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The investigation of nonelectrolyte-water interactions with respect to structure has been studied. An indirect method was used to determine some of the structural properties of these nonelectrolyte-water systems, since no direct method exists for these determinations. A titration calorimeter was used to collect thermodynamic data on the solute-water interactions at 25°. The enthalpy of transfer of sparingly soluble salts from pure water to water-nonelectrolyte solutions was used as the probe because it utilizes two structure sensitive probes instead of just one, as has been customarily used in this type of investigation. This method utilizes the heat of precipitation of these salts rather than the heat of solution of the ion.

The groups of solutes that were studied were carbohydrates and polyhydroxyalcohols. It was found that the simple carbohydrates (glucose, sucrose, and ribose) and the polyhydroxyalcohols (sorbitol and mannitol) used in this study did not exhibit normal hydrophobic water-solute interactions but rather showed a hydrophilic nature. This was expected because of the large number of polar groups of the carbohydrates and polyhydroxy alcohols.

THE INVESTIGATION OF SOME WATER--CARBOHYDRATE AND WATER--POLYHYDROXYALCOHOL SYSTEMS UTILIZING THE ENTHALPY OF TRANSFER OF SOME SLIGHTLY SOLUBLE SALTS AS A STRUCTURAL PROBE

by

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CHAPTER ONE

WATER STRUCTURE

As far back as the early Greeks water was realized to be a most important substance in life support. It was regarded as one of Aristotle's four basic elements: fire, air, water, and earth. When in the 18th century these four "elements" were finally analyzed, it was found that water was a mixture of two elements, hydrogen and oxygen, or as Lavoisier and Cavendish considered them, "ordinary air" (oxygen) and "inflamable air" (hydrogen). Water was synthesized, however, before the breakdown of the compound, by Priestly in 1781.

Some wrong conclusions were made by Dalton as to the ratio of oxygen to hydrogen in the compound. More work on this ratio was done by Gay Lussac, and he proved experimentaly that the more accurate the measurement, the closer the combination came to the two to one ratio. Cavendish found, based on Gay Lussac's work, that the actual ratio was two volumes of hydrogen to one volume of oxygen.

Work was continued on water without much regard to its actual structure. Aqueous solutions of electrolytes and non-electrolytes were studied. As the investigations went on, more and more data was collected which revealed that water was not a normal solvent.

Although Röntgen is usually given credit for the first proposal of water structure in 1892, others preceeded him. Basing his proposal for water structure on the mathematical theory of cohesion, Whiting[1] mentioned the "solid particles" of liquid water in his thesis on a "Theory of Cohesion" in 1884. Then in 1891, Vernon[2] tried to account for the phenomenon of maximum density by the presence of "water-molecules aggregating together" and by saying that the density of these aggregates was less than that of water but greater than that of ice. The aggregates were said to be $(H_2O)_4$ while the water molecule was thought to be $(H_2O)_2$.

Röntgen's[2] experiments on water and his theory of "ice molecules" comprising water structure were forerunners of our present view of the structure of liquid water. His theory was that liquid water is a saturated solution of ice molecules and that a decrease in temperature favors the formation of more ice molecules. Röntgen's theories were based on studies of pressure, temperature, and viscosity effects on liquid water.

Thermodynamic principles were applied by Van Laar in 1899[1] to study liquid water. An equilibrium was proposed to exist between the doubly and singly bound water molecules. When another material was introduced, e.g., alcohol, it was thought that some of the double bound water molecules were broken to single molecules with a resulting volume contraction.

An endeavor by Sutherland in 1901[1] to determine the amount of each component of water resulted in another mixture model for liquid water. He proposed a binary mixture of trihydrol $(H_2O)_3$, dihydrol $(H_2O)_2$, and unbound water, monohydrol. These predictions were based on the hexagonal structure of ice, probable density of ice, and Mendeléeff's equations for expansion of a normal liquid. Although no real experimental evidence was present at this time for Sutherland's model, he used this concept to try to explain various abnormalities of liquid water.

Many other attempts were made to determine the "actual" structure of liquid water. In the early 1900's, cryoscopic determinations[3] were used. This method was, however, not very productive. Another approach was the study of crystalline hydrates.[4,1] There was thought to be a relationship between water of crystallization and liquid water. However, the X-ray analysis of hydrates[5] showed the futility of these attempts in that it demonstrated that water was in H_2O units rather than the three states (H_2O), $(H_2O)_2$, and $(H_2O)_3$ predicted by the crystalline hydrates.

Modern Liquid Water Models

The Uniformist Model

Uniformist models are those in which hydrogen bonds are thought to bend and distort, but not completely break. The modern theories of water structure of this type were spawned by the model presented by Bernal and Fowler in 1933.[5] They, after having criticized the small-aggregate models, proposed that a better description of water was that of an irregular four-coordinate arrangement of molecules. The charge distribution was found to resemble a tetrahedron with two positive and two negative corners. This model was not followed up immediately even though the theory could explain properties that the older models could not explain, as well as some additional experimental data such as X-ray diffraction patterns. Their model was like the older models in that it described water as a mixture of components, although the components discussed by Bernal and Fowler involved no breaking of hydrogen bonds and thus no free water molecules. This model came to be known as the uniformist model.

In a 1951 paper based on the early work of Bernal and Fowler, Pople,[2] assuming that each bond bends independently of all others, applied classical statistical mechanics to obtain an average degree of hydrogen bond bending. By saying that the bond is bending, a large amount of energy and entropy absorption on melting of ice may be accounted for. When ice melts, it is proposed that the order of the lattice is disrupted, but no hydrogen bonds are broken. The bonds are stretched in such a way that the number of molecules around any one molecule increased and, thus, the volume decreases on melting. Although this model can account for many of the abnormalities of liquid water, it has been highly criticized.[6,7] Nevertheless, studies of this model have been continued.[8,9]

Mixture Models

The major recurring theme of mixture models is that they contain a small number, usually from one to four, of distinctly different molecular species. The major problem with some of the early mixture models is that they explained merely one or more properties of water, but could not account for several others. This problem was apparent in the early two-state theories of liquid water.[10,11,12]

The mixture theories can be broken into two categories: two-state models and the multi-state models. The two-state models explain the properties of water as an equilibrium, as do the other mixture models. The two species are usually a bulky portion which is tetrahedrally hydrogen bound ("ice-like" clusters) and denser species which are assumed to be more closely packed and of a higher energy than the bulky expanded species. The second species in ludes unbound water molecules and those that have one, two, or three available sites bound. An equilibrium exists between these two species:

$$(H_2O)_{bulky} \rightleftarrows (H_2O)_{dense}$$

One of the first, most famous, and most useful theories of this type was introduced by Frank and Evans in 1945.[13] In a paper on the thermodynamic treatment of solutions, the "iceberg" model was introduced. These "icebergs" were ice-like constructions, not necessarily the same as ice, found when a non-polar molecule was introduced to the system. These non-polar molecules were thought to find and occupy the area bordering an open structure being termed an "iceberg" and in fact were thought to cause "icebergs" to form.

With the 1950's came a more intense study of solute-solvent interactions and thus, the proposal of more molecular models. Haggis, Hasted, and Buchanan[14] studied properties of water in solutions and they proposed a "broken ice" structure. This is a model in which each water molecule is striving to be tetrahedrally bound to four neighboring molecules (as ice), but the bonds are continually breaking and reforming.

A theory which built on that of Frank and Evans was the "flickering cluster" model of Frank and Wen[15] in which the number of molecules in each cluster can vary. The hydrogen bonding in this system is considered cooperative because of the formation, the inverse also being true.

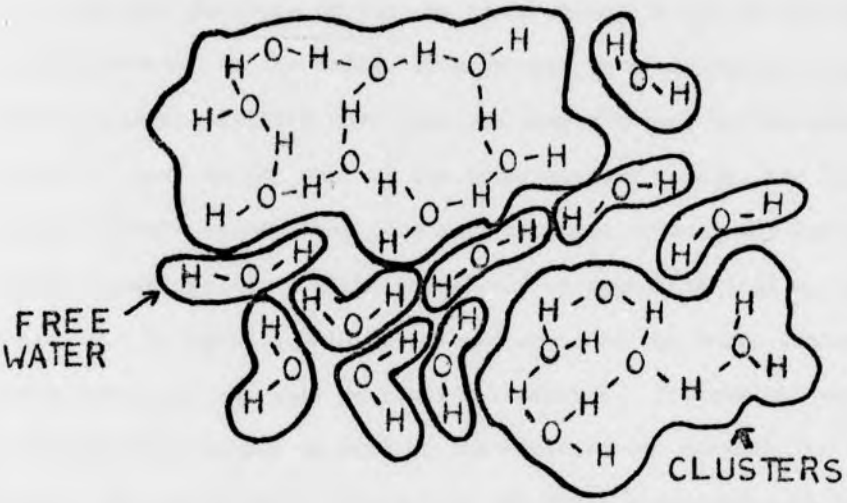


Figure 1. Frank's "Flickering Cluster" Mixture Model

This model is the basis for many modern theories of water structure. The (0, 1, 2, 3, 4) model of Walrafen[16] is thought to be one of the best to present. His model was experimentally based on Raman spectral studies in which he found the ratios of bound to unbound species at different temperatures.

The study of water structure intensified in the 1960's and was incorporated with the study of biological functions. Kauzmann's study[17] is regarded as the first step in the incorporation of water structure theories with that of the conformation of proteins in biological systems. Nemethy and Scheraga[18] wrote a series of papers concerning proteins and hydrophobic bonding with the water system.

They were the first to use a quantitative approach, although the mathematics they used were not totally correct.

Another division of the two state theory is the so-called interstitial model. As ice melts, some unbound water molecules from broken protions of the lattice move into the spaces formed by the expanding lattice. Just as for most of the other mixture models, the interstitial model assumes that some sort of three dimensional bulky framework exists along with the unbound or nontetrahedral water molecule. It again should be pointed out that the bulky framework is not necessarily the same as the ice framework. The unbound water molecules that reside in some of the cavities can account for the density of liquid water obtained by the X-ray experiments of Danford and Levy.[19] They found no large density variations as would be expected for large patches of bulky and dense water molecules. The X-ray diffraction results showed that water's nearest neighbor distance was 5.5% of that found for ice and that mnay occurred between the first and second neighbor distance of ice which could account for the additional density of water. This theory arose at the same time from three independent labs: Samoilov,[20] Forslind,[20] and Danford and Levy.[19] This model contains few non H-bonded molecules, as do other mixture models.

Another type of interstitial model was proposed by Pauling.[21] He proposed that water forms a cage where one unit is a pentagonal dodecahedron comprised of 20 water molecules enclosing a cavity 5.2 Å in diameter. The second cage unit is a tetrakaidecahedron containing 24 water molecules and a cavity 5.9 Å in diameter. These polyhedrals can be combined to form Pauling's framework structure of liquid water. His structures were based on those of gas hydrates and can be represented as in Figure 2.

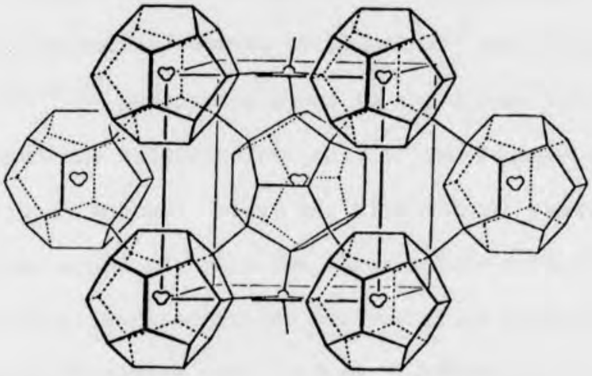


Figure 2. Pauling's Interstitial Model

Frank and Quist[22] reviewed the interstitial model in 1961 and concluded that as compared with other proposed models the interstitial model is most attractive because it conforms with results from X-ray and neutron scattering and it seems to be able to explain dielectric viscosity and diffusion properties. Work to develop the interstitial model continued through the 60's. As has already been mentioned, Danford and Levy[19] used X-ray diffraction and radial distribution functions to construct their interstitial model. Their model consisted of an expanded ice structure with the ice-like framework tetrahedrally surrounding the oxygen atoms and with an oxygen atom at each vertex of the tetrahedron. This formed puckered six membered ring layers. Interstitial water molecules inhabit some of the cavities formed by the puckered six membered rings. A systematic experimental approach was applied in forming this interstitial theory and it is an elaboration of past interstitial theories.

The last major division is the multi-state mixture model. This model contains more than two species in solution. Basing his model on the interstitial models of Samoilov[23] and Frank and Quist,[24] Mikhailov[24,25] proposed a model to accomodate large solute molecules. He claimed the existence not only of the framework water and the interstitial unbound water, but also a third type: a structureless water that could mix with the large solute molecule introduced. Many mathematical representations for solutions of gas molecules, alcohols, and non-electrolytes were derived by Mikhailov.

Hydrophilic and Hydrophobic Nature of Aqueous Solutions

When a small ion enters a water system the structure, as might be expected, is altered. According to Frank and Wen, the water will have a tendency to surround the ion with three concentric layers (Figure 3).[15,13] In the first layer the water is immobilized by the ion-dipole interaction which polarizes the water molecule. These polarized water molecules influence the bulk water in the second layer and disrupt the order slightly. The outer-most layer is unaffected by the ion-dipoles and is thus just bulk water.

The amount of disorder in the second layer may be affected by the type of ion in solution. The small or multicharged ion (e.g., Li^+, F^-, Mg^{2+}) can cause an ordering which extends into the second layer because of the large charge to size ratio leading to strong electrostatic attraction. A greater amount of disorder can be caused

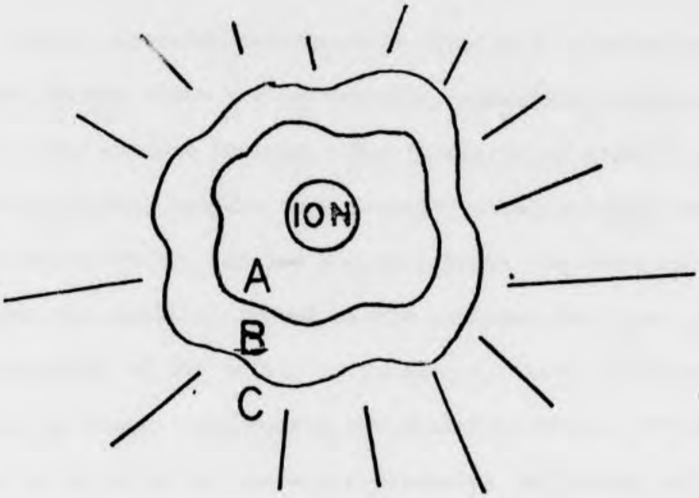


Figure 3. Frank and Wen's Ion-Water Model: A. Immobilized Layer B. Partially Polarized C. Bulk Water

in the second layer of a larger singularly-charged ion because of its small charge to size ratio or weak electrostatic attraction. Thus, the so-called electrostrictive bonding of an ion in water may be either overall structure making or structure breaking depending on the relative amounts of water in the first and second layers.

Some large electrolytes undergo hydrophobic interactions in aqueous solution. For example, some tetraalkylammonium ions have large positive heat capacities in solution, which reflects the influence of the apolar group.[26,27] These large ions (e.g., Bu_4N^+ and Pr_4N^+) induce increased water-water hydrogen bonding in bulk water[28] and are therefore termed hydrophobic structure makers. Some of the smaller tetraalkylammonium ions[29] can be structure breakers (Me_4N^+) or can have no net structuring effect on the water molecule (Et_4N^+). In general for this series of ions their hydrophobic structure making ability increases with the size of the apolar group.

When a nonpolar substance is dissolved in water the solute-solvent interactions are unfavorable, sometimes promoting solute-solute interactions instead. The interstitial model[17] can be used to describe what happens to a nonpolar nonelectrolyte when it is dissolved in water. At low concentrations the solute is thought to fit into the cavities formed by the expanded ice-type lattice. As the concentration of the solute is increased, these cavities become full and can no longer accommodate the apolar molecule. At this point, a reduction in order of the water molecules is present and some solute-solute interactions may occur. Other models, such as that of Frank and Evans,[43] have been used to describe the effect of apolar nonelectrolytes on water structure. They suggested that an increase in order and hydrogen bonding would take place in the water around the solute as a result of the molecules "dislike" for water, and vice versa. This model and others have been discussed in a previous section.

Many studies have been done to determine thermodynamic solution properties of apolar solutes at infinite dilution in water.[30,31,6] It was found that a large positive free energy change results when a hydrocarbon is introduced into water.[47] This is not because of an unfavorable enthalpy of solution, but rather because of the negative excess entropy of solution. This large entropy loss in combination with the large observed partial molal heat capacity implies that the change in hydrogen-bonded structure of water is an important factor.

As would be expected for nonelectrolytes, the shorter the carbon chain the more soluble in water, and the more polar substituents the more soluble in water. Generalizations about hydrophobic and hydrophilic bonds of nonelectrolytes in water can be made in the same way. The longer the carbon chain, the more hydrophobic the nature, and the more polar substituents there are the more hydrophilic the nature.

Ethyl alcohol is miscible in all proportions with water because of its short carbon chain and its polar hydroxyl group. Although the very polar hydroxyl group is present, the carbon chain causes the ethyl alcohol to interact hydrophobically. The alcohol is a highly hydrogen-bound compound before it enters the water system. Before the alcohol enters the water system, the water is highly hydrogen bound, and after the alcohol is added, an increase in the structure (hydrogen bonding) of the water results. Many investigators have discussed and experimented with the water-alcohol system.[32-36] As the temperature is increased, the structure making tendencies oor the ethyl alcohol-water system are diministed. As the concentration is increased, the water cannot accommodate the excess ethyl alcohol in its cavities, the structure begins to break down and the solute-solute interaciions increase. Ethyl alcohol is considered to be a structure making solute at low concentrations (0-0.22 mole percent) and although the structure is decreased at high concentrations, it is not considered to be a conventional structure breaker.

The interaction of a polar group with water is termed hydrophilic, that is, a "positive" hydrogen bonding attraction between the water molecule and the polar solute. The carbohydrates have an affinity for water and undergo these strong solute-solvent interactions because of the polar functional groups that are available for hydrogen bonding. They are also generally believed to form ideal solutions with water and have not been extensively studied because of this. Some early investigations of carbohydrates measured osmotic coefficients[37,38,39] but did not yield any information about the solution at infinite dilution. At infinite dilution only solute-solvent interactions occur and thus the effect of the polar solute on water structure may be determined.

