THESIS

AMERICAN UNIVERSITY OF BEIRUT

THE ASSOCIATION OF PYRROLE

AND

THE SYSTEM PYRIDINE-PYRROLE

by

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MASTER OF ARTS IN CHEMISTRY

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A thesis submitted to the Chemistry Department of the American University of Beirut in partial fulfillment of the requirements for the Degree of Master of Arts in Chemistry.

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ABSTRACT

In the present work the densities, viscosities and refractive indices of pyrrole-pyridine mixtures in different molar ratios, were measured at 30°C. The results plotted against mole fraction pyrrole gave the following curves: for density an S-shaped curve with a very slight curvature, for viscosity a slight maximum at mole fraction pyrrole 0.7 and for the refractive index a definite maximum at mole fraction pyrrole 0.5.

The heat of interaction between pyridine and pyrrole and the heat of dilution of pyrrole in CCl_4 were measured also at 30°C. and found to be -2.0 ± 0.1 kcal/mole and $+5.0 \pm 0.5$ kcal/mole, respectively. Assuming that pyridine is not associated in the pure state the corrected heat of interaction between pyridine and pyrrole is given as 7.0 ± 0.7 kcal/mole.

A simple equilibrium is then suggested for the system pyridine-pyrrole

$$C_5H_5N + C_4H_4NH \rightleftharpoons C_5H_5N...HNC_4H_4$$

where the complex consists of one molecule of pyridine bound to one molecule of pyrrole through the acidic hydrogen of the latter.

Using the corrected heat of interaction and assuming that in a given mixture the heat evolved is proportional to the amount of complex found the equilibrium constant is obtained $K = 1.3 \pm 0.2$. This is compared with $K = 1.2 \pm 0.2$ calculated from the infrared absorption data of Linnell on pyridine-pyrrole mixtures in CCl_4.

The thermodynamic quantities for the above equilibrium are given $\Delta F° = 110$ cal/mole and $\Delta S° = 23$ cal/deg. mole.

From examination of calorimetric and other data it is concluded that the pyridine-pyrrole complex is a one to one complex.

It is suggested that the complexing takes place through a hydrogen bond between the N of the pyridine and the NH of the pyrrole.

The association of pyrrole is discussed and it is pointed out that the large heat of dilution in CCl_4 asserts definitely the fact that pyrrole is associated and not existing in different molecular forms.

I ACKNOWLEDGEMENT

The experimental work for this thesis was carried out in the Research Laboratory of the Chemistry Department, American University of Beirut under the direct supervision of Dr. Robert H. Linnell.

The Author wishes to express his thanks for the valuable advice, patience and encouragement of Dr. Linnell without which this work would never have been possible.

II INTRODUCTION

The system pyridine-pyrrole has been studied by several workers. Dezelić [1] and Dezelić and Belia [2] measured the viscosity and density of a series of mixtures of pyridine and pyrrole. On plotting the viscosity against the mole fraction of pyrrole they obtained a slight maximum at mole fraction 0.7. The plot of density versus mole fraction of pyrrole gave a straight line. The two workers also observed a considerable heat of mixing. They interpreted their results as due to complex formation between one molecule of pyridine and two molecules of pyrrole. Although Dezelić [1] did not exclude the possibility of a one to one complex which dissociates.

Laurent[3] measured the specific inductive capacity of mixtures of pyridine and pyrrole in inert solvents and conclude that a one to one complex is formed.

In a study of hydrogen bonding Rodebush and coworkers [4] determined the infrared spectrum of a mixture of pyridine and pyrrole in a one to one mole ratio. Bands were formed at 2.95μ, 3.11μ, 3.25μ, 3.37μ and 3.47μ. The 3.11μ band was a new band and was attributed to hydrogen bonding between the N of the pyridine and the NH of the pyrrole.

More recently Zezyulenskii [5] studied the molecular interactions between pyrrole and several other compounds by solution absorption spectra in the two near infrared regions of 0.75 to 1.2μ and 1.3 to 1.6μ. He found that for pyridine-pyrrole mixtures the 1st overtone of the NH band is shifted

by 7.8% while the 2nd overtone disappears completely. To him
the latter part is an indication of the existence of a strong hydrogen
bond between pyrrole and pyridine molecules.

Still more recently Linnell[6] has measured the infrared
absorption of a series of mixtures of pyridine and pyrrole in
CCl_4. The only new band to appear in the region 2 to 15 was
the 3.11μ band. By using dilute enough solutions of pyrrole in
CCl_4 (o.1 molar or less) Linnell was able to eliminate the "asso-
ciated band" at 2.92μ[7] and hence using the optical density of
the fundamental NH vibration band of pyrrole at 2.84μ he calcu-
lated the concentration of "free" pyrrole molecules in the
pyridine-pyrrole-CCl_4 system. Using this data together with the
known initial concentrations of pyrrole and pyridine he calculated
the equilibrium constant for the following assumed equilibrium

$$C_5H_5N + C_4H_4N \rightleftharpoons (C_5H_5NHNC_4H_4)$$

The average of several values was K = 3.0 lit. moles^{-1}.
In the work described below the viscosity, density and refraction
index of pyridine-pyrrole mixtures were measured; it was deemed
of interest to see if the results obtained by Dezelić and Belia[2]
could be reproduced.

Since the heat of mixing of pyridine and pyrrole was observed
to be considerable it was thought that direct calorimetric measure-
ments could be used to determine the heat of interaction.

Also because it appeared that pure pyrrole is "associated"*
heats of dilution in CCl_4 at various concentrations were determined
calorimetrically.

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* For detailed discussion on the subject of "association" of pyrrole
  see Discussion part A page 20'.

Knowing the heat of interaction at different mole ratios of pyridine to pyrrole the equilibrium constant for the one to one equilibrium can be calculated in a manner similar to that used by McLeod and Wilson [8] to calculate the equilibrium constant for the equilibrium in ether-chloroform mixtures.

To compare the equilibrium constant calculated from viscometric and calorimetric data with one calculated from infrared absorption data it was thought worth while to recalculate the equilibrium constant from Linnell's data [6] using mole fractions to express concentrations.

Whether the pyridine-pyrrole complex is a π-electron complex [9] or one due to coordination* between the lone pair N atom electron [10] with the proton of the pyrrole can not be decided upon. The infrared evidence points to a latter type of interaction. The final answer may come from a study of the systems pyridine-N-substituted pyrrole.

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* Resonance will not play an important role in such a "hydrogen bond".

III EXPERIMENTAL WORK

A. MATERIALS

Pyridine Eastman Kodak reagent grade pyridine was distilled three times in a Fenske column having an efficiency of 22 theoretical plates. Each time only the portion distilling above 114°C was taken. The pyridine was stored over pure NaOH pellets in a ground glass stoppered flask and shaken vigorously every time before use.

The n_D^{30} of the pyridine measured by an Abbe refractometer (Bausch and Lomb Co.) with temperature control to 0.1°C was found to be 1.5033. This value did not vary by more than two units in the fourth place from day to day.

The d_4^{30} of the pyridine measured by an Ostwald-Sprengel type of pycrometer described below was 0.9730.*

The pyridine described above was used for most of the work.

The perchlorate method of purifying pyridine [11] was tried on crude synthetic pyridine (Reilly Tar and Chemical Corp.). The pyridine obtained after saturating the water azeotrope with NaOH, was distilled, the portion distilling between 114.115°C only, being collected. It was then allowed to stand over NaOH pellets for a week and its n_D^{30} was found to be 1.5035.

For comparison the same crude synthetic pyridine was distilled twice in the above mentione column. The portion distilling

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* Compare with d^{30} 0.9729 by Muller and Bunnneis, Z. Elektrochem. 38, 451 (1932) and 0.97281 by Trav. Bur. Int. Et. Phys. Chem. Bruxelles, J. Chem. Phys. 34, 693 (1937) quoted in J. Timmermans, Physico Chemical Constants of Pure Organic Compounds (Elsevier Publishing Co. 1950) p. 569.

above 114°C and below 115°C was taken and its n_D^{30} was found to be 1.5033.

Pyrrole Eastman Kodak pyrrole was distilled in the Fenske column before every determination the portion distilling over at 129 - 130°C being collected only. The freshly distilled pyrrole was always colorless, having an n_D^{30} 1.5046 ± 0.0001 and d_4^{30} 0.9613.

It was found that storing the freshly distilled pyrrole in a sealed flask in an atmosphere of nitrogen did not prevent the pyrrole from assuming the straw yellow color peculiar to it, previous to distillation*.

It was also found that no detectable change occurs either in the refractive index or the viscosity of the freshly distilled product, with time, even when strongly colored.

Carbon tetrachloride Merck pharmaceutical grade, sulfur free, carbon tetrachloride having an n_D^{18} of 1.4604** was used as solvent for measuring the heat of dilution of pyrrole.

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* Compare Conant ed., Organic Synetheses, IX, 79 (Wiley & Sons Inc., 1929)

** Compare with n_D^{18} 1.4615 in Timmermans, op. cit., p. 227.

B. EXPERIMENTS

Refractometry. The refractive indices of pure pyrrole and
pyridine and of the mixtures were determined on a Bauch and
Lomb Co. refractometer with temperature control to 0.1°C. In
each determination three readings were taken approaching from
above the intersection of the cross-hairs and three readings
from below, the average being then taken. Every reading was
accurate to 0.0002.   *how then to correct*

Viscometry. Viscosity measurments were made using a simple
Ostwald type viscometer clamped in a heavy sealed in, was placed   ?
on two rigid horizontal bars which were tightly clamped to
perpendicular bars on the circular iron frame supporting the
water bath, and which stood on three screws.

The water bath of a capacity of 20 liters was controlled
using a Fisher-Serfass electronic relay and a Fisher "Magnoset"
thermoregulator, to better than 0.02°C. The absolute tempera-
ture was read on a standardized thermometer with an accuracy
of 0.05°C.

The perpendicularity of the capillary of the viscometer was   ?
adjusted using the screws supporting the frame. It was checked
by looking through a cathetometer at the capillary from two
different positions at right angles to each other.

The clamp with the viscometer in it, was, after the adjust-
ment, left permanently in place all throughout the measurements.
Cleaning of the viscometer was effected by flushing it four
successive times with 95% ethyl alcohol solution filtered through
sintered glass under slight suction. Suction was then left on
until the viscometer was thoroughly dry.

The measurement was usually carried out by putting 5 ml. of

the solution, whose viscosity was to be measured, into the viscometer, applying a slight suction to bring the level of the liquid above the upper etched line and measuring the time of flow between the two etched lines with a stopwatch which could be read to 0.1 sec.

For each determination usually twenty such readings were made. Care was taken to examine carefully the sample in the viscometer, previous to starting the measurements, under good illumination so as to insure that no foreign particles were present in the solution.

Calorimetry. To measure the heat of interaction between pyridine and pyrrole calorimetric measurements were carried out on mixtures of pyridine and pyrrole in different molar proportions.

The calorimeter was designed after the one used by Zellhoefer and Copley [12]. It was found necessary to make the reaction vessel out of glass because of the reactivity of pyridine towards most metals. The capacity of the vessel was about 40 ml. Fig. 1 is a diagram of the calorimeter which consisted of a vacuum jacketed "thelma" flask of 600 ml. capacity. It was usually filled with 500 ml. of water and the reaction vessel immersed in it. The calorimeter was stoppered with a thick cork stopper which held the reaction vessel around which a short length of Nichrome wire No. 24 was wound with both ends soldered to thick copper wires No. 16 which led to the simple circuit shown in Fig. 2.

A hole in the stopper allowed a metallic stirrer driven by a small electric motor to be put in. Readings of the temperature were made using a Beckmann thermometer inserted into the calorimeter. Care was taken to avoid parallax error in reading the thermometer with the help of a lens.
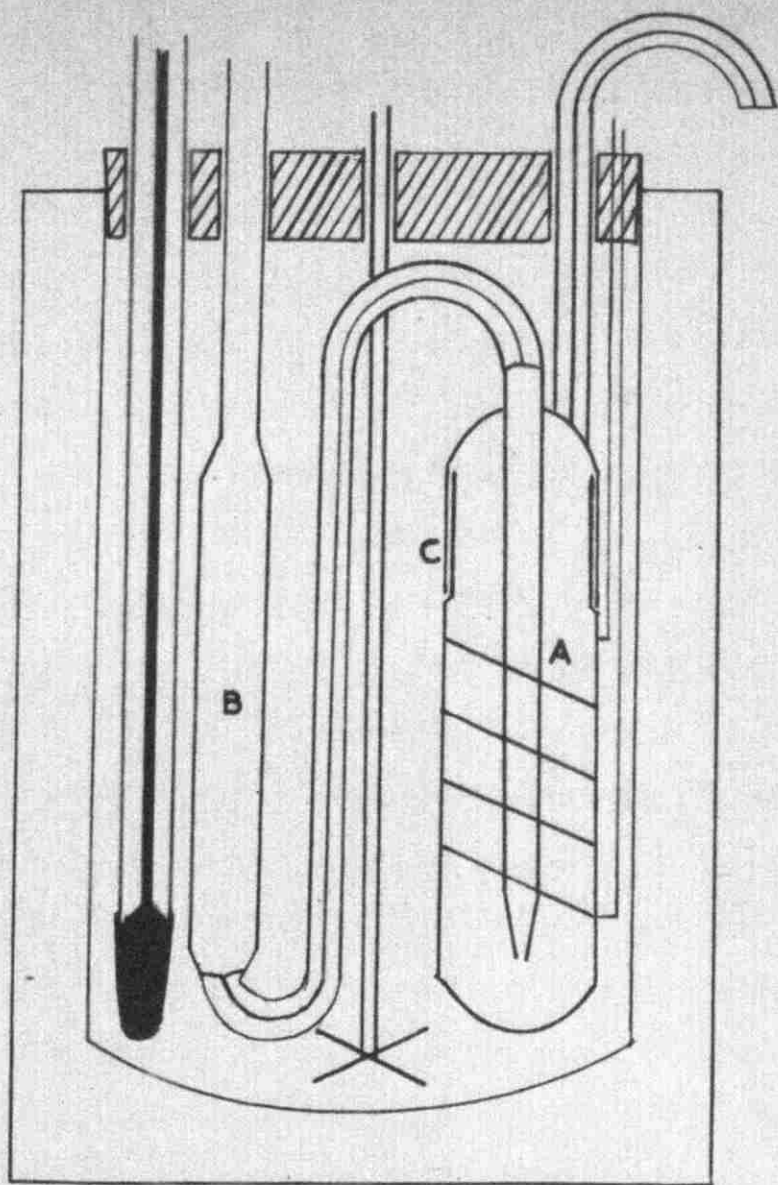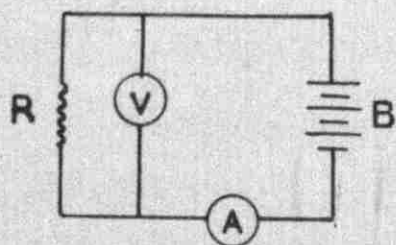
Because of the

FIG. I

R	Heater resistance $< 1\,\Omega$
V	$^0/_{10}{}^{V.}$ voltmeter
A	$^0/_{25}{}^{amp.}$ ammeter
B	Lead storage battery 6^V

FIG. 2
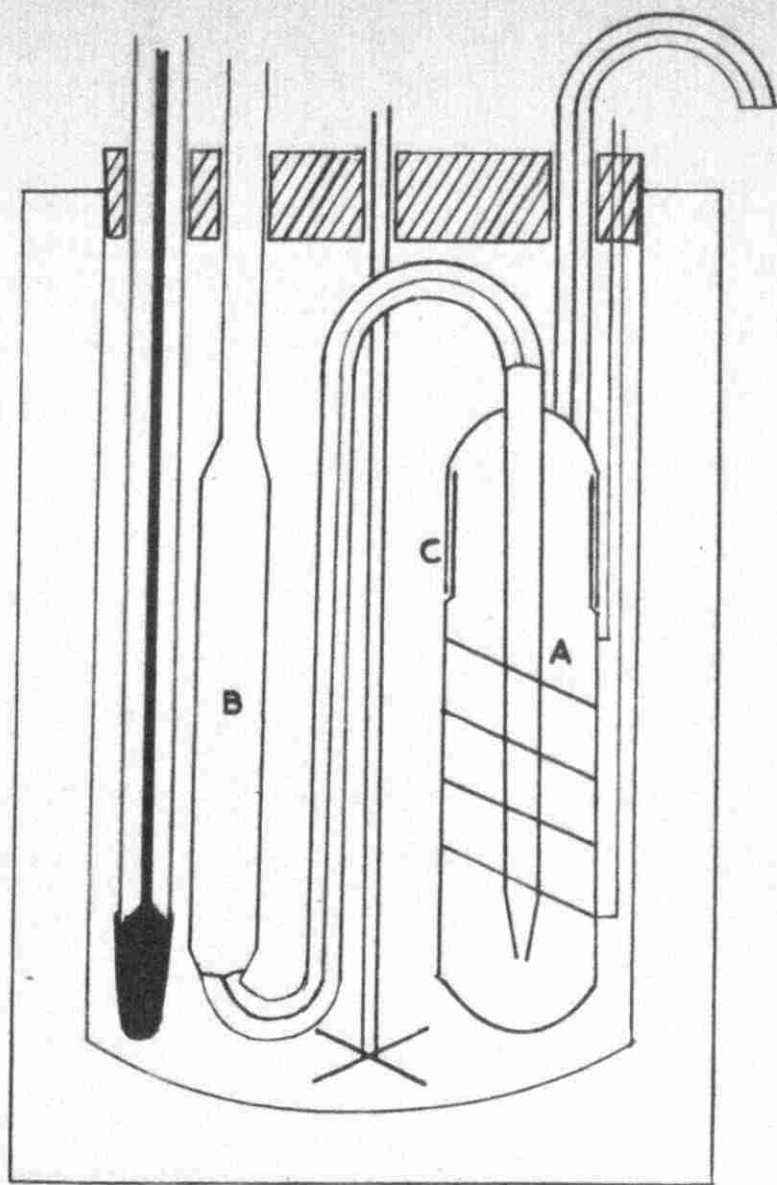
FIG. I
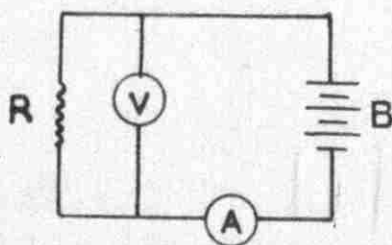
FIG. 2

R	Heater resistance < 1 Ω
V	0/10 v. voltmeter
A	0/25 amp. ammeter
B	Lead storage battery 6v

Because of the availability of only one storage battery, the resistance of the Nichrome wire was made small (less than 1 ohm) and hence it was important that the copper wire should be thick enough so that its resistance would be negligible in comparison.

