A SOLUTION CALORIMETRIC STUDY OF ION-PAIRING

AND COMPLEX FORMATION EQUILIBRIA

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GLOSSARY OF SELECTED SYMBOLS

α – Concentration of triiodide ion

β_2 – $K_1 \cdot K_2$ for $Tl(I_3)_2^-$ formation

C_1 – Analytical iodide concentration

C_2 – Analytical iodine concentration

C_K – Analytical potassium (I) concentration

C_m – Analytical thallium (II) concentration

γ – Activity coefficient of an univalent ion

δ – Concentration of $Tl(I_3)_2$

ΔG – Gibbs free energy of reaction

ΔG^o – Standard Gibbs free energy of reaction

ΔH_c – Conditional enthalpy of reaction

ΔH^o – Standard enthalpy of reaction

I – Ionic strength

$K\Omega$ – 1000 ohms

K_t – Thermodynamic equilibrium constant

K_3 – Equilibrium constant for triiodide formation

K_4 – Equilibrium constant for $K \cdot \cdot I_3$ ion-pair formation

Q_{tot} – Experimentally measured heat

$Q_{Reaction}$ – Heat due to the reaction of interest

Q_1 – Apparent heat due to a titrant temperature difference

GLOSSARY OF SELECTED SYMBOLS (Continued)

Q_{Hdil} — Heat of dilution of perchloric acid

Q_{Kdil} — Heat of dilution of potassium iodide

R — Ideal gas law constant

T — Absolute temperature

ΔS — Entropy of reaction

ΔS^o — Standard entropy of reaction

ω — Concentration of $K \cdot \cdot I_3$ ion-pairs

CHAPTER I

INTRODUCTION

This study consists of two major divisions, first the design and
construction of a precision titration calorimeter and second the appli-
cation of this calorimeter to several chemical systems, especially those
involving the formation of ion pairs in aqueous solution.

The Calorimeter

It was determined that the calorimeter to be constructed needed to
be capable of measuring very small heats on the order of 200 millicalo-
ries and to be capable of producing very accurate thermograms from con-
tinuous addition of titrant. The ability to accurately measure small
heats was necessitated by the small heats generally associated with ion-
pairing of the species to be studied and with the relatively low solubil-
ities associated with several of these species. The production of
accurate thermograms in general would make available the advantages of
titration calorimetry.

There are three major values to be obtained from titration calori-
metry. First it allows in one experimental run the determination of the
enthalpy change as a function of the degree of the completeness of the
reaction. Theoretically each point on the thermogram generated corre-
sponds to an experimental run in a conventional reaction calorimeter.
Second, as thermometric titrations have been used as analytical tools

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for a long time they can still be used in that manner so concentrations of reactants, numbers of reactions, and types of reactants may be determined from end points and slopes of the various parts of the thermogram (1,2). Third, in some cases, thermometric titration provides a method for determining free energy and entropy changes in addition to enthalpy change from a single titration thermogram as long as heat of dilution data for the titrant is available (3).

Such a calorimeter was constructed and employed in a series of calorimetric studies of ion-pairing and complexation reactions. A detailed description of the calorimeter is given in Chapter II.

<div align="center">Calorimetric Studies</div>

The formation of triiodide from iodine and iodide was one of the first complexation reactions known and has been studied from the time of Gay-Lussac (4) by large numbers of well known experimental chemists by techniques including solubility, conductivity, distribution, phase rule, potentiometry, spectrometry, and calorimetry (5-33). More recently the bonding and structure have been the subject of theoretical calculations (34,35). In the light of these past studies the question of why further study should be proposed for such a well known and fully explored reaction naturally arises. The answer is that this "well known" system is still one in which there is poor general agreement about the species present, the reactions taking place, and of course, the thermodynamic parameters of the system. If the concentrations are low, most experimenters agree that the simple reaction

$$I^- + I_{2\,(aq)} \rightleftharpoons I_3^- \qquad\qquad (1.1)$$

is adequate to describe the system but when concentrations approach 0.1

N there is a decrease in the apparent equilibrium constant which indi-

cates that some higher complex is present (28).

Foote and Chalker (21) carried out a phase rule study of the system

iodine–potassium iodide–water at 25° and reported three invariant solu-

tions which they considered were in equilibrium with 1. KI and KI_3, 2.

KI_3 and KI_7, and 3. KI_7 and I_2. Pierce and Eversole (36) used distribu-

tion between carbon tetrachloride and aqueous solutions of barium iodide

and concluded that only the triiodide was present in dilute solutions un-

saturated with iodine while a mixture of triiodide and pentaiodide was

present in solutions saturated in iodine. The presence of polyiodides

of the form $I^-\cdot I_{2n}$ have been the structures usually called on to explain

the variation with concentration of the apparent triiodide equilibrium

constant. The preference for polyiodides of this type has been support-

ed by studies in nonaqueous solvents such as those by Dawson and co-

workers (37) who found evidence of polyiodides as high as I_9^-. More re-

cently Davies and Gwynne (26) employing a distribution method proposed

the formation of I_6^{2-} from 2 I_3^- but Ramette and Sandford (31) in more

recent work still favor I_5^- as the major higher complex. Another possi-

ble complication was that most of the later studies were made in the

presence of an acid added to prevent hydrolysis of iodine (26,30,31).

Since this is a reaction that competes for iodine its suppression has

probably been useful but the value recorded by Bray and Mae Kay (13) of

the hydrolysis constant was low and the concentration of iodine was so

limited by solubility in all studies that this restriction was probably

a minor consideration (38). Determinations of the temperature coeffi-

cient of the reaction (1.1) have yielded values from -3.87 to -5.10 kcal

mol^{-1} for the enthalpy of complexing aqueous iodine with iodide ion. Indeed Ramette and Sandford (31) concluded that both the free energy and enthalpy changes found in the literature seemed dependent upon the particular technique used.

It was proposed that this study would use the advantages of the newly constructed calorimeter. Besides the advantages inherent in titration calorimetry the ability of the calorimeter to measure small heats could be used by starting at low concentrations and working upward in concentration to determine enthalpies and equilibrium constants for reactions taking place in dilute solution and moderately concentrated solutions up to approximately 1 M. It was felt that several other advantages over prior studies could be offered.

First, the development of lasers has made possible the determination of Raman spectra for ion-pairs and a study in this laboratory has indicated that a species present in solutions of iodine in potassium iodide is the potassium-triiodide ion-pair (39). This is a possibility not considered in prior studies although ion-pairs of potassium and iodates, bromates, chlorates, sulfates, ferrocyanide, and nitrates have been reported (40,41,42). Thus this study could perhaps determine if the new concept of the reaction

$$K^+ + I_3^- \rightleftharpoons KI_3 \qquad (1.2)$$

would more completely describe the higher complex (es) being formed in moderately concentrated species than would the types of polyiodides postulated before.

Second, prior calorimetric studies have been two step reactions in that solid iodine has been used (32,33). This means that the heat of

solution of iodine must be used as a correction to determine the heat of complex formation. One purpose of this study was to measure the heat of complex formation directly by mixing aqueous iodine with potassium iodide solution. Since this was necessarily to be done in dilute solution another advantage over prior calorimetric studies was possible in that activity coefficients and heats of dilution could be accurately obtained from Debye-Huckel Theory (43). Also in treating more concentrated solutions it was determined that dilution into water would displace the equilibrium sufficiently to allow measurement of ΔH for the reaction. This again included the advantage that no correction was necessary for heat of solution.

A calorimetric determination was also made to determine the solvent isotope effect (if any) for the formation of selected lanthanide mono-sulfate ion-pairs in D_2O versus H_2O. This became a question of special interest when ultrasonic relaxation kinetic studies and conductivity measurements by Farrow and Purdie (44) showed no solvent isotope effect on ΔG^o or the rate constants although Silber and co-workers (45) had reported solvent isotope effects of up to 6.0 for sulfate and anthranilate complexes of rare earths. The calorimetric study was undertaken to determine if ΔH and ΔS showed complimentary solvent isotope effects as is sometimes observed in weak acid ionizations (46).

A third study was made to determine the enthalpy of complexation of actinomycin D with a steroid which showed a capacity to multiply actinomycin D's antitumor activity by up to a factor of four in mice (47). This was an attempt to use the calorimeter to determine some of the chemical and thermodynamic properties which lead to this activity.

CHAPTER II

CALORIMETER DESIGN AND OPERATION

In order to meet the experimental requirements of a calorimeter capable of reproducibly measuring total heats of 200 millicalories in 50 milliliters of solution and also being able to produce accurate thermograms from continuous titration, several factors were considered essential in construction.

1. Low thermal conductance.

2. Low internal heat capacity (the heat capacity of the inner calorimeter vessel walls and insert).

3. High chemical resistance.

4. Thorough and rapid mixing.

5. Both heating and cooling for calibration and rapid operation.

6. Accurate maintenance of titrant at initial reactant temperature.

7. High sensitivity to temperature changes and low time delay in response to a temperature change.

8. Titration by a constant rate with delivery accurate to 0.001 ml.

9. Electrical stability and low noise to signal ratio.

10. Accuracy of 1% for a one calorie heat in 60 ml. of aqueous solution.

Thin walled Dewars were prepared as shown in Figure 1 for use as

$\frac{34}{28}$ GROUND GLASS JOINT

GLASS HOOK

SILVER FILM

.6 mm WALLS

EVACUATED

50 mL VESSEL   25 mL VESSEL
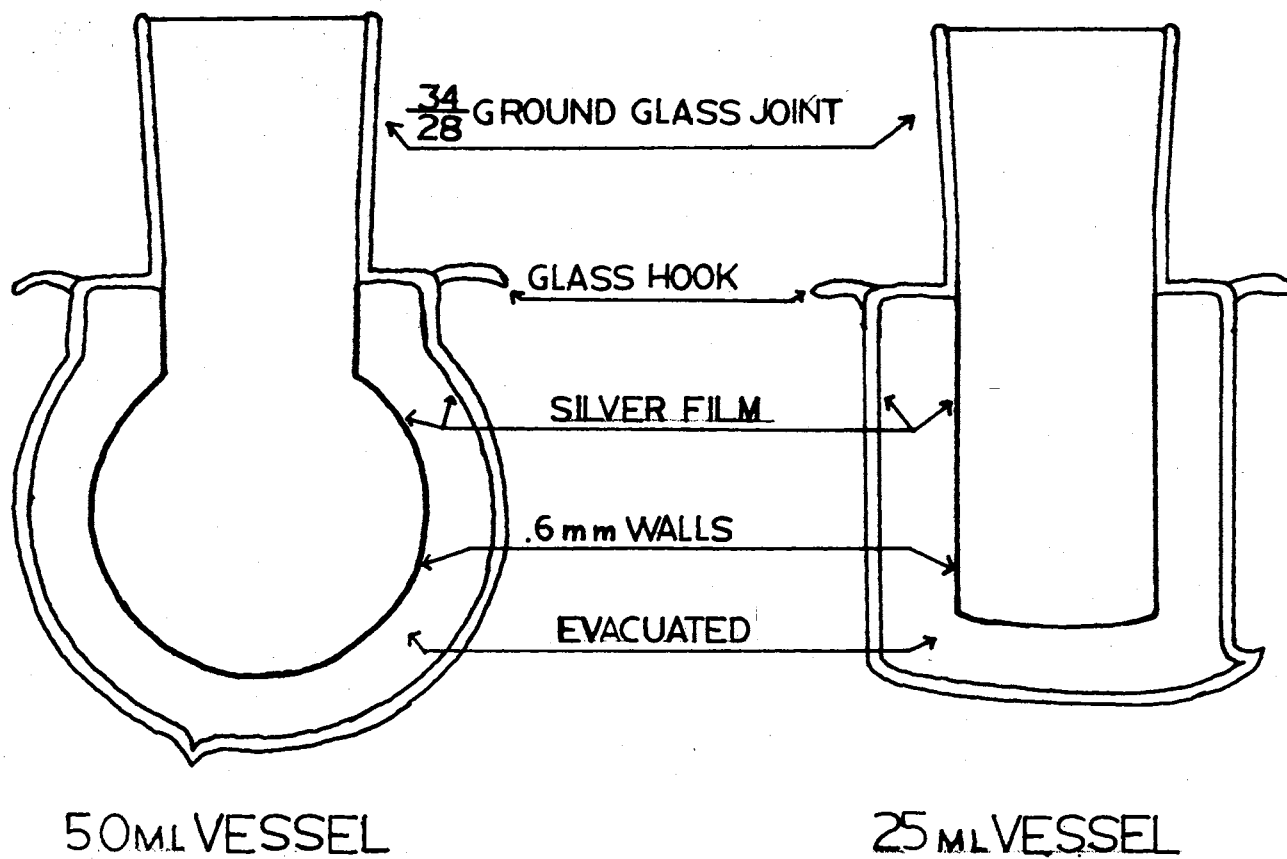
Figure I.   Calorimeter Dewars

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calorimeter vessels to meet the requirements for low thermal conductance and low internal heat capacity. Hutchinson and White (48) have compared the Newton's Law of Cooling modulus, for commercial Dewars to Dewars of 0.5 mm wall thickness and found a marked decrease in the modulus as shown in Table I.

TABLE I

A COMPARISON OF THIN-WALLED AND COMMERCIAL DEWARS

Type	Newton's Modulus
Commercial Dewar	0.0078 min^{-1}
0.5 mm Wall Dewar	0.0012 min^{-1}

This low heat leakage modulus is especially important in that it allows the calorimeter to be treated as essentially adiabatic over the period of titration.