Mutorotation studies[39,40,41] have been revealing as to the compatability of carbohydrates with water. Other thermodynamic studies have been performed in which carbohydrate-water structure was discussed. The exothermic heat of solution data[40,42] would seem to indicate extensive hydrogen bonding in the carbohydrate-water solution. Simple carbohydrates, unlike apolar solutes, show no extensive hydrophobic structuring of the water system. Rather, an increase in solute-solvent hydrogen bonding seems to be implied. Thus, simple carbohydrates could be classed as structure makers, but not in the conventional hydrophobic sense. The reason for the promotion of structure could be because the -OH groups are able to fit into the water system. It was deduced by Tait, et al.,[43] from relaxation studies of some simple monosaccharide solutions, that hydration of hexoses (i.e., glucose, mannose, and galactose) is quite different than that for ribose, which has one fewer -OH group. The difference was explained as due not only to the number of -OH groups, but also to the position on their respective carbon atoms and the conformation in solution. In solution, glucose, mannose, and galactose have a C1 conformation (see Figure 4).[44] Ribose, on the other hand, has 1C and

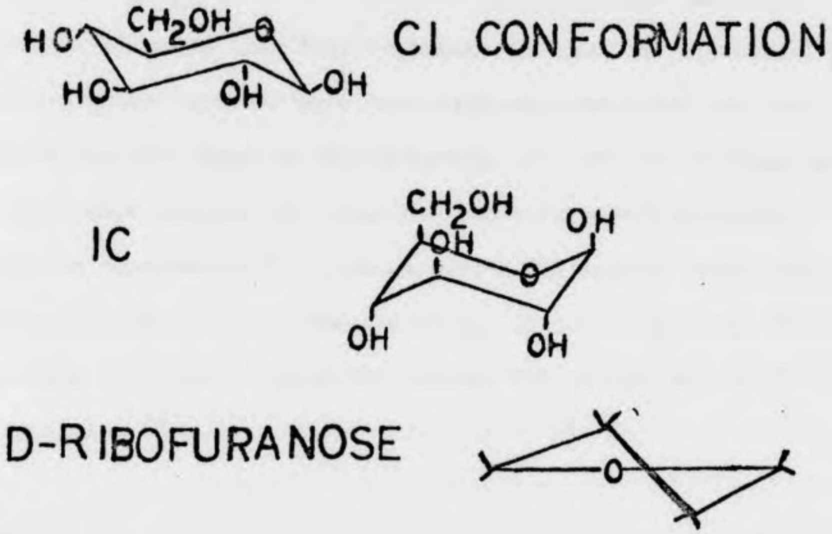
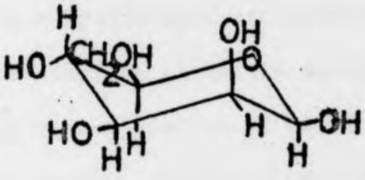


Figure 4. Monosaccharide Conformations

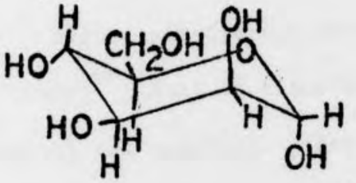
furanose conformations in water in addition to the C1 conformation (see Figure 4 above). Thus fewer than one half of the -OH groups on the ribose can be used for hydrogen bonding in the water lattice.

The hexoses in the C1 conformation have mostly equitorial -OH groups and are compatible with water structure. The distance between the -OH groups in the C1 conformation is about the same as the second nearest-neighbor distance for the oxygens in the ice-lattice, and thus the -OH groups on one side of the hexose can hydrogen bond with one layer of water while the -OH groups on the other side are hydrogen bonding to another layer of water molecules.[45]

The importance of the equatorial -OH group can be seen in the heat of solution studies of αand β-glucose.[40,42] A solution of β-glucose has a lower enthalpy of solution than does that of α-glucose. This may be attributed to the fact that α-glucose has one fewer equatorial -OH group than does β-glucose and that the equatorial groups in the β-glucose interact more favorably with the water lattice structure than do those on the α-glucose. The reverse is true for α and β-mannose because the β-mannose exhibits steric repulsion between the equatorial -OH group on carbon (1) and the axial -OH group on carbon (2) (Figure 5). The α-mannose, on the other hand, does not suffer from this severe repulsion because both groups are in the axial position.[46]



β-D-MANNOPYRANOSE



α-D-MANNOPYRANOSE

Figure 5. Stable Conformations of D-Mannose

Some investigators have proposed that monosaccharides hydrogen bond with four water molecules as do polysaccharides.[47] They claim that some of the -OH groups are H-bound within the sugar and thus are not available for reactions with water. It is evident that more study is needed into the structure and interactions of water-carbohydrate solutions.

Polyhydroxy alcohols are more like hydrophilic monosaccharides than simple alcohols in their reaction with water. Although some of the dihydric and trihydric alcohols retain the hydrophobic nature of monohydric alcohols. This can be seen in the heat of transfer studies[48] of ethylene glycol. At low concentrations, ethylene glycol is a hydrophobic structure maker (< 0.3M). As the concentration of ethylene glycol is increased, the water structure seems to become disrupted just as it would with some monohydric alcohols. The hydrophilic nature of the -OH group begins to predominate and solvent structure collapse begins to occur as seen in the negative enthalpies of transfer.

Higher polyhydroxy alcohols have been studied by Stern and O'Connor.[49] Heat of transfer studies were done on the steroisomers: sorbitol and mannitol. They found that at low concentrations (< 0.3M) mannitol shows a narrow endothermic peak which implies similar hydrophobic structure making abilities to the simple alcohols. Sorbitol, on the other hand, shows an increasingly negative heat of transfer with increasing concentration. This could result from its hydrophilic bonding with water. Stern and O'Connor thought that they had found a way to distinguish one steroisomer from another.

With some improvements in equipment, Wilson[50] tried to reproduce Stern and O'Connor's work without success. He found both sorbitol and mannitol to behave as hydrophilic structure breakers. Wilson proposed that these hexols act like simple carbohydrates. Their structure making or breaking ability depends not only on how well they fit into the water lattice, but also on how much hydrophobic character was retained. Thus, if a polyhydroxy alcohol has only slight hydrophobic character and cannot orient itself by rotation into the water environment (as does glucose), then it will be a net structure breaker or at most an electrostrictive structure maker. Clearly, additional work is needed to find support for either of these theories.

CHAPTER TWO

RESEARCH PROPOSAL

Little work has been done to study the solute-solvent interactions of simple carbohydrates and polyhydroxyalcohols, as has been mentioned previously in the section on hydrophilic bonding. A thermodynamic study of aqueous solutions of simple carbohydrates and polyhydroxyalcohols was undertaken to gain additional information on solute-solvent interactions. It was hoped that the systems studied would help in the understanding of the function of water in biological systems and would provide additional data to aid in the explanation of water structure. The thermodynamic function used to study these systems was the heat of transfer ($\Delta H_{(tr)}$) of some sparingly soluble salts from water to the nonelectrolyte-water mixtures. This data could aid in obtaining information on interactions in the system by determining structure breaking or making characteristics of the nonelectrolytes under investigation. Probe salts, such as tetrabutylammonium tetraphenylborate, which are structure making probes give an enthalpy of transfer in the same direction, but to different degrees, for aqueous solutions of both structure making and structure breaking solutes. The structure breaking salt silver iodide, however, may be able to be used to determine the structure making or breaking ability of the system in question because it exhibits endothermic heats of transfer in hydrophobic structure making systems and exothermic heats of transfer in structure breaking systems[51] (depending on how $\Delta H_{(tr)}$ is defined; see equation 2).

The heat of reaction of the system may be broken up into parts that reflect what is actually happening during the precipitation.

$$\Delta H(R) = \Delta H(\text{A desolvation}) + \Delta H(\text{M desolvation}) + \Delta H(\text{MA formation}) + \Delta H(\text{MA(s) formation}) + \Delta H\text{st}. \qquad \text{(equation 1)}$$

where:

$\Delta H(R)$ = the overall reaction enthalpy

ΔH(A desolvation)
ΔH(M desolvation) = the enthalpy of desolvating the anion and cation (respectively)

ΔH(MA formation) = the enthalpy of formation of the individual MA molecules

ΔH(MA(s) formation) = the enthalpy of MA solid formation

ΔH(st) = the enthalpy of any solvent reorganization which takes place upon removal of M and A from solution

The last term is the one of concern because it describes what is happening in the solution with respect to the structure of the solute and solvent. Since the ΔH(MA(s) formation) and ΔH(MA formation) can be assumed constant[51] and since the $\Delta H_{(tr)}$ can be represented as follows:

$$\Delta H_{(tr)} = \Delta H_{R(H_2O)} - \Delta H_{R(mix)} \qquad \text{(equation 2)}$$

equation 1 and 2 can be combined to give:

$$\Delta H_{(tr)} \approx \Delta H_{(st.\ H_2O)} - \Delta H_{(st.\ mix)} \qquad \text{(equation 3)}$$

A result which is representative of the change that occurs when the salts previously mentioned are used as probes. This assumes that the desolvation terms do not change significantly on changing the solvent. This is only true at high water concentrations where aqueous characteristics remain dominant.

Through these equations and the use of the structure making (Bu_4NTPB) and structure breaking (AgI) salts information about aqueous solutions of glucose, sucrose, ribose, mannitol, and sorbitol was found. This information was then related, in conjunction with spectroscopic data, to the structural properties of the nonelectrolye-water solutions.

CHAPTER THREE

THERMOMETRIC TITRATIONS

Basic Principles of the Method

Thermometric titration is a physical-analytical method in which the temperature of the reacting system is measured as a function of the volume of the titrant added. Most analytical titration methods, such as potentiometric, are based on the change in free energy of the system. In contrast thermometric titrimetry is primarily dependent on the enthalpy change of the system. The free energy methods depend only on the equilibrium constant correlated through the equation:

$$\Delta G = -RT\ln K \qquad \text{(equation 4)}$$

where:

ΔG = the change in free energy of the reaction system

R = The universal gas constant

T = the temperature in degrees absolute

K = the equilibrium constant for the system at temperature T

The only dependence of the thermometric titration method on the free energy is that ΔG must be large enough to give a good end point (<u>i.e.</u>, the reaction should be reasonably spontaneous). Free energy and the enthalpy of reaction are related through this equation:

$$\Delta H = \Delta G + T\Delta S \qquad \text{(equation 5)}$$

where:

ΔH = the change in enthalpy of the system

ΔG and T are defined as above

ΔS = the change in the entropy of the system

Where a titration based on free energy may not show a sufficient end point deflection, the same titration done thermotetrically will often show a greater inflection at the end point, assuming there is a sufficient heat given off. A good example[52] of this is the comparison of the potentiometric and thermometric titration curves for a weak acid (boric acid, H_3BO_3) as compared to a strong acid (hydrochloric acid, HCl) (Figure 6).[52] The strong acid shows a good end point potentiometicly, but the weak acid end point is not visible. Thermometric titrations of both show sharp end points (see Figure 6). This is true because the temperature change is independent of the amount of titrant added, just about up to the end point.

This method of analysis also has some advantages over electroanalytical and spectroscopic methods. Thermometric titrations can be done in many different solvent systems including emulsions and slurries.[53] This is true because thermometric titrations are independent of some properties of solution such as viscosity, optical clarity, and dielectric constants. Hume[54] has done studies on gaseous systems and other studies have been done on nonaqueous solutions,[55,56] as well as aqueous solutions. In contrast, most common solvents cannot be used in much of the U.V. range because of "intrinsic opacity." Due to the need for charge transfer in some electrochemical methods they cannot use solvents with low dielectric constants because no inert conductive

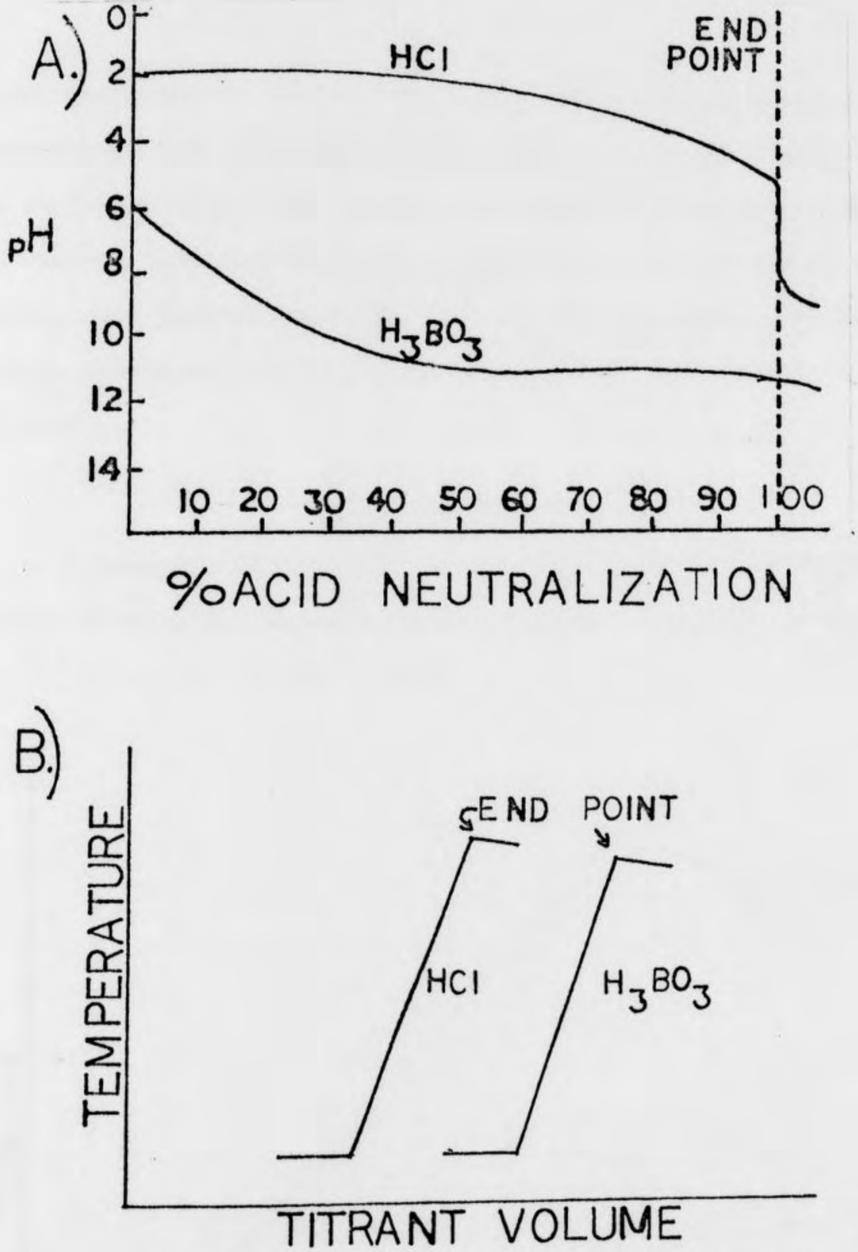


Figure 6. A. Potentiometric Titration of Weak Acid (H_3BO_3) and Strong Acid (HCl)
B. Thermometric Titration of Weak and Strong Acids

electrolyte exists. On the other hand, thermometric titrations may be done in almost any solvent in contrast to the restrictions placed on electroanalytical and spectroscopic analysis. Another advantage is that the calculations and interpretation of data are simple relative to the other methods mentioned. The apparatus is easily and inexpensively constructed which makes the use of this method rather attractive.

Idealized Titration Curves

A thermometric titration curve is essentially a temperature vs. volume (time) plot consisting of four regions. The first section is

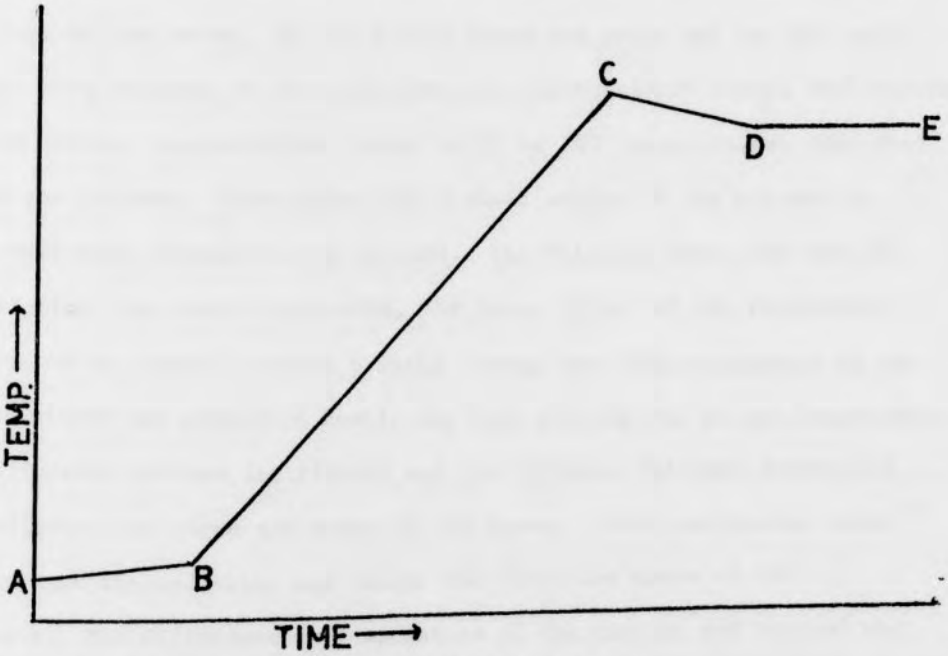


Figure 7. Idealized Thermometric Titration Curve

a "pre-reaction" region or baseline. This part of the curve, $\overline{AB}$, is where no titrant is added and shows the titrand temperature almost constant with time. The titrant is started at point B and curve $\overline{BC}$ is the reaction line. The reaction causes a change in temperature with time or volume of titrant added and thus the slope change from that of $\overline{AB}$. Point C is the end point of the reaction. The post-reaction line $\overline{CD}$ is often known as the excess reagent line. The titrant is stopped at point D and an afterslope $\overline{DE}$ is taken.

Factors Affecting the Shape of the Curve

The reaction, or reactions, involved in the titration and their equilibrium constants help determine the shape of the curve. Of course the magnitude of the heats of reaction have an effect on the slope of the curve. To get a good sharp end point and to make sure the heat capacity of the cell does not substantially change with volume, the titrant concentration should be 50 to 100 times greater than that of the titrand. This means only a small volume of the titrant is needed with respect to the titrand. The delivery rate, the heat of dilution, the heat of stirring, the Joule effect of the thermistor (caused by a small current passing through the high resistance of the thermistor and producing heat), the heat effects due to any temperature difference between the titrant and the titrand, and heat losses all influence the slope and shape of the curve. These extraneous heats may mask the end point and change the slope and shape of the curve. The difference in temperature of the titrant and titrand may mask the end point as can be seen in Figure 8.

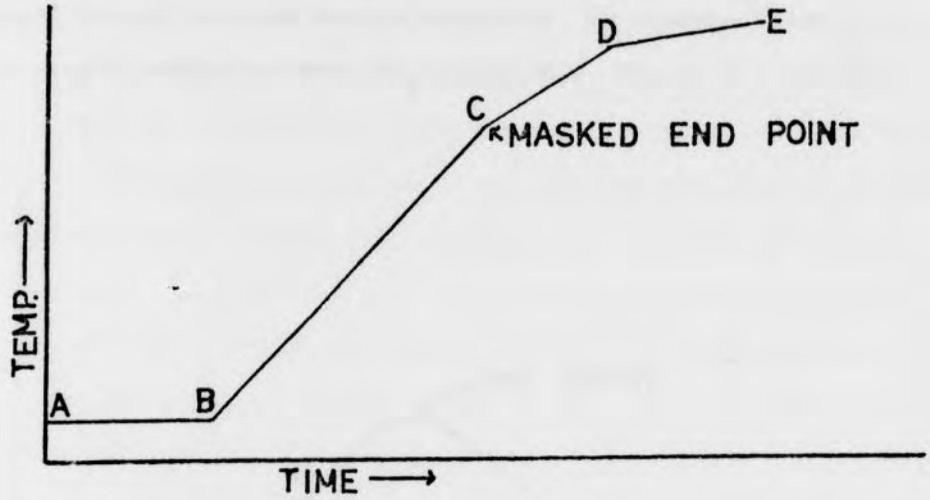


Figure 8. Thermometric Titration Curve With Masked End Point

Some of these heat effects may be eliminated by the use of a two cell (differential) system. In a one cell system the adiabatic or semi-adiabatic cell contains a heat sensing device, a stirring device, a titration delivery tube, and a heater. For a differential system, everything is duplicated allowing unwanted heats to be cancelled. The difference in a differential system is that the reaction of interest only takes place in one cell and thus since everything else is the same for both cells the circuitry cancels the extraneous effects. More details on this will follow in the section on apparatus.

