HEATS OF FORMATION OF
COBALT (II) AND NICKEL (II) DIPYRIDINE
SALTS OF FATTY ACIDS

by

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TABLE OF CONTENTS

LIST OF FIGURES

HEATS OF FORMATION OF
COBALT (II) AND NICKEL (II) DIPYRIDINE SALTS OF FATTY ACIDS

INTRODUCTION

The relative strength of metal-nitrogen coordinate bonds have been investigated by three different methods. These are the comparison of dissociation pressures of the complexes' volume changes during their formation and their heats of formation. Low dissociation pressures have been shown to indicate a relatively strong coordinate bond. A large volume shrinkage, and thus an increase in density, also indicate a strong coordinate bond. Recent work has been reported by Bush, Rogers, and Carle (1, 2, 6, 7) on the calorimetric determination of the heats of formation of nickel and cobalt cyanate and thiocyanate, the basis of comparison being that the stronger bond should have a higher heat of formation.

The dissociation pressures and volume changes of pyridine complexes of the cobalt (II) and nickel (II) salts of the fatty acids, acetate through valerate, were investigated by Davis and Logan. It was found that the complexes of the acid radicals of lower molecular weight had in general lower dissociation pressures and produced greater volume changes than those of higher molecular weight. This would suggest that the coordinate bond strength of the molecules of lower molecular weight is greater than for those in which the carbon chain is longer.

It was also shown that the volume changes and dissociation pressures followed the odd-even, saw tooth projection which is common with many properties of aliphatic acids.

The present work on the heats of formation of the complexes of the fatty acid series was undertaken to determine whether the heats of formation for the lower molecular weight complex salts are greater than for the higher members of the series and that the odd-even effect would carry over into this property.

Because it would be exceedingly difficult to form the pure complexes in a calorimeter, an indirect method was used to obtain the heats of formation of the complex salts. Since the complex salts are readily decomposed to form the amine hydrochloride and the simple salt in hydrochloric acid solutions, the calculation of the heats of formation becomes comparatively simple. If the heat of solution of the salt per mole, L_s, the heat of solution of the base per mole, L_a, and the heat of solution of the complex salt per mole, L_c, are known at $25^{\circ}C$ in 2 N HCl, then the heat of formation, H, is given by the relation:

$$H = L_s + 2 L_a - L_c.$$

The heats of solution are assumed to be identical with those at infinite dilution since the weight of sample used is small in comparison to the volume of acid in the calorimeter.

THE CALORIMETER

The calorimeter used was the same one that Bush (1) and Rogers (7) used for their determination of the heats of formation of pyridine complex salts of nickel (II) and cobalt (II) cyanates and thiocyanates. Their work gives a detailed description of the design and construction of the apparatus. The calorimeter consisted of a one-half gallon Dewar flask surrounded by a constant temperature bath. The bath was set at $25^{\circ}C$. The Dewar flask was arranged with a wooden lid which projected a stirrer, sample ejector, Beckmann thermometer, and heater. The heater was made out of #24 advance wire silver soldered at the ends to #12 copper wire so that the electrical resistance in the heating wire would be mostly in the advance wire portion which was immersed in the calorimeter. The wire was wrapped about a glass rod and then covered with tygon label glaze as a protective coating.

The calorimeter was standardized by passing a known amount of power through the heater and observing the increase in temperature. This power came from four recently recharged Edison batteries of seven volts each (Figure 1). By passing the power through a standardized one ohm resistor in series as shown in the diagram and observing the potential drop on a potentiometer across the standard
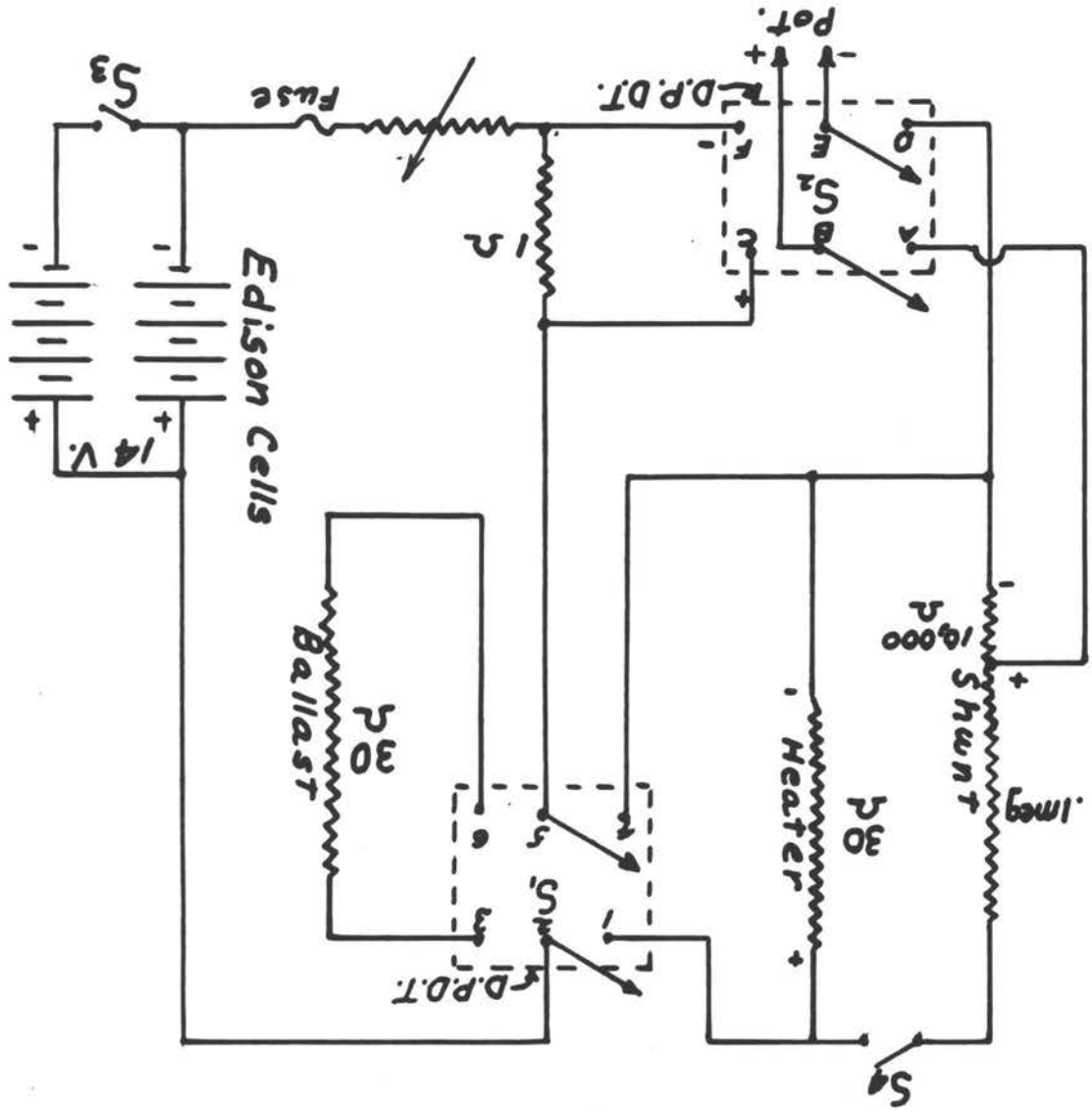
Figure I

