

HEATS OF FORMATION OF CERTAIN  
NICKEL-PYRIDINE COMPLEX SALTS

by

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## HEATS OF FORMATION OF CERTAIN NICKEL-PYRIDINE COMPLEX SALTS

### HISTORICAL BACKGROUND

Compounds of pyridine with inorganic salts have been prepared since 1870. In the next fifty years much work was done on the preparation and description of many metal pyridine salts. This early study was done in many instances with the idea of finding new qualitative tests for the anions and cations.

In the early nineteen twenties mention was made of the solubility characteristics of some of the pyridine complexes in chloroform. This opened a new procedure for preparing the metal pyridine cyanates and thiocyanates in a pure form.

At present, more and more quantitative analytical procedures are utilizing the precipitation of the complexes in a water solution as a means of separation and determination of the metals.

Other investigations have been made to gain further knowledge of the bonding of pyridine to the salt.

## INTRODUCTION

The relative strengths of the coordinate linkage between pyridine and the metals in pyridine complex salts have been studied by several investigators (1,3,4,5,6, and 8). Studies of the effect of different atoms and groups on these coordinate bonds have been attempted by two methods; the determination of the dissociation pressures of the complexes, and the determination of volume changes during the formation of the complexes. The change in volume during the formation of the complex gives an insight into the strength of the chemical bonding of the atoms in the complex salts. It has been shown that there is a relationship between the dissociation pressures and the volume changes during the formation of the complexes. There is a fair agreement that the complex that has the highest dissociation pressure and the least decrease in volume must have the weakest bond. The investigation reported in this paper deals with the actual measurement of the heat of formation of these coordinate linkages by an indirect means. The heats of formation so determined should produce further evidence concerning the strength of the coordinate bonds.

The method used involved measuring the heat of reaction of pyridine in a 2N hydrochloric acid solution. The heat of solution of the nickel salt in 2N hydrochloric acid solution was also determined. Finally the heat of reaction of the complex in the same strength acid solution was measured. When the complex is introduced into the acid, the pyridine-salt coordinate bonds are broken. Thus the heat of reaction of the complex will differ from heats of reaction of the pyridine and simple salt by an amount equal to the heat of formation of the complex. We can assume that the following formula will hold and give us the amount of energy necessary to break the pyridine coordinate linkage:

$$L_S + L_p - L_c = \Delta H$$

$L_S$  = heat of reaction of the salt.

$L_p$  = heat of reaction of pyridine.

$L_c$  = heat of reaction of the complex.

$\Delta H$  = heat of formation of the complex  
from pyridine and the salt.

Only the stable hexapyridinated nickel cyanates and tetrapyridinated thiocyanates have been investigated in this work. Hence, the total heat of formation of the bonds is reported. There could be a further study and a direct comparison of the effects of atoms and groups if the complexes had the same number of pyridine molecules. The

nickel cyanates with two, four and six pyridines have been reported (2). The nickel thiocyanates with two, four and seven pyridines have also been reported (1).

The heats were determined in a calorimeter similar to the one described by Lamb (7) in his determination of heats of solutions.

## EXPERIMENTAL

## Preparation of the Compounds

Hexapyridinated nickel cyanate was prepared by dissolving 0.5 mole of nickel chloride and one mole of potassium cyanate in separate vessels. These solutions were poured together in a large separatory funnel and a slight excess of the theoretical amount of pyridine was added. A voluminous light blue precipitate was formed. The precipitate was extracted in chloroform and the chloroform solution allowed to evaporate to dryness. The resulting complex was crushed and screened through a 60 mesh screen and stored in a dessicator in a pyridine atmosphere. The complex is a light blue color.

The tetrapyridinated nickel thiocyanate was prepared in a similar way using 0.5 mole of nickel chloride and one mole of potassium thiocyanate. After crushing and screening, the complex was stored in a dry dessicator without an open vessel of pyridine, since the tetrapyridinated thiocyanate of nickel takes up three more molecules of pyridine changing to the lavender color of the hepta-pyridinated nickel thiocyanate. The tetrapyridine thiocyanate is a light blue color.

An attempt was made to prepare the simple nickel cyanate and nickel thiocyanate by heating the pyridinated salts in a vacuum oven or in open atmosphere. However, in

the preparation of the large quantities of salt as were needed in this work there was a certain amount of decomposition of the salts before all the pyridine had been removed. The nickel cyanate was, however, prepared by a fast, hot heating to drive off the pyridine quickly. The salt produced was a dry almost non-wetting powder. The metal analysis checked out very well for the nickel cyanate. Other methods were investigated and the following procedures were finally used to prepare the salts.

In the preparation of nickel cyanate equivalent amounts of nickel nitrate and potassium cyanate, or a slight excess of nickel nitrate, were dissolved in a minimum amount of water. The solutions must be kept cold, since the cyanate tends to decompose in a water solution slightly above room temperature. These solutions were poured together with thorough stirring. No precipitate formed until a small amount of alcohol was added. The precipitate was filtered and washed with an alcohol-water solution, then with acetone, and finally with ether. The salt is a pale green color after drying in a vacuum oven at 40°-50°C. The excess of nickel nitrate was used to insure that no potassium cyanate be left, since its solubility is low in the alcohol-water solution. The nickel nitrate and potassium nitrate are quite soluble and were washed out, leaving only the nickel cyanate as the precipitate.

The nickel thiocyanate was prepared by dissolving equivalent amounts of barium thiocyanate and nickelous sulfate in separate vessels. The solutions were poured together and digested in boiling solution for about an hour to precipitate the barium sulfate. An excess of nickel sulfate is advisable to insure complete barium precipitation. The solution with the barium sulfate precipitate was allowed to stand and settle over night. It was decanted and filtered. The filtrate was evaporated to almost dryness with the aid of heat. A dark brown sludge formed which was filtered and washed with alcohol-water mixture and then dried in a vacuum oven at about 90°-100°C. The salt, when dried and crushed, was a yellowish brown color.

#### Analyses of the Compounds

The anhydrous salts and the complex salts were analyzed on the basis of the percent nickel content in the compound. The nickel was determined by the cyanide-silver titration method, using potassium iodide as an indicator.

The cyanide solution was standardized against a pure preparation of nickel dimethylglyoxime. Table I gives the results of these analyses. The results are not in exact accord with the calculated amount of nickel in the compound, but the results are good when one considers the instability

TABLE I

METAL ANALYSES,  
ANHYDROUS SALTS

	Found		Calculated
$\text{Ni}(\text{CNO})_2$	41.7%	41.8%	41.8%
$\text{Ni}(\text{CNS})_2$	33.3	33.5	33.1

METAL ANALYSES,  
PYRIDINE COMPLEX SALTS

	Found		Calculated
$\text{Ni}(\text{CNO})_2 \cdot 7 \text{ Pyr}$			8.4%
$\text{Ni}(\text{CNO})_2 \cdot 6 \text{ Pyr}$	9.69%	9.62%	9.52
$\text{Ni}(\text{CNO})_2 \cdot 5 \text{ Pyr}$			10.8
$\text{Ni}(\text{CNS})_2 \cdot 3 \text{ Pyr}$			10.3
$\text{Ni}(\text{CNS})_2 \cdot 4 \text{ Pyr}$	11.97	12.02	11.97
$\text{Ni}(\text{CNS})_2 \cdot 5 \text{ Pyr}$			14.3

of the complexes and the salts. The percent nickel is given for one more and one less pyridine so that the results show conclusively that the complex obtained is quite pure.

