AN INVESTIGATION OF SOLID MOLECULAR

COMPLEXES OF PICRIC ACID

By

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COMPLEXES OF PICRIC ACID

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INTRODUCTION

Picric acid is known to form complexes or molecular addition com-
pounds with aromatic hydrocarbons, amines, and phenols (24). In gener-
al, such complexes are formed with Lewis bases or electron-donating
nuclei.

Smith (27) and earlier workers (20,5,10) have utilized a rela-
tively simple and basically sound technique to study the nature of
these compounds. Molecular ratios and dissociation pressures were
determined for a number of new complexes by means of a differential
tensimeter. The heats of dissociation were then calculated from the
pressures observed at several temperatures and these are functions
of the stability of the complexes in the solid state.

The existence of several of the new addition compounds which were
claimed in earlier theses is questionable. This investigation was
undertaken to establish the reliability of the dissociation pressure
measurements and to determine the validity of previous workers' claims
for new complexes of certain aliphatic alcohols, ethers, nitriles,
esters, and olefins.

HISTORICAL

Organic molecular compounds have received a great deal of attention in the past, primarily owing to the apparent violation of rules for chemical bonding. A review by Pfeiffer (22) published in 1927 noted the additive combination of aromatic hydrocarbons with other organic compounds such as p-benzoquinone, polynitro aromatic compounds, and maleic anhydride. Inorganic acids such as sulfur dioxide, silver perchlorate, and hydrogen halides (2,26) may also participate in additive combination with certain aromatic and unsaturated compounds. Some of these complexes can be isolated as solids, but the majority exist only in solution.

Methods of investigating these compounds include vapor-pressure studies, measurements of solubility (25), melting point-composition data, dielectric constants, conductivities, diamagnetic susceptibilities, and crystal structure (23). Ultraviolet spectroscopy (15) has been widely used to study the electronic characteristics of the complexes and infrared spectra have been utilized to determine the effect of complex formation on the vibrational frequencies of the atoms within the molecule (17). For example, a paper published recently by Kross and Fassel (14) describes an interesting technique for determining the existence of a solid complex with picric acid.

The procedure consists of obtaining the infrared spectrum of the complex in the crystalline state by means of the mull technique.

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Forty picrates of various types were investigated and an effort was made to classify these compounds into three categories. The frequencies studied were the nitroasymmetric stretching and the carbon-hydrogen out-of-plane bending at 1525 and 783 cm^{-1}, respectively. The frequencies are sensitive to complex formation and some information as to type of interaction can be obtained.

Many previous workers have studied solutions of these complexes because of the instability of the solid complex. This work is based on the measurement of dissociation pressures of the solid complex, and therefore, the donor compounds studied were restricted to those with a conveniently measurable vapor pressure at 20 to 50°C. The data obtained for the dissociation constants of the solid complexes cannot be directly correlated with the equilibrium constants obtained in solution studies.

A number of theories have been advanced concerning the nature of the molecular addition complex. The covalent bond theory (3), which superseded Pfeiffer's residual valence field interaction concept, was based on the following structure:
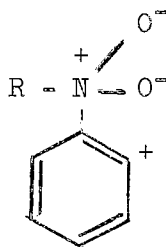
This theory has been rejected since the observed intermolecular distances are larger than predicted for covalent bonding. In addition, equilibrium conditions are rapidly obtained and this is not typical of covalent bond formation (2).

Briegleb's (4) polarization aggregate theory attributes complex formation to electrostatic interactions. These complexes could be formed between molecules with permanent dipoles and also with non-polar molecules subject to polarization by induction.

Weiss (28) explained the complex colors in his ionic complex theory as illustrated below:

$$D: \ + \ A \ = \ (D \cdot)^+ \ (\cdot A)^-$$
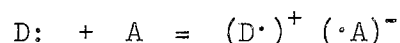
He states that the donor-acceptor complex results from the transfer of an electron to form odd molecules. Many investigators (21,8) have noted the correlation of color with complex formation. Although this is a qualitative indication of interaction, it is primarily of interest in studies of solutions. A distribution study for picric acid between water, amyl alcohol, and toluene pointed out that the colors of the layers are different, indicating a variation in molecular species (25, 2). The coloration is presumed to be associated with a "drift of electrons" from one component to the other when reactive centers are appropriately located (11). Weiss concluded that the stability of a complex increases as the ionization potential of the donor decreases and as the electron affinity of the acceptor increases.

Dewar's (8,9) representation of the donor-acceptor interaction is illustrated by the following structure. The coordinate linkage is shown by means of the arrow between the benzene nucleus and a vacant orbital of the acceptor molecule. (A)
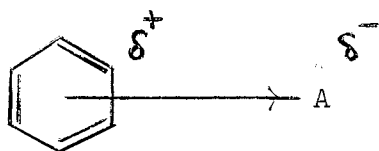
One of the most recent and widely accepted approaches is a quantum-mechanical treatment by Mulliken (18,19) and is known as the charge-transfer concept. The term "charge transfer" is defined as an intermolecular process whereby an electron is partially or completely transferred from one component of the complex to the other (21). A molecular complex is formed by the transfer of an electron from the π molecular orbital of a Lewis base to a vacant π molecular orbital of a Lewis acid. A second type of complex may be formed by the donation of an electron from the non-bonding orbital in the Lewis base to the vacant π-orbital in the Lewis acid and this is known as n-π interaction (14).

The donor component, which functions as the Lewis base, is usually aromatic and the ability to form an addition compound increases with the number of fused nuclei in the aromatic ring system. Benzene forms a relatively small number of unstable complexes while naphthalene forms a larger number of more stable ones (29). The Mulliken theory lacks the restrictions of Lewis acid-base interactions in that the electrons do not have to move from a particular atom in the donor to a specific atom in the acceptor component.

The strength of the interaction varies depending on the aromatic substituents present, from complete electron transfer to slight overlap of the orbitals, with resonance between the no-bond structure and the charge-transfer structure (16). The ionization potential of the donor, the electron affinity of the acceptor, and steric effects play an important role in the explanation of the charge-transfer concept.

A number of generalizations concerning the effect of substitution on the donor component for picric acid complexes are listed below:

1. Methyl substituents increase the stability of the complex.

2. Hydroxyl and amino groups increase the stability.

3. Nitro groups on the donor component decrease the tendency toward complex formation (29).

The relative stabilities of substituted benzene picrates vary as shown in the following table. These stability comparisons are based on distribution ratios for picric acid between a solvent and water when the aromatic substance is added to the solvent. The values are proportional to free energy changes for the alkylbenzenes and p-xylene has been arbitrarily taken as unity (1).

Substituent	Stability
H	0.70
CH_3	0.84
o-$(CH_3)_2$	1.03
m-$(CH_3)_2$	0.98
p-$(CH_3)_2$	1.00
1,3,5-$(CH_3)_3$	1.12
1,2,4,5-$(CH_3)_4$	1.65
$(CH_3)_6$	2.83
C_2H_5	0.74
n-C_3H_7	0.98
n-C_4H_9	0.57
s-C_4H_9	0.56
t-C_4H_9	0.51

THEORETICAL BASIS OF EXPERIMENTS

The first phase of this method is to isolate the complex (1:1 or 2:1) in such a manner as to exclude all foreign gases completely from the system. This is accomplished by using an excess of the volatile component over that which is required to form the complex in question. This excess volatile component is removed in increments by evacuating to obtain a "sweeping out" effect.

When all of the extraneous gases have been removed, constant pressure readings are obtained which correspond to a saturated solution of the complex. The pressure observed results from the dissociation of the dissolved complex and from the vaporization of the solvent. Continued evacuations are made to obtain constant pressure readings corresponding to the dissociation of the solid complex only and this equilibrium can be expressed as follows:

$$PA_x V_y \ (s) \ = \ xPA \ (s) \ + \ yV \ (g)$$
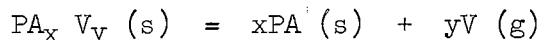
PA_x represents x moles of picric acid and V_y denotes y moles of the volatile component under study. The dissociation constant for this equilibrium is then:

$$K_d \ = \ \frac{(a_{PA})^x (a_V)^y}{(a_{PA_x\text{-}V_y})}$$

where a denotes the activity. The activities of the solids may be

taken as unity and at low pressures $(a_V)^y$ approaches P_V^y; therefore,

$$K_d = P_V^y$$

If K_d, the dissociation constant, is measured at two or more temperatures, the van't Hoff equation can be used to calculate the heat of dissociation for the complex.

$$\frac{d \ln K_d}{d T} = \frac{\Delta H}{RT^2}$$

This equation represents the variation of the equilibrium constant with temperature and can be integrated, by expressing ΔH as a function of temperature, to the following expression, where I is the constant of integration.

$$\log K_d = - \frac{\Delta H}{2.303RT} + I$$

A plot of $\log K_d$ vs $1/T$ will then yield a line with a slope of $-\Delta H/2.303R$ if the variation of heat capacities with temperature for the reactant and products is small. The standard free energy change can be calculated from the equilibrium constants with the following equation:

$$\Delta F = -RT \ln K_d$$

EXPERIMENTAL

Apparatus

The differential tensimeter illustrated in Figure 1 was employed for the majority of the pressure measurements. The U-tube is partially filled with mercury and overflow bulbs (E,F) prevent the mercury from being drawn into the cells by rapid changes in pressure. Picric acid and the volatile component are placed in cell A. The reference liquid is contained in cell B and three-way stopcocks (C,D) permit the cells to be opened to the manometer, the vacuum, or both. Additional stopcocks (G,H) are used to isolate the system from the vacuum line. The entire apparatus is placed in a constant-temperature bath.

The absolute manometer system is shown in Figure 2. Cell A is connected to the manometer and vacuum line by means of a three-way stopcock (B) and the system is further isolated from the vacuum by stopcock C. The mercury used in the manometer must be clean and one must be careful not to allow the closed end of the tube to become contaminated with a volatile substance. The manometer was checked before each reading by drawing a full vacuum and the pressure difference between the levels was always less than 0.5 mm.

