

THERMODYNAMICS OF THE IONIZATION OF
POLYBASIC ORGANIC ACIDS IN WATER

By

MASON BUTLER TOMSON

Bachelor of Science

Southwestern State College

Weatherford, Oklahoma

1967

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
DOCTOR OF PHILOSOPHY
May, 1972

Thesis
1972 D
T662t
cop. 2

AUG 16 1973

THERMODYNAMICS OF THE IONIZATION OF
POLYBASIC ORGANIC ACIDS IN WATER

Thesis Approved:

Neil Purdie

Thesis Adviser

John E. Moore

Horacio A. Mottola

H. Oliver Spivey

N. Hursham

Dean of the Graduate College

ACKNOWLEDGEMENTS

First, I would like to thank Dr. Purdie for his kindness and understanding through the past few years; without his patience and interest I would never have made it this far. Second, I would like to thank each and every faculty member who has answered one or many of my questions or encouraged me to learn more than required.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION.	1
Historical	1
Statement of Problem	4
II. EXPERIMENTAL.	6
Potentiometer.	6
Electrodes	6
Calibration of Glass Electrodes.	8
Solution Under Study	9
Harned Cells	9
Chemicals.	11
III. THEORY AND BACKGROUND	14
General Equation	14
Thermodynamic Equations.	15
General Extra Thermodynamic Conditions	17
Statistical Effects.	18
Intrinsic Ionization Constants	20
Electrostatics of Ionization	21
Models for Obtaining Thermodynamic Parameters.	23
Temperature Dependence of Electrostatics.	23
Gurney Model.	24
Nancollas Model	25
Structure Reactivity Relations	27
IV. EXPERIMENTAL RESULTS.	32
Temperature Independent Titrations	32
Temperature Dependent Titrations	38
Mixture Analysis	40
V. DISCUSSION.	49
Evaluation of the Calculation Procedure.	49
Interpretation of the Thermodynamics of Polybasic Acids.	50
Hammett Linear Free Energy Relationship for Tribasic Acids.	54

TABLE OF CONTENTS (Continued)

Chapter	Page
Analysis of a Mixture of Acids.	58
The Value of n at Which the Monomers Approach the Polymer Properties.	59
BIBLIOGRAPHY.	61
APPENDIX. OUTLINE OF PROGRAM TO CALCULATE K_1	64

LIST OF TABLES

Table	Page
I. Error Propagation.	16
II. Ionization of Methaemoglobins.	17
III. K-W Theory Data.	22
IV. (A) Data Verifying Gurney's Approach.	24
(B) Data in Conflict With Gurney's Separation Scheme.	25
(C) Data for the Separation of the ΔH_1°	26
V. Hammett Equation Data.	28
VI. Typical Titration Data Using Glass-Calomel Electrode As- sembly: 1,2,3,4,5,6-Benzenehexacarboxylic Acid	33
VII. Typical Data	34
VIII. Error Analysis of the Titration Data*.	35
IX. Harned Cell Titration Data	37
X. Thermodynamics of Ionization of Carboxylic Acids at 25 ^o	42
XI. Ionization Constants for 1,2,3,4,5,6-Benzenehexacarboxylic Acid	45
XII. Data for the Analysis of a Mixture of Dibasic Acids (DMSA)	47
XIII. (A) Sigma Parameters for Benzenedicarboxylic Acids ($\Delta G_0^{\circ} =$ 5.73 kcal.)	56
(B) Ionization Data for 1,2,4-Benzenetricarboxylic Acid	56
(C) Tabulated Data.	57

LIST OF FIGURES

Figure		Page
1.	The Statistical Ratio of Successive Ionization Constants as n Increases	19
2.	⊙ Polyacrylic Acid Results (28) by Equation (3.21). X Hypothetical Results With Equation (3.20) and Same pK_{int} .	20
3.	Graphical Representation of Data From Table X	41
4.	Test of Electrostatic Model	48
5.	Plot of SUM (Eq. 4.1) Vs. Mole % of Meso Isomer	48

CHAPTER I

INTRODUCTION

Historical

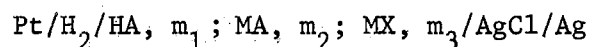
By 1850 Arrhenius' theory of ionic dissociation had not been proposed; acid strengths were referred to as their "avidities." In 1854 Julius Thomsen (1) attempted to compare avidities of acid pairs by thermochemical means as the acids competed for a common base. After studying hydrolysis rates of esters Ostwald (2) in 1884 attempted to put these avidities into a somewhat more quantitative scheme by Kohlrausch's technique of conductivity. Ostwald studied hydrochloric, acetic, dichloroacetic, and a few other acids. Still, these avidities did not seem to fit into any one scheme.

In 1883 Arrhenius published a paper (3) on the ionic dissociation of electrolytes. By 1889 Ostwald had measured more than 240 acids at various concentrations conductimetrically and was in a position to make a further breakthrough in explaining these avidities. In that year he published (4) the results of his conductivity studies and proposed that there exists a constant, K , such that for a particular acid $K = L_c^2 / (L_0(L_0 - L_c))$ where L_c is the conductivity at a given concentration, C , and L_0 is the conductivity extrapolated to infinite dilution.

In the next few years many systems were studied and the technique of conductivity refined. During this period of time the major contribution to electrolyte theory was the Debye and Huckel (5) theoretical der-

ivation of an activity coefficient expression, which explained the experimentally observed square root dependence of the logarithm of the activity coefficient, $\log (\gamma)$, upon the ionic strength, μ .

Harned and Ehlers in 1932 (6) were able to revolutionize the experimental study of acid strengths. They studied the emf for a buffered cell of the type:



where m_1 was the molality of the weak acid (they first studied acetic acid), m_2 was the molality of some alkali metal ion (generally Na^+ or K^+), and m_3 was the molality of some halide (generally Cl^-). The value obtained at 25°C , 1.750×10^{-5} , for the ionization constant of acetic acid was in excellent agreement with that obtained at 25°C from conductivity (7), 1.752×10^{-5} . At the same time Harned and Ehlers obtained the thermodynamic ionization constant at twelve other temperatures ranging from 0°C to 60°C . From this temperature dependence of the ionization constant they were able to calculate ΔH° , ΔS° , and ΔC_p° of the ionization reaction, each as a function of temperature.

The most recent assault on the problem of ionization thermodynamics has been made by a group at Brigham Young University (8) who perfected a titration calorimeter that can measure a total heat of 4 cal. to 0.1%. They obtain ΔH° , ΔS° , and ΔG° from a single experiment at one temperature.

So long as one has a monobasic acid, HA, straightforward extrapolation of emf data to zero ionic strength will yield the thermodynamic acidity constant (9). If the acid is dibasic, H_2A , or polybasic, H_nA , the problem is much more complex:

... 'overlapping of the successive ionization steps. When the ratio of the thermodynamic constants for the primary and secondary steps, K_1/K_2 , is less than 500 to 1000, as it is for most of the common aliphatic dicarboxylic acids and many substituted benzoic acids, the ionic and molecular concentrations cannot be established with sufficient accuracy by consideration of a single equilibrium. Hence, a determination of the constants often requires laborious arithmetical approximations'.

(10)

It can be shown that the minimum number of arithmetic operations required to evaluate n ionization constants is about $n^3(n-1)!$; for $n = 6$ this is 25920 and for $n = 10$ it becomes 362880000. These figures make it impossible to solve the problem "correctly" by hand for large n . Even for high speed computers some problems are encountered at n greater than 10.

Once the n ionization constants are available at various temperatures, ΔG_i° , ΔS_i° , ΔH_i° , and ΔS_i° can be calculated. Roughly, ΔS_i° is associated with solvation, ΔH_i° with bond breaking in the acid molecule, and ΔG_i° with the overall acidity (11). Often ΔG_i° is related to ΔH_i° by theory, as will be seen in Chapter III. Thus, ΔH_i° , and ΔS_i° are of potential value to a better understanding of ionization processes in solution.

Until this study only one carboxylic acid, citric acid (12) with n greater than 2 had been studied so as to yield ΔS_i° and ΔH_i° . All interpretations regarding acidity were previously based upon ΔG_i° . If the above association of ΔS_i° with solvation and ΔH_i° with bond breaking is at all correct, considerable insight into multiple ionizations should be obtained from ΔH_i° and ΔS_i° data.