Two pairs of calorimeter inserts were made as shown in Figure 2. One set was lucite and the second set glass. The lucite proved to have the lower internal heat capacity and was used in the lanthanide sulfate study but because of the corrosive nature of iodine solutions the glass inserts were used for the iodine studies. The inserts were made as light in weight as practical to reduce internal heat capacity which can be a problem in two ways. First, it reduces the observed temperature rise and second, since the solution must come to thermal equilibrium with the materials in the reaction vessel, there may be a significant time delay in reaching this equilibrium temperature. With the small heats involved in several of these studies this problem was compounded
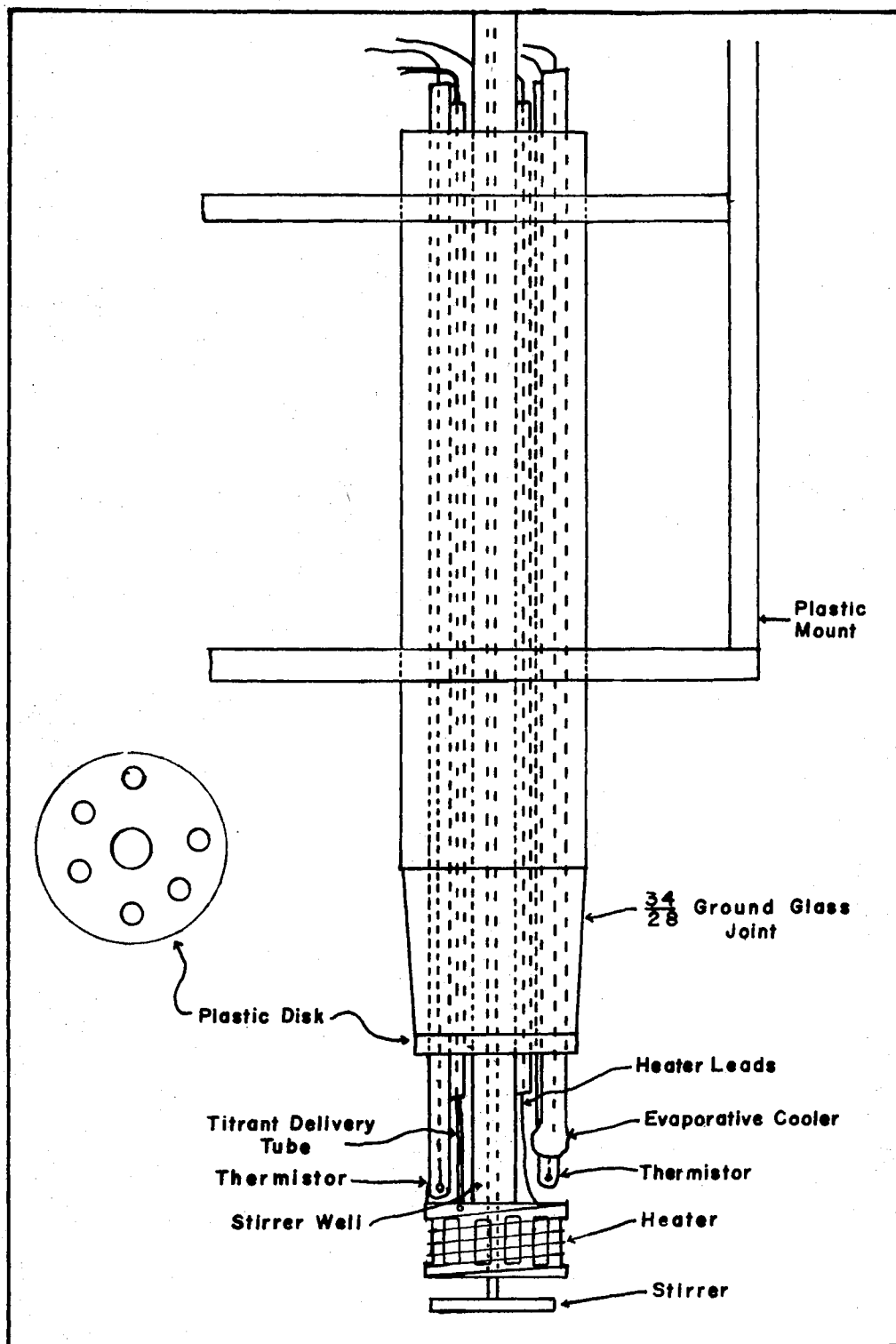
Figure 2. Calorimeter Inserts

due to the fact that the heat flow is proportional to the difference in temperature and this difference was often small. Normally this small heat flow would go unnoticed but in several experiments the signal was very highly amplified because the total heat being evolved was small and the heat flow to the internal heat capacity became easily observable. With heats of 200 millicalories, 20 to 25 seconds could pass before equilibrium was restored even with the steps taken to lower internal heat capacity. At one calorie the equilibrium was restored in approximately six seconds and this heat flow was usually only a very small correction.

High chemical resistance was extremely important because of the corrosive nature of the iodine solutions. It soon became apparent that materials such as epoxy, lucite, and polyethelene plastics were not suitable in iodine studies. The glass inserts containing the heater, cooler, and thermistor probes were used in conjunction with glass and teflon delivery tubes. The syringe was a Hamilton "Gastight" 2.5 ml. syringe (no. 1002) with a teflon piston head.

Rapid stirring was achieved using Corning LM-2 vibrating stirrers. These proved to have good stability in stirring rate and to be very efficient stirrers.

The use of both an electrical heating system and an enclosed evaporative cooling system enabled a rapid readjustment to the starting conditions at which the temperature of the reactants was that of the titrant for maximum use of the calorimeter. Since the electrical heating system was also used to calibrate the heat capacity before and after each titration care was taken to assure its proper function. The heater element was 80 cm. length of 40 gauge platinum wire which had a resistance of

16.979 ohm. The current was delivered by a Sargent Coulometric Current Source Model IV and the emf across a 7.667 ohm wire wound resistor was monitored by use of a Rubicon 1.5 volt potentiometer. Cooling was accomplished by evaporating acetone in a thin walled glass bulb immersed in the reactant solution by passing a stream of nitrogen over it. See Figure (2).

Both the titrant and the reaction vessels were placed in an 80 liter water bath which was insulated by a 7.5 cm layer of polyurethane foam. The temperature of the titrant and the environment for the calorimeter vessels was maintained at a temperature of $25 \pm 0.005^{\circ}C$ with a drift of less than 0.002° for the duration of any of the experiments by use of a Model PT-1 stainless steel temperature probe in conjunction with a Precision Temperature Controller and Heater–Cooler Model PTC-1000a (Tronac Inc., Orem, Utah). The temperature difference between the titrant and the reactants was a very important factor since the introduction of 2 ml. of water only 0.01° warmer than the reactants would introduce an extra 20 millicalories. If no correction was made this would amount to a 10% error in some of the experiments included in this study. The temperature of the titrant was monitored by measuring the resistance of a 15 KΩ thermistor (Fenwall GB 42 MMI2) to $\pm$ 1 ohm on a Leeds and Northrup Conductivity Bridge Model 4666. This should correspond to a temperature uncertainty of $\pm 0.0016^{\circ}$ for the titrant. During the experiment the temperature of the reactants was monitored for comparison with the titrant temperature by use of a 30 KΩ thermistor (Yellow Springs Instrument Co. no. 44008) mounted in a thin-walled glass probe with a drop of mineral oil for thermal contact.

The thermogram itself was produced from the out of balance signal

produced by a 30 KΩ thermistor probe identical with the one above used as one arm of a Wheatstone bridge. This second thermistor was balanced against a 27 KΩ standard resistor which was placed in the air cavity of the 80 liter thermostat bath. The Wheatstone bridge circuit is a slight modification of one recommended by Nancollas (49). See Figure 3. The out of balance signal was fed to an intermediate dc amplifier/nulldetector (Keithley Model 155) and displayed on a Sargent SRG chart recorder.

The 2.5 ml. Hamilton syringe which was filled directly from a titrant reservoir submerged in the thermostat, see Figure 4, was used for delivery of titrant. The syringe was driven mechanically by a gear driven variable speed motor (INSCO Corp.). The delivery motor was controlled by a circuit devised by Hall, Simpson, and Motolla (50) as shown in Figure 5. Calibration by delivery of mercury showed a delivery of $2.633 \pm 0.0009 \times 10^{-2}$ ml. per sec. at the fastest delivery speed.

Electrical noise was greatly reduced by proper grounding of the negative side of the circuit and by shielding the battery and battery leads of the Wheatstone bridge in a Faraday cage. Electrical noise was reduced sufficiently to allow amplification of a display of 200 millicalories so that it caused a deflection across the entire recorder sheet. The signal to noise ratio was still acceptable but at this signal amplification the heating due to the stirring motor caused the deflection to take place so rapidly just from stirring heat that no useful information could be obtained. This is not to say that 200 millicalories could not be measured as a fraction of the total chart width at a lower amplification but it was not possible to use amplification so high that 200 millicalories deflection occupied the full chart width. The calorimeter was easily converted to differential operation but the added electrical noise
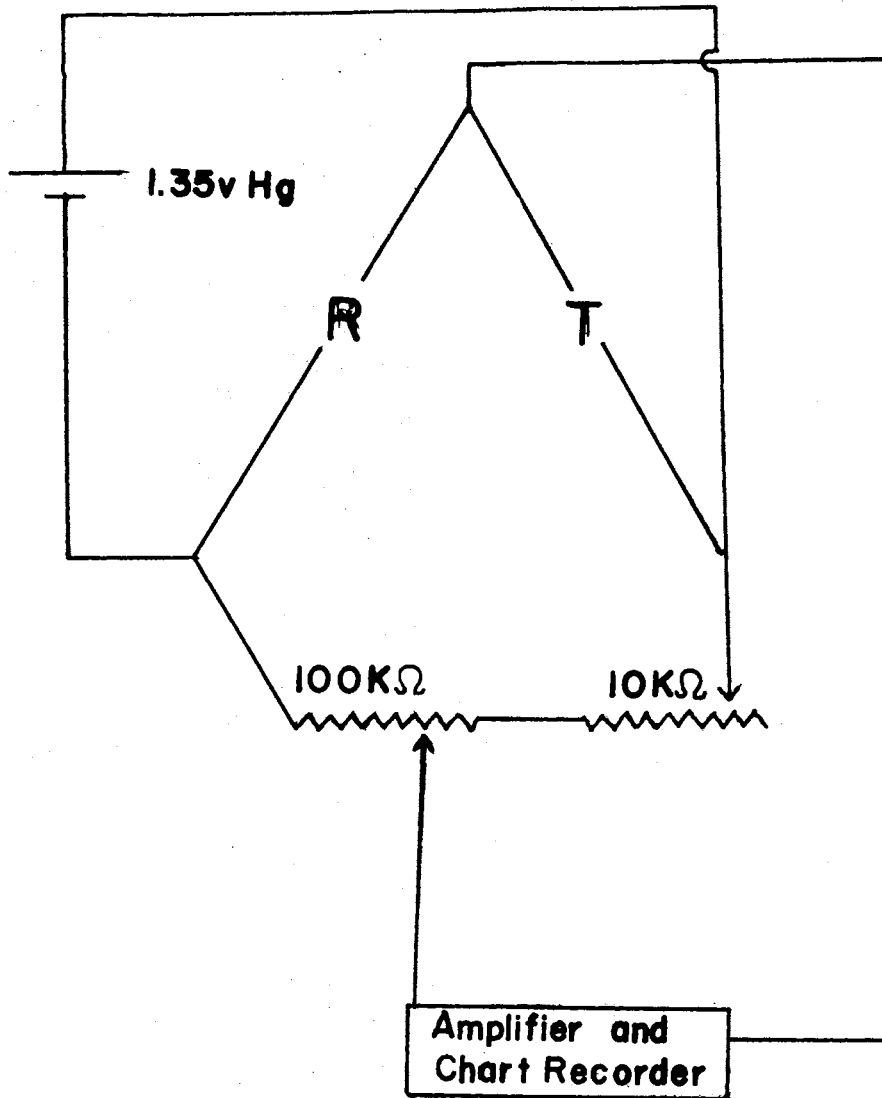
Figure 3. Wheatstone Bridge Circuit
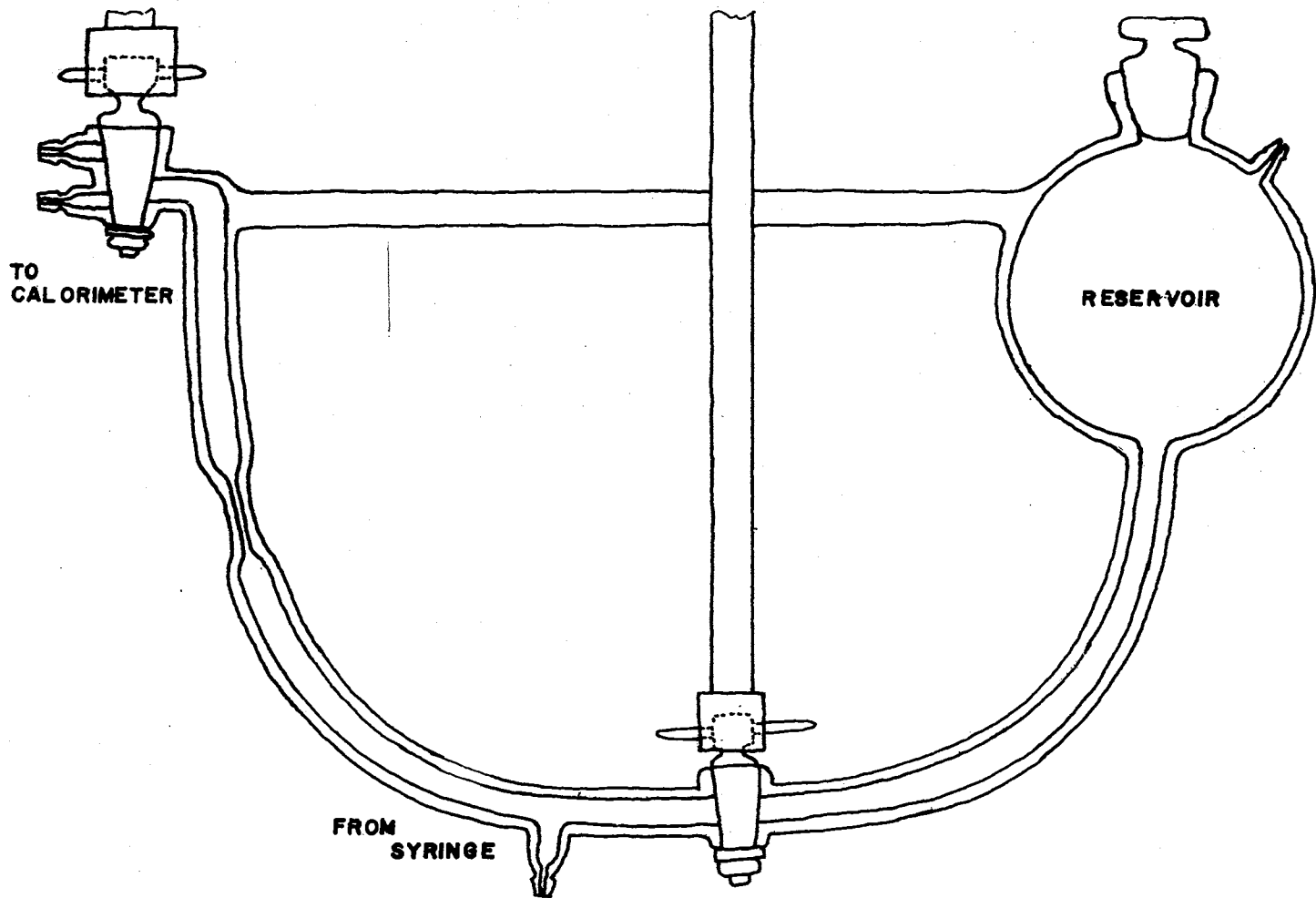
Figure 4. Titrant Reservoir
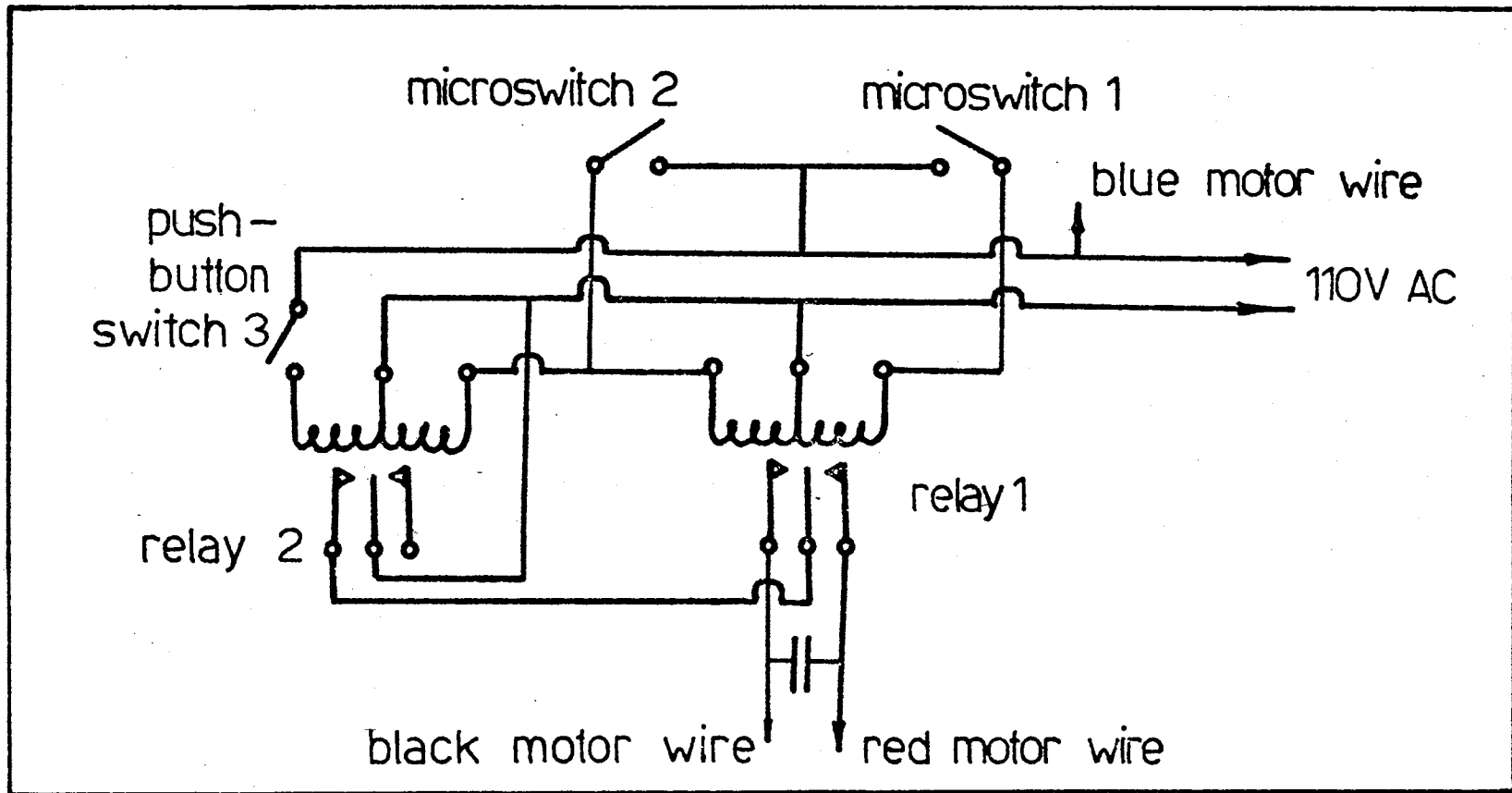
Figure 5. Delivery Motor Control Circuit

of the two thermistors made operation in this mode little better than single vessel operation for high amplification. In most cases the calorimeter was run nondifferentially and at amplification no greater than that which caused a heat of 500 millicalories to show a deflection across the total chart width.