Considerable difficulty was experienced with leaking stopcocks in the differential apparatus. Many varieties of grease were tried, but none appeared to be completely resistant to the organic vapors. Teflon plugs were tested but could not be used at low pressures.
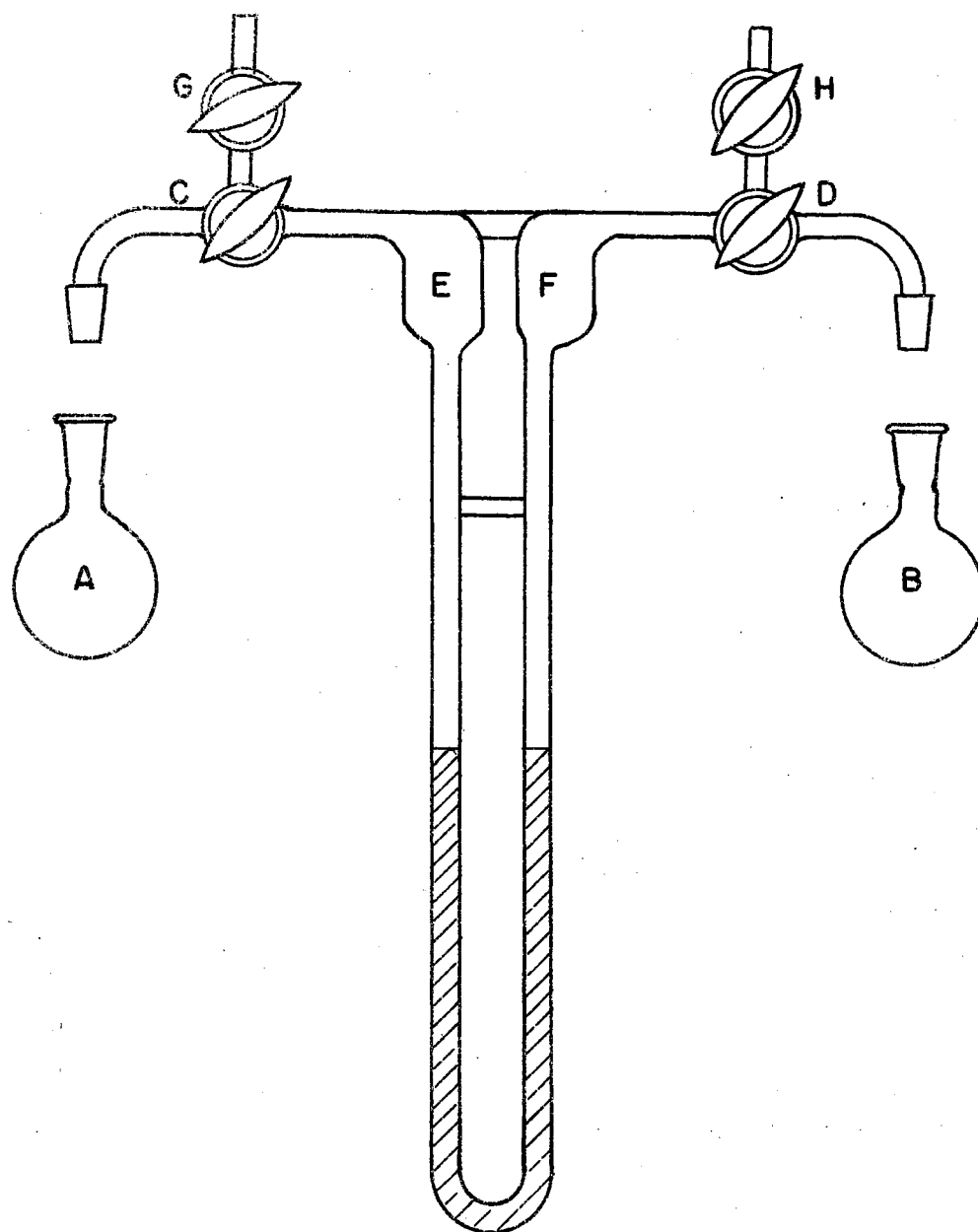
FIGURE (1)

DIFFERENTIAL MANOMETER APPARATUS
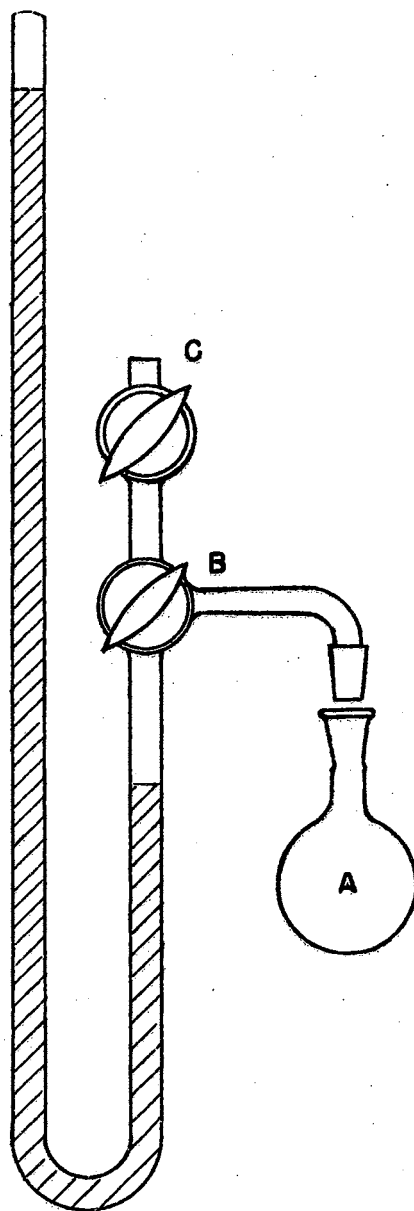
FIGURE (2)
ABSOLUTE MANOMETER APPARATUS

When water was used as the reference liquid, the leakage occurred much less frequently and always on the side containing the organic material. Ground glass joints were replaced with the o-ring seal type; such joints are very useful when one determines molecular ratios and infra-red spectra since the complex is then not contaminated with stopcock grease.

Pressure differences were measured with a cathetometer and could be obtained to 0.1 mm. The vacuum system consisted of a high-vacuum pump equipped with a drying tower and a cold trap to condense the vapors from the evaporation of the volatile component.

Chemicals

Picric acid - Reagent grade acid was dissolved in benzene and the water removed by azeotropic distillation. The air-dried crystals melted at 121.6 - 122°C.

Benzene - Reagent grade was dried over calcium hydride and passed through an alumina column. It was then distilled, the first and final 10% cuts being rejected.

n-Propyl alcohol - Reagent grade was distilled after drying. An 80% heart cut was taken and shown to be 99.5% pure by GLPC analysis.

Ethylbenzene - As for benzene.

Styrene - Reagent grade passed through alumina to remove inhibitor and impurities.

Xylene - As for benzene.

Cyclohexane - As for benzene.

Ethyl alcohol - Absolute, as for n-propyl alcohol.

Acrylonitrile - Eastman, used without further purification.

General Procedure

Two to three grams of picric acid are weighed into the sample cell and a considerable excess of the volatile component is added. The mixture is heated until complete solution of the picric acid is obtained and the contents of the cell are agitated slightly during cooling to prevent formation of a solid cake of crystals. In most cases glass wool was placed in the flask to obtain more finely divided crystals and to eliminate pockets of the volatile component.

Water or some other suitable reference liquid is placed in the opposite cell and both flasks are attached to the manometer, which has been previously filled with clean, dry mercury. Each cell is then connected to the vacuum by manipulation of the stopcocks and approximately one-third of the liquid is evaporated. The manometer is then alternately evacuated and connected to the cells to complete the removal of air from the system. A constant pressure for the saturated solution will be obtained when the air has been excluded and the system is at equilibrium. If the pressure is greater on the reference-cell side, the pressure in the test cell is equal to the vapor pressure of the reference liquid minus the difference between the two level readings. Conversely, the difference is added to the reference value if the pressure is greater on the test side.

The reference vapor pressure of water is readily obtained from tables (12) for any temperature. If benzene is used, its vapor pressure can be calculated for the temperature of the measurement. (See Table 1.)

The excess volatile component is then evaporated until the complex is near dryness. Evacuations are made in increments at this point and

readings are taken after each increment. If a complex exists, the pressure will reach a constant value corresponding to the dissociation pressure for the complex. If one wishes to determine the molecular ratio for the complex, the cell is capped and weighed to obtain the weight of the volatile component in the complex. Other dissociation constants for the complex are obtained by measuring the dissociation pressures at three degree intervals over a fifteen to twenty degree temperature range.

The procedure for using the absolute manometer apparatus is identical to the differential method except that the pressure is obtained directly from the differences in the mercury levels in the closed-end manometer. Equilibrium conditions were established more rapidly in this system and the smaller number of stopcocks made the leakage problem less severe. The differential system is considered to be the more exact, however, since the closed-end manometer is easily contaminated.

Infrared spectra were obtained on the solid complexes by the mull method. The freshly prepared moist crystals were mixed with Nujol and ground to a finely dispersed state with a mortar and pestle. The resulting paste was applied to the salt plates and the spectra obtained immediately. Spectra for several of the picrates were obtained by the smear technique in which a drop of the saturated solution was placed between the plates without Nujol. The picric acid bands appeared much sharper with this method than those observed by mulling the crystalline material.

Solubility determinations, when required, were made by titrating a weighed amount of saturated solution with 0.1 N sodium hydroxide to

the phenolphthalein endpoint.

Results of Pressure Measurements

The following tables and graphs represent the data obtained with the absolute and differential manometer systems. The heats of dissociation are calculated from the slopes of the lines as discussed in the theoretical section, and the lines corresponding to the vapor pressures of the pure volatile components are constructed from literature values.

Several experiments were performed in which the vapor pressure of a saturated solution was determined over a given temperature range. These runs were carried out in exactly the same manner as the dissociation runs except that the complex still contained, or was dissolved in, a visible excess of the volatile component.

Figures 3 and 7 illustrate the incremental pump-down technique used in searching for a constant pressure level proving the presence of a molecular complex.

The empirical equation expressing the pressure as a function of temperature for the various complexes is

$$\log P_{atm} = A/T + B$$

where A is the slope of the line and B is a constant.