Wiring Diagram
of
Heater Circuit

resistor as the power was passing into the heater, the
amount of current was obtained. Since the potentiometer
could read only 1.6 volts while the potential drop was on
the order of ten times that amount, the voltage was ob-
tained by shunting the heater with two large resistors
connected in series. The resistors were calibrated on a
Wheatstone bridge and found to have resistances of 111,400
ohms and 11,300 ohms. Because these resistances were
large only a very small portion of the power went through
the shunt, just enough to make the reading. The standard
one ohm resistor was found to have a resistance of 1.022
ohms.

DETERMINATION OF THE HEAT CAPACITY OF THE CALORIMETER

Because the calorimeter had to be reassembled, it
was necessary to redetermine its heat capacity. Fifteen
hundred ml. of 2 N HCl were added to the Dewar flask and
the contents adjusted to the same temperature as that of
the outside bath. While the calorimeter was coming to
equilibrium the batteries were placed on ballast for about
an hour so that they would come to constant voltage and
the potentiometer was calibrated against a Weston standard
cell. Time-temperature readings were then taken every
five minutes for about one-half hour to observe the heat
of stirring, heat of vaporization, and other heat effects.
An attempt was made to maintain the room at 25°C. The
circuit was then closed across the heater for a period of
twenty minutes, temperature readings being taken every
five minutes. During the heating the voltage drop across
the one ohm resistance and across the shunt were noticed
on the potentiometer. After the heating period was over
the temperature readings were taken every minute for a
period of five minutes to note the point of maximum
temperature and then every five minutes for a period of
one-half hour to observe the rate of cooling.

The time-temperature data were plotted in large
scale and the initial and final cooling curves were
extrapolated to the center of the heating curve. The

temperature difference between these two extrapolations was called the corrected temperature rise. A typical curve for 2 N HCl is given in figure II. The heat capacity was calculated by the formula:

$$\frac{H}{degree} = \frac{E \times I \times t}{4.1833 \times T}$$

where:

E = volts drop across heater
I = current in heater
t = time in seconds
T = corrected temperature change

E was calculated by taking the ratio of the sum of the two shunt resistances divided by the small resistance and multiplying it by the observed potential drop in the calorimeter. I was calculated by dividing the value of the standard resistance into the potential drop across the resistance. Since the shunt resistance was greater by a factor of over one hundred thousand, the loss through the shunt was negligible.

The values of the heat capacity are given on table I. As a rough check on the heat capacity of the calorimeter the heat capacity of 2 N HCl was found to be 1360 and the remainder of the calorimeter was assumed to have a heat capacity of 100 calories. This gives an approximate total of 1460 which is quite close to the observed value.
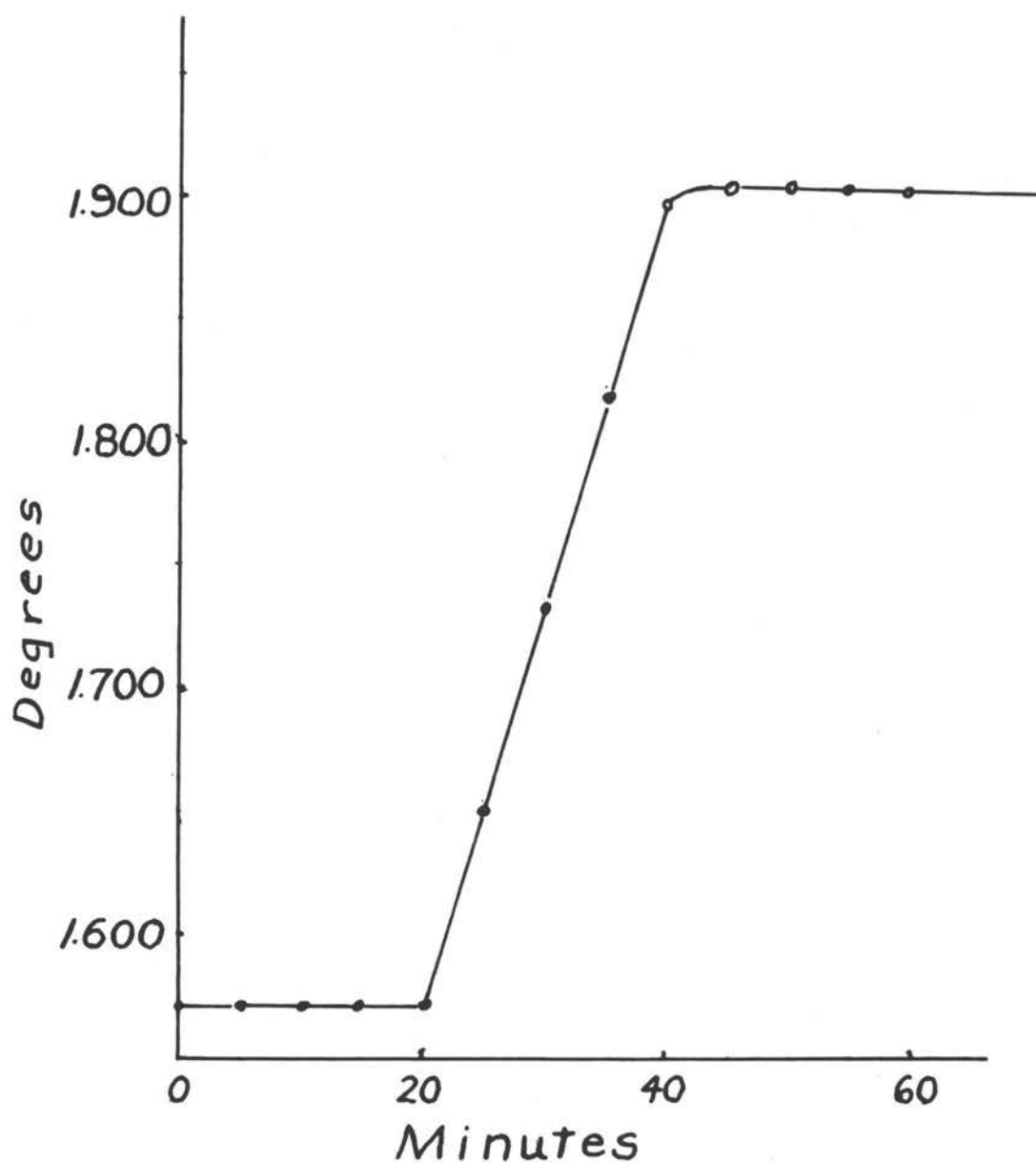
Heat Capacity of the Calorimeter Containing 2N HCl at 25°C

