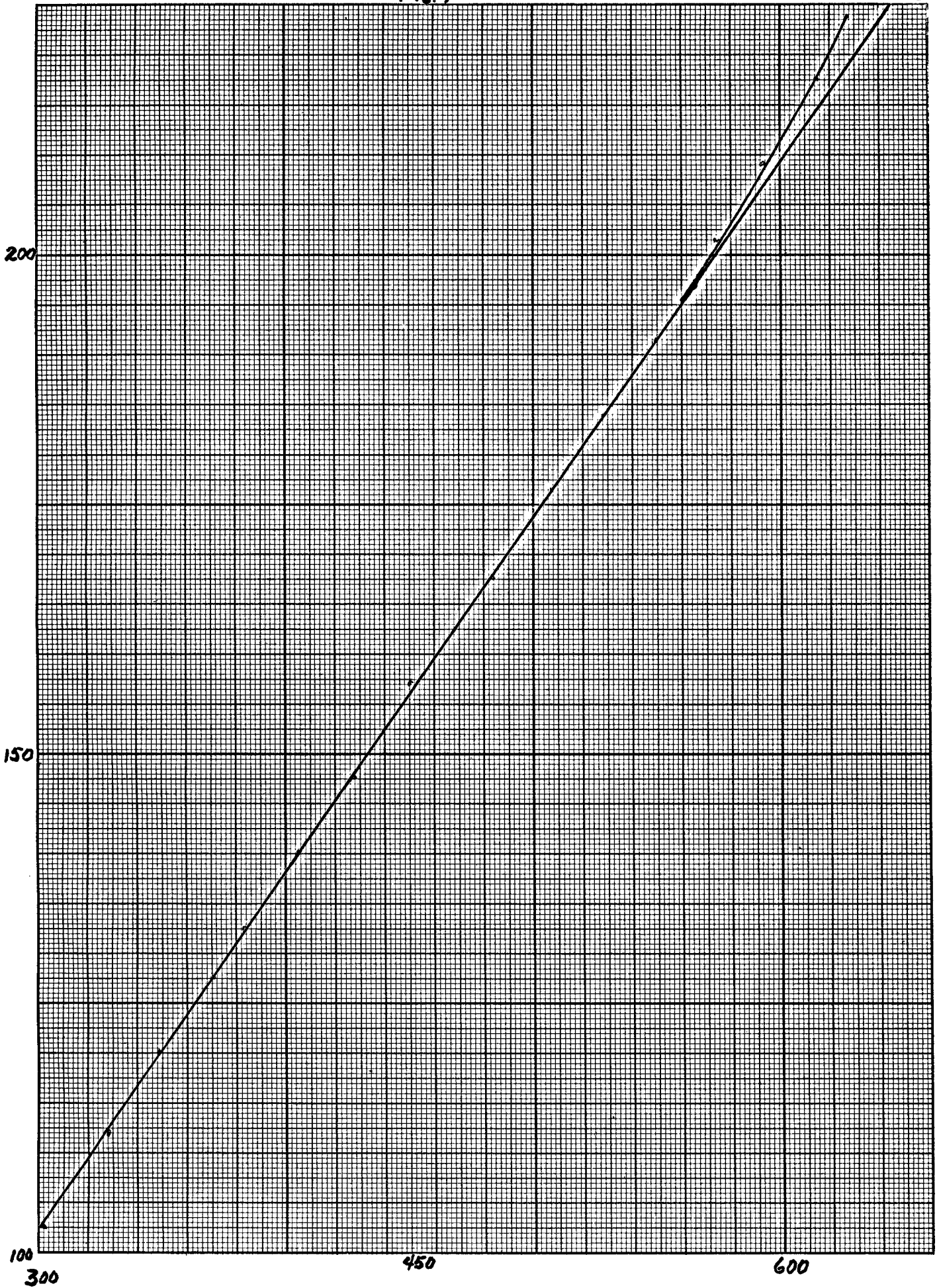
