

DISSOCIATION PRESSURES AND STABILITES OF  
SOLID PICRIC ACID COMPLEXES WITH  
SOME ALIPHATIC COMPOUNDS

By

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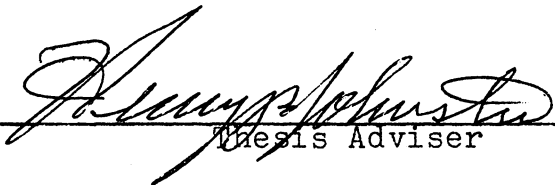
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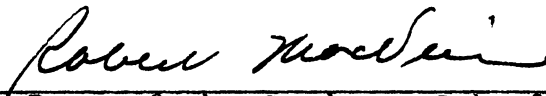
Submitted to the Faculty of the Graduate School of  
the Oklahoma Agricultural and Mechanical College  
in partial fulfillment of the requirements  
for the degree of  
MASTER OF SCIENCE  
August, 1955

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## ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. O. C. Dermer whose interest and guidance made this work possible. He also wishes to thank the Chemistry Staff and his fellow Graduate Students for their valuable suggestions.

Financial aid in the form of a Teaching Assistantship in the Department of Chemistry at Oklahoma Agricultural and Mechanical College is greatly appreciated.

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## INTRODUCTION

Harper (24) reported complexes of allyl chloride and allyl bromide with picric acid. Because these halides are similar to olefinic hydrocarbons it was thought that olefins, too, would complex with picric acid. Therefore, this work was undertaken in the hope that a method for the segregation of olefinic hydrocarbons from paraffins could be found.

If complexes of isomeric olefins should be found to have different stabilities, it might make the separation of the two compounds possible. The two compounds could simply be complexed, the less stable complex decomposed and the liquid olefin separated from the remaining complex. It was also thought that if such stabilities for an homologous series of the olefins could be determined, it would be possible to correlate structure with stability of these complexes.

Previous workers (10,41) have used various polynitro compounds as complexing agents. Picric acid was chosen as the complexing agent in this study for two reasons: stability of the complexes it forms, and ready availability in pure form.

The success of earlier workers (10,41,24,31) in determining equilibrium constants from vapor pressure measurements led to the use of this method in this study. Since activities can be determined more accurately in systems in which only one component is volatile, this study was restricted to solid molecular complexes of that type.

## HISTORICAL

In 1878 Mertens (35) reported the existence of a solid complex of picryl chloride with benzene. This complex was unstable and decomposed when exposed to air. Hepp (25) found several similar complexes of the naphthylamines with various polynitro compounds. Since that time many studies have been made on such addition complexes (1). This thesis will not review work that deals only with the existence of these complexes.

Many methods have been suggested for the study of the stability of these complexes. Most of these, however, can be used only in solution. Spectrophotometry (26,43), solubility (15), liquid-liquid partition (37), conductance (30), and diamagnetic susceptibility (2) measurements are the principal methods that have been employed, but it can be seen that none of these will give true thermodynamic equilibrium constants. Bell and Fendley (3) used a potentiometric method for one particular complex, but this could not be applied to other systems for lack of reversible electrodes.

Restricting this study to solid molecular complexes greatly reduces the number of pertinent investigations. The dissociation pressures of many hydrates of inorganic salts have been determined, but the method has such restrictions that it has been sparingly applied to organic molecular complexes. Table 1 gives a list of the solid molecular



complexes thus studied in which one component is organic, with the exceptions of hydrates of organic compounds and alcoholates of inorganic compounds.

There are several types of bonding proposed for this type of molecular complex. Each will be discussed separately on the following pages.

Sudborough (51) and others (5,6,32) thought that this bond was covalent. They proposed that the formation of this bond took place by the saturation of one of the double bonds of the aromatic ring. This would account for the observed increase in color intensity and for the small ratios of combination found in these complexes. This bond, however, would be impossible in the light of modern theories in that it would have to absorb the resonance energy of the aromatic ring. No such bond energies have been found in this type of complex. Kido (29) and Badder (2) have shown that the diamagnetic susceptibility of naphthalene picrate<sup>1</sup> is an additive property of its components; this indicates a much weaker type of bonding.

Weiss (54) and others (17) thought this bonding was essentially ionic in character, the aromatic component acting as the donor and the polynitro compound as the acceptor. This type of bonding would account for the almost instantaneous interaction between the two components. It, too, would account for the increased color intensity. However,

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<sup>1</sup>"picrate" is the name applied to complexes of picric acid. It erroneously suggests a salt-like structure, but it is used here in accordance with the literature.

TABLE 1

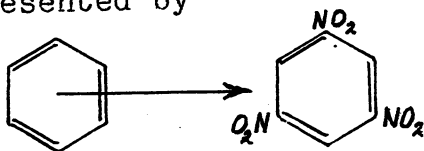
## Dissociation Constants of Organic Molecular Complexes

Complex	Ratio of Components	$K_p$ (atm)	H (kcal)	Temperature	Reference
Picryl chloride:hexamethylbenzene	1:1	-----	22.4	25	(42)
Aluminum bromide:trimethylamine	1:2	-----	15.2	25	(53)
Aluminum bromide:ethyl ether	1:2	-----	14.2	25	(53)
Antimony chloride:benzene	2:1	.0093	12.6	25	(31)
Aluminum bromide:toluene	2:1	-----	12.2	25	(12)
Carbon tetrabromide:benzene	1:1	-----	12.1	25	(28)
Aluminum chloride:ethyl ether	1:2	-----	11.3	25	(53)
Aluminum chloride:trimethylamine	1:2	-----	10.4	25	(53)
2,4-Dinitroiodobenzene:benzene	2:1	.067	10.4	30	(10)
Aluminum bromide:benzene	2:1	-----	10.1	25	(12)
Picric Acid:allyl chloride	1:1	.103	9.70	30	(24)
Antimony chloride:ethylbenzene	---	.0067	9.7	25	(31)
Antimony chloride:m-xylene	---	.0037	9.5	25	(31)
2,4-Dinitrobromobenzene:benzene	2:1	.070	9.35	30	(10)
Gallium chloride:methyl chloride	1:2	-----	9.34	25	(11)

Picric Acid:acrylonitrile	2:1	.048	9.29	30	(24)
Picric Acid:acrylonitrile	2:1	.048	9.29	30	(24)
Picric Acid:allyl bromide	1:1	.102	9.24	30	(24)
Gallium chloride:ethyl ether	1:1	-----	8.95	25	(53)
Picryl Chloride:benzene	1:2	.118	8.95	30	(10)
Picric Acid:benzene	1:1	.133	8.69	30	(10)
Picric Acid:benzene	1:1	.128	8.65	30	(41)
Picric Acid:allyl alcohol	1:1	.048	8.28	30	(24)
<u>s</u> -Trinitrobenzene:benzene	1:2	.148	8.05	30	(41)
2,4,6-Trinitro- <u>m</u> -cresol:benzene	1:1	.141	7.46	30	(41)
Antimony chloride:toluene	2:1	.0085	7.2	25	(31)
Gallium chloride:methyl chloride	1:1	-----	7.11	25	(11)
Gallium bromide:ethyl ether	1:1	-----	5.51	25	(53)
Picric Acid:vinyl acetate	2:1	.063	4.70	30	(24)
Picric Acid:cyclohexene	2:1	.089	4.39	30	(24)
2,4-Dinitrochlorobenzene:benzene	2:1	.085	-----	30	(10)

measurements in liquid sulfur dioxide have shown that there is no enhanced conductivity and, therefore, the bonding must not be ionic (33). Dewar (14,15) was also opposed to this view for two reasons: (1) there is no evidence that the transfer of a single electron takes place in organic chemistry and (2) the heats of formation of these compounds are too low for a salt-like structure to be possible.

Briegleb (8,9) considered the bonding in polynitro complexes to be due to dipole-induced dipole forces. This view is favored by many workers today (26,16,44). It has been shown that the intermolecular distances are too great for covalent bonding and that the crystal structure is not ionic by X-ray studies (46,47). Hammick and Yule (23) concluded that this was the type of bond formed because the reaction occurs almost instantaneously and, therefore, the activation energy is too small for the formation of a covalent bond. Nakamoto (40) and others (12) believed that this mutual polarization led to the formation of  $\pi$ -bonds perpendicular to the plane of the aromatic ring. This type of bond may be represented by



Rundle and Goring (48) found by X-ray measurements that silver perchlorate is bonded to two carbon atoms in different aromatic rings by  $\pi$ -bonds.

Brackman (7) proposed an interesting new type of chemical bonding which he called complex resonance. This is

represented as a covalent bond, the character of which lies between that of a single bond and no bond at all. Mulliken (38, 39) treated this type of bond quantum-mechanically and to him it is credible that all of the previous ideas are partly correct. He is in agreement with Weiss that the strength of the bond can be correlated with the ionization potential of the electron donor and supports the view that the predominant intermolecular forces are pair-wise donor-acceptor interactions.