Figure II

TABLE I

HEAT CAPACITY OF THE CALORIMETER AT
25°C CONTAINING 1500 ML 2 N HCl

time, seconds	shunt voltage	volts 1 ohm	temp. rise (corrected)	heat capacity calories per degree
1200	.7752	.3440	.547	1525
1200	.7681	.3434	.540	1530
1200	.7520	.3352	.390	1525
			Average	1525

CORRECTION OF THE HEAT CAPACITIES OF EARLIER WORKERS

The heat capacity of the calorimeter calculated by
Bush and Rogers was obtained by the use of a value for E
which was calculated by dividing the small shunt resistance
into the larger one and multiplying this ratio by the
observed potential drop. The previous workers should have
divided the small shunt resistance into the sum of the
shunt resistances. This would give them results of 1535
calories instead of 1403 calories.

PREPARATION OF COMPOUNDS

The preparation and isolation of many pyridine complex salts has been accomplished by previous workers using a method based upon the high solubility of these compounds in chloroform. Logan (5) prepared dipyridimated cobalt and nickel complex salts of the fatty acids by dissolving the anhydrous simple salt in a mixture of chloroform and pyridine. The lower members of the series were found to be much less soluble than the higher members. The acetates and propionates required a considerable excess of pyridine to produce a reasonably concentrated solution of the complex in chloroform.

After the chloroform solution of the complex was filtered through a filter paper which had been previously wet with chloroform, it was allowed to evaporate to dryness in the hood and the resulting crystals dried between filter papers and placed in a dessicator. The compounds were allowed to come to equilibrium with pyridine in an open vessel in the dessicator.

THE NICKEL SALTS

The simple nickel salts were prepared in the manner suggested by Davis and Logan (4). The nickel carbonate was refluxed with the respective acid in nearly molecular amounts with a little water. Care must be taken during refluxing that the mixture not be overheated, as

there is a tendency for foaming to occur from the freshly
released carbon dioxide in the solution.

After refluxing the resulting mixture which con-
tains the nickel salt, free acid, unreacted nickel car-
bonate and water was filtered. The filtrate was evaporated
in an oven at 120°C until a mass of fine powdery crystals
was obtained. The nickel salt was then placed in a des-
sicator over caustic potash and $CaCl_2$.

THE COBALT SALTS

The same procedure was followed in preparing the
cobalt salts. Cobalt carbonate was added to the respec-
tive acid and a little water. The mixture was allowed to
reflux slowly until no more cobalt carbonate appeared to
go into solution. After refluxing the mixture is filtered
and then carefully dried as cobalt salts tend to oxidize
in the air quite easily at elevated temperatures. The
solution was placed in the oven at 85°C and kept at that
temperature until crystals began to appear on the sides of
the dish. The saturated solution is then removed from the
oven and allowed to dry slowly in a dessicator over caustic
potash and $CaCl_2$. Finally the salts were washed with dry
ether to remove the last traces of acid which may remain
with the salt.

THE NICKEL COMPLEXES

The nickel complexes were made in a manner quite different from methods previously reported. The nickel salt was merely brought in contact with pyridine in an evaporating dish. The pyridine was allowed to completely mix and saturate the nickel salt. The immediate formation of a complex was quite noticeable as the color of the salt changed from green to blue when the pyridine was added. After the addition of pyridine the complex salt was placed in a dessicator and allowed to come to equilibrium with an open dish of pyridine in the dessicator.

THE COBALT COMPLEXES

The cobalt complexes, however, were prepared in a manner similar to that of Davis and Logan (4). The simple method which had been previously used on the nickel complexes was tried on the cobalt compounds. However, the cobalt compounds are less stable and the resulting complexes decomposed leaving black colored residues. It was found that all of the cobalt complex salts were difficultly soluble in chloroform. Nevertheless, with an excess of pyridine the complex will dissolve in chloroform. Upon solution of the complex salt into the chloroform and pyridine mixture it was found that quick evaporation of the chloroform solvent was necessary or decomposition would again result. This was accomplished by using only

a limited excess of pyridine with a considerable excess of chloroform as the solvent. This produced a solvent which was richer in chloroform and hence had a higher rate of evaporation. Upon evaporation of the chloroform the complex salt residue was placed in a dessicator under a pyridine atmosphere and allowed to come to equilibrium with the pyridine.

ANALYSIS

Both the simple salts and the complexes were ana-
lyzed for their metal content. The procedures used were
those followed by previous investigators (3, 4). In all
cases the results were reported as percent of nickel or
cobalt in the sample. The titration method using silver
nitrate and potassium cyanide was extensively used for
nickel (8,pp.613-615).

HEATS OF SOLUTION

The heats of solution of pyridine, the salts and
the complex salts were determined in the same manner as
done by previous investigators (1, 2, 6, 7).

The calorimeter was filled with 1500 ml of 2 N HCl.
The solid samples were placed in the sample ejector and a
thin cover glass was cemented in place with tygon label
glaze. The pyridine was placed in a rubber stoppered
ejector. The ejectors were of the same design as those
used by Bush and Rogers.