Determinations were carried out in the following way: the desired quantity of the first component introduced into the reaction vessel A which was then tightly fitted through the ground glass joint C to the rest of the apparatus and held in place by the resistance wire. Care was taken to grease the gound glass joint so that no water would leak into the reaction vessel. The desired quantity of the second component is then pipetted into the pipette B and a rubber tube attached to the outlet tube. The whole apparatus was then lowered into the calorimeter and the Beckmann and stirrer inserted. The stirrer was then turned on and time was given for the whole calorimeter to come to temperature equilibrium. Using a stopwatch readings of the calorimeter temperature were taken every 5 min. for a sufficient length of time.

To bring the two liquids in contact air is blown through the rubber tubing and the liquid in the pipette B forced into the reaction vessel A. To insure that the two components are well mixed, pipette B is flushed back and forth with the mixture in the reaction vessel at least two or three times. During the reaction time readings of the temperature are taken every 1 min.

After the temperature has ceased to rise quickly readings are taken again at 5 min. intervals.

The calorimeter is then calibrated by passing the current from a storage battery for known intervals of time, measured by a stopwatch and reading the temperature of the calorimeter both

before the current is switched on and then after it is switched off in the manner described above. Due to small flucturations in the battery current the voltage and current for every trial were recorded. A minimum of three, usually four such trials were made for every mixture.

The calorimeter described above had a low heat lag as can be seen from a typical example of graphical representation of calorimetric data for a mixture, shown below (Fig. 3 a,b & c). Densitometry. The densities of pure pyridine and pyrrole and their mixtures were measured using an Ostwald-Sprengel type of pycnometer of about 10 ml. capacity. The capillary arms were both 1 mm. in diameter and both were ground glass stoppered to reduce the error due to evaporation. The pycnometer gave better than 4th place accuracy as witnessed by the fact that four successive calibrations with water gave weights of the pycnometer filled with water differing by not more than 0.1 mg. The calibrations were made using freshly boiled distilled water.

C. Methods of Calculation

Density. In every determination at least three successive fillings and weighings were made. The wet and dry bulb thermometer temperatures were taken for every weighing. The relative humidity was then computed from tables [13].

The density of each solution was calculated by the method given in Weissberger [14].

The density of air D was calculated using the following formula:

$$D = \frac{0.001293 \ (P-K)}{(1 + 0.00367T) 760} \qquad (1)$$

where P is the barometric pressure in mm. of mercury, T the

balance room temperature in °C and K is given by:

$$K = 0.0038 \; H \; P_{H_2O} \qquad (2)$$

where H is the relative humidity in percent and P_{H_2O} is vapor pressure of water at temperature T°C.

The buoyancy correction was then found in the following way. If W' is the uncorrected weight, then the corrected weight W is given by:

$$W = W' + D(V_p + V_G - \frac{W'}{d}) \qquad (3)$$

where V_p is the volume of liquid in the full pycnometer V_G is the volume of the glass and d the denisty of the weights used to balance the pycnometer.

To evaluate V_p uncorrected weights may be used. Thus in calibration letting W'_1 and W'_2 be the uncorrected weights of the empty pycnometer and pycnometer filled with water, respectively, we have:

$$V_p = \frac{W'_2 - W'_1}{d^t_4 (H_2O)} \qquad (4)$$

where $d^t_4(H_2O)$ is the density of water at temperature t°C at which the measurement is made.

Since the pycnometer was left open while being weighed empty, we have for the corrected weight of the empty pycnometer:

$$W_1 = W'_1 + D(V_G - \frac{W'_1}{d})$$

then the corrected weight of the water is

$$W_2 - W_1 = \quad W'_2 + D(V_p + V_G - \frac{W_2'}{d}) \quad - \quad W_1' + D(V_G - \frac{W_1'}{d}) =$$

$$(W_2' - W_1') + D \; V_p - (\frac{W_2' - W_1'}{d})$$

It was found that as the relative humidity in the balance room never changed by more than 5% and the barometric pressure by

more than 0.25 mm. of mercury from one determination to another, the buoyarcy correction was practically constant for 4th place accuracy, being of the order of 0.0099 gm. The corrected weight W_8 of the pycnometer filled with the pyridine-pyrrole mixture is then also calculated.

The true volume of the pycnometer is then:

$$V_p = \frac{W_2 - W_1}{d_4^+ (H_2O)} \tag{5}$$

and hence the density of the solution is

$$d_4^+ (solution) = \frac{W_8 - W_1}{V_p} \tag{6}$$

Viscosity: Previous to all measurements on the time of flow of pyridine-pyrrole mixtures the viscometer was calibrated with distilled water. The density and viscosity of water at 30°C. were taken as 0.9957g./ml.[15] and 8.004[16] millipoises and the viscosity of the mixture calculated from the following relation

$$n_1 = n_2 \cdot \frac{d_1 t_1}{d_2 t_2} \tag{7}$$

where n_2, d_2 and t_2 are the viscosity, density and time of flow for water and d_1 and t_1 are the density and time of flow for the mixture.

No corrections were applied as the measurements were deemed accurate to only 1%.

Heat of interaction. The purpose of the calorimetric measurements was to obtain a roughly quantitative value for the heat of interaction between pyridine and pyrrole. The calorimeter was not designed to give the highest possible accuracy and hence a quick graphical method for the evaluation of the

rise in temperature was sufficient for the purpose. The method used is the one described by Sturtevant [17] in the chapter on calorimetry in Weissberger. It is suitable for rapid processes such as the one in this case; in a determination, temperature equilibrium was usually reached in one or two minutes while in a calibration run, temperature equilibrium was reached in one minute or less as evidenced in all cases by a straight line rise in temperature on the readings following the heating interval.

For each determination the temperature was plotted against time as shown in Fig. 3a.

If T_1 is the temperature of the water jacket just before the reaction and T_2 the temperature when equilibrium has been reached then the average temperature $T_a = \dfrac{T_1 + T_2}{2}$ was calculated. Through the point, when the line representing the average temperature intersects the straight line joining the point representing T_1 to the point representing the temperature after 1 min. interval, a vertical line is drawn. When this line cuts the extended lines joining the points representing the "fore" and "after" periods respectively, gives T_α the corrected initial temperature and T_β the corrected final temperature. Then the "true" temperature difference is $T_\alpha - T_\beta$. _dif. or change in temp_

Instead of finding the specific heat of the calorimeter and calculating the heat of interaction, a novel way of determining it was used, which although more laborious spared me the necessity of determining the specific heat of pyrrole as well as lengthy calculations.

Each pyrrole-pyridine mixture was "calibrated" by passing an electric current through a heater resistance at least four times

Mixture 16ml. pyridine + 4ml. pyrrole

$T_1 = 3.382$

$T_2 = 3.200$

$T_a = \dfrac{T_1 + T_2}{2} = \dfrac{6.582}{2} = 3.291$

$T_\alpha = 3.380$

$T_\beta = 3.202$

$T_\alpha - T_\beta = 0.178$
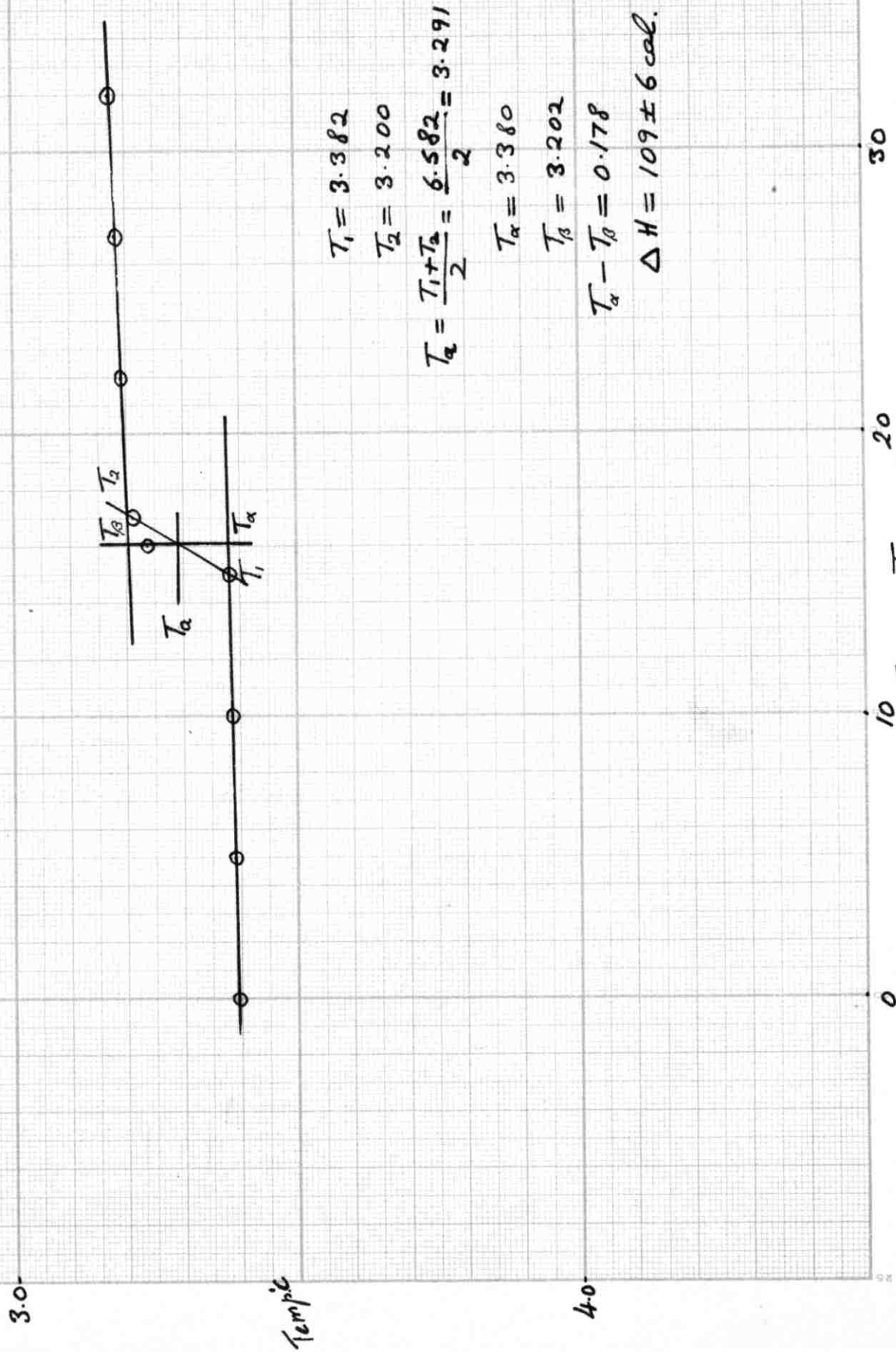
$\Delta H = 109 \pm 6 \; cal.$

Temp.

Fig 3a. Time, min.

for different periods of time. The temperature rises for the
different periods were then evaluated graphically as outlined
above (see Fig. 3b.) and then plotted against the heat equivalent
of the amount of current passed (see Fig. 3c.) In all cases the
plot gave a good straight line. The heat of interaction was
then determined directly from this graph.

The maximum error for each determination was obtained by
reading off from the graph of ΔH cal. versus $\Delta T^{\circ}C$ the amount
of heat in calories corresponding to an error of o.ol$^{\circ}$C in _in how much_
reading the thermometer. These errors are given together with
the experimental values for the heat of interaction in Table II
under results.

Calculations of the heat of dilutions of pyrrole in CCl_4
were carried out in a similar way. The results are given in
Table V under Results.

$T_1 = 2.570$

$T_2 = 2.360$

$\dfrac{T_1+T_2}{2} = 2.465$

$T_\alpha = 2.570$

$T_\beta = 2.365$

$T_\alpha - T_\beta = 0.205$

$\Delta H = 129.5 \text{ cal.}$

$T_1 = 2.940$

$T_2 = 2.798$

$\dfrac{T_1+T_2}{2} = 2.869$

$T_\beta = 2.800$

$T_\alpha = 2.940$

$T_\alpha - T_\beta = 0.140$

$\Delta H = 85.6 \text{ cal.}$

$T_1 = 2.775$

$T_2 = 2.597$

$\dfrac{T_1+T_2}{2} = 2.686$

$T_\alpha = 2.775$

$T_\beta = 2.598$

$T_\alpha - T_\beta = 0.177$

$\Delta H = 107 \text{ cal.}$

$T_1 = 3.082$

$T_2 = 2.970$

$\dfrac{T_1+T_2}{2} = 3.026$

$T_\alpha = 3.080$

$T_\beta = 2.970$

$T_\alpha - T_\beta = 0.110$

$\Delta H = 67.4 \text{ cal.}$

Temp. °C
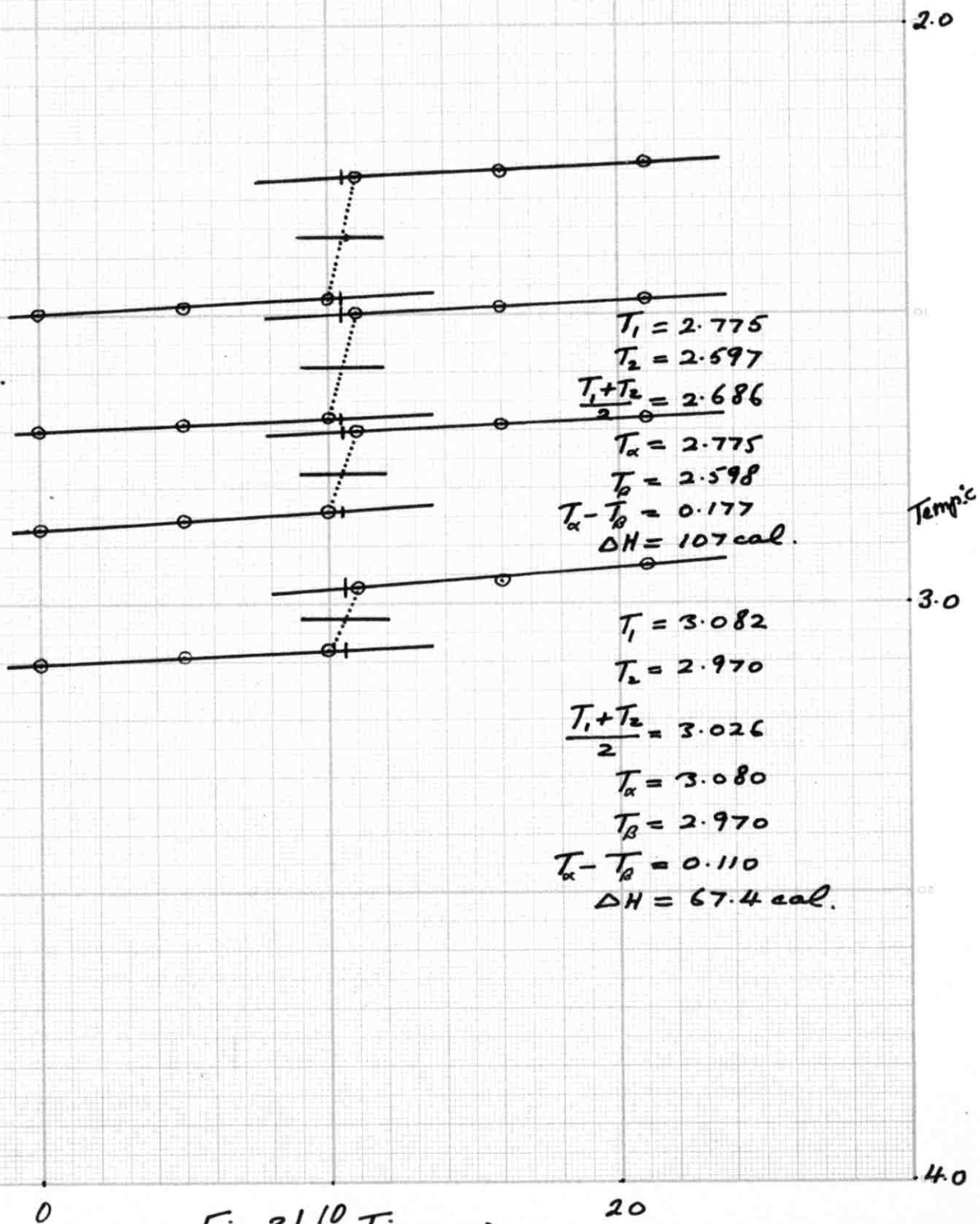
2.0

3.0

4.0

0

20

Fig. 3b[10] Time, min.