### The Calorimeter

The calorimeter consisted essentially of a Dewar flask seated in a thermostated bath with a stirrer, differential thermometer, heating element and sample ejector, in the wooden lid of the Dewar. Figure 1 is a detailed cutaway drawing of the calorimeter.

The Dewar flask is pyrex of about two liter capacity. It came equipped with a solid metal stand. Sections were cut out of the stand to insure complete circulation of water all around the flask. The flask was placed in a thermostated water bath. The bath was insulated with a cotton batting covered by a parchment type paper to keep it dry. The flask was centered in the bath with the aid of plastic prongs on three sides and a wooden wedge on the fourth side to insure a firm position for the flask. The bath was stirred by a variable speed motor and stirrer. The stirring paddle was housed in a separate metal tube soldered to the side of the bath. This arrangement forced the water down the tube, out at the bottom, and the intake of the tube took water from the top of the bath solution.

## THE CALORIMETER

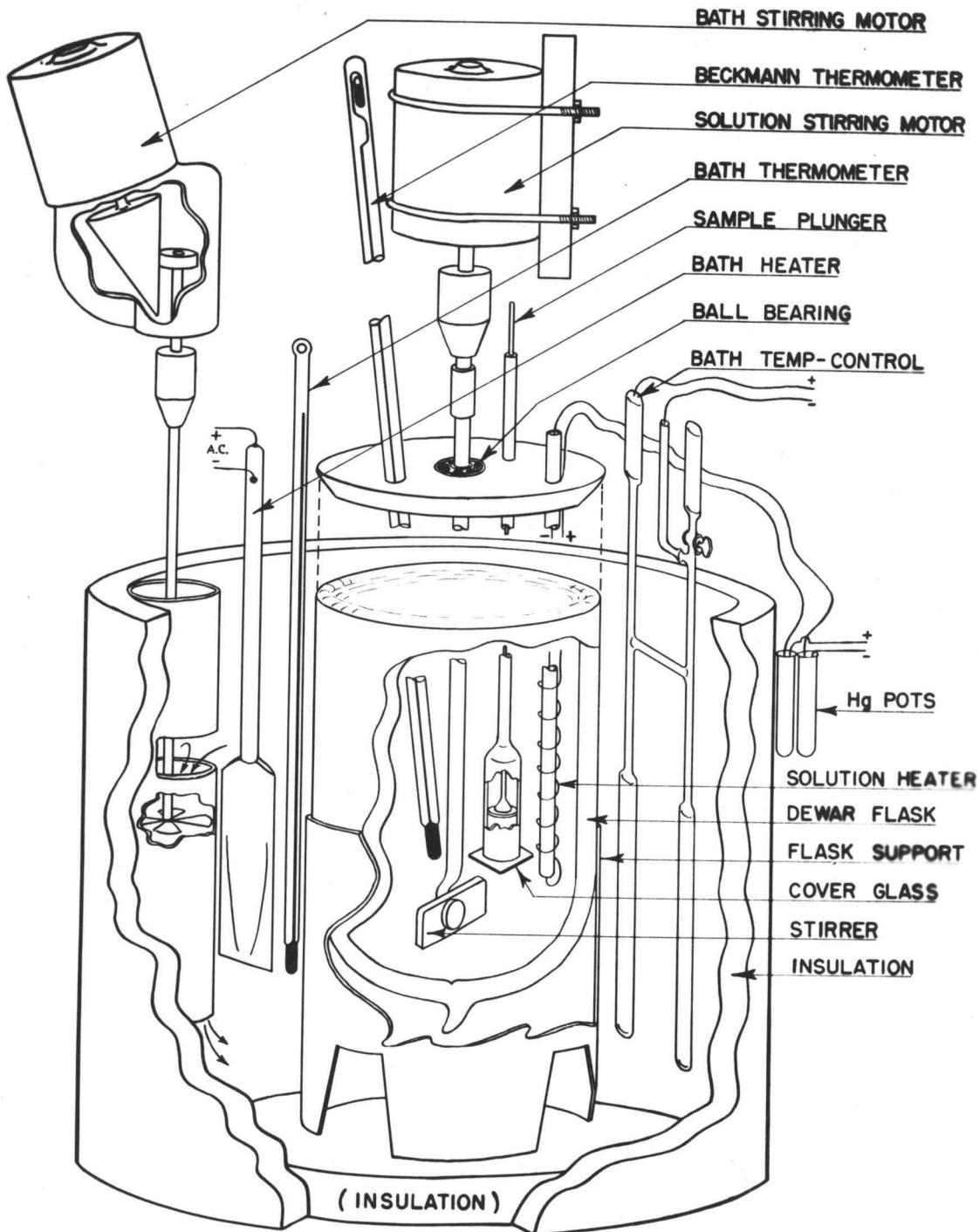


FIGURE 1

The bath was heated by 250 watt Cenco knife heater controlled through a variable resistor by a Cenco-Gilson electronic relay, which was in turn controlled by a mercury type thermoregulator. The thermoregulator consisted of an H tube about nine inches in height made from 16 mm tubing. Electrical contact for one side of the circuit was made by a permanent wire-mercury contact and the other side in a capillary tube for increased sensitivity. The bath was operated at  $25^{\circ}\text{C}$ . which was controlled to  $0.002^{\circ}\text{C}$ . The bath temperature was checked by a thermometer standardized by the National Bureau of Standards.

The Dewar flask was fitted with a wooden lid equipped with a rubber gasket. The whole lid was coated several times with Tygon Primer TP107B. The lid was held secure by placing a metal piece over the top of it. The metal piece was pulled down tight on the lid by using two hooks that fastened to the metal base of the Dewar flask. The hooks were threaded on the end that passed through the metal piece so that by tightening up with wing nuts, the lid was pressed firmly into the mouth of the Dewar flask.

The lid had four holes drilled to hold the equipment that was necessary for the operation of the calorimeter. The center hole was fitted with a stirrer. The stirrer consisted of a 10 mm glass rod hooked on the end, over which was fitted a glass paddle about two inches long and one half inch wide. The rod was cemented to the inside of

a metal sleeve and the sleeve pressed into a ball bearing. The outside of the bearing was pressed into the hole in the lid to give rigid structure. The stirrer was driven by a selsyn generator stator of low torque at slow speeds, but which could be set at various constant speeds. Due to the low torque of the motor the low friction bearing was needed. Also, the ball bearing aided in keeping the heat of stirring to a minimum. The selsyn generator was attached by two U bolts to a wooden bracket made of three quarter inch plywood. The bracket was hinged to the wall. This was necessary because of the weight of the stirring motor and also allowed easy access to the bath, since the motor could be swung back out of the way. It could also be centered easily over the stirrer by the use of a small turn buckle attached to the end of the bracket and the wall. This gave a three bar structure which was rigid. Rigidity was needed to cut down vibration and hence heat of stirring.