When n becomes large as in the ionization of a protein or polymer several simplifying assumptions are made (13) to treat the ionization data. In such treatments a large number of the ionizing groups is treated as if the individual ionization steps had approximately the same ther-

modynamics. Therefore, along with these simplifying assumptions, goes any insight into the detailed differences between the individual ionizations that might otherwise have been obtained.

Statement of Problem

It became obvious from an analysis of pK data that these or ΔG° data alone do not convey too much information on ionization processes. Other thermodynamic properties lend themselves to a wider interpretation and to this end a number of theories have been developed which attempt to correlate trends in ΔH_i° and ΔS_i° . In summary the content of this thesis describes the accumulation of thermodynamic data and our effort to bring these theories to bear to interpret the data by changes at the microscopic level.

It was observed that ΔH_i° becomes more negative upon successive ionization for dibasic aliphatic acids and citric acid. Since the carboxyl and/or the carboxylate groups were able to rotate and possibly interact in nearly all of the aliphatic acids examined, it was postulated that the trends to a more negative ΔH_i° on higher ionizations might be related to a proximity effect involving the carboxyl and carboxylate moieties. The first objective was to test this hypothesis by selecting acids in which the groups were in a locked configuration. Among the aliphatics, maleic and fumaric had already been characterized. In the beginning 1,3-benzenedi and 1,3,5-benzenetricarboxylic acids were chosen. To close the cycle proximity effects, if they are real, must be examined in the aromatic series. Consequently a number of acids with ortho-pair arrangements were examined, these were: 1,2,3-benzenetri, 1,2,4-benzenetri, 1,2,4,5-benzenetetra, 1,2,3,4,5,6-benzenehexacarboxylic acid. Citric

acid does not fit into the general scheme of acids examined by virtue of the presence of a hydroxyl group on the 3-carbon position. It does offer an opportunity, however, to investigate the effect of the OH on ionization by making comparison with 1,2,3-propanetri-carboxylic acid. This has been done.

The majority of ionization studies on carboxylic acid polymers or copolymers have been made on polymers of aliphatic acids. To prepare oligomers of these which have a characteristic molecular weight is difficult. Interpretation of the polymer propagation process produces oligomer fractions within which the molecular weight and tacticity vary. A significant question which was raised from the consideration of polymertacticity was the interpretation of the difference in ionization properties of diastereoisomer forms of the same acid. A method is described which permits the composition of a mixture of diastereoisomers to be analyzed. Stereospecific synthesis poses innumerable and individual problems. Rather than change the emphasis of the work, the aromatic acid results were used to test how large 'n' would have to be before convergence with the results for polymers was obtained.

CHAPTER II

EXPERIMENTAL

Potentiometer

All experimental emf measurements were made on a Beckman 101900 Research pH meter with a readability of 0.05 mV, and a standard deviation of 0.051 mV.

Electrodes

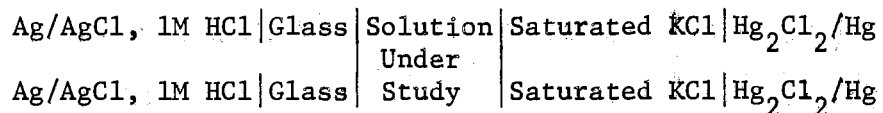
The glass electrodes were Beckman 39301 electrodes with Ag/AgCl internal elements in reference solutions of 1.0 M HCl. Electrodes were stored in an 0.0500 M potassium acid phthalate solution at least a week before use and later at all times between titrations.

Beckman 39071 Frit Junction Calomel Reference electrodes were tested but found to be unsatisfactory (i.e., nonreproducible to within 0.3 mV.) on going from a buffer solution to a test solution and back to the same buffer solution within a period of about an hour. The inconsistency was attributed to the nonreproducible liquid junction across the frit. Consequently, calomel electrodes were prepared (14) in which the liquid junction was maintained across an 0.1 mm. aperture. In this way reproducibility in the liquid junction, e_j , was achieved. To use the electrode, 2-3 drops of fresh salt solution were drained from the tip and the stopcock reclosed before the tip was put into the solution (and after removing the tip from the solution) under study. Electrodes of this type

combined with the same glass electrode in a buffer solution of 4.008 pH would typically produce the same emf to within 0.2 mV. over an extended period of normal use. The only electrical contact was made around the closed stopcock; this reduced the change in ionic strength of the 0.01 M solution under study by the saturated KCl solution of the calomel electrode. Care must be taken not to allow the saturated KCl solution (about 4.5 M at 25°C) to leak into the 0.01 M acid solution because 0.01 ml. of this KCl solution would change the ionic strength of 50 ml. of water by 0.001 M, which is approximately 10% of the total ionic strength of a 0.01 M solution. This would change the logarithm of the activity coefficient by around 5% or a pH of 4.053 to a pH of 4.050, which corresponds to a decrease in the observed emf of about 0.3 mV.

Temperature independent measurements were made on a cell of the type:

Cell I



This permitted four measurements of emf to be made at each point of neutralization and served as an internal check on the individual electrodes. If the differences in the emf between each calomel and a single glass electrode were greater than 0.3 mV., the measurements were discarded from further calculations. This was usually caused by a mismatch of reference potential, and, if no mechanical or electrical failure was found, the calomel electrodes were remade. Disagreement in emf's measured between two glass electrodes and one calomel was frequently found because of differences in asymmetry potentials, e_a , of the glass elec-

trode. The difference, generally near 4 mV., was readily accommodated in the calibration procedure. When the difference was greater than this and not a function of an improperly prepared calomel electrode, the glass electrode was normally replaced.

Calibration of Glass Electrodes

Glass electrodes are reversible to hydrogen ions but are not primary electrodes and must be calibrated relative to a primary standard. This is done by testing the linear response of the cell emf with pH, ($\text{pH} = -\log a_{\text{H}^+}$). Two buffer solutions (NBS standards) are used for this purpose, 0.0500 M potassium acid phthalate ($\text{pH} = 4.008$ at 25°C) and 0.0100 M borax ($\text{pH} = 9.180$ at 25°C). In practice the system was calibrated before and after the titration experiment. The linear response, (the Nernst slope of k) was calculated using the equations and compounds with the theoretical values:

$$k = (E_{4.008} - E_{9.180}) / (9.180 - 4.008) \quad (2.1)$$

where $E_{4.008}$ and $E_{9.180}$ are the observed emf's in the indicated solutions. If the calculated value of k differed from the theoretical value, 0.05916 V at 25°C , by more than 0.3 mV., the cell assembly was examined for possible causes of failure. Using the calculated k , the pH of an unknown solution was calculated from:

$$\text{pH} = 4.008 + (E_{4.008} - E_{\text{obs}}) / k \quad (2.2)$$

where E_{obs} was the measured emf of the unknown acid solution. This assumption of a linear emf-pH response was occasionally checked by an independent measurement on an 0.0250 M KH_2PO_4 - 0.0250 M Na_2HPO_4 solution

with an NBS defined pH of 6.86 at 25°C; the results were always within experimental error.

Solution Under Study

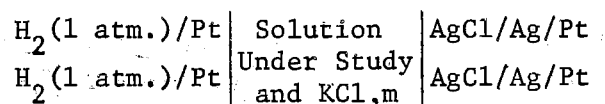
The solution under study was always degassed to remove dissolved carbon dioxide by bubbling dry nitrogen through the solution for about 15 minutes. A slow bubble rate of about 20 ml./min. was maintained during the titration. As a rule the titration was completed in approximately fifteen minutes.

The temperature was controlled to within 0.05°C with a Braun Thermomix II circulator-heater. The temperature-controlled water from a constant-temperature bath was circulated around a jacketed beaker and through the lid.

Harned Cells

The previous glass-calomel assembly was not found to be satisfactorily reproducible at temperatures other than ambient. The problem seemed to be located in the calomel electrode; possibly the Hg_2Cl_2 in the KCl solution was not given sufficient time to equilibrate at the temperatures further removed from ambient. To investigate this problem would have meant completely redesigning the calomel electrodes, possibly by making them completely submersible. Rather than perfect the calomel electrode assembly and still have the uncertainty of a liquid junction, a Harned cell was constructed (6):

Cell II



As before, this assembly allows four independent measurements to be made on the solution under study. Furthermore, the uncertainties of a liquid junction and of a secondary standard for hydrogen ion activity or pH are no longer a problem.