$T_1 = 2.570$

$T_2 = 2.360$

$\dfrac{T_1 + T_2}{2} = 2.465$

$T_\alpha = 2.570$

$T_\beta = 2.365$

$T_\alpha - T_\beta = 0.205$

$\Delta H = 129.5$ cal.

$T_1 = 2.940$

$T_2 = 2.798$

$\dfrac{T_1 + T_2}{2} = 2.869$

$T_\alpha = 2.940$

$T_\beta = 2.800$

$T_\alpha - T_\beta = 0.140$

$\Delta H = 85.6$ cal.

$T_1 = 2.775$

$T_2 = 2.597$

$\dfrac{T_1 + T_2}{2} = 2.686$

$T_\alpha = 2.775$

$T_\beta = 2.598$

$T_\alpha - T_\beta = 0.177$

$\Delta H = 107$ cal.

$T_1 = 3.082$

$T_2 = 2.970$

$\dfrac{T_1 + T_2}{2} = 3.026$

$T_\alpha = 3.080$

$T_\beta = 2.970$

$T_\alpha - T_\beta = 0.110$
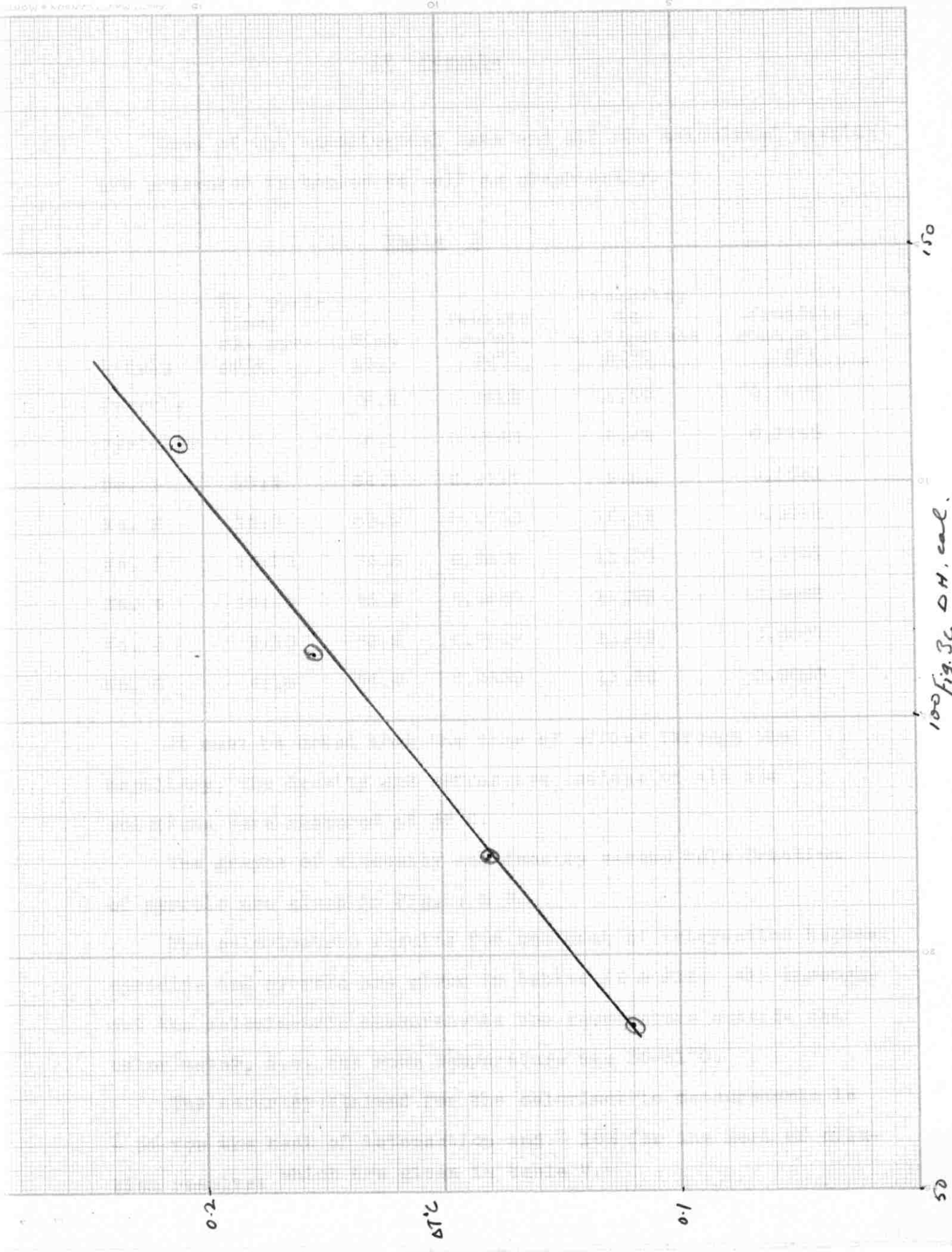
$\Delta H = 67.4$ cal.

0   10   20

Time, min.

Fig. 3c. ΔH, cal.
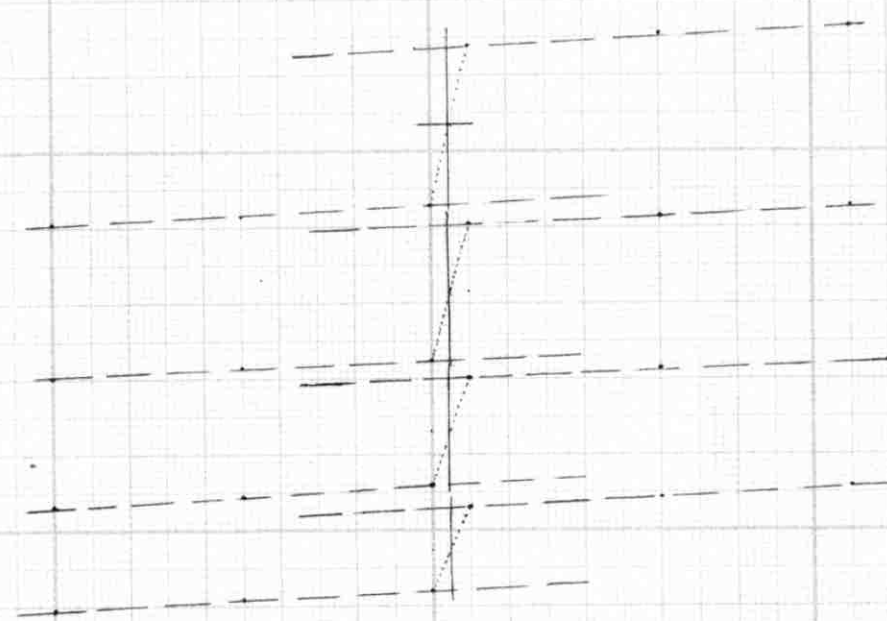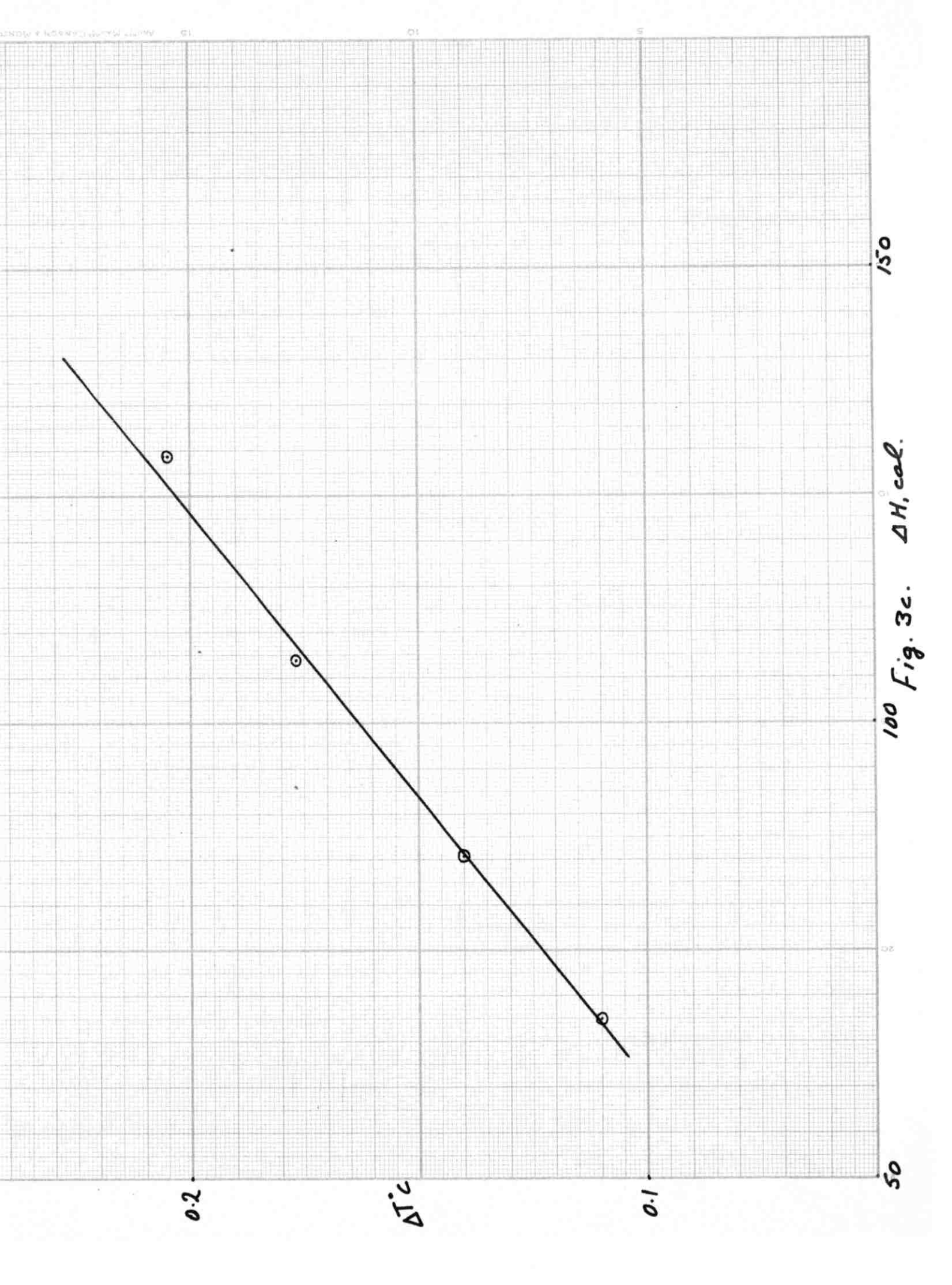
Fig. 3c $\Delta H.$ cal.

IV Results

Some of the experimental data and all the calculated results are presented in tables as well as graphically.

Table I

Liquid	Ml. pyridine; ml. pyrrole	Time sec.	Density gm/ml. 30°C	Viscosity in millipoises 30°C	Fluidity rhes x 10^{-3} 30°C
Pyrrole	-	76.2	0.9613	11.29	0.0886
Pyridine	-	56.1	0.9730	8.42	0.1188
No. 1	16:4	64.1	0.9717	9.61	0.1041
No. 2	10:5	69.2	0.9700	10.35	0.0966
No. 3	10:10	74.3	0.9676	11.10	0.0901
No. 4	10:15	75.6	0.9658	11.26	0.0888
No. 5	5:10	76.2	0.9647	11.35	0.0881
No. 6	4:16	76.2	0.9632	11.32	0.0883

It must be noted that the time of efflux through the capillary, the density and refractive indices of all the solutions were measured at 30°C.

The graphs of viscosity and density versus mole fraction of pyrrole are given in Fig. 4 & 5.

The calorimetric results for the heat of interaction between pyridine and pyrrole are given in tables II & III. All throughout the calorimetric measurements the temperature outside the calorimeter, i.e. the room temperature was 30-31°C.