TABLE 1

Vapor Pressures for Benzene

$T°,K$	$1/T \times 10^3$	P_{atm} *	log P_{atm}
290.6	3.441	0.0874	-1.0585
298.0	3.356	0.1234	-0.9087
303.3	3.297	0.1570	-0.8041
307.6	3.251	0.1900	-0.7213
313.1	3.194	0.2411	-0.6178
318.0	3.145	0.2949	-0.5303
322.9	3.097	0.3553	-0.4494

* Calculated from the following equation (13):

$$\log P_{atm} = (0.05223/T)(A) + B$$

where A = 34,172 and B = 7.9622 for 0 to 42°C
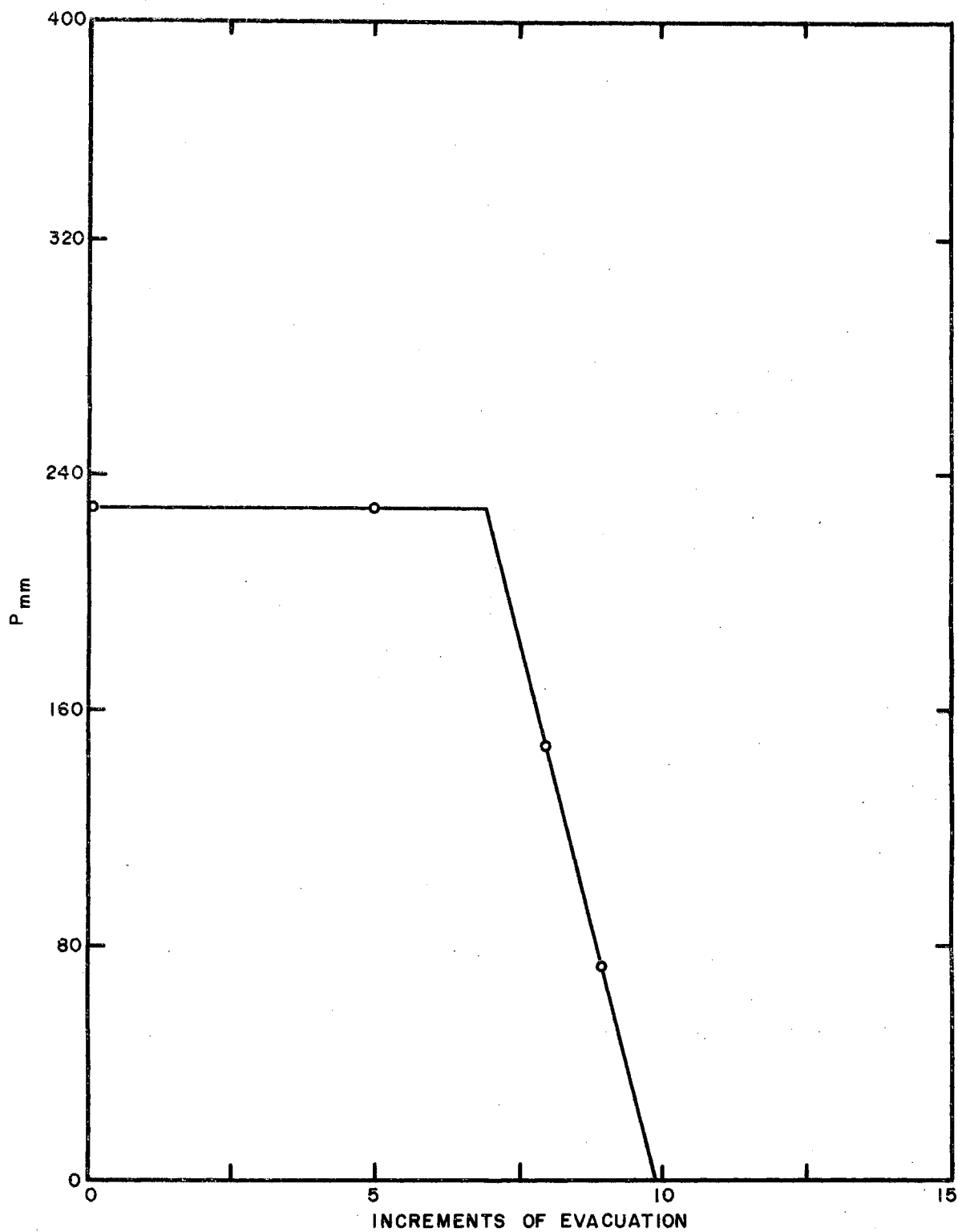
FIGURE 3

PRESSURE vs INCREMENTS OF EVACUATION FOR
BENZENE – PICRIC ACID SYSTEM (47.0°C.)

TABLE 2

<u>Vapor Pressures for the Benzene-Picric Acid System</u>

$T°,K$	$1/T \times 10^3$	P_{mm}	P_{atm}	$\log P_{atm}$
303.4*	3.296	114.7	0.1509	-0.8213
309.3*	3.233	146.1	0.1923	-0.7160
312.4*	3.201	166.8	0.2195	-0.6586
313.1*	3.194	174.3	0.2293	-0.6396
320.1*	3.124	230.0	0.3021	-0.5198
320.1	3.124	147.0	0.1934	-0.7135
320.1	3.124	67.5	0.0888	-0.9112

* Saturated solution; the data was obtained with the dif-
ferential manometer using water as the reference liquid.
(See Figures 3 and 4.)

TABLE 3

Dissociation Pressures of Benzene Picrate*

$T°$, K	$1/T \times 10^3$	P_{atm}	$\log P_{atm}$
294.2	3.399	0.0739	-1.1311
295.2	3.387	0.0779	-1.1085
296.5	3.373	0.0829	-1.0815
297.5	3.361	0.0879	-1.0560
298.1	3.354	0.0913	-1.0390
299.1	3.343	0.0986	-1.0060
300.1	3.332	0.1051	-0.9788
301.2	3.320	0.1124	-0.9492
302.1	3.310	0.1192	-0.9237
304.9	3.280	0.1345	-0.8713
306.3	3.265	0.1545	-0.8111
307.2	3.255	0.1624	-0.7894
308.1	3.245	0.1721	-0.7642
309.1	3.235	0.1821	-0.7397
310.2	3.224	0.1913	-0.7183

* Absolute manometer apparatus used on this run. Six ad-
ditional runs were made using both the absolute and dif-
ferential systems. The dissociation pressures obtained
in each experiment agreed very well with those tabulated
above. (See Figure 4.)

$$\log P_{atm} = 6.93 - 2370/T$$

$$\Delta H \text{ dissociation} = 10.97 \text{ Kcal/mole}$$

TABLE 4

Vapor Pressures for Benzene-Picric Acid System*

$T°$, K	$1/T \times 10^3$	P_{atm}	log P_{atm}
296.7	3.370	0.1129	-0.9473
299.7	3.337	0.1280	-0.8928
301.7	3.315	0.1408	-0.8514
305.7	3.271	0.1664	-0.7789
309.7	3.229	0.1967	-0.7062
311.7	3.208	0.2137	-0.6702

* Excess benzene was present for the entire determination.
  The data was obtained with the differential tensimeter
  using benzene as the reference liquid. (See Figure 4.)
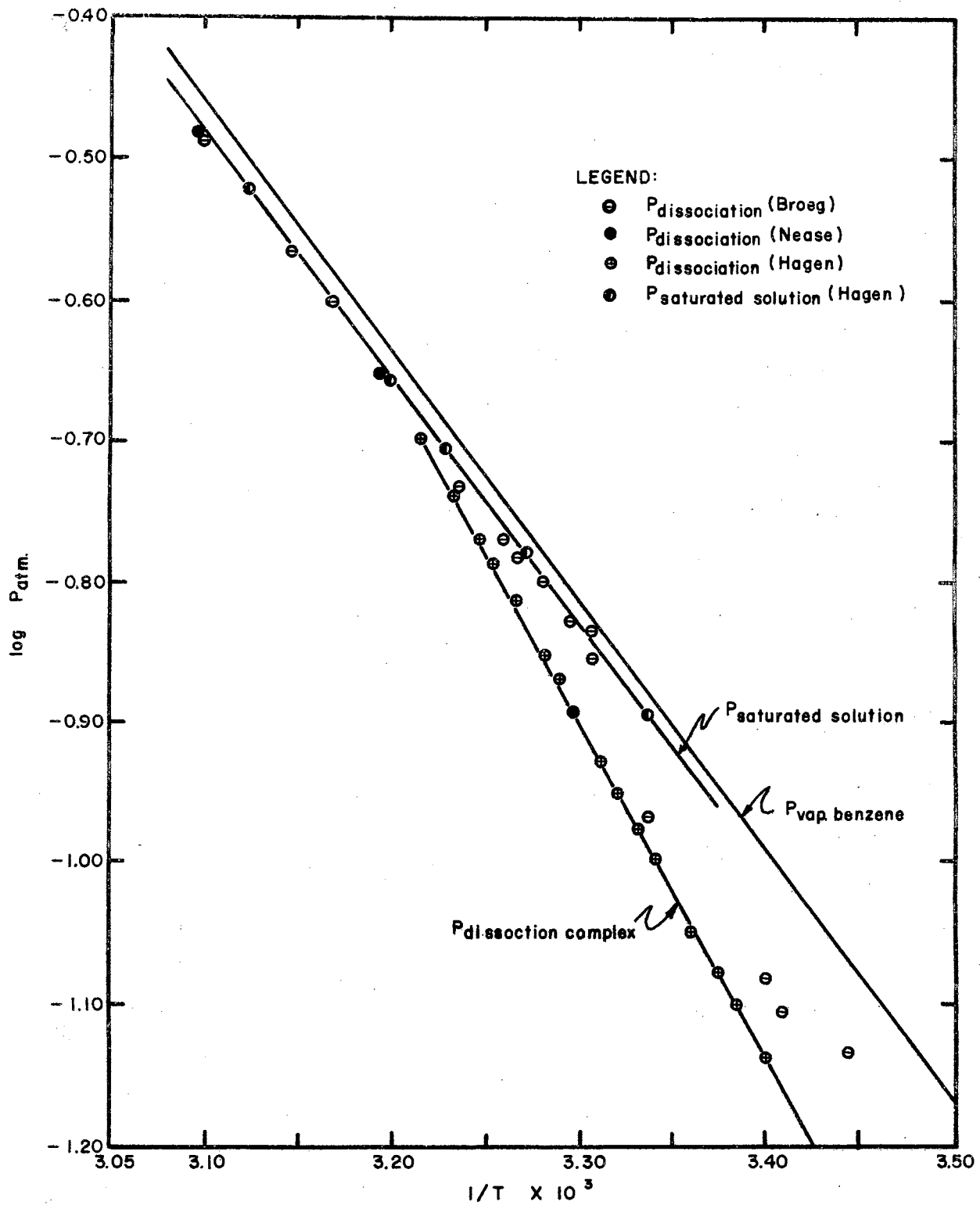
FIGURE 4

GRAPH OF PRESSURE, TEMPERATURE DATA FOR THE
BENZENE - PICRIC ACID SYSTEM

TABLE 5

Vapor Pressures of Ethylbenzene Picrate (13)

$T°,K$	$1/T \times 10^3$	P_{atm}	$\log P_{atm}$
307.5	3.252	0.0211	-1.6768
313.4	3.191	0.0287	-1.5424
316.3	3.162	0.0336	-1.4743
319.4	3.131	0.0387	-1.4125

* Calculated from $\log P_{mm} = 6.95366 - 1421.9/(t + 212.9)$

(See Figure 5.)