Type III (16), electrolytic, Ag/AgCl electrodes were used. These were found to be very sensitive to mechanical shock, to the lack of cleanliness, to the smoothness of the Pt surface, and to oxygen in the electroplating and storage solutions. For this last reason all solutions had to be strictly degassed by N_2 before use.

The H_2 /Pt electrodes were made (17) on a 22 gauge platinum wire. These were easily prepared, always reproducible, and extremely rugged.

In a typical experiment three to six of the Harned cell assemblies weighted by sheets of lead were lowered into a styrofoam ice chest. Dry H_2 (Linde Gas Co., Union Carbide) was passed over a catalytic deoxygenator (Engelhard Industries) and then through about 25 ft. of $\frac{1}{4}$ in. copper tubing in the styrofoam ice chest before use. It was found that the emf of a 0.01 M HCl solution changed at most about 0.3 mV. in 8 hrs. using dry H_2 , so the H_2 was often not presaturated. The barometric pressure was read from a Taylor aneroid barometer, which was checked against a mercury barometer; agreement was within 1 mm. The H_2 was bubbled at a rate of one to two bubbles per second which caused an oscillation of solution of about $\frac{1}{4}$ cm. on the Pt black. The electrodes were equilibrated at 25°C for 1-2 hrs. before the first emf was recorded. The temperature was subsequently lowered to 0°C and held for about 3 hrs. to reach the new equilibrium before readings were begun. Emf measurements were then taken at 5°, 15°, 25°, 35° and finally again at 25°. An equilibrium time of approximately one hour was allowed at each tempera-

ture. If the data at 25° differed by more than 0.3 mV., the data was excluded from further analysis. The temperature was held to within 0.05°C by a Braun circulating pump and heater, as before, which was opposed by ice water running through a 6 ft. copper cooling coil. The ice water flow rate was adjusted such that the Braun was heating for only a few seconds, every 2-3 minutes.

The overall Harned cell was checked by using 0.01 molal HCl made from constant boiling HCl. The reported (6) value was reproduced to 0.1 mV. after corrections (17) for molarity to molality, for observed pressure to one atmosphere, and the partial pressure of water vapor were made. These same corrections were made on all subsequent measurements. Other more general checks will be pointed out in the results section.

Chemicals

2,3-butanedi, 1,2,3-propanetri, 1,2,3-benzenetri, 1,2,4-benzenetri, 1,3,5-benzenetri, 1,2,4,5-benzenetetra, and 1,2,3,4,5,6-benzenehexacarboxylic acids were obtained from Aldrich Chemical Co., Inc., and were reagent or purissima grade. The molecular weight of each checked to within 0.1% by neutralization with KOH. Reagent grade meso-1,2,3,4-butanetetracarboxylic acid was obtained from Petro-Tex Chemical Corporation and 1,3-benzenedicarboxylic acid from Eastman Kodak Co. The 2,3-butanedicarboxylic acid was obtained from Aldrich as a mixture of meso-dl isomers of unknown composition. About 80% of it was found to be the meso form by recrystallization from concentrated HCl. Further analysis was done by titration and will be discussed in the section on results.

Standard 0.1 N KOH was prepared according to Vogel (18) using reagent grade KOH (Mallinckrodt). A 10.00 ml. Kimax class A automatic buret

equipped with an Ascarite filled drying tube to exclude CO_2 was generally used; it had a readability of 0.01 ml. A Teflon needle (C.R.C., Inc.) was attached to the end of the buret for delivery of the KOH without exposing the KOH to the atmosphere. The KOH was standardized using Baker analyzed potassium acid phthalate dissolved in degassed and deionized water.

The deionized water used in all experiments was prepared by passing distilled water through about 3 ft. of reagent grade Rexyn #300 (H-OH) mixed bed resin (Fisher Scientific Co., Inc.). The water was then passed over a 3 ft. column of activated charcoal and stored in two twelve liter flasks, which were vented to the atmosphere through Ascarite (8-20 mesh) (Arthur H. Thomas Co.) to remove CO_2 .

The KCl used in the Harned cells was Baker analyzed KCl with less than 0.05% KBr as recommended by Bates (19). AgNO_3 was 0.10 N Fisher Scientific Co. certified grade. The KCN was certified ACS grade (Fisher Scientific Co.). The chloroplatinic acid and lead acetate were Baker Analyzed reagent grade.

The acid concentration was about 0.01 M in most of the work. The KCl concentration was about the same as the acid concentration in all of the temperature dependent work. Several exceptions to the 0.01 M acid concentration rule were necessary: the 1,3-benzenedicarboxylic acid was studied at about 0.0005 M due to its low solubility: the 1,3,5-benzenetricarboxylic acid was studied at about 0.05 M also due to its very low solubility: the first buffer regions of 1,2,3,4,5,6- and 1,2,4,5-benzenehexa and tetracarboxylic acids were studied near 0.05 M because they are relatively strong acids and this increase in concentration significantly reduces the error in the corresponding ionization constant. The

base was made about 0.8 N for these first buffer regions to avoid excess dilution. All molarities, M, were changed to molalities, m, for the temperature dependent work.

CHAPTER III

THEORY AND BACKGROUND

General Equation

At a given temperature and pressure the n thermodynamic ionization constants, K_1, K_2, \dots, K_n , can be calculated from the following six equations (20):

- 1) the definition of the ionization constant is given by

$$K_i = (a_{H^+} a_{H_{n-i}A}) / a_{H_{n-i+1}A} \quad (3.1)$$

where $i = 1, 2, 3, \dots, n$ and a_x is the activity of X . (For simplicity the charges are omitted and it is assumed that H_nA is a neutral molecule.)

- 2) the ionization constant of water

$$K_w = a_{H^+} a_{OH^-} \quad (3.2)$$

- 3) the mass balance condition for the total acid concentration, T_a ,

$$T_a = \sum_{i=0}^n (H_{n-i}A) \quad (3.3)$$

where round brackets are used to signify concentrations.

- 4) the electroneutrality condition

$$L = T_b + (H) - (OH) = \sum_{i=1}^n i(H_{n-i}A) \quad (3.4)$$

5) the definition of the ionic strength, μ ,

$$\mu = \frac{1}{2} \{ T_b + (H) + (OH) + 2(Cl) + \sum_{i=1}^n i^2 (H_{n-i}A) \} \quad (3.5)$$

where T_b represents the concentration of base added in the titration of H_nA .

6) the activity of X, a_x , is defined as the concentration of X, (X), times the activity coefficient of X, γ_x , therefore an assumed functional form for the activity coefficient is needed.

$$\log(\gamma_i) = -A^1 i^2 \{ \mu^{1/2} / (1 + \mu^{1/2}) - 0.3\mu \} \quad (3.6)$$

with i as the charge on the X ion and A^1 as the standard Debye Huckel, D-H, constant. This is the extended form of the D-H equation developed by C. W. Davies (21), accurate to $\mu = 0.1$ M.

Equations (3.1) through (3.6) can be combined to give

$$-L = \sum_{i=1}^n ((L - iT_a) a_H^{-1} f_i^{-1} \prod_{j=1}^i K_j) \quad (3.7)$$

This is an equation linear in the products πK_j . For every n points in the titration of H_nA , n equations can be solved simultaneously for the ionization constants, K_1, K_2, \dots, K_n .

Thermodynamic Equations

The thermodynamic variables ΔS_i^0 , ΔH_i^0 , and $\Delta C_{p,i}^0$ can be obtained from the temperature dependence of the ionization constants using the following four equations (22);

$$\Delta G_i^0 = -RT \ln(K_i) \quad (3.8)$$

$$\Delta S_1^{\circ} = -(\partial \Delta G_1^{\circ} / \partial T)_p \quad (3.9)$$

$$\Delta H_1^{\circ} = \Delta G_1^{\circ} + T \Delta S_1^{\circ} \quad (3.10)$$

$$\Delta C_{p,i}^{\circ} = (\partial \Delta H_1^{\circ} / \partial T)_p \quad (3.11)$$

The standard state is taken to be at one molal activity extrapolated from infinite dilution by use of Equation (3.6).