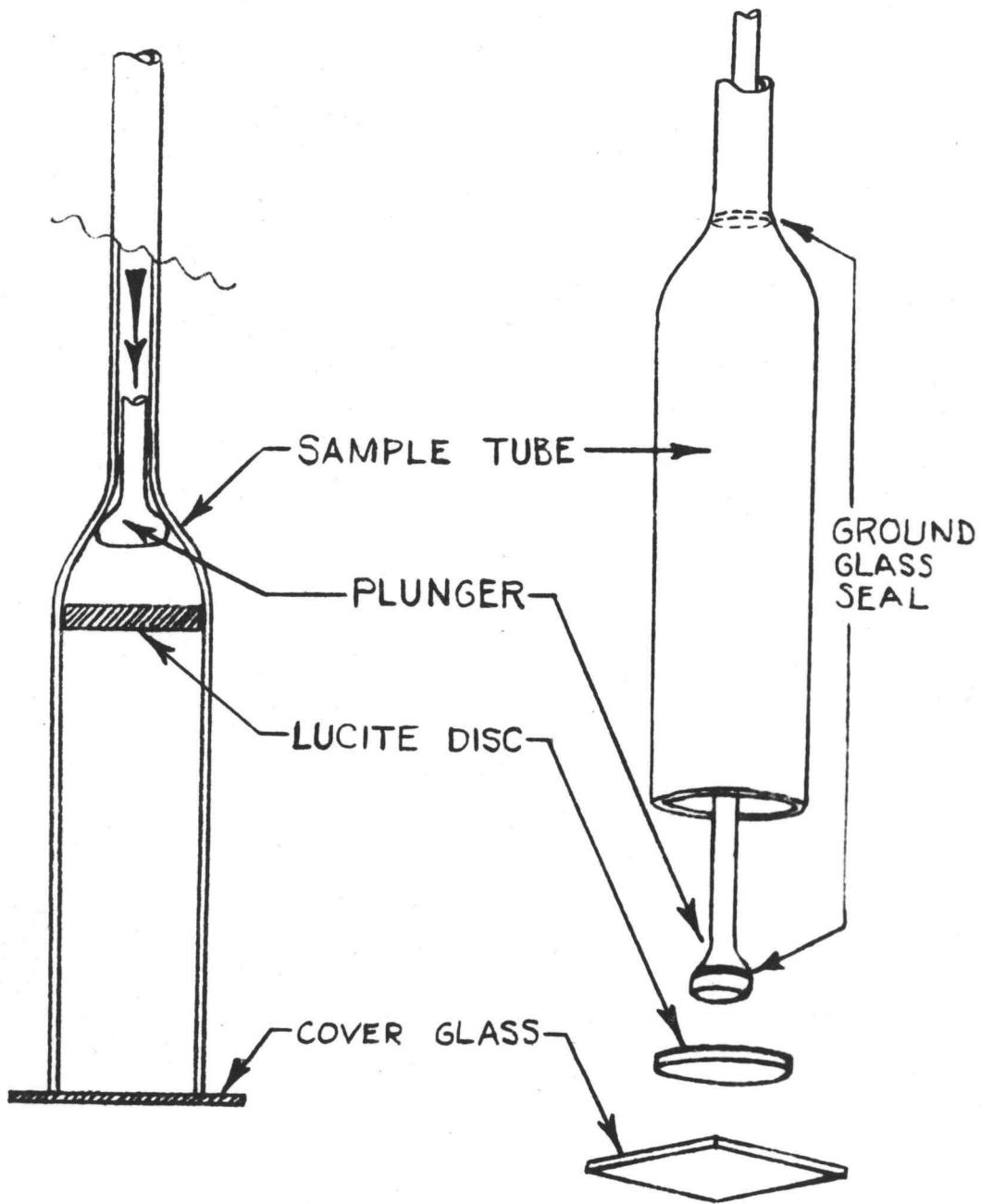
The selsyn generator takes a two phase 110V-60 cycle circuit to operate. Since the laboratory was equipped with only 110 volt, 60 cycle, single phase line, the power supply for the stator was made from a variable transformer and a 60 micro farad condenser. Two ends of the Y wound field were connected directly to the variable transformer. The third end was connected through the 60 micro farad condenser to one side of the line. This gave a typical

induction-capacitor arrangement. The speed of the stirrer was controlled by the variable transformer.

The second hole in the lid was fitted with a Beckmann type differential thermometer held in place by a rubber stopper. The thermometer was read with the aid of a small tubular reading lens attached to the stem of the thermometer.

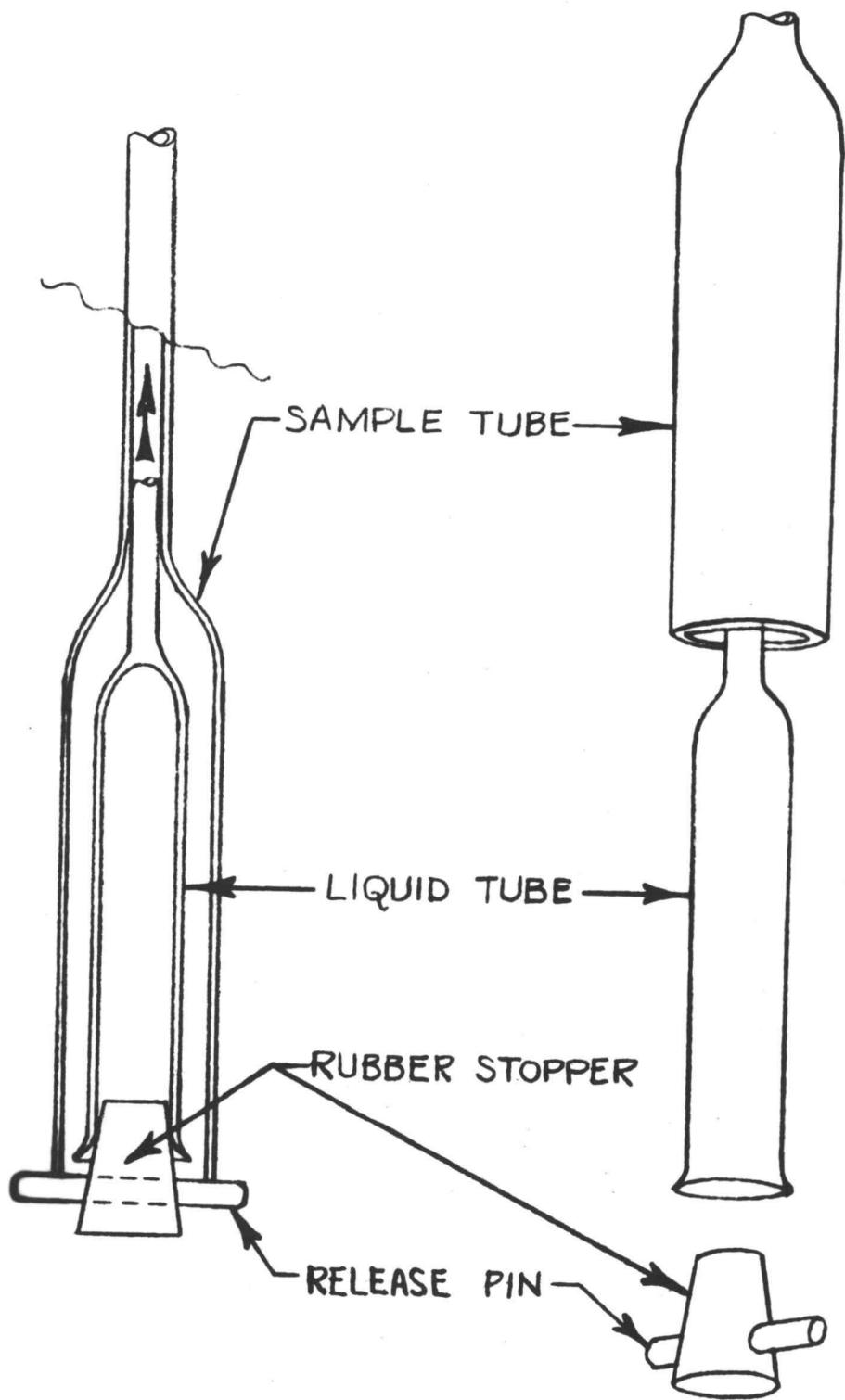
In the third hole in the lid of the flask was a solution heater made by winding three feet of #32 advance wire, about 30 ohms, around a glass tube. Copper leads were silver soldered to the ends of the heater wire. One wire going up the center of the glass tube and the other continuing up the outside of the glass tube from the top of the heater winding. The leads passed into two mercury pots on the side of the bath. The mercury pots were necessary so as to reproduce the same contact with the heating circuit to be described later. The whole of the heating element was given more than a dozen coats of Tygon Primer.

