THE HEATS OF REACTION OF SOME SILVER

AND ETHYLENEDIAMINE COMPLEXES

by

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This thesis is dedicated to my mother.

ACKNOWLEDGEMENT

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INTRODUCTION

The purpose of this investigation was to determine the heats of reaction of the silver ethylenediamine (ethylenediamine = en) complexes; $AgHen^{++}$, $Ag_2(en)_2^{++}$, $Ag(en)^+$, and $Ag(en)_2^+$; by solution calorimetry. In the past two decades interest in metal complexes has greatly increased because of the demands from the government and industry for new materials with properties that are not found in conventional organic compounds. Consequently, metal complexes have found practical application in polymeric products, analytical chemistry and as catalysts.

The chemical literature contains numerous thermodynamic studies on metal complexes. In general, two approaches are employed. The first approach utilizes one cation and a series of ligands; the second varies the cations with respect to a given ligand. Several extensive studies have concerned the series of divalent transition metal ions: Cu^{++}, Zn^{++}, Cd^{++}, Mn^{++}; and, occasionally, one or two other metal ions (1,2,3). Relatively few of these studies include silver - probably because of the limited number of complexing cations with the same charge or charge to radius ratio as silver.

Although silver can form three and four monodentate
ligand complexes (4,5), it generally accepts two groups in
its complex formation with non-chelating agents and only
one with chelating species. The ligands add stepwise,
and under favorable conditions the formation constant for
each step can be evaluated. In the case of silver ethylene-
diamine, the unshared pairs of electrons on the amine
groups are coordinated with the silver ion. Schwarzenbach
believes that the first ethylenediamine chelates with the
silver ion to form a strained five-membered ring (6). He
also attributes the greater stability of $Ag(NH_3)_2^+$ as
compared to $Ag(en)^+$ to this strained ring (7). If the
first ethylenediamine group does chelate, the entry of the
second group would necessitate the breaking of one of the
silver-amine bonds and bring about a correspondingly large
change in the entropy of the system. Coupled with the
formation constants for each step, the evaluation and
discussions of the respective ΔS terms will appear under
Discussion of Results, page 30.

The following work concerns three series of solutions
whose concentrations have been chosen to render the concen-
trations of the species under study as large as possible

while making the concentrations of the other species as small as possilbe. However, it was necessary to obtain the thermodynamic functions for the $Ag(en)^+$ and $Ag_2(en)_2^{++}$ simultaneously due to the nature of the system.

Structural formulas appear on page 11.

$$A_G^+ - NH_2 - CH_2 - CH_2 - NH_3^+$$

AgHen^{++}

$$NH_2 - CH_2 - CH_2 - NH_2 - A_G^+ - NH_2 - CH_2 - CH_2 - NH_2$$
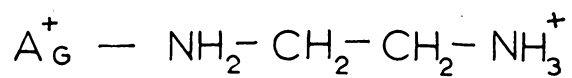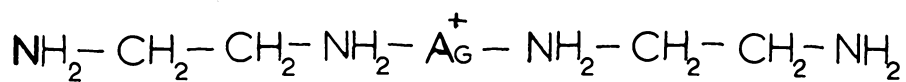
Ag(en)$_2^+$
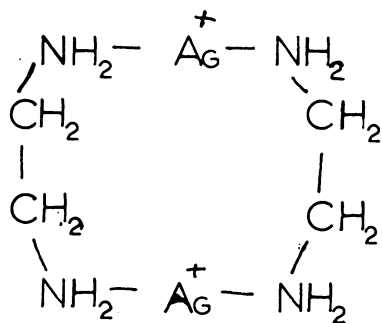
Ag$_2$(en)$_2^{++}$
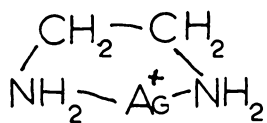
Ag(en)$^+$
(distorted linear)

or
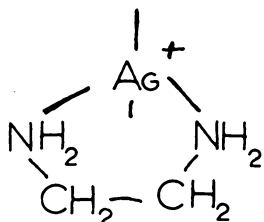
Ag(en)$^+$
(tetrahedral)

HISTORICAL

With reference to the work done in this thesis, only three publications have primary importance. The first of these is a series of papers on silver amine complexes by Schwarzenbach (6,7,8,9); these studies contain the measurement of the stability constants for the entire silver ethylenediamine system and provide the values used for the calculations of the concentrations of the various species present in the systems investigated in this work. The second (10) is a very recent paper dealing with the infrared determinations of the structure of some silver ethylenediamine species present in the crystalline state; these results were used in the analysis of the thermochemical data obtained here. The third is an extensive work by Fernelius, Bertsch, and Block giving ΔF, ΔH, and ΔS for a number of metal amine complexes - including silver 1,3-propane diamine and silver 1,4-butanediamine (1). Other papers dealing with silver ethylenediamine are by 1. Luca and Armeanu (11,12), 2. Harris (13), and 3. Pfeiffer, Schmitz, and Böhm (14). The first deals with the determination of the formation constants for $Ag(en)_2^+$ and $Ag(en)_3^+$ -

the latter in alcoholic solution only; the results are in good agreement with the data obtained by Schwarzenbach (6). The other papers concern only the preparation of some silver ethylenediamine salts. It should be mentioned that other work has been done on systems that contain silver ethylenediamine complexes in one form or another (15,16,17,18), but their results do not directly concern this line of investigation.

EXPERIMENTAL

The basic principles of the calorimeter have been covered by several authors (19,20), and many references to specific designs are given by them. The calorimeter employed in this work is a modification of several which have appeared in the literature in the last few years (21,22,23). A cross section of the calorimeter and surroundings is shown in Fig. 1; a detailed cross section of the calorimeter itself is shown in Fig. 2.

A silvered Dewar flask of approximately two liters volume constituted the main body of the calorimeter. This flask was fitted with a double wooden cover shaped so that it fitted snugly inside the Dewar flask. Six holes were drilled through the wooden top to accommodate the two variable resistance arms of the thermometer, the stirrer, sample holder, bulb breaker, and heater. The stirrer was a steel shaft with a brass pulley, and it rotated in a brass bearing. In order to protect the steel from corrosion that might be caused by any solution in the calorimeter, the stirrer was given several coatings of MARASET 780, a very highly chemically resistant epoxy resin

produced by the Marblette Corp. No detectable heating was caused by the stirrer under normal calorimeter heat flow. Throughout the months of use, no observable chemical attack occurred to the stirrer.

The sample holder and bulb breaker were two glass rods extending above the first wooden top down into the solution inside the Dewar flask. The bulb holder was ground on the end so that thin walled glass bulbs with short necks fitted closely at both the top and sides of their necks. These bulbs were sealed to the holder by wrapping chemically resistant plastic tape around the neck and then coating this tape with paraffin. The bulb breaker was an "L" shaped glass rod that was rotated into the bulb thereby breaking the thin glass wall. Both the bulb breaker and bulb holder were well beneath the surface of the liquid.