If the heat capacity is assumed to be independent of temperature, it can be shown (23) that the functional form of $\ln(K_i)$ vs. temperature, $^{\circ}\text{K}$, is

$$\ln(K_i) = A + B/T + C \ln(T) \quad (3.12)$$

with A, B, and C as temperature independent constants to be obtained by curve fitting the $\ln(K_i)$ vs. T, $^{\circ}\text{K}$, data. This assumption of a temperature independent heat capacity is valid for all but the most accurate work. Successive differentiation to obtain ΔH_1° and the $\Delta C_{p,i}^{\circ}$ magnifies the error in the original $\ln(K_i)$ data as can be seen from the following Table I (24).

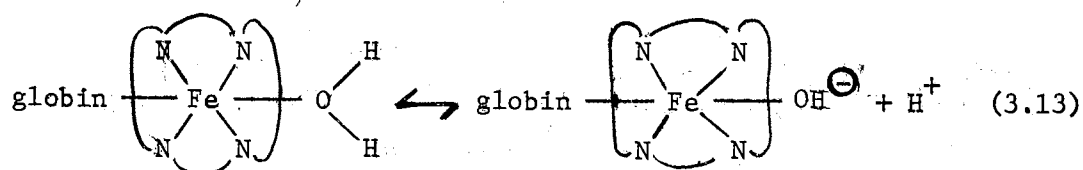
TABLE I
ERROR PROPAGATION

T, $^{\circ}\text{C}$, values at which pK is measured	20, 22, 24, 26, 28, 30,	0, 10, 20, 30, 40, 50,	5, 10, 15, 20, 25, 30, 35, 40, 45, 50
ΔpK probable error	0.02	0.001	0.02 0.001
S.D. in H in cal*	0.970	50	200 10
S.D. in S in eu	3.3	0.16	0.65 0.033
S.D. in C_p in eu	666	33	27 1.3
			28 1.4

* S.D. represents the standard deviation.
eu represents cal./deg.-mol.

General Extra Thermodynamic Conditions

Before accurate temperature dependent data became available comparisons of relative acid strengths were made based solely upon ΔG° data (25). However, as can be seen from Equation (3.10) a constant value of ΔG_i° can result from a compensating change in ΔH° and ΔS° . This is illustrated by Table II for the ionization of three methaemoglobins (26)



which differ in the charge distribution over the globin portion of the molecule.

TABLE II

IONIZATION OF METHAEMOGLOBINS

Animal	ΔG° kcal/mol	ΔH° kcal/mol	$-T\Delta S^\circ$ Kcal/mol
Shrew	11.1	10.2	0.9
Cow	11.0	1.6	9.4
Guinea Pig	11.0	5.8	5.2

Clearly ΔH° and ΔS° data reveal a difference that is undetected if only the free energy data is studied.

To understand which molecular parameters affect the change in a given thermodynamic variable models outside the framework of thermody-

namics, extrathermodynamic conditions, must be used. The procedure for using such conditions is to calculate, from a chosen model, a contribution, X_c , to the thermodynamic variable X . When X_c is added to some ideal part, X_{id} , X is obtained.

$$X = X_{id} + X_c \quad (3.14)$$

If the values of X for two compounds (or one compound at two conditions), X_1 and X_2 , are to be compared, the difference is generally assumed to be due to the change in the X_c values, $X_{c2} - X_{c1}$. The extent to which the equality

$$(X_2 - X_1)_{\text{observed}} = (X_{c2} - X_{c1})_{\text{calculated}} \quad (3.15)$$

holds is a measure of the goodness of the model.

Statistical Effects

The most widely accepted extrathermodynamic condition, the statistical effect, predicts that for an n -basic carboxylic acid in the limit of widely separated (i.e., noninteracting) carboxyl groups, the ratio of K_i to K_j is (27)

$$K_i/K_j = (j(n-i+1))/(i(n-j+1)) \quad (3.16)$$

for a dibasic acid this yields

$$K_1/K_2 = 4 \quad (3.17)$$

Several general deductions can be made from Equation (3.16):

- 1) $\lim_{n \rightarrow \infty} K_i/K_j = j/i$ for $i, j \ll n$. In particular: $\lim_{n \rightarrow \infty} K_1/K_2 = 2$.

2) A plot of K_i/K_{i+1} vs. i is symmetrical about the i axis at

$i = \frac{1}{2}n$ where $K_{\frac{1}{2}n}/K_{\frac{1}{2}n+1} = 1$ in the limit of large n .

These ideas can be illustrated by the following figure:

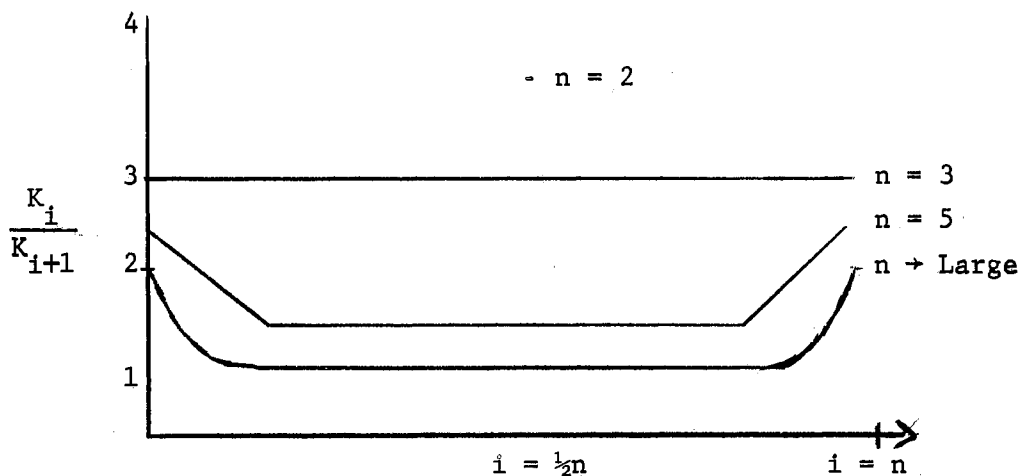


Figure 1. The Statistical Ratio of Successive Ionization Constants as n Increases

3) The difference in the free energy of the i -th ionization of an n -basic acid and the j -th ionization of an m -basic acid is

$$\Delta G_i^n - \Delta G_j^m = -RT \ln \left(\frac{i(m-j+1)}{j(n-i+1)} \right) \quad (3.18)$$

and similarly for the entropy difference. In particular, if the 4-th ionization of a hexabasic acid is compared with the 3-rd ionization of a pentabasic acid at 25°C.

$$\Delta G_4^6 - \Delta G_3^5 = -RT \ln \left(\frac{4(5-3+1)}{3(6-4+1)} \right) = -171 \text{ cal./mol.} \quad (3.19)$$

which often amounts to 10-20% of the total difference.

Intrinsic Ionization Constants

Statistical arguments based upon Equation (3.16) are used extensively in polymer and protein research (28). If it is assumed that the only reason successive ionizations in a polymer differ is a statistical effect and that the inherent or intrinsic strength of an ionization is represented by K_{int} , then from the same assumptions, which lead to Equation (3.16), it can be shown that

$$pK_{int} = pH - \log \left(\frac{\alpha}{1-\alpha} \right) \quad (3.20)$$

where α is the fraction of the total charge ionized at a given pH. Because the charge on the polymer increases and the carboxyl groups are not far enough apart to be considered noninteracting, an electrostatic correction, $w_{el}(\alpha)$, is generally added to Equation (3.20).

$$pK_{int} = pH - \log \left(\frac{\alpha}{1-\alpha} \right) + w_{el}(\alpha) \quad (3.21)$$

Often $w_{el}(\alpha)$ is considered to be a linear function of α , in which case a plot of $pH - \log \left(\frac{\alpha}{1-\alpha} \right)$ vs. α is a straight line of intercept pK_{int} .