The final piece of equipment in the lid of the flask was the sample ejector. Figures 2 and 2A give a clear picture of the sample ejector. It consisted of a 22 mm glass tube about 7 cm long attached to a piece of 8 mm tubing, which protruded up through the lid. This outer jacket was held in place by a rubber stopper. The tube was equipped with a plunger which was ground into the conical



SAMPLE EJECTOR  
(SOLID SAMPLE)

FIGURE 2



SAMPLE EJECTOR  
(LIQUID SAMPLE)

FIGURE 2A

end of the sample holder in order to reduce evaporation of pyridine. Directly below the plunger and on top of the sample a lucite disc was placed so that all the sample would be forced out of the tube with a minimum amount adhering to the side walls. The bottom of the sample holder was ground flat so that a microscope cover glass could be cemented to it with Duco household cement. After allowing the cement to dry, the end was dipped in Tygon Primer for a waterproof seal. The plunger was held in place in the up position by a piece of rubber tubing.

When liquid samples were run, a sample tube as shown in Figure 2A was used. This consisted of the sample ejector into which was inserted a glass rod with the bottom of a small test tube sealed to the end. The test tube opening was closed with a rubber stopper. A short piece of glass rod passed through the sides of the stopper. To introduce the sample, the sample tube was raised by means of the glass rod up the center of the ejector. This movement pulled the stopper from the end of the liquid sample tube when the rod through the stopper caught on the side of the sample ejector.

An electrical source of energy was used in determining the heat capacity of the calorimeter. A complete wiring diagram can be found in Figure 3. The source was provided by four Edison batteries which consisted of five

WIRING DIAGRAM  
OF  
HEATER CIRCUIT

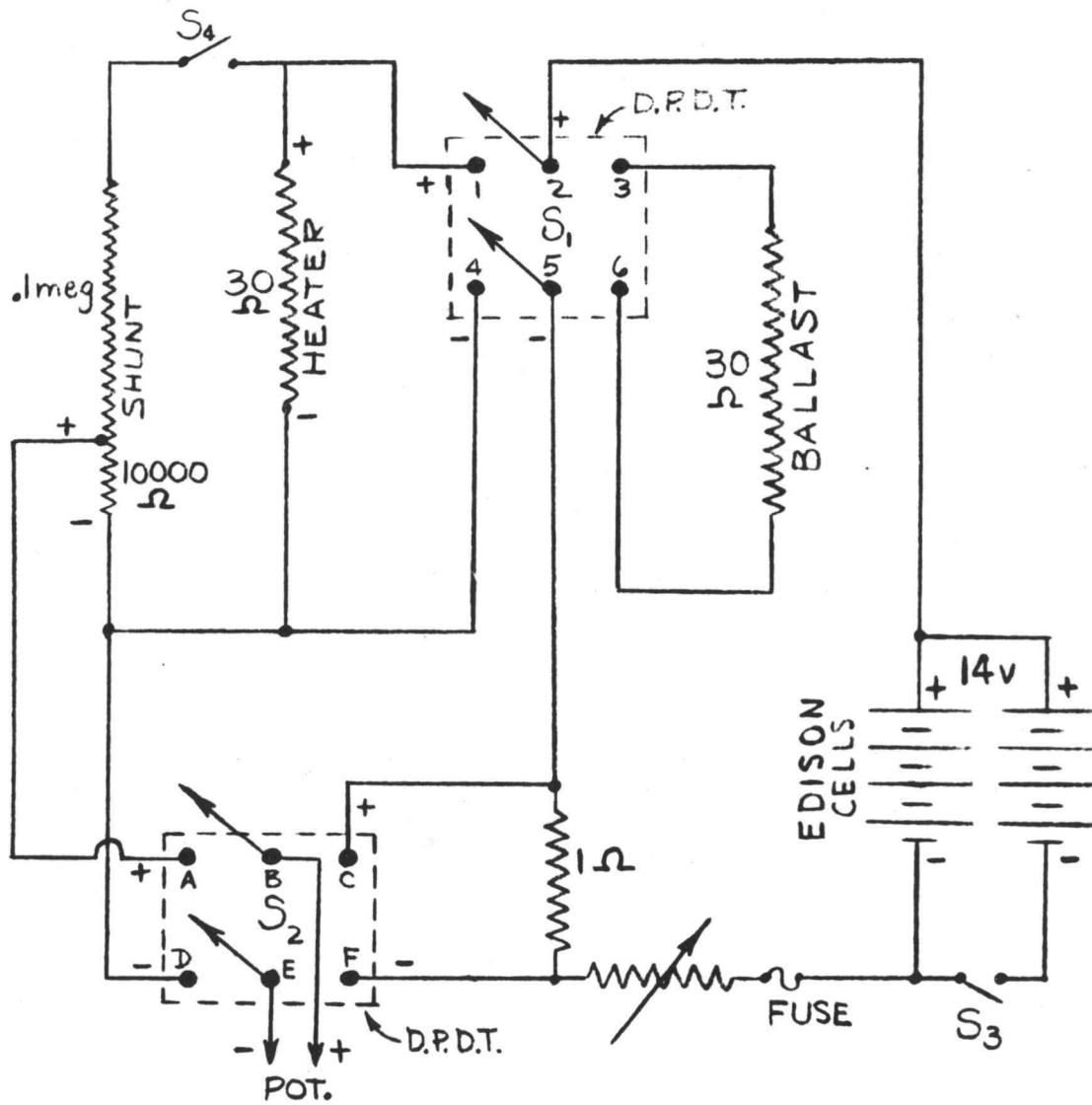


FIGURE 3

cells to a battery. Two batteries were connected in series giving emf of 14 volts. Two of these sets were connected in parallel to give added stability to the voltage on the power source. A switch  $S_3$  was placed between the two sets of series connected batteries so that when all circuits were open the batteries would not discharge into one another. The positive terminal of the power source was led to the center pole of a double pole double throw switch,  $S_1$ . The negative side of the batteries was wired to the other center pole of switch  $S_1$  through variable resistance and a standardized one ohm resistor. The fuse was used to protect the one ohm resistor in case of a short in the heater circuit. The variable resistor was wired in to give flexibility to the voltage on the power source. The one ohm resistor was made in the laboratory and standardized against a National Bureau of Standards, 0.9997 ohm, resistor by use of a potentiometer circuit to a value of 1.000 ohms. The one ohm resistor was made of #18 nichrome wire. One side of switch  $S_1$  is connected across a ballast equal in resistance to the calorimeter heater. Switch  $S_1$  is thrown across this ballast for about an hour before each heat capacity determination to allow the batteries to come to a constant voltage. The calorimeter heater is wired on Switch  $S_1$ . The heater was made of #32 advance wire and has a resistance of about 30 ohms.