Performance of the calorimeter was checked by the measurement of the heat of ionization of water. A value of 13.32 kcal. mol^{-1} was obtained which agrees to within 0.1% of the accepted literature value (51).

CHAPTER III

TRIIODIDE FORMATION

The direct determination of the heat of the reaction when potassium
iodide is added to iodine solution was chosen as the first in a series
of studies of triiodide and higher polyiodide complex formation. Sever-
al factors were considered in this choice. Solubility limited the con-
centration of iodine to approximately 10^{-3}M, the potassium iodide con-
centration was also restricted to about 5×10^{-3}M, and even with the
presence of 10^{-2}M HClO$_4$ the activity coefficients and other solution
parameters could be accurately determined by an extended form of the
Debye-Huckel limiting law. Also of major importance, these low concen-
trations made formation of possible higher complexes unimportant allow-
ing a direct measurement of the enthalpy of the triiodide reaction
alone. A survey of the literature produced no record of this type of
study having been made as the usual method of study has involved dis-
solving solid iodine into a potassium iodide solution (31,32). This
required several corrections, which must have introduced additional un-
certainties into the data, before even a conditional ΔH could be calcu-
lated. It should be admitted that the direct determination had a major
disadvantage in that there was only a small amount of heat produced in a
large heat capacity. Because of this the means of determining the tem-
perature change had to be very sensitive and considerations such as in-
ternal heat capacity in the calorimeter insert and vessel became

important.

Experimental

The calorimeter vessels used were the 50 ml. Dewars fitted with plastic calorimeter inserts. The iodine was purified by triple sublimation of Baker Analyzed reagent grade material. Potassium iodide was also Baker Analyzed reagent grade. Solutions were prepared by weight and the iodine content checked after the calorimetric titrations by titration with standardized H_3AsO_3 (52). The iodine solution was 1.159 x 10^{-3}M in iodine and 1.0 x 10^{-2}N in $HClO_4$, the latter being introduced to prevent iodine hydrolysis to HI and HOI (13,14). The potassium iodide solution was 5.4334 x 10^{-3}F.

Treatment of Data

The thermograms were treated strictly as incremental additions because of the low signal to noise ratio. This was caused primarily because the pen deflections were so small that the signal had to be highly amplified. As incremental additions the thermograms were first analyzed by a graphical method (53). This is illustrated in Figure 6. The anterior base line was extrapolated linearly and the posterior line was extrapolated from the straight line portion following a curved section which appeared just after completion of the titration. This curved "relaxation" portion was caused by equilibration of the solution with the internal heat capacity of the calorimeter vessel as discussed in Chapter II. The steady state portion of the thermogram was extended to establish the beginning of the titration because of the thermistor lag in registering the heat change. At a distance corresponding to half the
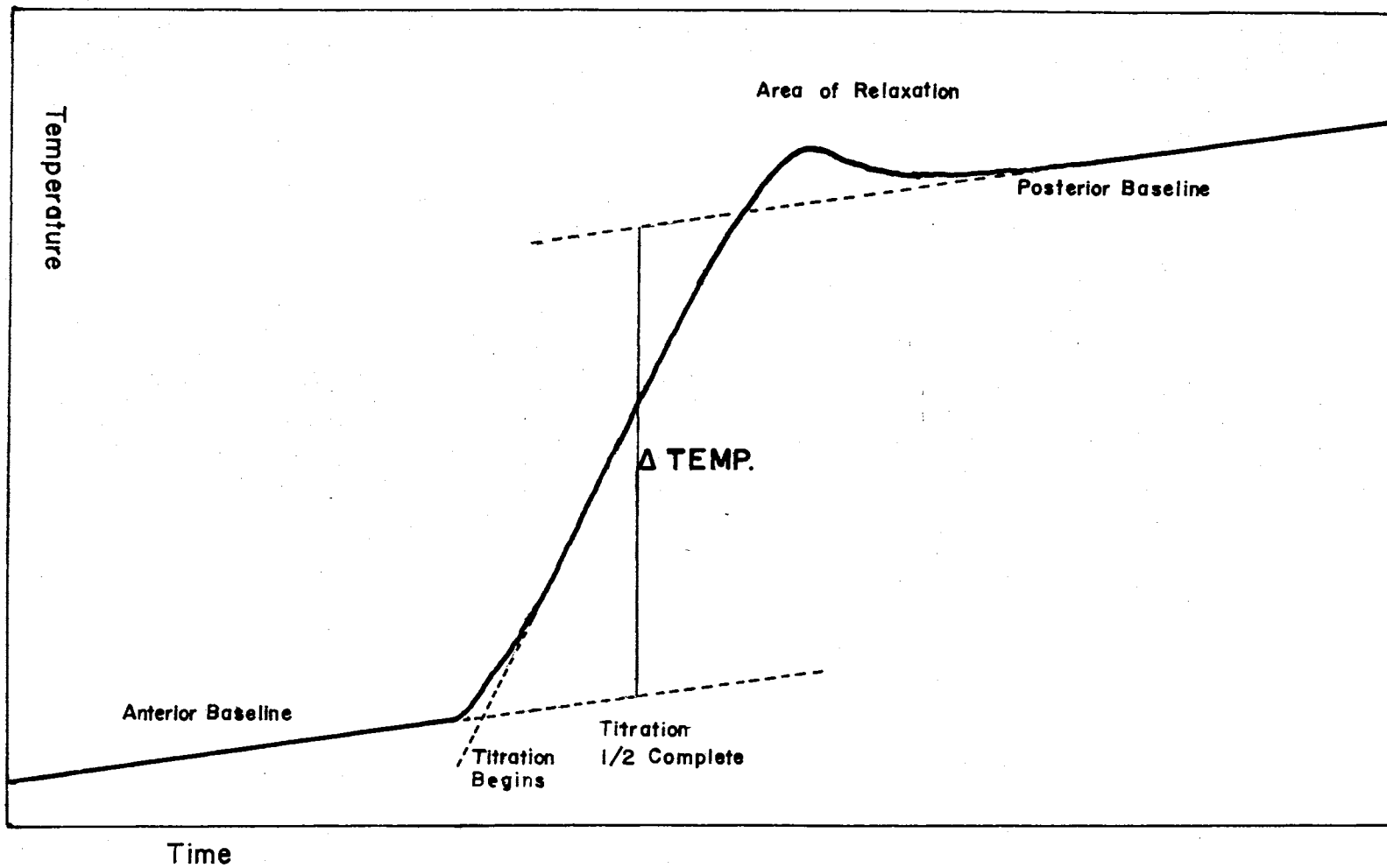
Figure 6. Graphical Treatment of Thermograms

time of the titration the distance between the two base lines was taken
to represent the change in temperature in chart units. The use of this
average value assumes that the change in the slope of the base lines was
linear with addition of titrant. This was based on the assumption that
the heat capacity changed linearly with the addition of titrant and that
the calorimeter was so nearly adiabatic that the higher (or lower) tem-
perature caused by the reaction did not change the slope of the base
lines through heat loss. This last assumption was well verified by ex-
amination of a thermogram produced by adding a known amount of heat
through the electric heaters. The anterior and posterior base lines
were parallel.

A second method employed to obtain the correct temperature change
due only to the heat of the titration was the method of Regnault–
Pfaundler (53). A computer program was prepared which took the experi-
mental thermogram in a digitalized form, computed the best base lines by
linear least squares, and applied the Regnault–Pfaundler formulas. The
results of the graphical and the calculational methods were essentially
the same. The mathematic treatment would probably be more important in
the case of a less satisfactorily adiabatic condition as it includes a
correction for increased cooling during the posterior portion.

After the temperature change was available an average heat capacity
was needed to determine the total titration heat (Q_{tot}). This was ob-
tained in each case by determining the heat capacity before and after
each titration by electrical calibration. The electrical heating thermo-
grams were treated by the graphical and Regnault–Pfaundler methods as
shown above for a temperature change which was then divided into the
amount of heat introduced to give the heat capacity in calories per

chart space. The average value of the heat capacity before and after addition was taken as the heat capacity of the system during the titration.

Another important experimental variable was the difference in the temperature of the titrant and the solution in the reaction vessel at the start of the titration. These temperatures were measured as mentioned in Chapter II by separate thermistors in the thermostat bath and in the reaction vessel. A correction was made for any difference in temperature by considering the titrant to have the same heat capacity as water and determining the amount of heat necessary (Q_1) to bring the titrant temperature exactly to the reactant temperature at the beginning of the reaction.

The last two experimental variables considered were the heat of dilution of $HClO_4$ (Q_{Hdil}) and the heat of dulution of KI (Q_{Kdil}). These were available from the National Bureau of Standards listing (54). Since

$$Q_{tot} = Q_{Reaction} + Q_1 + Q_{Hdil} + Q_{Kdil} \qquad (3.1)$$

it can be said that

$$Q_{Reaction} = Q_{tot} - Q_1 - Q_{Hdil} - Q_{Kdil} \qquad (3.2)$$

At the low concentrations used formation of higher complexes should be unimportant and the simple equilibrium

$$I^- + I_2 \rightleftharpoons I_3^- \qquad (3.3)$$

should be sufficient to describe the system. Because conditions of the study prevented a direct determination of the equilibrium constant, the

value from G. Daniele (30), K_t = 723 at $25^\circ C$, which was obtained by

spectrophotometry of dilute solutions in $10^{-3}M$ $HClO_4$, was taken to be

the most reliable.

The equilibrium constant for I_3^- formation is therefore:

$$K_3 = 723 = \frac{[I_3^-]\, \gamma}{[I^-][I_2]\, \gamma} \tag{3.4}$$

Activity coefficients for the monovalent ions were assumed to be equal

and thus to cancel and the activity coefficient of the uncharged iodine

was set equal to one. Given the following definitions:

$$C_1 = \text{analytical } [I^-]$$

$$C_2 = \text{analytical } [I_2]$$

$$\alpha = [I_3^-]$$

and the mass balance equations

$$[I^-] = C_1 - \alpha \tag{3.5}$$

$$[I_2] = C_2 - \alpha \tag{3.6}$$

Equation (3.4) was written as

$$\alpha^2 - (C_1 + C_2 + \frac{1}{K_3})\, \alpha + C_1 C_2 = 0 \tag{3.7}$$

which was easily solved for α. The conditional enthalpy of formation

of I_3^-, ΔH_c, is calculated from

$$\Delta H_c = \frac{Q_{Reaction}}{\alpha(\text{Volume of reactant solution})} \qquad (3.8)$$

ΔH^o, the standard enthalpy change, was obtained from ΔH_c by correcting the conditions to zero ionic strength as illustrated in the following Born-Haber cycle.

$$\begin{array}{ccccccccccc}
HClO_4 & + & I_2 & + & I^- & + & K^+ & \xrightarrow{\;\Delta H_c\;}_{I\neq 0} & I_3^- & + & K^+ & + & HClO_4 \\
\downarrow{\scriptstyle \Delta H_{Hdil}} & & \downarrow{\scriptstyle \Delta H_{I_2dil}\approx 0} & & \downarrow{\scriptstyle \Delta H_{I^-dil}} & & \downarrow{\scriptstyle \Delta H_{K^+dil}} & & \uparrow{\scriptstyle -\Delta H_{I_3^-dil}} & & \uparrow{\scriptstyle -\Delta H_{K^+dil}} & & \uparrow{\scriptstyle -\Delta H_{Hdil}} \\
HClO_4 & + & I_2 & + & I^- & + & K^+ & \xrightarrow{\;\Delta H^o\;}_{I=0} & I_3^- & + & K^+ & + & HClO_4
\end{array}$$
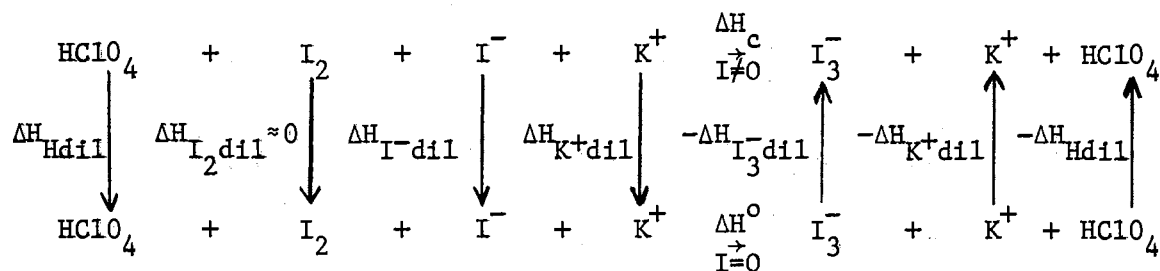
Proceeding anticlockwise the cycle shows

$$\Delta H_{I^-dil} + \Delta H^o - \Delta H_{I_3^-dil} = \Delta H_c \qquad (3.9)$$

Since the ionic strength was low the Debye-Huckel Limiting Law gave assurance that $\Delta H_{I^-dil} \approx \Delta H_{I_3^-dil}$ and therefore $\Delta H_c = \Delta H^o$ in this particular case. From the equation relating standard free energy change and the formation constant

$$\Delta G^o = - RT \ln K_t \qquad (3.10)$$

and from the Gibb's free energy equation

$$\Delta S^o = \frac{\Delta G^o - \Delta H^o}{-T} \qquad (3.11)$$

The experimental data and values for the basic thermodynamic functions as well as literature comparisons are shown in Table II and Table III.

TABLE II

CALORIMETRIC DATA FOR TRIIODIDE FORMATION IN DILUTE SOLUTIONS

Q_{tot} cal.	Q_1 cal.	Q_{KIdil} cal.	Q_{Hdil} cal.	Final $[I_3^-]$ F.	ΔH^o kcal mol^{-1}	Titrant Vol. ml.
−.09874	.01331	−.0026	−.0002	2.033×10^{-5}	−4.06	1.120
.1337	.1762	−.0015	−.0001	9.92×10^{-6}	−4.12	.535
−.1115	.0009	−.0040	−.0003	2.926×10^{-5}	−3.69	1.887
					Average 4.0 ± .5[a]	

[a]Error limit is the approximation of σ, 1 standard deviation.