End Point Determination

If the parameters are chosen carefully, a clearly defined end point can be obtained. Sometimes, however, when a small ΔH is present the end point is hard to determine. For example,[57] the titration of sodium malonate (Na_2A) with $HClO_4$ (Figure 9). One of

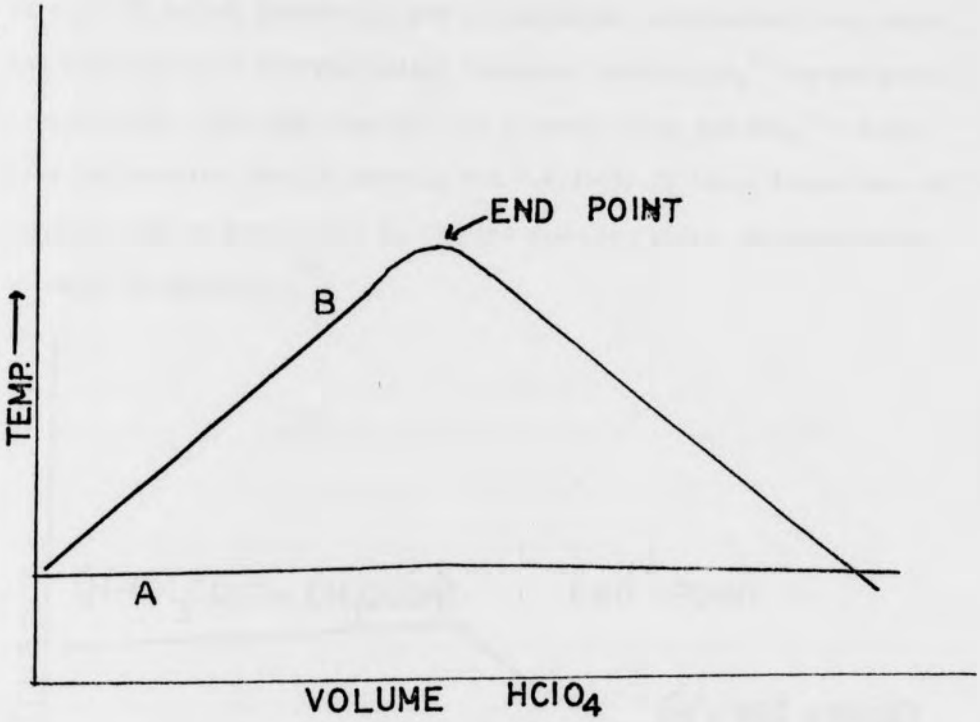


Figure 9. Thermometric Titration Curve
(a) Without Amplification
(b) With Electrical Amplification

the solutions to this problem is amplification of the signal (Figure 9) to increase sensitivity of the temperature axis of the graph and give a better end point by increasing the slope.

Another way to accentuate the end point is to use a thermochemical indicator. The reaction of the titrant with the indicator, which only occurs beyond the end point gives a larger ΔH than does the reaction of the titrant with the titrand; thus, the end point is more visible. For example,[58] in the titration of the acetate ion with strong acid, $\Delta H = -0.01 \pm 0.01$ kcal/mole, and no end point is observed; but, with the addition of a thermochemical indicator such as SO_4^{2-} an end point is observed. Although the SO_4^{2-} is a weaker base (pK HSO_4^- = 1.97) than the acetate ion (pK acetate ion = 4.766), it has a large heat of reaction and is protonated by the hydrogen ion after the acetate is consumed (Figure 10).[58]

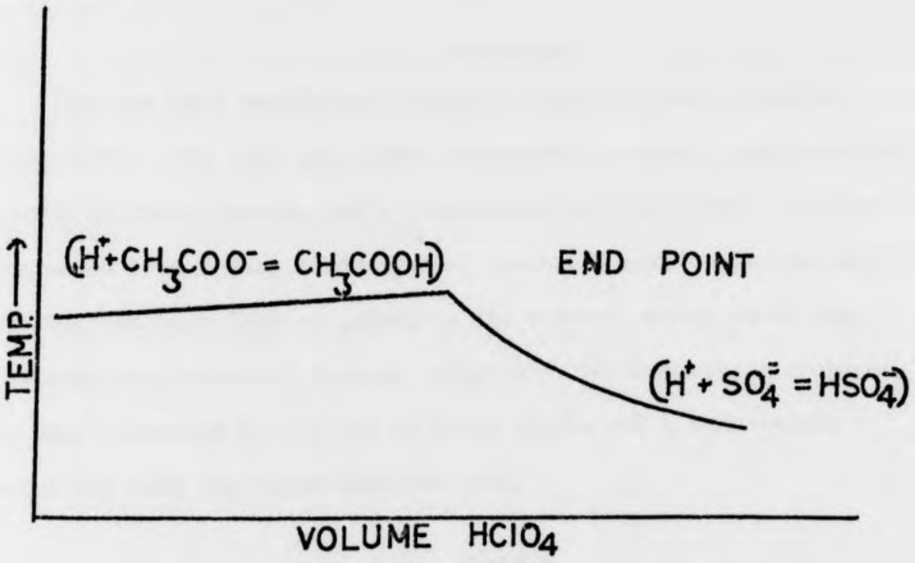


Figure 10. Thermometric Titration Curve--Use of "Thermometric Indicator"

End Point Sharpness

Rounding of the end point is usually a result of the titration not having come to completion. An equilibrium constant smaller than desired is the cause of this complication. If the free energy term is sufficient then the slope at the end point depends on the enthalpy term. However, if the free energy term is not sufficient then the end point will be rounded no matter what the enthalpy term. These factors do not totally restrict the determination of the end point because an extrapolation of the linear portion of the titration curve ($\overline{BC}$) on section $\overline{CD}$ can be performed.

Apparatus

The one cell system was the first type used for titration calorimetry. The cell has always contained a stirrer, some kind of titrant delivery system, and a temperature sensing device. It has progressed from a very crude system, which did not compensate for any unwanted heat loss or gains, to the present system which can eliminate many unwanted thermal energies. The heat escape problem has been decreased by the use of Dewar flasks and a temperature controlled bath that surrounds the cell.

History

In 1910, Howard[59] proposed the use of heats of reaction as an analytical tool. Soon after this, in 1913, Bell and Cowell[60] published the first article on thermometric titrations. The study of this analytical method was not solely conducted in the United States, but also in Switzerland, France (1920's), and other European countries.[61]

The method then being used was a discontinuous flow technique. The equipment consisted of a volumetric burette, a Beckman thermometer, a Dewar flask, and a glass stirrer. After an addition of titrant the temperature of the solution was taken using the Beckman® thermometer and the system was then allowed to come to thermal equilibrium before another addition of titrant. This equilibrium was necessary because of the low conductivity of the glass bulb of the thermometer which causes a slow response and because of the large heat capacity of the immersed portion of the thermometer. This method was therefore not useful unless the concentrations were high enough to produce a large temperature change. Another problem was the time element (the process took quite a long time to complete, from about one half to one hour). The heat exchange with the environment was apparent from the fact that the data was often not reproducible.

Dutoit and Grobel in 1922[62] showed that the method could be used for a variety of reactions: acid-base, precipitation, and complexation. A thermostated burette, a Beckman thermometer, and a Dewar flask were used. Since the conversion of the system for different determinations was relatively easy, this system was used by many people for a variety of analyses. Acid-base titrations and compleximetric titrations were the main types studied and will be discussed in detail in a later section.

The cell, the Dewar flask, had to be large to accomodate the large sensing device, the Beckman thermometer. Thus, a large amount of titrand had to be used to submerge the thermometer stirrer on the tip of the burette. The tip of the burette had to be submerged to prevent any titrant from hanging on the end when the flow was stopped. To produce a sufficient amount of heat for detection and recording, a larger volume of titrant was used. However, this presented a problem, because as the volume in the cell is changed, the heat capacity is changed. On changing the heat capacity, the linear relationship between volume of titrant and heat produced is no longer valid. To try to alleviate the problem, another one was created. If the concentration of the titrant is increased then a smaller, more acceptable, volume will be used. However, as the concentration increases, so does the heat of dilution in some cases. The only solution at that time was to lower the concentration, but, as expected, the accuracy suffered.

The next major advance came in 1953. Linde, Rogers, and Hume[53] published a paper on the use of a thermistor as a temperature sensing device. This was the first published account on the use of thermistors, although Müller[63] used one in the 1940's. A thermistor is a semiconductor material, usually a mixture of ferrites and a trace amount of oxides. In contrast to that for normal (<u>e.g.</u>, platinum) conductors, these semiconductors have a large negative temperature coefficient of resistance, a low heat capacity, and, therefore, respond quickly to the heat change of the system. The resistance of the thermistor can be best described by equation 6.[64]

$$R = \exp(A + \frac{B}{T + C}) = \exp A \cdot \exp\left|\frac{B}{(T + C)}\right| \qquad \text{(equation 6)}$$

where: A, B, and C are constants for a given thermistor.

Thermistors are very sensitive (large $\frac{\Delta R}{\Delta T}$) and can detect very small temperature changes. They do not (usually) measure exact temperature, but rather the temperature change in the system. However, they can be calibrated (as the H_g height is for a thermometer) to be able to read temperature directly. In many applications, the thermistor is used as one arm of a Wheatstone bridge.

Linde, Rogers, and Hume[53] also used a constant flow burette. Thus the use of an automatic recording device was made possible. They also made improvements in the electronics of the system. A buck out circuit was added which was useful when the recorder was being used. The buck out voltage produced from this system was used to zero the recorder. The titration of HCl with NaOH in different solvent systems was studied by Linde, Rogers, and Hume. They found that even when their solutions were thick slurries no change in end point volume was observed compared to that in normal aqueous solutions.

First and second derivative of titration curves are useful in analysis of data, and can locate the end point with more ease, precision, and accuracy. In the late 1950's Zenchelsky and Segatto[65] devised a resistance-capacitance network to record the first and second derivative curves automatically. This was done through the output of the thermistor bridge. This method helped to isolate the end point without having to extrapolate the base lines.

Continual progress was being made toward an automatic system. Priestly[66] devised an automatic digital titration in 1963. The flow rate of the titration could be varied to a maximum of 10 ml/min. The glass stirrers were abandoned and a vibrator was used. A large amount of turbulence was produced by the vibrator using vertical motion. The thermistor was housed in the stem of the vibrator. Titrant was added with a constant flow piston burette, controlled by the signal from a modified Wheatstone bridge. The signal was filtered to eliminate stirrer noise, and differentiated to give a square well voltage. The signal was sent through a resistance-capacitance network and had an amplitude proportional to the rate of temperature change. The time period was equal to the length of the titration from begining to end point. The differentiated signal was amplified to a workable size to be recorded on a strip chart recorder or a digital counter. This system enabled the operator to use low concentrations of reactants and to detect small temperature change with some accuracy.

A multi-function thermopile and galvanometer were used in 1941 by Müller.[66] This system was used to replace the Beckman thermometer. He also used one of the first differential systems. To compensate for the heat of reaction in the sample vessel, a second vessel was used that contained a heater and a temperature sensing device. A photoelectric relay was used to switch the reference heating on and off in order to compensate for the temperature change in the sample cell. A clock was used to record the time of heating which was proportional to the temperature change in the titration vessel. This improved apparatus was used by Müller for titrations of ferrous iron with potassium permanginate. He thought the thermometric method was only useful if the data was directly recorded. Otherwise, the method was too time consuming.

The differential, or two cell, system was used and improved upon by Tyson, McCurdy, and Bricker.[67] Their two cell system contained two thermistors per cell, matched glass stirrers, and two motor-driven syringes. The set of thermistors were matched for temperature and resistance response over the range of anticipated investigation. The stirrers were each run by a variac controlled motor and were thus synchronized. The motor-driven syringes had capillary tips, a three-way stopcock, and a reservoir. The flow rates were known and matched for the two 5cc syringes so the rate of addition to each cell was the same. The tips of the capillary tubes were below the solution in the cell so the volume of titrant would not be in error due to lingering drops. The desired chemical reaction only took place in one cell, the sample cell, while the reference cell cancelled out many of the extraneous heat effects. This was possible because the same conditions were applied to both cells except for the actual reaction. For example, the heat of stirring was cancelled because the stirrers were moving at the same rate.

Many simplified differential systems were used, such as those of Keily and Hume,[68] and Rondeau, Legrand, and Paris.[66] These systems tried to compensate for specific unwanted heats by duplication of minimal amounts of equipment. For example, Rondeau, et. al., used a reference cell that did not receive the titrant. They claimed to be able to cancel the Joule effect of the thermistor and the heat of stirring by duplication only of the stirrer and the thermistor.

A two cell system was used by Nakanishi and Fujieda in 1972[69] with some major changes in conventional thinking. A system which allowed the escape of heat from the non insulated glass cells into the surrounding water was used. They used an analog computer circuit with an operational amplifier to treat the observed temperature change. Curves that closely resembled those for an adiabatic system were observed for the reaction of hydrochloric acid and phenol with sodium hydroxide. One major assumption was made about this system, that is, the titrant was assumed to mix instantaneously, keeping the temperature uniform in the glass vessels and the surrounding water. They felt that some of the major advances of the system were its rapid attainment of thermal equilibrium (less than ten minutes); the temperature changes in the system followed Newtonian behavior exactly and, thus, a series of mathematical equations may be applied; and no great difference in the temperature of the titrand and titrant exists with this system, as the cell temperature is always nearly that of the bath and titrant.

When a system can be studied with other titration methods, such as potentiometric or coulometric, thermometric titrations may, in some cases, not be preferred by the investigator because of their often poorer precision. Smith, et al.,[70] found the major problems in precision were the noise level, base line drift caused by stirring heats and the loss of heat from the cell, and the reproducibilities of the flow rate of the delivery burette. They made some changes in the electronics to try to eliminate these problems. To improve the signal to noise ratio, a phase sensitive amplifier was used. Alleviation of base line drift was accomplished by a ramp function generator which was to offset the heat effects. To improve the reproducibility of the flow rate, the volume of the titrant added was monitored by a linear position transducer. The modifications were tested by performing known reactions that gave sharp end points even at low concentrations. It was found that the limiting factor for the precision of the instrument was now the reproducibility of the flow rate of the titrant. The improvements solved the basic problems for which they were designed; however, with the new sensitivity came other problems. Noise levels that had previously been swamped out were now beginning to come into the picture. As is always the case, more improvements may be necessary.

Other advances have been made in equipment design[71,72] and mathematical interpretation.[73,74] The state of the art now is such that titration systems can be fully automated. A computer can be incorporated into the system not only to run the experiment, but also to calculate data. Improvements will continually be made as the technique is more widely used. Thermometric titrations can be used for a variety of reactions and some of these will be reviewed in the following section.

Applications

The application of thermometric titrations may be divided into two groups: analytical applications and fundamental or calorimetric applications. The analytical group contains studies of concentration of an unknown, and amount of an unknown, while the fundamental group contains studies such as heat of reaction, free energy of reaction, entropy of reaction, and reaction mechanism determination.

Analytical Applications

Acid-base or neutralization reactions can usually be thought of as being in the analytical group as they are usually used for determination of concentration or amount of reagent. As mentioned, the first thermometric titration recorded was in 1913, a neutralization reaction by Bell and Cowell.[60] A new method was needed to determine the amount of ammonia necessary to generate a neutral solution of ammonium citrate. The first attempt was based on solubilities. This was an extraction method followed up by a visual titration. A temperature method was suggested and tried. This was done with early titration equipment previously described in the section on apparatus. Each point was taken after the addition of a small increment of titrant. The system was checked by utilizing twice normal solutions of sulfuric acid and ammonia. The results from this agreed exactly with those found from the visual titration of the ammonia, sulfuric acid system.

Organic acids were used again in a study by Jordan and Dunbaugh in 1952.[75] They chose four acids: boric, acetic, monochloroacetic, and tricholoacetic. These acids were chosen because they have comparable neutralization enthalpies and cover a wide range of acid strengths. When the ionization constant is small for an acid-base system, conventional methods cannot be used without difficulties in determining the end point. Thus, to be used as a quantitative method of analysis, thermometric titrimetry must show less dependence on the ionization constant than classical procedures. The results showed that in fact this was a valid analytical method for the titration of weak acids even in the low concentration ranges.

The determination of free acid in the presence of a hydrolizable cation was described in 1959 by Miller and Thomason.[76] The study was done on the free acid in hydrofluoric acid solution of zirconium. When this system is titrated the result is the neutralization of the free acid and the hydrolysis of the zirconyl ions. Problems were encountered when the authors made up the standard acid solution: the perchloric acid would not complex the zirconium ion. These solutions had to be made indirectly. Other systems studied were uranyl sulfate-sulfuric acid and thorium nitrate-nitric acid.

Much more work has been done on this type neutralization reaction than has been mentioned here.[77] Strong acid-strong base reactions have been tried. Also, mixtures of strong and weak bases have been titrated to determine the concentration of the weak base.

Precipitation reactions can also be studied thermometrically. As is expected, the heat of precipitation is a result of the removal of the ions from their solvent molecules and the formation of a solid. The concentration is not the only effect on the ΔH (enthalpy) of a precipitation reaction that may be investigated; the thermal stabilization of the precipitate may also be determined.

In the case of precipitation reactions, the volume of the titrant must be kept small, not only to avoid change in the heat capacity of the system, but also to avoid change in the ionic strength of the system. For example, if a solution $X^+ + Y^-$ were titrated with Z^+ and W^- and gave the precipitate XW, then for every X^+ that is removed from solution, a Z^+ will be added, thus keeping the ionic strength constant during the actual titration.

The precipitate may undergo a rearrangement after formation to a more stable form. Thus, the overall free energy change may be thought of as two terms (equation 7).[78]

$$\Delta G = \Delta G_i - \Delta G_s \qquad \text{(equation 7)}$$

where:

ΔG_i = the instantaneous free energy

ΔG_s = the stabilization free energy

Both terms mentioned in equation 7 must be negative because they refer to spontaneous processes. It was also thought by Ewing and Maze[78] toward the negative unless $T\Delta S$ was large and positive. An example is the cooling when KCl is dissolved in water or the endothermic chelation of magnesium by EDTA.

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Thermometric titration was first used for a precipitation reaction in 1921 by Dutoit and Grobet[62] who found that the precipitation of basic salts and hydroxides, i.e., zinc, lead (II), and magnesium, gave three, four, and three end point breaks respectively when treated with sodium hydroxide. Precipitation thermometric titrations were applied in 1924 by Dean and Watts[79] when they took an approximately 0.5N solution of $BaCl_2$ and titrated it against

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a 0.5g portion of a soluble sulfate. The precipitate was barium sulfate and the amounts compared well with those determined by a gravimetric analysis that had been done previously. The new method was then successfully applied to the determination of sulfur in an ore. Samples containing from 20 to 44% sulfur were tested. The results were compared with those determined from gravimetric analysis and it was determined that the method was useful. Time is a factor, and the thermometric titration is often less time consuming and tedious than the classical gravimetric analysis.