The accuracy claimed for the calorimetric measurements is ± 5% for the heat of interaction and ± 10% for the heat of dilution results: which are given in table V.
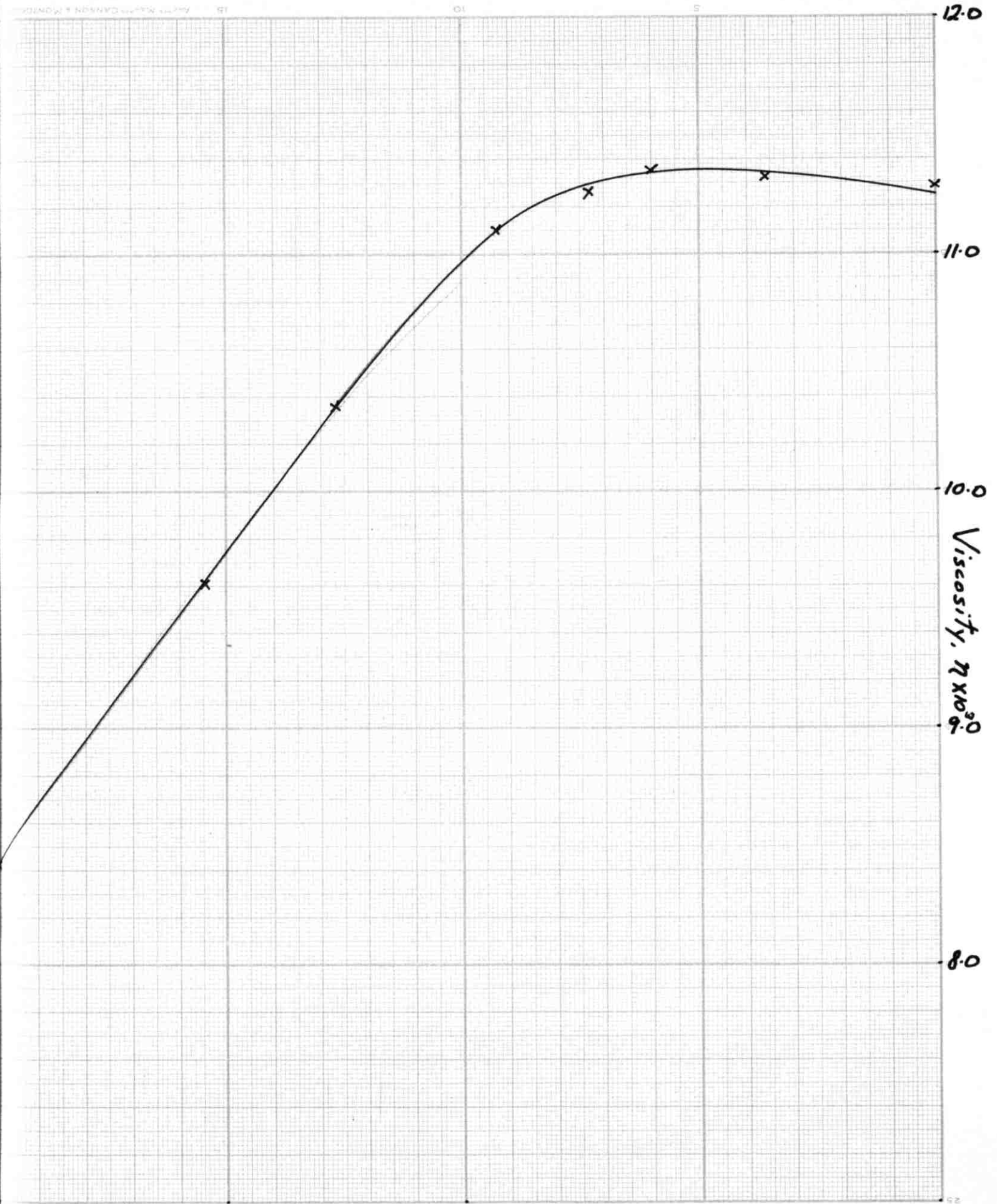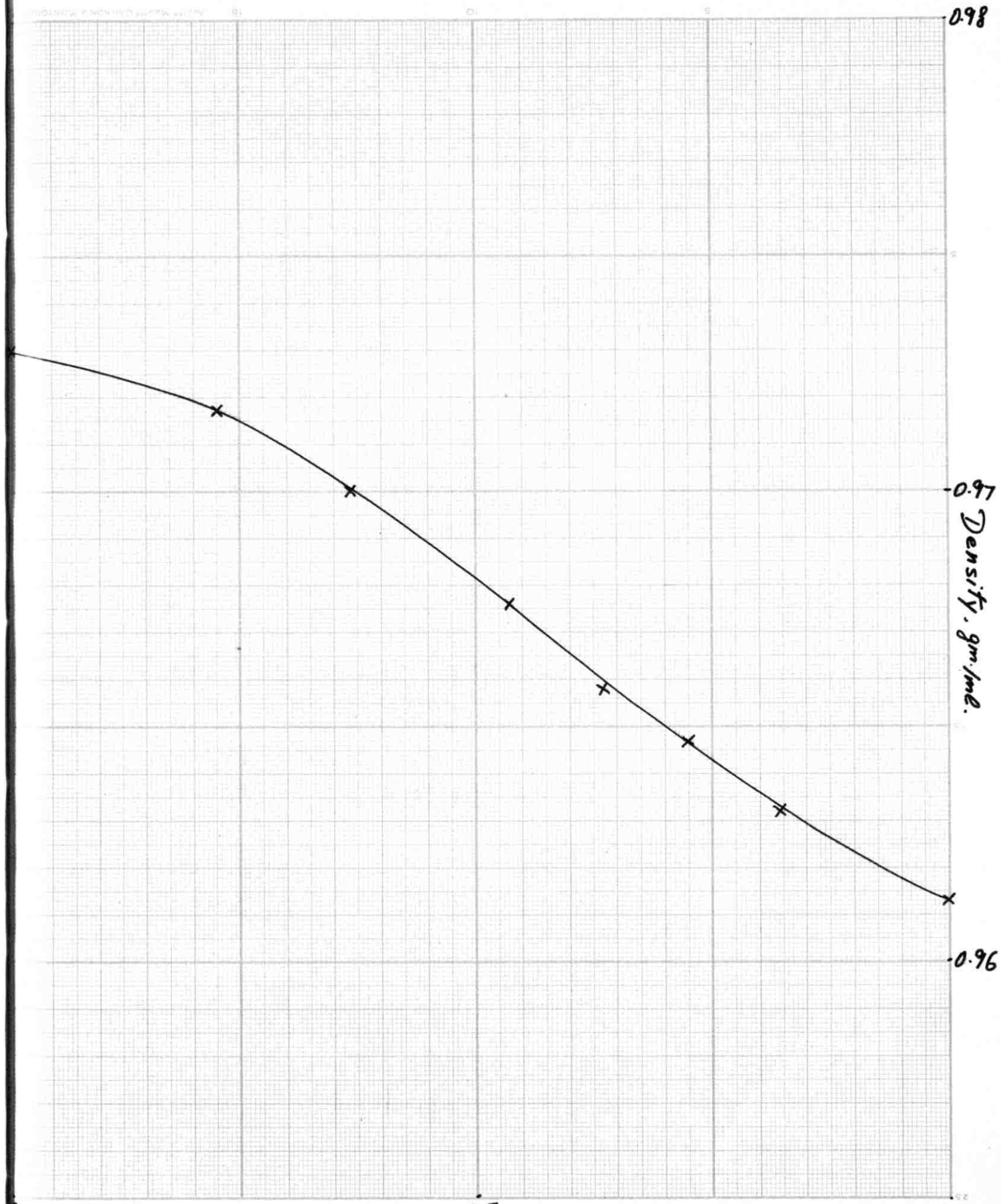
Fig. 4   Mole fr. pyrrole

Fig. 5 Mole fr. pyrrole

Table II

Liquid	Mole fraction of pyrrole	Ref. Ind. 30°C	Moles of pyrrole	Moles of pyridine	ΔH experimental in calories.
Pyrrole	1	1.5046	-	-	-
Pyridine	0	1.5033	-	-	-
No. 1	0.226	1.5056	0.057	0.197	109^+_-6
No. 2	0.368	1.5064	0.072	0.123	127^+_-7
No. 3	0.538	1.5070	0.144	0.123	166^+_-7
No. 4	0.636	1.5069	0.215	0.123	192^+_-7
No. 5	0.700	1.5062	0.144	0.062	108^+_-6
No. 6	0.823	1.5059	0.230	0.049	88^+_-6

The graph of refractive index versus mole fraction of pyrrole is given in Fig. 6. The vertical lines represent the allowable error for each reading.

The calorimetric data given in Tables II & III (was) treated in a more elaborate way than the rest.

First the heat of the interaction between pyrrole and pyridine was calculated for each mixture, as kcal. per mole by dividing the experimental ΔH by the number of moles of the deficient component (see Table III column 6).

The above values of ΔH were then plotted against the molar ratio for each mixture of pyridine to pyrrole and pyrrole to pyridine (Fig. 7 & 8).

As can be seen from the two graphs there is clearly a minimum in ΔH for the molar ratio of one.

Second the method of Copley and Zelloheefer [9] for calculating the heat of the interaction per mole of solution, was
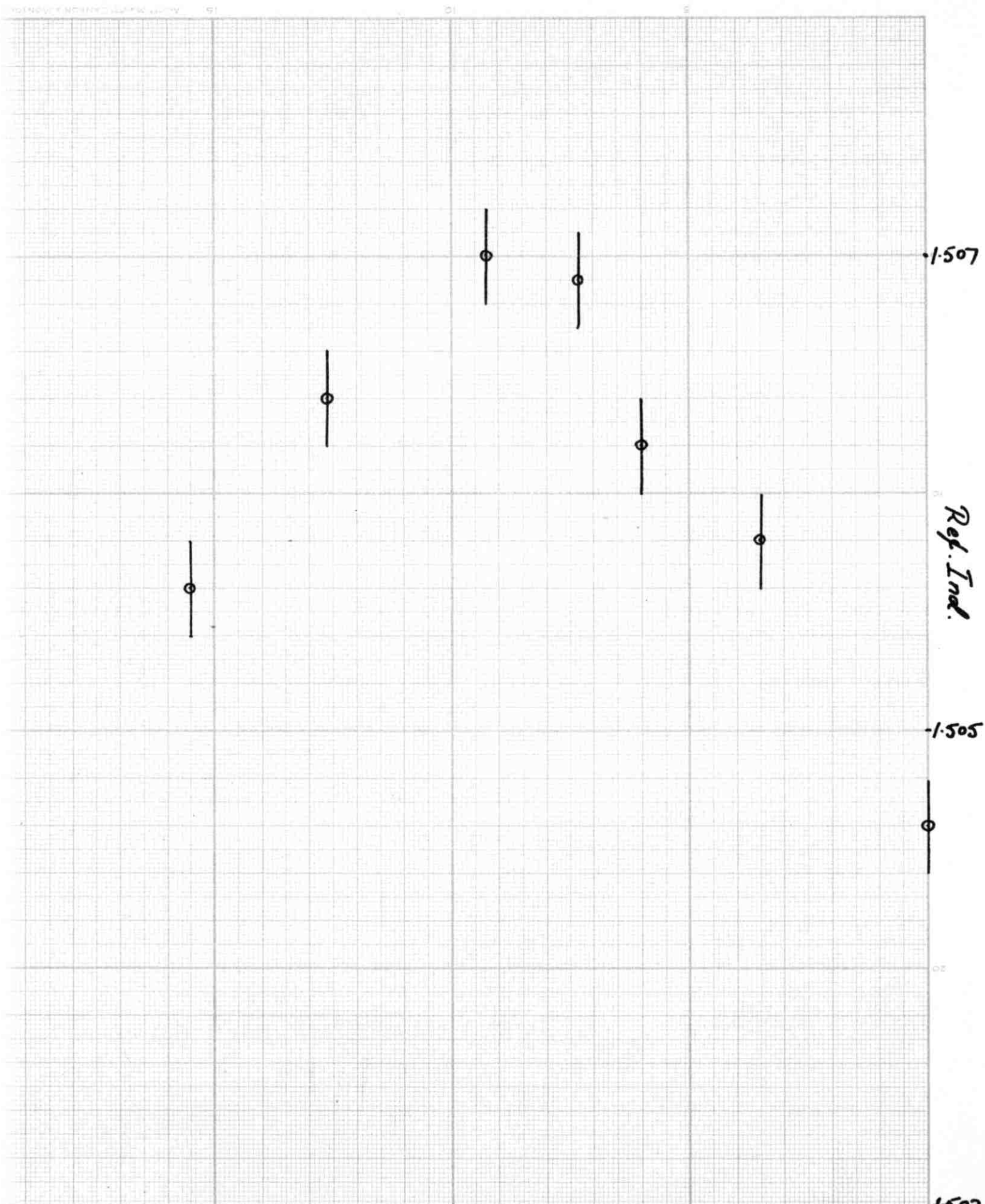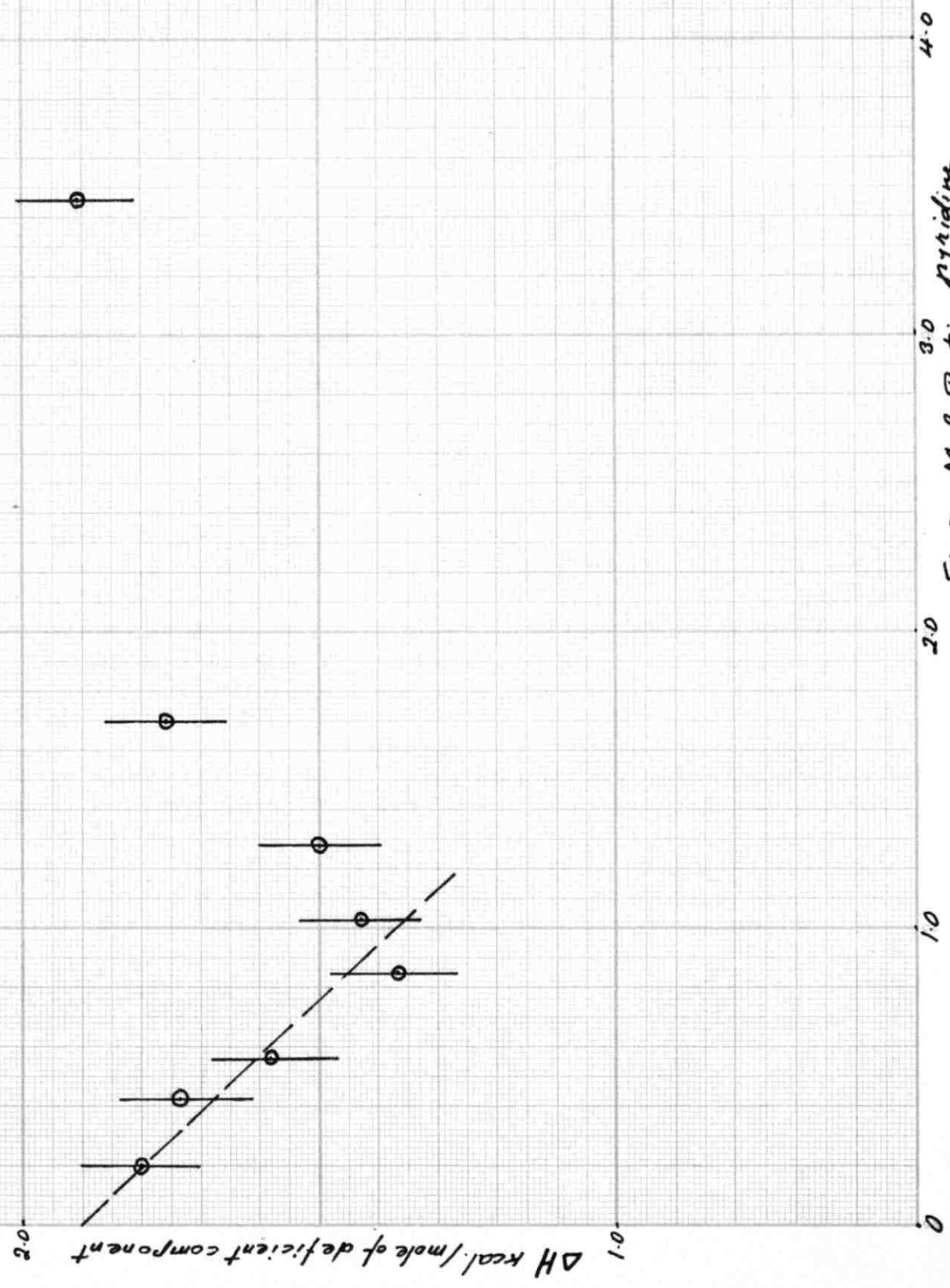
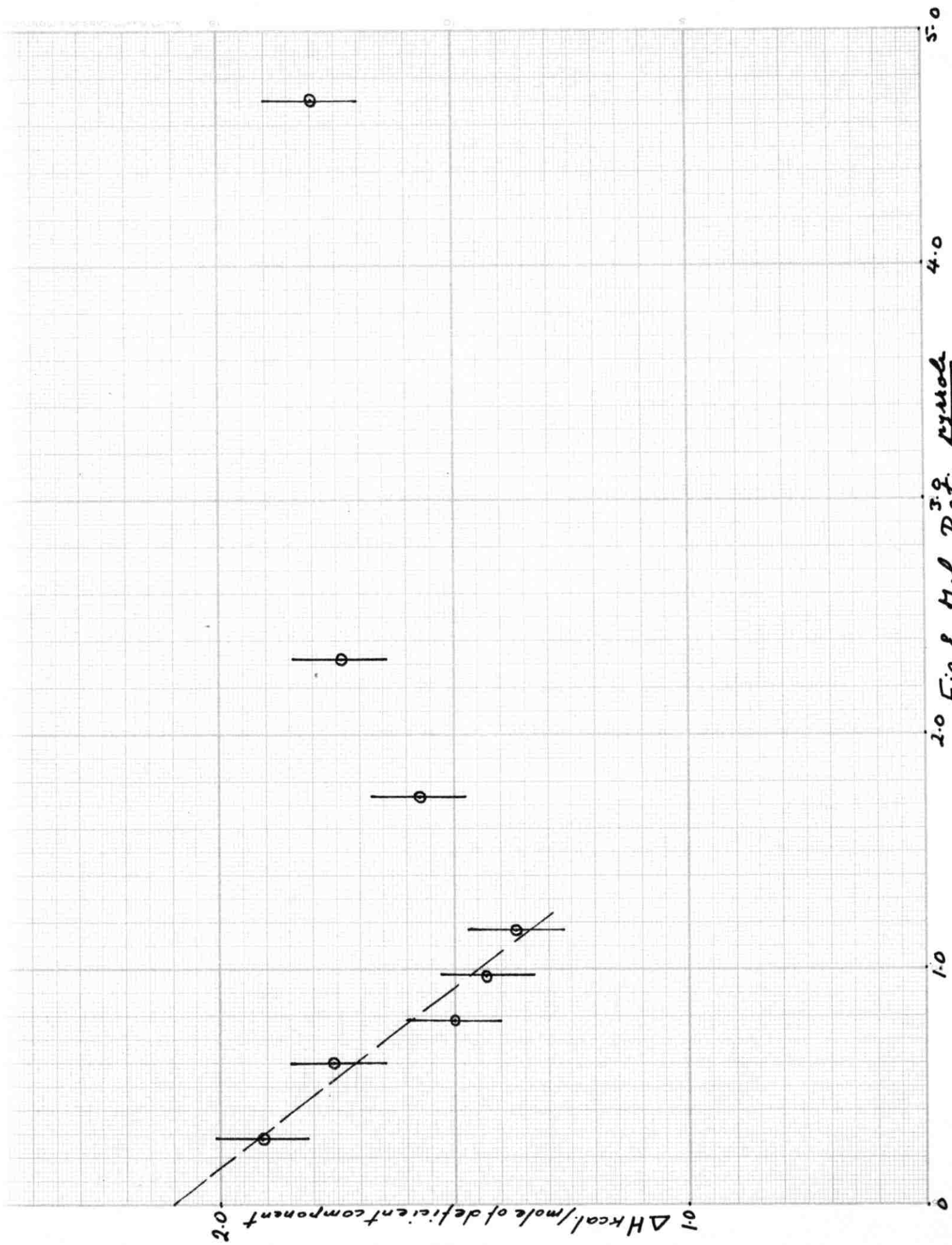Fig. 6 Mole fr. pyrrole

Fig.7. Mole Ratio $\frac{Pyridine}{Pyrrole}$.