Also shown in Figure 7 and Figure 8 are examples of experimental titra-
tion thermograms and electrical heating thermograms. The agreement with
some of the latest values in the literature where work has been done at
low concentration tends to confirm that in dilute solution a model of
the system is now established. For higher concentrations Figure 9 taken
in part from Ramette and Sanford (31) clearly shows that the simple
model is inadequate.

TABLE III

A COMPARISON WITH LITERATURE VALUES

	ΔG^o kcal mol^{-1}	ΔH^o kcal mol^{-1}	ΔS^o e.u.	K_t
This Study	-3.9	-4.0	.2	723[a]
Reference (28)	-3.9[b]	-4.3		714
Reference (25)	-3.8[b]	-3.60		675
Reference (26)	-3.9[b]	-3.80		768
Reference (33)		-3.9		
Reference (30)	-3.9	-4.76	-2.88	723

[a]From Reference (30).

[b]Calculated by this author.
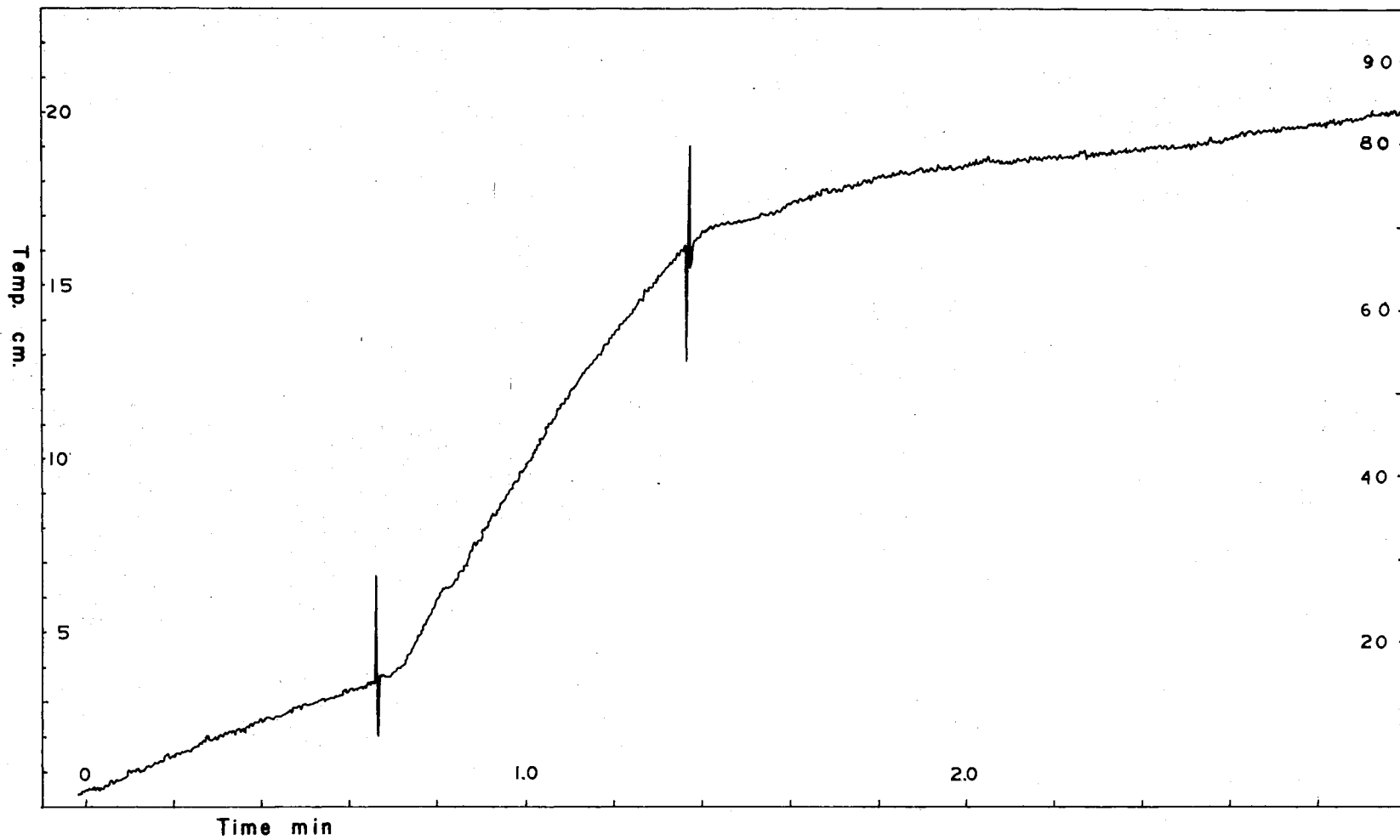
Figure 7. Titration Thermogram

Temp. cm.

90

80

60

40

20

0

1.0

2.0

Time min.
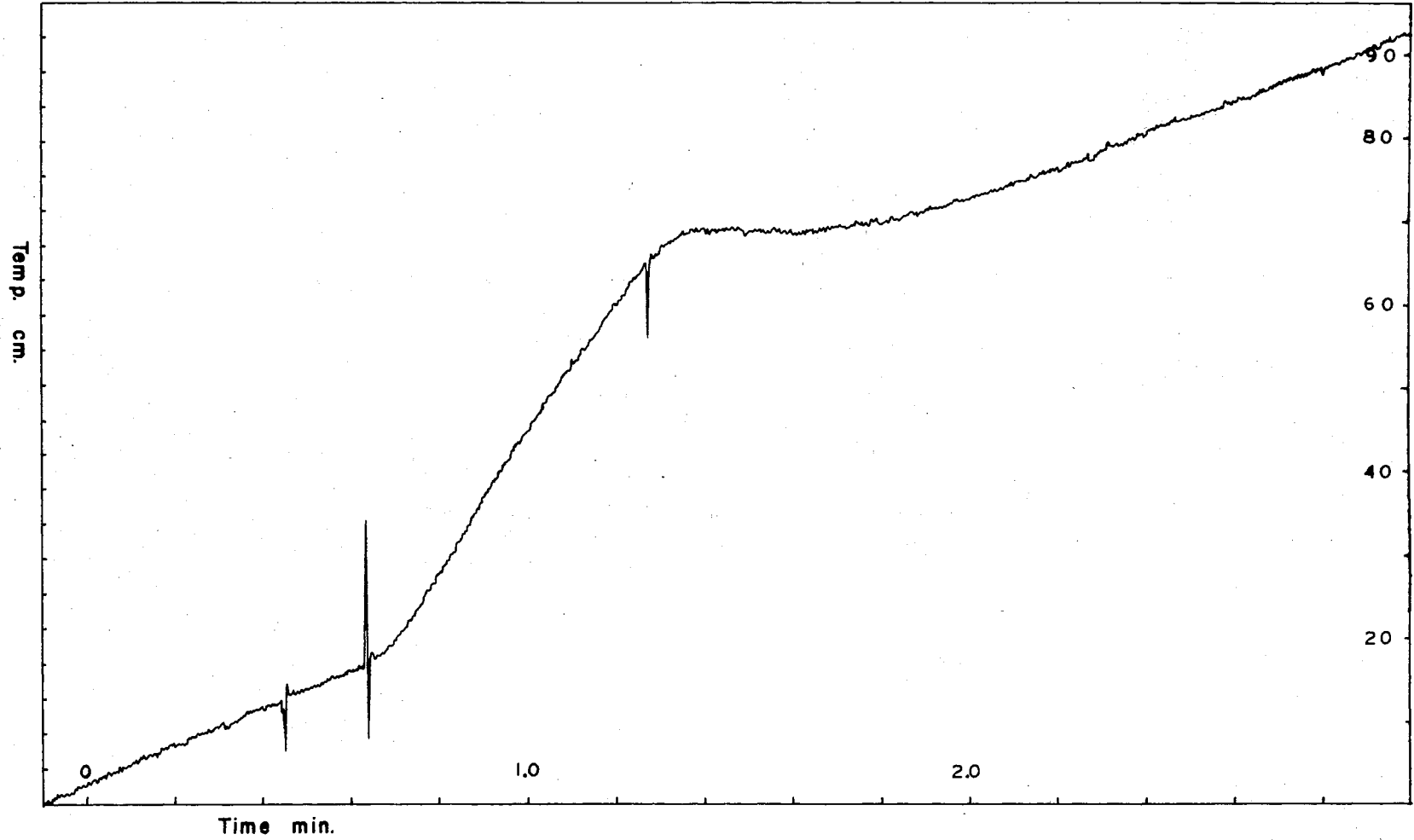
Figure 8. Electrical Heating Thermogram

27
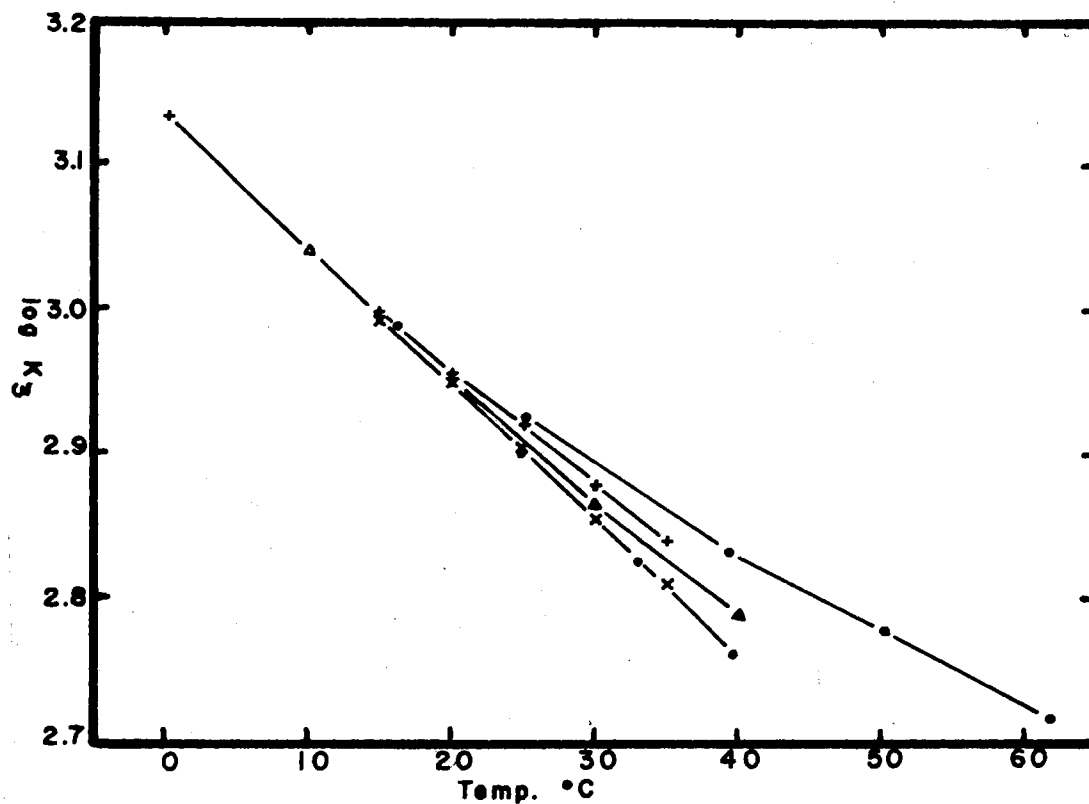
Figure 9. Temperature Variation of K_3: O, Ref. (26), Distri-
bution; +, Ref. (31), Solubility; Δ, Ref. (27),
Distribution, ●, Ref. (29), Spectrophotometric;
x, Ref. (30), Spectrophotometric

CHAPTER IV

A CALORIMETRIC STUDY OF THE FORMATION OF

POTASSIUM AND TRIIODIDE ION-PAIRS

After direct titration of potassium iodide solution into idoine

solution had been used to determine the molar enthalpy change for the

iodine-iodide complex formation reaction in dilute solution a second

series of experiments was undertaken to study the reaction in moderately

concentrated solutions to determine which additional complex or complexes

were formed. Since the solubility of iodine in water is approximately

10^{-3}M and there is probably salting out at higher concentrations, the

study of more concentrated solutions called for a different experimental

procedure than that used in Chapter III.

Determination by Dilution

The method of diluting a solution of concentrated potassium tri-

iodide into water was chosen. This method offered the advantage of

starting and ending with all reactants in solution so that knowledge of

the heat of solution of iodine would not be necessary. It was also pre-

dicted that the absolute value of the experimental heat would be larger

than that of the direct determination of Chapter III. This last factor

was important in that it allowed a better per cent accuracy in the heat

measurement.

For treatment of the heats of dilution, the heat of dilution of

potassium iodide was available in a listing from the National Bureau of

Standards (54) and although some uncertainty was introduced, the heat

of dilution of potassium triiodide was taken to be equal to the heat of

dilution of potassium iodide. This treatment as justified by ionic

solution theory was considered to be a reasonable approximation. Reagents

for the titrant solution were prepared from materials listed in Chapter

III. The solution used for titration was 1.006 F in potassium iodide

and 0.6356 M in iodine. The larger calorimeter vessels were used an

initially contained 50 ml. of water to which the triiodide solution was

added. More concentrated solutions were tried but this resulted in pre-

cipitation of iodine as the titrant was diluted.

The thermograms were treated as incremental additions as detailed

in Chapter III to obtain the heat due to the reaction. Results of this

treatment are given in Table IV. Reaction heats were first analyzed

assuming no complexes beyond triiodide. The concentrations of the tri-

iodide in the titrant and in the reaction vessel were determined by ap-

plication of Equation (3.6). Then the molar enthalpy change is given by

$$\Delta H_c = \frac{Q_{Reaction}}{\alpha_{final}(\text{Volume of Water} + \text{Volume of Titrant}) - \alpha_{titrant}(\text{Volume of Titrant})}$$

$$(4.1)$$

Application of a Born-Haber Cycle leads exactly to Equation (3.8) so,

within the accuracy of the approximation from the Debye-Huckel Limiting

Law that $\Delta H_{I^- dil}$ equals $\Delta H_{I_3^- dil}$, it could be said that $\Delta H_c = \Delta H^o$.

Results of this treatment are given in Table V. It can readily be

seen that values of ΔH are not constant for different concentrations

which indicates that other competing equilibria are probably important.

TABLE IV

CALORIMETRIC DATA FROM DILUTION OF POTASSIUM TRIIODIDE

Titrant Volume ml.	Total Heat cal.	Q1[a] cal.	Total Volume ml.
1.442	0.821	0.007	51.442
0.658	0.585	−0.020	50.658
1.117	0.773	−0.066	51.775
0.813	0.426	0.000	50.813
0.721	0.482	−0.036	51.534

[a]Apparent heat caused by temperature difference in titrant and calorimeter solution.

TABLE V

TREATMENT OF TRIIODIDE DILUTION AS ONE COMPLEX

Heat of Dilution cal.	Heat of Reaction cal.	ΔH^o kcal mol^{-1}
0.148	0.457	− 6.2
0.186	0.240	− 2.4
0.241	0.276	−22.0
0.364	0.580	− 6.4

The Raman spectroscopic studies of Miller (39) had led to the conclusion that the first complex formed after triiodide in more and more concentrated potassium triiodide solutions was the potassium-triiodide ion-pair:

$$K^+ + I_3^- \rightleftharpoons K\cdot\cdot I_3 \qquad (4.2)$$

The formation of I_5^- or I_6^{2-} had been ruled out from symmetry considerations. Because of this evidence equilibrium (4.2) was the first to be considered from the point of view of competing equilibria.