The remaining hole in the lid accommodated the electrical heater which was used to determine the energy equivalent of the system. The heater consisted of a tight coil of noninductively wound number 36 Advance wire of 208.2 ohms resistance with number 24 copper leads which was contained

in a glass tube bent into a coil around the stirrer; a

paraffin oil provided the heat transfer medium. The

electrical energy for the heater was furnished by a

Power Designs Inc. constant current source, Model Number

4005.

The Dewar flask was lowered into a copper can two

inches larger in diameter than the flask and about twice

as deep. A second double top, attached to the top fitting

inside the Dewar by means of long bolts, fitted snugly

inside the copper can and flush with the top of a large

wooden box (30 inches x 30 inches x 30 inches) thus forming

a dead air space. The distance from the bottom of the

second top to the top of the first top was six and one

half inches. In order to minimize conduction of heat into

or out of the calorimeter system _via_ the metal stirrer,

a glass rod was connected to the top of the stirrer shaft

and attached to another shaft in a motor driven pulley

above the second double top.

In order to measure the energy input to the heater,

the electrical circuit in Fig. 3 was used. During any given

heating period (usually one minute) no current variation

greater than one part in 10,000 was observed; usually the

variations were of the order of a few parts in 100,000. The heating period was measured by means of an electrical stopclock that was read directly to 0.01 seconds and estimated to 0.002 seconds.

The appearance of the temperature sensing devices, Fig. 4, is exactly the same as that of a Wheatstone bridge. The device was constructed as follows: The resistances of the two manganin arms contained number 40 wire plus pieces of larger wire soldered to the smaller wire so that the resistances could be matched as closely as possible. The total resistance of each arm was 366.4 ohms at 25.15°C. The variable resistance arms (thermistors) were contained in glass tubing filled with paraffin oil to provide an efficient heat transfer medium. The four arms of the bridge were connected with short pieces of number 20 copper wire of matched resistance. Only the thermistors were inside the calorimeter. Copper leads connected the bridge to the potentiometer and battery as indicated in Fig. 4.

Manganin wire has a very low temperature coefficient of resistance over a temperature range of 15° - 35°C. Thermistors, on the other hand, have a rather large negative

temperature coefficient of resistance (4.4%). When all
the resistances are equal, the potential across the bridge
is zero. At any temperature other than this transition
temperature, the resistances of the matched thermistors
will differ from that of the manganin coils, and a potential
will exist across the bridge; this potential is measured
by means of a potentiometer. Above the transition point
the potential exists one way and below the transition
point the potential exists the other way. It should be
noted that the temperature - resistance relationship over
the small temperature range encountered in our measurements
is linear.

For any given run it is necessary to maintain a constant
current through the temperature bridge. If there is a size-
able current variation, the potential drop across the bridge
will also vary, and this will produce a potential change
without a temperature change. The source of current was
lead storage batteries connected in series to give 40 volts.
A resistance of 20,000 ohms was connected in series with
the circuit to give the desired current of 0.002 amperes.
The heating effect of this current inside the calorimeter

was about 0.6 calories per hour, an insignificant amount.
In order to maintain the desired current and correct for
any deviations, a decade resistance box with a range of
one ohm to 111,111 ohms (adjustable in one ohm steps) was
connected in series with the circuit. The potential drop
across a fixed resistance in the circuit was checked
periodically with the potentiometer. Since a deviation
in the potential drop corresponds to a change in current,
any deviations in the current could be compensated for
by changing the resistance of the decade. The average
constancy of current was better than one part in 20,000.

The potentiometer used for these measurements was a
White double potentiometer (Model Number 7622) capable
of reading a maximum of 9,999 microvolts in one microvolt
steps. However, with a lamp and scale and a galvanometer
of sufficient sensitivity, the instrument can give at
least one more significant figure. Calibration of the
potentiometer against itself showed the internal consistency
to be better than 0.05 microvolts. The present galvanometer
setup, a two meter light path and a scale that is magnified
by a lens, enables us to read to plus or minus 0.5 microvolts.

However, since the galvanometer (sensitivity of 0.05 micro-volts per millimeter) is used as a null instrument for determining the temperature change, our accuracy is better than 0.5 microvolts because when the galvanometer passes the zero, the time is recorded and no attempt is made to interpolate between the units on the scale. The sensitivity of this system is about 0.00001°C. The overall circuit for the setup is given in Fig. 5.

In a typical run, the calorimeter is loaded with 1400 grams of water, weighed to 0.3 grams on a large balance. The bulb containing the sample is attached to the bulb holder which is then secured in the tops. The calorimeter is then assembled in the copper can. It is necessary to wait about an hour before making a run in order to permit the system to come to thermal equilibrium. All current sources are also discharged before a run to minimize current fluctuations. The potentiometer batteries are discharged by means of resistances equal to the internal resistance of the potentiometer, the thermometer current is connected to the temperature bridge, and the heater current is discharged through a dummy resistance of about the same resistance as the actual heater. After the

potentiometer is in balance, the heat leak either into or out of the calorimeter is measured by setting the potentiometer dials "ahead" of the drift and marking the time when the galvanometer passes the null for the reading. When the heat drift is constant, the heater inside the Dewar flask is turned on. From the current, the resistance of the heater, and the time of heating; the heat input is calculated. The after drift is recorded after the heat is turned off, and the temperature change is corrected for the before and after heat leaks assuming that all the heating occurred at 0.6 (24) of the heating time. Similarly, the drifts are measured before and after the sample bulb is broken, and the temperature change is again corrected by extrapolation to the point where half of the reaction has occurred. There was a second and sometimes a third heat capacity determination after the sample has gone into the solution. From the temperature change of the sample, the enthalpy is computed. Temperature changes are approximately $0.1^{\circ}C$.

Before performing any chemical reactions, several heat capacities of the system were determined to check for internal consistency. Secondly, it was necessary to check

the accuracy of the instrument by measuring the heat of
solution of potassium chloride, a substance whose heat
has been determined quite accurately. These results agree
to plus or minus 0.3% of the accepted values. Determina-
tions of the heat of solution of potassium chloride were
also made after obtaining the data for the chemical re-
actions under investigation. There was no detectible
difference in the results (Table 1).