Fig. 8. Mol Ratio $\dfrac{pyrole}{pyridine}$

used*. The calculated results are shown in Table IV and plotted
in Fig. 9.

Table III

Ml. pyridine: ml. pyrrole	Moles of pyrrole	Moles of pyridine	Ratio pyrrole: pyridine	Ratio pyridine: pyrrole	ΔH kcal/mole of deficient component 1st	2nd
16:4	0.057	0.197	0.29	3.45	1.91	
10:5	0.072	0.123	0.59	1.70	1.76	
11:9	0.129	0.136	0.97	1.03	1.43	1.45
10:10	0.144	0.123	1.17	0.85	1.37	1.35
5:10	0.144	0.062	2.32	0.43	1.74	
15:10	0.144	0.185	0.78	1.28	1.50	
10:15	0.215	0.123	1.75	0.57	1.58	1.55
4:16	0.230	0.049	4.69	0.21	1.80	

The reproducibility of the results can be judged by
comparing the values in the two subdivisions of column 6. In all
cases it was found to be within the range $\pm$ 5% of the experimental
ΔH (in calories). In Fig. 7 & 8 the vertical lines represent the
allowable 5% error in ΔH (in kcal/mole of deficient component.

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* One mole of solution is defined as $L = M_A x_A + M_B x_B$ where M_A, M_B
  are the molecular weights of the two components and x_A, x_B are the
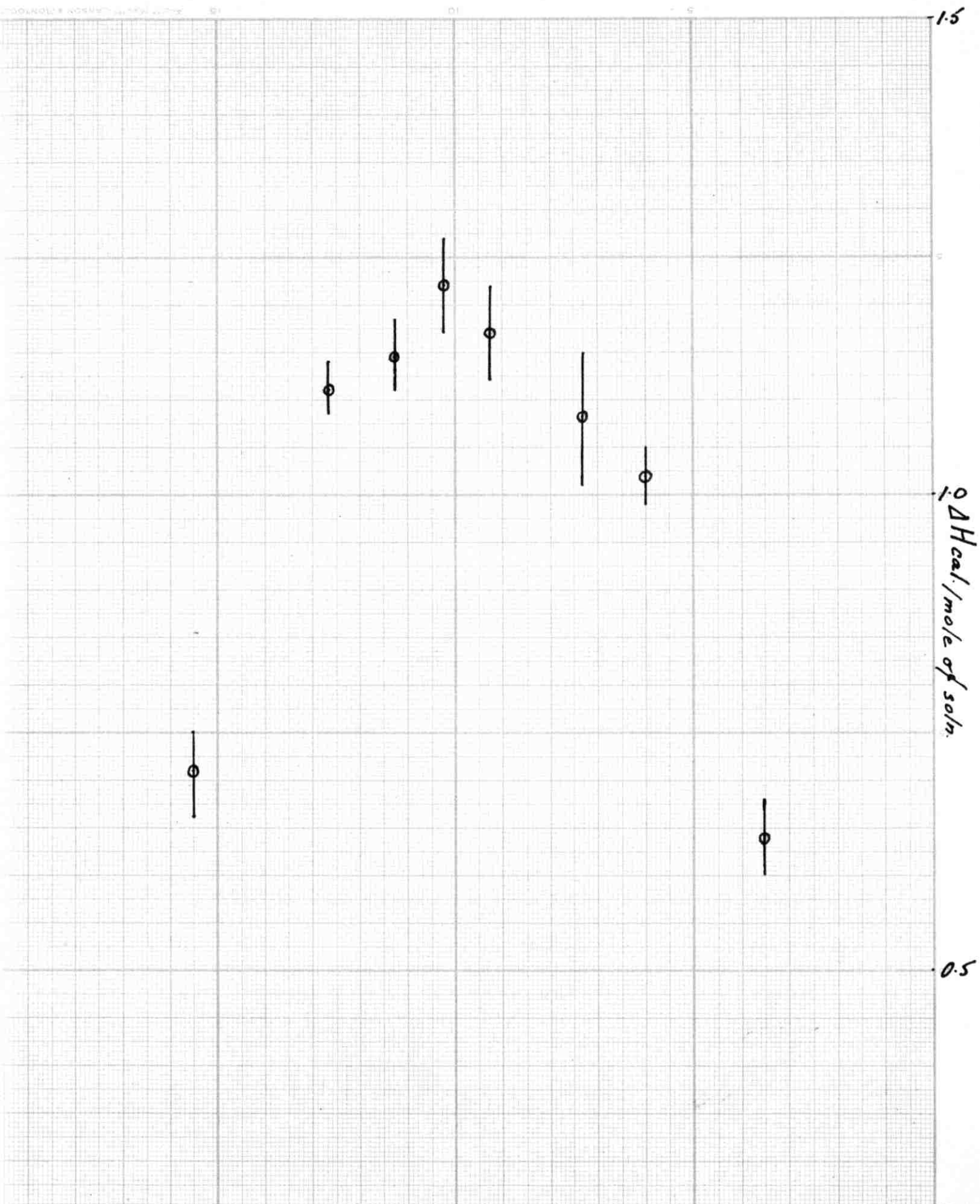 mole fractions of the two components respectively.

Fig. 9   Mol. fr. pyrrole

Table IV

Ml. pyridine: ml. pyrrole	Mole fraction pyrrole	Mole fraction pyridine	ΔH cal. experimental	density gm / ml.	Moles of Solu.	ΔH cal.* (const. volume)	ΔH cal./ mole of solution
16:4	0.226	0.774	109 ± 7	0.9717	76.4	54.6	0.72 ± 0.04
10:5	0.368	0.632	127 ± 7	0.9700	74.6	84.7	1.11 ± 0.03
15:10	0.438	0.562	216 ± 5	0.9690^a	73.8	86.4	1.13 ± 0.04
11:9	0.488	0.512	184 ± 8	0.9683^a	73.2	91.9	1.22 ± 0.05
10:10	0.538	0.462	166 ± 7	0.9676	72.5	83.1	1.17 ± 0.05
10:15	0.636	0.364	192 ± 7	0.9658	71.4	76.8	1.08 ± 0.07
5:10	0.700	0.300	108 ± 6	0.9647	70.6	71.9	1.02 ± 0.03
4:16	0.823	0.177	88 ± 6	0.9632	69.2	44.0	0.64 ± 0.04

a These two values were taken from the plot of density versus mole fraction of pyrrole.

The $\pm$ in column 8 indicate the allowed error range in the values for the ΔH cal/mole of solution assuming an error of $\pm$ 5% in the experimental ΔH in calories.

The results of the measurements of the heat of dilution of pyrrole in CCl_4 are given in table V. The two subdivisions under each of columns 4 & 5 give a measure of the reproducibility of the results.

* This ΔH represents the experimental value in cal. reduced to a a volume of 10 ml. Assuming that the change in volume on mixing pyridine with pyrrole is negligible.

Table V

Mixture	Moles pyrrole	Moles CCl_4*	Exp. ΔH in calories	ΔH kcal/ mole of pyrrole	Ratio: Pyrrole/ CCl_4
20 ml.C_4H_4N + 10ml.CCl_4	0.288	0.102	165	0.57	2.82
10 ml. " + 10ml. "	0.144	0.102	125	0.87	1.41
10 ml. " ¥ 20ml. "	0.144	0.204	241	1.67	0.71
5 ml. " + 15 ml. "	0.072	0.153	162	2.24	0.47
5 ml. " + 20ml. "	0.072	0.204	200 178	2.78 2.47	0.36
5 ml. " + 30ml. "	0.072	0.306	253 235	3.51 3.27	0.24
3ml. " + 30ml. "	0.043	0.306	166 184	3.95 4.38	0.14
1 ml. " + 30ml. "	0.014	0.306	83 97	5.98 6.93	0.05

The plot of ΔH in kcal. per mole of complex versus the molar ratio pyrrole to CCl_4 is given in Fig. 10. Linear extrapolation gives the final heat of dilution of pyrrole as 5.0 ± 0.5 kcal./mole.

The last point was not included in the extrapolation for the reason that with dilution the relative error grows too large to make accurate extrapolation possible.

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* The density of CCl_4 was taken as 1.575g/ml. at 30°C (Timmermans, loc. cit. p. 226). Since this part of the work was performed at a room temperature of about 15°C there will be an error in the calculations which however will be must less than the experimental error. The calorimeter itself was placed in an oil bath kept at $30° \pm 1°C$. all throughout the heat of dilution experiments.
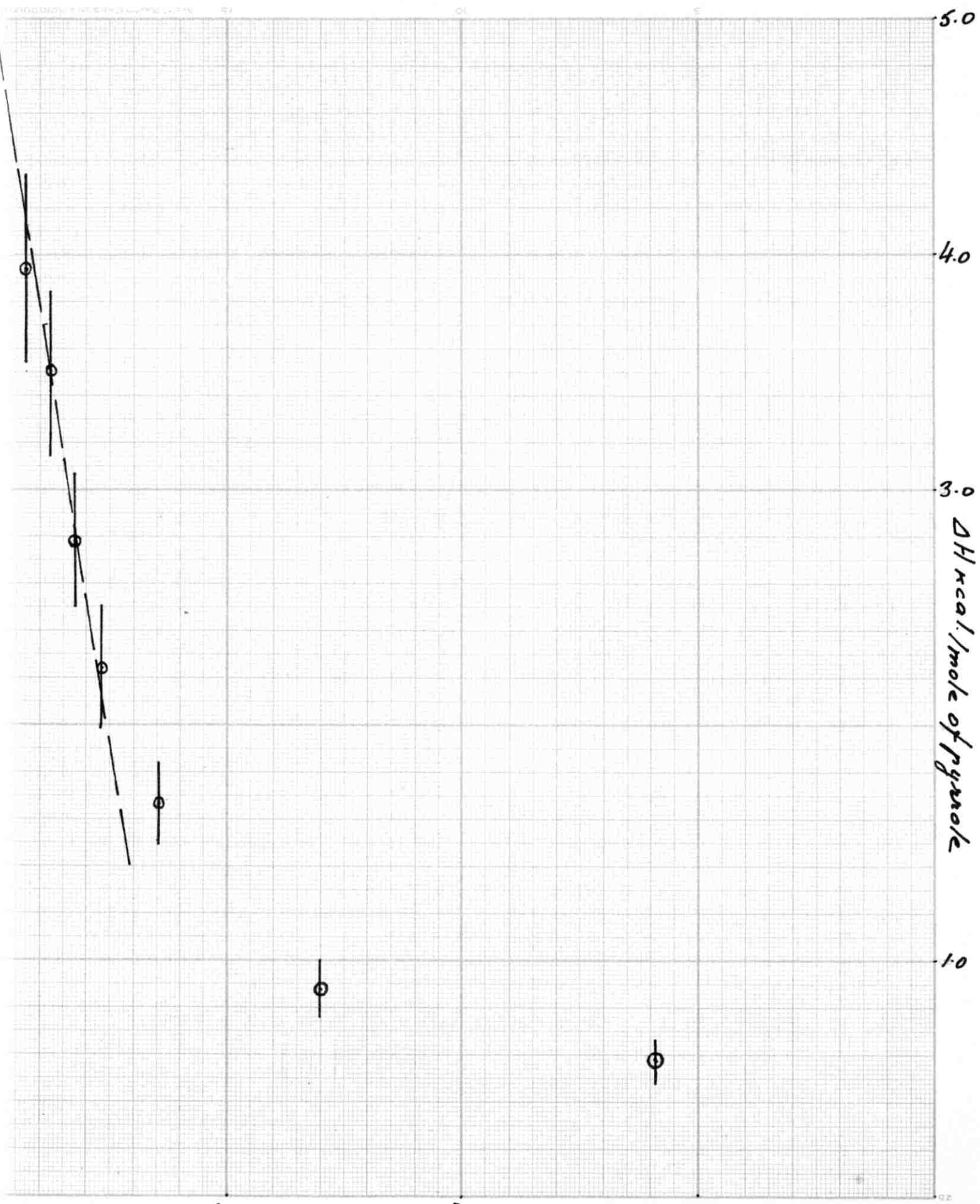
Fig. 10. Ratio $\dfrac{pyrrole}{CCl_4}$

V Discussion

A. The association of pyrrole
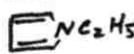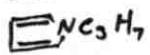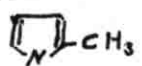
The plots of density and viscosity versus mole fraction pyrrole, although by no means linear, exhibits no well defined maxima or minima in the case of the density and bout a slight maximum in the case of the viscosity.

The absence of well-defined curvatures in the two plots is probably due to the fact that in this particular case complex formation between pyridine and pyrrole molecules changes but little such properties as density and viscosity. This points to the possibility of association in pyrrole, in the liquid state. More than that, it points to the possibility of a predominance of a dimer over the other possible polymers of higher order.

It should be noted that all the mixtures of pyrrole with basic amines, studied by Dezelić [1], with the exception of the system piperidine pyrrole, exhibited very slight maxima in the viscosity versus mole fraction plots and nearly linear density versus mole fraction relationships.

The association of pyrrole is also supported by a comparison of the boiling points of the following compounds

Table VI
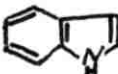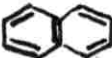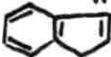
Compound	Formula	B.P.*	Compound	Formula	B.P.
Pyrrole		130°	N-methyl pyrrole	NCH_3	114.5°
Furan		32° (758)	N-ethyl pyrrole	NC_2H_5	130°
Thiophen		84°	N-propyl pyrrole	NC_3H_7	146°
Cyclopentane		49.5°	N-acetyl pyrrole	$NCOCH_3$	181°
Pyridine		115.5°	2-methyl pyrrole	CH_3	148°

* The boiling points are at 760 mm. unless otherwise indicated in a subscript.

The high boiling point of pyrrole compared with the boiling
points of other compounds having nearly the same molecular weight,
as well as the marked change in the boiling point of pyrrole on
substitution in the 1 position, are very definitely in favor
of the suggestion that pyrrole is associated through its acidic
hydrogen.

The comparison made above can be extended to indole, which
also might be expected to associate.

Table VII

Compound	Formula	B.P.	Compound	Formula	B.P.
Indole		254°	Naphthalene		182.4°
Indene		182.4°	N-acetyl indole		152°
Quinoline		237.7°	2-methyl indole		272°

The association of pyrrole was studied by several workers
mainly through absorption in the infrared.

In 1935 Wulf and Liddell [18] found a small subsidiary
maximum on the long wavelength side of the main absorption peak
of the 2nd, NH vibration harmonic*. They interpreted the two
peaks as resulting from resonance of the NH vibration with neigh-
bouring CH groups**.