Attempts have been made to classify the effects of substitution on the components of these complexes. The ability of the nitro component to combine increases with the number of nitro groups. Halogens and hydroxyl and amino groups enhance the ability of the nitro component to complex while methyl groups decrease it (55). The ability of the hydrocarbon to complex increases with the size of the ring system and also with substitution of methyl, amino and hydroxyl groups. Its ability to complex decreases with nitro substitution (19). Hammick and Hellicar (20) concluded from experiments with 1,3,5-trichloro-2,4,6-trinitrobenzene and trinitromesitylene that the above effects were due to polar and not to steric causes.

## EXPERIMENTAL

### Apparatus:

The apparatus used for the determination of dissociation pressures was a modified tensimeter devised by Gibson and Adams (18) and adapted to this work by Harper (24) and Langford (31). The advantages of this apparatus are that all foreign gases may be swept from the system and the unknown pressure is opposed to a known pressure.

Figure 1 is a diagram of this apparatus. The system was immersed in a constant-temperature water bath. A battery jar twelve inches in diameter and twenty-four inches high served this purpose. The bath was fitted with a stirrer and a thermoregulator. The temperature was controlled to  $\pm 0.05^{\circ}\text{C}$ . A thermometer graduated in tenths of a degree which had been compared to a Bureau of Standards thermometer was used to determine the temperature.

### Procedure:

Approximately a two-gram portion of picric acid was placed in cell A, an excess of the volatile component introduced, and the cell warmed until solution was complete. Benzene, the reference liquid used in this work, was introduced into cell B and both cells were attached to the system.

With stopcocks 1 and 2 closed and 3,4,5 and 6 open the system was evacuated with a Welch Duo-Seal vacuum pump.

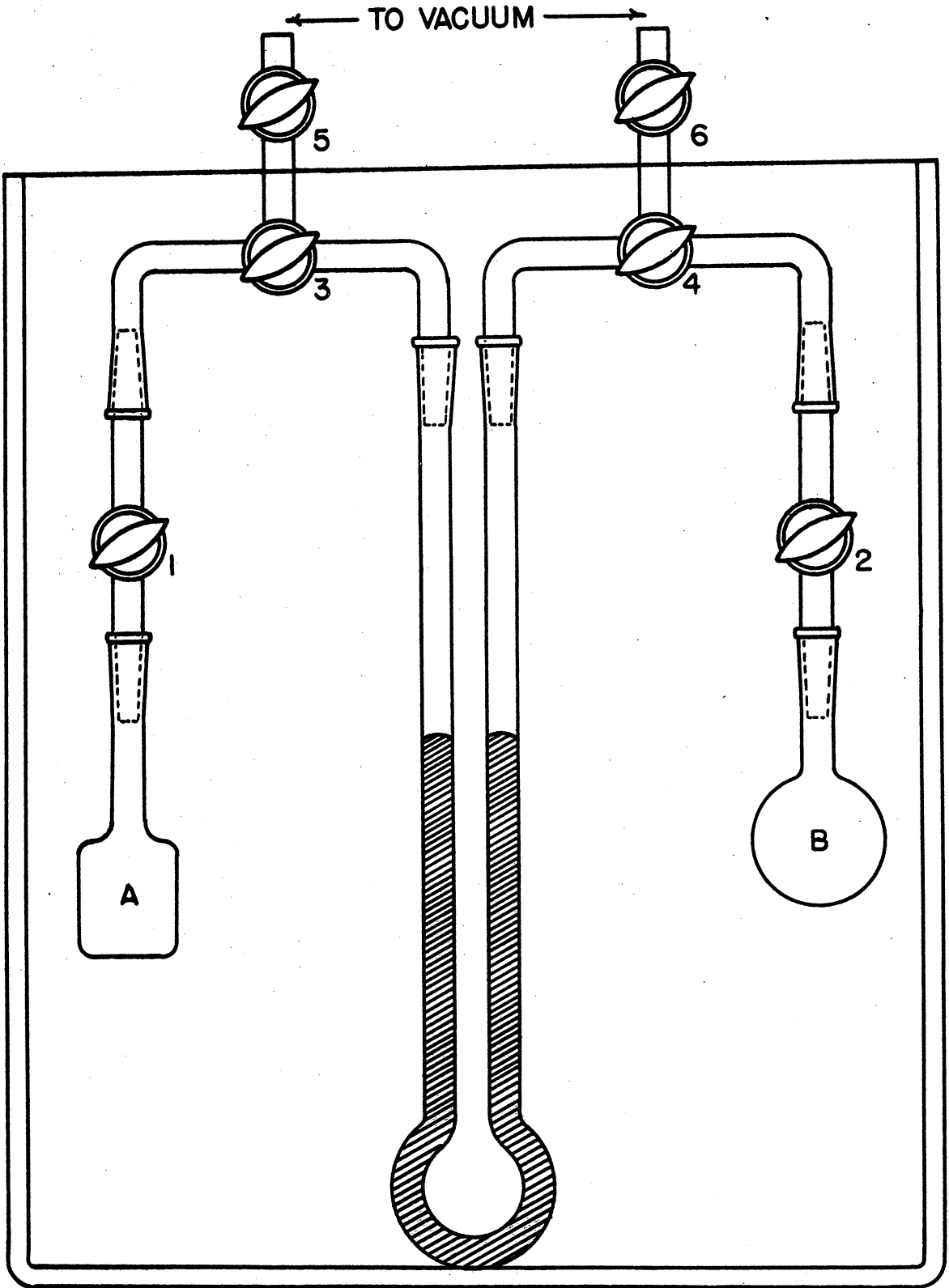


Figure 1  
Vapor Pressure Apparatus

Stopcocks 5 and 6 were then closed and 1 and 2 were opened allowing the vapor of the volatile component and the reference liquid to diffuse throughout the system. These procedures were repeated until a constant vapor pressure was obtained for the saturated solution of the complex in the volatile component. The constancy of the vapor pressure of the saturated solution was taken as a criterion that all foreign gases had been swept from the system. Cell A was then further evacuated in small increments until there was an abrupt lowering of the vapor pressure. At this point only the solid complex remained in the cell. At least two more evacuations were made to make sure that the system was in equilibrium and the dissociation pressure was constant. The dissociation pressure was determined at three-degree intervals over a temperature range of about twenty degrees. Further stepwise evacuations were then made in search of a second constant dissociation pressure which would indicate the presence of another complex.

Mercury was used as the manometer liquid and manometer levels were read to one-tenth of a millimeter with a cathetometer having a vernier.

Considerable difficulty was encountered in the form of leaking stopcocks. The leaking was found to be through the stopcocks to the vacuum line and not to the atmosphere. Stopcocks 5 and 6 were therefore used for all preliminary evacuations and 3 and 4 were used to isolate the system when measurements were taken. Dow Corning high-vacuum



silicone lubricant was used on all ground glass joints as it was found to be less soluble in organic compounds.

Molecular ratios were determined by weighing a known amount of picric acid into cell A, complexing it with an excess of the volatile component and evacuating as above. Immediately upon reaching the dissociation pressure of the complex, stopcock 1 was closed. Cell A with stopcock 1 was then removed from the system and weighed. The amount of volatile component in the complex was determined by the difference in weight.

If A represents the solid picric acid, B the volatile component, and  $A_m B_n$  the solid complex, the reaction may be expressed as  $A_m B_n(s) = mA(s) + nB(g)$ . The dissociation constant for this reaction will be

$$K(\text{diss}) = \frac{a_A^m \times a_B^n}{a_{A_m B_n}}$$

in which activity is represented as  $a$ . The activities of the solid complex and solid picric acid may be taken as unity and the dissociation constant reduces to

$$K(\text{diss}) = a_B^n$$

or, substituting fugacities,

$$K(\text{diss}) = \left( \frac{f_B}{f_B^\circ} \right)^n$$

If the fugacity in the standard state is chosen as one atmosphere,  $K(\text{diss}) = f_B^n$ .

As the pressure approaches zero the fugacity approaches the pressure. In this manner the equilibrium constant can be obtained from the dissociation pressure.

From the integrated form of the van't Hoff reaction isochore

$$\ln K = - \frac{\Delta H}{RT} + C$$

it is seen that a plot of  $\ln K$  versus  $1/T$  will give a straight line with a slope of  $-\Delta H/R$ . The heat of dissociation was found by multiplying the slope by  $-R$ .

The free energy of dissociation was determined by means of the reaction isotherm,  $\Delta F = \Delta F^{\circ} - RT \ln K$ .

#### Purity of Chemicals:

Picric acid-----Reagent grade with ten percent added water. The water was removed by azeotropic distillation with benzene, and the benzene removed by air drying. M. p. 121.5-122° C.

Benzene-----Reagent grade was dried over sodium, distilled and the first ten percent of the distillate rejected.

Acetonitrile-----Eastman Kodak practical grade was distilled through a Todd column. The first ten percent of the distillate was rejected and a constant boiling fraction taken.

Acrylonitrile-----As for acetonitrile.

Propionitrile-----As for acetonitrile.

Allyl alcohol-----As for acetonitrile.

Allyl ether-----As for acetonitrile.