The following definitions and equations applied:

$$[I_3^-] = \alpha$$

$$[K\cdot\cdot I_3] = \omega$$

$$C_1 = \text{analytical } [I^-]$$

$$C_2 = \text{analytical } [I_2]$$

$$C_K = \text{analytical } [K^+]$$

$$I = \text{ionic strength}$$

$$\gamma = \text{activity coefficient of a univalent ion}$$

From mass balance considerations

$$[I^-] = C_1 - \alpha - \omega \qquad (4.3)$$

$$[I_2] = C_2 - \alpha - \omega \qquad (4.4)$$

$$[K^+] = C_K - \omega \qquad (4.5)$$

The equation for the formation constant of the potassium triiodide ion pair is:

$$K_4 = \frac{\omega}{(C_K - \omega)\,\alpha\gamma^2} \qquad (4.6)$$

and the modified equation for the formation constant of the triiodide complex is:

$$K_3 = 723 = \frac{\alpha}{(C_1 - \alpha - \omega)(C_2 - \alpha - \omega)} \qquad (4.7)$$

The activity coefficient γ was obtained from the Davies equation (40,55)

$$\gamma = 10^{\exp\{-.509\,[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I]\}} \qquad (4.8)$$

where I is the ionic strength given by the equation:

$$I = \frac{1}{2}\,([K^+] + [I^-] + [I_3^-]) \qquad (4.9)$$

or

$$I = C_1 - \omega \qquad (4.10)$$

There are four unknown quantities K_4, α, ω, and γ and only three linearly independent equations (4.6), (4.7), and (4.8). It was easily shown that a fourth equation could be generated by considering two data points with different concentration conditions. However, the treatment chosen for analysis was not the straight forward substitution which would lead to one final equation but rather an iterative numberical technique (56). Because of the exponential character of Equation (4.8) this iterative technique is probably the one most commonly used to determine activity

coefficients and is easily and accurately extended as long as a high speed computer is available.

Equations (4.6) and (4.7) were solved for ω and α respectively.

$$\omega = \frac{\alpha\gamma^2 K_4 C_K}{\alpha\gamma^2 K_4 + 1} \qquad (4.11)$$

$$\alpha = \frac{(C_2+C_1+1/K_3-2\omega) - \sqrt{(2\omega-C_1-C_2-1/K_3)^2 - 4(C_1C_2-C_1\omega+\omega^2)}}{2} \qquad (4.12)$$

Only the negative value of the square root term is considered in Equation (4.12) because the positive value corresponds to an imaginary root.

A computer program was written to carry out the iteration following the logic shown below:

(1) Guess initial values for α and γ.

(2) Supply a starting value for K_4.

(3) Read in analytical concentrations and volumes for titrant conditions.

(4) Calculate ω_t from Equation (4.11).

(5) Calculate α_t from Equation (4.12).

(6) Calculate γ_t from Equation (4.8).

(7) Calculate ω_t from Equation (4.11).

(8) Cycle through item (6) for a constant value of γ_t.

(9) Cycle through item (5) for a constant value of α_t.

(10) Calculate analytical concentrations and final volumes for calorimeter vessel conditions from the analytical titrant concentrations, titrant volume, and original calorimeter vessel volume.

(11)   Calculate ω_v from Equation (4.11).

(12)   Calculate α_v from Equation (4.12).

(13)   Calculate γ_v from Equation (4.8).

(14)   Calculate ω_v from Equation (4.11).

(15)   Cycle through item (13) for a constant value of γ_v.

(16)   Cycle through item (12) for a constant value of α_v.

(17)   Read heats of dilution from the NBS table (54).

(18)   Calculate heat of reaction and ΔH_c of reaction and save ΔH_c for graphical presentation.

(19)   Add an incremental value to K_4 and cycle through item (5) for as many values of K_4 as desired.

(20)   Move to next data point and cycle through item (2) for as many data points as desired.

The subscripts t and v refer to titrant and calorimeter vessel properties respectively.

Plots of ΔH_c vs K_4 were prepared as shown in Figure 10. It was hoped that varying the ion concentrations, and in particular $[K^+]$, by adding different titrant volumes would give the mathematical solutions at different titration points sufficient "independence" to allow a simultaneous graphical determination of K_4 and ΔH_c. However, there was sufficient scatter in the data and the concentrations could not be varied over a wide enough range using only this procedure for this goal to be fully realized.

Considerable information was available from the graph even though an exact solution was not possible. Toward the left hand portion of Figure 10 the concentration of the ion-pair $K \cdot \cdot I_3$ was tending to zero because of the steadily decreasing formation constant. This left the
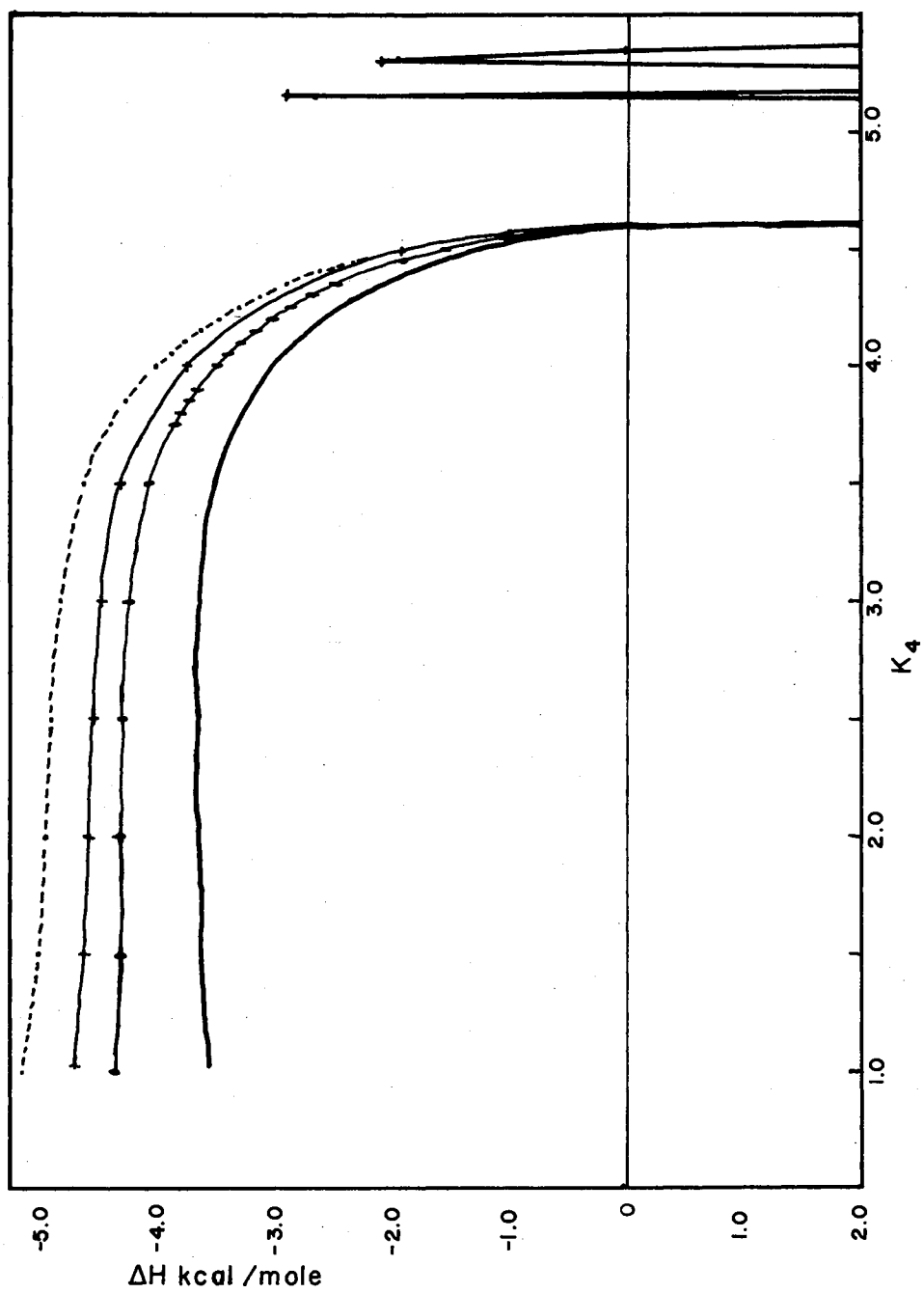
Figure 10. ΔH_c Vs. K_4

heat in excess of I_3^- formation to be accounted for in terms of the for-
mation of progressively smaller quantities of $K \cdot \cdot I_3$. In the limit this
corresponds to division by zero and an infinite molar ΔH. However, be-
fore the limit was reached, the solution of Equation (4.13) gave imagin-
ary roots. These roots were observed at values of K_4 just greater and/or
just less than one. Acceptance of the mathematical model allowed values
of K_4 less than one to be rejected. At values of K_4 between four and
five the mathematical model again broke down as the amount of $K \cdot \cdot I_3$ con-
verted by dilution to K^+ and I_3^- went from a negative to an indeterminate
amount and the value of ΔH oscillated between large positive and negative
values before an imaginary root was again generated. There was no firm
reason for rejecting the values of K_4 between 4 and 4.7 except to say
that this was where the breakdown of the model appeared to take place.
This allowed the value of K_4 to be set at 2.5 ± 1.5 and the correspond-
ing value of ΔH_c to be $-4.3 \pm .6$ kcal mol^{-1}. The limits on ΔH_c are the
95% confidence limits for all values of ΔH_c at K_4 equal to 2.5. Although
it was not certain that this value represented the maximum possible error
it did represent the scatter of the data.

One additional item of interest from this treatment was that under
syringe conditions and using a K_4 of 2.5, 69.3% of the iodine was in the
form of $K \cdot \cdot I_3$ and after dilution to an analytical iodine concentration
of 2.179×10^{-2} M only 7.2% was in the form of the ion pair.

Variation of Potassium Ion Concentration

This result itself was an unsatisfactory conclusion to the identifi-
cation of the competing equilibrium as $K \cdot \cdot I_3$ formation. Further justifi-
cation called for a repetition under wider variations of potassium ion

concentration. Not only should the reaction (4.2) show a very large dependence on potassium ion concentration, but none of the other complexes usually mentioned as the competing complex e.g., I_6^{2-} or $I_3-I_{2n}^-$, could explain a dependence on potassium ion. Unfortunately, a meaningful increase in potassium ion concentration increases the ionic strength completely out of the range of applicability of the extensions to the Debye-Huckel Limiting Law. Because of this and the loss of correspondence with the first dilution experiment dilutions had to be repeated both in a solution containing potassium ion and in a solution of inert electrolyte which would reproduce the conditions of ionic strength. There was no way in which a direct comparison between the titration into water and these high ionic strength solutions could be made.

KClO$_4$ was chosen as the source of additional potassium ion because the perchlorate ion does not readily ion pair. The limited solubility of potassium perchlorate dictated that the variation in potassium ion must be done in the dilute solution in the calorimeter vessel and not in the titrant. A new titrant solution was prepared by diluting 0.994 gram formula weights of potassium iodide, 0.483 moles of iodine, and 0.127 moles of perchloric acid to one liter with water. The perchloric acid served to eliminate hydrolysis of iodine and the concentration chosen simplified heat of dilution corrections when the titrant was delivered. One dilutant solution was 0.127 F KClO$_4$ and the other 0.127 F HClO$_4$ which provided for a fourfold variation in the final potassium ion concentrations.

The ionic strengths of the final solutions were constant for equivalent amounts of titrant added so long as complex formation did not deplete the potassium ion concentration significantly. Even where greater

or lesser volumes of titrant had been added the ionic strengths were very similar because the predominatn contribution to the ionic strength was from the electrolyte originally in the calorimeter vessel.

Thermograms were again treated as incremental additions as detailed in Chapter III. A comparison of four equivalent titrations under the conditions of high ionic strength is given in Table VI. Titrations into solutions containing added potassium ions gave markedly different heats than those into solutions of equal ionic strength without added potassium ions. An interaction between the potassium ions and the titrant is indicated. The formation of polyiodides either I_S^- or I_6^{2-} could not explain this dependence on potassium ion concentration and consideration was again given to reaction (4.2).

TABLE VI

THE EFFECT OF ADDITIONAL POTASSIUM ION ON THE HEAT OF REACTION

Titration Number	Volume Added (ml.)	Total Heat[a]	Electrolyte in Calorimeter Solution
K2	1.023	.3013	$KClO_4$
K6	0.964	.2132	$HClO_4$
K3	1.004	.3242	$KClO_4$
K7	1.001	.1801	$HClO_4$

The treatment of the data was very similar to that described for the dilution of triiodide in water. The computer program was modified to accommodate the change in ionic strength due to the added electrolyte

$$I = C_1 - \omega + 0.127$$

and the variation in the potassium ion concentration.

Experimental results are given in Table VII. The plot of ΔH_c vs K_4 (Figure 11) has the same properties as those depicted in Figure 10 in that imaginary roots are encountered near K_4 equals one and a rapid oscillation followed by imaginary roots occurs as values of K_4 become larger than four. As before a definite value of ΔH_c could not be assigned without a prior determination of the equilibrium constant. It seemed reasonable, however, to conclude that there was some mathematical justification in eliminating values of K_4 less than one and greater than four. This would set the equilibrium constant at 2.5 ± 1.5 and ΔH_c at $-3.4 \pm .3$ kcal mol^{-1}. The limits of the ΔH_c given are the 95% confidence limit for all values of ΔH_c at K_4 equal to 2.5. Although it was not certain that this value represented the maximum possible error it did represent the scatter of the data.

As an additional test of the mathematical procedure used, Equations (4.6), (4.7), and (4.8) were combined to give a quartic equation in α:

$$\alpha^4 + A\alpha^3 + B\alpha^2 + C\alpha + D = 0 \tag{4.14}$$

where

$$A = \frac{2}{d^2} + \frac{1}{K_4} - C_2 - C_1 + 2C_K \tag{4.15}$$

$$B = \frac{2}{d^2} - \frac{2}{K_3 d} - \frac{2C_2}{d} - \frac{2C_1}{d} + \frac{2C_K}{d} + C_K^2 - C_K C_2 - C_K C_1 + C_1 C_2 \tag{4.16}$$

$$C = \left(\frac{1}{K_3 d} - \frac{C_2}{d} - \frac{C_1}{d} - C_K C_2 - C_K C_1 + 2C_1 C_2\right)d \tag{4.17}$$
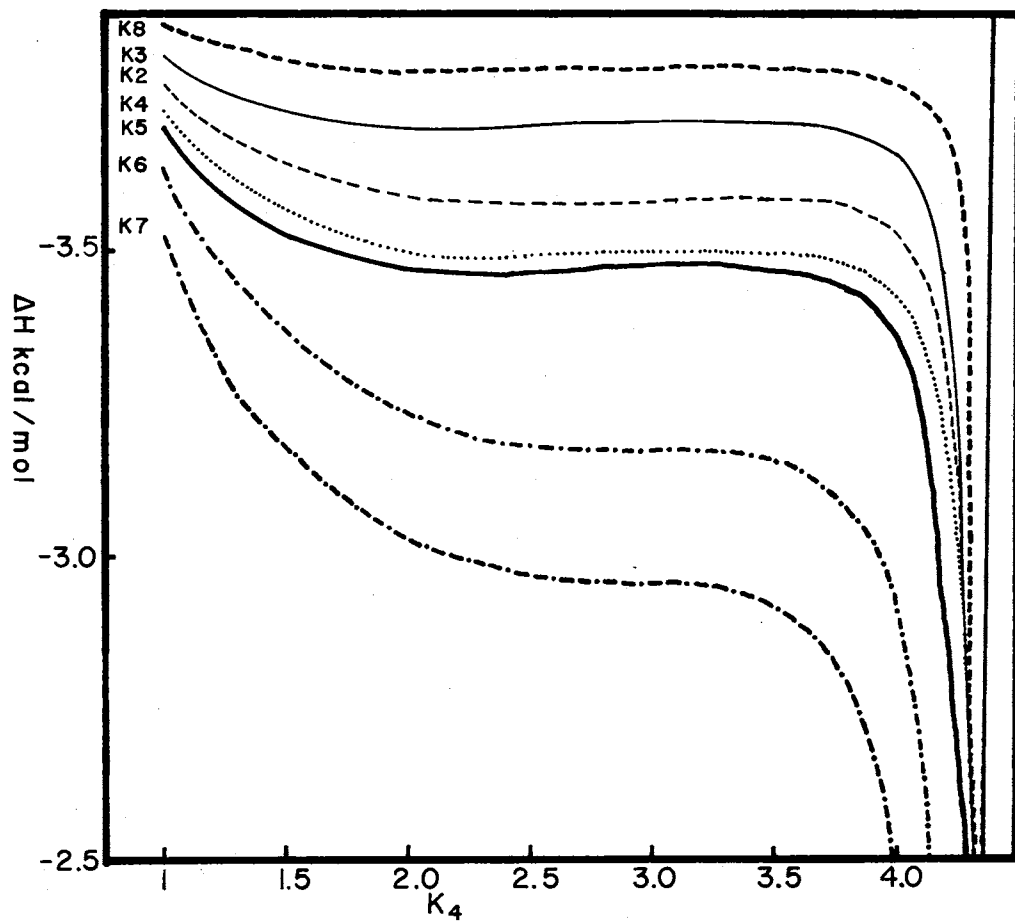
Figure 11. ΔH_c Vs. K_4 From $[K^+]$ Variation

$$D = \frac{C_1 C_2}{d^2} \qquad (4.18)$$

and

$$d = \gamma^2 K_4 \qquad (4.19)$$

A computer program was written which used numeric methods to solve for all roots of α between zero and the analytical concentration of iodine, cycled between Equations (4.11) and (4.8) for a constant activity coefficient, and repeated these operations for all values of K_4 used in the original program. Concentrations calculated in this manner were the same as those produced by incrementation which showed the validity of the method.