All electrical measurements were made with a Leeds and Northrup student potentiometer that could measure a potential of only 1.6 volts. Since the potential drop across heater was on the order of 10 to 14 volts, a shunt was needed to measure the heater voltage. The heater was shunted with a 100,000 ohm resistor and a 10,000 ohm resistor connected in series. These were accurate to only seven per cent. The shunt was therefore calibrated on a Wheatstone bridge against standard resistors. The 100,000 ohm resistor has a value of 107,350 ohms and the 10,000 ohm resistor has a value of 10,556 ohms. The heater voltage was therefore measured by switching the potentiometer across the small shunt resistor and measuring only 9.8332 per cent of the total potential drop across the heater. The center poles of double pole double throw switch  $S_2$  were connected to the potentiometer. The two sides of switch  $S_2$  were wired across the small shunt resistor and also across the one ohm resistor. This enables the operator to measure potentials across either resistor at will.

#### Determination of Heat Capacity

In order to investigate energy changes in chemical reactions, the heat capacity of the calorimeter must be known. The most accurate and most convenient method is accomplished by passing into the calorimeter a known

quantity of electrical energy. The current is passed through a resistance wire changing electrical energy into heat energy, which can be measured by a temperature rise read on a Beckmann differential thermometer. Then by knowing the energy put into the calorimeter and the temperature rise, one can determine the heat capacity in terms of calories per degree.

The electrical energy can be measured by a silver or copper coulometer. However, a more convenient method is to measure the voltage and current flowing for a definite period of time and converting these values to heat units. The formula used in this conversion was:

$$H = \frac{EIt}{4.1833}$$

H = energy in calories.

E = voltage across the heater.

I = current passing through the heater.

t = time of heating in seconds.

4.1833 = conversion factor in changing watt seconds or joules to calories.

In determining the heat capacity the following procedure was used. The bath temperature was kept at  $25^{\circ}\text{C}$ . An attempt was made to keep the room temperature at about  $25^{\circ}\text{C}$ . also. The Dewar flask was filled with 1500 ml of 2N hydrochloric acid and the lid fastened in place. The stirring motor was attached to the calorimeter stirrer and set

at a low speed to keep the heat of stirring to a minimum yet fast enough to insure thorough mixing.

The wires from the calorimeter solution heater were placed into the mercury junction pot. The current was then sent through the heater and the solution heated to the temperature of the bath. At this time the switch  $S_1$  was thrown across the ballast for about an hour to allow the batteries to come to a constant voltage. This time interval also allowed the bath and calorimeter to come to equilibrium. When no change in the solution temperature could be noted, a stop watch was started and Beckmann temperature readings taken for ten minutes to determine the heating or cooling effects due to evaporation and heat of stirring. At the end of ten minutes the switch  $S_1$  was thrown from the ballast to the heater and a temperature reading was taken immediately. The thermometer was read at intervals of five minutes for 20 minutes and then the heater turned off. Readings were then taken for five minutes at intervals of one minute and then cooling readings taken for an additional 25 minutes at five minute intervals.

During the time the heater was on several electrical measurements were taken to determine the voltage and current utilized.

These readings were made by measuring potential drops across the shunt and one ohm resistor with the aid

of the potentiometer. By throwing switch  $S_2$  across the one ohm resistor, the potential drop could be measured. Knowing the voltage and resistance and utilizing Ohms Law, the current could be measured. By throwing switch  $S_2$  across the small resistor in the heater shunt, a known fraction of the potential across the heater could be measured. When one knows the potential and current in a heater wire and the length of time applied, the heat energy liberated can be calculated. By dividing the calories liberated by the temperature rise in degrees the heat capacity in calories per degree can be found. Temperature rise as read must be corrected for heat losses or heat of stirring. This is done by plotting on a large scale time versus temperature and drawing curves. Extrapolate the curves before and after each heating curve to the middle of the heating time and measure the distance between the lines at this time. This gives a corrected temperature rise. An example of the curves drawn can be found in Figure 4. Heat capacity values can be found in Table II.

#### Heat of Formation

In determining the heat of reaction of pyridine in 2N hydrochloric acid, a sample tube, as previously described and also drawn in Figure 2A, was used. Weight of

TABLE II

## HEAT CAPACITY OF THE CALORIMETER

(Soln. is 1500 ml. of 2N HCl.)

Run	Temperature rise (corrected)	One ohm amps	Shunt voltage	Heat capacity cal/degree
1	1.014	0.4084	1.1925	1402
2	1.005	.4067	1.1883	1404
3	1.014	.4087	1.1932	1404
Average....				1403

All runs starting at 25°C and heating time  
of 1200 seconds.