A year later Pauling in analyzing their results [19] sug-
gested that pyrrole molecules exist in solution in a coplanar form,
the NH hydrogen bring in the plane of the ring, and also, to a

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* The satellite bond was approximately 50 cm^{-1} from the main band
 and had roughly one twentieth the intensity of the main band.

** They also found a subsidiary maximum in indole but none in
 carbazole which does not posses adjacent CH groups.

smaller extent, in a non-coplanar form.

In 1937 M. Freymann and R. Freymann studied the N-H vibration of pyrrole in the region of the 3rd harmonic ($0.8-1.2\mu$) in solution[20] and in the vapor [21] phases. They found a strong band at 1.02μ, a weaker one at 1.01μ and a very faint band at 1.00μ. The three bands were attributed to three molecular species of pyrrole.

Zumwalt and Badger [22] repeated the work of Freymann. They measured the 3rd harmonic of pyrrole vapor both with low and high dispersions at two temperatures (150° and 250°). In the low dispersion studies they observed that with rise in temperature the 1.01μ and the 1.00μ bands show moderate and large increases in intensity, respectively, relative to the 1.02μ band. From the fact that under high dispersion at $250^\circ C$ the 1.02μ and the 1.01μ bands* exhibit narrow Q branches which have in both cases the same intensity relative to the rest of the band, Zumwalt and Badger conclude that the two bands originate from the same molecular species.**

Hence they attribute the main band to absorption from the ground level and the two subsidiary maxima to absorption from two different excited states.

In the same year Rodebush and Coworkers [4][23] as a result of their work on hydrogen bonding and infrared absorption mention that the fundamental NH vibration absorption band lies at 2.93μ

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* The 1.00μ band being too faint to be photographed.

** The intensity of the Q branch of the NH vibration absorption depends on the electric moment in the N-H vibration and will, therefore, be sensitive to different orientations of the N-H bond.

for liquid pyrrole and at 2.85μ for a dilute solution in CCl_4*. Their conclusion was that pyrrole does not associate appreciably.

Gordy and Stanford [24] in 1940 observed a shift in the fundamental from 2.92μ to 2.78μ on going from pure liquid to 0.1 molar solution and conclude that pyrrole is associated in the pure liquid.

In 1951 Fuson, Josien et al [7] studied the NH vibration fundamental of pyrrole, indole, carbazole and other compounds in several different solvents. For CCl_4 solutions of pyrrole and indole at different concentrations they find two well-defined bands which they attribute to "unassociated" molecules and to "associated" molecules. For pyrrole the "unassociated" band changes from 2.87μ to 2.86μ in going from 3.8 molar to 0.039 molar while the "associated" band changes from 2.945μ to 2.924μ in going from pure liquid to 0.039 molar solutions.

In pure pyrrole only the "associated" band is present. In CCl_4 solutions both bands are present and going towards more dilute solutions the "associated" band disappears in the region 0.1 to 0.01 molar while the "unassociated" band becomes sharper and sharper while staying at 2.860μ.

From the above Fuson and co-workers conclude that pyrrole is associated through the NH-N hydrogen bond.

It is interesting to compare their results with those of Zezyulinskii [5] who found that the three harmonics shifted from 2.857μ, 1.460μ and 0.995μ respectively in pure pyrrole to 2.933μ, 1.490μ and 1.005μ respectively in dilute CCl_4 solution.

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* Both Wulf and Liddell, and Rodebush and co-workers do not mention the concentration of the pyrrole in CCl_4 solutions.

Tuomikoski [25] in 1952 criticized both Zezyulinskii and Fuson and co-workers on the ground that the slight shift observed in the frequencies of the harmonics on dilution is not sufficient e evidence for an NH-N hydrogen bond. He contends that the relative frequency shifts of the order of 3% or less do not necessarily indicate hydrogen bonding, as they may be due to dipole-dipole interaction between the solute and the solvent*.

Recently Fuson and Jasien [26] have measured the frequency of the fundamental of pyrrole in the vapor state at room temperature and found it to lie at 3535 cm^{-1} (2.829μ) and have no noticeable structure which should be present if M. Freymann's [20][21] and Zumwalt and Badger's [22] findings are correct**.

Some additional evidence can be found in the literature for the association of pyrrole.

In an X-Ray study of the structure of phthalocyanine, Robertson [27] found that the molecule was not tetragonally symmetrical and suggested that the departure may be due to internal hydrogen bonding. In the case of porphyrine and di-pyrrylmethenes the question as to whether they exist as hydrogen bonded isomers or as N isomers has not yet been answered [28] although
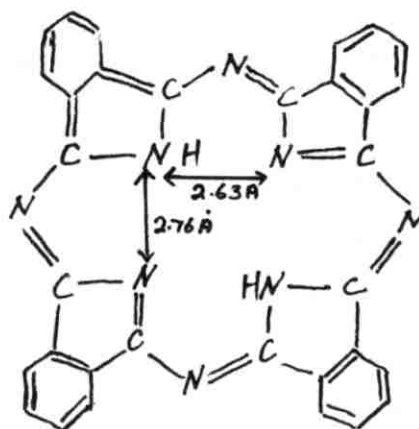
Phthalocyanine

Dipyrrylmethene

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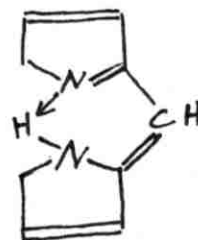
* In the wording of the author "the shift may be derived from electrostatics".

** The 70cm^{-1} spacing between the main band and the stronger subsidiary in the 3rd harmonic region suggests that for the fundamental

infrared studies [29][28] point out that hydrogen bonding may exist, the distance between the adjacent nitrogens being favorable for the formation of such a bond.

Kumler [30] measured the electronic and total polarizations for ms-tetraphenylporphine and found that the dipole moment of the molecule was zero or very nearly zero. This would obviously necessitate the hydrogens to be symmetrically distributed. Hence hydrogen bonding to the adjacent nitrogen and a bifurcated hydrogen bond (see Figure) were proposed as possible structures.

As can be easily seen from the literature survey made above the question of the "association" of pyrrole has not been answered in any definitive way [26]. We believe that the calorimetric work performed on the heat of dilution of pyrrole in CCl_4 has definitely settled the question in favor of association.

Porphine

Tetraphenylporphine

The value given for the heat at infinite dilution -5.0 ± 0.5 kcal/mole

one should observe a shoulder separated from the main peak by 20 to 30 cm^{-1}.
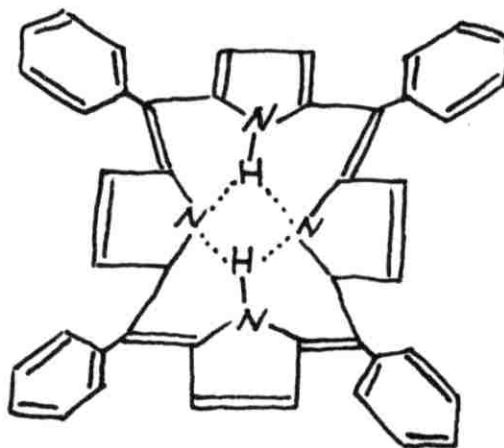
is not unreasonalbe if one compares it with -3.5 kcal/mole

the heat of association of some aliphatic and aromatic [31]*

acid amides.

The magnitude of the value is much larger than what one

would expect from the shift of the associated bond on dilution.

However the question as to what kind of association takes

place in liquid pyrrole and in CCl_4 solutions of sufficient

concentration has yet to be answered. Some calculations have

been tried using the data of Fuson and co-workers [7], Linnell[6]

and our own calorimetric data. The former covers a large concen-

tration range without sufficient accuracy. Linnell's data, on

the other hand, covers a rather small concentration range. Five

points from his calibration curve (see Fig. 13, Appendix) were

taken and Kempter and Mecke's [33] treatment applied to them.

Assuming a set of equilibrium constants of the kind

$$K_1 = \frac{(P)^2}{(P_2)} \quad , \quad K_2 = \frac{(P)^3}{(P_3)} \quad \cdots\cdots\cdots \quad K_n = \frac{(P)^{n+1}}{(P_{n+1})}$$

where $K_1 = K_2 \cdots\cdots = K_n$

Kempter and Mecke derived the equation

$$K_c = \frac{\alpha c}{1 - \sqrt{\alpha}} \qquad \text{where } K_c \text{ is the general dissociation}$$

constant, c is the total concentration in moles per liter and α

is the fraction of unassociated molecules.

If their assumptions are valid for the association of pyrrole

* Davies and Hallam [32] give the heat of association of acetamide
as -3.3 kcal/mole trimer.

then a plot of αc versus $\sqrt{\alpha}$ should give a straight line.

The experimental points and the calculations are given in Table VIII.

<p style="text-align:center">Table   VIII</p>

Ml. Pyrrole Made to 25ml. with CCl_4	Concentration Moles / lit.	OPtical density 2.84 bond	Optical density/ concent.	$\sqrt{\dfrac{Optical\ Density}{Concentration}}$
2.0	1.152	0.675	0.586	0.766
1.5	0.848	0.530	0.625	0.791
1.0	0.576	0.375	0.651	0.807
0.5	0.288	0.210	0.729	0.854
0.25	0.144	0.130	0.903	0.956

In the plot of $\sqrt{\dfrac{D}{C}}$ versus C which is equivalent to plotting αC versus $\sqrt{\alpha}$ [34] the first four points lie approximately on a straight line while the fifth is way off. However as can be seen the concentration range is too small to give an adequate test of the assumption.

Coggeshall and Saier's [34] treatment using two equilibrium constants could not be applied successfully to Linnell's data. The first-order equilibrium constant* increases with decreasing concentration in the case of alcohols and phenols [33] which in our case (it) decreased in a rapid manner.

We tried to use our calorimetric data to calculate the equilibrium constant of equilibria of the type

$$P \rightleftharpoons \frac{1}{n} P_n$$

making the assumption that the concentration of free pyrrole is

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* Both Kempter & Mecke & Coggeshall and Saier use the dissociation constant while we use association constants.

proportional to the experimental quantity of heat liberated or

$$H_{exp.} = (P).\ 5.0$$

Then, if C is the total concentration the total number of moles T will be given by

$$T = (P) + \frac{(C-P)}{(n)} + (CCl_4)$$

hence

$$K_{n-1} = \frac{\frac{(C-P)}{(n)} \cdot \frac{1}{T}^{1/n}}{(P) \cdot \frac{1}{T}}$$

$$= \frac{(C-P)}{(n)}^{1/n} / (P) \cdot \frac{1}{T^{1-1/n}}$$

K calculated for values of n from 2 to 8 gave a marked trend with concentration.

More careful infrared work over a large concentration range would give more material for interpretation. Moreover measurement of the heat of dilution of pyrrole in CCl_4 at different temperatures should give an independent value for the equilibrium constant.

how conceived?

B. The interaction between pyridine and pyrrole

The equilibrium constant for the one to one equilibrium can be easily calculated from the viscometric and calorimetric datas if we make the following assumptions: first, that the pyridine, pyridine-pyrrole complex, and pyrrole mixture behaves ideally; second, that the volume change on mixing pyrrole and pyridine is negligible; and third, that the heat of interaction is proportional to the concentration of the complex.

Having made the assumptions we can put down the three basic relations.

$$\phi = x_1\phi_1 + x_2\phi_2 + x_{12}\phi_{12} \qquad (5)$$

$$K = \frac{x_{12}}{x_1 \cdot x_2} \qquad (6)$$

$$\text{and } n_{12} = \frac{H'}{H} \qquad (7)$$

where K is the equilibrium constant.

x_1 = mole fraction of pyrrole at equilibrium.

x_2 = " " " pyridine " "

x_{12} = " " " the complex at equilibrium.

ϕ = fluidity of the mixture.

ϕ_1 = " " pyrrole.

ϕ_2 = " " pyridine.

ϕ_{12} = " " the complex.

n_{12} = moles of the complex at equilibrium.

H' = experimental heat of interaction.

H = actual heat of interaction obtained by extrapolation to zero mole ratio. (see Fig. 10)

if n_1' = moles of pyrrole present initially.

and n_2' = " " pyridine " "

$N' = n_1' + n_2'$ = total moles

Then $x_1 = \dfrac{n_1' - n_{12}}{N' - n_{12}}$ $\qquad\qquad$ (8)

$x_2 = \dfrac{n_2' - n_{12}}{N' - n_{12}}$ $\qquad\qquad$ (9)

and $x_{12} = \dfrac{n_{12}}{N' - n_{12}}$ $\qquad\qquad$ (10)

then eq. (5) can be rewritten as

$$n_{12} = \frac{\emptyset N' - n_1'\emptyset_1 - n_2'\emptyset_2}{\emptyset + \emptyset_{12} - \emptyset_1 - \emptyset_2} \qquad (11)$$

substituting from eqs. (8,9 & 10) into eq. (6) and solving for n_{12} we obtain

$$n_{12} = \frac{N'}{2} \pm \sqrt{\frac{N'^2(K+1) - 4n_1'n_{12}'K}{4(K+1)}} \qquad (13)$$

Setting eq. (11) equal to eq. (13) and letting

$$\emptyset_1 + \emptyset_2 = a \quad \text{we have}$$

$$2n_1'\emptyset_1 + 2n_2'\emptyset_2 + \emptyset_{12} \quad N' \pm\sqrt{\frac{(N'^2 - 4n_1'n_2')K + N'^2}{(K+1)}} \; =$$

$$N'(a+\emptyset)\mp\emptyset \sqrt{\frac{(N'^2 - 4n_1'n_2')K + N'^2}{(K+1)}} \pm a\sqrt{\frac{(N'^2 - 4n_1'n_2')K + N'^2}{(K+1)}} \qquad (14)$$

substituting the numerical values for a, $\emptyset$, and $\emptyset_2$

$$\emptyset_{12} = (0.2074 - \emptyset) + \frac{2N'\emptyset - c}{N' \pm\sqrt{\frac{(N'^2 - 4n_1'n_2')K + N'^2}{K+1}}} \qquad (15)$$

where $c = 0.1772n_1' + 0.2376n_2'$

substituting eq. (13) into eq.(7) we obtain

$$K = 1 + \frac{H^2n_1'n_2'}{H'(HN' - H') - H^2n_2'n_2'} \qquad (16)$$

A graphical method of solution was tried on eq. (15) assuming: $\emptyset_{12}$ and K to be constant variables values of K ranging from 0.1 to 20 were substituted into eq. (15) and the corresponding $\emptyset_{12}$'s calculated.

Plotting one against the other for the six experimental points (see Tables I & II) gave paralled curves. The failure of

this method is attributed to the fact that $\emptyset_{12}$ is not sensitive
to changes in K.

For eq. (16) the above method also failed mainly because
the sensititity of K to H' was larger than the experimental
error.

A more direct way of the two equations was then tried. H_1
the he at of interaction at infinite dilution of pyrrole was
corrected for the heat of dissociation of pyrrole assuming that
the heat of dilution in pyridine would not differ appreciably
from that in CCl_4. This assumption is permissible since the pyri-
dine is not associated.*

The correction was performed in the way shown in Tables IX &
X and in Fig. 11.

Table IX

Moles of pyrrole	Ratio pyrrole/ CCl_4	ΔH experimental in cal.	ΔH experimental calculated for 0.144 moles of pyrrole
0.288	2.82	165	83
0.144	1.41	125	125
0.144	0.71	241	241
0.072	0.47	162	324
0.072	0.36	200	400
0.072	0.24	252	504
0.042	0.14	157	568
0.014	0.05	83	830

The experimental heat of dilution ΔH calculated to 0.144 moles
of pyrrole is plotted versus ratio pyrrole to CCl_4 in Fig. 11.

For corresponding values of the ratio pyrrole to pyridine
the correction was read from Fig. 11 and added to the experimental
heat of interaction as shown in Table X.