TABLE VII

CALORIMETRIC DATA FROM THE VARIATION OF POTASSIUM ION CONCENTRATION

Titrant Vol. ml.	Total Heat cal.	Q_1[a] cal.	$KClO_4$ Conc. F
1.998	0.236	−0.059	0.0
1.023	0.278	−0.023	0.0
1.004	0.327	−0.003	0.0
1.006	0.276	0.0	0.0
0.999	0.271	0.0	0.0
0.964	0.215	0.002	0.127
1.001	0.180	0.0	0.127
0.998	0.350	0.0	0.0

[a]Apparent heat from introduction of a titrant at a temperature different than the temperature of the reactants.

Summary

Although rigorous solutions for the values of K_4 and ΔH_c for the ion-pair reaction

$$K^+ + I_3^- = K \cdot \cdot I_3$$
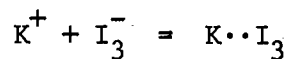
have not been made, several things of value have been accomplished by this study. This study fully supports the concept that formation of potassium-triiodide ion-pairs explains the variation of the apparent equilibrium constant for triiodide formation in solutions of ionic strength less than one (31). This study has shown that the formation of $K \cdot \cdot I_3$ can successfully explain heats measured from the dilution experiments with an equilibrium constant of 2.5 ± 1.5 and a ΔH_c of $-4.3 \pm .6$ kcal mol^{-1} for conditions of dilution from an ionic strength of 1.6 to 0.03 or a ΔH_c of $-3.4 \pm .3$ kcal mol^{-1} for dilution from an ionic strength of 1.6 to 0.15. Since the ΔH_c values must be something of an average, their close agreement argues that they apply well over a large range of ionic strengths. Not only does the ion-pair model fit the experimental facts, there is evidence of a dependence of the heats of reactions taking place in dilution on potassium ion concentration. This dependence is independent of ionic strength. Since neither the I_5^- formation nor I_6^{2-} formation can explain this dependence their presence under these conditions must be questioned. To be complete, calculations fitting polyiodide models to experimental results should be attempted. These calculations are now in progress but no results are available at this time.

CHAPTER V

THALLOUS TRIIODIDE FORMATION

As an extension of the work indicating the formation of an ion pair

between K^+ and I_3^- a series of experiments with thallium (I) and the tri-

iodide ion were designed. Thallium (I) was chosen primarily because it

is an ion known to be more favorable than the potassium ion toward ion

pair formation. Also another worker was concurrently studying this same

system with Raman and ultraviolet spectroscopy in this laboratory and

his findings were readily available for comparison (39).

Experimental

In order to correspond more completely with the Raman and ultra-

violet spectroscopic studies and to prevent hydrolysis of the iodine all

of the solutions prepared contained 10^{-2} moles of $HClO_4$ per liter.

It was soon determined that a complex formed which had a low solu-

bility. Because of the low solubilities the final solution prepared as

titrant was 1.248×10^{-2} F $TlNO_3$ and the solution for the reaction vessel

was 9.5796×10^{-4} F in KI and 4.8494×10^{-4} M in I_2. The iodine was pre-

pared by triple sublimation of Baker Analyzed Reagent and the thallous

nitrate was Fisher purified.

The calorimeter vessels chosen were the 50 ml. Dewars fitted with

glass calorimeter inserts and Teflon delivery tubes. The titrant was

delivered at the maximum rate of 2.633×10^{-2} ml sec^{-1}. Several thermo-

grams were taken and because of the low total heat, titrations were made

by adding two allquots of one milliliter each so that the data could be

treated as incremental additions. The first appearance was that the

thermograms would not be accurate enough to be analyzed as continuous

thermograms. The addition of two milliliters titrant leads to a two to

one ratio of Tl^+ to $(I_3)_2^{2-}$ but the relative smoothness of the thermogram

and the continuing evolution of heat was assurance that the second milli-

liter addition would have useful information, see Figure 12.

<div align="center">Treatment of the Data</div>

Analyzing the calorimeter runs in terms of incremental additions

the data in Table VIII was obtained by the graphical treatment outlined

in Chapter III. This information was then treated to obtain the best β_2

in the following manner: Based upon the results from Miller's study

(39) it was first assumed that the thallous complexation can be describ-

ed completely by the reaction

$$Tl^+ + 2I_3^- \rightleftharpoons Tl(I_3)_2^- \qquad (5.1)$$

Then

$$\beta_2 = \frac{[Tl(I_3)_2^-] \; \gamma}{[Tl^+][I_3^-]^2 \; \gamma^3} \qquad (5.2)$$

where $\beta_2 = K_1 \times K_2$ and K_1 and K_2 are the stepwise equilibrium constants.

As discussed in Chapter IV there was evidence from the Raman study

that other postulated species such as $I_3 \cdot \cdot I_3^{2-}$ or I_5^- were not involved

(39). It was hoped that this study might be able to determine the step-

wise equilibrium constants since in the spectroscopic approach only β_2
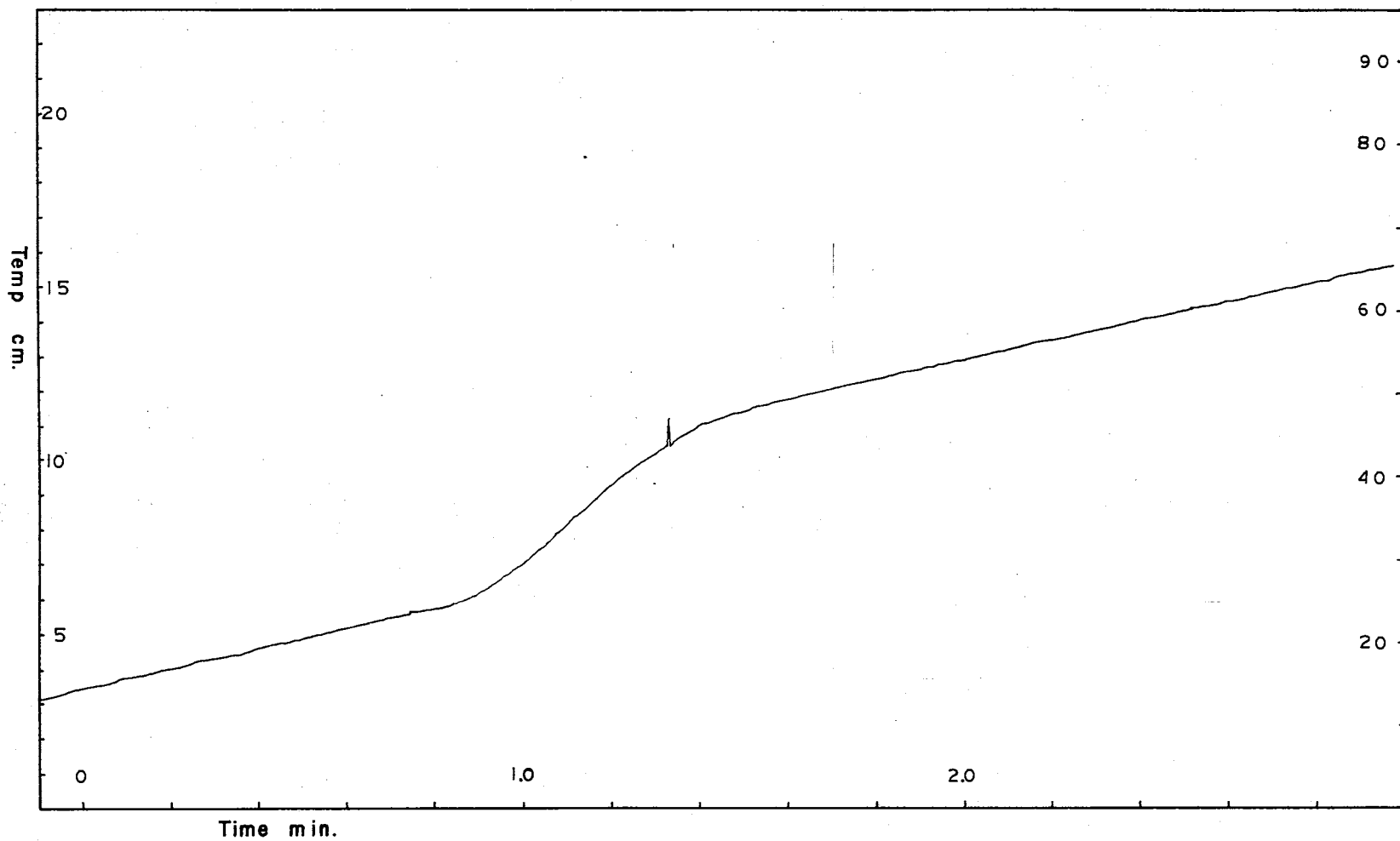
Figure 12. Thallous Triiodide Thermogram

could be determined. This result indicates that $[TlI_3] \ll [Tl(I_3)_2^-]$.

TABLE VIII

RESULTING HEATS FROM GRAPHICAL TREATMENT

Titrant ml.	Q_{tot} cal.	Q_1 cal.
1.8468	-.2716	-.0029
1.8768	-.3146	.0000
1.8413	-.2770	.0000
.9250	-.1769	.0000
1.8397	-.2959	.0000
.9239	-.2049	.0000

Where Q_{tot} is the observed heat evolved by the reaction and Q_1 is the apparent heat added when the titrant is not at the temperature of the reactants.

The other reactions of the system are

$$I^- + I_2 \rightleftharpoons I_3^- \tag{5.3}$$

and

$$K^+ + I_3^- \rightleftharpoons KI_3 \tag{5.4}$$

Since these last two equations represent the only important reactions occurring before thallous ion is added, initial conditions may be calculated from them as shown in Chapter IV. These conditions must be known in order to evaluate the heat contributions of these two reactions

as the concentrations of the species are changed.

After the thallous ion is added all three reactions must be con-
sidered. The following definitions and equations mathematically describe
the system:

$$[I_3^-] = \alpha$$

$$[KI_3] = \omega$$

$$[Tl(I_3^-)_2] = \delta$$

$$C_1 = \text{analytical } [I^-]$$

$$C_2 = \text{analytical } [I_2]$$

$$C_m = \text{analytical } [Tl^+]$$

$$C_K = \text{analytical } [K^+]$$

$$\gamma = \text{activity coefficient of a univalent ion}$$

From mass balance considerations

$$[I^-] = C_1 - \alpha - 2\delta - \omega \qquad (5.5)$$

$$[I_2] = C_2 - \alpha - 2\delta - \omega \qquad (5.6)$$

$$[Tl^+] = C_m - \delta \qquad (5.7)$$

$$[K^+] = C_K - \omega \qquad (5.8)$$

Given these mass balance expressions Equation (5.2) may be shown to
yield

$$\delta = \frac{C_m \beta_2 \alpha^2 \gamma^2}{1 + \beta_2 \alpha^2 \gamma^2} \tag{5.9}$$

Likewise the mass balance equations when substituted into Equation (4.7), the KI_3 formation constant equation, and Equation (3.4), the I_3 formation constant equation produce expressions for ω and α respectively:

$$\omega = \frac{\alpha C_K \gamma^2}{\alpha \gamma^2 + 1/K_4} \tag{5.10}$$

$$\alpha^2 - [C_1 + C_2 - 4\delta - 2\omega + 1/K_3]\alpha + C_1 C_2 - 2C_1 \delta - C_1 \omega$$
$$- C_2 \gamma + 4\gamma^2 + 4\delta\omega - C_2 \omega + \omega^2 = 0 \tag{5.11}$$

The extended Davies Equation (40,55) may be employed to obtain activity coefficients

$$\gamma = 10^{\exp\{-.509[\frac{\sqrt{I}}{1\sqrt{I}} - 0.3I]\}} \tag{5.12}$$

where the ionic strength I is given by

$$I = \frac{1}{2}([I^-] + [K^+] + [I_3^-] + [Tl^+] + [Tl(I_3^-)_2] + [H^+] + [ClO_4^-]) \tag{5.13}$$

or

$$I = \frac{1}{2}[C_1 + C_K + C_m - 2\delta - 2\omega + 2 \times 10^{-2}] \tag{5.14}$$

Equation (5.11) may be solved for α as

$$\alpha = \frac{-P - \sqrt{P^2 - 49}}{2} \tag{5.15}$$

where

$$P = -[C_1 + C_2 - 4\delta - 2\omega + 1/K_3]$$

$$g = C_1C_2 - 2C_1\delta - C_1\omega - 2C_2\gamma + 4\gamma^2 + 4\delta\omega - C_2\omega + \omega^2$$

Examination now shows that there are five unknowns β_2, α, δ, ω, and γ but only four independent equations. The solution for β_2 then must involve some type of simultaneous solution for two data points. There are a number of procedures possible but perhaps the simplest and most direct involves an iterative procedure very similar to the one presented in Chapter IV which leaves the equations in their present form (56). This procedure would be impractical without the availability of a high speed computer. The logic for the program may be represented as follows:

(1) Guess initial values of α and γ.

(2) Supply a minimum starting value for β_2.

(3) Read in analytical concentrations and volumes for the potassium triiodide solution in the calorimeter vessel.

(4) Calculate ω_v from Equation (4.12).

(5) Calculate α_v from Equation (4.13).

(6) Calculate γ_v from Equation (4.9).

(7) Calculate ω_v from Equation (4.12).

(8) Cycle through item (6) to a constant value of γ_v.

(9) Cycle through item (5) to a constant value of α_v.

(10) Calculate analytical concentrations and final volumes for calorimeter vessel conditions from the analytical titrant concentrations, titrant volume and original calorimeter vessel volume.

(11) Solve for δ_a and ω_α from Equations (5.9) and (5.10).

(12) Solve for γ_α from Equation (5.12).

(13) Cycle through item (11) to a constant value of γ_a.

(14) Solve for α_a from Equation (5.15).

(15) Cycle through item (11) for a constant value of α_a.

(16) If an additional titration increment was added, calculate

analytical concentrations and final volumes as item (10).

(17) Solve for δ_b and ω_b from Equations (5.9) and (5.10).