The chemicals used in this investigation were reagent
grade silver nitrate, potassium chloride, nitric acid,
potassium nitrate, and ethylenediamine. A freshly opened
bottle of reagent grade Fisher Chemical Co. silver nitrate
was used; the purity of the sample was established gravi-
metrically by precipitation as the chloride. The ethylene-
diamine was distilled once, discarding the first and last
portions and collecting only the middle fraction under a
nitrogen atmosphere. The solution was stored under nitrogen
in a wax lined bottle. Throughout the course of this
work, no decomposition was detected. The ethylenediamine
solutions used in the calorimeter were prepared by diluting
the stock solution (13.00 molar) to give the various

concentrations needed for each series. The dilute ethylene-
diamine solutions were standardized with 0.1N hydrochloric
acid which had been standardized against sodium carbonate
using bromcresol green indicator. The ethylenediamine
was also standardized with bromcresol green indicator
(the titration carried out to the second equivalence
point). The silver nitrate crystals were broken up and
kept in a dark desiccator after being heated for an hour
at $140^{\circ}C$. A freshly opened bottle of Mallinckrodt reagent
grade potassium chloride was used for standardization of
the calorimeter. The potassium nitrate used to boost
the ionic strength of some of the series was Fisher
reagent grade. The nitric acid in the $AgHen^{++}$ series was
a 4.58 molar solution prepared from reagent grade con-
centrated nitric acid. The nitric acid stock solution was
standardized against sodium carbonate both before and after
the $AgHen^{++}$ series.

The three concentration systems used to determine
the heats of reaction were as follows: a. 0.014 molar
silver nitrate in 0.15 molar ethylenediamine; b. equimolar
ratios of ethylenediamine and silver nitrate in the range

of 0.02 to 0.03 molar each; and c. 0.04 molar ethylene-

diamine neutralized with an acid concentration of 0.065

molar with the silver nitrate concentration around 0.034

molar. Since the equilibrium constants were determined

at 0.1m ionic strength, potassium nitrate was added to

the above systems, when necessary, to raise the ionic

strength.

Calculations of the concentrations in system a. were

facilitated by the assumption that all the silver existed

as the species $Ag(en)_2^+$. From the concentration of the

excess ethylenediamine and the equilibrium expression

$[Ag(en)_2^+] / [Ag(en)^+] [(en)] = 10^3$ (6), the $Ag(en)^+$

present could be approximately calculated; and, therefore,

the concentration of the dimer, from the expression

$[Ag_2(en)_2^{++}] / [Ag(en)^+]^2 = 10^{3.83}$ (6). These approximate

values were used to correct the concentration of the

$Ag(en)_2^+$. Since the concentrations of the $Ag(en)^+$ and

$Ag_2(en)_2^{++}$ were small, two or three successive approximations

gave consistent results.

For system b. it was necessary to assemble the equation

for the complete system of $Ag(en)^+$, $Ag_2(en)_2^{++}$, and $Ag(en)_2^+$

from the equilibrium expressions for each of the species

and the mass balance and electroneutrality relationships.
The solution to a typical system showed that the $Ag(en)_2^+$
was present to only a small extent. This permitted the
final calculations to be performed by means of the expressions:
$$C_{Ag^+} = [Ag(en)^+] + 2[Ag_2(en)_2^{++}] \text{ and } [Ag_2(en)_2^{++}] / [Ag(en)^+]^2 =$$
$10^{3.83}$ (6), where C_{Ag^+} represents the total silver con-
centration. The equation was then corrected for free silver
ion and the small $Ag(en)_2^+$ concentration. (It was assumed
that approximately half the excess ethylenediamine was
used in forming $Ag(en)_2^+$.) Several successive approxima-
tions produced consistent results.

System c. presented the greatest difficulties in
calculation since no ready simplification was available.
The equilibrium expressions for the entire system were
too difficult to solve. The pH of the solution was there-
fore measured. From this pH one can calculate the ratio of
the species $[Ag_2(en)_2^{++}] / [AgHen^{++}]^2$ and the species
$[H_2(en)^{++}] / [Hen^+]$; from these ratios and equilibrium
expressions, one may calculate the concentrations of the
species.

A table of the equilibrium expressions determined by
Schwarzenbach (6) is given in Table 2. The concentrations

of the various species in each solution used in calculating the enthalpies is given in Tables 3 and 4.

From the algebraic sum of the observed calorimetric heat, the heat of solution of silver nitrate (25), and the heat produced by the shift in the concentrations of the various protonated ethylenediamine species (26), the overall heat, Q, is obtained. This Q divided by the concentration of the species given the enthalpy of the reaction. For the $Ag(en)^+ - Ag_2(en)_2^{++}$ system, the enthalpy was determined from the heats of pairs of runs in two simultaneous equations. These heat corrections appear in Table 5.

DISCUSSION AND RESULTS

A. DISCUSSION OF RESULTS

The free energies, enthalpies, and entropy changes for the silver ethylenediamine complexes appear in Table 6; these values are for 0.1m ionic strength.

Although many determinations of free energies for silver complexes are in the literature, very little thermodynamic work has been done on the enthalpies and entropies. Therefore, comparisons with these data can not be extensive. The data here, however, do seem to be in line with the work done by Fernelius (1) and Fyfe (27). Although Fernelius did not determine thermodynamic functions for silver ethylenediamine complexes, he did determine the thermodynamic functions for 1,3-diaminopropane, 1,4-diamino-butane, and 1,3-diamino-2-hydroxypropane complexes with silver for the first formation constant. The enthalpy value obtained here for the Ag(en)$^+$ complex, $\Delta H = -25 \pm 5$ kcal./mole, although much larger, is in line with the enthalpies obtained by Fernelius, -10.7 kcal./mole for 1,4-diaminobutane, -14.6 kcal./mole for 1,3-diaminopropane, and -13.2 kcal./mole for 1,3-diamino-2-hydroxypropane.

For the Ag(en)$_2^+$ enthalpy, -13.0 kcal./mole, the value

quoted by Fyfe (27) for Ag(NH$_3$)$_2^+$, -13.5 kcal./mole, shows

a more reasonable comparison. Both complexes involve

similar groups attached to a silver ion. The data by

Datta and Gryzbowski (28) for the enthalpies of the silver

complexes with glycine and arginine do not compare too

favorably with the above. The enthalpies for the 1:1

complexes are -14 ±1 kcal./mole and -24 ±4 kcal./mole,

respectively; and for the 2:1 complexes are -33.7 ±2.5

kcal./mole and -30.3 ±4 kcal./mole, respectively. However,

one could expect some discrepancies because of the different

nature of the ligands and the difference in ionic strength

for the determinations -0.1m for these data and 0.02m for

the glycine and arginine data. The value for the 1:1

silver glycine complex agrees with the data in this work

for the AgHen^{++} complex, -14 kcal./mole, but this is pro-

bably a coincidence. In light of the data by Fyfe (27)