With the sample in place, the calorimeter lid was
closed and the contents of the calorimeter brought to
25°C by means of the heater. Temperature readings were
then observed every five minutes until an even, steady
cooling curve was obtained. When this condition was
attained, the sample was introduced into the HCl. Tem-
perature readings were then taken in thirty second

intervals, for the first five minutes, and at one minute intervals after that until a maximum point was reached and cooling curves began to appear. At that time the reading intervals were increased to five minutes and continued until an even cooling curve was observed.

With some salts particularly the complexes the reaction period was quite short, often under five minutes. With nickel valerate, however, the reaction period was very long, 40 minutes. The attempts made to obtain the heat of solution of cobalt valerate were confronted by this to an even greater degree. After an hour or so cooling curves would be obtained but upon inspection of the contents after the run it would be observed that some of the material had remained unreacted. Further work is in progress on the heat of solution of cobalt valerate.

The corrected temperature rise was extrapolated in the same manner as the heat capacity measurements. The pyridine used had been redistilled through a ten plate Oldershaw fractionation column.

TABLE II

HEAT OF SOLUTION OF PYRIDINE IN 2 N HCl AT 25°C

weight sample (grams)	temp. change (corrected)	heat of solution calories per mole
2.874	.191	−7980
2.9369	.197	−8100
	Average	−8040

TABLE III

HEAT OF SOLUTION OF NICKEL ACETATE IN 2 N HCl AT 25°C

weight sample (grams)	temp. change (corrected)	heat of solution calories per mole
3.9728	.157	−10,670
3.9550	.153	−10,450
4.1305	.160	−10,450
	Average	−10,500

TABLE IV

HEAT OF SOLUTION OF NICKEL ACETATE· 2 PYRIDINE IN 2 N HCl AT 25°C

weight sample (grams)	temp. change (corrected)	heat of solution calories per mole
3.9067	.113	−14,650
3.9337	.111	−14,430
	Average	−14,550

Heat of Solution of Pyridine
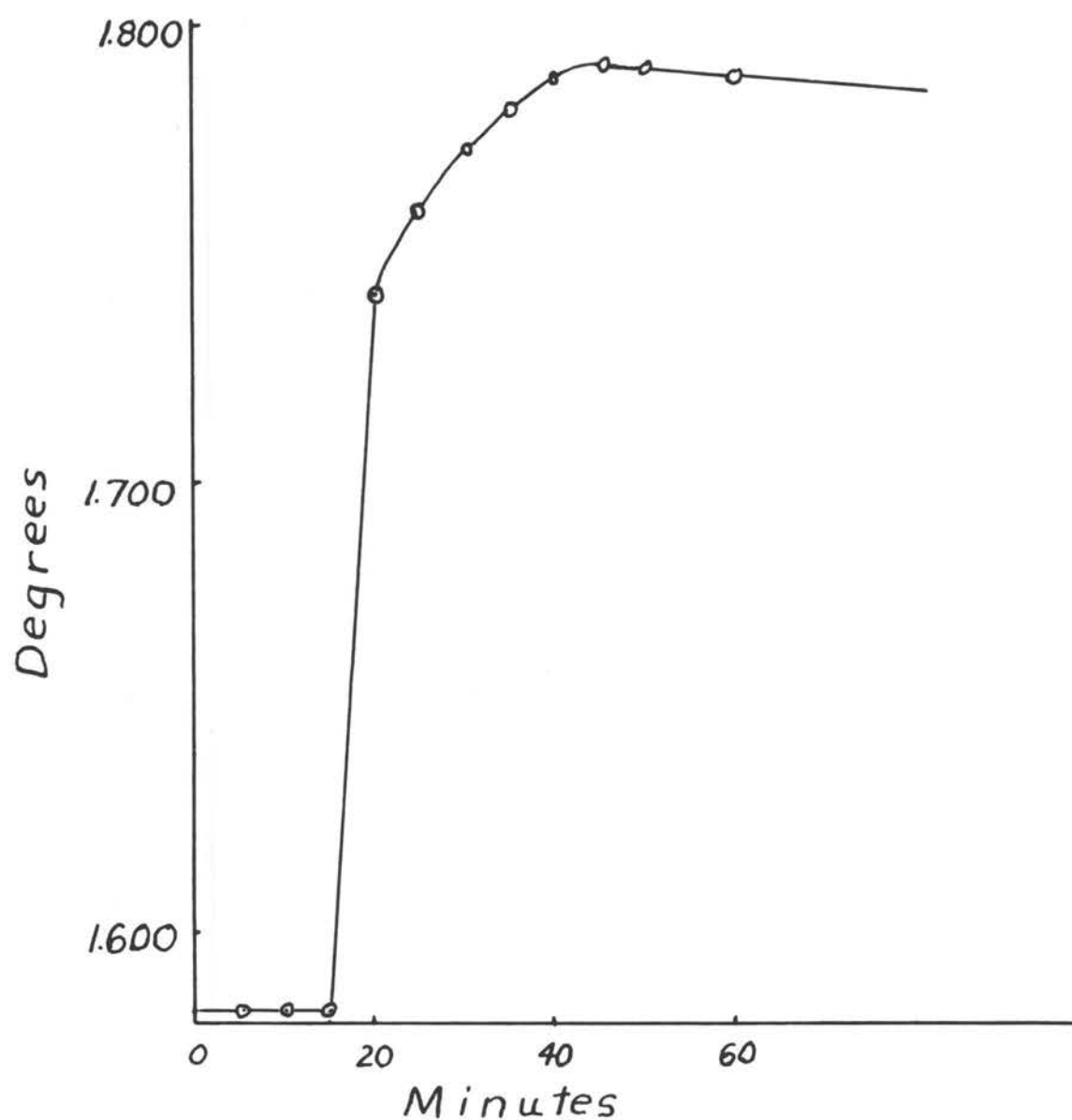in 2 N HCl at 25° C

Figure III

TABLE V

HEAT OF SOLUTION OF NICKEL PROPIONATE
IN 2 N HCl AT 25°C

weight sample (grams)	temp. change (corrected)	heat of solution calories per mole
3.8169	.176	−14,400
3.9509	.182	−14,400
	Average	−14,400

TABLE VI

HEAT OF SOLUTION OF NICKEL PROPIONATE·
2 PYRIDINE IN 2 N HCl AT 25°C

weight sample (grams)	temp. change (corrected)	heat of solution calories per mole
3.9530	.118	−16,550
3.9890	.120	−16,650
	Average	−16,600