The precipitation of silver halides has long been a good analytical tool in gravimetric analysis. Dean and Newcome[80] experimented with silver chloride and cyanide compounds. They used the same technique as did Dean and Watts[79] and found that the amount of chloride could be thermometrically determined, using $AgNO_3$ as the titrant, with some degree of accuracy. When the cyanide ion was introduced to the chloride solution and titrated, one break was found at the completion of both precipitations. They thought they could get two breaks, one for each ion's end point, if no coprecipitation was taking place. This was not found to be true; they concluded that the method was good for the determination of the chloride ion if no other ions were present.

The improvements made to the apparatus by Linde, Rogers, and Hume[53] (mentioned in the section on apparatus) also improved the accuracy of the silver halide precipitation reaction.
Their system was tested with 1.0M hydrochloric acid as the titrant and a 1 gram sample of $AgNO_3$.

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In 1959, Jordan, Meier, Bellingham, and Pendergast[81] used thermometric titrations to determine the concentration of KCl by precipitation titration in fused lithium potassium nitrate. They made many changes in the conventional system to accomodate the molten salts. The NaCl was precipitated with $AgNO_3$ at 158° in a Dewar flask.

The white crystals of AgCl precipitate were formed instantaneously with the addition of the titrant.

The differential system of Tyson, McCurdy, and Bricker[82] was also tested with the silver halide precipitation reaction. The silver chloride precipitation reaction had been well established as a calibration reaction. They also tried the mecuric nitrate-hydrochloric acid system for which they saw two breaks in the titration curve. The heat of reaction for the first step was slightly higher than that for the second step. The first break was thought to be the reaction: $Hg^{+2} + Cl^{-} = HgCl^{+}$ while the second break was $HgCl^{+} + Cl^{-} = HgCl_2$. This system was tested with other titrations such as the ferous ethylene diammonium sulfate-ceric sulfate and the volume results were within 99.8 ± 0.7% of the theoretical value.

The precipitate of potassium with sodium tetraphenylborate was one of the first examples of back titrations using a precipitation.[83] The back titration was necessary in this case because the solubility in water of sodium tetraphenylborate was not high enough to obtain the concentrations needed for a normal thermometric titration. When using this back titration procedure, ions such as NH_4^+, Ag^+, Tl^+, and Hg^{2+} cannot be present because they will precipitate along with the potassium ion.

Mixed halides were determined in 1966 by Harris.[78] He introduced a thermopile as a temperature sensing device in the thermometric apparatus. This new sensitive device was able to determine mixtures of halides, precipitated with $AgNO_3$, to some degree of accuracy. Mixtures of Cl^- and I^- gave the best results, but even then co-precipitation presented some difficulties.

Other mixtures can be quantitatively studied, such as that of calcium and magnesium, by thermometric titrimetry. The calcium and magnesium mixture was titrated with ammonium oxalate at pH 8. At this pH the calcium will give a well defined titration curve instantaneously, but the magnesium seemed to give isothermal lines.[84] The reason the magnesium gives no signal is because the precipitation of magnesium oxalate dihydrate proceeds via a complex reaction sequence. The magnesium was "kinetically masked" and thus the determination of calcium could be carried out without interuption or coprecipitation of the magnesium.

A good instrumental method for the determination of SO_4^{2-} and ClO_4^- did not exist until Carr and Jordan[85] utilized thermometric titrations for these analyses. Tetraphenylphosphonium, tetraphenylarsonium, and tetraphenylantimonium ions were found to form sparingly soluble salts with perchlorate ion. After testing, the tetraphenylarsonium chloride was found to be the best titrant for this precipitation reaction. Solutions of perchlorate were tested between concentrations of 0.003 and 0.008M with a precision of ±0.5%. The lower concentrations had the same precision although there was a lag in the precipitation reaction due to the slow kinetics. Of the common ions tested for interference, only the permaganate ion was found to introduce any error. This is true because the permaganate will precipitate out along with the perchlorate. The major features of this method were that it was rapid and convenient in the presence of most other cations and anions.

Complexation reactions can be used to determine the concentrations of metal ions in solution. For example, Jordan and Billingham[83] have determined the concentration of $Ca^{+2}(aq)$ in the presence of $Mg^{+2}(aq)$ using ammonium oxalate as the titrant at pH 8. The calcium will give a well defined titration curve and a precipitate immediately, but no signal or precipitate is visible for magnesium. The lack of a signal for magnesium is due to the complex reaction sequence for the precipitation of magnesium oxalate dihydrate. The magnesium is "kinetically masked" and thus the determination of calcium can be carried out without interruption or coprecipitation of the magnesium.

The analytical use of thermometric titrations with many other reaction types is feasible. The method can be used, not only in aqueous media, but also in the study of non-aqueous reactions. Forman and Hume in 1959[86] determined the strength of amines in acetonitrile. The initial slopes of the titration curves were used to estimate the heats of neutralization of the amines. They found the method to be a good measure not only of the strengths of aromatic amines, but also alphatic, primary, and straight chain secondary amines in acetonitrile.

Although oxidation-reduction reactions generally have high heats of reaction not much work has been done to apply thermometric techniques to these systems. The more common oxidation-reduction reactions have at least been tried. One example of the study of redox reactions in thermometric titrations is the work of Billingham and Ries in 1964.[87] They used a standard solution of thio-sulfate to determine the copper concentration of a solution. The copper concentration ranged from 5×10^{-2} to 2×10^{-2}M and was determined with 1 to 3% relative error.

As can be seen from the above examples, thermometric titrimetry is quite versatile in its applications to analytical methods.

Calorimetric Applications

Information other than concentrations of unknows may be determined by titration calorimetry. These studies determine other properties about the solutions being studied, such as heats of transfer, reaction, dilution, and mutarotation; and reaction mechanisms.

In 1954, Persach and Brescia[88] determined the mechanism of the precipitation of magnesium oxalate from supersaturated solutions. This was useful in explaining the gravimetric determination of calcium oxalate in the presence of magnesium. To prevent deficiencies in the precipitation of calcium oxalate, enough oxalate to combine with both the calcium and magnesium is added. The procedure and the reasoning for this reaction was discussed in the previous section.

Calorimetric titrations may be used to determine properties of metal ions or the chelating agent itself in complexation reactions. The most frequently used complexing agent is ethylenediamenetetra-acetic acid (EDTA). The stability of metal chelates was discussed in a paper by Carini and Martell in 1954.[89] Thermodynamic equilibrium constants were reported for the reaction of a M^{+2} (aq) and Y^{-4} (aq) where M^{+2} is an alkaline earth ion and Y^{-4} is the tetranegative anion of EDTA. He found the high stability of these complexes was due to the large entropy increase of complex formation. Charles continued this work and in a later paper[90] that same year published a series of heats of reaction for some mono- and divalent metal ions with EDTA in aqueous solutions. A direct calorimetric method was used to determine the heats of formation of the reactions. The entropy change was then calculated from the enthalpy change of the reaction and the known equilibrium constant. There are two major reasons for the choice of EDTA for use in this investigation. It is versatile in that it forms stable, water soluble chelates with many metal ions and the equilibrium constants are available for many of the systems.

The study of the complexation of metals with EDTA continued with the work of Jordan and Alleman.[91] Their results for the heats of reaction were within 0.5% of expected values for cadmium, calcium, cobalt, copper, lead, magnesium, nickel, and zinc bivalent ions. The accuracy and precision for the heats of reaction for lead were within 0.1% of the expected values because the heat of formation of lead is higher than for other complexes with EDTA. Mixtures of the bivalent metals have been complexed with EDTA. The titration for an equimolar mixture of 0.0005M calcium and magnesium with 1.0M EDTA was found to have an accuracy of 0.4% for calcium and 2% for magnesium. However, when the number of ions in the solution is increased, the equilivance points do not correspond exactly to the theoretical values. Many other studies have been done using EDTA as a chelating agent to determine equilibrium constants for the complex.[92,93]

Other chelating agents have been studied thermometrically besides EDTA.[94] However, at times, more conventional methods for complexing ions are found to yield more accurate and precise data. In the work of Rasmussen and Nielsen[40] two clear breaks were expected by the investigators in the silver cyanide-potassiumdicyanoargenate (II) ions compexation. The end points turned out to be blurred because the reaction was too slow to be followed thermometrically.

Weak complexes of metal ions with Cl^-, Br^-, I^-, or SO_4^{2-} were studied by Christensen, et al.[95] They developed a series of equations to calculate ΔH, ΔS, ΔG from the same thermometric titration. The equations were tested by finding the pK values of samples with fairly large ΔH values. For example, the pK values were found for the proton ionization from HSO_4^- and HPO_4^{2-}. The values obtained with the new method were in good agreement with ionization constants found in the literature.

The heats of transfer of slightly soluble salts were used in a study by Bright and Jezorek[51] of the structural interactions of nonelectrolyte-water solutions. The reactions used were precipitation reactions of the salts silver iodide, silver tetraphenylborate, tetraphenylarsonium tetraphenylborate, and tetra-n-butylammonium tetraphenylborate. The enthalpy of transfer from water to the nonelectrolytes was measured using the colorimetric titration technique. The results obtained in this study show that these salts act as good probes for the indirect determination of the structural interactions in water-nonelectrolyte solutions.

Thermometric titrations may be used to determine the heats of proton dissociation of various substances. Christensen and Izatt[96] found the heats of proton dissociation from ribonucleotides and other biologically related compounds. A series of equations was developed in this study to determine thermodynamic functions (e.g., ΔH for each protination) taking into consideration some extraneous heat effects. These equations are applicable to other acid-base type reactions as well.

The pK (equilibrium constant for proton ionization reaction), ΔH° (enthalpy change of the reaction), and ΔS° (entropy change of the reaction) values for carbohydrates were obtained from ionization studies by Izatt, et al., in 1966.[97] They determined that the acidity found to exist for the monosaccharides is associated with the proton ionization in the first position on the compound. Christensen, et al.,[98] continued studies of this kind in 1967 on dilute aqueous solutions of o-, m-, and p-aminobenzoic acids. Entropy titrations and pH (potentiometric) titrations were used to determine the pK_1 and ΔH° values for m- and p-aminobenzoic acids and the pK values for the methylamino benzoates. The values calculated using the entropy titrations agreed well with the values obtained by the pH titration.

The thermodynamic functions for other acid-base systems can be determined by thermometric titrimetry. Strong acid (base) systems as well as weak acid (base) systems have been extensively studied. Christensen, Wrathall, and Izatt[93] extended the study of acid-base systems to the intermediate pK range ($4<pK<10$). They determined pK, ΔH°, and ΔS° values for the proton dissociation of metanilic acid, pyridinium ion, protanated THAM, and glycine with acetic acid as the titrant.

The procedure and the guidelines for the use of titration calorimetry in the determination of equilibrium constants was outlined in a series of papers by Christensen, et al.[99] The calculations of the equilibrium constants for proton ionization and metal-complex formation as well as those for the entropy and enthalpy were explained. Examples of various systems and calculations were included in this review as well as an explanation of usefulness of the system.

As can be seen from these examples, thermometric titrations may be applied to many different systems. The method is versatile and fast compared to many conventional techniques.

CHAPTER FOUR

EXPERIMENTAL

Chemicals and Solutions

The water used in this system was distilled once using a Barnstead Still (Model SM-10, Barnstead Still and Sterilizer Co., Inc., Forest Hills, Boston, Massachusetts) and further purified by running it through a mixed bed ion exchange column (Barnstead Hose Type Cartridge, Fisher Scientific Company) to remove inorganic impurities. The removal of organic impurities was insured by a second distillation in a vented all glass distillation apparatus. The water was collected and stored in a Nalgene carboy (Nalge Sybron Corporation) which prevented contamination from carbon dioxide. The water was used without further purification directly from the polyethylene container.

The carbohydrates and polyhydroxy alcohols, ribose (Eastman Organic Chemicals), d-Sorbitol (reagent grade, Fisher Scientific Company), mannitol, glucose, and sucrose (certified ACS, Fisher Scientific Company) were used without further purification. They were, however, dried in an oven, at an appropriate temperature and then stored in a dessicator with indicating Drierite (W. A. Hammond Drierite Company), as were all solid chemicals.

The water--sugar or water-alcohol solutions were prepared by weight as follows. The amount of solid needed for the desired concentration, using 400 ml of water, was calculated using the equation:

$$\text{wt. of solid} = \frac{\dfrac{\text{mole \% desired}}{100}\;\dfrac{\text{vol. H}_2\text{O in ml. density H}_2\text{O}}{\text{M. W. H2O}}}{1-\dfrac{\text{mole \%}}{100}}\;(\text{M. W. solid}) \qquad \text{(equation 8)}$$

A clean air dried amber bottle was weighed to a tenth of a gram. The sugar or alcohol was then added to the approximate weight needed by tapping the powder in the bottle using a funnel on the balance. The funnel was then removed and the bottle and its contents weighed. The desired volume of water was then added and the contents reweighed. The weight of the sugar (or alcohol) and the water were determined by difference and the actual concentration in mole % of solute was calculated using this equation:

$$\text{mole \%} = \frac{\dfrac{\text{wt. solute}}{\text{M. W. solute}}}{\dfrac{\text{wt. H}_2\text{O}}{\text{M. W. H}_2\text{O}} + \dfrac{\text{wt. solute}}{\text{M. W. solute}}} \times 100 \qquad \text{(equation 9)}$$

These solutions were kept cool when not in use to help deter the growth of microorganisms.

Since glucose is a reducing sugar, problems were encountered with $AgNO_3$ solutions in the water-glucose solvent mixtures, namely some silver(I) reduction occured yielding a concentration change. In order to get a handle on this problem a study of the kinetics of this reduction was performed. A solution of known concentration was prepared and samples were taken at various time intervals and the silver(I) concentration determined. No significant concentration changes were seen (Table 1). Observation of the solution detected no further formation of metallic silver after about two hours.

Solutions were thereafter made up, allowed to stand in a cool dark place for two hours, filtered to remove the solid silver metal particles formed, and then used for the titration series. Since six sets of titrations were normally run, the concentration of Ag(I) was checked between the third and fourth titration assuming a more or less linear concentration change from the last run. The concentration was determined by normal gravimetric analysis using excess hydrochloric acid.

Table 1

Time period (hrs)	Concentration of the $AgNO_3$-water-glucose solution (Molar)
0 (based on wt. of $AgNO_3$)	0.1179
1	0.1207
3	0.1148
6	0.1081
12	0.1132
24	0.1142

The hydrochloric acid (reagent ACS, Fisher Scientific Company) solution was made by adding distilled water from the carboy to about 0.1 M to be used as a titrant for THAM as well as for $AgNO_3$ gravimetric analyses. The actual concentration of the hydrochloric acid solution was determined by normal gravimentric procedures using excess silver nitrate-water solution.

All solutions using silver nitrate (analytical reagent, Mallinckrodt Chemical Works) were made of the $AgNO_3$ dried in an oven at 115° for at least one hour, but no more than two hours. The solutions of $AgNO_3$ used as thermometric titrant were approximately 0.1M.

The sodium iodide (ACS certified, Fisher Scientific Company) was dried before use as titrand.

The tris(hydroxymethyl)aminomethane, THAM (certified primary standard, Fisher Scientific Company) was made up fresh periodically and not allowed to stand for long periods of time (more than a week or so).

The tetrabutylammonium bromide (Eastman Organic Chemicals) was dissolved in a small amount of acetone (Fisher Certified), filtered, and precipitated with absolute ether[100] (reagent grade, ACS, Matheson Coleman and Bell Manufacturing Chemists). The precipitate was dried under vacuum at 40-50° for at least one hour and then at 80° overnight at atmospheric pressure. It was cooled (in a dessicator) for at least one half hour before use. The titrant solutions of $Bu_4N^+Br^-$ were approximately 0.1M concentration. All titrant solutions were made at 25.00°.

The titrand for the $Bu_4N^+Br^-$ was sodium tetraphenylborate and was used without purification.

Apparatus

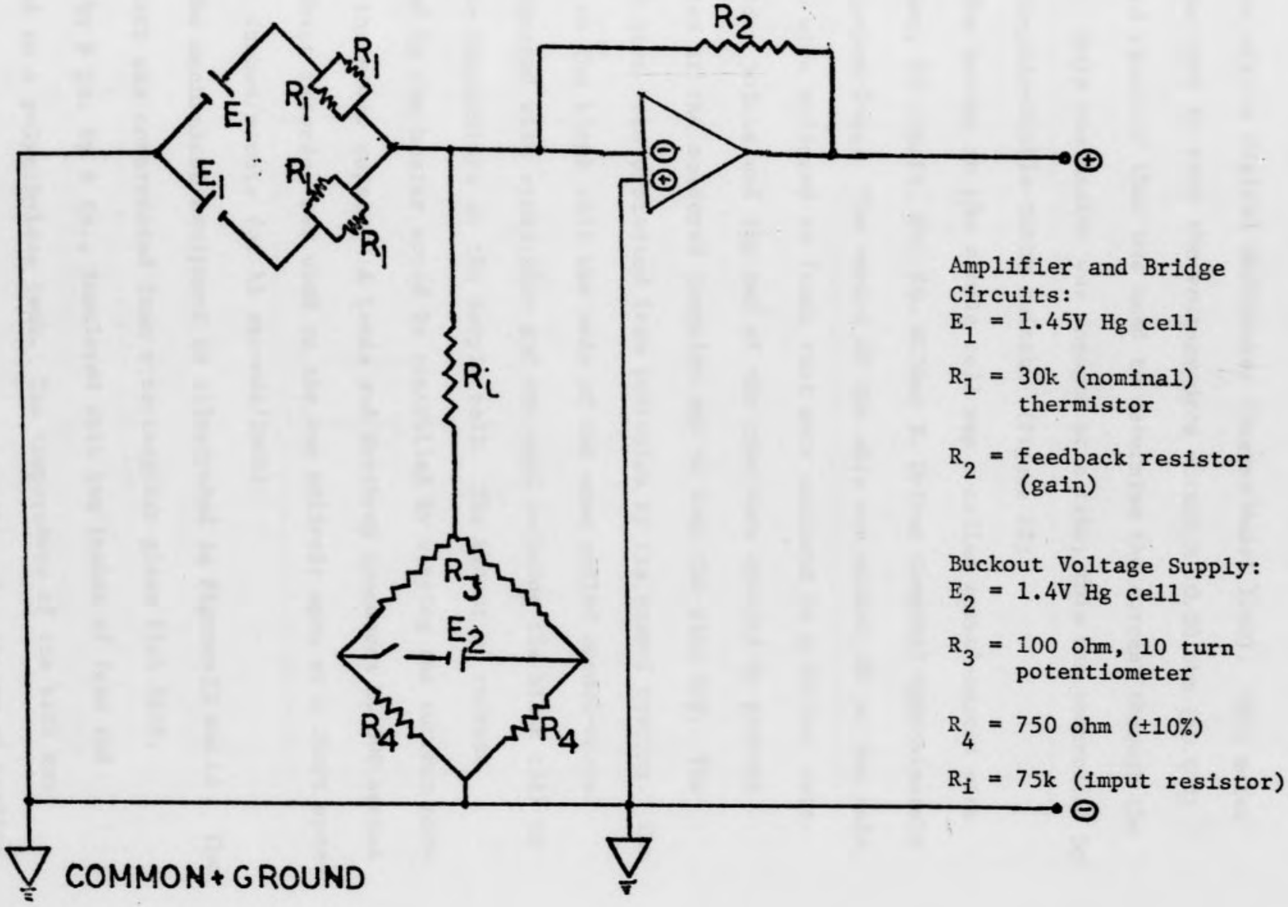
A differential system is one in which many extraneous heat effects are cancelled electronically as has been previously described in the section on the history of thermometric titrations. The differential system used in this investigation was fashioned after that described by Tyson, McCurdy, and Bricker.[82]

The equipment used in this study can be broken into two major divisions, electrical and mechanical. The temperature detecting circuit utilized the bridge shown in Figure 11. This bridge contained a 1.45 volt Hg cell in each of two arms while the other two arms each contained a pair of two inch glass probe type thermistors (Victory Engineering Company, Type A43R). The thermistors were paired to decrease the amount of thermal noise by balancing sudden localized heat gradients in the solutions. This bridge provides a more linear resistance vs. temperature response than does a conventional Wheatstone bridge.[51] An amplifier was available at the bridge output, but was not used in this study. In the sample cell the thermistors were encased in a Teflon (register by DuPont) tube closed at the end using silicon rubber and/or epoxy glue. Only the tip of the thermistor was exposed to the system. The leads of the thermistors were connected to the bridge using a shielded cable, which in turn was grounded to help minimize electrical noise.