and the data here for Ag(en)$_2^+$, this AgHen^{++} enthalpy is

somewhat anomalous since the heat of formation for its

one silver-nitrogen bond equals that for the formation

of the two silver-nitrogen bonds for the others. Secondly,

one would expect a lower enthalpy because one end of the

ethylenediamine has been protonated. Since the bonding
in each of the cases should be the same (linear sp bond),
no ready explanation is available except that the method
for determining the AgHen^{++} concentration may have intro-
duced a large error. Comparison of the AgHen^{++} enthalpy
with that of Ag(en)$^+$, and Ag(tmn)$^+$ is not desirable because
the latter are all chelates. The enthalpy for the dimer,
Ag$_2$(en)$_2$$^{++}$, falls in line with the data for Ag(en)$_2$$^+$,
Ag(NH$_3$)$_2$$^+$, Ag(tn)$^+$, Ag(tmn)$^+$ and Ag(thn)$^+$ (1). (Where
tn = 1,3-diaminopropane, tmn = 1,4-diaminobutane, and
thn = 1,3-diamino-2-hydroxypropane.) In the cases of the
latter compounds, each silver-nitrogen bond contributes about
6 kcal./mole. If the dimer is the 10-membered ring pro-
posed by Schwarzenbach (6), then the enthalpy, -25.57
kcal./mole, divided among the four silver-nitrogen bonds
gives about this value, 6 kcal./mole. However, the linear
polymeric structure found for the mercury ethylenediamine
complex is also proposed for the Ag$_2$(en)$_2$$^{++}$ complex by
Newman and Powell (10) based on their infrared spectra
data for the sulfate. Since the spectra were taken on the
crystalline compound, a strict comparison can not be made,
and both structures could exist.

Due to the large uncertainties in the entropy values,
a quantitative discussion can not be undertaken; however,
certain qualitative conclusions can be drawn. The entropies
all strongly oppose the formation of the complexes $Ag(en)^+$,
$Ag_2(en)_2^{++}$, and $AgHen^{++}$.

The entropy value for the formation of $Ag(en)^+$, ΔS =
-60 e.u. ± 20 e.u., may seem unusually large, but comparison
with data obtained by Fernelius (1) shows that this value
can be in line. Fernelius obtains ΔS = -11 e.u. for
1,4-diaminobutane and -23 e.u. for 1,3-diaminopropane;
consequently, one could easily expect above -30 e.u. for
ethylenediamine since it is next in that series of decreasing
carbon atoms, and the chelated complex would be severely
strained. Since this large entropy for $Ag(en)^+$ is plausible,
the large enthalpy for the reaction does not seem unreason-
able. The infrared studies of Newman and Powell (10)
also indicate that $Ag(en)^+$ is not chelated; but since
their measurements were done on the crystalline chloride,
the results are not strictly comparable. Both structures
could exist.

The ΔS for $Ag(en)_2^+$ of -8.4 e.u. is in line with that
for $Ag(NH_3)_2^+$ quoted above (28); no other data was available

for comparison here. A negative value is obtained because three particles form one, thereby producing a more ordered system. In the case of the dimer, the effect is similar since four particles form one. The -25.2 e.u. for the formation of the dimer is not unreasonable when considered from the restriction imposed by the 10-membered ring. The entropy for AgHen^{++}, -38 e.u., is anomalous and can be explained only on the same basis as the enthalpy for this complex. The entropys for the glycine and arginine silver complexes (28) do not compare especially well here due to the differences in the ligands. The entropy data for these complexes is as follows:

glycine 1:1 ΔS = +19 ± 3 e.u.   1:2 ΔS = -47 ± 8 e.u.

arginine 1:1 ΔS = -20 ± 12 e.u.   1:2 ΔS = - 32 ± 12 e.u.

From the obtained thermodynamic data additional data was calculated (see Table 6).

B. DISCUSSION OF ERROR

All total silver and potassium chloride concentrations are accurate to better than 0.1%. The concentrations of the ethylenediamine for each system are accurate to 0.2%. Plus or minus values on the enthalpies refer to calorimetric precision; entropy uncertainties were determined mainly by the enthalpy uncertainties. The uncertainties in the equilibrium constants are those given by Schwarzenbach and, therefore, determine the free energy uncertainties. Volumes for the calorimetric runs are accurate to 0.1%. Ionic strengths are accurate to about 1% except where uncertainties in the calculated concentrations would give greater error. Heat correction uncertainties depend on the concentration of the species concerned and acquire additional uncertainty because of concentration uncertainties. Therefore, it is preferable to list all the uncertainties in the heats given by those authors for each source. The heat of solution of silver nitrate is accurate to 0.2% (25). The ethylenediamine heats of neutralization are accurate to about 1% (26). Due to the

uncertainties in the logarithms of the stability constants, the calculated concentrations have less than one significant figure; however, the tabulated concentrations have three and four significant figures. This does not imply these values were understood to have that much accuracy but simply that they were carried out to the limit of experimental error, usually about 0.3%, in order to provide enough digits to calculate the enthalpies. All concentrations of species other than major species are little better than order of magnitude. In the case of $AgHen^{++}$, the uncertainty in concentration is about 20%. Consequently, no plus or minus values appear for the concentrations.