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* The heat of dilution of pyrdine in CCl_4 is only -10cal/moles$^{(35)}$ =
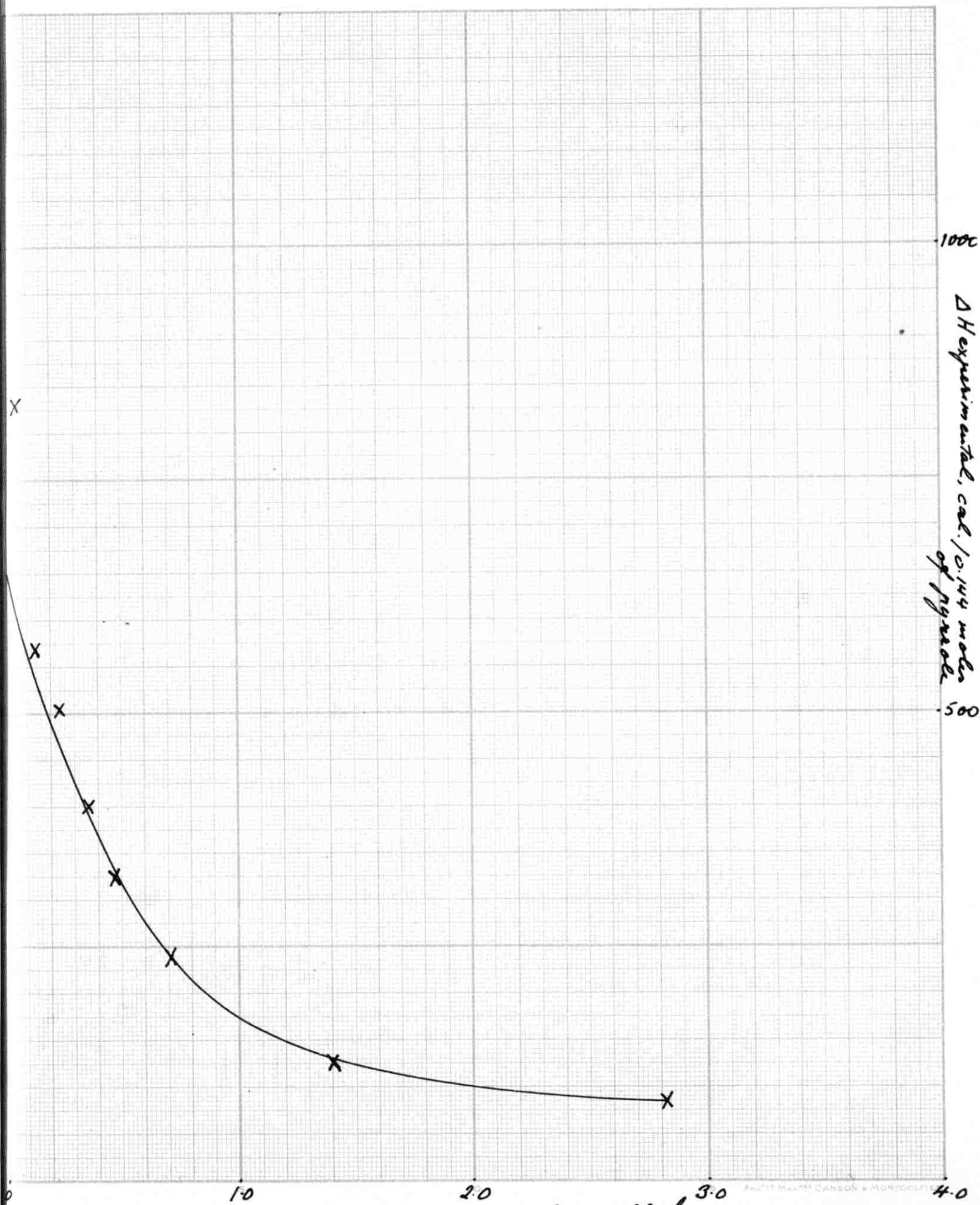
Fig. 11 Mole Ratio $\frac{pyrrole}{CCl_4}$

ΔH experimental. cal./0.144 moles of pyrrole

Table X

Ratio pyrrole/ pyridine	Moles of pyrrole	ΔH exp. in cal.	ΔH exp. corrected to 0.144 moles of pyrrole in cal.	ΔH exp. corr. for associa- tion of pyr- role, cal.	ΔH exp. corr. re- duced to org.no.of moles
0.29	0.057	109	275	730	289
0.59	0.072	127	254	549	275
0.78	0.144	216	216	446	446
0.95	0.129	184	205	390	349
1.17	0.144	166	166	316	316
1.75	0.215	192	128	233	348
2.32	0.144	108	108	193	193
4.69	0.230	88	55	95	151

Table XI gives the heat of interaction calculated as kcal. per mole of pyrrole and Fig. 12 gives the plot versus mole ratio pyrrole to pyridine. The vertical lines indicate the ± 10% error allowable. As seen the extrapolated value gives the heat of interaction as 7.0 ± 0.7 kcal/mole.

Substituting 7.0 as the value for ΔH, the equilibrium constants obtained from eq. (16) are listed in Table XII.

Applying statistics for small numbers of observation[35] we reject the value 2.89 and obtain the average K = 1.3 ± 0.2 (95% confidence level).

Obviously it is of interest to compare the above value of K

Table XI

Ratio pyrrole/ pyridine	ΔH kcal. per mole of pyrrole
0.29	5.07
0.59	3.82
0.78	3.01
0.95	2.71
1.17	2.20
1.75	1.62
2.32	1.34
4.69	0.66

Fig. 12 Mole Ratio. $\frac{pyrrole}{pyridine}$
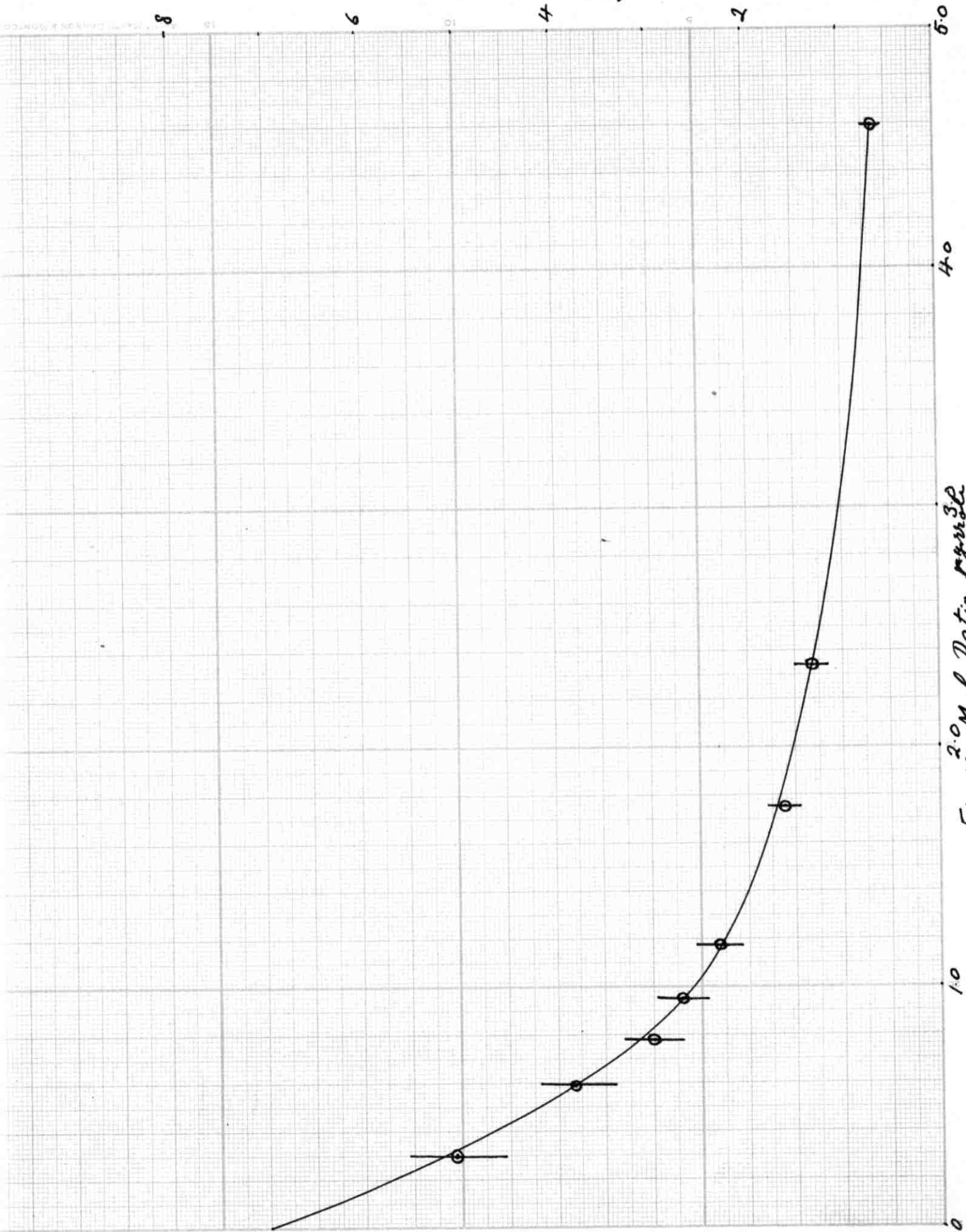
ΔH kcal./mole of pyrrole

with the one obtainable from Linnell's data (Appendix).

Since the concentrations used by Linnell were less than one molar we can assume that the equilibrium between pyridine and pyrrole in his solutions was mainly a one to one equilibrium unaffected by the still present associated pyrrole.

Table XIII gives the results of the calculations.

Table XII

Ratio Pyrrole/ Pyridine	K
0.29	2.89
0.59	1.02
0.78	1.66
0.95	1.28
1.17	1.30
1.75	1.19
2.32	1.54
4.69	0.97

Average K = 1.3 $\pm$ 0.2

ml.C₄H₄N : ml.C₅H₅N	Moles CCl₄	Moles of free pyrrole	Moles of complex pyrrole	Moles of pyridine	Total moles fraction pyrrole	Moles fraction complex pyrrole	Moles fr. of pyridine	K.
1.00:1.00	0.237	0.0087	0.0053	0.0211	0.412	0.251	0.337	1.8
1.00:0.50	0.243	0.0111	0.0029	0.0173	0.771	0.168	0.191	1.4
0.50:0.70	0.246	0.0049	0.0021	0.0136	0.369	0.154	0.485	0.9
0.50:0.60	0.247	0.0046	0.0024	0.0121	0.380	0.198	0.422	1.2
0.50:0.60	2.46	0.0046	0.0051	-	-	-	-	1.2
0.50:0.60	0.247	0.0056	0.0024	0.0074	0.757	0.189	0.054	4.6
0.50:0.15	0.251	0.0056	0.0014	0.0040	0.524	0.144	0.333	0.8
0.50:0.40	0.249	0.0055	0.0015	0.0105	0.515	0.164	0.520	1.0
0.50:0.30	0.244	0.0046	0.0024	0.0146	0.709	0.105	0.186	1.0
0.50:0.20	0.251	0.0061	0.0009	0.0036	0.630	0.141	0.239	0.8
0.50:0.25	0.250	0.0057	0.0013	0.0092	0.395	0.169	0.435	1.0
0.50:0.60	0.247	0.0049	0.0021	0.0124	0.395	0.169	0.435	1.0
0.50:1.00	0.243	0.0037	0.0033	0.0091	0.230	0.205	0.565	1.6

Rejecting the value 4.6 we obtain K = 1.2 ± 0.2 (95% confidence) which is in good agreement with the value obtained from our calorimetric data. This fact indicates that our approach to the study of the pyridine-pyrrole system is a sound one.

C. The nature of the pyridine-pyrrole complex

The conclusion of Dezelic [1] that the pyridine-pyrrole complex consists of one molecule of pyridine to two molecules of pyrrole is contradictory to Linnell's results [6] * as well as to those obtained by the author.

The plot of the refractive indices of pyridine-pyrrole mixtures versus mole fraction pyrrole, indicate that the complex is in a one to one ratior. That the complex exists as a result of an equilibrium and not as a product of a simple reaction, can be concluded from an examination of the calorimetric data. In the latter case the heat of interaction calculated as kcal. per mole of the deficient component plotted against the mole ratio of one component to the other would give a straight line. The presence of the minima at a 1:1 mole ratio, is strong evidence for the equilibrium idea with a 1:1 complex formed.

Moreover assuming equilibrium and correcting for the association of pyrrole it is possible to obtain a consistent value for K the equilibrium constant, as well be shown in the next section.

Treatment of Linnell's data on the assumption gives a value for K which is nearly identical to that obtained from calorimetric results.

It can be then concluded that the pyridine-pyrrole complex is definitely a one to one complex.

It is interesting to compare the thermodynamic quantities calculable from the calorimetric results and the equilibrium constant obtained above, for the two equilibria.

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* See Appendix.

$$C_5H_5N + C_4H_4N_4 \rightleftharpoons C_5H_5N...HNC_4H_4 \qquad (i)$$

$$\text{and } C_5H_5N + (C_4H_4NH)n \rightleftharpoons C_5H_5N...HNC_4H_4 + C_4H_4NH \; n-1 \qquad (ii)$$
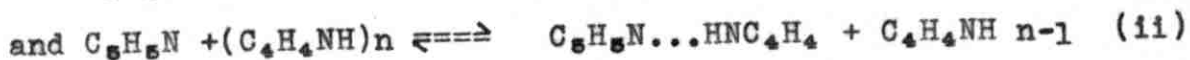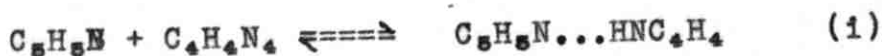
For equilibrium (i) $\Delta H = + 7.0$ kcal/mole and $K = 1.2$

Then $\qquad \Delta F = -RT \ln K$

$$= -2.3 \times 2.0 \times 303 \log 1.2$$

$$= -110 \text{ cal/mole.}$$

using the relation

$$\Delta S = \frac{\Delta H - \Delta F}{T}$$

$$= \frac{7000 + 110}{303}$$

$$= 23 \text{ cal./deg.mole.}$$

For equilibrium (ii) $\Delta H = + 2.0$ kcal/mole

and $\quad \Delta S = \dfrac{2000 + 110}{303}$

$$= 7 \text{ cal./deg.mole.}$$

The large entropy change in the former case would indicate that pyridine-pyrrole complex is a tightly packed complex, while the much smaller entropy change in the second case indicates that the pyrrole complex is more loose than the pyridine-pyrrole complex, but only slightly so. This would provide a reasonable explanation for the slight curvatures in the viscosity and density versus mole fraction plots.

SUMMARY

In the present work the densities, viscosities and refractive indices of pyrrole-pyridine mixtures in different molar ratios, were measured at $30^\circ C$.

The heat of interaction between pyridine and pyrrole and the heat of dilution of pyrrole were measured also at $30^\circ C$ and found to be $+2.0 \pm 0.1$ kcal/mole and -5.0 ± 0.5 kcal/mole, respectively. The corrected heat of interaction between pyridine and pyrrole is then given as 7.0 ± 0.7 kcal/mole.

Using this value and assuming a simple equilibrium

$$C_5H_5N + C_4H_4NH \rightleftharpoons C_5H_5N...NHC_4H_4$$
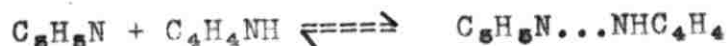
a value for K, the equilibrium constant is obtained 1.3 ± 0.2. This is compared to $K = 1.2 \pm 0.2$ calculated from the infrared absorption data of Linnell on pyridine-pyrrole mixtures in CCl_4.

The association of pyrrole is discussed and it is pointed out that the large heat of dilution in CCl_4 asserts definitely the fact that pyrrole is associated and not existing in different molecular forms.

For the above equilibrium $\Delta F = 110$ cal/mole and $\Delta S = 23$ cal/mole.

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VIII APPENDIX

Infrared Studies on the Pyridine-Pyrrole System

Below are given the results of the work done by Dr. R.H. Linnell on the infrared absorption of pyridine-pyrrole mixtures in CCl_4 solutions. They have been published in the J.Chem.Phys. 21, 179 (1953).

As given here the results have been recalculated by Dr. Linnell yielding only slightly differing results.

The experimental technique was as follows: in each case a certain volume of pyrrole was pipetted into a 25 ml. volumetric flask, a certain volume of pyridine, accurately measured, added, and the whole made up to volume with CCl_4.

The absorptions from 2 to 15μ of the solutions thus made up, were measured in a double beam Perkin-Elmer Model 21 Spectrophotometer, using a NaCl prism.

NaCl cells 0.145 cm thick were used for the measurements with a reference cell of identical thickness filled with the solvent.

The table gives the experimental data and the calculated results assuming a simple one to one complex and equilibrium.