The sensing circuit was connected in series with a buck out circuit used to keep the pen of the recorder on scale. This Wheatstone bridge buck out circuit contained a variable 100 ohm ten turn potentiometer which was set at about the middle placing about 50 ohms in each of two arms; a 75 kohm resistor in series with the bridge served as the imput resistance when the amplifier was in use. The two other arms of the Wheatstone bridge contained fixed 750 ohm (±10%) resistors. The bridge was powered by a 1.40 volt Hg cell.

The heating circuit was powered by a Heathkit Regulated Low-Voltage Power Supply (Model IP-27). Voltage across the heater was

Figure 11. Amplifier Circuit, Bridge Circuit, and Buckout Voltage Supply



Amplifier and Bridge Circuits:
E_1 = 1.45V Hg cell

R_1 = 30k (nominal) thermistor

R_2 = feedback resistor (gain)

Buckout Voltage Supply:
E_2 = 1.4V Hg cell

R_3 = 100 ohm, 10 turn potentiometer

R_4 = 750 ohm (±10%)

R_i = 75k (imput resistor)

measured with a digital multimeter (Weston Model 1240). This meter also was used to read the voltage drop across a 10.00 ohm (±0.01%) standard resistor that was used to determine the current through the heater. Only one heater was engaged at a time; this was controlled by a double-pole-double-throw switch. (Figure 12)

The heater in the sample cell was a coiled enamel-coated wire (Evanohom, 83 ohm/ft, No. 40, Wilber B. Driver Company) approximately three inches long. The enamel of the wire was sanded off at the ends and the wire soldered to leads that were enclosed in a Teflon tube. The solder joints and the end of the tube were epoxied to prevent corrosion at the soldered junction and to keep the wire dry. The exposed wire was protected from corrosion by its enamel coating. The heater in the blank cell was made of the same coiled enamel-coated wire covered with epoxy glue and was used to bring the blank cell to the same temperature as the sample cell. The amount of current received by the heater would be controlled by varying the current output of the power supply. A Leeds and Northrup Speedomax XL 600 series strip chart recorder was used on the one milivolt span at a chart speed of four inches/minute (or 15 seconds/inch).

The mechanical equipment is illustrated in Figures 13 and 14. The water bath was constructed from a rectangular glass fish tank, 11 in. by 8 in. by 8 in., insulated with two inches of foam and enclosed in a polyethylene tank. The temperature of the bath was regulated with a Haake Controller (Model E 52) and a system of cooling coils to 25 ± 0.002°. The bath was placed on a wooden structure containing two magnets both turned by a 1800 rpm sychronous motor

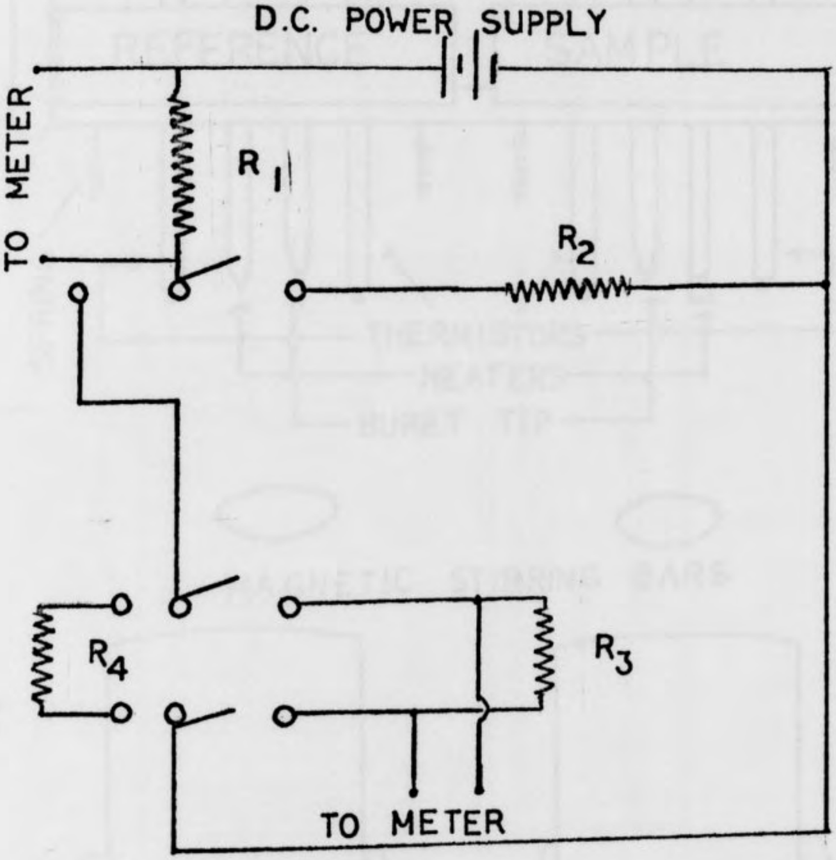


Figure 12. Heating and Calibration Circuit

R_1 = standard resistor (10 ohmes)

R_2 = dummy resistor

R_3 = sample cell heater

R_4 = reference cell heater

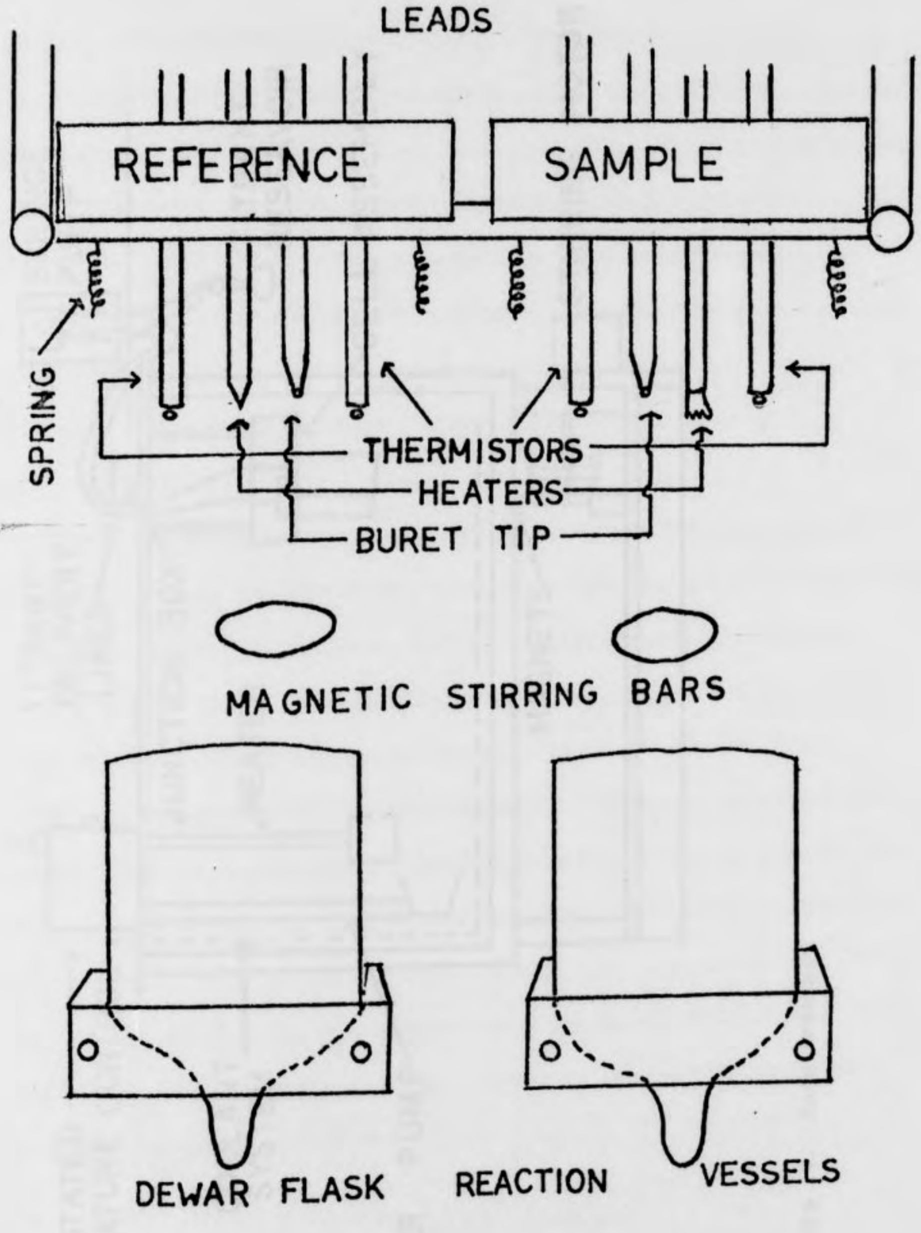


Figure 13. Cell Assembly

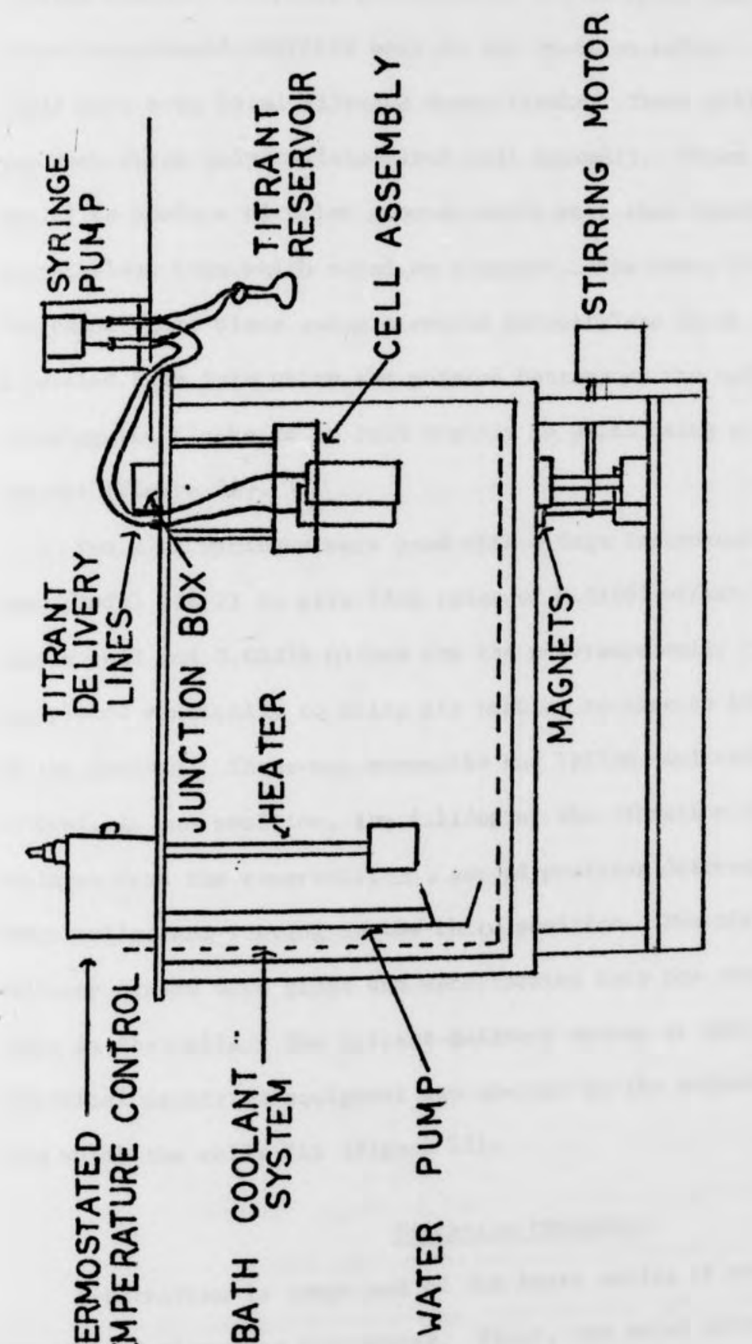


Figure 14. Bath Assembly

(Bodine Electric Company) gear-reduced to 480 rpm. These magnets turned egg-shaped stirring bars in the reaction cells. The reaction cells were twin 25 ml silvered dewar flasks. These cells fit into the one inch thick polyethylene-block cell assembly. These blocks had been milled to produce circular grooves which were then lined with polyethylene foam which acted as a gasket. The dewar flasks were "squeezed" into place using a second polyethylene block provided with a beveled hole into which the pointed bottoms of the cells fit allowing the flasks to be held tightly in place using a series of springs (Figure 13).

Two 2 ml syringes were used with a Sage Instruments syringe pump (Model 234-2) to give flow rates of 0.01062 ml/sec for the sample cell and 0.01070 ml/sec for the reference cell. This pump was placed vertically to allow air bubbles to rise to the top (back) of the syringe. Three-way stopcocks and Teflon delivery lines allowed, in one position, the filling of the titration lines and the syringes from the reservoir, in a second position delivery to the Dewar cells, and venting in the third position. The tips of the delivery system were glass and were epoxied into the ene of the Teflon® tubes in the cells. The titrant delivery system as well as the electrical detection equipment was mounted in the polyethylene block into which the cells fit (Figure 13).

Titration Procedure

A titration is comprised of two basic series of events, the equilibration and titration procedures. First, the water bath was brought to temperature, 25 ± 0.002°, by activating the heater and pump and by adjusting the coolent flow. The bath system took approximately twenty-five minutes to come to constant temperature. During this time, solvent for the sample and reference was equilibrated in the water bath. The approximate temperature was obtained from a mercury thermometer. The temperature of the bath was periodically checked using a Hewlett-Packard Quartz Thermometer (Model No. 2801A).

The Teflon titrant lines were then purged with the titrant to make sure no air was left in them. To fill the syringes titrant was drawn up from the reservoir. Air was drawn up to the top of the polyethylene block (about 5.5 cm) in the tips of the syringes to prevent premature mixing of the titrant with the solution in the cell and to allow for some thermal expansion of titrant in the lines. During equilibration, then, the titrant was in the part of the lines exposed to the bath temperature. Thus, the titrant received by both cells was at the same constant temperature. The titrant reservoir was kept cool with an ice bath to prevent concentration changes and the growth of bacteria when water-carbohydrate solvent systems were being studied. The exposed barrels of the syringe were wiped clean with a clean damp towel to prevent the build-up of titrant and sugar deposits which could cause concentration changes and sticking of the syringe.

Twenty-five ml of equilibrated solvent was placed in each Dewar flask. Stirrers were added to both cells and the solid titrand for the reaction was added to the sample cell. The cells were fitted into their polyethylene blocks and secured after which the cell assembly platform was lowered into the water bath and allowed to equilibrate for at least 25 minutes. Before the platform was put into the water bath, a bottle containing solvent was secured in the water bath allowing it to equilibrate for the next run.

The heater power supply and other circuity was warmed up during the equilibration of the bath. The pen was brought on scale using the buckout circuit preparatory to performing the heating run. After a baseline of constant slope was obtained (approximately two to three inches) the sample cell heater was turned on for 20 or 30 seconds, and an appropriate afterslope was obtained. During the heating run the voltages across the standard resistor and across the sample heater were read and recorded. To rebalance the reference cell with respect to the sample, the reference cell was heated until the pen returned to its initial point and a few minutes were allowed for equilibration after heating. Three or four of these calibration heating runs were done before each titration. These were used to find the heat capacity of the system being studied.

A titration was begun in the same manner as a heating run by obtaining a baseline of relatively constant slope, and then the delivery system for the titrant was activated. Of course, the slope of the pen trace changed in proportion to the heat of reaction After the end point break, an excess reagent line was recorded, the titrant shut off, and an afterslope obtained. After removal of the cells from the assembly, the thermistors, heaters, and the tip of the delivery tubes were rinsed well with deionized, doubly-distilled water and were blotted dry. Generally, five or six titrations were performed for each solvent compostion and particular probe reaction.

Calibration of Equipment

For the calculations of enthalpy values, information is needed on the flow rate of the titrant delivery system and the heat capacities of the sample cell. The delivery rate in a continuous-titration, differential calorimeter must not only be constant over the entire titration time, but must also be the same or nearly the same for both cells. Two mililiter syringes were used in conjunction with a Sage Instruments 234-2 syringe pump. The entire assembly was stood on end so that the syringes were in a vertical position. They were attached via Hamilton three-way Teflon® stopcocks to Teflon® delivery lines which led to the reaction cells and to the titrant reservoir. To determine the flow rate the syringes were filled with deionized, doubly-distilled water, and the delivery lines purged to remove air bubbles. A weighing bottle was filled about half way with water and initially weighed. The syringe pump was turned on, and water collected over a timed interval with the tip of the delivery line submerged. The bottle was again weighed and the procedure repeated a number of times for each syringe. The temperature of the water was taken at some time during the procedure so the density could be used to calculate flow rate in ml/min or ml/sec (equation 10).

$$\text{delivery rate} = \frac{\text{wt. water}}{\text{density } H_2O \times \text{time interval}} \qquad \text{(equation 10)}$$

Since the heat capacity of the total system is used in the calculations of the enthalpy of reaction, the heat capacity of the reaction carbohydrate (sugar alcohol) solvent, the heat capacity of the reaction cell itself must be determined. The following procedure is used to determine the heat capacity of the cell. The sample and blank vessels are each filled with 25 ml of deionized, doubly-distilled water. A number of heating runs were done in this volume of water and the procedure was then repeated in 26 ml of water. The average of several runs at each volume was used to determine the total heat capacity of the system at each volume. Using the height and length of the heating curve along with the voltages across the heater and the standard resistor voltages, equation 11 can be used to calculate the heat capacity of the system.

$$\frac{\dfrac{\dfrac{\text{Time (cm)}}{2.54\ \frac{\text{cm}}{\text{in}}\ \text{chart speed}\ \frac{\text{in}}{\text{min}}}}{60\ \frac{\text{s}}{\text{in}}}\cdot\dfrac{\text{Heater voltage (v)}}{4.184\ \frac{\text{joules}}{\text{cal}}}\ \dfrac{\text{Std. Resistor voltage (v)}}{\text{standard resistance }(\Omega)}}{\text{height of heating curve (cm)}} = C_p \text{ of the system} \qquad \text{(equation 11)}$$

That obtained for the 25 ml system was subtracted from that for the 26 ml system giving the heat capacity for one ml of water. This in turn was multiplied by 25 to give the heat capacity for 25 ml of water which in turn was subtracted from the total for the 25 ml system value leaving the heat capacity of the cell. The value was checked by repeating the procedure using 27 ml and 25 ml volumes.