TABLE 6

Dissociation Pressures of Ethylbenzene Picrate

(Weighings showed the complex to be 1:1)

$T°,K$	$1/T \times 10^3$	P_{atm}	$\log P_{atm}$
313.4	3.191	0.0211	-1.6768
316.3	3.162	0.0274	-1.5629
319.4	3.131	0.0343	-1.4642

$$\log P_{atm} = 9.67 - 3555/T$$

$$\Delta H = 16.27 \text{ Kcal/mole}$$

FIGURE 5

**DISSOCIATION PRESSURES OF ETHYL BENZENE PICRATE
AND VAPOR PRESSURES OF ETHYL BENZENE**

TABLE 7
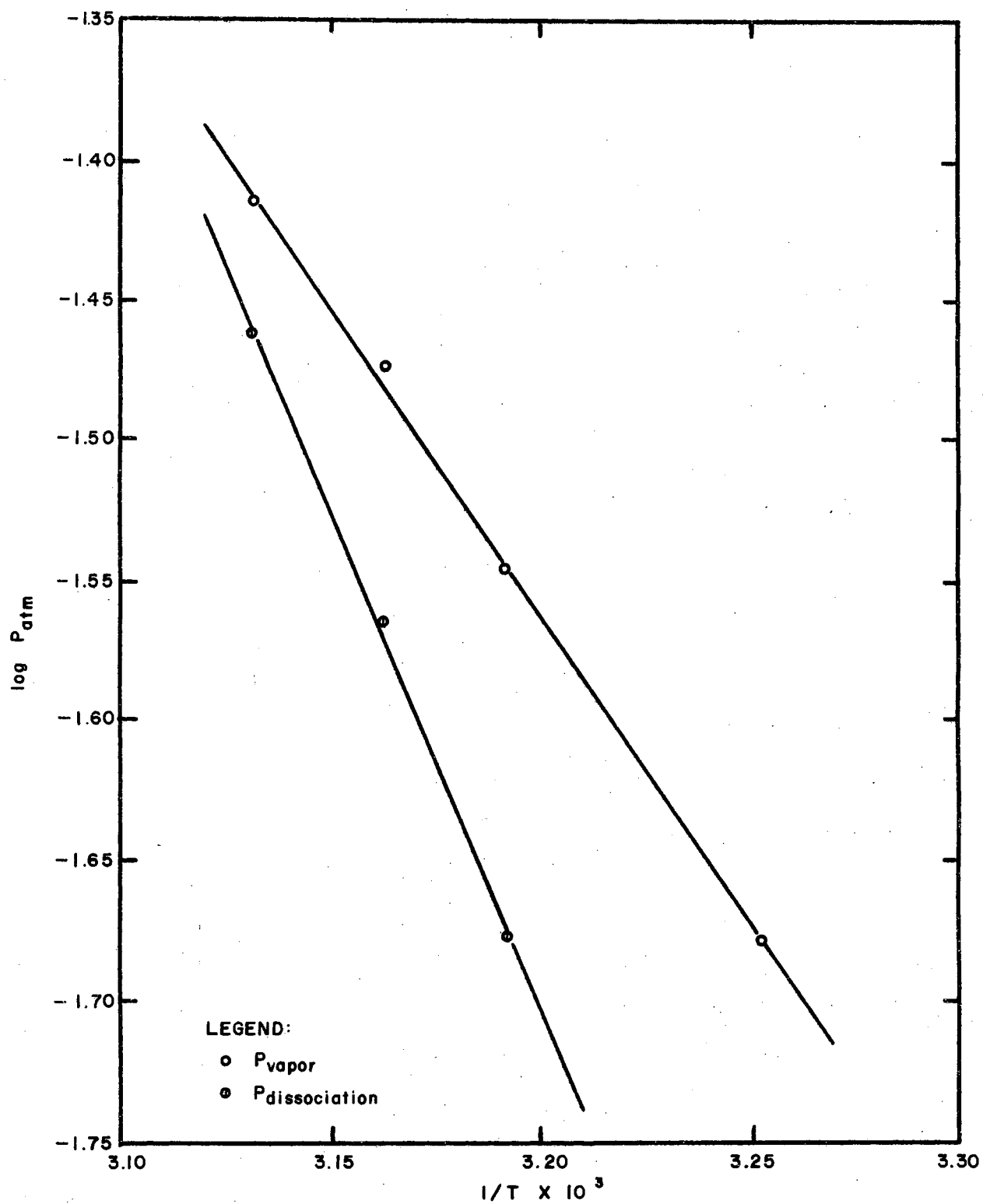
Vapor Pressures of Styrene (13)

$T°,K$	$1/T \times 10^3$	P_{atm}*	log P_{atm}
308.1	3.246	0.0149	-1.8268
313.1	3.194	0.0195	-1.7100
318.1	3.144	0.0252	-1.5986

* Calculated from log P_{mm}= 7.2788 - 1649.2/(t + 230)

(See Figure 6.)

TABLE 8

Dissociation Pressures of Styrene Picrate

(Weighings showed the complex to be 1:1)

$T°,K$	$1/T \times 10^3$	P_{atm}	log P_{atm}
309.2**	3.234	0.0134	-1.8729
312.8**	3.197	0.0163	-1.7878
317.1**	3.154	0.0199	-1.7012
309.3	3.233	0.0113	-1.9469
312.6	3.199	0.0129	-1.8894
316.8	3.157	0.0136	-1.8664
318.5	3.140	0.0146	-1.8357

** This run was on the saturated solution.

$$\log P_{atm} = 1.79 - 1153/T$$
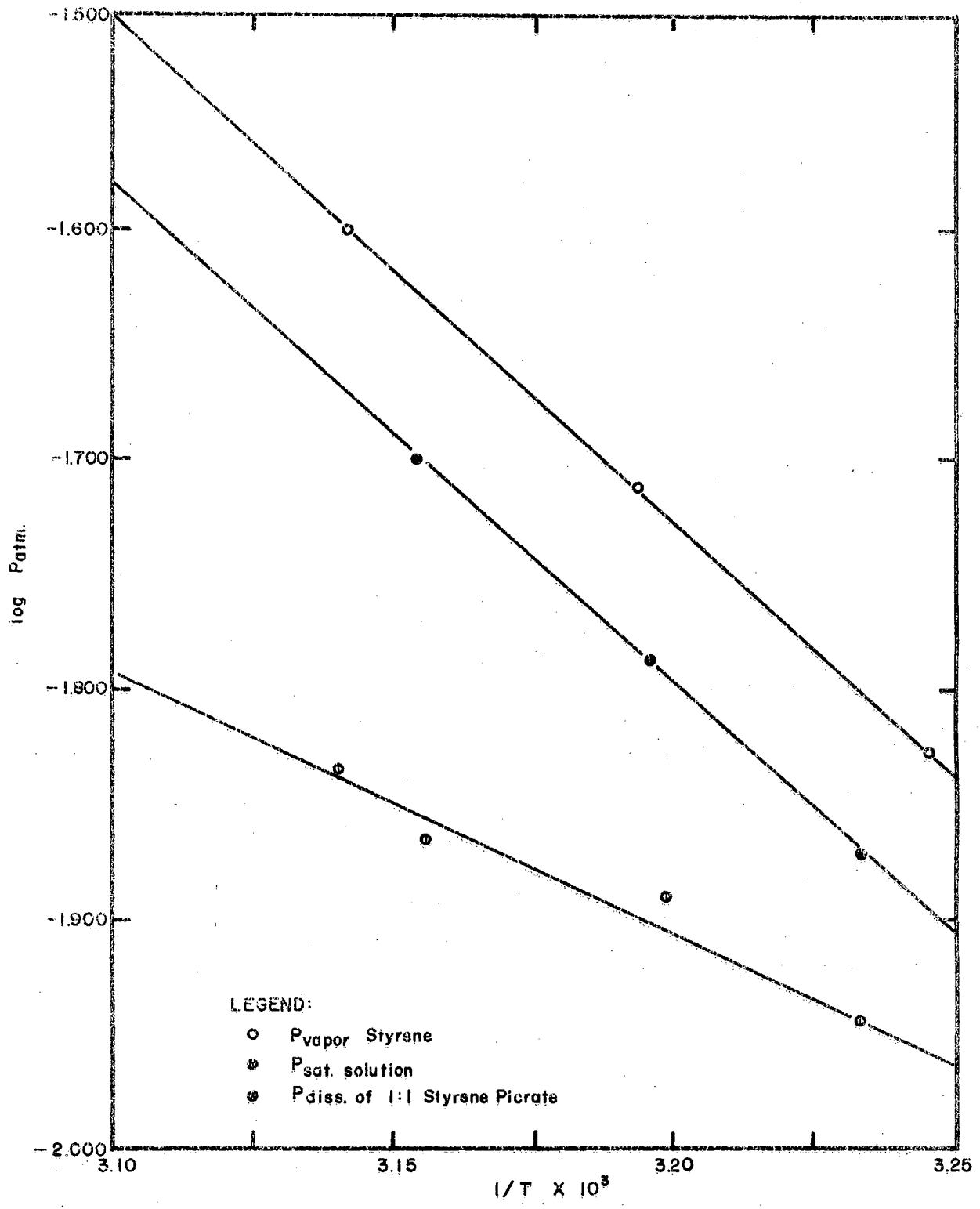
Δ H dissociation = 5.28 Kcal/mole

FIGURE 6

DISSOCIATION PRESSURES OF STYRENE PICRATE
AND VAPOR PRESSURES OF STYRENE

TABLE 9

Pressure Data for n-Propyl Alcohol-Picric
Acid System vs. Evacuations

Region A.   Large increments of alcohol were removed for
            each evacuation . . . . 12.4 mm
                                                  12.4
                                                  12.1
                                                  12.3
                                                  12.3

Region B.   Five increment evacuations in this region,
            complex approaching the dry state . 11.7
                                                 11.5
                                                 11.3
                                                 11.6