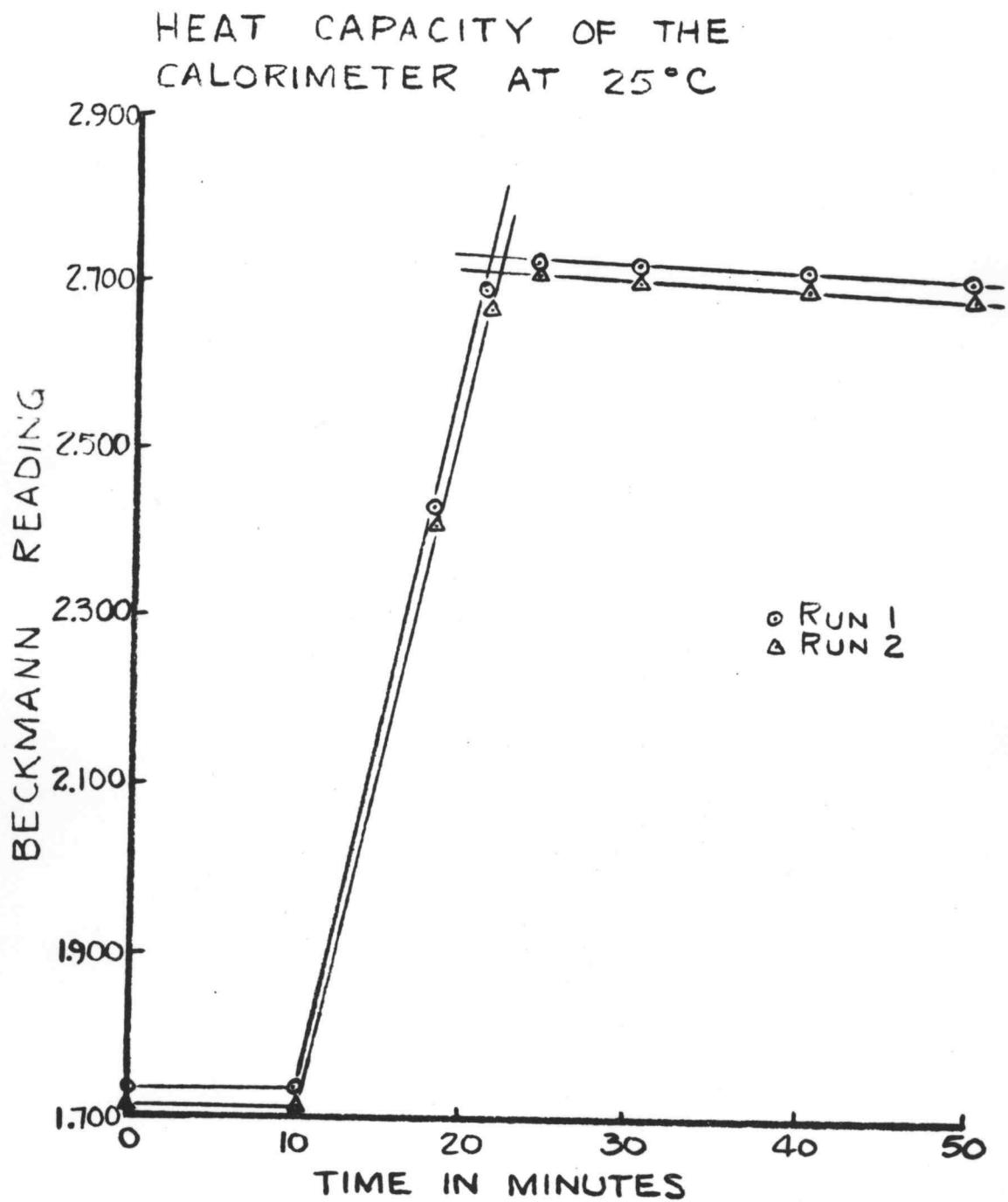


FIGURE 4

the tube and stopper was taken. Then the pyridine was poured into the tube, the tube stoppered and weighed again to get the weight of sample used. The sample tube was inserted into the sample ejector and then the ejector was fastened in the calorimeter lid. The calorimeter with 1500 ml of 2N hydrochloric acid was raised to the bath temperature by the aid of the same heater used in the heat capacity determination. The system was allowed to come to equilibrium. Readings were taken for ten or fifteen minutes before the sample was emptied into the solution, then they were taken at 30 second intervals until the temperature stopped rising. Readings were then taken again at five minute intervals to get the slope of the correction curve. A similar sample run on nickel cyanate can be seen in Table IV. Values obtained for the heat of reaction of pyridine per mole are to be found in Table III and curves drawn are to be found in Figure 5.

When the solid salt and complex samples were run, the sample ejector was used with the plunger, lucite disc and cover glass arrangement. This is shown in Figure 2. The solid sample was weighed in a weighing bottle and introduced into the sample tube with the aid of a metal funnel. The sample bottle was reweighed and by difference the weight of sample could be obtained. The bottom of the sample tube was covered with a cover glass, glued in place,

TABLE III

HEAT OF REACTION OF PYRIDINE  
IN 2N HCl AT 25° C.

---

Run	Weight of Sample in gms	Temperature rise (corrected)	Heat of reaction cal/mole ( $\Delta H$ )
1	3.2152	0.228	- 7870
2	3.2284	.229	- 7870
3	2.9966	.212	- 7850
4	2.8693	.204	- 7890
5	2.9258	.207	- 7850
6	2.9166	.206	- 7840
Average.....			7860

---

TABLE IV

## SAMPLE RUN

Compound	$\text{Ni}(\text{CNO})_2$
Weight	10.8387 gms.
Room temperature	24.5°
Bath temperature	25°

<u>Time</u>	<u>Beckmann reading</u>
0	1.690
5	1.692
10	1.694
11	2.245
12	2.970
13	3.440
14	3.458
15	3.458
16	3.455
21	3.445
26	3.437

Temperature rise	1.764
correction	.005
	1.769

## Sample Calculation

$$\frac{1403 \times 142.73 \times 1.769}{11.0451} = 32080 \text{ cal/mole}$$

HEAT OF REACTION OF  
PYRIDINE in 2N HCl at 25°C

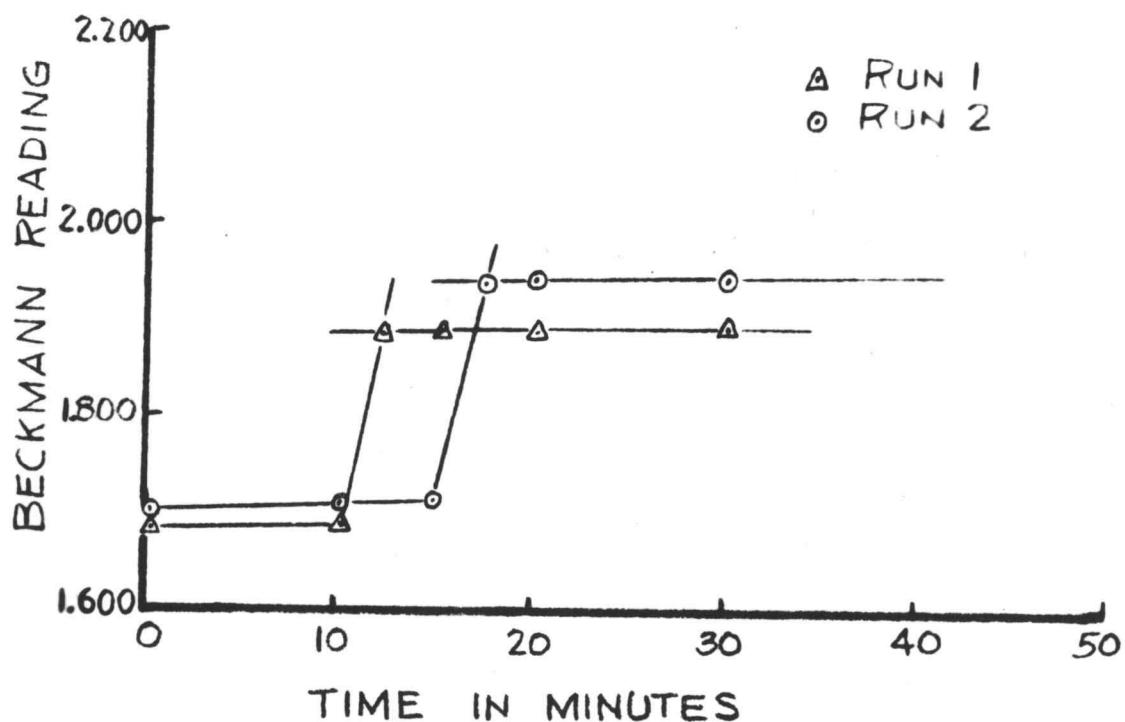


FIGURE 5

and then dipped in the Tygon Primer to waterproof the ejector. The tube was set in the lid and runs made in the same manner that the pyridine samples were run. Values obtained will be found in Tables V through VIII, and curves drawn to correct the temperature will be found in Figures 6 through 9.

Table IX contains the values for the heat of formation of the nickel cyanate and thiocyanate complexes from the salt and pyridine.

TABLE V

HEAT OF REACTION OF HEXAPYRIDINATED  
NICKEL CYANATE IN 2N HCl AT 25°C.

---

Run	Weight of Sample in gms.	Temperature rise (corrected)	Heat of reaction cal/mole ( $\Delta H$ )
1	4.4685	0.317	-61,430
2	3.8838	.275	-60,900
3	6.8522	.479	-60,500
4	6.1219	.429	-60,650
5	3.1029	.218	-60,720
Average.....			-60,850

---

TABLE VI

HEAT OF REACTION OF TETRAPYRIDINATED  
NICKEL THIOCYANATE IN 2N HCl AT 25°C.

Run	Weight of Sample in gms.	Temperature rise (corrected)	Heat of reaction cal/mole ( $\Delta H$ )
1	8.5908	0.097	7780
2	10.0131	.110	7990
3	10.7474	.120	7700
4	8.5039	.101	8180
5	8.8557	.103	8020
6	9.0146	.104	7950
Average.....			7940

TABLE VII

HEAT OF REACTION OF NICKEL CYANATE  
IN 2N HCl AT 25°C.