TABLE VII

HEAT OF SOLUTION OF NICKEL BUTYRATE
IN 2 N HCl AT 25°C

weight sample (grams)	temp. change (corrected)	heat of solution calories per mole
3.8826	.157	−14,350
3.9000	.154	−14,050
	Average	−14,200

TABLE VIII

HEAT OF SOLUTION OF NICKEL BUTYRATE·
2 PYRIDINE IN 2 N HCl AT 25°C

weight sample (grams)	temp. change (corrected)	heat of solution calories per mole
3.9300	.088	−13,350
3.8215	.082	−12,800
3.7976	.084	−13,200
	Average	−13,100

TABLE IX

HEAT OF SOLUTION OF NICKEL VALERATE
IN 2 N HCl AT 25°C

weight sample (grams)	temp. change (corrected)	heat of solution calories per degree
3.9125	.163	−16,550
3.7465	.151	−16,150
3.0031	.125	−16,600
	Average	−16,400

TABLE X

HEAT OF SOLUTION OF NICKEL VALERATE·
2 PYRIDINE IN 2 N HCl AT 25°C

weight sample (grams)	temp. change (corrected)	heat of solution calories per degree
2.7840	.067	−15,350
1.5434	.036	−14,950
	Average	−15,200

TABLE XI

HEAT OF SOLUTION OF COBALT ACETATE IN 2 N HCl AT 25°C

weight sample (grams)	temp. change (corrected)	heat of solution calories per degree
3.8313	.138	$-9,720$
3.8319	.138	$-9,720$
	Average	$-9,720$

TABLE XII

HEAT OF SOLUTION OF COBALT ACETATE· 2 PYRIDINE IN 2 N HCl AT 25°C

weight sample (grams)	temp. change (corrected)	heat of solution calories per degree
3.9439	.019	$-2,460$
3.4493	.018	$-2,670$
	Average	$-2,500$

TABLE XIII

HEAT OF SOLUTION OF COBALT PROPIONATE
IN 2 N HCl AT 25°C

weight sample (grams)	temp. change (corrected)	heat of solution calories per degree
3.7056	.137	−11,580
3.7058	.136	−11,470
	Average	−11,500

TABLE XIV

HEAT OF SOLUTION OF COBALT PROPIONATE·
2 PYRIDINE IN 2 N HCl AT 25°C

weight sample (grams)	temp. change (corrected)	heat of solution calories per degree
3.9714	.083	−11,550
4.1740	.088	−11,670
	Average	−11,600

TABLE XV

HEAT OF SOLUTION OF COBALT BUTYRATE
IN 2 N HCl AT 25°C

weight sample (grams)	temp. change (corrected)	heat of solution calories per degree
4.0476	.115	− 10,050
4.0476	.112	− 9,860
	Average	− 9,950

TABLE XVI

HEAT OF SOLUTION OF COBALT BUTYRATE·
2 PYRIDINE IN 2 N HCl AT 25°C

weight sample (grams)	temp. change (corrected)	heat of solution calories per degree
3.8879	.086	−13,175
3.9400	.085	−12,900
	Average	−13,100

TABLE A

ANALYSIS OF COMPOUNDS

Compound	per cent metal		
	calc.	Found	
Nickel acetate	33.1	32.72	33.06
Nickel propionate	28.6	28.6	28.75
Nickel butyrate	25.15	28.81	25.3
Nickel valerate	22.5	23.3	22.86
Nickel acetate·2 pyridine	17.5	17.40	17.25
Nickel propionate·2 pyridine	16.15	16.65	16.65
Nickel butyrate·2 pyridine	15.0	15.55	15.42
Nickel valerate·2 pyridine	14.0	14.72	14.85
Cobalt acetate	33.3	32.81	
Cobalt propionate	28.7	28.9	28.93
Cobalt butyrate	25.3	25.06	26.0
Cobalt acetate·2 pyridine	17.6	17.6	17.56
Cobalt propionate·2 pyridine	16.2	16.0	
Cobalt butyrate·2 pyridine	14.2	14.01	14.51

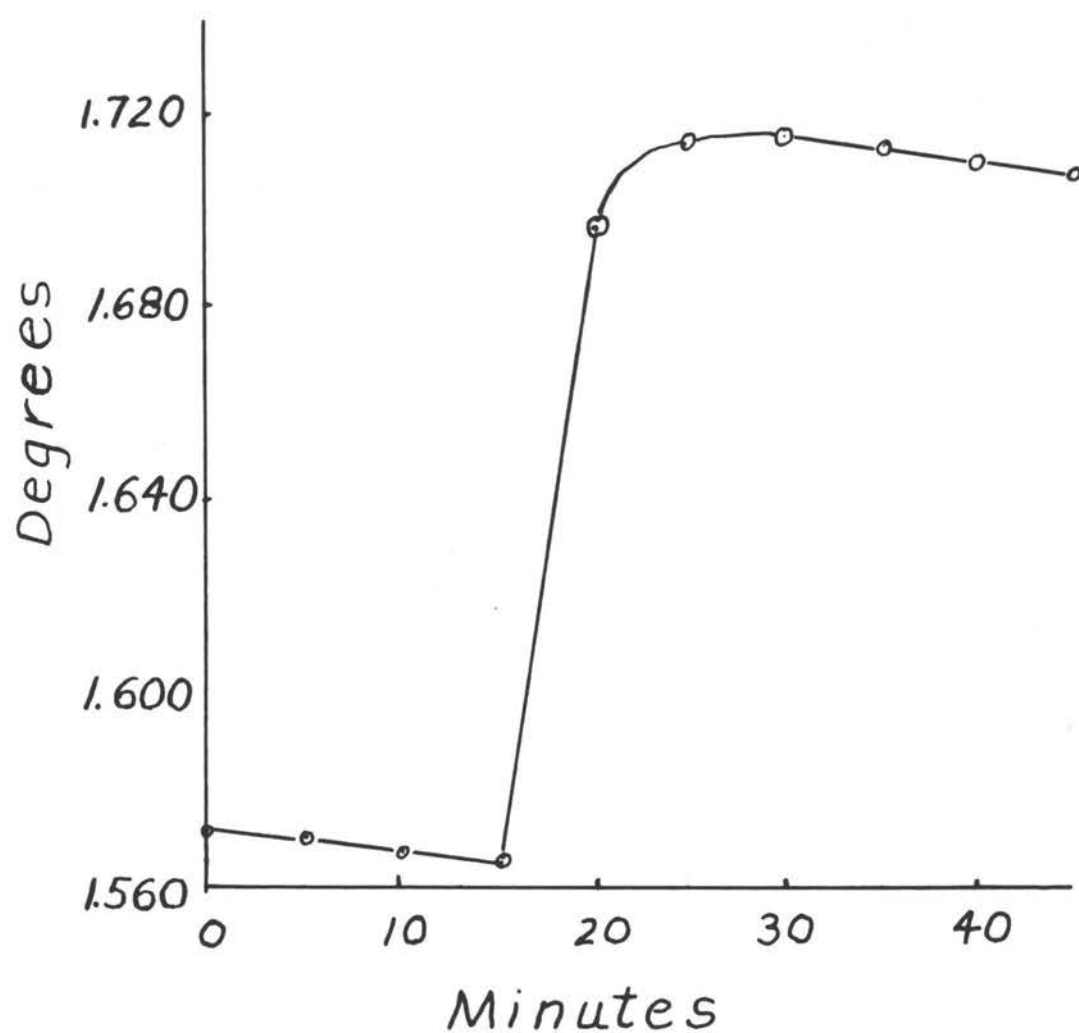Heat of Solution of Nickel
Acetate in 2 N HCl at 25°C