Region C.   One increment evacuation from this point
            onward 10.5
                                                  8.8
                                                  7.6
                                                  6.0
                                                  4.7
                                                  3.2
                                                  1.9
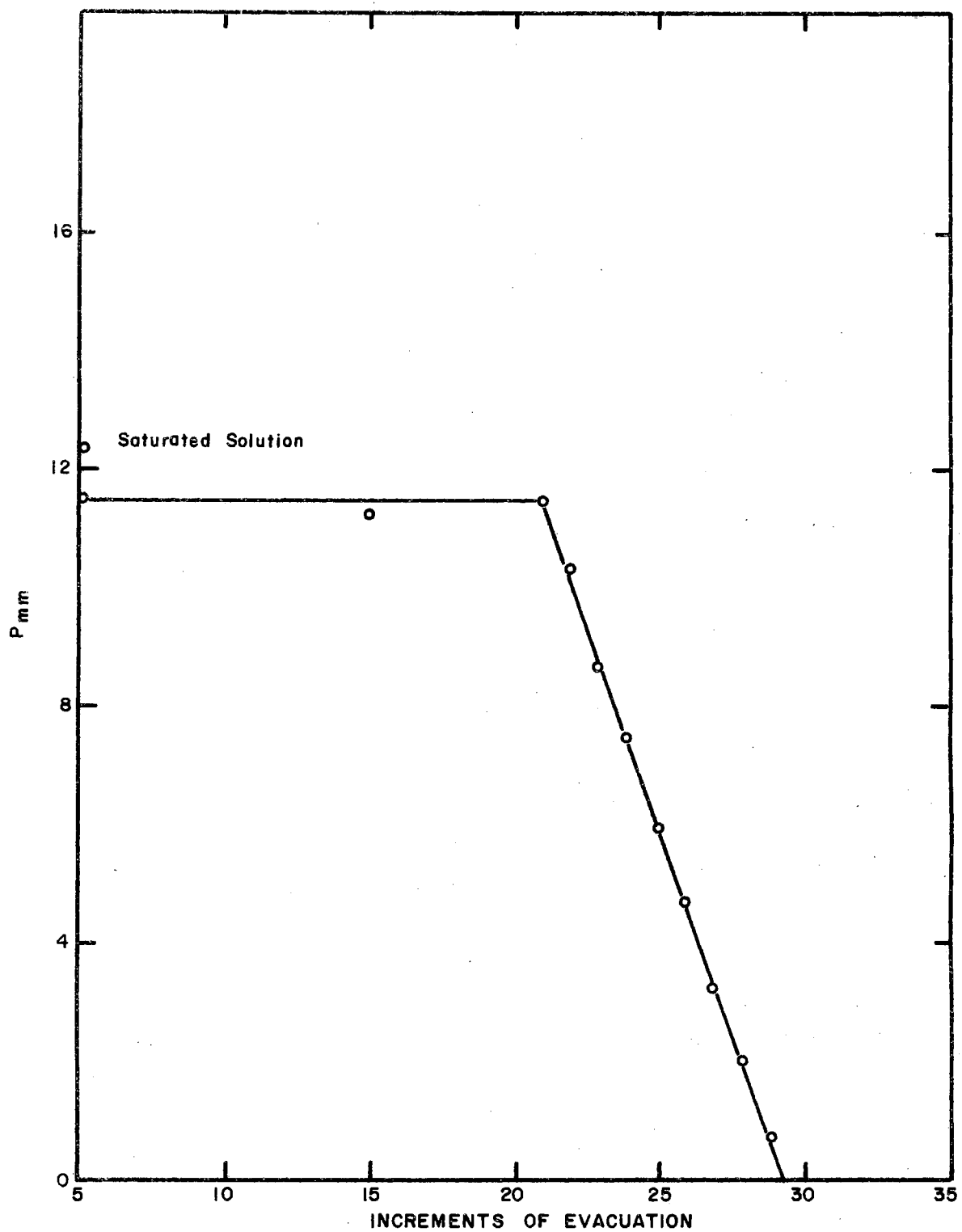   0.7

The complex was weighed at this point and all of the
alcohol was exhausted from the system.   (25°C.)

FIGURE 7

PRESSURE vs INCREMENTS OF EVACUATION FOR
n- PROPYL ALCOHOL – PICRIC ACID SYSTEM

TABLE 10

Vapor Pressure of n-Propyl Alcohol (13)

$T°,K$	$1/T \times 10^3$	P_{atm}	log P_{atm}
283.1	3.531	0.0096	-2.020
293.1	3.411	0.0191	-1.719
303.1	3.299	0.0363	-1.440
313.1	3.194	0.0661	-1.180

(See Figures 7 and 8)

TABLE 11

Dissociation Pressures of "Picrate" (Smith)

$T°,K$	$1/T \times 10^3$	K_p	log K_p
291.8*	3.461	0.0133	-1.8762
292.3**	3.241	0.0162	-1.7905
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

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

ΔH dissociation = 11.8 Kcal/mole
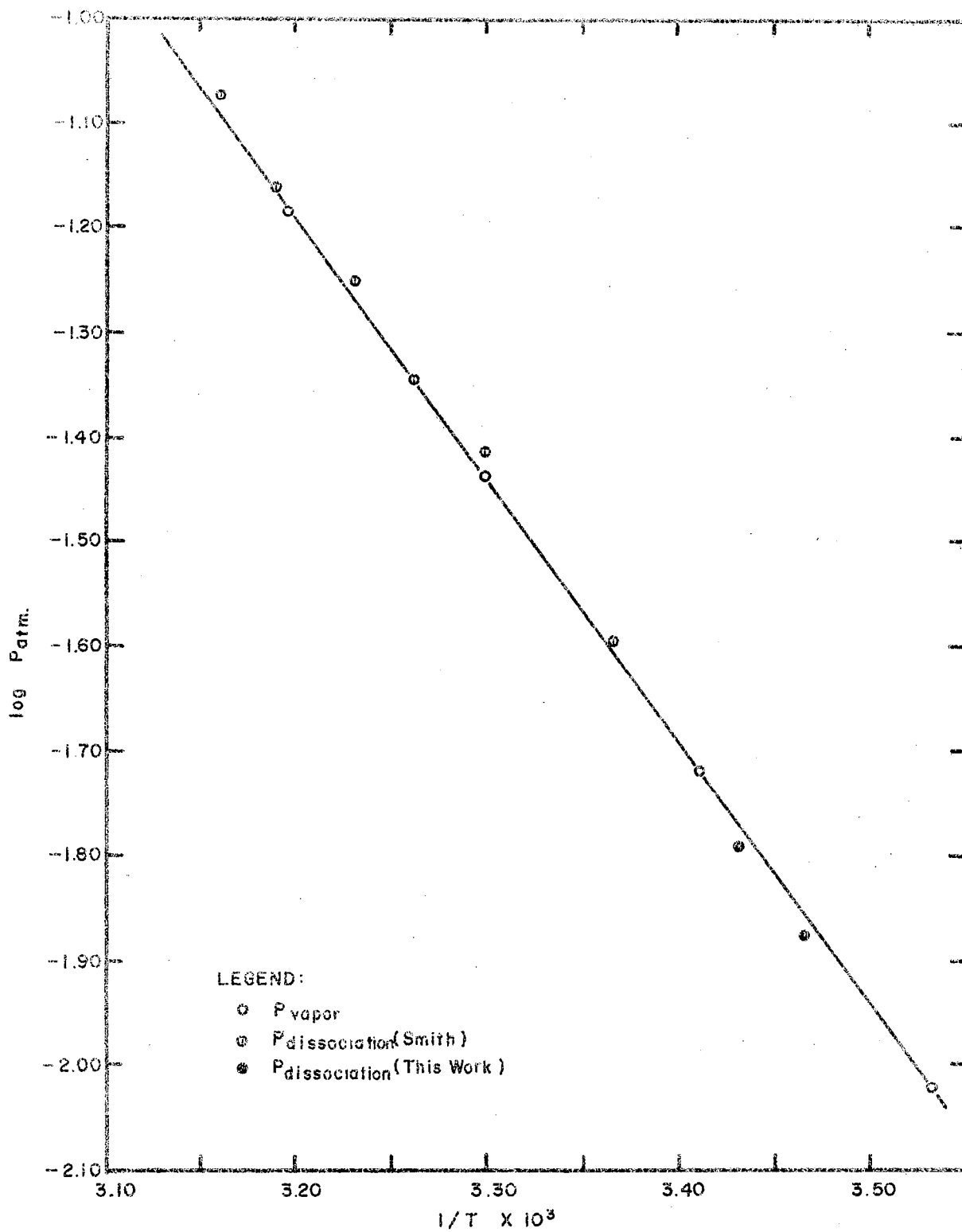
* This work Run I
** This work Run II

FIGURE 8

GRAPH OF PRESSURE , TEMPERATURE DATA FOR THE
PROPYL ALCOHOL — PICRIC ACID SYSTEM

TABLE 12

Vapor Pressures of Allyl Alcohol (13)

$T°,K$	$1/T \times 10^3$	P_{atm}	$\log P_{atm}$
283.7	3.525	0.0132	-1.879
306.6	3.261	0.0526	-1.279
323.2	3.094	0.1320	-0.879

TABLE 13

Dissociation Pressures of Allyl Alcohol Picrate

$T°,K$	$1/T \times 10^3$	K_p	$\log K_p$	
303.1	3.299	0.0375	-1.4260	(Smith)
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	
303.2	3.298	0.04816	-1.3164	(Harper)
306.6	3.261	0.05842	-1.2334	
308.1	3.243	0.06001	-1.2218	
313.2	3.192	0.07697	-1.1142	