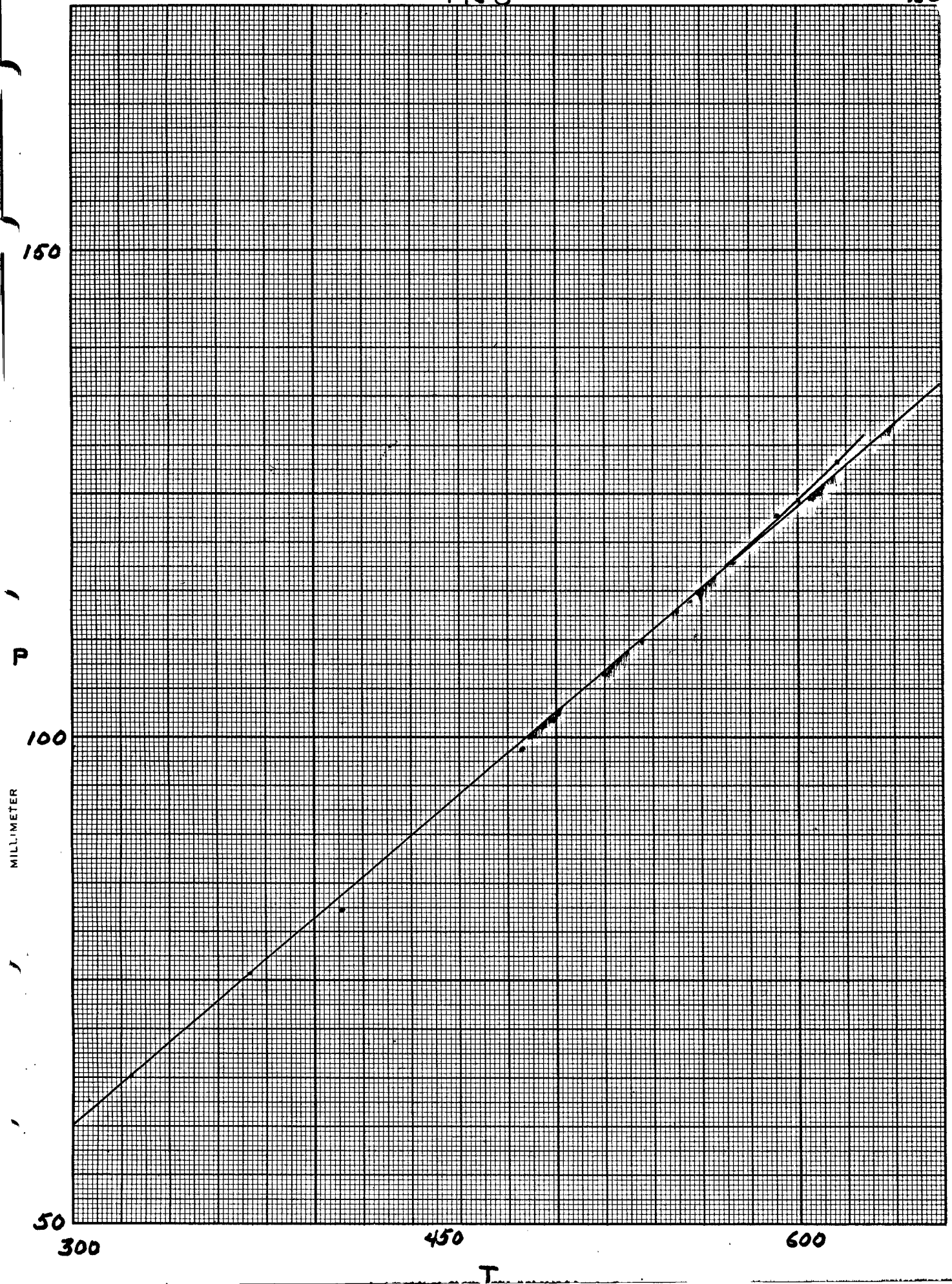