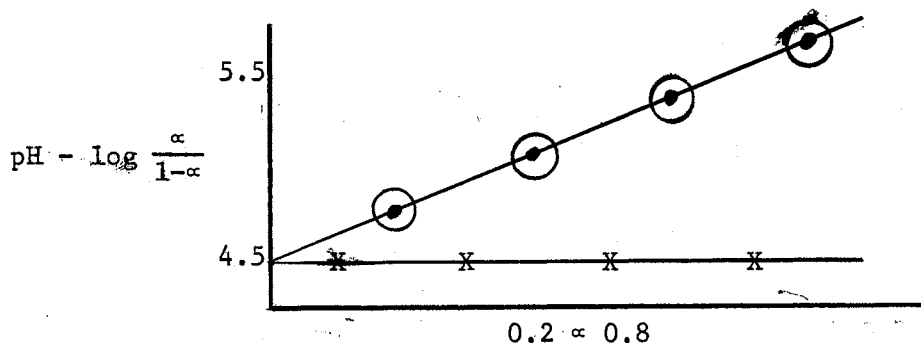


Figure 2. \odot Polyacrylic Acid Results (28) by Equation (3.21).
 X Hypothetical Results With Equation (3.20) and Same pK_{int}

Regardless of which semiempirical correction is applied to Equation (3.18), the pK_{int} values obtained are generally compared with the pK values from monobasic acids.

Electrostatics of Ionization

Bjerrum (29) was among the first to make progress in correlating ionization constants and molecular structure. He developed an electrostatic model to predict the ratio of K_1/K_2 for dibasic acids

$$K_1/K_2 = 4 \exp\left(\frac{-ze^2}{rk'T\epsilon}\right) \quad (3.22)$$

where z is the net charge left by the first ionization (-1 for dicarboxylic acids), e is the charge on the proton (4.80×10^{-10} esu), ϵ is the bulk dielectric constant of water (79 at 25°C), k' is the Boltzmann constant (1.38×10^{-16} erg/deg.-molecule), r is the distance in cm. of the proton to be ionized from the charge already present, and 4 is the statistical factor for a dibasic acid derived from Equation (3.16). This model treats the acid as a molecule without structure and without volume in a continuous dielectric medium with ϵ equal to that of the bulk dielectric. In fact, many of the lines of force from the carboxylate ion to the leaving H^+ must pass through both the molecule and the solvent adjacent to the molecule. In both regions the dielectric constant must be less than the bulk value.

Kirkwood and Westheimer (K-W) (30) later developed a model to account for this reduced dielectric constant cavity. The K-W model may be looked upon, for dibasic acids, as a modification of ϵ in the Bjerrum Equation (3.20)

$$K_1/K_2 = 4 \exp \left(\frac{-ze^2}{rkT \epsilon_{\text{eff}}} \right) \quad (3.23)$$

where ϵ_{eff} is essentially an adjustable parameter. This is an oversimplification, though, because the K-W theory provides an algorithm based upon electrostatics for the calculation of ϵ_{eff} . In Table III ϵ_{eff} is the value which, together with the best value of r , gives the experimentally determined ratio of K_1/K_2 . On the other hand, $r_{\text{K-W}}$ is the value obtained by using the experimentally determined K_1/K_2 ratio and ϵ_{eff} as prescribed by the K-W model. The r_{B} values are obtained by using the experimental K_1/K_2 ratio along with ϵ equal to the bulk dielectric constant of water.

TABLE III
K-W THEORY DATA

Acid	Log ($K_1/4K_2$)	r (A $^\circ$)	$r_{\text{K-W}}$ (A $^\circ$)	r_{B} (A $^\circ$)	ϵ_{eff}
Oxalic	2.36	3.50	3.85	1.30	30
Malonic	2.26	4.12	4.10	1.36	26
Succinic	0.84	4.66	5.75	3.65	63
Dimethylmalonic	2.29	4.12	4.15	1.34	26
Diethylmalonic	4.48	4.12	3.75	0.69	13

As Table III indicates, the value of ϵ_{eff} is generally much less than the bulk dielectric value.

To extend these ideas to polybasic acid ionizations to calculate K_i/K_j based upon a viable electrostatic model is no more difficult mathe-

matically, but it is more tedious, because the symmetry, charge position, and statistical correction must all be applied simultaneously.

Models for Obtaining Thermodynamic Parameters

Temperature Dependence of Electrostatics

If the temperature dependence of the dielectric constant ϵ can be represented by (32)

$$\epsilon(T) = 315 e^{-T/219^\circ\text{K}} \quad (3.24)$$

it can be shown from the Bjerrum theory that for processes whose enthalpy difference is electrostatic in origin, a plot of ΔH_i° vs. ΔS_i° should be a straight line of slope 79°K . For succinic acid this slope $\frac{\Delta H_2^\circ - \Delta H_1^\circ}{\Delta S_2^\circ - \Delta S_1^\circ}$

is about 80°K (see Table III). If a plot of ΔH_i° vs. ΔS_i° has a slope of 79°K , then a plot of ΔG_i° vs. ΔS_i° will have a slope of -219°K . However, the value of the slope obtained experimentally for ΔH_i° vs. ΔS_i° is often close to the experimental temperature, T , and thus ΔG_i° changes very little (see Table II); this effect is referred to as " $\Delta H_i^\circ - \Delta S_i^\circ$ compensation" (33). This $\Delta H_i^\circ - \Delta S_i^\circ$ compensation has been qualitatively explained by the more complete K-W model (22). Yet, the K-W model often predicts a value much too low (34) for the slope of ΔG_i° vs. ΔS_i° , whereas, in these cases the Bjerrum theory is in better agreement with experiment. It is hoped that in the future the more complete K-W model will be modified to better account for the change in ΔG_i° with temperature without affecting its excellent prediction of the ratio of ionization constants at a given T .

Gurney Model

It is observed experimentally that when $\ln(K_1)$ is plotted against T the curve has a maximum. To explain this Gurney (32) has suggested that ΔG° be broken into two parts

$$\Delta G^\circ = \Delta G_{\text{non}}^\circ + \Delta G_{\text{el}}^\circ \quad (3.25)$$

where $\Delta G_{\text{int}}^\circ$ should be considered to be due to internal or quantum mechanical effects and not dependent upon T, and $\Delta G_{\text{non}}^\circ$ should be considered to be due to an electrostatic contribution, which because of the variation of ϵ with T, is T dependent. Using this model and Equation (3.24) for $\epsilon(T)$ Gurney was able to show that the temperature at which a plot of $\ln(K)$ vs. T reaches a maximum, T_{max} , is

$$T_{\text{max}} = 219 \left(1 + \frac{G_{\text{non}}}{G_{\text{el}}} \right) \quad (3.26)$$

The general results of this prediction in terms of the significance of $\Delta G_{\text{non}}^\circ$ vs. $\Delta G_{\text{el}}^\circ$ to the value of T_{max} are correct (Table IV(A) (22)).

TABLE IV(A)

DATA VERIFYING GURNEY'S APPROACH

Ionizing Ion	T_{max} ($^\circ\text{K}$)	Explanation
NH_4^+	1520	Low $\Delta G_{\text{el}}^\circ$ and large $\Delta G_{\text{non}}^\circ$
$\text{NH}_3\text{CH}_2\text{CO}_2^-$	792	Large $\Delta G_{\text{non}}^\circ$
$\text{NH}_3\text{CH}_2\text{CO}_2\text{H}$	324	Low $\Delta G_{\text{el}}^\circ$ from $-\text{NH}_3^+$ assistance
$\text{CH}_3\text{CO}_2\text{H}$	296	Taken as normal
$\text{HO}_2\text{CCH}_2\text{CO}_2^-$	277	Large $\Delta G_{\text{el}}^\circ$

Equation (3.26) fails to explain many specific examples (34). Polar derivatives of acetic acid are expected to have a lower ΔG_{el}° but not much change in ΔG_{non}° , because the OH bond of the acid is four or five bonds away from the polar bond and therefore polar derivatives are expected to have a higher T_{max} (see Table IV(B)). Also, it is difficult to see how an alkyl group could affect either ΔG_{el}° or ΔG_{non}° , yet, generally T_{max} for alkyl-substituted acetic acids is less than that for acetic acid (Table IV(B)). (See Table I of reference 53 for further examples.) Another disappointment with the theory is that it in no way allows for the separation of ΔG_{el}° and ΔG_{non}° .