Allyl ethyl ether--As for acetonitrile.

Vinyl acetate-----As for acetonitrile.

Cyclohexene-----As for acetonitrile.

n-Propyl ether-----Matheson technical grade purified as for acetonitrile.

n-Propyl alcohol---As for acetonitrile.

iso-Propyl ether---As for acetonitrile.

Methyl acrylate-----Eastman Kodak practical grade purified like acetonitrile except that a twelve-bulb Snyder column was used for the distillation.

Acetone-----Merck reagent grade.

Ethyl ether-----Baker reagent grade.

Ethyl acetate-----Mallinckrodt reagent grade.

Ethyl alcohol-----Absolute.

Isoprene-----Phillips pure grade.

1-Hexene-----As above.

2-Heptene-----As above.

In these experiments benzene was used as the reference liquid. The vapor pressure of benzene was calculated from the equation (27)  $\log P_{(\text{mm})} = -0.05223 A/T + B$  where

$$A = 34,172 \quad B = 7.9622 \quad \text{from } 0^{\circ} \text{ to } 42^{\circ} \text{C}$$

$$A = 32,295 \quad B = 7.6546 \quad \text{from } 42^{\circ} \text{ to } 100^{\circ} \text{C}$$

Table 2 shows the calculated values for the vapor pressure of benzene.

TABLE 2

## Vapor Pressure of Benzene

---

T, °C	T, °K	Vapor Pressure mm. of Hg
24.9	298.1	94.4
29.9	303.1	118.5
32.9	306.1	135.3
36.4	309.6	157.5
39.9	313.1	182.7
42.9	316.1	207.9
45.9	319.1	233.7

---

The dissociation pressures of benzene picrate were determined. The heat of dissociation was found to be 8.84 kcal. per mole of complex. This is in agreement with the values found by Broeg (10), Nease (41) and Harper (24).

## RESULTS

### TABLE 3

Dissociation Pressures of n-Propyl Alcohol Picrate

Molecular ratio of picric acid to <u>n</u> -propyl alcohol (1:2)			
T, °K	1/T x 10 <sup>3</sup>	K <sub>p</sub>	log K <sub>p</sub>
298.1	3.355	0.0270	-1.5691
303.1	3.299	0.0380	-1.4199
306.1	3.267	0.0457	-1.3405
309.6	3.230	0.0559	-1.2524
313.1	3.194	0.0695	-1.1582
316.1	3.164	0.0846	-1.0726
319.1	3.134	0.1009	-0.9960

Figure 2 on the following page is a plot of log K<sub>p</sub> versus 1/T. The slope of the best straight line through the points is -2580. The following equation relates the dissociation pressure to the temperature:

$$\log P_{(\text{mm})} = 7.533 - 2580/T$$

The heat of dissociation was found to be 11.8 kcal. per mole.

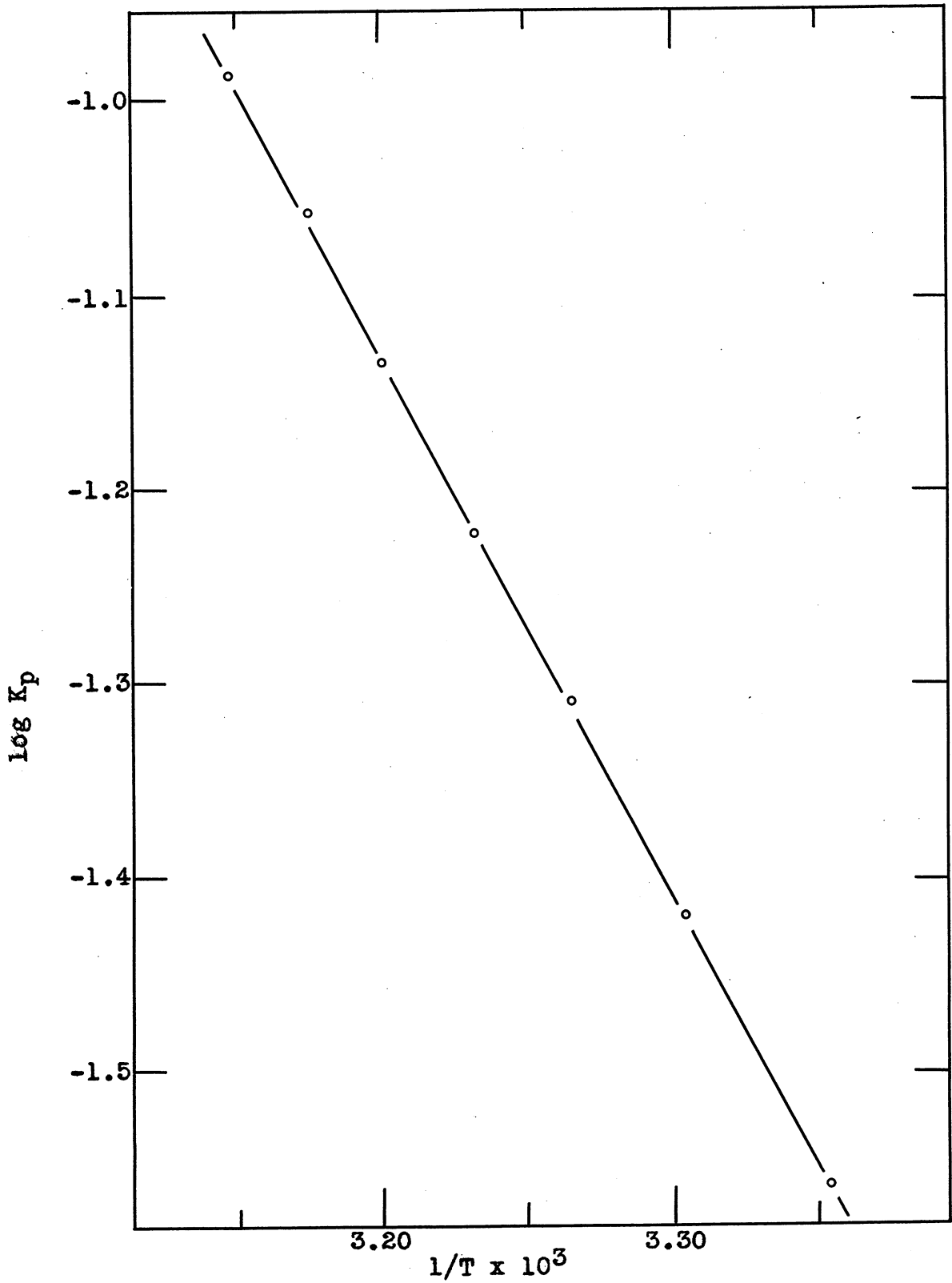


Figure 2

Graph of the Dissociation Pressures of  
n-Propyl Alcohol Picrate

TABLE 4

Dissociation Pressures of n-Propyl Ether Picrate

Molecular ratio of picric acid to <u>n</u> -propyl ether (1:2)			
T, °K	1/T x 10 <sup>3</sup>	K <sub>p</sub>	log K <sub>p</sub>
298.1	3.355	0.04355	-1.3610
303.1	3.299	0.05803	-1.2364
306.1	3.267	0.06842	-1.1648
309.6	3.230	0.08487	-1.0713
313.1	3.194	0.1034	-0.9854
316.1	3.164	0.1228	-0.9109

Figure 3 on the following page is a plot of log K<sub>p</sub> versus 1/T. The slope of the best straight line through the points is -2350. The following equation relates the dissociation pressure to temperature:

$$\log P_{(\text{mm})} = 6.552 - 2360/T$$

The heat of dissociation was found to be 10.8 kcal. per mole.