---

Run	Weight of Sample in gms.	Temperature rise (corrected)	Heat of reaction cal/mole ( $\Delta H$ )
1	11.0451	1.769	-32,080
2	10.8385	1.735	-32,060
Average.....			-32,070

---

TABLE VIII

HEAT OF REACTION OF NICKEL THIOCYANATE  
IN 2N HCl AT 25° C.

---

Run	Weight of Sample in gms.	Temperature rise (corrected)	Heat of reaction cal/mole ( $\Delta H$ )
1	10.0354	0.046	1,120
2	9.7661	.046	1,150
3	8.0232	.037	1,130
Average.....			1,135

---

TABLE IX

HEAT OF FORMATION OF THE PYRIDINE COMPLEXES  
FROM THE SALT AND PYRIDINE

---

Complex	Heat of formation cal/mole ( $\Delta H$ )
$\text{Ni}(\text{CNO})_2 \cdot 6 \text{ Pyr}$	-18,400
$\text{Ni}(\text{CNS})_2 \cdot 4 \text{ Pyr}$	-38,300

---

HEAT OF REACTION OF  
 $\text{Ni}(\text{CNO})_2 \cdot 6\text{Py}$  in 2N HCl @ 25°C

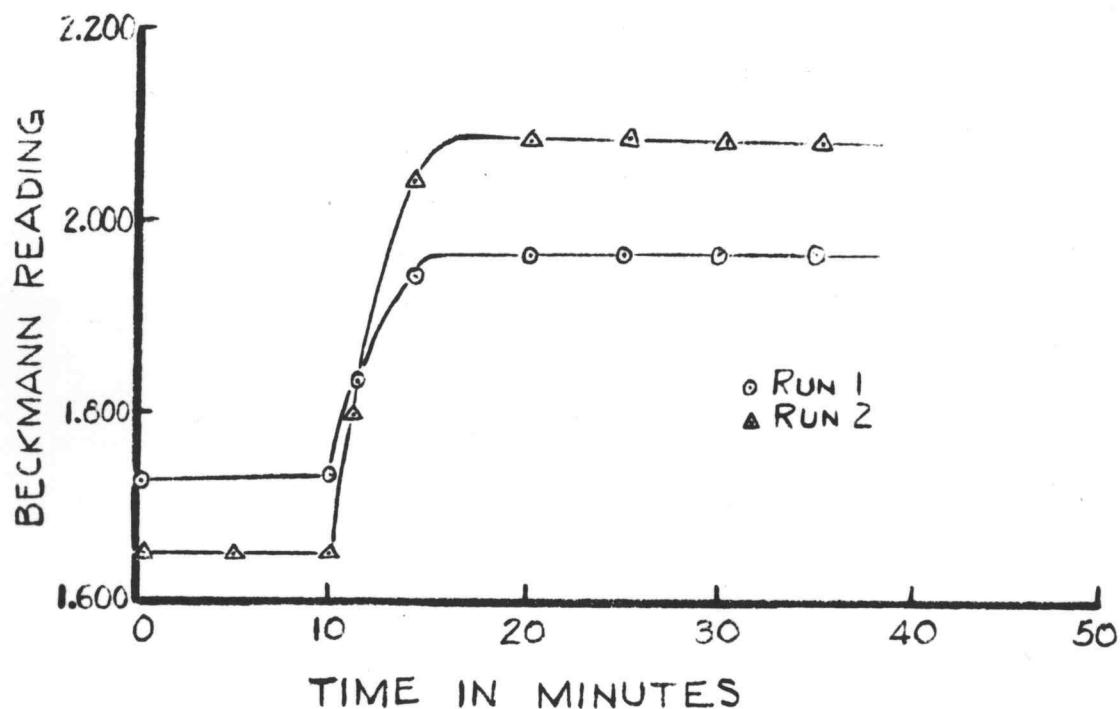


FIGURE 6

HEAT OF REACTION OF  
 $\text{Ni}(\text{CNS})_2 \cdot 4\text{R}_2$  in 2N HCl @ 25°C