Figure IV

Heat of Solution of Nickel
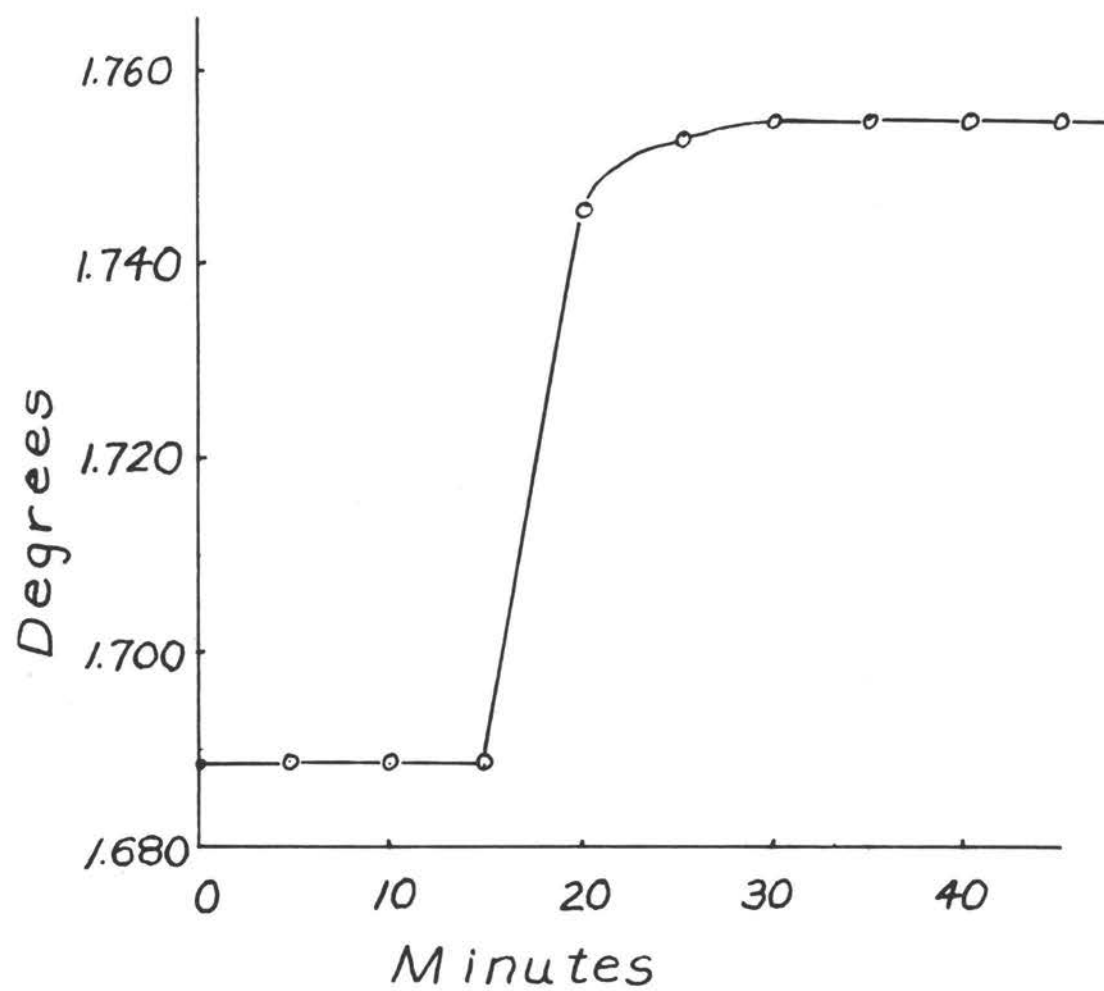Valerate · 2 Pyridine in
2 N HCl at 25° C