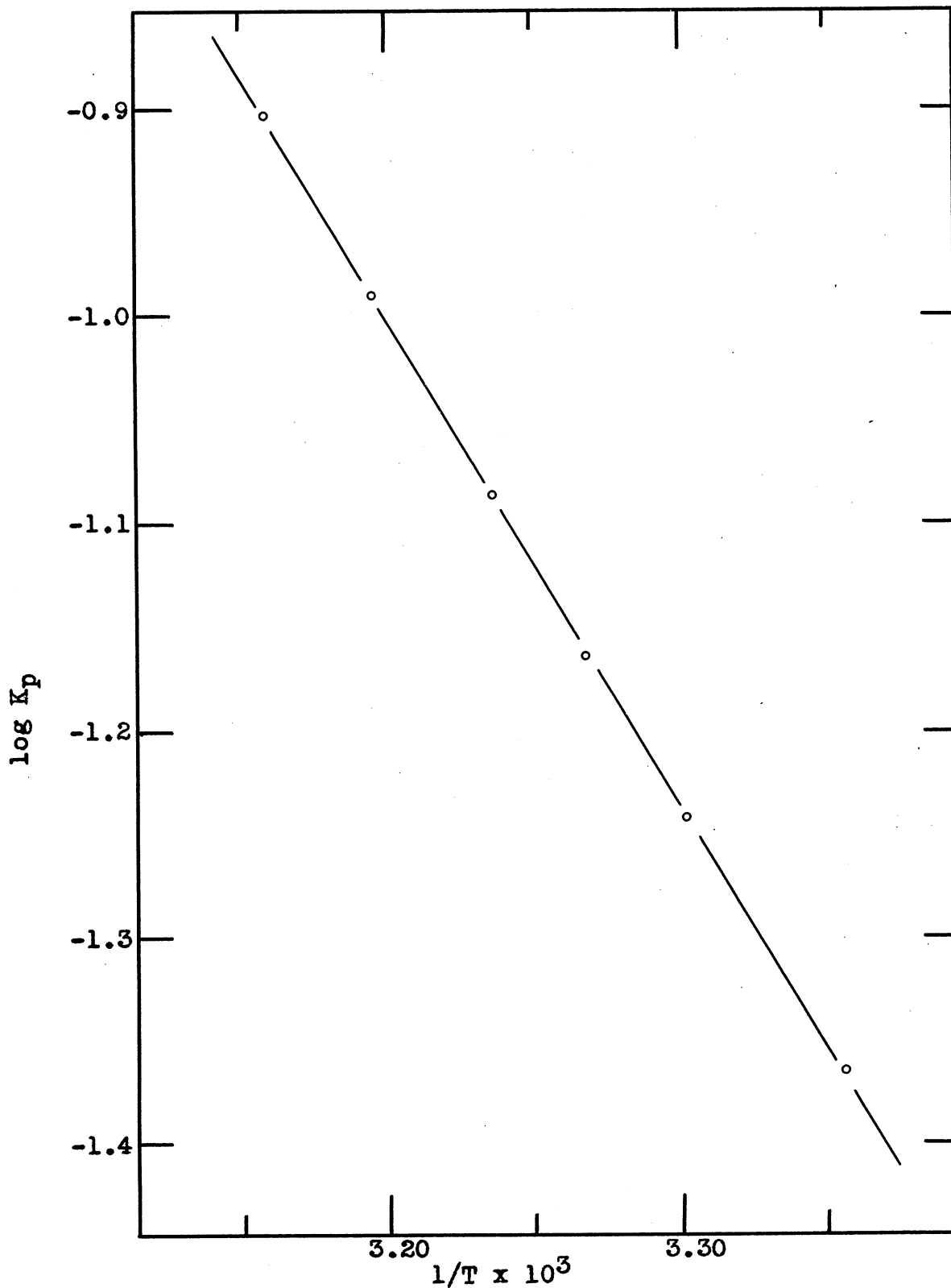


Figure 3

Graph of the Dissociation Pressures of  
n-Propyl Ether Picrate



TABLE 5

## Dissociation Pressures of Allyl Alcohol Picrate

---

Molecular ratio of picric acid to allyl alcohol (1:1)

---

T, °K	1/T x 10 <sup>3</sup>	K <sub>p</sub>	log K <sub>p</sub>
303.1	3.299	0.0375	-1.4260
306.1	3.267	0.0459	-1.3381
309.6	3.230	0.0582	-1.2354
313.1	3.194	0.0725	-1.1397
316.1	3.164	0.0887	-1.0522
319.1	3.134	0.1043	-0.1816

---

Figure 4 on the following page is a plot of log K<sub>p</sub> versus 1/T. The slope of the best straight line through the points is -2730. The following equation relates the dissociation pressure to the temperature:

$$\log P_{(\text{mm})} = 7.581 - 2730/T$$

The heat of dissociation was found to be 12.5 kcal. per mole.

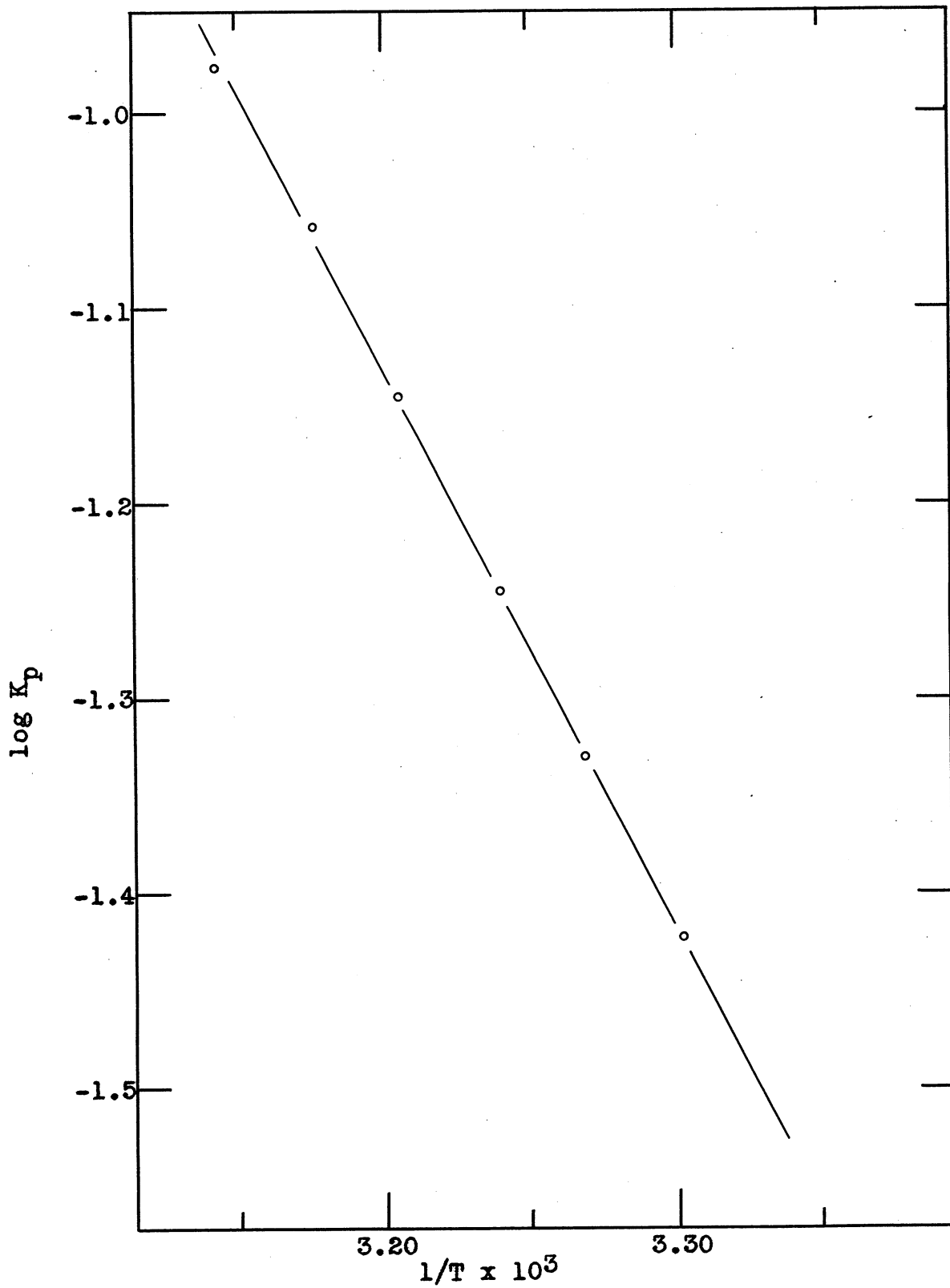


Figure 4

Graph of the Dissociation Pressures of  
Allyl Alcohol Picrate

TABLE 6

## Dissociation Pressures of Acrylonitrile Picrate

Molecular ratio of picric acid to acrylonitrile (2:1)

T, °K	1/T x 10 <sup>3</sup>	K <sub>p</sub>	log K <sub>p</sub>
303.1	3.299	0.1424	-0.8465
306.1	3.267	0.1617	-0.7913
309.6	3.230	0.1875	-0.7270
313.1	3.194	0.2146	-0.6684
316.1	3.164	0.2417	-0.6167
319.1	3.134	0.2709	-0.5672

Figure 5 on the following page is a plot of log K<sub>p</sub> versus 1/T. The slope of the best straight line through the points is -1660. The following equation relates the dissociation pressure to the temperature:

$$\log P_{(\text{mm})} = 4.667 - 1660/T$$

The heat of dissociation was found to be 7.65 kcal. per mole.