(18) Solve for γ_b from Equation (5.12).

(19) Cycle through item (17) to a constant value of γ_b.

(20) Solve for α_b from Equation (5.15).

(21) Cycle through item (17) to a constant value of α_b.

(22) Read heats of dilution from NBS tables (54).

(23) Calculate heats of reaction and enthalpies of reaction at

both points and save for a graph.

(24) Add an incremental value to β_2 and cycle through item (11)

for as many values of β_2 as desired.

(25) Graph values of ΔH_c vs values of β_2.

(26) Move to the next data point and cycle through item (2) for

all data points.

Plots of ΔH_c vs β_2 were prepared as shown in Figure 13. Inspection of these graphs indicated that the most likely area for a solution was in the range from $\beta_2 = 3.5 \times 10^6$ to 12.5×10^6.

Runs T10, T11, T12A, and T14A were taken to essentially the same final concentrations from the same initial concentration conditions so Q_{tot} should be very similar and the calculated ΔH_c values should be very much the same no matter which β_2 is used. However, the runs T12o and
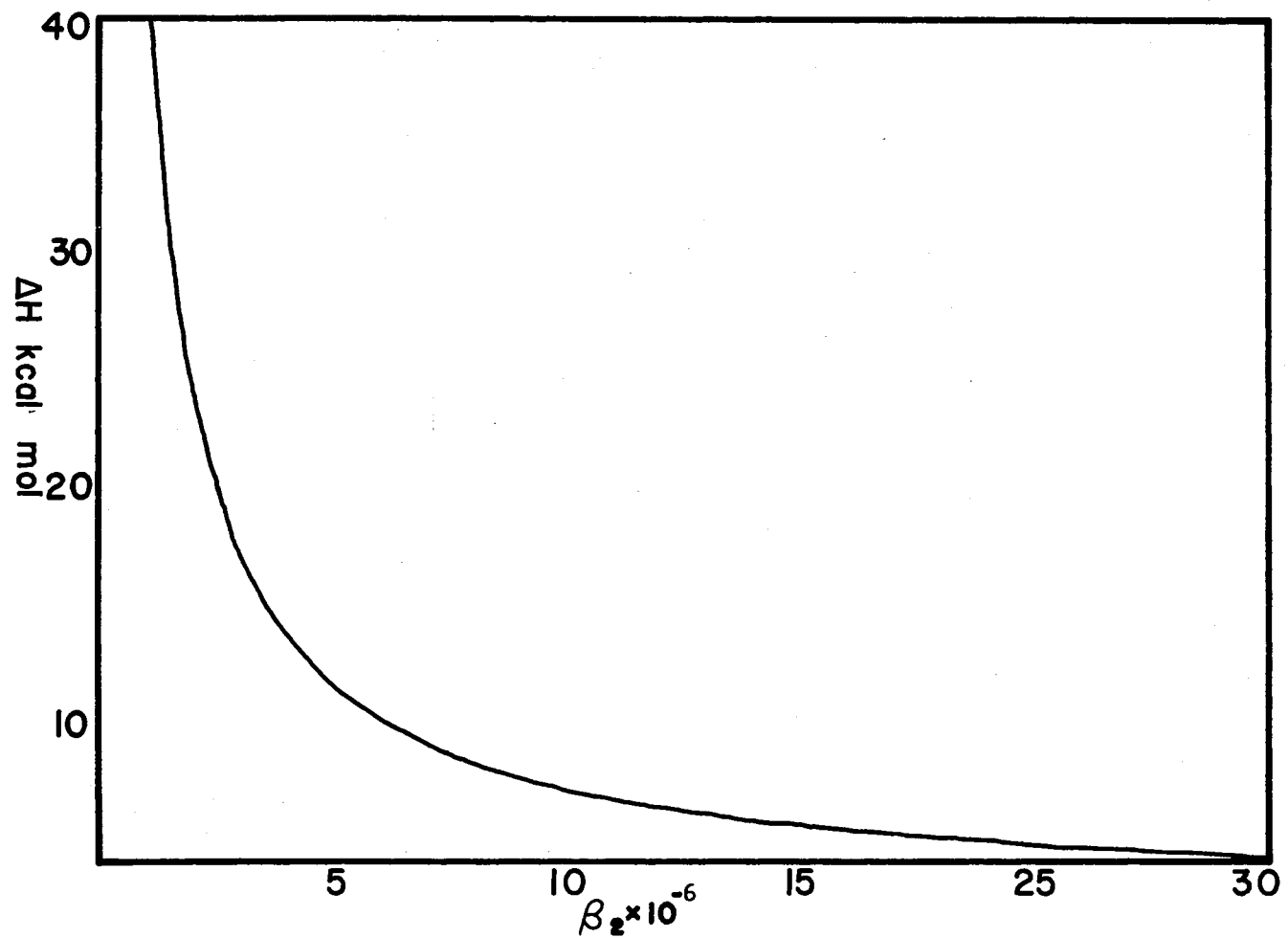
Figure 13. Typical Variation of ΔH_c With β_2

T14o were run to only one half the final concentration of the other runs so Q_{tot} is not the same and a real dependence on β_2, different from the other runs should be apparent. The value of β_2 taken was that which best fit both sets of curves. The best fit was determined by comparison of the average relative deviation, see Table IX and Table X.

Since the average relative deviations were the same for $\beta_2 = 7.5 \times 10^6$ and 9.5×10^6 the mean, 8.5×10^6, was taken as the best value. The average ΔH_c is then -7.3 kcal mol^{-1}. Using these values the thermograms were calculated as shown in Figure 14. The fits were excellent as far as reproducing the shape of the entire curve.

Conclusions

The fact that the thermograms could be so exactly reproduced using only a β_2 indicates that K_1 and K_2 must be very similar in magnitude. It also means that there is little chance of determining the separate values of K_1 and K_2.

The values obtained for ΔH, β_2, and ΔS are compared to those obtained by ultraviolet spectroscopy in Table XI (39). The agreement is fairly good. Both experimental methods give evidence for a very strong complex, formed with a fairly large exothermic heat change. The weak point in this study is the fact that β_2 is determined by the interaction of two families of shallow curves as shown in Figure 15 and thus cannot be determined with the desired accuracy. The heat measurements have a higher accuracy than the determination of ΔH_c but the inaccuracies in β_2 are carried over in ΔH_c. Little reliance may be put on ΔS because of the error in ΔH_c and ΔG.

TABLE IX

DEVIATIONS BETWEEN ONE MILLILITER AND TWO MILLILITER INCREMENTS

ΔH_c kcal/mol 2 3.5×10^6	dev from T12o	ΔH_c kcal/mol 2 5.5×10^6	dev from T12o	ΔH_c kcal/mol 2 7.5×10^6	dev from T12o	ΔH_c kcal/mol 2 9.5×10^6	dev from T12o	ΔH_c kcal/mol 2 12.5×10^6
-13.28		- 9.34		-7.46		-6.36		-5.35
-15.19		-10.68		-8.53		-7.27		-6.11
-12.44	.16	- 9.04	.30	-7.41	.05	-6.44	-.08	-5.54
-14.18	-.90	-10.31	-.97	-8.46	-1.00	-7.35	-.99	-6.32
-12.80	.48	- 9.30	.04	-7.62	- .16	-6.62	-.26	-5.69
-13.58	-.30	- 9.86	-.52	-8.08	- .62	-7.02	-.66	-6.04
	dev from T14o		dev from T14o		dev from T14o		dev from T14o	
-12.44	2.61	- 9.04	.82	-7.41	.45	-6.44	.25	-5.54
-14.18	1.01	-10.31	.37	-8.46	.07	-7.35	-.08	-6.32
-12.80	2.39	- 9.30	1.38	-7.62	.91	-6.62	.65	-5.69
-13.58	1.61	- 9.86	.86	-8.08	.45	-7.02	.25	-6.04

TABLE X

RELATIVE DEVIATIONS

	β_2 3.5×10^6	β_2 5.5×10^6	β_2 7.5×10^6	β_2 9.5×10^6	β_2 12.5×10^6
Average ΔH_c in kcal/mole	-13.58	-9.76	-7.93	-6.84	-5.84
Average |deviation|	1.183	.658	.464	.403	.370
Average Relative |deviation|	.087	.067	.059	.059	.063

TABLE XI

COMPARISON OF THERMODYNAMIC PROPERTIES

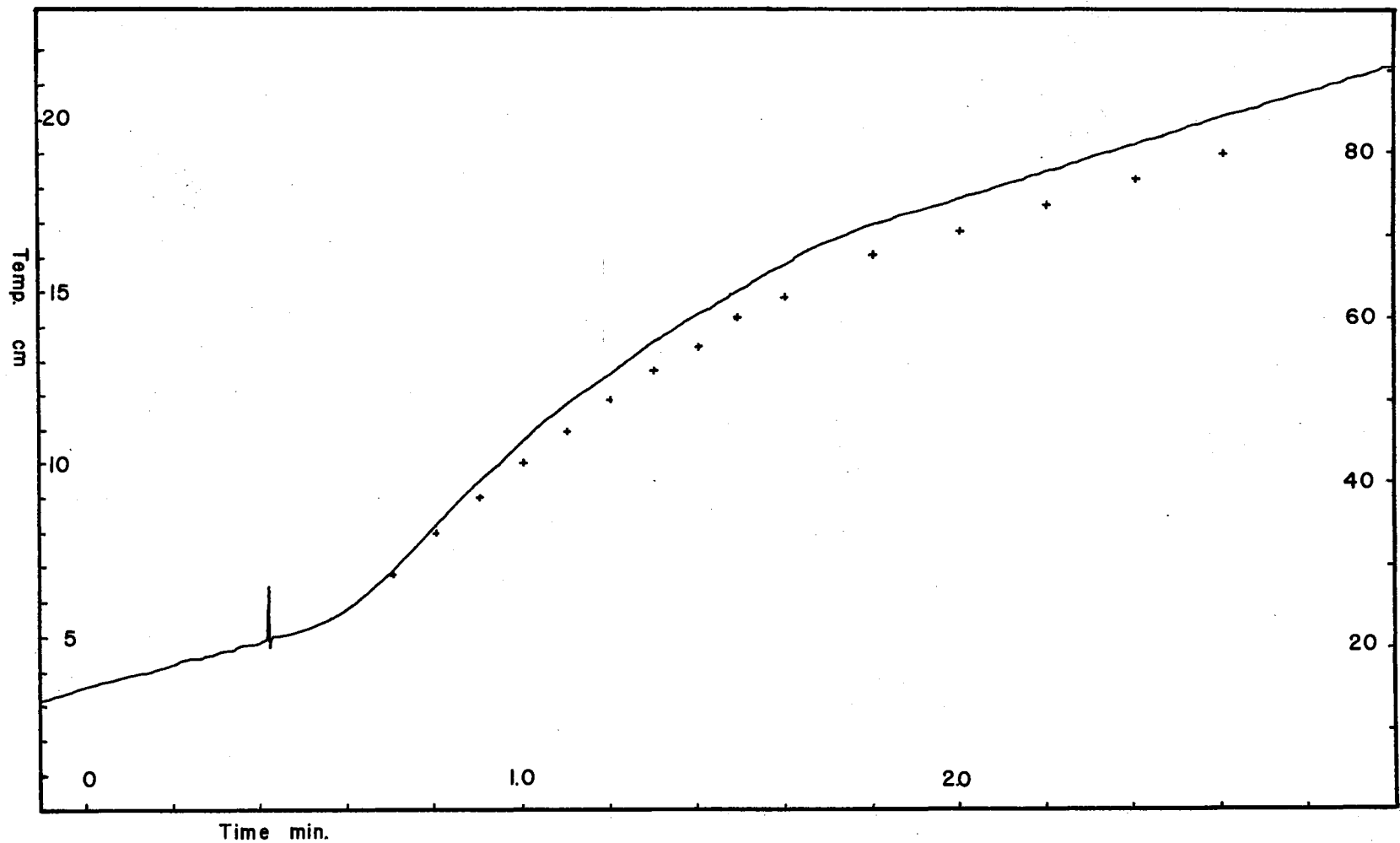|	This Work		Ref (39)
ΔG^o	-9.45 kcal mol.$^{-1}$	ΔG^o	-10.32 kcal mol^{-1}
ΔH_c	-7.3 kcal mol.$^{-1}$	ΔH^o	- 9.12 kcal mol^{-1}
ΔS_c	7 e.u.	ΔS^o	4 e.u.
β_2	8.5×10^6	β_2	3.9×10^7

Figure 14. Regeneration of Thermogram T11 by Calculation: ———, Original Thermogram; ++++, Thermogram Generated With $\beta_2 = 8.5 \times 10^6$, $\Delta H = -7.3$ kcal mol^{-1}
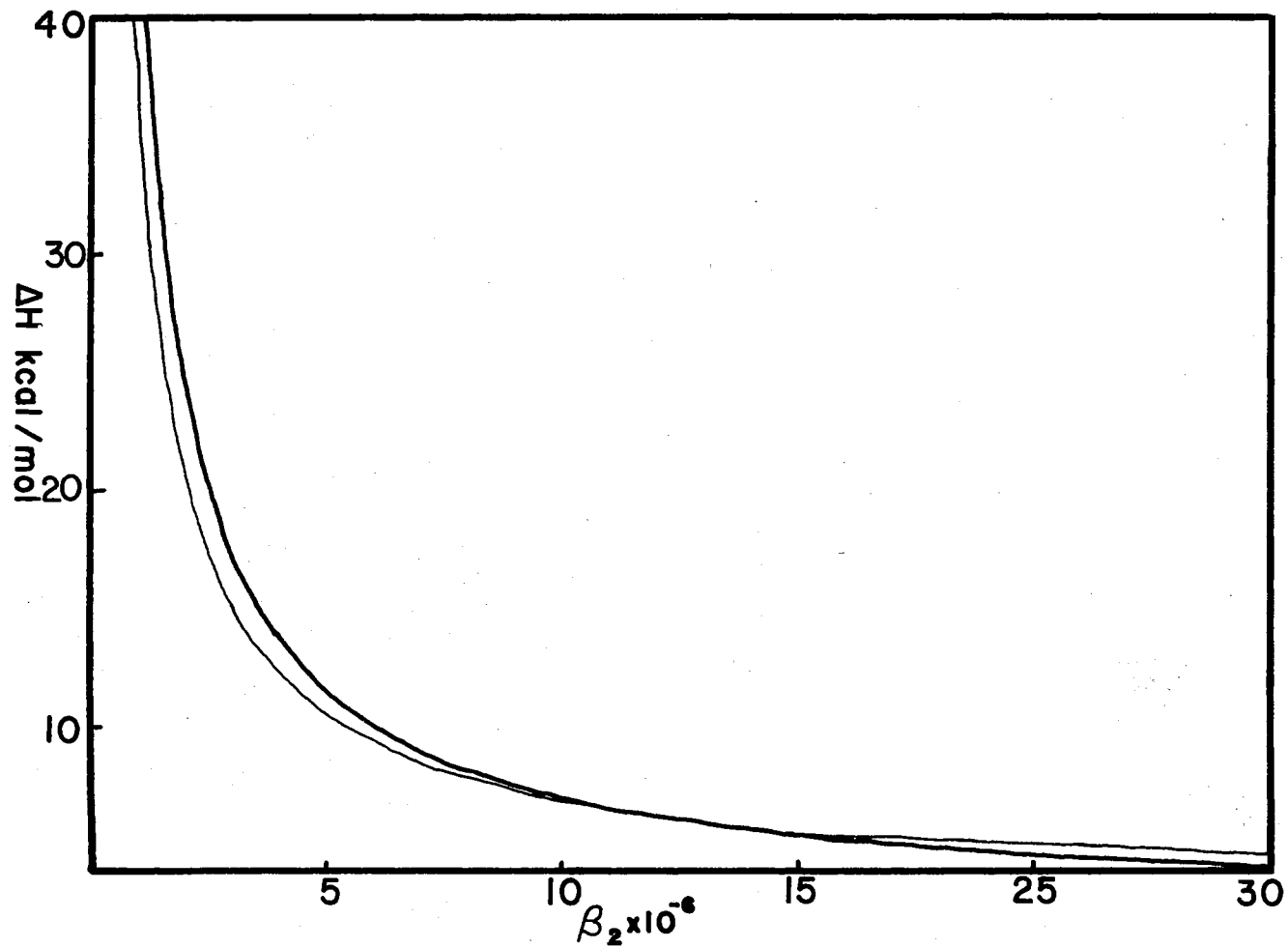
Figure 15. Typical Intersection of Plots of ΔH_c
vs. β_2

CHAPTER VI

HEATS OF FORMATION OF LANTHANIDE MONOSULFATE

COMPLEXES IN D_2O

Previous studies in this laboratory of stabilities of trivalent rare-earth monosulfate ion-pairs as measured by conductance and rate studies by sound absorption in D_2O, when compared to the analogous results in H_2O, indicated that there was no observable solvent isotope effect (SIE) on either property; however, Silber et al (45) had reported that large kinetic SIE's had been observed for sulfate and anthranilate complexes of rare-earths (57,58). This calorimetric study was undertaken to determine if the remaining thermodynamic properties, ΔH_c and ΔS_c of ion-pair formation, were also unaffected or if the two terms were changed in a self-compensating manner as has frequently been observed for weak acid ionizations (46). D_2O should be a more structured solvent than H_2O and a difference in entropy terms might be expected (59). Representatives from both heavy and light rare earths were included to observe if there might be any difference in behavior, particularly in ion solvation.