TABLE IV(B)

DATA IN CONFLICT WITH GURNEY'S SEPARATION SCHEME

Acid	T_{max}
Cl-CH ₂ CO ₂ H	268
MeO-CH ₂ CO ₂ H	270
CN-CH ₂ CO ₂ H	277
Et ₂ -CH ₂ CO ₂ H	228
Et-CH ₂ CO ₂ H	278

Nancollas Model

Nancollas (35) has extended Gurney model to ΔH_1° of reaction

$$\Delta H_1^{\circ} = \Delta H_{non}^{\circ} + \Delta H_{el}^{\circ} \quad (3.27)$$

where $\Delta H_{\text{non}}^{\circ}$ and $\Delta H_{\text{el}}^{\circ}$ are analogous in meaning to $\Delta G_{\text{non}}^{\circ}$ and $\Delta G_{\text{el}}^{\circ}$, respectively, of Equation (3.25). This treatment differs in a very important respect that is an algorithm is provided for the calculation of both $\Delta H_{\text{el}}^{\circ}$ and $\Delta H_{\text{non}}^{\circ}$ from experimental measurements.

$$\Delta H_{\text{el}}^{\circ} = (T - 219^{\circ}\text{K})(\Delta S_{\text{i}}^{\circ} + R \ln 55.5) \quad (3.28)$$

where $R \ln (55.5)$ is the cratic contribution to the entropy change, because two particles are formed from one in an ionization, and the $(T-219)$ at 25°C is recognized as the slope of $\Delta H_{\text{i}}^{\circ}$ vs. $\Delta S_{\text{i}}^{\circ}$, 79°K , from electrostatics. To calculate $\Delta H_{\text{non}}^{\circ}$, $\Delta H_{\text{el}}^{\circ}$ is subtracted from the experimental $\Delta H_{\text{i}}^{\circ}$. Again, qualitative agreement is good.

TABLE IV(C)
DATA FOR THE SEPARATION OF THE $\Delta H_{\text{i}}^{\circ}$

Ionizing Species	$\Delta H_{\text{i}}^{\circ}$	$\Delta H_{\text{non}}^{\circ}$	$\Delta H_{\text{el}}^{\circ}$	T_{max}
NH_4^+	12.48	13.08	-0.60	1520
$\text{NH}_3^+\text{CH}_2\text{CO}_2^-$	10.57	10.47	0.10	792
$\text{NH}_3^+\text{CH}_2\text{CO}_2\text{H}$	0.94	0.97	-0.03	324
$\text{CH}_2\text{CO}_2\text{H}$	- 0.10	1.21	-1.11	296
$^- \text{O}_2\text{C}-\text{CH}_2\text{CO}_2\text{H}$	- 1.15	0.58	-1.73	277

Those species which were expected to have a large $\Delta G_{\text{non}}^{\circ}$ from Table IV(C) also have a large $\Delta H_{\text{non}}^{\circ}$ from Equation (3.27). Also, $\Delta H_{\text{el}}^{\circ}$ is seen to be

small for NH_4^+ just as ΔG_{e1}^0 was argued to be small for the same ion. This model may prove to be more informative than the Gurney model when more generally applied.

Structure Reactivity Relations

In a completely different type of extrathermodynamic model ionization strengths can be correlated and predicted based upon some semiempirical data fitting procedure. The most successful procedure (36,37) of this type is based upon the assumption of a linear additivity of free energy: the "Hammett sigma-rho" equation

$$\log K - \log K_0 = \rho\sigma \quad (3.29)$$

where K is the ionization constant of a substituted acid, K_0 is the ionization constant of the reference acid (for aromatic acids generally benzoic acid), ρ is a constant which depends upon temperature, solvent, and reaction type (ρ is defined as one for ionizations in water at 25°), and σ is a parameter which relates to a given substituent at a particular position relative to the reaction site and which is independent of ρ . For example: the sigma value for a methyl group in the 2, 3, or 4 position can be calculated from the ionization constants (38) of 2, 3, or 4 toluic acids relative to benzoic acid by use of Equation (3.27). (See Table V.) Then the additivity of these σ values (this is the same as the additivity of the free energy) can be used to compute the ionization constants of the di, tri, tetra, and pentamethylbenzoic acids.

When Hammett originally (39) proposed Equation (3.27), he explicitly warned against using this additivity relationship for ortho groups because of specific proximity effects such as resonance and steric effects.

TABLE V
HAMMETT EQUATION DATA

Acid	pK	Sigma		
benzoic	4.202	0.00		
2-toluic	3.898	0.304		
3-toluic	4.274	-0.072		
4-toluic	4.367	-0.165		
Me-substitution Positions	pK _{obs}	Sigma Values Used	pK _{calc}	Difference (pK _{obs} - pK _{calc})
2,3	3.716	$\sigma_2 + \sigma_3$	3.972	-0.256
2,4	4.219	$\sigma_2 + \sigma_4$	4.063	+0.156
2,5	4.001	$\sigma_2 + \sigma_3$	3.972	+0.029
2,6	3.354	$2\sigma_2$	3.594	-0.240
3,5	4.298	$2\sigma_3$	4.346	-0.048
3,4	-----	$\sigma_3 + \sigma_4$	4.439	-----
2,4,6	3.446	$2\sigma_2 + \sigma_4$	3.759	-0.313
2,3,5,6	3.416	$2\sigma_3 + \sigma_2$	3.738	-0.322

With this in mind, agreement with experiment would only be expected for the 3,5; 3,4,5; and 3,4 substituted acids of the acids in Table V; the calculation for the only one for which results are available, 3,5-dimethylbenzoic acid, is in excellent agreement with experiment.

Laidler (40) combined statistical thermodynamics, the temperature independence of ΔC_p^0 , and the additivity of ΔH^0 in the gas phase compared with the additivity of ΔG^0 in solution to partially explain, in terms of three molecular properties the linear free energy relationships in solution:

1) Polar effects (induction and resonance) affect both ΔG° and ΔH° but leave ΔS° unchanged. For example: For the meta and para methoxybenzoic acids (40) $\Delta H_m^\circ = 0.06$ kcal./mol and $\Delta H_p^\circ = 0.57$ kcal./mol, but $\Delta S_m^\circ = \Delta S_p^\circ = -18.5$ eu.

2) Steric effects (as from an ortho group) affect ΔG° , ΔH° , and ΔS° in a complicated manner, but sometimes a partial compensation of ΔH° and ΔS° is observed. In ortho methoxybenzoic acid $\Delta H^\circ = -1.60$ kcal./mol and $\Delta S^\circ = -24.1$ eu., or a partial compensation (40).

3) Solvation effects produce a nearly complete $\Delta H^\circ - \Delta S^\circ$ compensation, leaving ΔG° virtually constant (40).

Acid	ΔG°	ΔH°	ΔS°
Phenol	13.63	5.60	-27.0
3,5-xyleneol	13.67	7.51	-20.7

In the continuation of an intensive approach at the molecular level, progress has been made toward calculations by quantum mechanics of energy differences between conformations. Based upon extended Huckel calculations (41) propionic acid is expected to be most stable in a conformation in which the β carbon (the methyl group) eclipses the carbon-oxygen double bond (Figure 4). However, in α -hydroxypropionic acid the OH group on the α -carbon atom occupies this position eclipsing the carbon-oxygen double bond. This unexpected eclipsed, rather than staggered conformation has been verified by microwave studies of the gas phase and x-ray studies of the solid phase.

Even though quantum mechanics gives no hope of being able to calculate from first principles thermodynamic properties in solution, such

calculations can serve to guide experiments to the most interesting systems for study. For example: based upon the previous calculations, it would be worth while to study the dimethylsuccinic acid and the tartaric acid stereoisomers.