Figure V

Heat of Solution of Cobalt
Propionate in 2 N HCl at 25°C
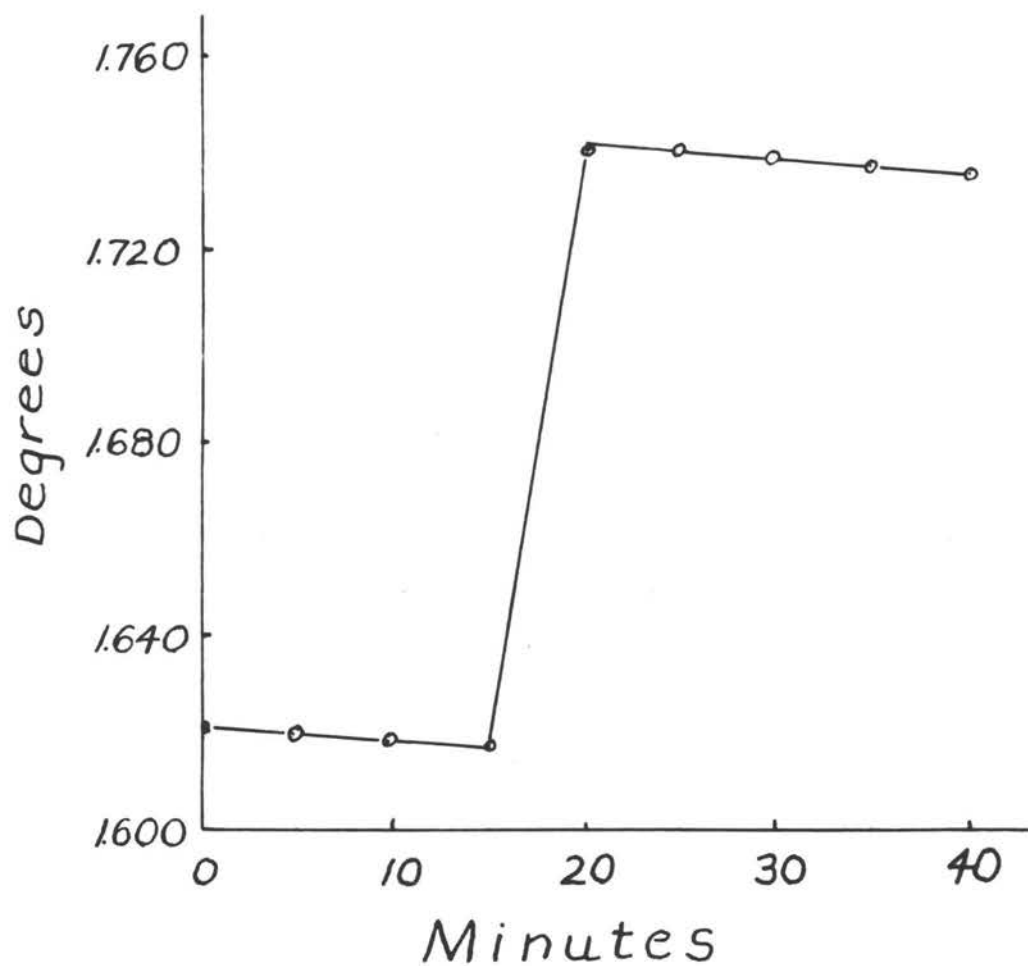

Figure VI

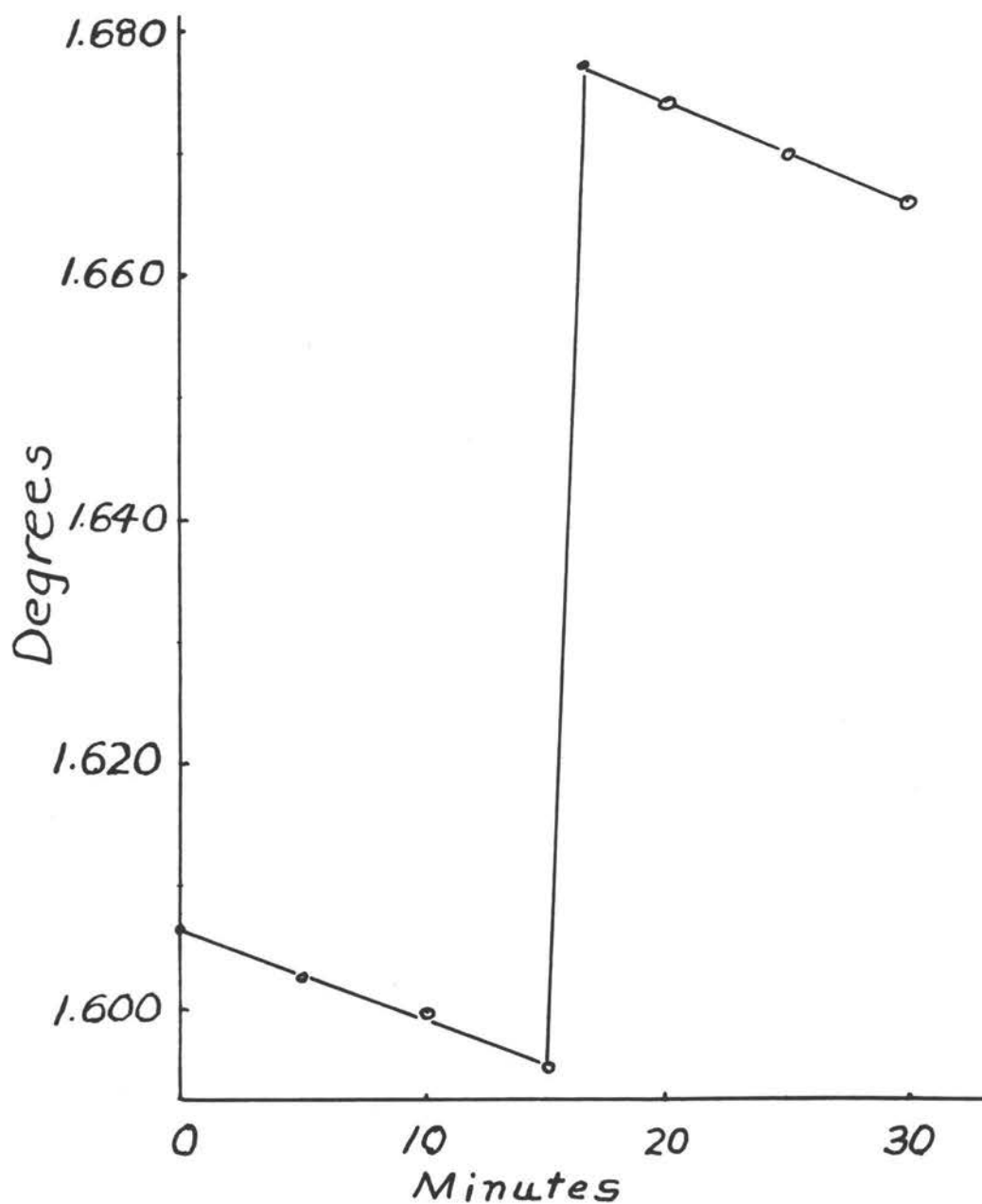Heat of Solution of
Cobalt Butyrate·2 Pyridine
in 2N HCl at 25°C
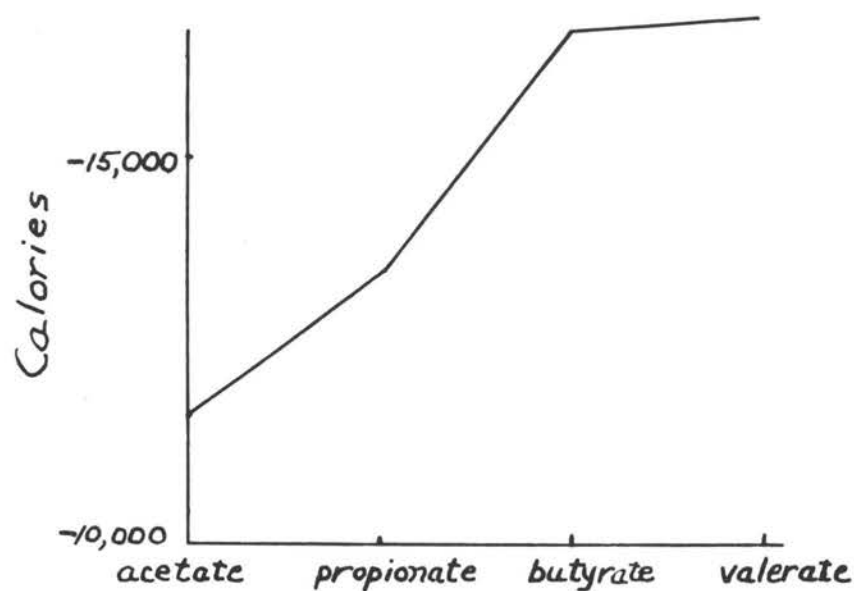
Figure VII