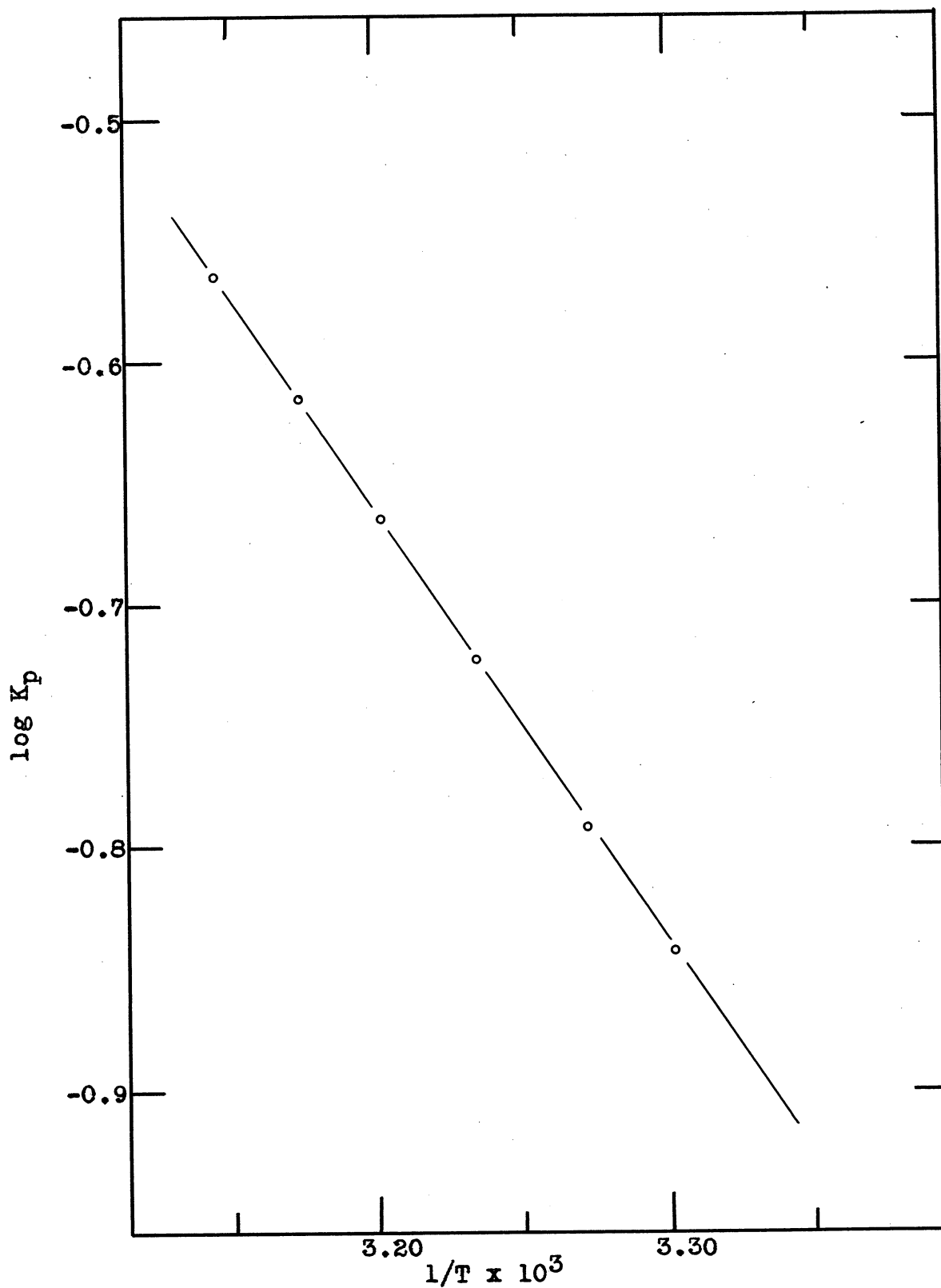


Figure 5

Graph of the Dissociation Pressures of  
Acrylonitrile Picrate

TABLE 7

## Dissociation Pressures of Acetonitrile Picrate

---

Molecular ratio of picric acid to acetonitrile (1:1)

---

T, °K	1/T x 10 <sup>3</sup>	K <sub>p</sub>	log K <sub>p</sub>
298.1	3.355	0.0922	-1.0351
303.1	3.299	0.1120	-0.9508
306.1	3.267	0.1263	-0.8986
309.6	3.230	0.1496	-0.8251
313.1	3.194	0.1709	-0.7673
316.1	3.164	0.1933	-0.7138

---

Figure 6 on the following page is a plot of log K<sub>p</sub> versus 1/T. The slope of the best straight line through the points is -1700. The following equation relates the dissociation pressure to the temperature:

$$\log P_{(\text{mm})} = 4.663 - 1700/T$$

The heat of dissociation was found to be 7.78 kcal. per mole.

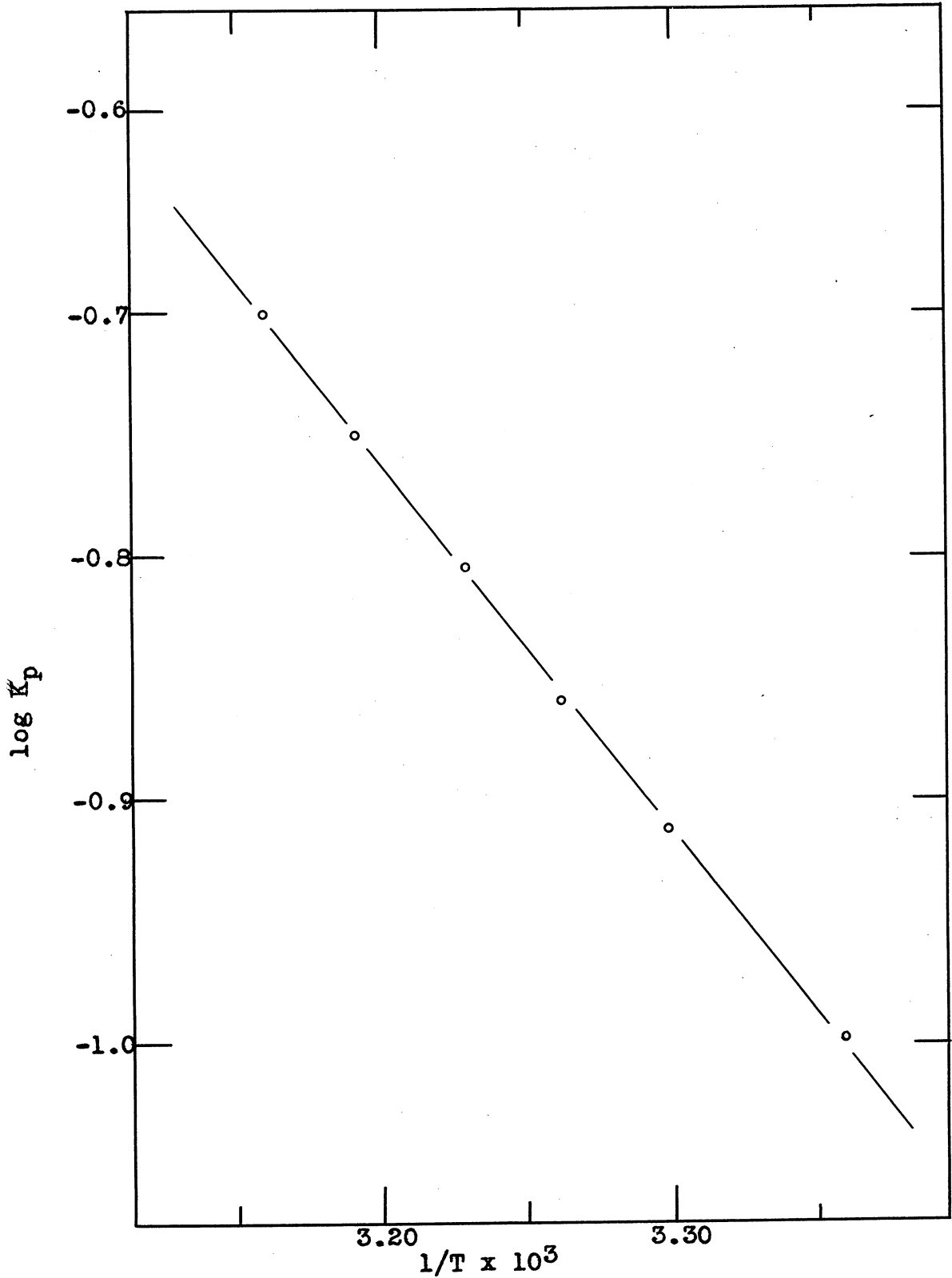


Figure 6

Graph of the Dissociation Pressures of  
Acetonitrile Picrate

TABLE 8

## Dissociation Pressures of Propionitrile Picrate

---

Molecular ratio of picric acid to propionitrile (1:1)

---

T, °K	1/T x 10 <sup>3</sup>	K <sub>p</sub>	log K <sub>p</sub>
298.1	3.355	0.0492	-0.3080
303.1	3.299	0.0622	-0.2059
306.1	3.267	0.0726	-0.1389
309.6	3.230	0.0851	-0.0699
313.1	3.194	0.0983	-0.0075
316.1	3.164	0.1124	-0.9494
319.1	3.134	0.1257	-0.9008

---

Figure 7 on the following page is a plot of log K<sub>p</sub> versus 1/T. The slope of the best straight line through the points is -1790. The following equation relates the dissociation pressure to the temperature:

$$\log P_{(\text{mm})} = 4.678 - 1790/T$$

The heat of dissociation was found to be 8.15 kcal. per mole.