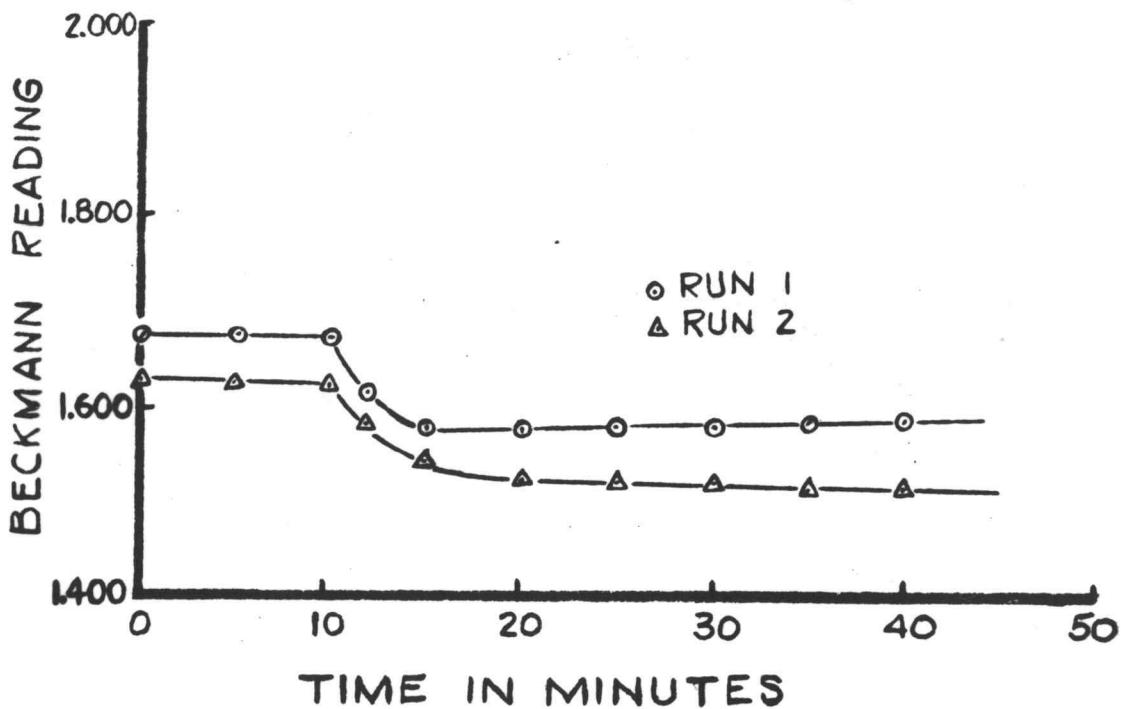


FIGURE 7

HEAT OF REACTION OF  
 $\text{Ni}(\text{CNO})_2$  in 2N HCl at 25°C

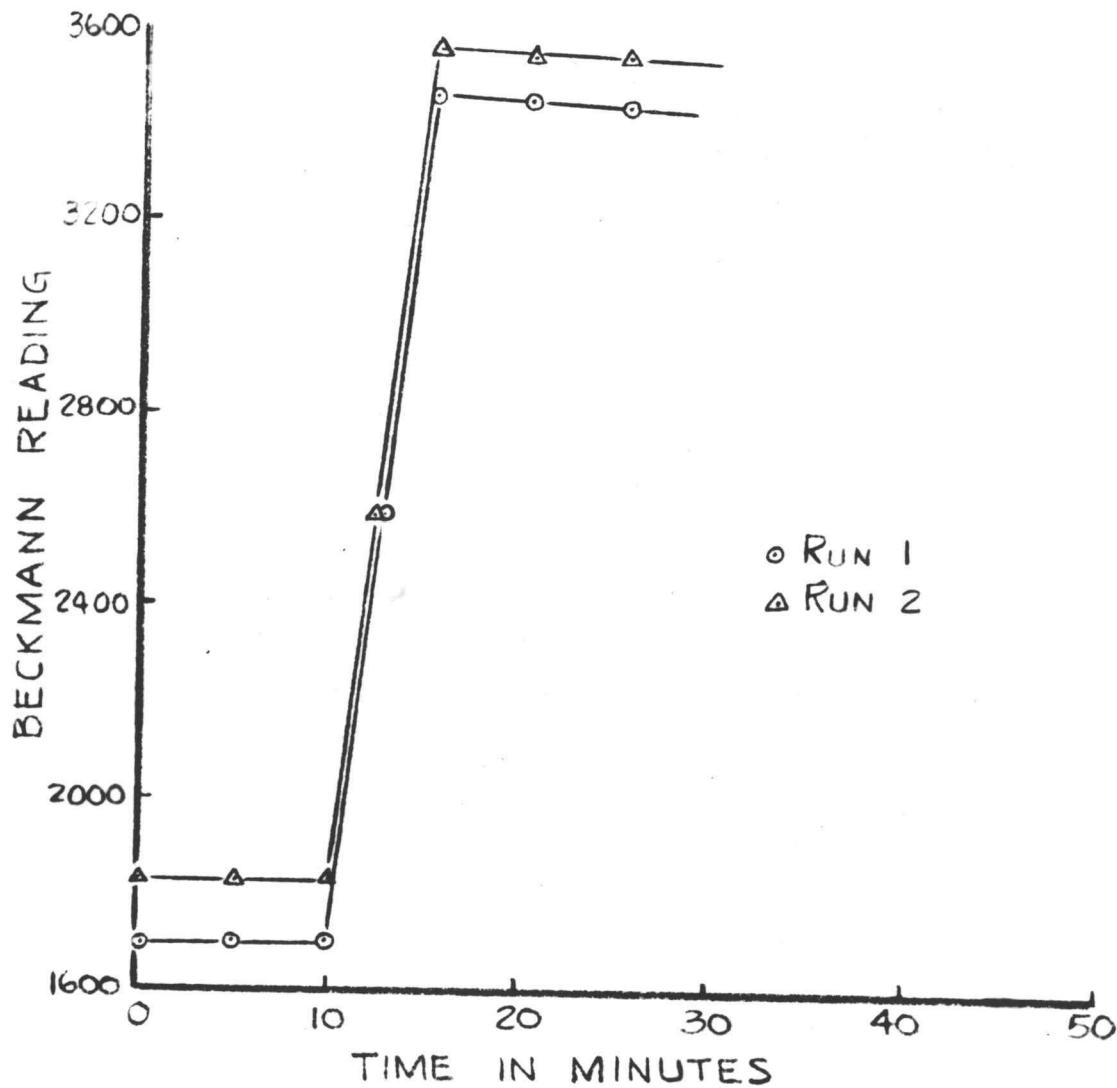


FIGURE 8

HEAT OF REACTION OF  
 $\text{Ni}(\text{CNS})_2$  in 2N HCl at 25°C

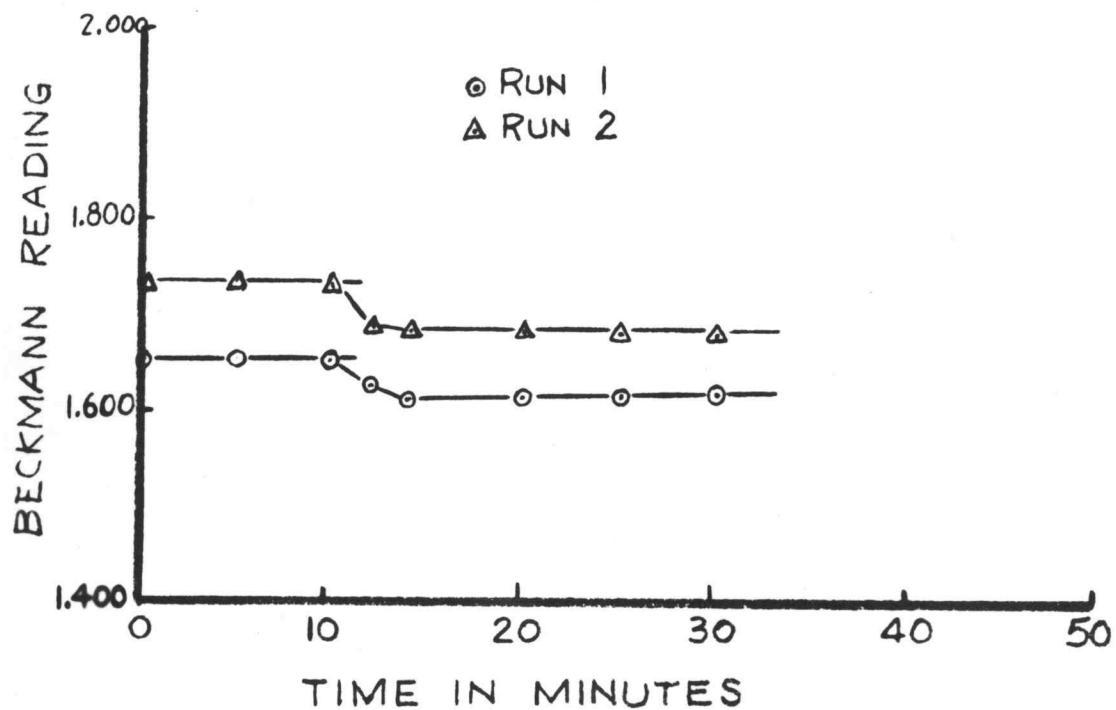


FIGURE 9

## DISCUSSION

The results of this investigation, Table IX, show that the heat of formation of the tetrapyridinated nickel thiocyanate is much greater than the heat of formation of the hexapyridinated nickel cyanate. A comparison cannot be drawn between these two compounds because of the different number of pyridine molecules coordinated in the complex. A comparison could be obtained by determining the heats of formation of the di and tetra pyridinated compounds of nickel cyanate and thiocyanate.

Another good comparison can be made between metals of the same anion and number of pyridines in the compound. There is work being done on the cobalt complexes on this same calorimeter.

The Beckmann thermometer was definitely the limiting factor as far as the accuracy of the work was concerned. One thousandth of a degree could make the results vary by as much as 300 calories in some cases, and as small as 25 calories in others, depending upon the molecular weight of the compound and weight of sample taken. For this reason the heat of formation values were rounded off to the nearest hundred calories.

If further work is to be done on this calorimeter another means of measuring the temperature should be used to give more exact results. A resistance thermometer or thermistor would probably suffice.

## SUMMARY

A calorimeter was designed, constructed, and its heat capacity determined. The compounds; nickel cyanate, nickel thiocyanate, hexapyridinated nickel cyanate, and tetrapyridinated nickel thiocyanate were prepared and analyzed. The heats of reaction of pyridine and the compounds that were prepared were determined in 2N hydrochloric acid solution at 25°C.

From these values the heats of formation of the complexes were calculated. The heat of formation of hexapyridinated nickel cyanate from the salt and pyridine is 18,400 calories per mole of complex. The heat of formation of tetrapyridinated thiocyanate from the salt and pyridine is 38,300 calories per mole of complex.

## LITERATURE CITED

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