In an attempt to add a molecular interpretation to the Hammett equation, Hepler (42) et al., have made progress by a dichotomized approach, similar to the electrostatic models of Gurney and Nancollas. If the Hammett Equation (3.29), is written as $\ln(K_+) = \rho\sigma$ where K_+ is K_o/K and the corresponding free energy, $\delta\Delta G^\circ$, obtained as $-RT\ln K$, then the thermodynamic variables $\delta\Delta S^\circ$ and $\delta\Delta H^\circ$ can be separated into internal and environmental contributions and written as

$$\delta\Delta G^\circ = \delta\Delta G_{int}^\circ + \delta\Delta G_{env}^\circ \quad (3.30)$$

$$\delta\Delta S^\circ = \delta\Delta S_{int}^\circ + \delta\Delta S_{env}^\circ \quad (3.31)$$

$$\delta\Delta H^\circ = \delta\Delta H_{int}^\circ + \delta\Delta H_{env}^\circ \quad (3.32)$$

When K and K_o refer to similar acids, $\delta\Delta S_{int}^\circ$ can be taken as zero (43).

$$\delta\Delta S_{int}^\circ = 0 \quad (3.33)$$

Also, it has been shown that $\delta\Delta H_{env}^\circ$ approximately proportional to $\delta\Delta S_{env}^\circ$ (42)

$$\delta\Delta H_{env}^\circ \approx \beta' \delta\Delta S_{env}^\circ = \beta' \delta\Delta S^\circ \quad (3.34)$$

where β' is a constant found to be about equal to the temperature. If β' is taken equal to T and Equation (3.34) is treated as an equality then

$$\delta\Delta G^{\circ} = \delta\Delta H_{int}^{\circ} \quad (3.35)$$

or $\delta\Delta G_{env}^{\circ}$ is zero. This leads to the prediction that ρ of Equation (3.29) should be environment independent; which is false. This contribution can be removed by modifying Equation (3.34) to

$$\delta\Delta H_{env}^{\circ} - \beta\delta\Delta S^{\circ} = \gamma'\delta\Delta H_{int}^{\circ} \quad (3.36)$$

where γ' is a parameter which depends upon the solvent. With this modification the proportionality between $\delta\Delta G^{\circ}$ and $\delta\Delta H_{int}^{\circ}$ is maintained, but more important ρ is now expected to depend upon the solvent and $1/T$

$$\rho\sigma = \{C(1 + \gamma)/2.3 RT\}\{-\delta\Delta H_{int}^{\circ}/C\} \quad (3.37)$$

where the first term is associated with the reaction condition parameter ρ , and the second with the substituent parameter, σ . The $1/T$ dependence of ρ has been verified experimentally, the association of ΔH_{int}° with σ seems reasonable, but the relationship between ρ , γ , and T awaits further investigation.

CHAPTER IV

EXPERIMENTAL RESULTS

Temperature Independent Titrations

As we discussed in Chapter II, measurements to be made at 25°C only were made with glass-calomel electrode assembly. When a titration to determine the ionization constants by this method was performed 5-10 data points in each buffer region and around the end point were generally taken. The first and last fourth of the first and last buffer regions, respectively, were not used because in these regions the pH changes too rapidly with the number of ml. of base added. Typically 50 sets of randomly chosen data points were used to obtain 50 sets of ionization constants; then the average, standard deviation, S.D., and relative S.D.-% were calculated for each K_1 .

Table VI contains a sample set of experimental data at 25°C; the acid being used for illustration is 1,2,3,4,5,6-benzenehexacarboxylic acid or mellitic acid. All of the data necessary for the determination of the 6- K_1 's is contained in Table VI. About one minute was required to obtain each data point or about 1½ hours for the whole titration; the $E_{4.008}$ and $E_{9.180}$ agreed before and after the titration.

The results in Table VII were all obtained from the data in Table VI. The error in K_1 and K_2 is unusually large; this type of experiment was repeated on mellitic acid many times; each time similar results were obtained. Finally, a reasonably rigorous error analysis was per-

TABLE VI

TYPICAL TITRATION DATA USING GLASS-CALOMEL ELECTRODE
 ASSEMBLY: 1,2,3,4,5,6-BENZENEHEXACRBOXYLIC ACID

Base-Vol.	emf x 10	Base-Vol.	emf x 10	Base-Vol.	emf x 10
0.00	3.095	10.00	2.371	22.00	0.525
2.00	3.004	10.50	2.308	22.50	0.453
2.25	2.990	11.00	2.235	23.00	0.377
2.50	2.980	11.50	2.161	23.50	0.292
2.75	2.967	12.00	2.084	24.00	0.205
3.00	2.954	12.50	1.999	24.50	0.103
3.25	2.943	13.01	1.910	25.00	-0.002
3.50	2.929	13.50	1.816	25.10	-0.053
3.75	2.915	14.00	1.729	25.25	-0.103
4.02	2.900	14.50	1.643	25.35	-0.138
4.25	2.885	15.00	1.558	25.50	-0.208
4.50	2.874	15.50	1.485	25.60	-0.255
4.75	2.856	16.00	1.400	25.75	-0.359
5.00	2.840	16.50	1.324	25.85	-0.447
5.25	2.827	17.00	1.247	25.95	-0.584
5.50	2.809	17.50	1.171	26.00	-0.680
6.01	2.769	18.00	1.094	26.05	-0.804
6.50	2.731	18.50	1.020	26.10	-0.965
7.00	2.689	19.00	0.949	26.15	-1.132
7.51	2.648	19.50	0.879	26.20	-1.278
8.00	2.599	20.00	0.810	26.25	-1.395
8.50	2.547	20.50	0.740	26.30	-1.499
9.00	2.493	21.00	0.667	26.35	-1.583
9.50	2.434	21.50	0.598	26.50	-1.811

$T_a = 0.01137$ M; Base concentration = 0.06530 M; Initial volume of acid = 25.00 ml.; $T = 25^\circ\text{C}$; $E_{4.008} = 0.1822$ V.; $E_{9.180} = -0.1230$ V.; $pK_w = 14.00$.

TABLE VII

TYPICAL DATA

i	I	II	III	IV	V	VI
pK_i	1.08	2.08	3.50	5.05	6.30	7.43
K_i	8.24×10^{-2}	8.38×10^{-3}	3.14×10^{-4}	8.99×10^{-6}	5.05×10^{-7}	3.70×10^{-8}
S.D. _i	3.62×10^{-2}	1.03×10^{-3}	3.14×10^{-4}	8.99×10^{-6}	5.05×10^{-7}	3.70×10^{-8}
$\frac{S.D.}{K_i}$	23%	12%	2.5%	1.7%	1.4%	1.4%

TABLE VIII

ERROR ANALYSIS OF THE TITRATION DATA*

X	(X _i)	K ₁ ⁻¹ 2.24X10 ⁻¹	K ₂ ⁻³ 6.18X10 ⁻³	K ₃ ⁻⁴ 3.03X10 ⁻⁴	K ₄ ⁻⁶ 8.18X10 ⁻⁶	K ₅ ⁻⁷ 4.81X10 ⁻⁷	K ₆ ⁻⁸ 2.66X10 ⁻⁸
a _H ⁺ of 0.5%	2.998X10 ⁻²	+8.90	-0.38	+0.05	- - -	- - -	- - -
	5.582X10 ⁻³	-5.29	+1.92	-0.27	+0.06	- - -	- - -
	7.099X10 ⁻⁴	+1.61	-0.60	+0.89	-0.07	+0.03	- - -
	3.807X10 ⁻⁵	-0.18	+0.07	-0.11	+0.74	-0.14	+0.02
	3.372X10 ⁻⁶	+0.04	-0.01	+0.02	-0.14	+0.79	-0.13
	2.480X10 ⁻⁷	- - -	- - -	- - -	+0.06	-0.12	+0.61
T _a of 0.1%	0.05047	-1.73	+0.08	-0.01	- - -	- - -	- - -
	0.02124	+3.02	-1.00	+0.14	+0.01	+0.01	- - -
	0.01056	-1.73	+0.68	-1.04	+0.15	-0.01	- - -
	0.00992	+0.33	-0.12	+0.20	-1.30	+0.31	-0.05
	0.00973	-0.07	+0.03	-0.05	+0.36	-1.64	+0.29
	0.00954	+0.02	- - -	+0.01	-0.05	+0.44	-2.12
T _b of 0.1%	0.02536	+0.72	-0.03	- - -	- - -	- - -	- - -
	0.03321	-2.37	+0.83	-0.12	+0.04	+0.01	- - -
	0.02612	+1.76	-0.67	+1.02	-0.09	+0.04	- - -
	0.03482	-0.35	+0.13	-0.22	+1.37	-0.28	+0.04
	0.04373	+0.09	-0.03	+0.05	-0.35	+1.71	-0.29
	0.05250	-0.02	- - -	-0.01	+0.13	-0.48	+2.18
(KCl) of 0.1%	0.04654	-1.50	+0.07	- - -	- - -	- - -	- - -
	0.02171	+1.17	-0.38	+0.05	+0.02	+0.01	- - -
	0.01292	-0.28	+0.11	-0.17	+0.04	+0.01	- - -
	0.00936	+0.01	- - -	- - -	-0.11	+0.04	- - -
	0.00918	- - -	- - -	- - -	+0.04	-0.13	+0.02
	0.00900	- - -	- - -	- - -	+0.03	+0.01	-0.11