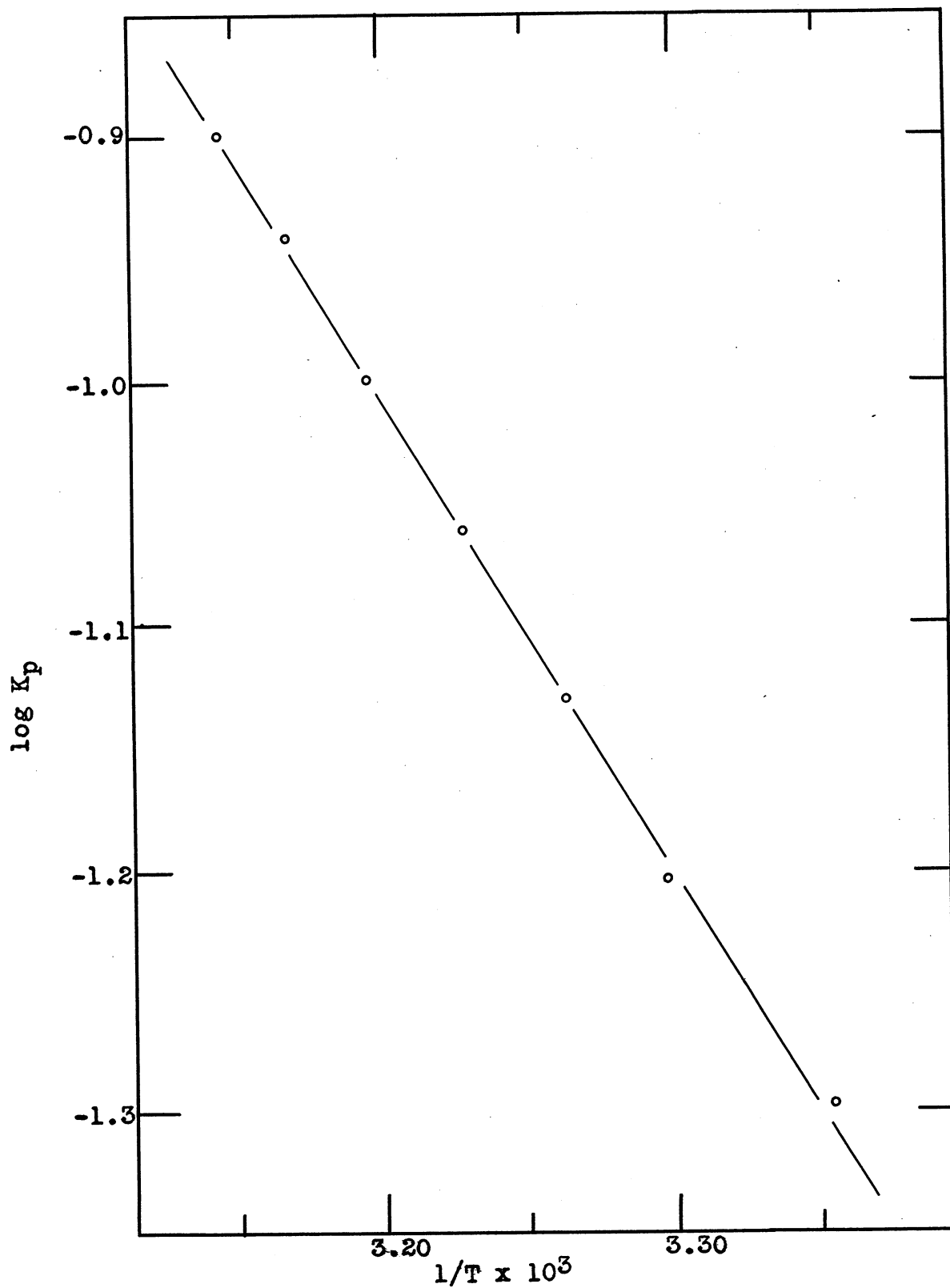


Figure 7

Graph of the Dissociation Pressures of  
Propionitrile Picrate



TABLE 9

## Dissociation Pressures of Allyl Ether Picrate

---

Molecular ratio of picric acid to allyl ether (2:1)

---

T, °K	1/T x 10 <sup>3</sup>	K <sub>p</sub>	log K <sub>p</sub>
298.1	3.355	0.0529	-1.2766
303.1	3.299	0.0708	-1.1500
306.1	3.267	0.0826	-1.0829
309.6	3.230	0.0983	-1.0075
313.1	3.194	0.1163	-0.9344
316.1	3.164	0.1363	-0.8654

---

Figure 8 on the following page is a plot of log K<sub>p</sub> versus 1/T. The slope of the best straight line through the points is -2110. The following equation relates the dissociation pressure to the temperature:

$$\log P_{(\text{mm})} = 5.776 - 2110/T$$

The heat of dissociation was found to be 9.62 kcal. per mole.

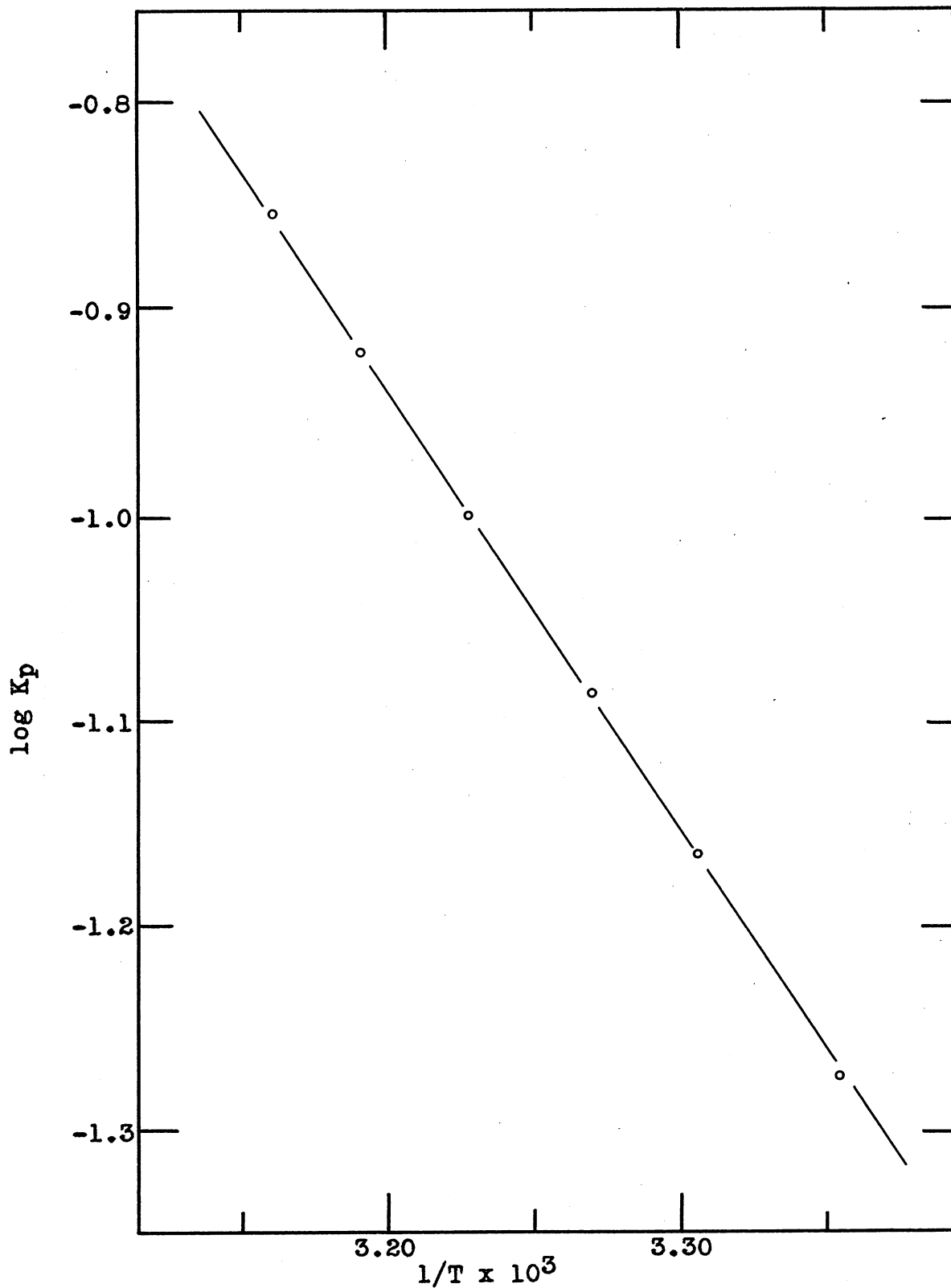


Figure 8

Graph of the Dissociation Pressures of  
Allyl Ether Picrate

TABLE 10

## Dissociation Pressures of Allyl Ethyl Ether Picrate

Molecular ratio of picric acid to allyl ethyl ether (1:2)

T, °K	1/T x 10 <sup>3</sup>	K <sub>p</sub>	log K <sub>p</sub>
298.1	3.355	0.1841	-0.7350
303.1	3.299	0.2289	-0.6404
306.1	3.267	0.2629	-0.5802
309.6	3.230	0.3046	-0.5163
313.1	3.194	0.3524	-0.4530
316.1	3.164	0.3997	-0.3983

Figure 9 on the following page is a plot of log K<sub>p</sub> versus 1/T. The slope of the best straight line through the points is -1760. The following equation relates the dissociation pressure to the temperature:

$$\log P_{(\text{mm})} = 5.169 - 1760/T$$

The heat of dissociation was found to be 8.06 kcal. per mole.