FIG 8



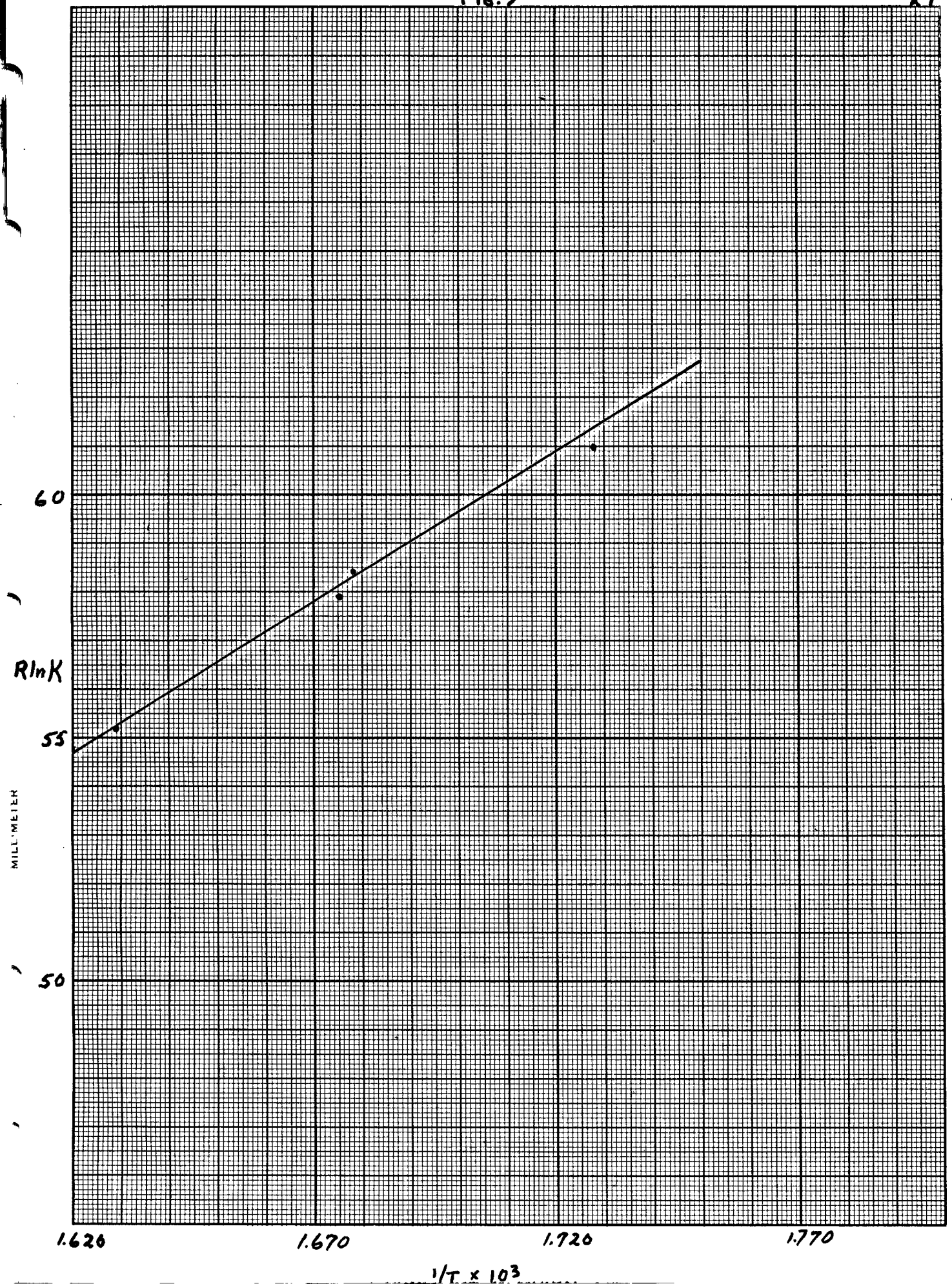