To know the concentration of free pyrrole at equilibrium from the optical density of the 2.84μ band, Dr. Linnell ran the absorption curves of solutions of pyrrole in CCl_4, for various concentrations of pyrrole and then plotted the optical density of the 2.84μ band of pyrrole versus the concentration. Assuming that in the concentration range measured (1 to 0.1 moles/liter) the 2.84μ band obeys Beer's law, Dr. Linnell drew the best straight line through his experimental points and used it as a calibration curve. Fig. 13 shows the curve.

Optical Density 2.84 μ band.

The equilibrium constant for the equilibrium

$$C_4H_4NH + C_5H_5N \rightleftharpoons (C_4H_4NH...NC_5H_5)$$
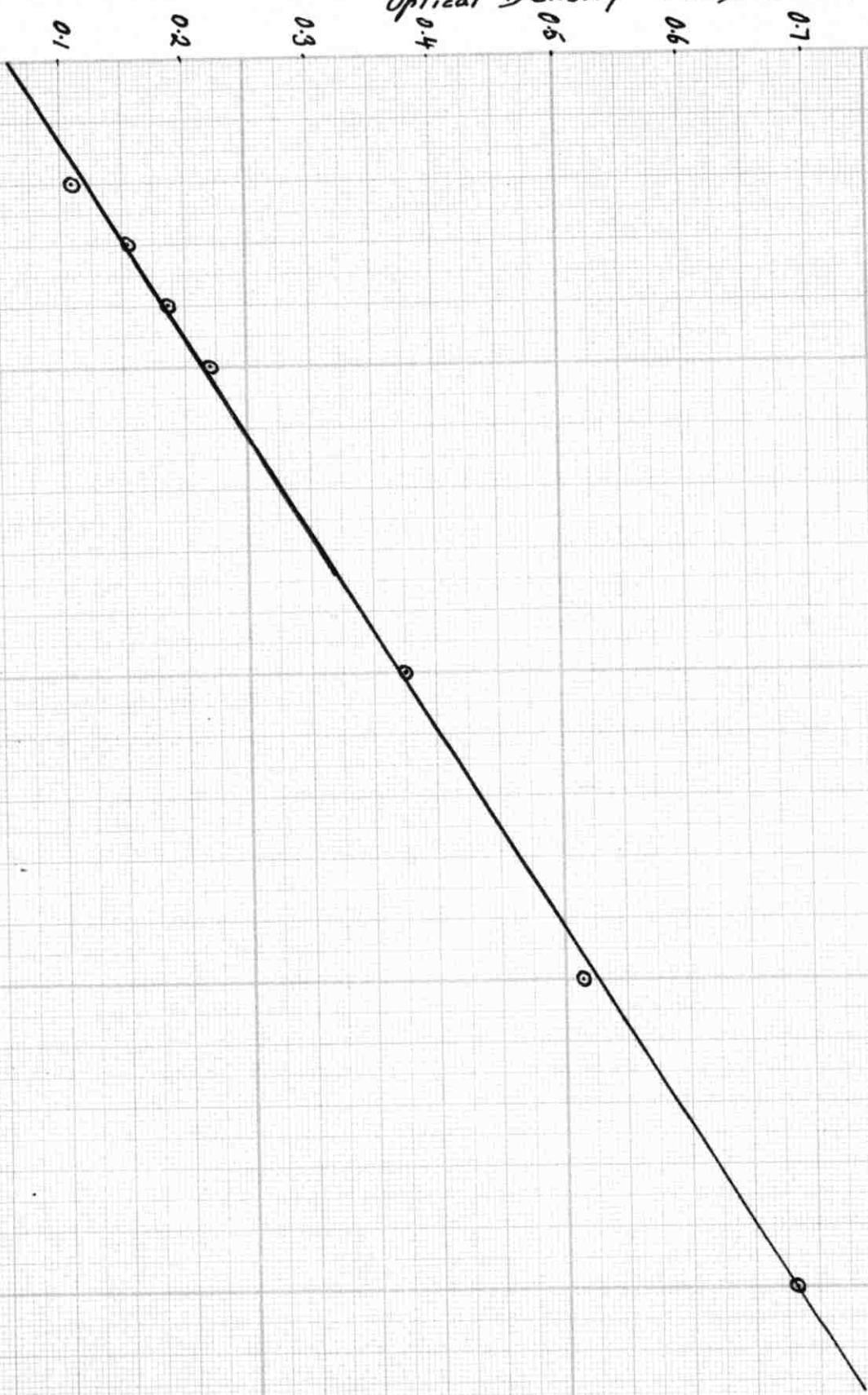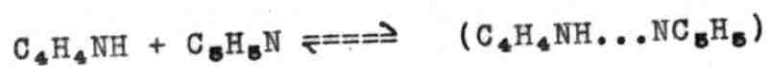
is calculated in lit/mole units from

$$K = \frac{\text{millimoles complex x } 10^3}{(\text{millimoles free pyrrole})(\text{millimoles free pyridine}) \text{x} 40}$$

In Fig. 14 the optical density of the 3.11 μ band due to association between pyridine and pyrrole is plotted versus the calculated concentration of the complex. The fact that a straight line can be drawn through the points bands support to the equilibrium idea and to the assumption of linearity. The number near each experimental point is the equilibrium constant.

It should be remarked that the points whose equilibrium constant is way off from the average are the ones that deviate most from a straight line.

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Optical Density 3.11 μ band
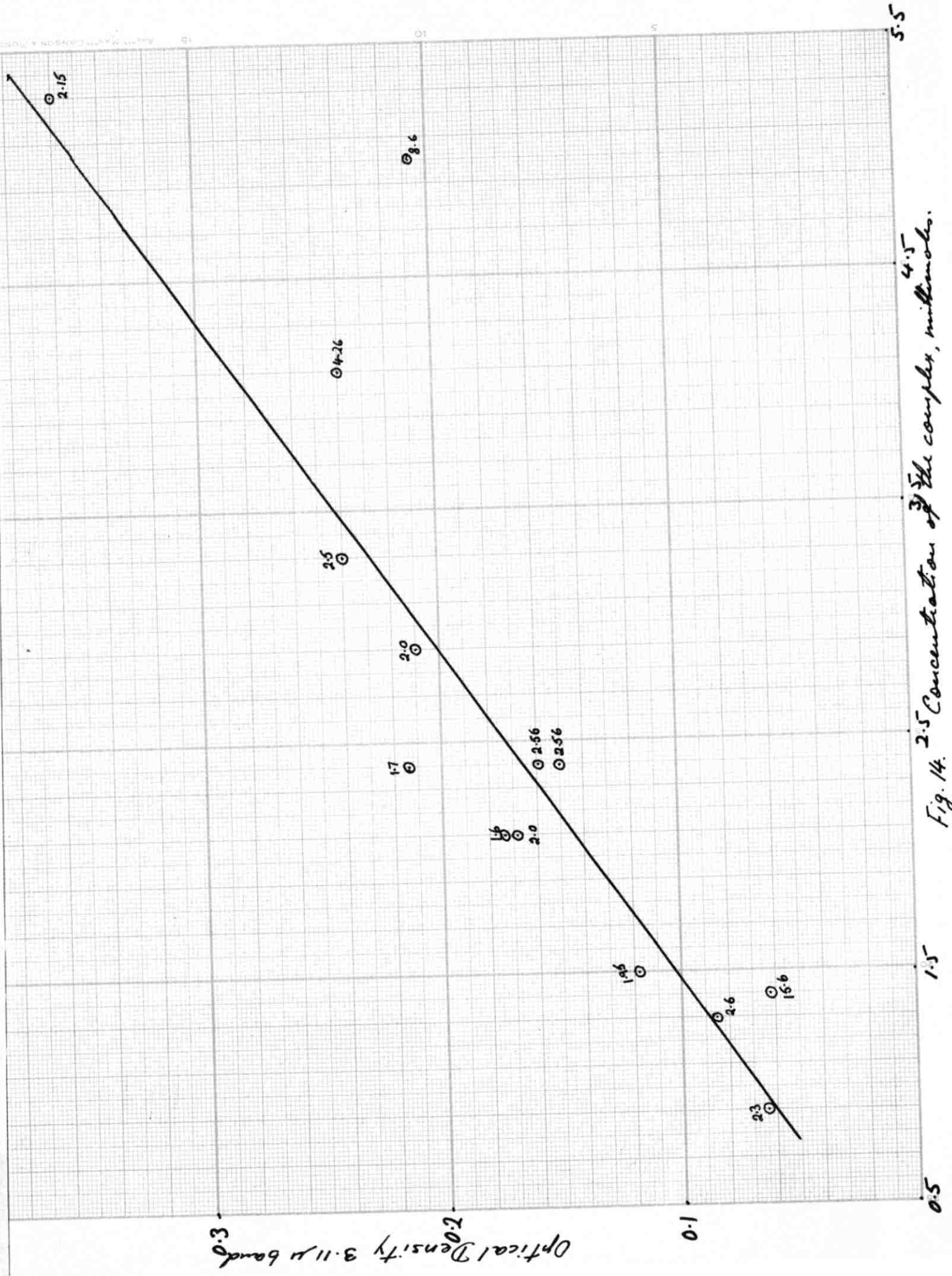
Concentration of the complex, millimols.

Fig. 14.

0.5   1.5   2.5   4.5   5.5

0.3   0.2   0.1

2.15
9.6
4.26
2.5
2.0
2.56
2.56
1.7
1.6
2.0
1.45
2.6
15.6
23

Table XIV

Ml. of pyrrole	ml. of pyridine	Ratio pyrrole/ pyridine	Total* moles pyrrole $\times 10^5$	Total** moles pyridine $\times 10^5$	ml. of CCl_4	Moles*** of CCl_4	Optical density 3.11μ band	optical density 2.84μ band	moles of free pyrrole $\times 10^5$	Moles of complex $\times 10^5$	Moles of free pyridine $\times 10^5$	K lit/mole
0.50	0.15	3.75	6.98	1.86	24.35	0.251	0.062	0.189	5.6	1.4	0.4	15.6
0.50	0.20	2.92	6.98	2.48	24.30	0.251	0.084	0.204	6.1	0.9	1.6	2.3
0.50	0.25	2.01	6.98	3.48	24.22	0.250	0.085	0.193	5.7	1.3	2.2	2.6
1.00	0.50	2.24	13.96	6.22	23.50	0.243	0.240	0.310	11.1	2.9	3.3	2.0
0.50	0.40	1.40	6.98	4.97	24.10	0.239	0.199	0.184	5.5	1.5	3.5	1.95
1.00	1.00	1.13	13.96	12.4	24.36	0.237	0.357	0.260	8.7	5.3	7.1	2.15
0.50	0.60	0.936	6.98	7.46	23.90	0.247	0.159	0.162	4.6	2.4	5.1	2.56
0.50	0.60	0.936	6.98	7.46	23.90	0.246	0.150	0.162	4.6	2.4	5.1	2.56
0.50	0.60	0.936	6.98	7.46	23.90	0.247	0.160	0.169	4.9	2.1	5.4	2.0
0.50	0.70	0.804	6.98	8.69	23.80	0.246	0.176	0.170	4.9	2.1	6.6	1.6
0.50	0.80	0.703	6.98	9.94	23.70	0.244	0.214	0.162	4.6	2.4	7.6	1.7
0.50	1.00	0.563	6.98	12.4	23.50	0.243	0.240	0.108	2.9	4.1	8.3	4.26
0.50	1.00	0.563	6.98	12.4	23.50	0.243	0.208	0.121	1.96	5.0	2.4	8.6
0.50	1.00	0.563	6.98	12.4	23.50	0.243	0.240	0.133	3.7	3.3	9.1	2.5

\# Taking the density of pyrrole as 0.935gm/ml. and the mol. wt. as 67.

\## Taking the density of pyridine as 0.982gm/ml. and the mol. wt. as 79.

Table XIV

Ml. of pyrrole	ml. of pyridine	Ratio pyrrole/pyridine	Total* moles pyrrole x 10⁵	Total** moles pyridine x10⁵	ml. of CCl₄	Moles*** of CCl₄	Optical density 3.11μ band	optical density 2.84μ band	moles of free pyrrole x 10⁵	Moles of complex x 10⁵	Moles of free pyridine x10⁵	K lit/mole
0.50	0.15	3.75	6.98	1.86	24.35	0.251	0.062	0.189	5.6	1.4	0.4	15.6
0.50	0.20	2.82	6.98	2.48	24.30	0.251	0.064	0.204	6.1	0.9	1.6	2.3
1.00	0.50	2.24	13.96	6.22	23.50	0.243	0.310	0.310	11.1	2.9	3.3	2.0
0.50	0.25	2.01	6.98	3.48	24.22	0.250	0.085	0.193	5.7	1.3	2.2	2.6
0.50	0.40	1.40	6.98	4.97	24.10	0.299	0.199	0.184	5.5	1.5	3.5	1.95
1.00	1.00	1.13	13.96	12.4	24.36	0.237	0.357	0.260	8.7	5.3	7.1	2.15
0.50	0.60	0.936	6.98	7.46	23.90	0.247	0.159	0.162	4.6	2.4	5.1	2.56
0.50	0.60	0.936	6.98	7.46	23.90	0.246	0.150	0.162	4.6	2.4	5.1	2.56
0.50	0.60	0.936	6.98	7.46	23.90	0.247	0.160	0.169	4.9	2.1	5.4	2.0
0.50	0.70	0.804	6.98	8.69	23.80	0.246	0.176	0.170	4.9	2.1	6.6	1.6
0.50	0.80	0.703	6.98	9.94	23.70	0.244	0.214	0.162	4.6	2.4	7.6	1.7
0.50	1.00	0.563	6.98	12.4	23.50	0.243	0.240	0.108	2.9	4.1	8.3	4.26
0.50	1.00	0.563	6.98	12.4	23.50	0.243	0.208	0.131	1.96	5.0	2.4	8.6
0.50	1.00	0.563	6.98	12.4	23.50	0.240	0.133		3.7	3.3	9.1	2.5

\# Taking the density of pyrrole as 0.935 gm/ml. and the mol. wt. as 67.

** Taking the density of pyridine as 0.982 gm/ml. and the mol. wt. as 79.

Table XIV

Ml. of pyrrole	Ml. of pyridine	Ratio pyrrole/ pyridine	Total* moles pyrrole x 10⁵	Total** moles pyridine x 10⁵	ml. of CCl₄	Moles*** of CCl₄	Optical density 3.11μ band	Optical density 2.84μ band	moles of free pyrrole x 10⁵	Moles of complex x 10⁵	Moles of free pyridine x 10⁵	K lit/mole
0.50	0.15	3.75	6.98	1.86	24.35	0.251	0.062	0.189	5.6	1.4	0.4	15.6
0.50	0.20	2.82	6.98	2.43	24.30	0.251	0.064	0.204	6.1	0.9	1.6	2.3
1.00	0.50	2.24	13.96	6.22	23.50	0.243	0.240	0.310	11.1	2.9	3.3	2.0
0.50	0.25	2.01	6.98	3.48	24.22	0.250	0.085	0.135	5.7	1.3	2.2	2.6
0.50	0.40	1.40	6.98	4.97	24.10	0.299	0.198	0.184	5.5	1.5	3.5	1.95
1.00	1.00	1.13	13.96	12.4	24.36	0.237	0.357	0.260	8.7	5.3	7.1	2.15
0.50	0.60	0.936	6.98	7.46	23.90	0.247	0.152	0.162	4.6	2.4	5.1	2.56
0.50	0.60	0.936	6.98	7.46	23.80	0.246	0.150	0.162	4.6	2.4	5.1	2.56
0.50	0.60	0.936	6.98	7.46	23.90	0.247	0.160	0.169	4.9	2.1	5.4	2.0
0.50	0.70	0.804	6.98	8.69	23.50	0.246	0.176	0.170	4.9	2.1	6.6	1.6
0.50	0.80	0.703	6.98	9.94	23.70	0.244	0.214	0.162	4.6	2.4	7.6	1.7
0.50	1.00	0.563	6.98	12.4	23.50	0.243	0.240	0.108	2.9	4.1	8.3	4.26
0.50	1.00	0.563	6.98	12.4	23.50	0.243	0.208	0.201	1.96	5.0	2.4	8.5
0.50	1.00	0.563	6.98	12.4	23.50	0.243	0.240	0.133	3.7	3.3	9.1	2.5

* Taking the density of pyrrole as 0.955gm/ml. and the mol. wt. as 67.

** Taking the density of pyridine as 0.982gm/ml. and the mol. wt. as 79.

*** Taking the density of CCl₄ as 1.59gm/ml. and the mol. wt. as 154.