The heats involved were large enough for easy measurement but the SIE if present would be observed only as a small difference so precision measurements were again called for. Since neither H^+ nor D^+ was directly involved, the SIE would be due to solute-solvent interactions and as the primary SIE in acid ionizations are on the order of only a few hun-

dred calories the heat differences might be expected to be on the order

of tens of calories per mole (60). Literature values for ΔH^o in water

were sufficiently scattered and difficult to correct to experimental

conditions that it was felt necessary to repeat these measurements under

conditions identical to those for D_2O (61,62,63).

99.8% w/w deuterium oxide was supplied by Stohler Isotope Chemicals

Inc. H_2O enrichment was periodically checked by measuring the velocity

of sound at ultrasonic frequencies (64). It was never observed to ex-

ceed 0.5 mole percent. The water used was steam-distillate subsequently

deionized by passage over a mixed-bed ion exchange resin and trace organ-

ic residues from this step were removed by further passage over a four

foot long column of activated charcoal.

Rare-earth nitrate hydrates of 99.9% purity (American Potash and

Chemical Corp.) were dehydrated under vacuum at 25^oC for several days

and stored over silica gel in a vacuum desiccator. Equivalent weight

determinations by cation exchange and titration with standard potassium

hydroxide showed the salts to contain 0.1 to 0.3 moles of water per

equivalent. Reagent grade $NaNO_3$ and Na_2SO_4 (Baker "Analyzed" Reagents)

were dried and equivalent weights determined in the same way. Solution

concentrations were calculated on the basis of these experimentally de-

termined equivalent weights.

Experimental Procedure

Twenty milliliter samples of 1.4×10^{-2}F solutions of rare-earth

nitrates were placed in the small Dewars and attached to the plastic

calorimeter head. These were then placed in the thermostat bath and

titrated with 0.6F Na_2SO_4. The thermograms were treated as single in-

crement additions with the temperature change determined as in Chapter III. Also the heat of dilution of Na_2SO_4 in a $NaNO_3$ solution of ionic strength equivalent to the ionic strength of the rare-earth solution was determined. No correction was made for the heat of dissociation of the $NaSO_4^-$ complex in the rare-earth solution as compared to the $NaNO_3$ solution as this correction would be minimal and in the comparison between solvents the effects would be offsetting (65).

Treatment of the Data

A typical set of the pertinent information required to calculate the molar enthalpies of complexation of the La^{3+}, Sm^{3+}, Gd^{3+}, and Er^{3+} ions with sulfate and the values obtained are given in Table XII for La^{3+} in D_2O. From the measured pH (or pD) of the solutions and the dissociation constants of HSO_4^- and DSO_4^- the calculated concentration of the bisulfate ion wa- found to be insignificantly small and could be ignored (66). The system was then described as simply

$$Ln^{3+} + SO_4^{2-} \rightleftharpoons LnSO_4^+ \tag{6.1}$$

Definitions and mass balance equations were

$$C_m = \text{analytical } [Ln^{3+}] = [Ln^{3+}] + [LnSO_4^+] \tag{6.2}$$

$$C_s = \text{analytical } [SO_4^{2-}] = [SO_4^{2-}] + [LnSO_4^+] \tag{6.3}$$

$$\sigma = [LnSO_4^+] \tag{6.4}$$

Values for the formation constant K, given by the equation

TABLE XII

TYPICAL EXPERIMENTAL DATA FOR LANTHANUM SULFATE IN D_2O

C_m 10^2F	Total Volume ml	C_1 $\times 10^2 F$	$LaSO_4$ $\times 10^2 F$	Heat Capacity $\times 10^2$ h cal/cm	Pen Deflection D, cm	$Q = \bar{h} \times D$ cal	ΔH_c kcal/mol	Mean[a] ΔH_c kcal/mol
4.862	20.42	1.485	1.416	4.11	22.76	0.935	3.12	
4.889	20.06	1.515	1.445	4.06	23.60	0.958	3.19	3.16

[a]The mean is calculated from a number of experiments, usually three to six repetitions.

[b]This term includes the heat of mechanically injecting that volume of titrant.

$$K = \frac{[LnSO_4^+]}{[Ln^{3+}][SO_4^{2-}]\ \gamma^{12}} = \frac{\sigma\ \gamma^{12}}{(C_m-\sigma)(C_s-\sigma)\ \gamma^{12}} \tag{6.5}$$

have been measured in a previous study (65). In Equation (6.5) γ was the mean activity coefficient of an univalent ion which was evaluated using a modified form of the Davies equation (40)

$$-\log \gamma = 0.509 \left[\frac{I^{\frac{1}{2}}}{1 + \overset{o}{Ba}\ I^{\frac{1}{2}}} - 0.31\right] \tag{6.6}$$

Where I, the ionic strength, was given by

$$I = 0.5\ [[Na^+] + [NO_3^-] + 9[Ln^{3+}] + 4[SO_4^{2-}] + [LnSO_4]] \tag{6.7}$$

A customary simplification of the Davies equation is to set $\overset{o}{a}$, the distance of closest approach, equal to 30 nm so that $\overset{o}{Ba} = 1$. In order to fully compare with the previous rate and conductance studies, and for the reasons presented there, a value of 88.6 nm was taken for $\overset{o}{a}$ (57,58).

Equation (6.5) may be solved for σ as

$$\sigma = \frac{C_m + C_s + \frac{\gamma^{12}}{K} - \sqrt{(-C_m - C_s - \frac{\gamma^{12}}{K})^2 - 4C_m C_s}}{2} \tag{6.8}$$

A reiterative calculation around Equations (6.7) and (6.8) was used to determine the complex concentration by converging on a value for γ. The calculation terminated when successive values of γ agreed to within 0.1%

Thermodynamic parameters are listed in Table XIII. Calculated ΔH_c values were not too sensitive to the proposed error of $\pm$ 10% in the con- ductimetrically determined formation constants (57,51). From repetitive measurements the standard deviation in ΔH_c was better than 100 cal/mole.

TABLE XIII

THERMODYNAMIC VALUES OF THE FORMATION OF L_nSO_4 COMPLEXES AT $25^{\circ}C$

Ion	$K^a \times 10^{-3}$	ΔG kcal mol^{-1}	ΔH kcal mol^{-1}	ΔS cal mol^{-1} deg^{-1}
			D_2O	
La	4.69	5.00	3.16	27.4
Sm	4.82	5.01	3.76	29.4
Tb	4.42	4.96	3.30	27.7
Er	3.85	4.88	3.51	28.1
			H_2O	
La	4.43	4.96	3.13	27.1
Sm	4.78	5.00	3.42	28.3
Tb	4.36	4.95	3.70	29.0
Er	3.79	4.87	3.37	27.6

[a]Values of K from reference 3.

Discussion

From the positive signs of the free energies, enthalpies, and entropies of transfer for electrolytes and individual ions from H_2O to D_2O it is suggested that solvation of the ions produces a greater "structure-breaking" effect on D_2O (59). Transfer heats, which are equal to the differences in heats of solution, for non-reacting solutes are typically 0.2 to 0.7 kcal mol^{-1} (59). No values for rare-earth salts are available but there is no a priori reason to presume that they will behave differently. What has been measured here are the relative heats of solute-solute, solute-solvent interactions and apparently no other data is available for comparison. It is to be concluded from the results of this study that, within the limits of experimental error there is no evidence for a SIE on the enthalpies and entropies of ion-pair formation of the rare-earth monosulfates in light and heavy water.

Allowing for a difference in the solvation parameters for the free ions the reaction heats signify an equivalent difference in the hypothetical partial molal heats of solution of the ion-pairs. This should not be taken to mean that the parameters for the ion-pairs are the simple sums of the values for the free ions but only that the differences are the same. Any structural change on forming the ion-pair in light water is apparently duplicated in heavy water.

Related to this is the observation from sound absorption studies that the maximum absorption in excess of the solvent, and attributed to the chemical relaxation process of ion-pair formation, is exactly the same for both solvent media (44). This means that the partial molal volume changes for the equivalent reactions, which are related directly to the square root of the absorption amplitudes, are also unaffected by

the changes in solvent.

These results are probably not generally true for all ion-pair interactions. A number of other complexation reactions have been examined where a change in the stability constant has been observed on changing solvents. The ligands in these cases however are either the anions of weak acids, e.g., azide and oxalate or are hydrolysis reactions (67,68, 69). It would not be an unexpected result there to find the primary SIE on ΔG transmitted to the other thermodynamic parameters.

CHAPTER VII

HEAT OF COMPLEX FORMATION OF A STEROID

WITH ACTINOMYCIN D

In recent studies Durham, Berlin, and Hasslim (47) have shown by
spectrophotometric means that a complex is formed between the drug
actinomycin D and the steroid
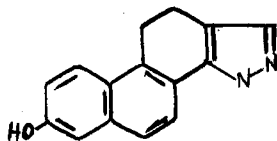
These same investigators have shown that the steroid-actinomycin D com-
plex demonstrates enhanced antitumor activity over either substance
separately in treating tumors in mice. It was hoped that the heat of
the complex formation would be great enough to allow calculation of an
equilibrium constant or at least confirm the presence of the complex.

The main drawback to the calorimeter study proved to be the low
solubility of the steroid in both water and D_2O. The steroid solutions
prepared were $2.3 \times 10^{-5}M$ and the large vessels would hold only 60 ml or
1.4×10^{-6} moles. A simple calculation showed that a molar ΔH of -10
kcal would have produced only 14 millicalories which is near the limit
of possible measurement. A temperature difference of $0.014^{\circ}C$ in titrant
and reactant temperatures would produce an apparent heat that large.

66

The addition of actinomycin D to the steroid was carried out in both
water and D_2O but in both cases the results were indecisive. The change
in the heat capacity with the addition of the titrant appeared to be the
major feature of the thermogram however in each case there was a positive
pen displacement indicating some slight exothermicity. The values were
so close to the noise level that no confidence could be placed in them.

The conclusions were that heats on the order of less than −10 kcal
per mole of reactant might have been present but the current equipment
was unable to measure them. More exothermic heats of complex formation
were ruled out as they would have been observable. This is not to say
that a molar ΔH more exothermic than −10 kcal can be ruled out because
the equilibrium constant might have been small and at such low concen-
trations the complex formation might have been far from complete.

CHAPTER VIII

SUMMARY AND SUGGESTIONS FOR FUTURE STUDY

The major goal of building a precision titration calorimeter was ac-
complished. The studies of complex and ion-pair formation have demon-
strated that the calorimeter was useful in a variety of cases especially
in the area where low solubility or small ΔH values were encountered.

The goals represented by studies undertaken with the completed
calorimeter produced some useful and somewhat surprising information.
Combined with the other studies by Miller (38) the problem of describing
the "well known" triiodide equilibrium in moderately concentrated solu-
tions seems to have been solved. The suggestion of the importance of
ion-pairing of potassium is somewhat surprising because potassium is not
noted as an ion that easily ion-pairs. However, many texts point out
that one of the first problems in calculating activity coefficients is
caused by the formation of ion-pairs and recent studies have shown ion-
pairing of potassium salts (39,40,41). The realization of the importance
of ion-pairing of such ions as potassium and the demonstration that they
may be treated in this manner may allow other systems that have shown
similar variation in the equilibrium constant to be explained in a like
manner. The characterization of the thallous triiodide system lends
support to the ion-pair model of the potassium trioodide system and is
itself now adequately described.

Suggestions for the future use of the calorimeter are inexhaustible

but some of the more obvious ones include a temperature study to confirm ΔG° and measure ΔC_{p} and studies into nonaqueous solvents. By choosing the dielectric constant and other properties of the solvent the formation of polyiodides might be further confirmed and studied (36). Compounds with higher enthalpies and greater solubility could be studied so that the calorimeter could be used as continuous titration calorimeter.

Some compounds of particular interest would be metal complexes of phthalic acid and other polycarboxylic aromatic acids. These are especially interesting in that they should represent a series of compounds whose chemical and physical properties can be varied slightly. This allows a good chance to relate changes in thermodynamic properties to structural changes in solution and so could be valuable as a model for other acids. There is also some industrial interest in these compounds as some consideration has been given to their use in replacing phosphates in detergents and it might become important to know which, if any, metal ions will cause them to precipitate (70).

A somewhat related study would be the comparison of heats of ionization of cis and trans dicarboxylic acids such as fumaric and maleic acid. Again this could be useful in relating changes in physical structure to thermodynamic parameters in solution. Molecular statistical mechanics is generally considered the bridge between thermodynamics and molecular structure but it works best in the gas phase. In solution the application of statistical mechanics is usually hindered because the systems become complex and many of the necessary parameters for a full treatment are often either unknown or at best only poorly defined. For this reason, at least in solution, general empirical studies still seem to have

a good deal to offer to the practicing chemist.

Also of special interest in the light of recent important advances in biochemistry would be the observations of heats of reaction of biologically active compounds. Presently much of the current literature data must be considered unreliable (60). Many of the enzyme reactions have large enthalpies but are scarce or expensive and often somewhat limited in their solubilities. The ability to measure small heats in volumes of 15 to 20 milliliters will prove to be very useful.

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VITA

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Candidate for the Degree of

Doctor of Philosophy

Thesis: A SOLUTION CALORIMETRIC STUDY OF ION-PAIRING AND COMPLEX FORMATION EQUILIBRIA

Major Field: Chemistry

Biographical:

Personal Data: Born in Bpswell, Oklahoma, January 15, 1943, the son of Rev. and Mrs. Elvin White.

Education: Graduated from Guthrie High School, Guthrie, Oklahoma, in June, 1961; received the Bachelor of Arts degree in Chemistry, from Oklahoma City University, in May, 1966; received the Master of Science degree in Chemistry, Oklahoma State University in May, 1968, and completed requirements for the Doctor of Philosophy degree in July, 1973.

Professional Experience: Taught in a sophomore analytical laboratory September, 1965, to January, 1966, at Oklahoma City University; was a materials engineer at the Marshall Space Flight Center, Huntsville, Alabama, June, 1966, to July, 1966; served as a teaching or research assistant from September, 1966, to August, 1967, and again from January, 1971, to May, 1973, at Oklahoma State University; and served as a 1st Lieutenant in the U.S. Army Chemical Corps from August, 1967, to August, 1971.