TABLES AND FIGURES
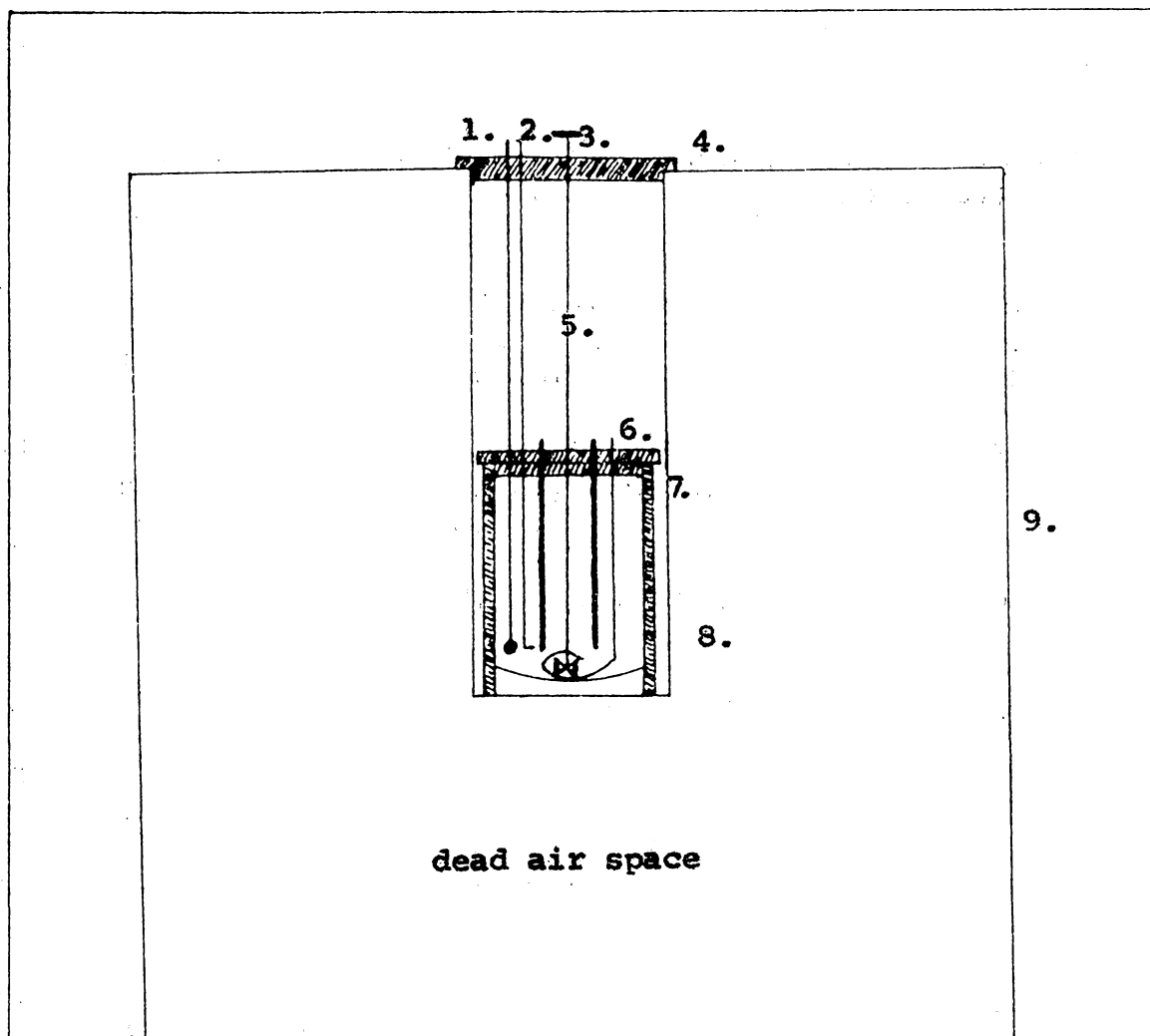
1. bulb holder

2. bulb breaker

3. pulley rotating stirrer shaft

4. second double top

5. stirrer shaft

6. first double top

7. Dewar flask

8. copper can

9. wooden box (30" x 30" x 30")

Figure 1. Cross Section of the Calorimeter and Surroundings
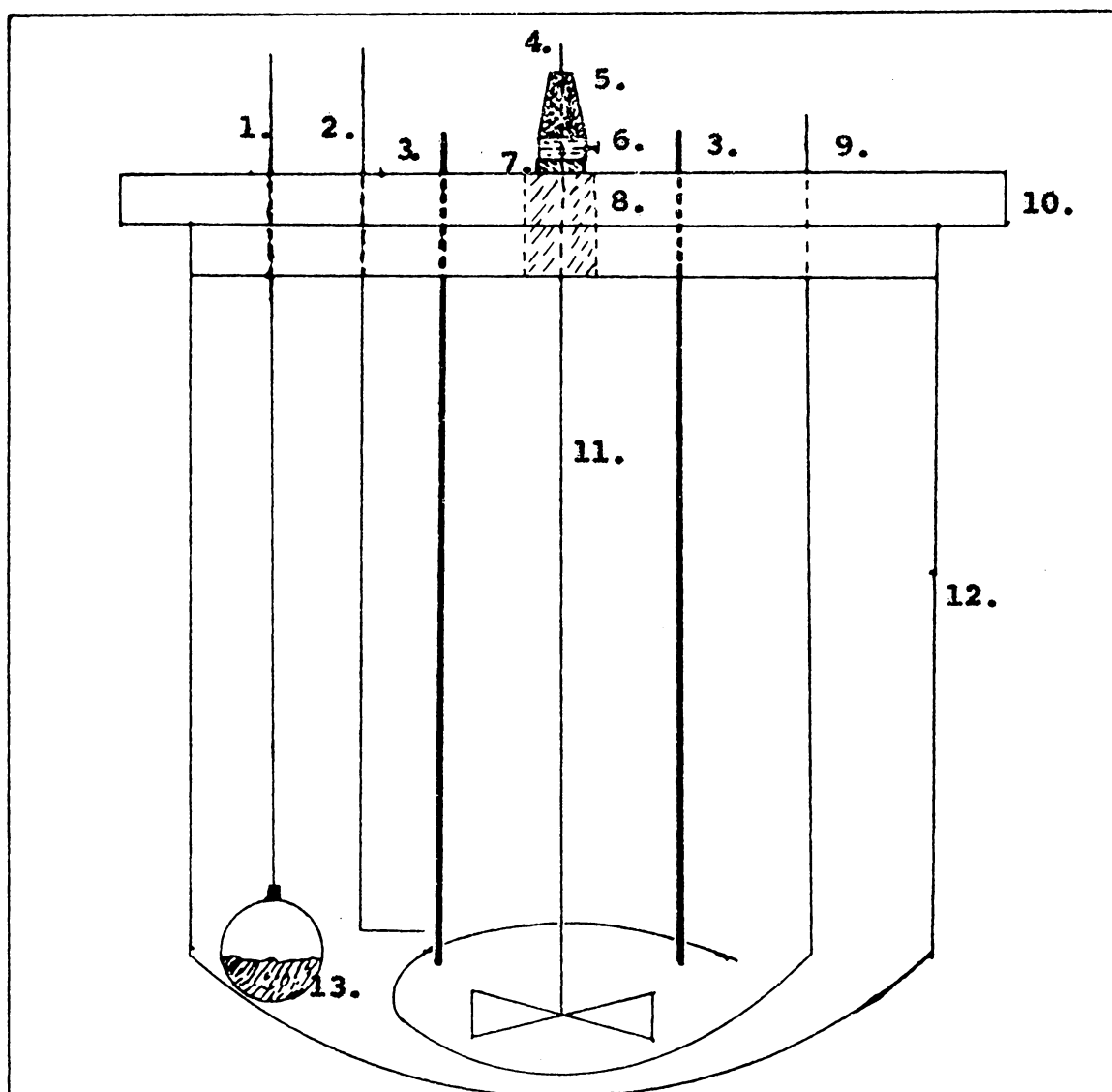
1. bulb holder   7. teflon washer
2. bulb breaker   8. brass bearing
3. thermistor tube   9. heater
4. glass rod   10. first double top
5. rubber stopper   11. steel stirrer shaft
6. brass screw clamp   12. Dewar flask
                       13. sample