Calculation of $\Delta H_{(R)}$

Data is extracted from the titration curves essentially by comparing the slope of the titration curve to that of the heating curve using the basic equation given below:

$$\Delta H_R = \frac{E_{HC}}{4.184} \frac{E_{SR}}{R_{SR}} \frac{S_T}{S_{HC}} \frac{1}{\text{conc.}} \frac{1}{\text{flow}} \qquad \text{(equation 12)}$$

where:

ΔH_R = enthalpy of reaction in kcal/mole

E_{HC} = heater voltage

E_{SR} = standard resistor voltage

R_{SR} = standard resistor, resistance in ohmes

S_T = final slope of the titration curve

S_{HC} = final slope of the heating curve

conc. = concentration of titrant in moles/liter

flow = flow of the titrant in ml/sec

4.184--conversion factor, 1 cal = 4.184 joules

In the determination of the titration slope several correction factors must be considered.[51] The baseline slope and the after-slope are a result of the Newton cooling of the cells. This cooling is produced as both cells tend to come to the same temperature. This effect at any point P on the titration curve is calculated by linear interpolation of drift before and after the titration (P being the point at which the titration slope $\overline{BC}$ is measured).

Since the titrant is likely to be at a slightly different temperature than the titrand this must also be considered in the calculation of the titration slope. Again by knowing that the Newton cooling rate is linear and that the slope due to the titrant temperature effect is the difference between the slopes $\overline{DE}$ and $\overline{CD}$, interpolation can be used to determine this titrant correction.

As a titration progresses the volume in the cell increases, changing the heat capacity of the system. The corrected heat capacity of the cell plus contents is calculated at point P by using the time from the beginning of the titration to this point, the heat capacity of the cell, the flow rate of the titrant, and the heat capacity per mililiter of solution. These values are used to determine the amount of additional titrant added up to point P and from this volume to determine the new heat capacity. The heat capacity per ml of solution was calculated using the slopes of the heating curves in conjunction with the heating rate in cal/sec. These slopes are determined at the midpoint by extrapolating the baseline and the after slope drifts and measuring the height and time of the extrapolated heating curve at the midpoint. The overall heat capacity is assumed to change linearly with time. These corrections are used to calculate the final titration slope to be used in equation 12 for the enthalpy calculation.

Standard Reaction

Since there is always the possibility of some unforseen problem with the electrical equipment used in the collection of data for calculation of the heat capacity of the system, an alternate method for checking the heat capacity is advisable. The use of a reaction with a well-documented enthalpy change is a convenient check of this problem. The reaction used for this was a solution of THAM [tris (hydroxymethyl)amionomethane] with 0.1M HCl. This protonation reaction is known to have an enthalpy of reaction of -11.35 cal/mole[52] which is easily reproducible. Utilizing normal titration procedure as previously mentioned in this chapter and the computer program (see Appendix) the heats of reaction for the solution were calculated. The average enthalpy of reaction was -11.50 ± 0.29 (error limits standard deviation) which did not indicate significant error is the value calculated for the heat capacity of the system.

CHAPTER FIVE

RESULTS AND DISCUSSIONS

The nature of solutions of some nonelectrolytes in water have been studied using two probe reactions, one structure making (equation 13) and one structure breaking (equation 14).

$$Bu_4N^+Br^- + Na^+TPB^- \rightleftarrows Bu_4NTPB(s) + Na^+Br^- \qquad \text{(equation 13)}$$

$$Ag^+NO_3^- + Na^+I^- \rightleftarrows AgI(s) + Na^+NO_3^- \qquad \text{(equation 14)}$$

The enthalpy of transfer of sparingly soluble salts from one solvent to another was used as a probe because it permits the utilization of two sensitive probe ions[51] instead of just one as has been customarily used in solution calorimetry. For example, very often salts such as NaCl have been used as a probe to obtain the heat of transfer of the Cl^- ion.[49] In the present study, it is not the heat of solution of the probe that was determined, but rather the heat of precipitation (which is numerically the same but opposite in sign).

An explanation of these probes is in order and can be accomplished by referring to previous results obtained with known structure making and breaking nonelectrolytes. Tert-butyl alcohol is a hydrophobic structure maker as has been previously discussed in Chapter One.[51] The structure breaking nonelectrolyte to be discussed is urea. It seems to disrupt the structure of the water lattice by bonding with the free (unbound) water molecules.[51]

The structure-making probe used in the water-tert-butyl alcohol system results in an exothermic heat of transfer from water to tert-butyl alcohol--water mixtures, calculated from equation 2. Since the water-alcohol system is more structured than pure water, the Bu_4N^+ and TPB^- ions cannot induce as much structure as they can in pure water. When the structure-making ions are precipitated from the water-alcohol system the structure promoted by the alcohol remains intact, but that promoted by the ions collapses, an endothermic structural contribution which leads to an exothermic heat of transfer as this endothermic term is smaller in the mixture than in pure water.

On the other hand, the structure breaking probe salt (AgI) in the water-alcohol system has more structure to break than in pure water. This leads to a reorganization of this broken water-alcohol structure on precipitation of the AgI. An exothermic structurel contribution greater in the mixture than in pure water results which again causes an exothermic heat of transfer.

Urea seems to break up the structure of water such that for the structure making probe salt an exothermic $\Delta H_{(tr)}$ is also seen. The magnitude of this $\Delta H_{(tr)}$ is less for the urea than for the alcohol as would be expected. In contrast to the tert-butyl alcohol-water system, an endothermic $\Delta H_{(tr)}$ was found for the AgI probe in the urea-water system. This is because the structure breaking probe is less effective than in pure water because it must compete with urea for the "disruptibility" of water and thus there is less exothermic reorganization of water structure upon precipitation of the AgI than there is in pure water. To summarize these findings, in hydrophobically promoted water-nonelectrolyte systems, both structure promoting and disrupting salts have increased reaction heats and therefore $\Delta H_{(tr)}$ is exothermic (from water to the mixture). In structure disrupted water--nonelectrolyte systems structure making probe salts exhibit increased reaction heats (exothermic $\Delta H_{(tr)}$) while structure disrupting salts exhibit a decreased reaction heat (endothermic $\Delta H_{(tr)}$).

Glucose has previously been reported as being a structure maker in solution with water based on dielectric,[102] thermodynamic,[42] and ^{17}O NMR.[45] This ordering of the system was not thought to be long range, however. Glucose seems to follow ideal or semi-ideal behavior in water; that is, only solute-solvent interactions occur. Six equatorial hydroxyl groups exist on the predominate glucose conformer in solution (see section on hydrophilic bonding, this work). These equatorial groups are thought to be able to fit into the tetrahedral water structure to increase the structuring of the water-sugar system.[45] The water-sugar bonds apparently closely resemble the water-water bonds of pure water, but appear to be stronger. This could suggest that for the solution fewer water-water bonds are able to exist than in pure water because the glucose is hydrogen bonding with the water, thus disrupting some water-water structure, but promoting the overall structure of the system. This was observed by Taylor and Rowlinson when they concluded that aqueous glucose solutions resembled water-H_2O_2 systems rather than water-alcohol mixtures.[42] Stokes and Robinson have suggested that indeed this is the case, basing their predictions on the concentration dependence of thermodynamic quantities.[102]

The entropy of reaction for the precipitation of the probe ions, $\Delta H°$, vs. mole % glucose appears in Figures 15-6.Heats of transfer calculated from equation 2 were plotted vs. mole % glucose (Figures 17-8) to see if the trends follow those previously established for other structure makers. Since glucose is a structure maker the Bu_4N^+ and TPB^- ions should not be able to induce as much structure as they can in pure water because the water is already tightly bound to the sugar. This would result in an exothermic $\Delta H_{(tr)}$ for the probe reactions, which indeed it does (Figure 22). AgI, on the other hand, showed a steady decrease in ΔH_R with increasing concentration leading to an endothermic heat of transfer, to be contrasted with an exothermic $\Delta H_{(tr)}$ in the t-butyl alcohol-water system. If glucose were a hydrophobic solute an exothermic $\Delta H_{(tr)}$ would be expected (as for t-butyl alcohol) suggesting structure making tendencies. As has previously been mentioned (Chapter One), glucose is apparently not hydrophobically bound, but rather, due to the large number of -OH groups, it is hydrophilically bound in water. Thus our data seems to corroborate earlier results in this regard.

The results for sucrose are similar to those for glucose (Figures 20-23) as the structure making probe shows a steady increase in the heat of reaction with the increase in concentration. It might be noted that at around seven mole % sucrose no further data was able to be obtained because of the high viscosity of these solutions. With the high viscosity came a large standard deviation, not only for the results of sucrose, but also for the other sugars and the alcohols investigated, and the kinetics did not permit good data

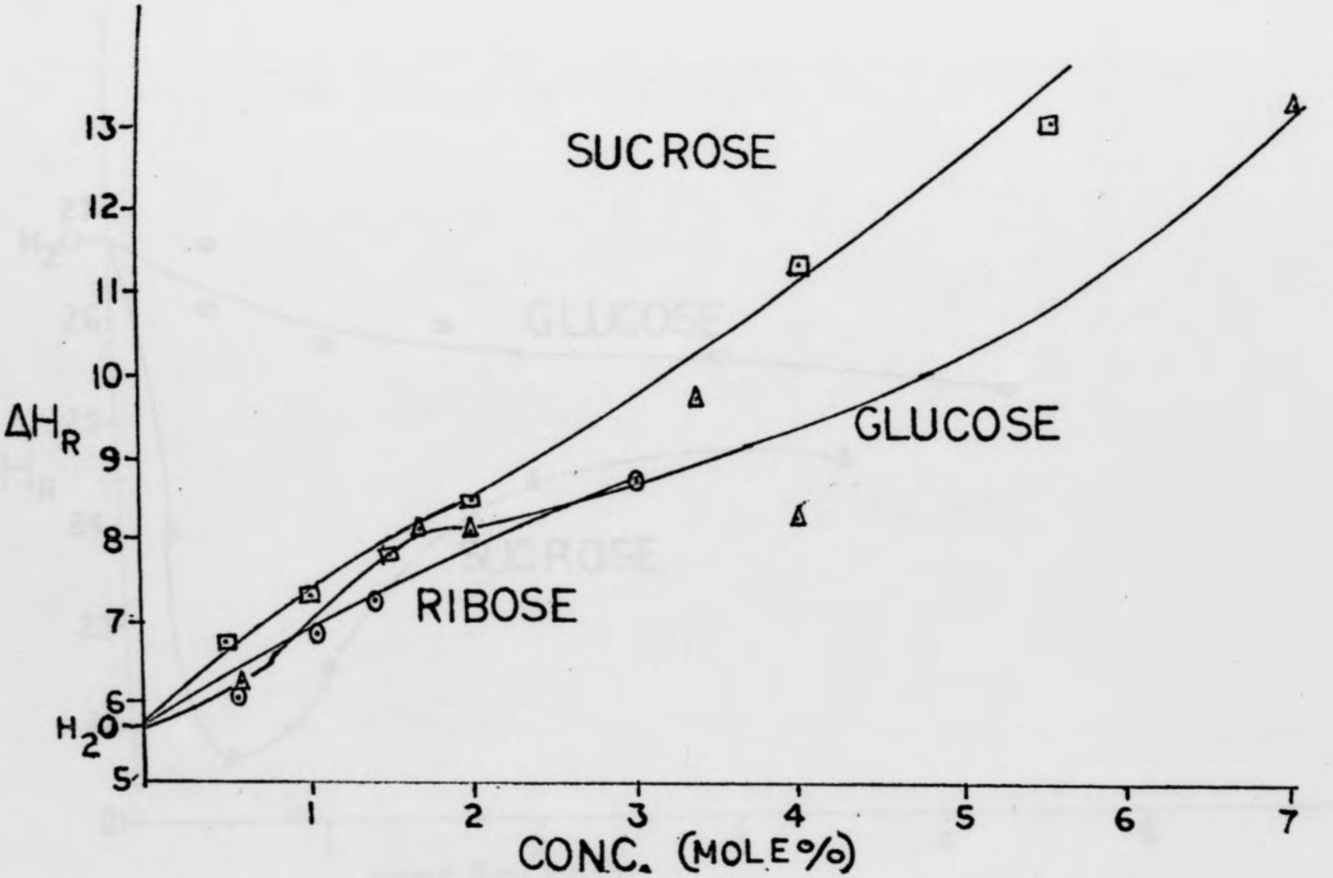


Figure 15. Enthalpy of Reaction for Bu_4NTPB Precipitation in Sucrose-Water ⊡ , Glucose-Water ∆ , and Ribose-Water ⊙ Solutions

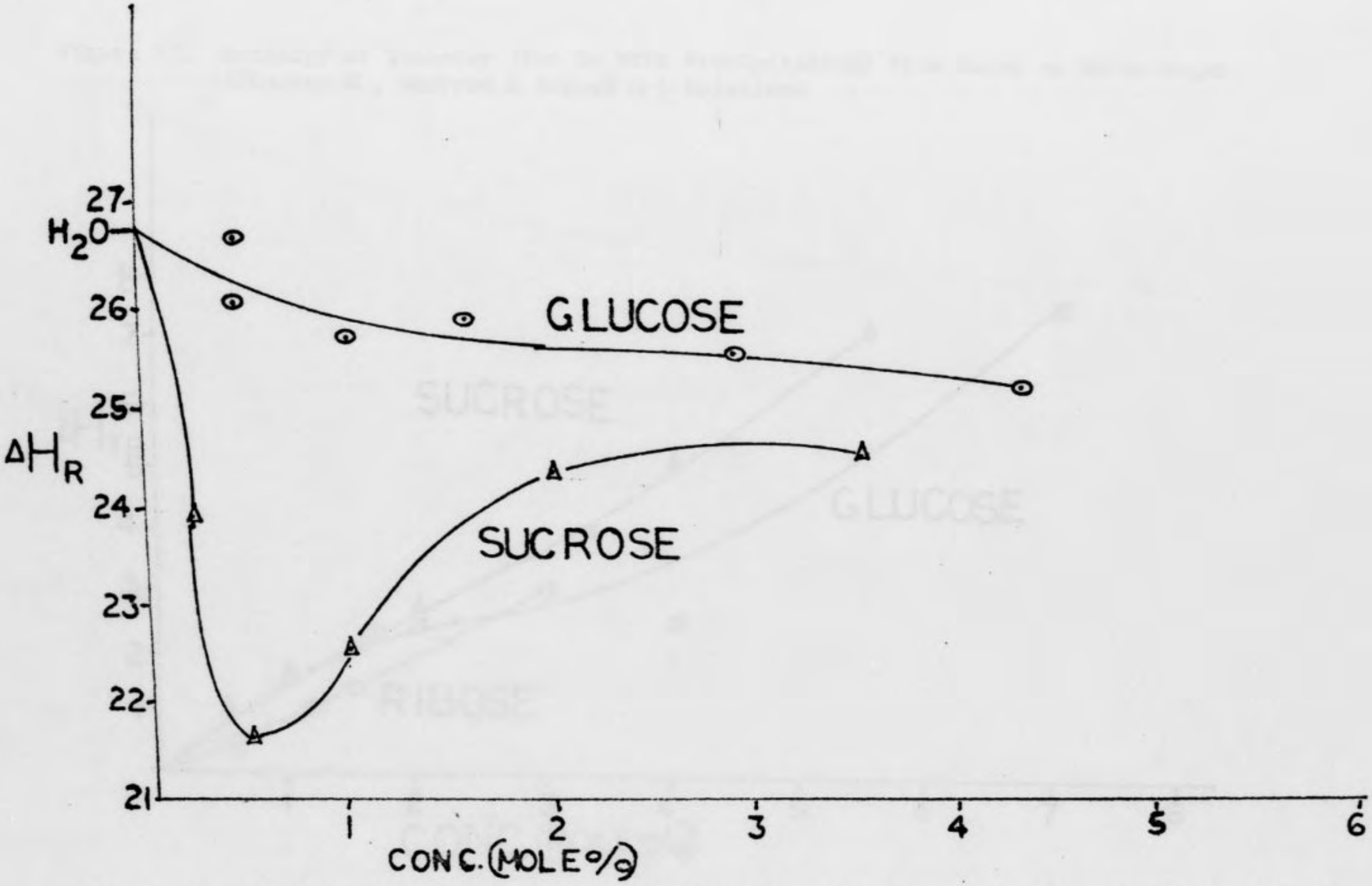
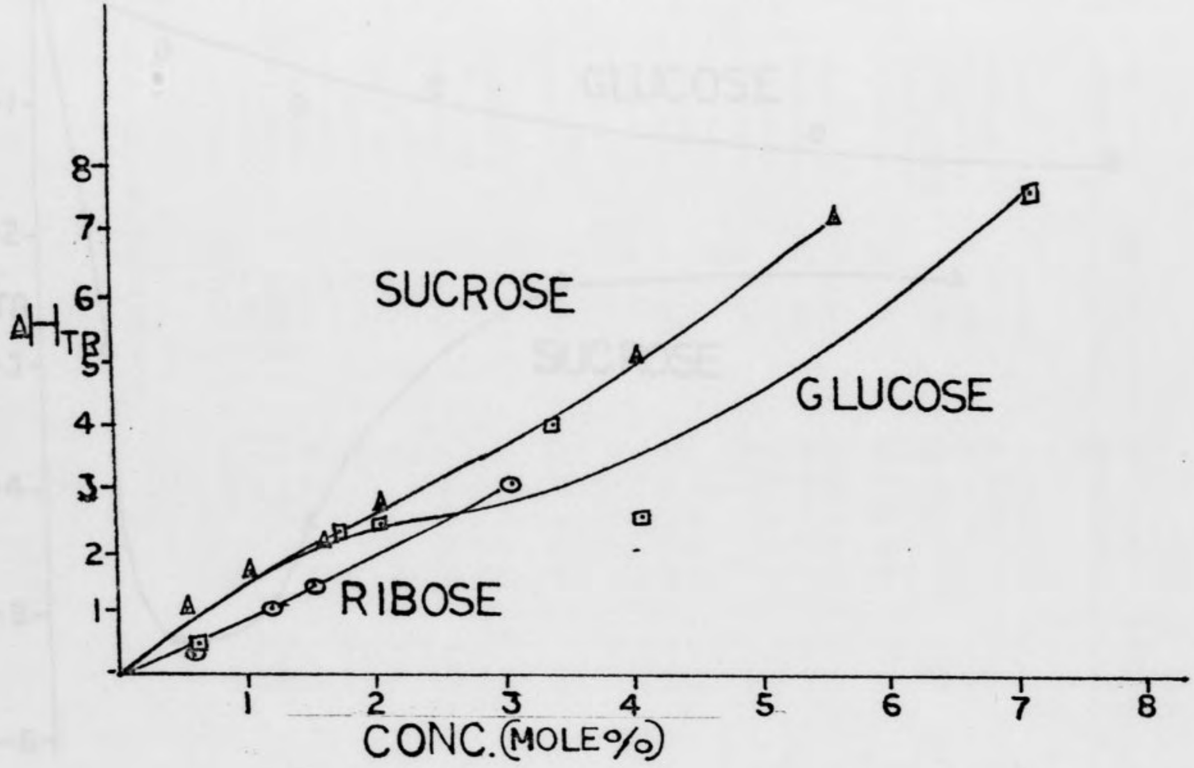