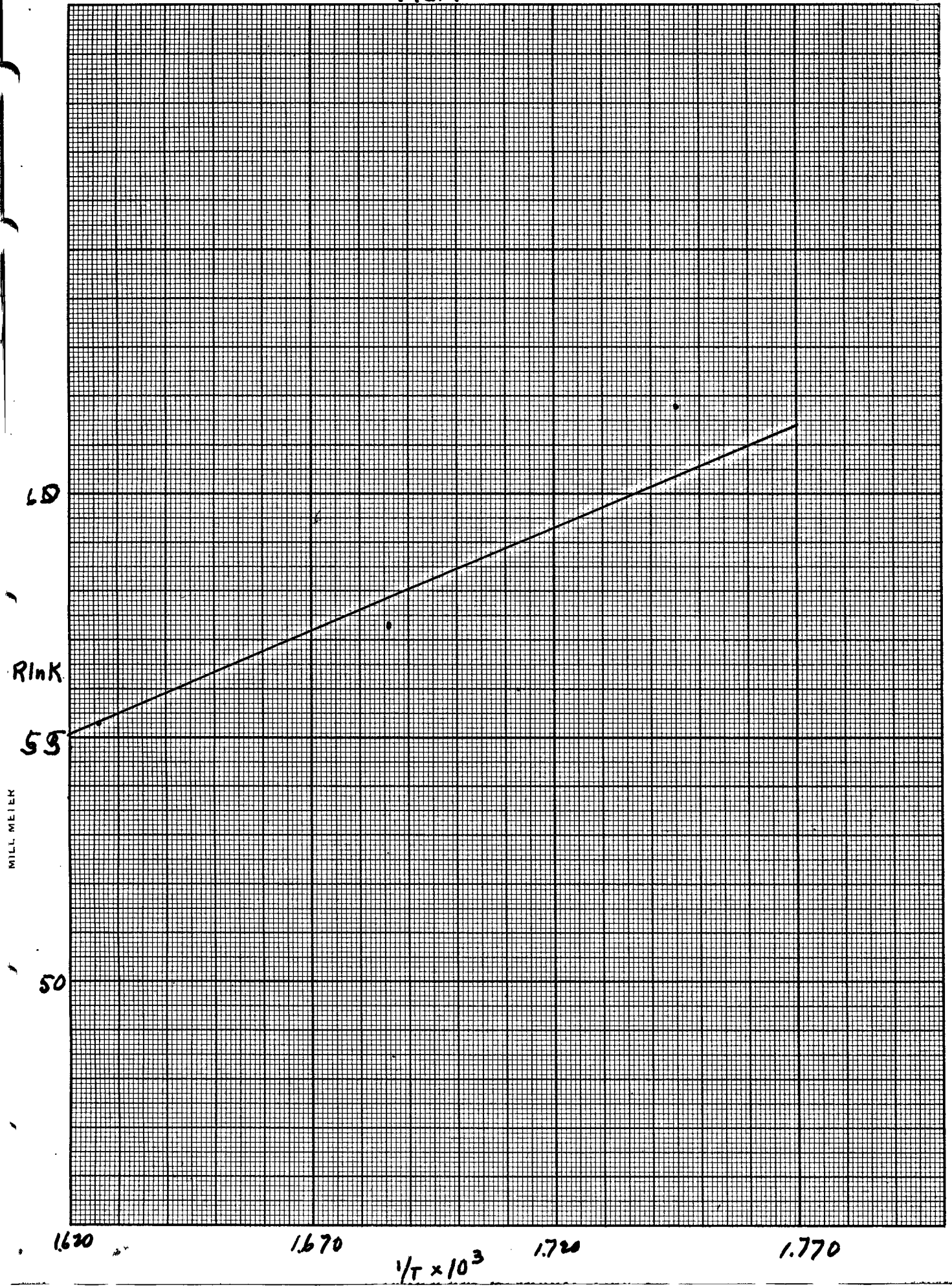
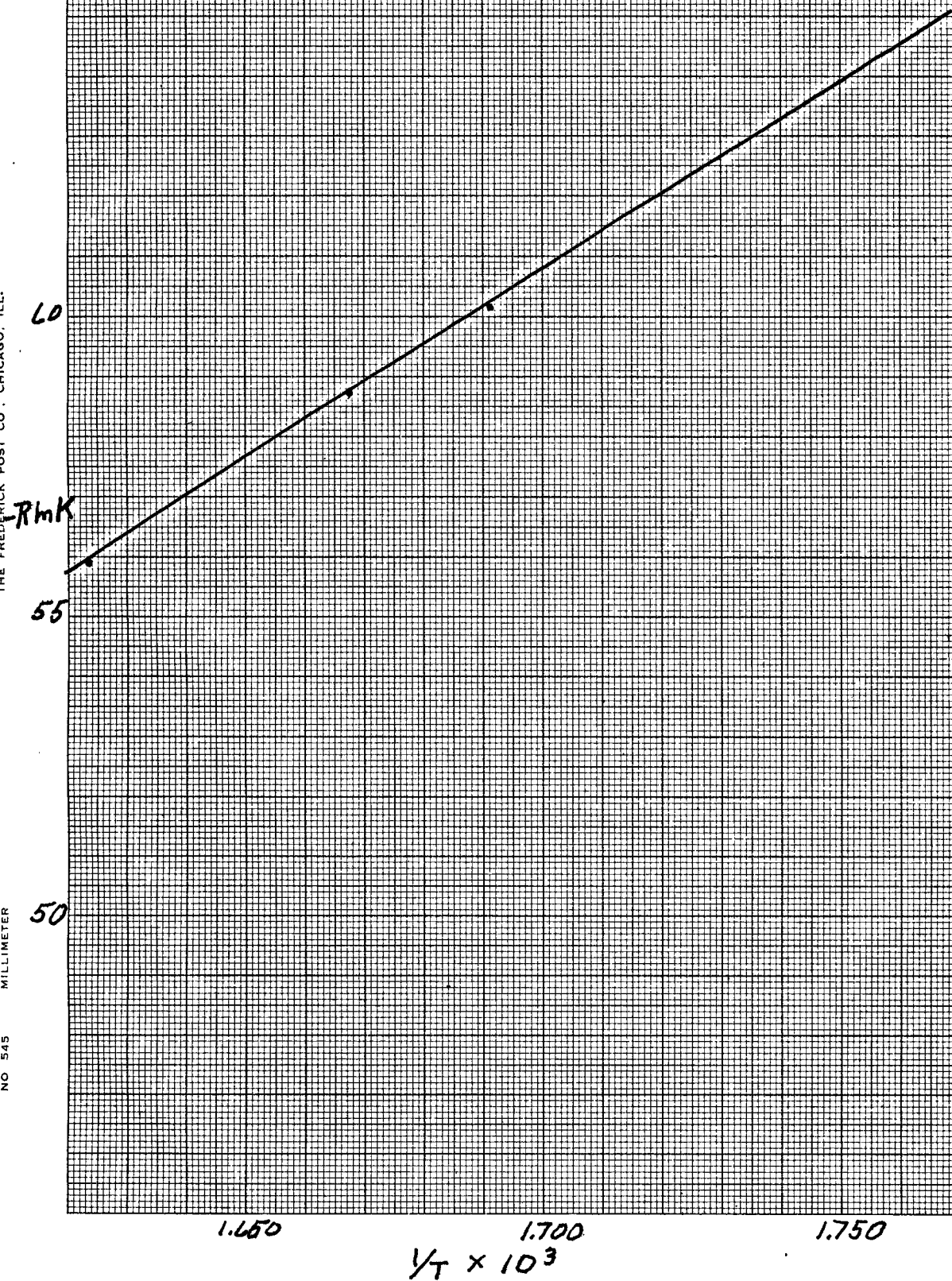