Figure 2. Detailed Cross Section of the Calorimeter
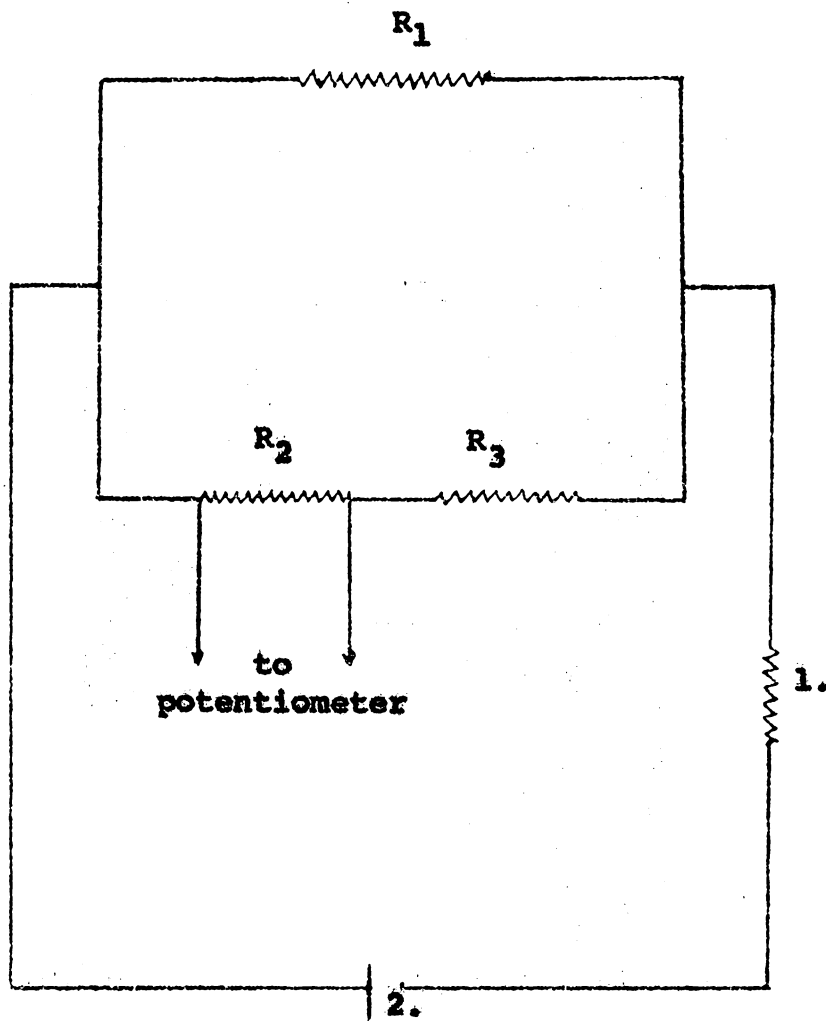
$R_1 = 1.1178$ ohms

$R_2 = 1.2159$ ohms

$R_3 = 19.8958$ ohms

1. heater

2. power source

Figure 3. Heater Circuit Diagram

Figure 4. Temperature Sensing Bridge Diagram

thermometer
current

1.

2.

2.

1.

3.   to potentiometer
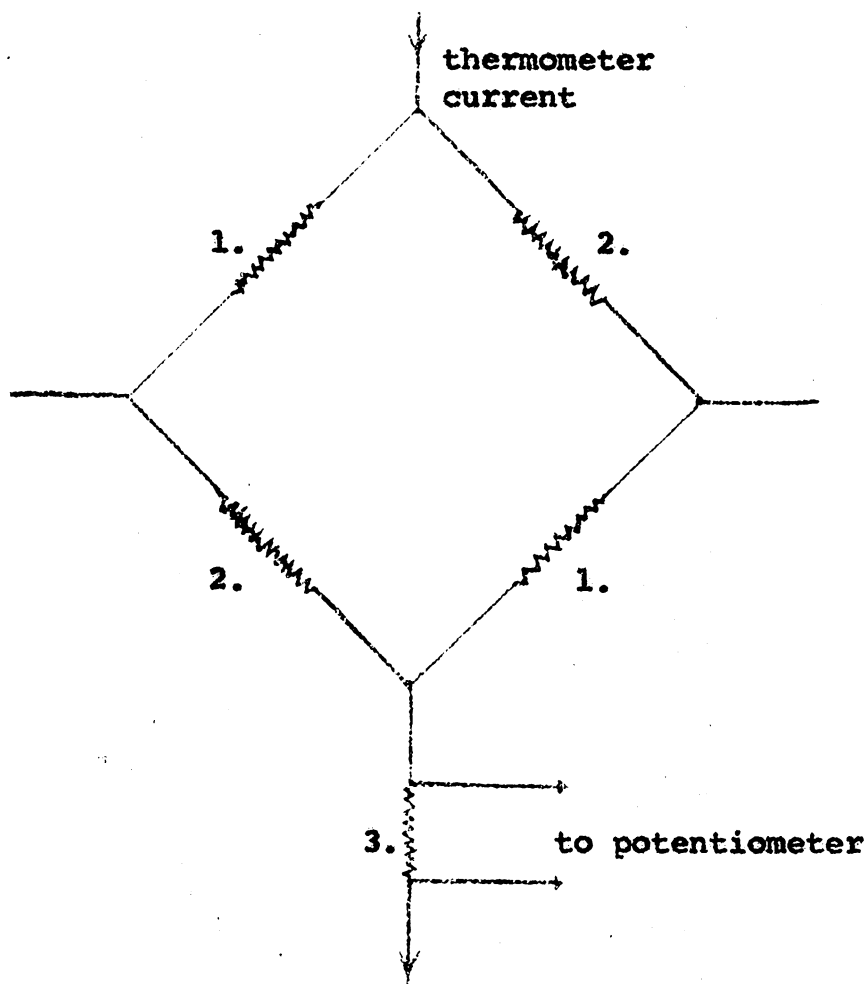
1.   thermistor
2.   Manganin resistance
3.   fixed resistance (about four ohms)

1. galvanometer   7. double pole double throw switch
2. potentiometer   8. constant current source
3. heater   9. voltage stabalizer
4. to 110 volts A.C.   10. 40 volts (lead storage batteries)
5. stopclock   11. decade resistance
6. dummy heater

Figure 5. Complete Circuit Diagram

TABLE 1

Heats of Solution of KCl

Run	Moles KCl	Molarity	ΔH (kcal./mole) This Work	N.B.S. (29)
1.	0.033829	0.056512	4.22	4.19
2.	0.029093	0.029093	4.18	4.18
3.	0.038475	0.067568	4.20	4.19
4.	0.056439	0.124007	4.20	4.20

Runs 1-4 were done before the silver determinations;
runs 5-7 were done after the silver determinations.