Smith had obtained a value of 12.5 Kcal/mole for the heat of dissociation and Harper reported 8.28 Kcal/mole. Their results, however, appear to be based on vapor pressures for allyl alcohol rather than on dissociation pressures of a picrate. (See Figure 9.)
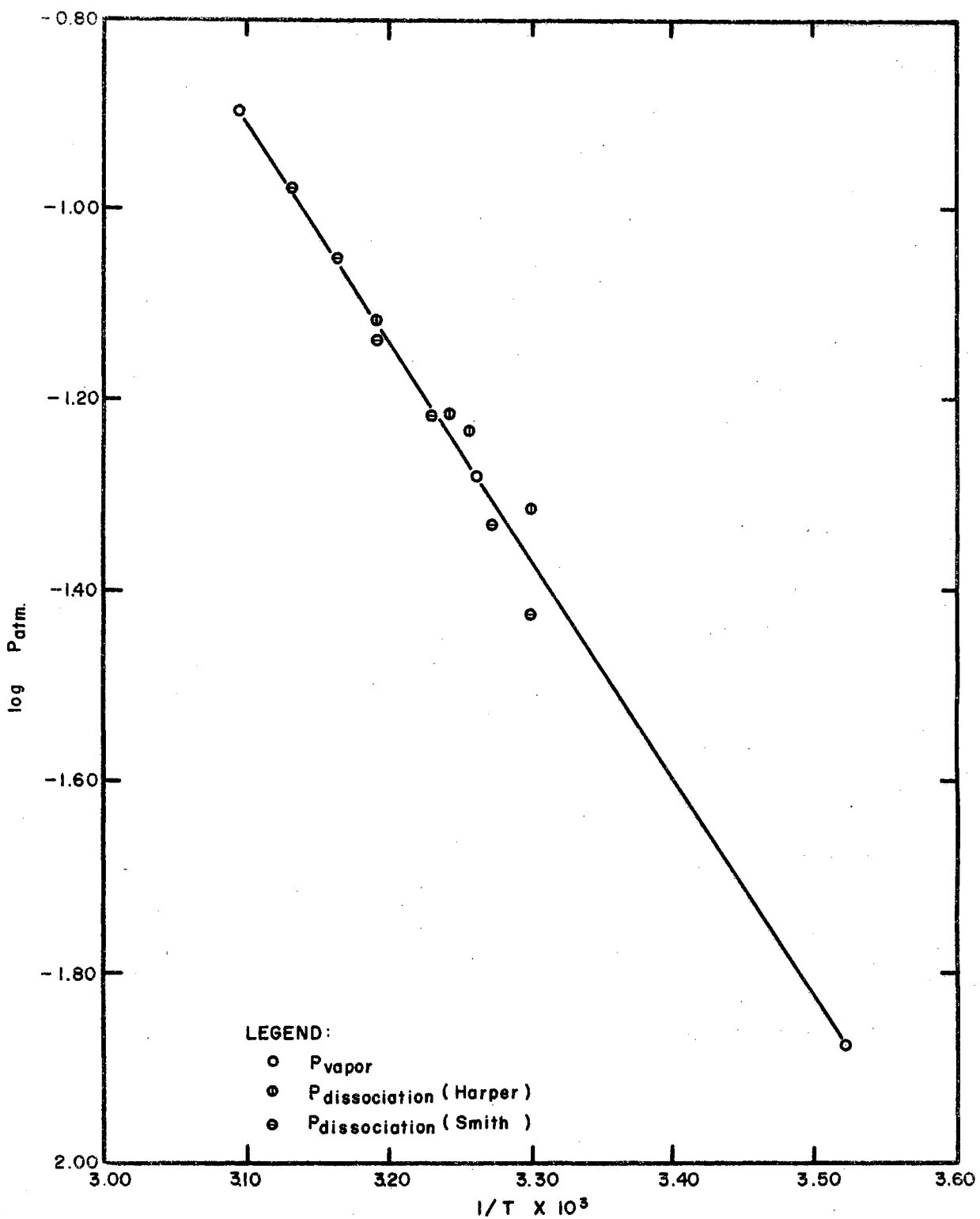
FIGURE 9

GRAPH OF PRESSURE, TEMPERATURE DATA FOR THE
ALLYL ALCOHOL – PICRIC ACID SYSTEM

TABLE 14

Vapor Pressures of Acrylonitrile (13)

T°,K	$1/T \times 10^3$	P_{atm}	log P_{atm}
284.1	3.519	0.0789	-1.1029
295.9	3.378	0.1316	-0.8807
311.8	3.207	0.2632	-0.5797

(See Figure 10.)

TABLE 15

Dissociation Pressures of Acrylonitrile Picrate

T°,K	$1/T \times 10^3$	P_{atm}	log K_p	
303.2	3.298	0.0476	-1.3221	(Harper)
308.1	3.243	0.0617	-1.2096	
313.2	3.192	0.0793	-1.1006	
318.2	3.141	0.1013	-0.9944	
303.1	3.299	0.1424	-0.8465	(Smith)
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	

(Harper) log P = 5.36 - $2030/T$, ΔH = 9.29 Kcal/mole

(Smith)   log P = 4.667 - $1660/T$, ΔH dissociation = 7.65 Kcal/mole

An incremental pump down conducted on the acrylonitrile-picric acid system indicated that Smith's data was obtained with an excess of acrylonitrile present. A constant pressure level was obtained corresponding to Harper's data for the 2:1 complex.
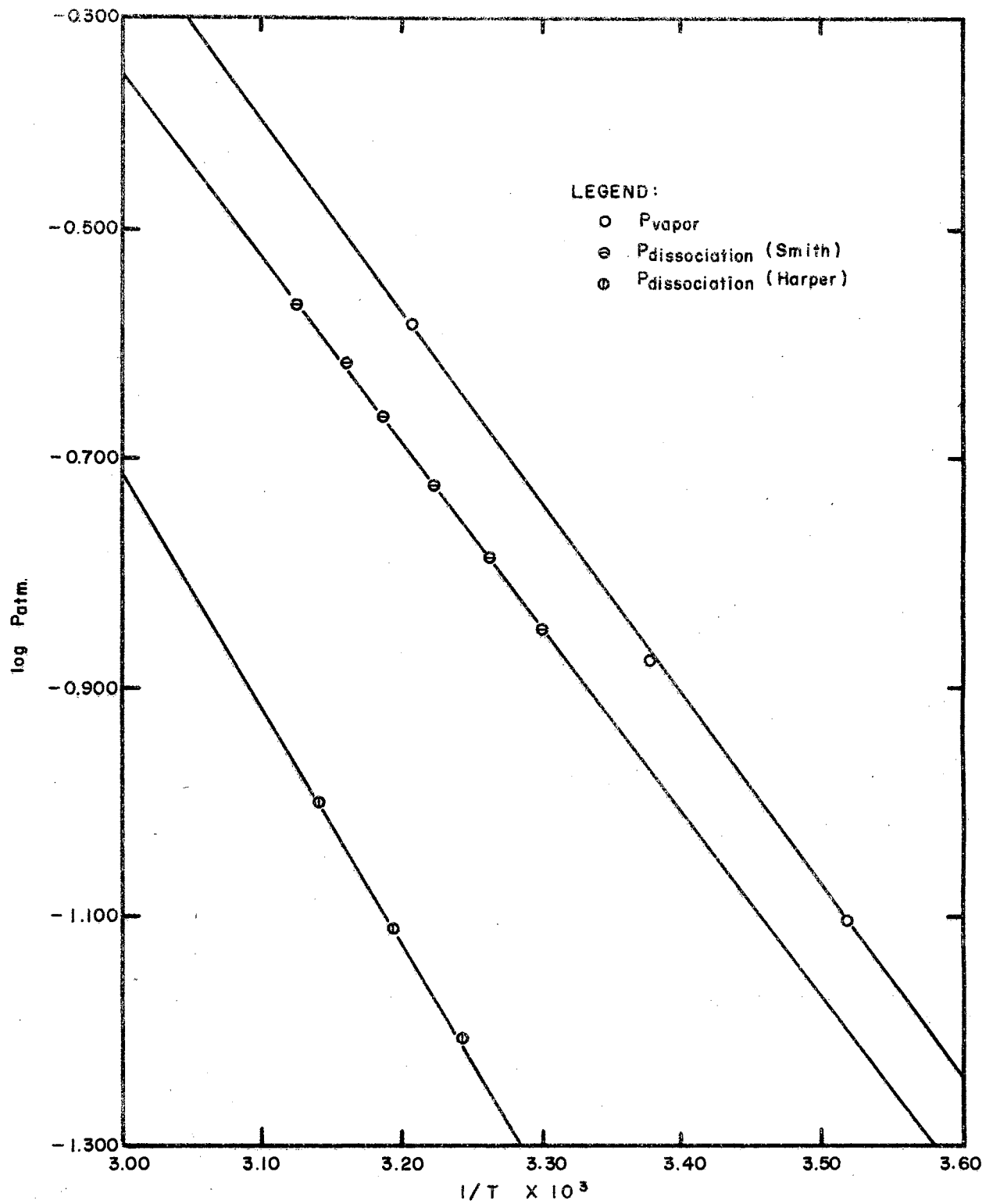
FIGURE 10