TABLE XVII

HEATS OF FORMATION AT 25°C

Compound	heat of formation calories per mole
Nickel acetate·2 pyridine	−12,000
Nickel propionate·2 pyridine	−13,800
Nickel butyrate·2 pyridine	−17,000
Nickel valerate·2 pyridine	−17,200
Cobalt acetate·2 pyridine	−23,200
Cobalt propionate·2 pyridine	−16,000
Cobalt butyrate·2 pyridine	−12,900

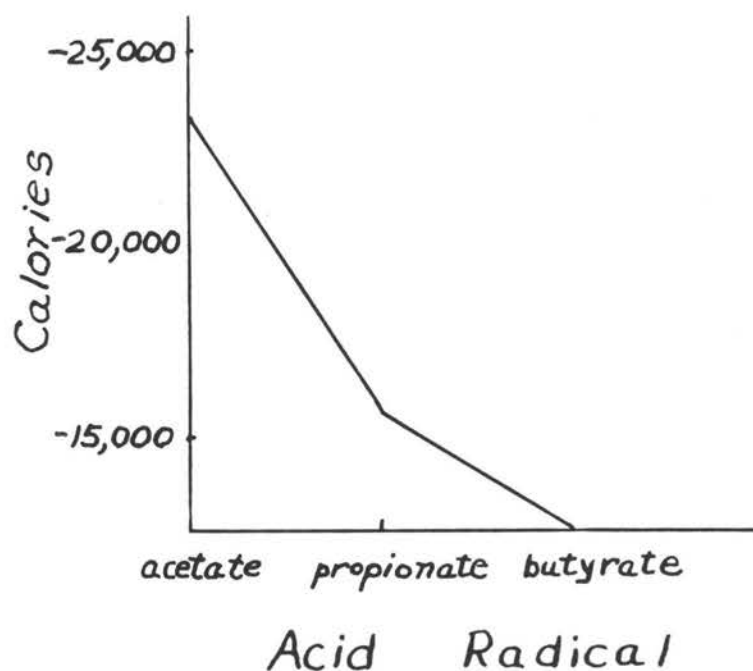Heat of Formation of Pyridine
Complexes with Fatty Acid Salts

Figure VIII

COMPARISON OF HEATS OF FORMATION

The values for the heats of formation of the nickel
and cobalt series of pyridine complexes of the fatty acids
show a striking dissimilarity. The cobalt series seems to
confirm previous work that the lower members of the fatty
acid series would possess a greater heat of formation of
the pyridine complex because the coordinate bond is strong-
er than the higher molecular weight acids. However, nickel
completely reverses the situation. In this case the lower
members have a smaller heat of formation than the upper
members (Table XVII, Figure VIII). The results of the
nickel salts also run counter to the previous work on dis-
sociation pressures and volume shrinkages (5,pp.12-14).
Further work must be done to verify this conclusion.
Since the differences between compounds were on the order
of one to five thousand calories, these differences are
beyond that of experimental error.

The odd-even, saw tooth effect that was displayed
in the dissociation pressures was not observed in either
of the two series. However, the heats of solution both
of the simple salt and the complex salt exhibited this
effect. Since the heats of formation were obtained by
subtracting one heat of solution from the other, this
effect was canceled out. Nevertheless, in nickel a slight

odd-even effect does take place as difference in heat of
formation between the propionate and butyrate is greater
than the differences between acetate and propionate on one
side and butyrate and valerate on the other. The series
would have to be extended in order that this effect could
be verified.

SUMMARY

The nickel (II) and cobalt (II) salts of fatty acids and the dipyridine complexes have been prepared and analyzed. The heats of solution of these compounds and pyridine were determined in 2 N HCl at 25°C in a calorimeter. From these values the heats of formation of the complexes were calculated.

BIBLIOGRAPHY

1. Bush, David Clair. Heats of formation of certain nickel-pyridine complex salts. Master's thesis. Corvallis, Oregon state college, 1950. 42 numb. leaves.

2. Carle, Don W. The preparation of nickel (II) thio-cyanate complex compounds with certain organic bases and the determination of their heats of formation. Master's thesis. Corvallis, Oregon state college, 1952. 44 numb. leaves.

3. Davis, Tenney L. and Albert Victor Logan. Chloroform-soluble metal pyridine cyanates. Journal of the American chemical society 50:2493-2499. 1928.

4. _____ and Albert Victor Logan. Metal pyridine complex salts. VI. Cobaltous and nickelous dipyridine salts of fatty acids. Journal of the American chemical society 62:1276-1279. 1940.

5. Logan, Albert Victor. Effect of atoms and groups upon coordinate linkages in pyridine complex compounds. Doctoral thesis. Cambridge, Massachusetts institute of technology, 1938. 39 numb. leaves.

6. Logan, Albert Victor, David C. Bush and Charles J. Rogers. The heats of formation of cobalt (II) and nickel (II) pyridinated cyanates and thiocyanates. Journal of the American chemical society 74:4194. 1952.

7. Rogers, Charles Junior. Heats of formation of certain cobalt pyridine complexes. Master's thesis. Corvallis, Oregon state college, 1950. 34 numb. leaves.

8. Treadwell, F. P. and William T. Hall. Analytical chemistry, Vol. II. New York, Wiley, 1924.