5.	0.035300	0.035300	4.19	4.18
6.	0.042892	0.07819	4.20	4.20
7.	0.053493	0.132685	4.21	4.20

TABLE 2 (6)

Ethylenediamine and Silver Ethylenediamine Equilibrium Expressions

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$$[Ag(en)^+] / [Ag^+][en] = 10^{4.7 \pm 0.1}$$

$$[Ag_2(en)_2^{++}] / [Ag(en)^+]^2 = 10^{3.83 \pm 0.15}$$

$$[Ag(en)_2^+] / [Ag^+][en]^2 = 10^{7.7 \pm 0.1}$$

$$[AgHen^{++}] / [Ag^+][Hen^+] = 10^{2.35 \pm 0.05}$$

$$[Ag_2(en)^{++}] / [Ag^+][Ag(en)^+] = 10^{1.76 \pm 0.3}$$

$$[Hen^+] / [H^+][en] = 10^{10.03}$$

$$[H_2(en)^{++}] / [H^+][Hen^+] = 10^{7.22}$$

TABLE 3

Chemical Composition of Each Run

Run	c_{H^+} (M.)	Moles Ag^+	Volume (Ml.)	c_{en} (M.)	c_{Ag^+} (M.)	μ*
system a.						
L-1		0.014791	1409.9	0.1535	0.010501	0.103
L-2		0.017647	1710.2	0.1535	0.012526	0.104
L-3		0.014874	1410.2	0.1535	0.010557	0.104
L-5		0.014198	1409.8	0.1535	0.010081	0.102
L-6		0.014004	1410.3	0.1535	0.009940	0.101
L-7		0.014038	1411.0	0.1535	0.010000	0.102
system b.						
C-6		0.024527	1403.5	0.017476	0.017575	0.105
D-1		0.039550	1398.0	0.028290	0.028255	0.095
D-3		0.028132	1397.6	0.020375	0.020129	0.098
D-4		0.026997	1397.8	0.019806	0.019314	0.097
D-5		0.041587	1397.8	0.029992	0.029752	0.096
system c.						
H-1	0.06536	0.051760	1402.9	0.042298	0.036895	0.102
H-4	0.06550	0.050022	1400.0	0.042386	0.035730	0.102
H-5	0.06532	0.048647	1403.9	0.042268	0.034651	0.114
H-6	0.06545	0.051029	1401.0	0.042355	0.036423	0.102
H-7	0.06550	0.047136	1400.0	0.042386	0.033669	0.100

*μ = ionic strength

TABLE 4

Concentrations of Principal Species for "L" Series

Part a

Concentration Before Reaction in Moles per Liter

Run	en	Hen$^+$	H$_2$en^{++}
L-1	0.1494	0.004000	0
L-2	0.1494	0.004000	0
L-3	0.1494	0.004000	0
L-5	0.1494	0.004000	0
L-6	0.1494	0.004000	0
L-7	0.1494	0.004000	0

Concentration After Reaction in Moles per Liter

Run	en	Hen$^+$	Ag(en)$_2^+$	Ag(en)$^+$	Ag$_2$(en)$_2^{++}$
L-1	0.1289	0.003715	0.01033	0.000080	0.000043
L-2	0.1249	0.003659	0.01229	0.000099	0.000068
L-3	0.1288	0.003714	0.01038	0.000081	0.000044
L-5	0.1297	0.003729	0.00992	0.000076	0.000040
L-6	0.1299	0.003731	0.00979	0.000075	0.000038
L-7	0.1298	0.003730	0.00984	0.000076	0.000039

TABLE 4

Concentration of Principal Series for "D" Series

Part b

Concentration Before Reaction in Moles per Liter

Run	en	Hen$^+$	H$_2$en^{++}
C-6	0.01616	0.00132	0
D-1	0.02660	0.00169	0
D-3	0.01895	0.00143	0
D-4	0.01840	0.00140	0
D-5	0.02825	0.00174	0

Concentration After Reaction in Moles per Liter

Run	en	Hen	H$_2$en^{++}	Ag(en)$_2^+$	Ag(en)$^+$	Ag$_2$(en)$_2^{++}$
C-6	0.0001	0	0	0	0.00110	0.00818
D-1	0.0001	0.00004	0	0	0.00141	0.01335
D-3	0.0001	0.00003	0	0.00013	0.00118	0.00940
D-4	0.00015	0.000008	0	0.00026	0.00115	0.00889
D-5	0.0001	0.00004	0	0.00014	0.00144	0.01403

TABLE 4

Concentration of Principal Species for "H" Series

Part c

Concentration Before Reaction in Moles per Liter

Run	en	Hen^+	H_2en^{++}
H-1	$2.46 \ 10^{-5}$	0.019181	0.023092
H-4	$2.47 \ 10^{-5}$	0.019223	0.023138
H-5	$2.47 \ 10^{-5}$	0.019167	0.023076
H-6	$2.47 \ 10^{-5}$	0.019210	0.023120
H-7	$2.47 \ 10^{-5}$	0.019223	0.023138
H-8	$2.47 \ 10^{-5}$	0.019223	0.023138

Concentration After Reaction in Moles per Liter

Run	en	Hen^+	H_2en^{++}	$AgHen^{++}$	$Ag_2(en)_2^{++}$	$Ag(en)^+$
H-1	$3.4 \ 10^{-7}$	0.002370	0.02072	0.01200	0.00102	0.00039
H-4	$3.5 \ 10^{-7}$	0.002399	0.02074	0.01202	0.00102	0.00039
H-5	$3.4 \ 10^{-7}$	0.002359	0.02072	0.01200	0.00102	0.00039
H-6	$3.5 \ 10^{-7}$	0.002390	0.02073	0.01202	0.00102	0.00039
H-7	$3.5 \ 10^{-7}$	0.002399	0.02074	0.01202	0.00102	0.00039
H-8	$3.5 \ 10^{-7}$	0.002399	0.02074	0.01202	0.00102	0.00039

TABLE 5

Heat Corrections and Overall Heat in Calories for Each Run

Run	Calorimeter Heat	$AgNO_3$ Heat	Hen^+ Heat	H_2en^{++} Heat	Heat of Reaction
system a.					
L-1	-110.57	80.76	7.15		-198.48
L-2	-129.81	96.35	8.62		-234.78
L-3	-109.24	81.21	7.20		-197.65
L-5	-103.69	77.52	6.85		-188.06
L-6	-102.56	76.46	6.76		-185.78
L-7	-103.19	76.65	6.80		-186.64
system b.					
C-6	-174.82	134.68	21.54		-331.04
D-1	-282.19	215.67	27.46		-525.32
D-3	-201.84	153.60	23.28		-378.72
D-4	-195.57	147.40	21.96		-264.93
D-5	-299.78	227.07	28.28		-555.13
system c.					
H-1	145.07	282.61	80.32	76.04	-293.90
H-4	134.24	273.12	80.04	76.71	-295.63
H-5	129.62	265.61	80.32	76.57	-291.88
H-6	144.20	278.62	80.03	76.51	-290.96
H-7	130.98	269.36	80.03	76.71	-295.12
H-8	120.94	257.36	80.03	76.71	-293.16