GRAPH OF PRESSURE , TEMPERATURE DATA FOR THE
ACRYLONITRILE - PICRIC ACID SYSTEM

The following figures illustrate the data for the vapor pressures
(13) of propionitrile, acetonitrile, methyl acrylate, and vinyl acetate.
The dissociation pressures (27) obtained are reported to be for 1:1
complexes in each case. Experimental data obtained in this work
indicate that if a slight excess of volatile component is present,
the slopes of the vapor pressure and dissociation pressure lines will
be equal. Additional increments of evacuation are needed to reach
the pressure level corresponding to the exact molecular ratio of the
complex. The slope of the line corresponding to the true complex is
usually different than that of the vapor pressure of the pure solvent,
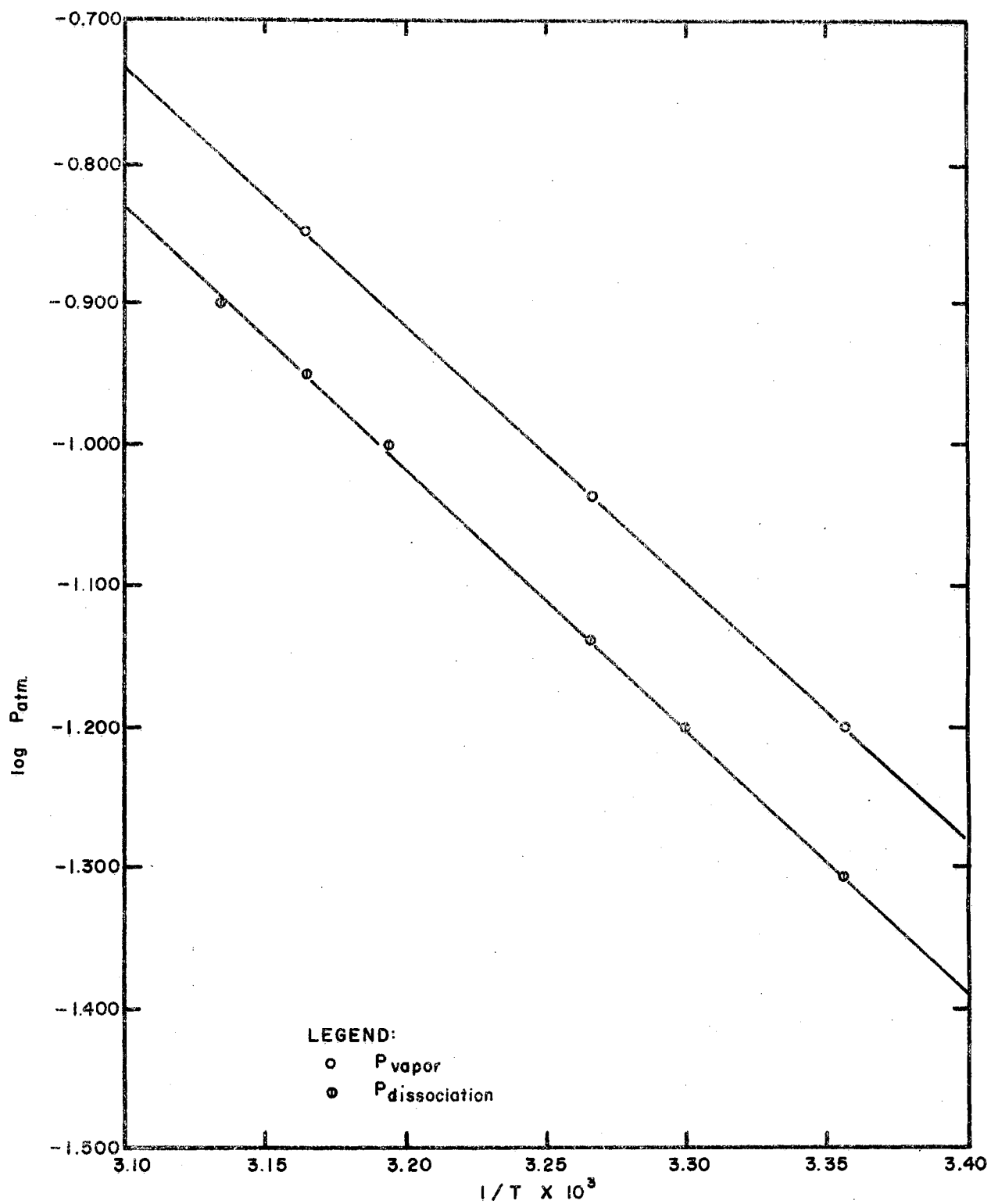as illustrated in the benzene and styrene experiments.