FIG. 10





PART V
SUMMARY AND CONCLUSIONS

A carefully purified sample of thionyl chloride shows its boiling point to be 76.5°C . This boiling point is in agreement with that established by other investigators.

By the methods described in this work it seems possible that the equilibrium constant for the dissociation of thionyl chloride may be obtained at several temperatures with a reasonable degree of precision.

Upon the examination of the methods of thermodynamics, it becomes apparent that the knowledge of the value of the equilibrium constant of a reaction at several temperatures is a useful one. One employs it in the calculation of ΔF° and also in the calculation of the enthalpy of the reaction.

Since thermodynamic functions are related to one another, one may derive properties of reactions and substances without the use of direct measurements. This is, indeed, fortunate since some properties may not be measured directly. Frequently, as is the case with enthalpy and free energy, one may calculate free energy changes and enthalpies of reactions by mere addition and subtraction of known values of these variables.

The enthalpy of the reaction studied was found to be 61,000 and the values of ΔF and K at several temperatures are given in the following table.

TABLE IV

T	K	ΔF
	I A	
579	4.8×10^{-14}	35,400
596	1.65×10^{-13}	34,800
597	2.21×10^{-13}	34,600
614	9.2×10^{-13}	33,800
	II A	
573	3.3×10^{-14}	35,400
593	1.96×10^{-13}	34,000
615	8.08×10^{-13}	34,000
	III A	
573	8.0×10^{-16}	30,600
591	7.18×10^{-14}	35,600
600	1.6×10^{-13}	35,200

PART VI
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