TABLE 6

Thermodynamic Data for the Indicated Reactions

Reaction

1. $Ag^+ + en = Ag(en)^+$

2. $Ag^+ + 2en = Ag(en)_2^+$

3. $2Ag^+ + 2en = Ag_2(en)_2^{++}$

4. $Ag^+ + Hen^+ = AgHen^{++}$

Derived relationships:

5. $Ag(en)^+ + en = Ag(en)_2^+$

6. $2Ag(en)^+ = Ag_2(en)_2^{++}$

7. $Ag_2(en)_2^{++} + 2en = 2Ag(en)_2^+$

Reaction	$-\Delta F$(kcal./mole)	$-\Delta H$(kcal./mole)	$-\Delta S$(e.u.)
1.	6.4 ± 0.14	25 ± 5	60 ± 20
2.	10.5 ± 0.14	13.016 ± 0.02	8.43 ± 0.3
3.	18.0 ± 0.3	25.57 ± 0.5	25.21 ± 2
4.	3.0 ± 0.06	14.45 ± 2	38.3 ± 20
5.	4.1 ± 0.2	-12.0 ± 5	-54 ± 20
6.	5.2 ± 0.3	-24.4 ± 8	-99 ± 40
7.	3.0 ± 0.4	0.46 ± 0.5	-8.4 ± 2

SUMMARY

A solution calorimeter was constructed. The temperature measuring device used thermistors as the temperature sensitive elements. The heat capacity was determined by electrical calibration. The heats for the following reactions were determined:

1. $Ag^+ + en = Ag(en)^+$

2. $Ag^+ + 2en = Ag(en)_2^+$

3. $2Ag^+ + 2en = Ag_2(en)_2^{++}$

4. $Ag^+ + Hen^+ = AgHen^{++}$

From the equilibrium constants reported by Schwarzenbach (6), the free energies and entropies were calculated; thereby, providing insight into the nature and structures of the reactants.

	-ΔF (kcal./mole)	-ΔH (kcal./mole)	-ΔS (e.u.)
1.	6.4 ± 0.14	25 ± 5	60 ± 20
2.	10.5 ± 0.14	13.016 ± 0.02	8.43 ± 0.3
3.	18.0 ± 0.13	25.57 ± 0.5	25.2 ± 2
4.	3.0 ± 0.6	14.45 ± 2	38.3 ± 10

The data indicate that the $Ag(en)^+$ is chelated. Data for $AgHen^{++}$ is anomalous. The data for $Ag(en)_2^+$ and $Ag_2(en)_2^{++}$ are in line with work done by others (1,27).

BIBLIOGRAPHY

1. W. C. Fernelius, C. R. Bertsch, and B. P. Block, J. Phys. Chem., 62, 444 (1958).

2. M. Campolini, P. Paoletti, and L. Sacconi, J. Chem. Soc., 1960, 4553.

3. W. C. Nicholas and W. C. Fernelius, J. Phys. Chem., 65, 1047 (1961).

4. L. H. Jones and R. A. Penneman, J. Chem. Phys., 22, 965 (1954).

5. S. Ahrland and J. Chatt, Chemistry and Industry, 1955, 96.

6. G. Schwarzenbach, H. Ackermann, B. Maisson and G. Anderegg, Helv. Chim. Acta, 35, 2337 (1952).

7. G. Schwarzenbach, C.A., 47, 7362b, (1953), ibid, 36, 23, (1953). Original not seen.

8. G. Schwarzenbach, H. Ackermann and B. Maisson, ibid, 35, 2333 (1952).

9. G. Schwarzenbach, ibid, 35, 2343 (1952).

10. G. Newman and D. Powell, J. Chem. Soc., 1962, 3477.

11. C. Luca and V. Armeanu, Z. physik. Chem (Leipzig), 217, 389 (1961).

12. C. Luca and V. Armeanu, ibid, 218, 149 (1961).

13. C. M. Harris and H. N. S. Schafer, C.A., 47, 1927a (1953), J. Proc. Roy. Soc. New South Wales, 85, 142 (1952). Original not seen.

14. P. Pfeiffer, E. Schmitz and A. Böhm, Z. anorg. u. allgem. Chem., 270, 287 (1952).

15. R. Stokes and H. Walton, J. Am. Chem. Soc., 76, 3327 (1954).

16. B. Hibbard and F. Schmidt, J. Am. Chem. Soc., 77, 225 (1955).

17. S. Bruckenstein and L. Mukheejee, J. Phys. Chem., 64, 1601 (1960).

18. T. Muniyappen and B. Anjaneyalee, C.A., 52, 9724i (1958), Proc. Indian Acad. Sci., 46A, 454, (1957). Original not seen.

19. J. M. Sturdevant in "Physical Methods of Organic Chemistry," A. Weissberger, Ed. Vol. I, Part I, Interscience Publishers, Inc., New York, New York, 1949, Ch. XIV.

20. F. D. Rossini, "Experimental Thermochemistry," Interscience Publishers, Inc., New York, New York, 1956, Chs. 1, 2, 3, 11 and 14.

21. F. H. Spedding and C. F. Miller, J. Am. Chem. Soc., 74, 3158 (1952).

22. R. L. Graham and L. G. Hepler, ibid, 78, 4846 (1956).

23. J. E. McDonald, J. R. King and J. W. Cobble, J. Phys. Chem., 64, 1345 (1960).

24. H. C. Dickinson, Bull. Natl. Bur, Standards, 11, 189 (1915).

25. R. L. Graham and L. G. Hepler, J. Am. Chem. Soc., 80, 3538, (1958).

26. T. Davies, S. S. Singer and L. A. K. Staveley, J. Chem. Soc., 1954, 2304.

27. W. S. Fyfe, J. Chem. Soc., 1952, 2023.

28. S. P. Datta and A. K. Grzybowski, J. Chem. Soc., 1959, 1091.

29. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Circular of the National Bureau of Standards, United States Government Printing Office, Washington, D. C., 1952.

ABSTRACT

A solution calorimeter was constructed with a temperature range of one degree in the region of 25°C. The precision of the calorimeter was about 0.3%. The heats of reaction of the following silver ethylenediamine complexes were measured: $Ag(en)^+$, $Ag_2(en)_2^{++}$, $Ag(en)_2^+$, and $AgHen^{++}$. With the formation constants determined by Schwarzenbach (6), the respective entropies were calculated. Enthalpy and entropy data for the $Ag(en)^+$, $Ag_2(en)_2^{++}$, and $Ag(en)_2^+$ complexes are reasonable. The data for the $AgHen^{++}$ complex seems anomalous.