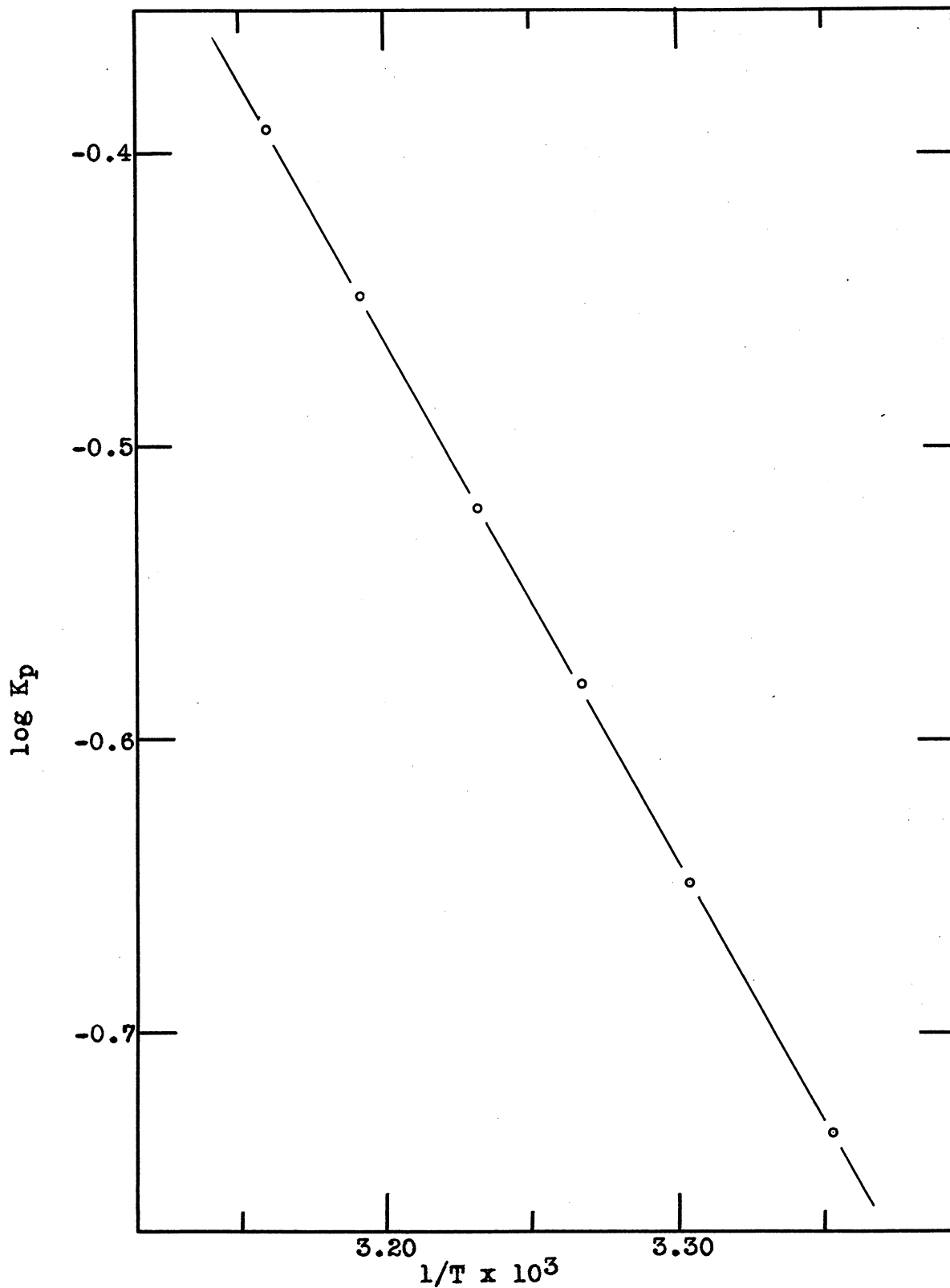


Figure 9

Graph of the Dissociation Pressures of  
Allyl Ethyl Ether Picrate

TABLE 11

## Dissociation Pressures of Vinyl Acetate Picrate

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Molecular ratio of picric acid to vinyl acetate (1:1)

---

T, °K	1/T x 10 <sup>3</sup>	K <sub>p</sub>	log K <sub>p</sub>
298.1	3.355	0.1326	-0.8775
303.1	3.299	0.1667	-0.7781
306.1	3.267	0.1897	-0.7219
309.6	3.230	0.2204	-0.6568
313.1	3.194	0.2546	-0.5941
316.1	3.164	0.2895	-0.5384

---

Figure 10 on the following page is a plot of log K<sub>p</sub> versus 1/T. The slope of the best straight line through the points is -1770. The following equation relates the dissociation pressure to the temperature:

$$\log P_{(\text{mm})} = 5.027 - 1770/T$$

The heat of dissociation was found to be 8.08 kcal. per mole.

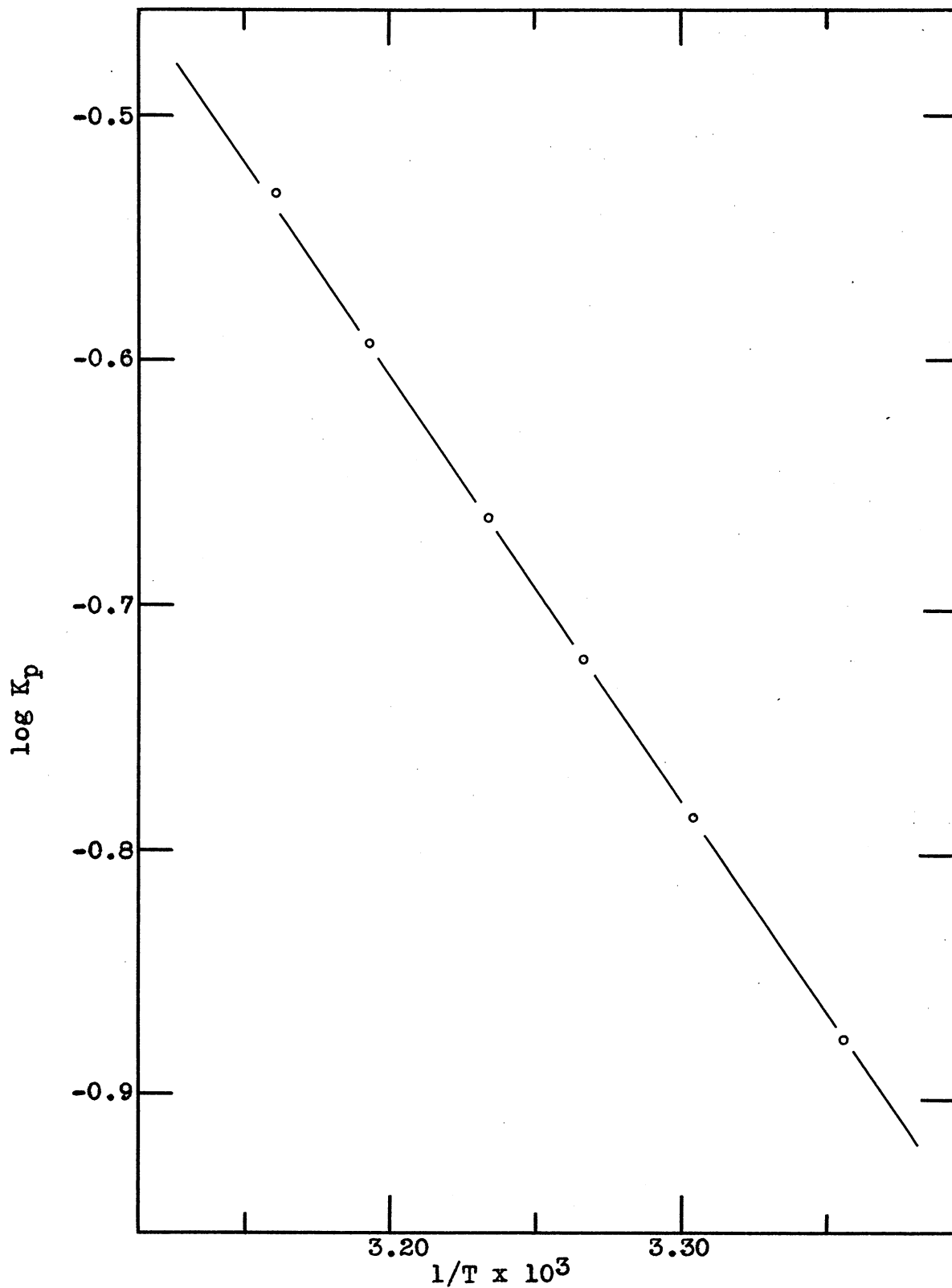


Figure 10

Graph of the Dissociation Pressures of  
Vinyl Acetate Picrate

TABLE 12

## Dissociation Pressures of Methyl Acrylate Picrate

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Molecular ratio of picric acid to methyl acrylate (1:1)

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T, °K	1/T x 10 <sup>3</sup>	K <sub>p</sub>	log K <sub>p</sub>
298.1	3.355	0.0932	-1.0308
303.1	3.299	0.1179	-0.9285
306.1	3.267	0.1312	-0.8821
309.6	3.230	0.1559	-0.8072
313.1	3.194	0.1842	-0.7347
316.1	3.164	0.2049	-0.6885

---

Figure 11 on the following page is a plot of log K<sub>p</sub> versus 1/T. The slope of the best straight line through the points is -1780. The following equation relates the dissociation pressure to the temperature:

$$\log P_{(\text{mm})} = 4.910 - 1780/T$$

The heat of dissociation was found to be 8.12 kcal. per mole.