FIGURE II

GRAPH OF PRESSURE, TEMPERATURE DATA FOR THE
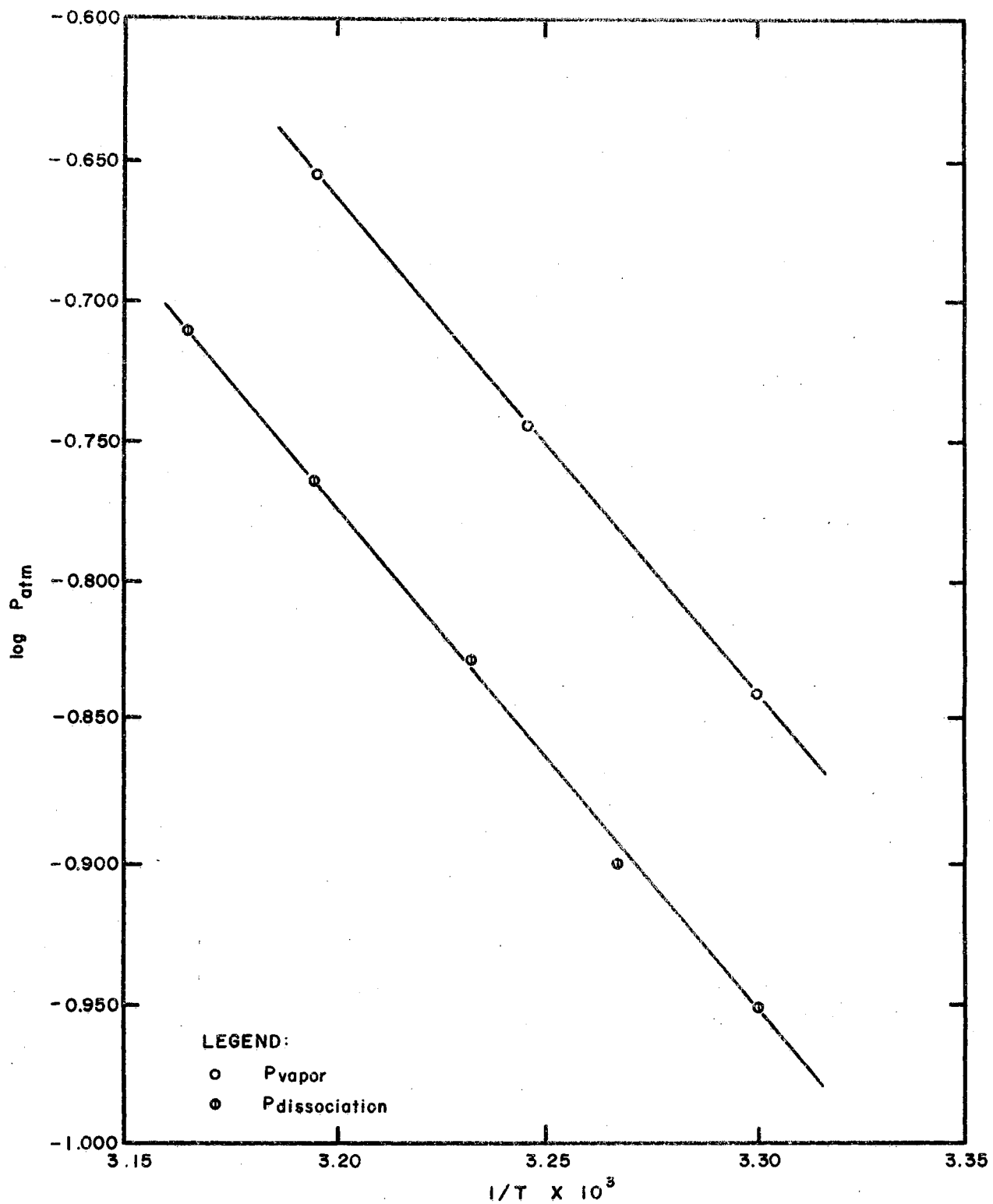PROPIONITRILE – PICRIC ACID SYSTEM

FIGURE 12

GRAPH OF PRESSURE, TEMPERATURE DATA FOR THE
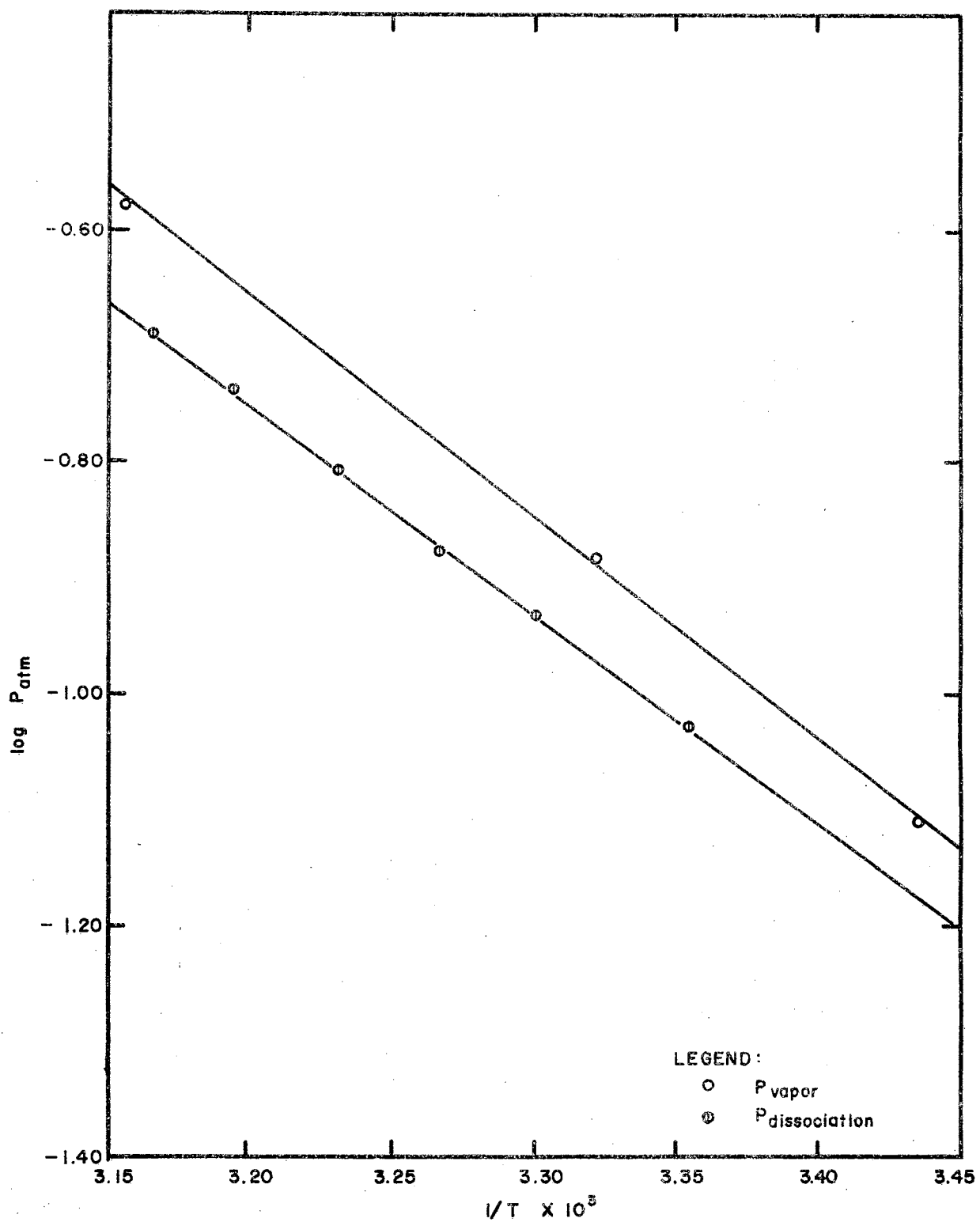ACETONITRILE - PICRIC ACID SYSTEM

FIGURE 13

GRAPH OF PRESSURE, TEMPERATURE DATA FOR THE
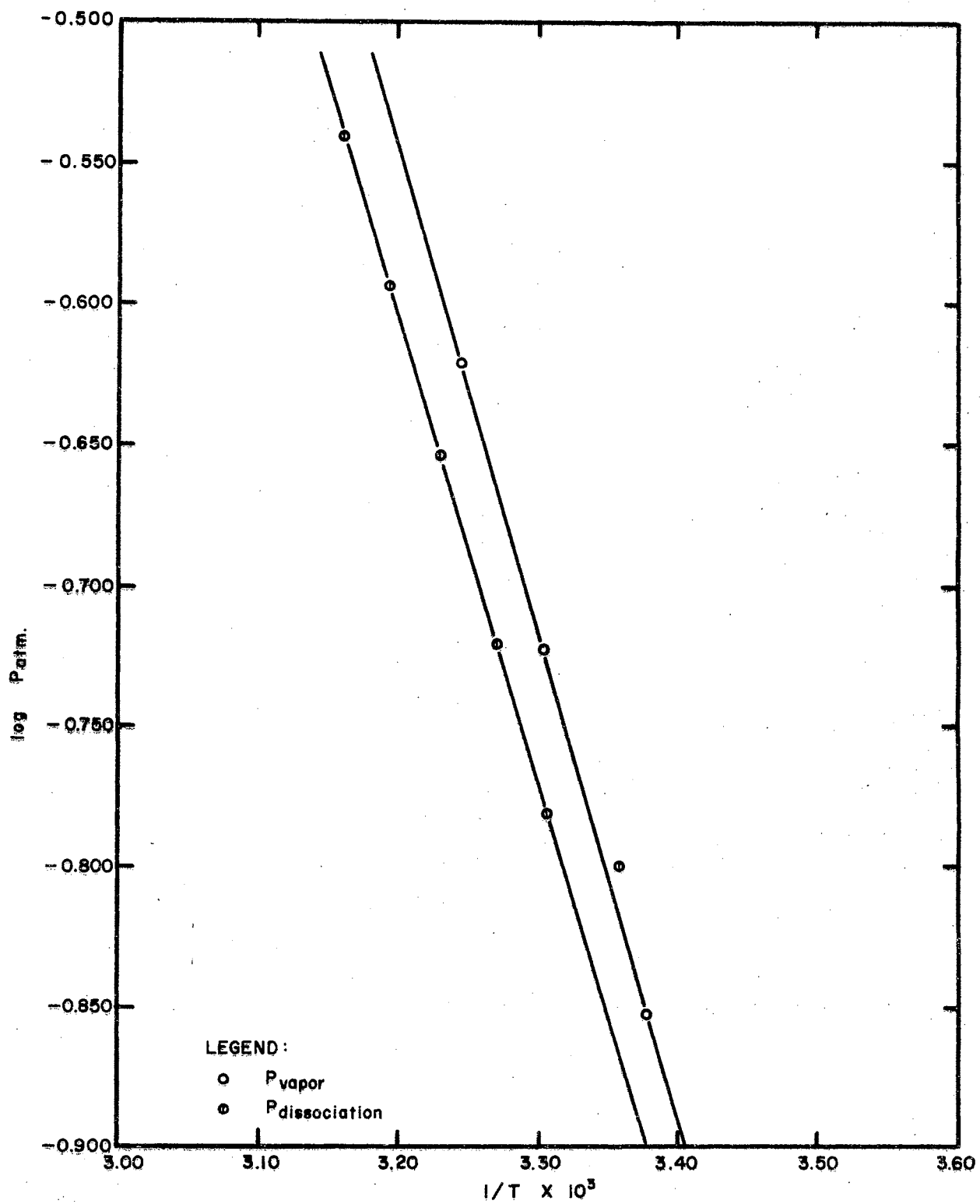METHYL ACRYLATE — PICRIC ACID SYSTEM

FIGURE 14

GRAPH OF PRESSURE , TEMPERATURE DATA FOR THE
VINYL ACETATE - PICRIC ACID SYSTEM

DISCUSSION OF RESULTS

The benzene-picric acid system was carefully investigated to
determine the reliability of the dissociation pressure measurements.
Seven experiments were conducted on this system using both the absolute
and the differential apparatus.

Earlier investigations pointed out an apparent change in slope for
the line obtained from the dissociation pressure-temperature plot.
A good deal of effort was made to define this line, and it was veri-
fied that the slope does change at approximately 30°C. The earlier
work offered the speculation that the complex changed form in some
way at this temperature. It has now been shown that the slope above
30°C is identical to that of the saturated solution, and if one
attempts to prepare the 1:1 complex, or indeed any complex, above
30°C, the only constant pressure observed is that of the saturated
solution. This indicates the presence of a single form of benzene
picrate from 20° to 30°C., above which the complex breaks down into
a saturated solution of picric acid in benzene, mixed with solid
picric acid. Indications of the same phenomenon were observed by
Dermer (6), who observed a change of slope in the plot of log (solu-
bility of picric acid in benzene) vs. 1/T in the neighborhood of 27°C.

The ethylbenzene and styrene complexes have been made before (2a)
but not studied systematically. A comparison of thermodynamic constants
found for the complexes of the three aromatic hydrocarbons investigated

is of interest. The fundamental measure of stability is $\Delta F°$, which as already noted is directly proportional to K_p, the dissociation pressure. Unfortunately, measurements could not conveniently be made below 30°C. for ethylbenzene and styrene, whereas above that temperature, as already noted, the benzene complex does not exist. Nevertheless, it is possible to extrapolate the plot of log P vs. 1/T for benzene picrate to 316.5° and so derive a hypothetical K_p of 0.27 for that temperature. At the same temperature the K_p value for ethylbenzene picrate is 0.027, and that for styrene picrate 0.013. These are in just the order that would be expected from the literature records (e.g., (1)) of the potency of the hydrocarbons as Lewis bases.

It will be noted that the heats of dissociation for the complexes are not in the same order: benzene picrate, 10.97 Kcal/mole; ethyl-benzene picrate, 16.27; styrene picrate, 5.28. This presumably means that the entropy change, ΔS, is not about the same for all three dissociations.

The n-propyl alcohol-picric acid system showed only one constant pressure level on evacuation, and that nearly identical to the vapor pressure of the pure alcohol. Smith (27) claimed that a complex was formed with n-propyl alcohol but not with isopropyl alcohol. This difference is surprising and under suspicion, since the solubility of picric acid at 25°C. is greater in isopropyl alcohol (8.7 g/100g) than in n-propyl alcohol (3.7 g/100g) (25). The present work shows that no stable solid complex of propyl alcohol exists at room temperatures.

For allyl alcohol, both Harper (10) and Smith (27) reported a 1:1 complex to exist. Inspection of their data and comparison with the vapor pressures of the pure alcohol indicates that both workers were

measuring the vapor pressure of the saturated solution rather than that of alcohol from the complex. Since the observed pressure is so near that of the alcohol itself, it is considered very unlikely that a solid complex exists.

The acrylonitrile-picric acid system was found by both Smith (27) and Harper (10) to yield a 2:1 complex. Their values for dissociation pressures disagreed considerably, however, and limited restudy of this system now shows that Smith's values are those for the saturated solution. Evacuations beyond this pressure yield a dissociation pressure in agreement with that of Harper.

Smith also found 1:1 complexes of picric acid with acetonitrile and propionitrile. Once more it is apparent that his data for these "compounds" came from saturated solutions and not solid complexes. It is extremely unlikely, for example, that the heat of dissociation of the complex should be exactly the same as the heat of vaporization of the solvent; but this is what the parallel lines of Figures 11 and 12 show. Several experiments (see Figures 4, 6, 8, 9, and 10) demonstrate that if an excess of the volatile component is present, the heat of "dissociation" calculated from the slope of the log P vs. 1/T line will be substantially equal to the heat of vaporization of the volatile component. The deviation from the line for the pure solvent must depend on two things: the solubility of picric acid in the liquid at the temperature involved, and the boiling point elevation constant for that liquid.

The vinyl acetate and methyl acrylate experiments carried out by Smith (see Figures 13 and 14) gave results very similar to those of present runs in which a slight excess of the solvent was known to be

present. This indicates that the reported dissociation values are in error but, as for acetonitrile and propionitrile also, does not prove the absence of a molecular complex.

Picrates of benzene, ethylbenzene, styrene, and xylene were prepared and the infrared spectra obtained by the mull technique. An attempt was made to determine complex formation by this method, but no observable shift was found. The instrument (Perkin-Elmer #221) has a resolution of approximately 1 cm^{-1} in the region of interest and this indicates that the shift was either less than 1 cm^{-1} or the complex decomposes in the process of preparing the mull. This technique does apply to solid complexes and may be of great value in future work. Information obtained by this method is qualitative in nature; whereas, the dissociation pressure approach provides data on solid state stabilities and molecular ratios.

Solubility data were obtained for picric acid in styrene and ethylbenzene at 25°C. The value obtained for picric acid in styrene (12.8 g. PA/100g) is slightly greater than that in benzene (12.7) and correspondingly lower than the literature value (25) for toluene (13.2). Ethylbenzene contained 5.8 g. of PA/100g at 25°C.

A variation of color intensity was noted and may have some bearing on the tendency for complex formation as discussed earlier. These observations were as follows: styrene > xylene > toluene > benzene ethylbenzene > cyclohexane.

SUMMARY

The differential tensimeter was used to investigate molecular addition complexes formed between picric acid and a number of donor compounds. Molecular ratios and heats of dissociation were determined for benzene, ethylbenzene, and styrene picrates. Thermodynamic stabilities of ethylbenzene and styrene picrate were compared with that of the benzene picrate.

A careful examination of the benzene-picric acid system demonstrated the reliability of the pressure measurements and the pump-down technique used to isolate the molecular complex. The complex with benzene is unstable above 30°C and the data reported by earlier workers corresponds to saturated solution pressures rather than dissociation pressures for the complex.

Data from earlier theses for complexes of picric acid and some aliphatic alcohols and nitriles were compared with the known vapor pressures of the pure solvents. It appears that the earlier measured "dissociation" pressures were in fact vapor pressures of solutions, not solid complexes.

This technique is of great value in the determination of molecular ratios and dissociation constants for the solid complex. One must be especially careful, however, to remove the volatile component in excess of that required in the molecular ratio before attempting to measure the dissociation pressures of the complex.

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