Figure 16. Enthalpy of Reaction for AgI Precipitation in Sucrose-Water △ and Glucose-Water ⊙ Solutions

Figure 17. Enthalpy of Transfer (For Bu_4NTPB Precipitation) From Water to Water-Sugar (Glucose ⊡ , Sucrose Δ Ribose ⊙) Solutions



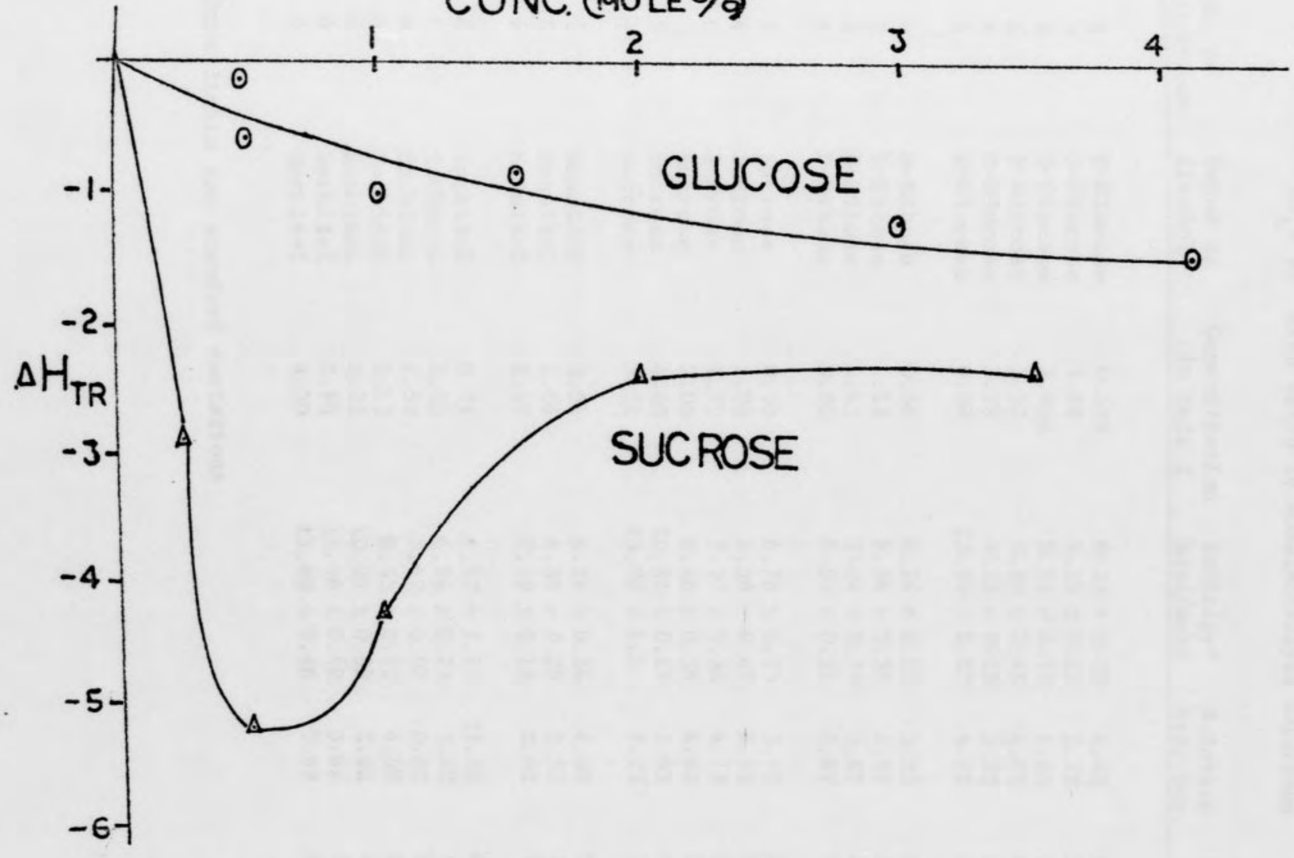


Figure 18. Enthalpy of Transfer (For AgI Precipitation) From Water to Water-Sugar (Glucose ⊙ , Sucrose ▲) Solutions

Table 2

Enthalpies of Reaction and Transfer for the Probe Reaction $Bu_4N^+Br^-$ with NaTPB in Nonelectrolyte Solutions

No. of Titrations	Sugar or Alcohol	Concentration in Mole %	Enthalpy* kcal/mole	Relative Std. Dev.	ΔH_{tr}
4	D-Glucose	0.599	6.23 ± 0.28	4.4%	0.47
5	D-Glucose	1.68	8.12 ± 0.17	2.1%	2.36
6	D-Glucose	1.996	8.21 ± 0.13	1.6%	2.45
6	D-Glucose	3.32	9.80 ± 0.45	4.6%	4.034
6	D-Glucose	3.99	8.33 ± 0.19	2.3%	2.57
4	D-Glucose	6.98	13.40 ± 0.63	4.7%	7.64
4	D-Ribose	0.56	6.14 ± 0.13	2.1%	0.38
5	D-Ribose	1.16	6.86 ± 0.34	4.9%	1.13
6	D-Ribose	1.45	7.24 ± 0.39	5.4%	1.48
5	D-Ribose	3.00	8.81 ± 0.51	5.8%	3.05
6	Sucrose	0.50	6.78 ± 0.25	3.7%	1.02
4	Sucrose	1.00	7.39 ± 0.47	6.3%	1.63
6	Sucrose	1.52	7.97 ± 0.38	4.7%	2.21
5	Sucrose	2.00	8.46 ± 0.39	4.6%	2.70
5	Sucrose	4.00	10.81 ± 0.17	1.6%	5.05
4	Sucrose	5.51	13.02 ± 1.2	9.2%	7.26
5	Mannitol	0.55	6.14 ± 0.24	4.0%	0.38
6	Mannitol	1.04	6.88 ± 0.23	3.3%	1.12
6	Mannitol	1.49	7.19 ± 0.18	2.6%	1.43
6	Sorbitol	0.51	6.37 ± 1.10	17.3%	0.610
6	Sorbitol	1.03	6.94 ± 0.23	3.2%	1.18
6	Sorbitol	1.50	7.67 ± 0.07	0.9%	1.91
4	Sorbitol	2.12	8.55 ± 0.42	4.9%	2.79
4	Sorbitol	3.21	10.04 ± 0.39	3.9%	4.28
6	Sorbitol	3.98	11.44 ± 0.42	3.6%	5.68
6	Sorbitol	4.30	11.62 ± 0.88	7.6%	5.86

*Error limits are standard deviations

Table 3

Enthalpies of Reaction and Transfer for the Probe Reaction $AgNO_3$ with NaI in Nonelectrolyte Solutions

No. of Titrations	Sugar or Alcohol	Concentration in Mole %	Reaction Enthalpy kcal/mole	Relative Std. Dev.	ΔH_{tr}
4	D-Glucose	0.49	26.67 ± 1.21	4.6%	-0.11
6	D-Glucose	0.49	26.17 ± 0.65	2.5%	-0.61
5	D-Glucose	1.04	25.78 ± 0.94	3.6%	-1.00
6	D-Glucose	1.59	25.91 ± 1.46	5.6%	-0.87
4	D-Glucose	2.96	25.56 ± 0.50	2.0%	-1.22
4	D-Glucose	4.30	25.30 ± 0.63	2.5%	-1.48
6	Sucrose	0.25	23.98 ± 1.86	7.8%	-2.80
4	Sucrose	0.51	21.62 ± 1.28	5.9%	-5.16
5	Sucrose	1.01	22.57 ± 1.10	4.9%	-4.21
6	Sucrose	2.00	24.44 ± 1.07	4.4%	-2.34
5	Sucrose	3.53	24.50 ± 0.81	3.3%	-2.28
	Mannitol	0.10	24.18 ± 1.00	4.1%	-2.60
	Mannitol	0.21			
6	Mannitol	0.30	25.66 ± 1.11	4.3%	-1.12
	Mannitol	0.40	18.98 ± 3.00	15.8%	-7.80
6	Mannitol	0.57	24.27 ± 1.76	7.2%	-2.51
6	Mannitol	1.07	24.05 ± 1.99	8.3%	-2.73
6	Mannitol	1.55	19.41 ± 2.80	14.4%	-7.37
6	Sorbitol	0.11	24.76 ± 1.01	4.1%	-2.02
5	Sorbitol	0.21	23.86 ± 1.21	5.1%	-2.92
4	Sorbitol	0.27	20.58 ± 0.86	4.2%	-6.20
5	Sorbitol	0.28	25.13 ± 1.85	7.4%	-1.65
6	Sorbitol	0.43	24.88 ± 2.05	8.2%	-1.90
4	Sorbitol	0.51	27.85 ± 1.15	4.1%	-1.07
6	Sorbitol	1.04	25.90 ± 1.23	4.7%	-0.88
5	Sorbitol	1.5	25.43 ± 1.85	7.3%	-1.35
6	Sorbitol	1.98	24.59 ± 0.97	3.9%	-2.19
6	Sorbitol	3.0	24.74 ± 2.13	8.6%	-2.04

to be taken. Heats of reaction for Bu_4NTPB were somewhat higher in sucrose systems than glucose systems which might be attributed to the increased number of hydroxyl groups available for hydrogen bonding in the sucrose molecule causing more structuring effects in aqueous media. Sucrose is a disaccharide containing one glucose and one fructose monomer and therefore the resemblence to glucose is not unfounded.

The AgI heat of reaction exhibited a minimum at about 0.5% sucrose increasing to a plateau at around 2% which could imply the sucrose-water and water-water structures were collapsing with increasing concentration. The $\Delta H_{(tr)}$ of glucose was progressively endothermic over a much larger range in concentration than that of sucrose, probably due to the difference in size of the sugar molecules.

Due to the conformations of ribose in water, α- and β-furanose and α- and β-pyranose, and its small number of -OH groups it is thought not to be able to fit into the tetrahedral water lattice as effectively as either glucose or sucrose.[45] These conformations are discussed at length in the previous section on hydrophilic bonding. Due to the cost of ribose, only a few data points were obtained. It is clear that much more data is needed for ribose before any major conclusions can be drawn.

Studies previously done on sorbitol and mannitol have resulted in a conflict as to their structure making or structure breaking tendency.[49,50] As discussed earlier, Stern and O'Connor claimed that mannitol was a hydrophobic structure maker over the concentration range from pure water to about 0.3 mole % while sorbitol was a structure breaker over the entire range of concentrations. They claimed that the difference in the position of one -OH group could cause a qualitative difference in structuring between these steroisomers. Mannitol was said to be a hydrophobically bound alcohol from 0-0.3 mole % while sorbitol was found to exhibit structure breaking qualities over the entire concentration investigated, from 0-1.0 mole % sorbitol.

In contrast to this, Wilson,[50] with improvements in equipment design and hence precision, found totally different results for mannitol. He claimed that in fact, in this case, the difference in geometry of one -OH group did not lead to hydrophobic bonding in one case and hydrophilic bonding in the other. Sorbitol and mannitol both showed the same structural properties giving endothermic heats of transfer of NaCl (a structure disrupting probe salt) from water to the polyhydroxy alcohol--water mixtures. It was also theorized by Wilson that, since these alcohols are free rotating, they would adapt to the most favorable conformation possible.

In our study of these alcohols, the entropy of reaction for Bu_4NTPB probe increased with increasing concentration. Further, the heat of reaction studies were severely limited because of the low solubility of mannitol which is approximately one-fourth as soluble in water as sorbitol. Although the precision of the silver iodide results is not good, the trend seems to be similar for both sorbitol and mannitol. The heat of reaction for this probe (Figure 20) seems to decrease from its value in pure water and then decrease only slightly or level out. Absolutely no evidence of an increase in $\Delta H_{(tr)}$ in the 0-0.3 mole % mannitol range was observed. It would

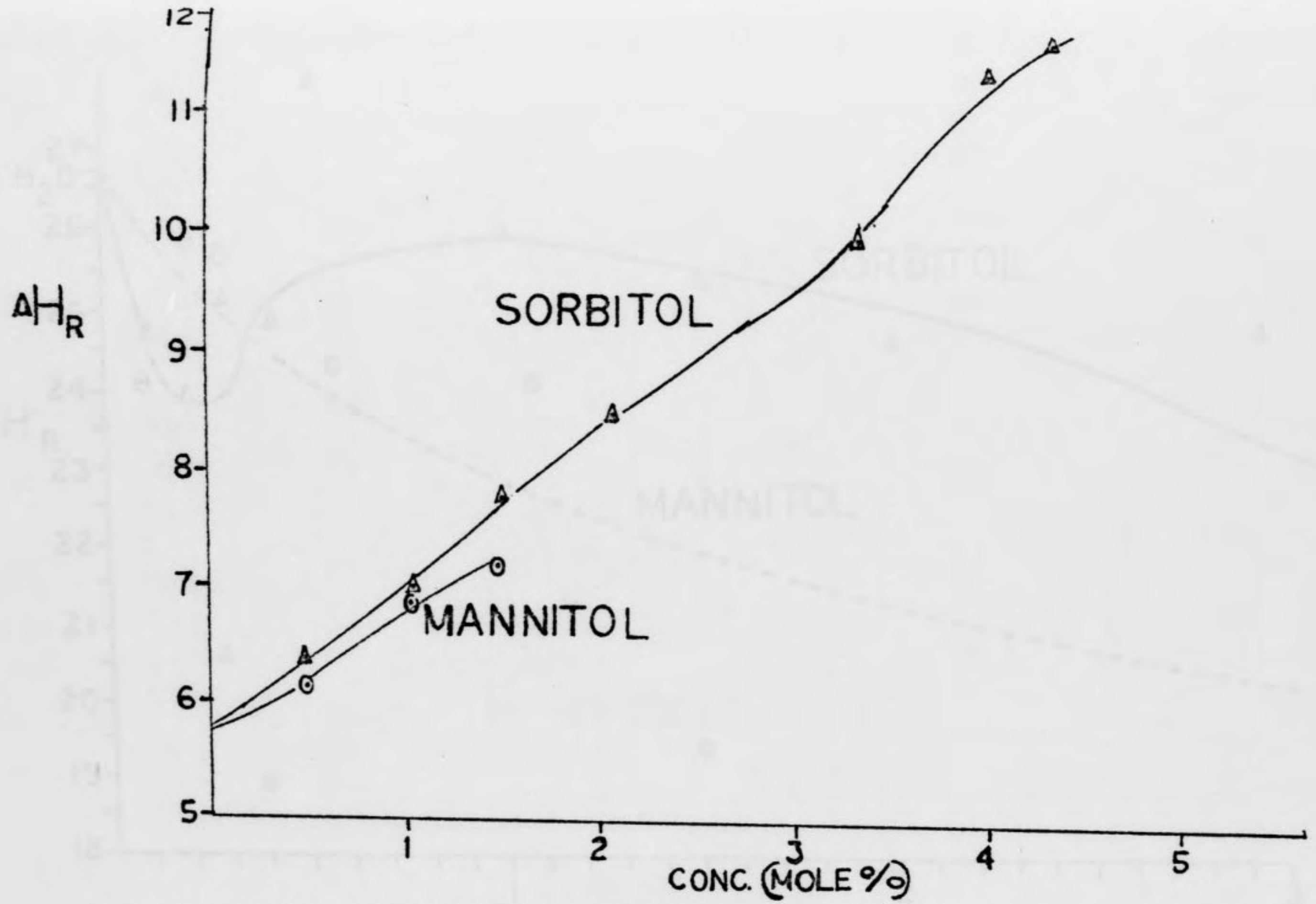


Figure 19. Enthalpy of Reaction for Bu_4NTPB Precipitation in Sorbitol-Water ▲ and Mannitol-Water ⊙ Solutions

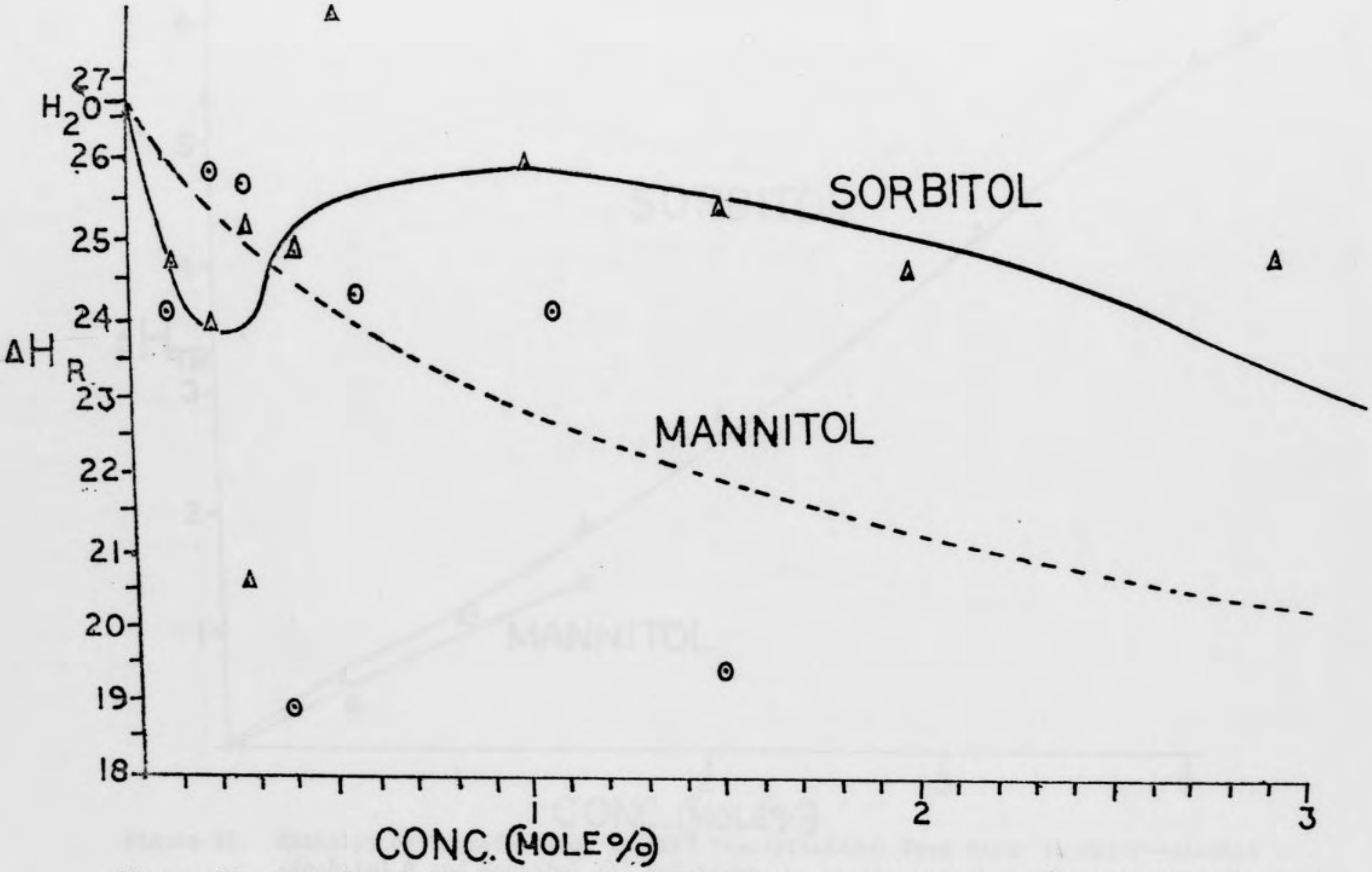


Figure 20. Enthalpy of Reaction for AgI Precipitation in Sorbitol-Water Δ and Mannitol-Water ⊙ Solutions