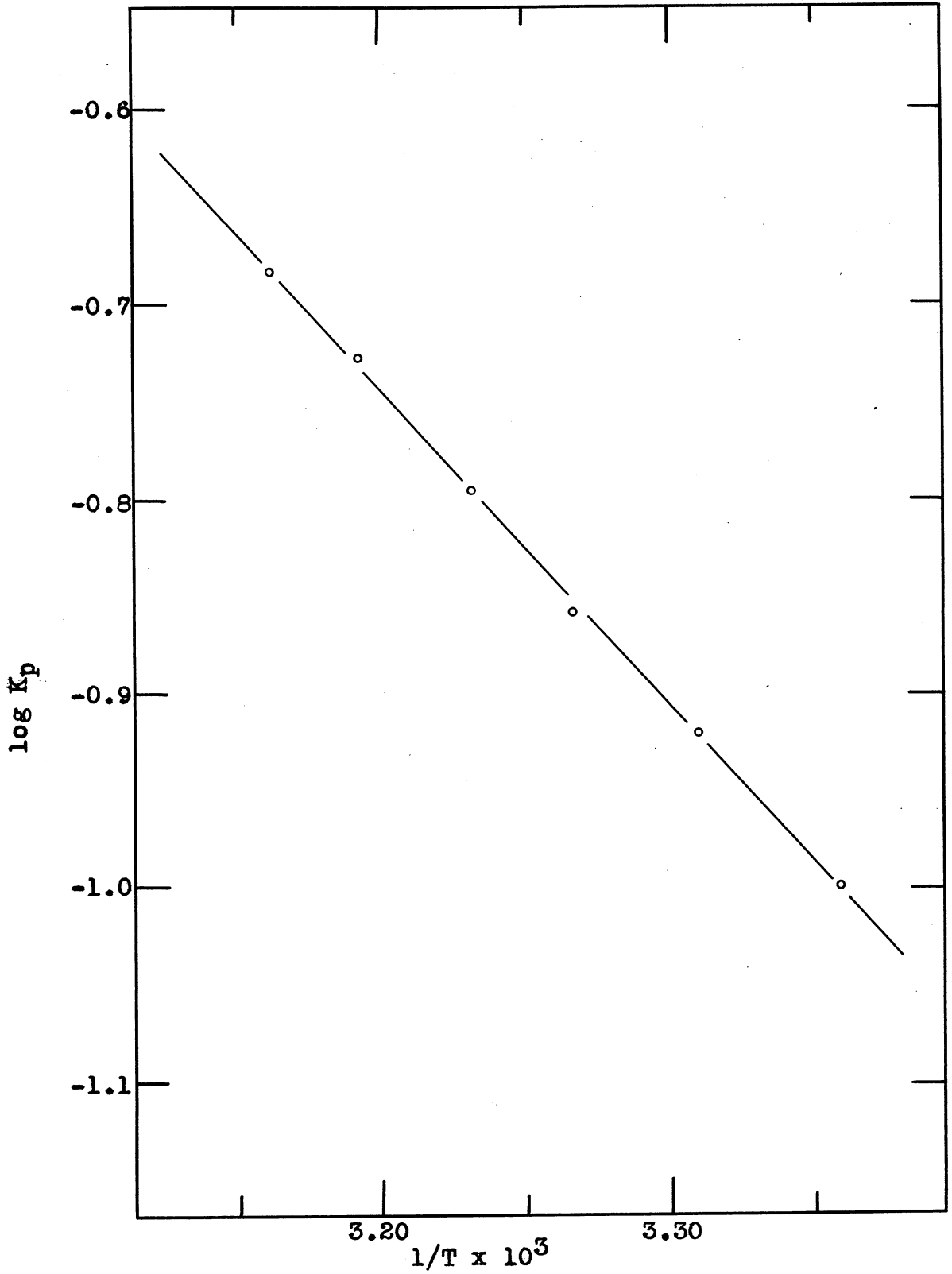


Figure 11

Graph of the Dissociation Pressures of  
Methyl Acrylate Picrate



The following compounds were found to give no complex with picric acid.

Acetone	Cyclohexene
Ethyl alcohol	Allyl chloride
Ethyl ether	1-Hexene
<u>iso</u> -Propyl ether	2-Heptene
Ethyl acetate	Isoprene

Upon evacuation as previously described the only constant pressure obtained was that of the saturated solution.

TABLE 13

## Summary of Results

Complex of Picric Acid with	Mole Ratio Picric Acid to Aliphatic Component	K p(303°)	$\Delta H$ (kcal.)	$-\Delta F$ (303°) cal.
Allyl Alcohol	1:1	0.038	12.5	820
<u>n</u> -Propyl Alcohol	1:2	0.05	11.8	860
<u>n</u> -Propyl Ether	1:2	0.058	10.8	750
Allyl Ether	2:1	0.071	9.62	690
Benzene	1:1	0.131	8.84	530
Propionitrile	1:1	0.062	8.15	730
Methyl Acrylate	1:1	0.118	8.12	560
Allyl Ethyl Ether	1:2	0.229	8.06	390
Vinyl Acetate	1:1	0.167	8.06	470
Acetonitrile	1:1	0.112	7.78	570
Acrylonitrile	2:1	0.142	7.65	510

## CONCLUSIONS

The apparatus used for the determination of the dissociation pressures and molecular ratios functioned very well. It was found that values could be duplicated fairly easily. The only point left to be desired is the availability of a stopcock lubricant that is completely insoluble in organic compounds.

In the determinations of molecular ratios it was assumed that the ratio of combination was a small integral number. If the determinations were fairly close to some small integral ratio that ratio was taken as the ratio of combination. The values found to be one-to-one are as expected. The ratios of acrylonitrile and allyl ether can be explained on the basis of two points of unsaturation and, therefore, two points of interaction with picric acid. It does not follow, however, that  $\text{>C} = \text{C}'$  and  $-\text{C} \equiv \text{N}$  contribute an equal amount to the interaction. Vinyl acetate and methyl acrylate have two points of unsaturation and yet form one-to-one complexes. This, however, may be due to the inability of  $\text{>C} = \text{O}$  groups to affect complexing, as acetone and especially ethyl acetate were found to form no complexes.

The values obtained for the molecular ratios of n-propyl ether, n-propyl alcohol and allyl ethyl ether are for complexes of a different type. It is thought that the complexes with two molecules of volatile component dissociate

into complexes that are not stoichiometric and, therefore, do not exhibit any further constant dissociation pressures.

The heats of dissociation of all of the compounds studied are within a very small range. So little information was obtained that no attempt could be made to correlate the heats of dissociation with the nature of functional groups present. An attempt was made to find some relation between the heats of dissociation and the heat of vaporization of the volatile component, but no relation could be found. There was a qualitative relation found between the ability of the substance to complex and the color intensification of the picric acid immediately upon contact with the volatile component.

Repeated attempts failed to yield the complexes Harper (53) reported of picric acid with cyclohexene and allyl chloride. It is assumed that the complex of picric acid with allyl bromide that he reported also does not exist. Values found for the dissociation pressures of complexes of allyl alcohol and acrylonitrile are not in agreement with those found by Harper.

This study yielded thermodynamic equilibrium constants, and comparisons with work done in solution would be invalid.

The free energies of formation of these complexes were found to be negative in all cases indicating that they are thermodynamically stable over the temperature range studied.

## SUMMARY

The dissociation pressures and heats of dissociation of new molecular complexes were determined by the use of a differential tensimeter. The molecular ratios of these complexes were determined.

New molecular complexes of picric acid with allyl alcohol, acrylonitrile, propionitrile, acetonitrile, n-propyl ether, n-propyl alcohol, allyl ether, allyl ethyl ether, vinyl acetate, and methyl acrylate were isolated. Picric acid was found not to complex with ethyl alcohol, water, ethyl acetate, acetone, cyclohexene, ethyl ether, iso-propyl ether, 1-hexene, 2-heptene, or isoprene.

All of the complexes were found to decrease in stability as the temperature increases. The complexes were shown to be thermodynamically stable over the temperature range studied.

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## VITA

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