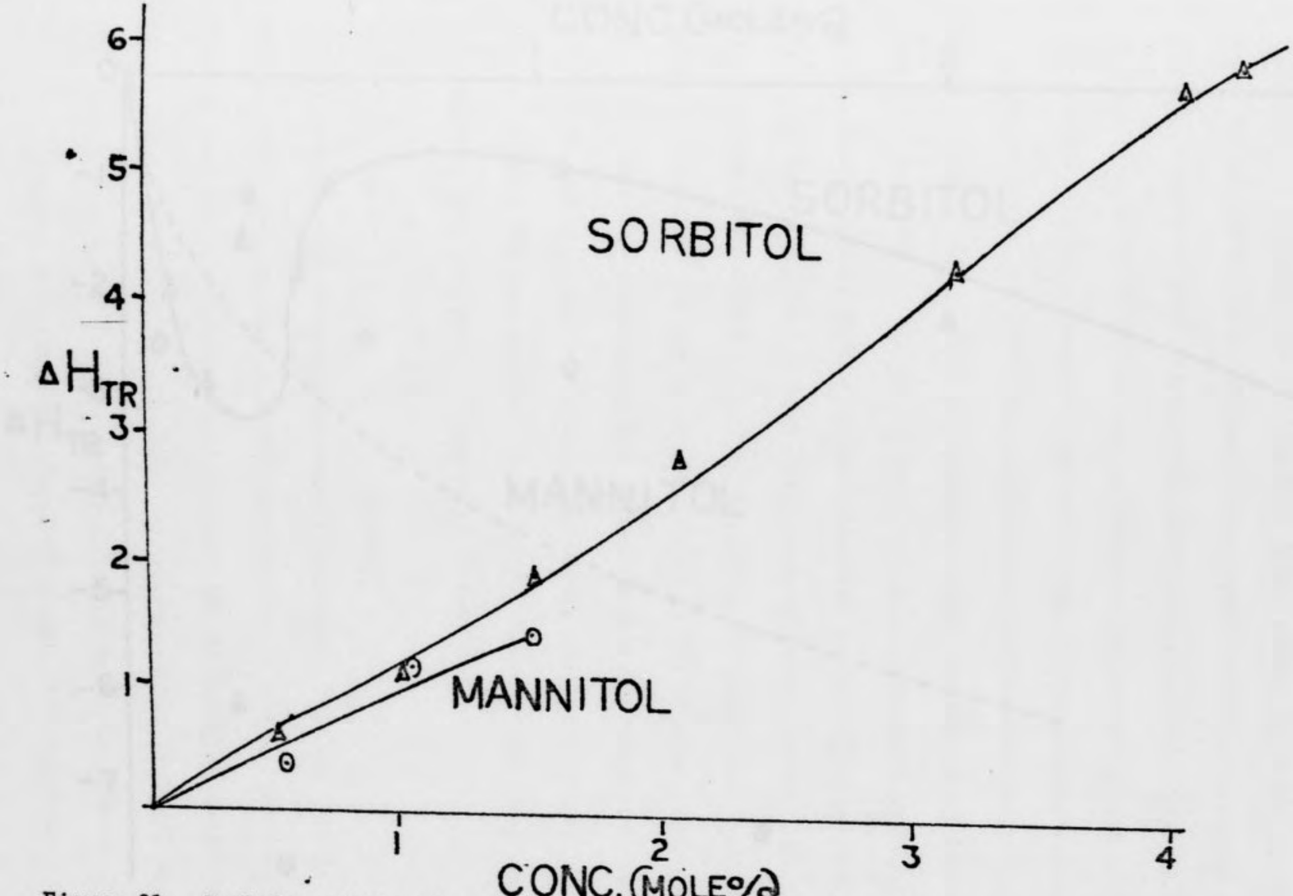


Figure 21. Enthalpy of Transfer (for Bu_4NTPB Precipitation) From Water to Water--Alcohol (Sorbitol Δ and Mannitol ⊙) Solutions

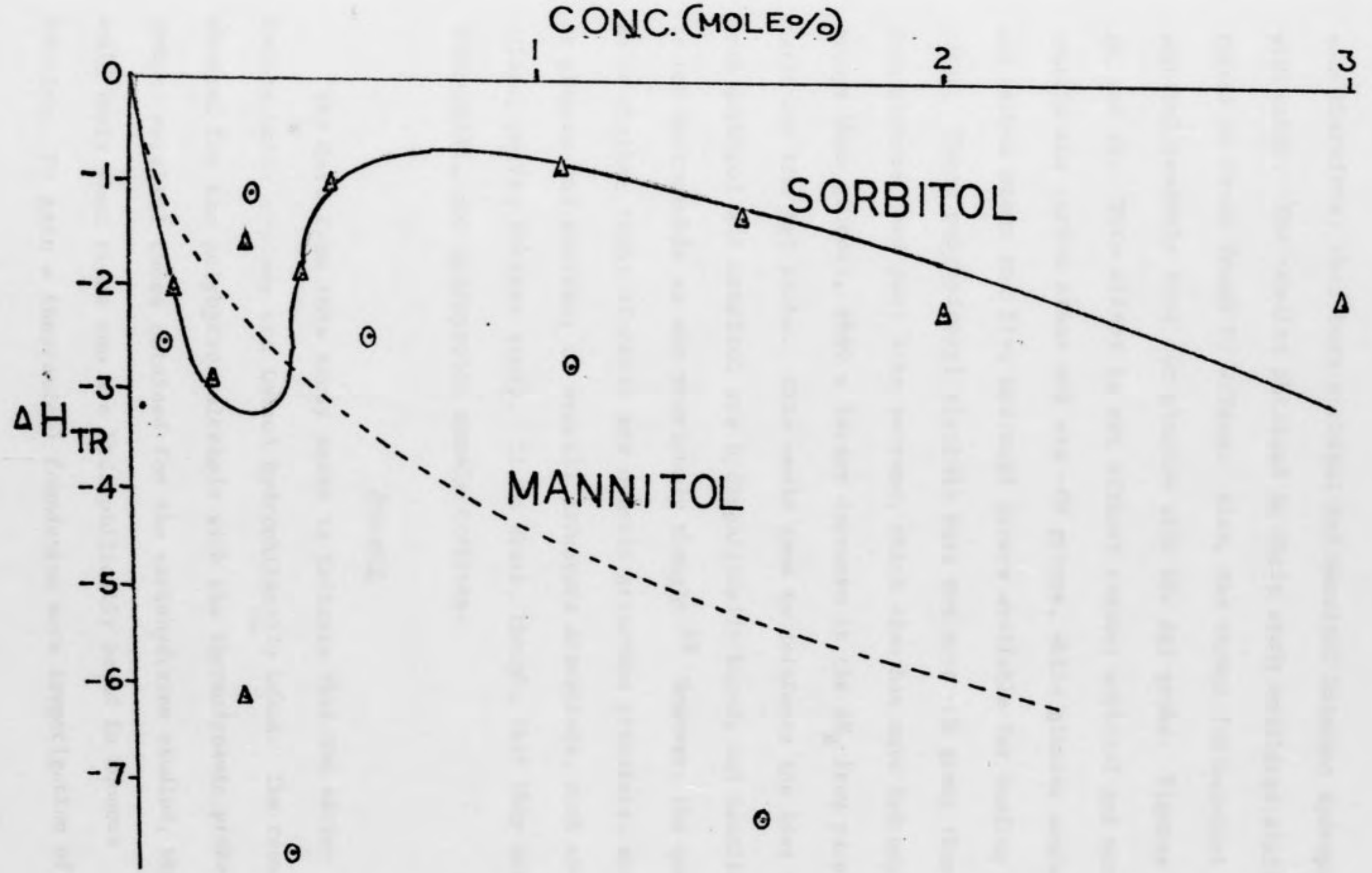


Figure 22. Enthalpy of Transfer (For AgI Precipitation) From Water to Water--Alcohol (Sorbitol ▲ and Mannitol ⊙) Solutions

seem therefore, that both sorbitol and mannitol interact hydrophilically with water. The results obtained in their study exhibited similar trends to those found by Wilson. Also, the curves for mannitol and sorbitol resemble that for glucose with the AgI probe. Figures 19, 20, and 22. This effect is not without reason; sorbitol and mannitol contain six carbon atoms and six -OH groups, while glucose contains six carbon atoms and five hydroxyl groups available for bonding with water. These polyhydroxyl alcohols have one more -OH group than does glucose, and just like sucrose, which also has more hydroxyl groups than glucose, show a larger decrease in the ΔH_R from pure water for the AgI probe. This would seem to reinforce the idea that both sorbitol and mannitol are hydrophilically bound, and mannitol is not hydrophobic as was previously thought.[49] However, the question as to whether these alcohols are overall structure promoters, such as glucose and sucrose, or overall structure disrupters, such as ribose, awaits further study. It is clear, though, that they are hydrophilic, not hydrophobic nonelectrolytes.

Summary

The data from this study seems to indicate that the carbohydrate water systems are indeed hydrophilically bound. The results obtained for the polyhydroxyalcohols with the thermodynamic probes seem to parallel those obtained for the carbohydrates studied, which would imply that these too are hydrophilically bound in aqueous solution. To gain a theoretical foundation more investigation of such systems and other associated systems is necessary. A need for a new structure breaking probe reaction is indicated by the bad precision obtained when using AgI as a structural probe.

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APPENDIX

Computer Program For Calculation of ΔH_R

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      DIMENSIØN HEIGHT(10), TIME(10), HTSLP(10), HTVØLT(10), SRVØLT(10),
     *ENTSLP(10),DEVSLP(10),HTSLAV(10)
     *, TITSSL(10), SLPRAT(10),DEVSQR(10),AVPWR(10)
C THE NUMBER ØF TITRATIØNS IS READ IN
      READ, M
C  THE CØNCENTRATIØN IN MØL/LIT, THE FLØW RATE IN ML/SEC, THE VØLUME
C  IN ML, THE CHART SPEED IN SEC/IN, THE HEAT CAPACITY ØF THE CELL IN
C  JØULES/CM, AND THE STANDARD RESISTØR VALUE IN ØHMS ARE READ IN
      READ, CØNC, FLØW
      READ, V
      READ, CRTSPD
      READ, CPCELL
      READ, R
C THE SUM ØF THE ENTHALPYS IS INITIALIZED
      SUMSLP = 0
      DØ 50 J=1,M
C THE NUMBER ØF HEATING CURVES IS READ IN
      READ, N
C THE HEIGHT AND TIME FØR EACH HEATING CURVE IA READ IN
      READ, (HEIGHT(I), TIME(I), I = 1,N )
C THE HEATER AND STD. RES. VØLTAGES ARE READ IN
      READ, ( HTVØLT(I), SRVØLT(I), I = 1, N )
C EACH HEATING SLØPE IS CALCULATED
      DØ 10 I=1,N
   10 HTSLP(I) = HEIGHT(I)/TIME(I)
```

```
C THE AVERAGE HEATING SLØPE IS CALCULATED
      SLØPE = 0
      DØ 20 I=1,N
   20 SLØPE = SLØPE + HTSLP(I)
      HTSLAV(J) = SLØPE/FLØAT(N)
C TGE AVERAGE PØWER IS CALCULATED
      SUMHTV = 0
      SUMSRV = 0
      DØ 30 I=1,N
   30 SUMHTV = HTVØLT(I) + SUMHTV
      AVHTVL = SUMHTV/FLØAT(N)
      DØ 40 I=1,N
   40 SUMSRV = SRVØLT(I) + SUMSRV
      AVSRVL = SUMSRV/FLØAT(N)
      AVPWR(J)=AVHTVL*AVSRVL/R
C THE AVERAGE SLØPE TØ PØWER RATIØ IS CALCULATED FØR EACH TITRATIØN
      SLPRAT(J) = HTSLAV(J)/AVPWR(J)
      PRINT, ' THE HEATER VØLTAGES ARE: ', (HTVØLT(I), I = 1,N)
      PRINT, ' THE STD. RES. VØLTAGES ARE: ', (SRVØLT(I), I = 1,N)
      PRINT, ' THE HEATING SLØPES ARE: ', (HTSLP(I), I=1,N)
      PRINT, ' THE AVERAGE HEATING SLØPE = ', HTSLAV(J)
      PRINT, ' THE AVERAGE SLØPE TØ PØWER RATIØ = ', SLPRAT(J)
      PRINT,'****'
   50 CØNTINUE
 C THE AVERAGE SLØPE/PØWER RATIØ ØF ALL THE HEATING CURVES IS
 C  CALCULATED
      SUMSP=0
      DØ 60 J=1,M
   60 SUMSP=SUMSP+SLPRAT(J)
      AVSLPR=SUMSP/FLØAT(M)
 C  THE HEAT CAPACITY PER ML, CPML, IS CALCULATED IN JØULES PER CM
      CPTØT=CRTSPD/(AVSLPR*2.54)
      CPML=(CPTØT-CPCELL)/V
      DØ 70 J=1,M
 C THE TITRATIØN CURVE DATA IS READ IN
```

```
      READ, ABNUM, ABDEN, BCNUM, BCDEN, CDNUM, CDDEN, DENUM, DEDEN
C THE TIME AT WHICH THE TITRATIØN SLØPE IS MEASURED IS READ IN
      READ, TIMCM
C  THE FRACTIØNAL TEMPERATURE RISE AT ANY PØINT  P ØN THE TITRATIØN
C  CURVE IS READ IN AS FRACTR, WHERE FRACTR = (TP-TX)/(TY-TX). X =
C  BEGINNING AND Y = END ØF THE TITRATIØN
      READ, FRACTR
C THE SLØPES ØF THE FØUR PARTS ØF THE ØVERALL TITRATIØN CURVES ARE
C CALCULATED.  AB AND DE ARE DUE TØ NEWTØN CØØLING ØNLY.
      AB = ABNUM/ABDEN
      BC = BCNUM/BCDEN
      CD = CDNUM/CDDEN
      DE = DENUM/DEDEN
C THE HEAT CAPACITY CØRRECTIØN IS CALCULATED AS CPCØR, WHERE
C CPCØR = CP(CELL)+CP(PER ML)*V+CP(PER ML)(FLØW(TIME)/
C CP(CELL) + CP(PER ML)*V
      TIMSEC = TIMCM*CRTSPD/2.54
       CPCØR = (CPCELL+CPML*(V+(FLØW*TIMSEC)))/(CPCELL+(V*CPML))
C  THE NEWTØN CØØLING SLØPE CØRRECTIØN AT ANY PØINT P ØN THE
C  TITRATIØN CURVE IS CALCULATED BY LINEAR INTERPØLATIØN ØF DRIFT
C  BEFØRE AND AFTER TITRATIØN
      XNEWTØ  = AB + ((DE - AB)*FRACTR)
C  THE CØRRECTIØN FØR THE EFFECT ØF TITRANT TEMPERATURE IS CALCULATED
C  AS ( CD - DE)* (NEWTØN CØØLING AT P/ NEWTØN CØØLING AT Y )
        TITCØR = (CD-DE)*(XNEWTØ/DE)
C  THE CØRRECTED TITRATIØN SLØPE IS CALCULATED AS ( BC - TITCØR -
C  NEWTØN ) * CPCØR
      TITSSL(J) = ( BC - TITCØR - XNEWTØ)*CPCØR
C THE ENTHALPY FØR EACH TITRATIØN IS CALCULATED
      ENTSLP(J)=AVPWR(J)*TITSSL(J)/(4.184*CØNC*FLØW*HTSLAV(J))
      PRINT, ' THE ENTHALPY BY THE SLØPE METHØD = ', ENTSLP(J)
      PRINT, ' THE SLØPE METHØD TITRATIØN SLØPE = ', TITSSL(J)
      PRINT, ' AB = ', AB, ' BC = ', BC
      PRINT, ' CD = ', CD, ' DE = ', DE
      PRINT, 'THE FRACTIØNAL TEMPERATURE RISE = ',FRACTR,
```

```
     * ' NEWTØN CØØLING CØRRECTIØN = ', XNEWTØ
      PRINT, ' THE TITRANT TEMPERATURE CØRRECTIØN = ',TITCØR,
     * ' THE HEAT CAPACITY CØRRECTIØN = ', CPCØR
      PRINT, '      ****    '
      PRINT, '      ****    '
   70 CØNTINUE
C THE AVERAGE ENTHALPY FØR ALL TITRATIØNS IS CALCULATED
      SUMSLP=0
      DØ 80 J=1,M
   80 SUMSLP = SUMSLP+ENTSLP(J)
      AVENSL = SUMSLP/FLØAT(M)
      PRINT, '****************'
      PRINT, '****************'
      PRINT, ' THE ENTHALPY AVERAGE ØF THE SLØPE TITRATIØNS  = ', AVENSL
      PRINT, '****'
      SUMDSL = 0
      DØ 100 J=1,M
      DEVSLP(J) = AVENSL-ENTSLP(J)
  100 SUMDSL = SUMDSL + ABS(DEVSLP(J))
      AVDESL = SUMDSL/FLØAT(M)
      RELDSL = 100.0*AVDESL/AVENSL
      PRINT, ' THE DEVIATIØNS FRØM THE MEAN ( SLØPE METHØD) ARE : ',
     *(DEVSLP(J), J = 1,M)
      PRINT, ' THE AVERAGE DEVIATIØN FRØM THE MEAN( SLØPE METHØD ) = ',
     *AVDESL
      PRINT, ' THE RELATIVE AVERAGE DEVIATIØN FRØM THE MEAN (SLØPE METHØ
     *D) IN % = ', RELDSL
C THE STANDARD DEVIATIØN AND RELATIVE STANDARD DEVIATIØN ARE CØMPUTED
      DØ 110 J = 1, M
  110 DEVSQR(J) = DEVSLP(J)**2
      SUMSQR = 0
      DØ 120 J = 1, M
  120 SUMSQR = SUMSQR + DEVSQR(J)
      STDDEV = SQRT(SUMSQR/(FLØAT(M)-1.0))
      RELSTD = (STDDEV/AVENSL)*100
```

```
      PRINT, ' THE STANDARD DEVIATIØN ØF THE SLØPE METHØD = ', STDDEV
      PRINT, ' THE RELATIVE STANDARD DEVIATIØN ØF THE SLØPE METHØD
     * IN % = ', RELSTD
      PRINT, ' CØNC = ', CØNC, ' FLØW RATE = ', FLØW
      PRINT, ' SØLUTIØN VØLUME = ', V, ' THE CHART SPEED = ', CRTSPD
      PRINT, ' THE CELL HEAT CAPACITY = ', CPCELL,
     *' THE STD. RES. VALUE = ', R
      PRINT, ' THE HEAT CAPACITY PER ML = ', CPML
      PRINT, ' THE ØVERALL SLØPE/PØWER RATIØ = ', AVSLPR
      PRINT, ' THE TØTAL HEAT CAPACITY = ', CPTØT
      PRINT, ' ########## '
      PRINT, ' ########## '
      STØP
      END
$DATA
/*
//
/*EØF
```