TABLE VIII (Continued)

X	(X _i)	K_1^{-1} 2.24X10 ⁻¹	K ₂	K_3^{-3} 6.18X10 ⁻³	K_4^{-4} 3.03X10 ⁻⁴	K_5^{-7} 4.81X10 ⁻⁷	K_6^{-8} 2.66X10 ⁻⁸
SUM % ** =		31.28	7.23	3.50	5.23	6.31	5.94

* An example of how to read the table: Looking at the second buffer region where $T_a = 0.02124$ m. if a 0.1% error is made in the value of T_a in this buffer region, it would cause K_1 to be too high by 3.02% and K_2 to be too low by 1.00%.

** SUM |%| is the sum of the absolute values of the errors for a given ionization constant. It is expected to be an upper limit to the per cent of error in the experimentally determined ionization constants as is verified by Table VII.

NOTE: The table was constructed by increasing each of the experimental variables a_H , T_a , T_b , and (KC1) by the listed amount one at a time and then resolving for six K's and comparing results. In the range of small error (less than about 1%) the error is approximately linear for most practical purposes.

TABLE IX

HARNED CELL TITRATION DATA

	$T_a \times 10^2$	$T_b \times 10^2$	$(C1) \times 10^2$	Emf-observed				
				25°	5°	15°	25°	35°
1,3-benzenedicarboxylic acid								
I	0.0532	0.0278	0.1139			0.6139	0.6212	0.6282
II	0.0551	0.0871	0.0829			0.6752	0.6844	0.6923
1,3,5-benzenetricarboxylic acid								
I	0.4367	0.2224	0.999	0.6324	0.6163	0.6239	0.6323	0.6404
II	0.3994	0.5957	1.041	0.5767	0.5661	0.5713	0.5768	0.5820
III	0.4118	0.1023	1.025	0.5315	0.5245	0.5279	0.5314	0.5347
1,2,4-benzenetricarboxylic acid								
I	2.001	1.007	2.143	0.4788	0.4718	0.4753	0.4787	0.4812
II	0.980	1.364	1.015	0.5629	0.5524	0.5576	0.5627	0.5675
III	1.024	2.492	0.999	0.6446	0.6287	0.6365	0.6446	0.6531
1,2,3-benzenetricarboxylic acid								
I	1.081	0.540	1.509	0.5095	0.5006	0.5055	0.5095	0.5133
II	0.955	1.520	1.120	0.6189	0.6065	0.6125	0.6187	0.6248
III	0.942	2.326	1.253	0.7325	0.7132	0.7226	0.7323	0.7416
1,2,3-propanetricarboxylic acid								
I	0.982	0.492	1.064	0.5531	0.5442	0.5489	0.5530	0.5569
II	0.929	1.392	1.021	0.6208	0.6041	0.6123	0.6207	0.6290
III	0.873	2.175	0.959	0.7016	0.6777	0.6891	0.7006	0.7119
1,2,4,5-benzenetetracarboxylic acid								
I	1.019	0.641	1.097	0.4836	0.4753	0.4798	0.4834	0.4865
II	0.881	1.321	0.771	0.5336	0.5211	0.5278	0.5336	0.5385
III	1.007	2.503	0.881	0.6106	0.5965	0.6035	0.6105	0.6180
IV	0.975	3.359	0.853	0.6806	0.6605	0.6705	0.6806	0.6910
1,2,3,4,5,6-benzenehexacarboxylic acid								
I	5.047	2.536	4.654	0.3986	0.3963	0.3971	0.3986	0.3995
II	2.124	3.221	2.171	0.4599	0.4518	0.4560	0.4602	0.4636
III	1.056	2.612	1.292	0.5255	0.5125	0.5195	0.5256	0.5315
IV	0.992	3.482	0.936	0.6089	0.5942	0.6016	0.6089	0.6182
V	0.973	4.373	0.918	0.6717	0.6557	0.6637	0.6717	0.6797
VI	0.954	5.250	0.900	0.7393	0.7192	0.7293	0.7393	0.7493

formed, and this large error in K_1 and K_2 was related to the fact that $T_a < (K_1 \text{ or } K_2)$ which makes both ionizations behave as if they were "strong" acids.

The only data from the temperature dependent calomel-glass studies used was for 1,2,3,4-butanetetracarboxylic acid. This data was used because all of the pure compound was consumed in the studies at 25° and no more could be obtained commercially.

Temperature Dependent Titrations

Accurate temperature dependent data was finally obtained by the use of Harned cells (Chapter II). Typical data from the use of these cells is represented in Table IX for every acid whose thermodynamics is reported in Table IX. In all cases in Table VIII the emf over a 10 degree temperature range varies by only 4-10 mV. If the emf on going back to 25° varied by more than 0.2 mV., that cell was not used in further calculations. The 1,3-benzene data is an exception, since the acid precipitated on lowering the temperature.

The Ag/AgCl electrodes were made 12 at a time; aged for 2-3 days in 0.01 M HCl; and checked against each other before use. Any electrode which differed in emf from the others by more than about 0.2 mV. was discarded. If more than 3 or 4 electrodes failed to zero, relative to each other, the whole set was remade. Each electrode pair was used in only one experiment. The H_2/Pt electrodes always checked against each other to within 0.1 mV. When 6 cells as described by Cell II in Chapter II were filled with 0.01006 m HCl, the emf reported by Harned was reproduced to within 0.1 mV. with a S.D. of about 0.05 mV. This reproducibility is considered to be fortuitous, but serves to indicate the

care taken in the preparation of the electrodes used in the experiments with the Harned cells.

Results of the temperature dependent studies are summarized in Table X. A detailed discussion of temperature independent error will be presented in Chapter V. Based upon the reproducibility of the emf at 25° it is estimated that from one temperature to another a given pK_i is in error by about 0.003. According to Table I this error in pK_i corresponds to an error of about 0.1 kcal./mole in ΔH_i° , an error of about 0.5 eu. in ΔS_i° , and an error of about 20 eu. in $\Delta C_{p,i}^\circ$. None of the interpretations in Chapter V necessitate ΔH_i° or ΔS_i° data of any more accuracy than this. The $\Delta C_{p,i}^\circ$ data, although of the right order of magnitude and sign, is not accurate enough to warrant any further detailed interpretation. Table IX also contains ΔH_c° data from Equation (3.27). The A, B, and C constants in Table IX are the least squares curve fitted results from Equation (3.12). With these numbers the pK_i data from experiment could generally be reproduced with a S.D. of about 10^{-4} , but this has little meaning because the sample size, in all cases, was too small. The T_{\max} data not derived from Equation (3.12) will be discussed in Chapter V. The ΔH_i° data for 1,3-benzene and 1,2,3,4-butane were derived by use of the van't Hoff equation treating ΔH_i° as a constant and independent of temperature; no attempt was made to estimate the error in the pK_i 's as a function of temperature for these two acids. Figure 3 is a graphical summary of the pK_i data as a function of temperature for the acids in Table X that were studied by the Harned cells.

The electrostatic theory of Gurney (Chapter III) predicts that a plot of ΔG_i° vs. ΔS_i° will be a straight line of slope $-219^\circ K$. Figure 4 is a test of this hypothesis with the data from Table X. The least

squared line through the data, not blocked out by the hashed marks, has a slope of -224°K with a correlation coefficient of 0.97. All data in the hashed box is believed to be from the first ionization of an ortho-pair and is discussed in Chapter V.

In an attempt to understand how accurately concentration variables would need to be measured to produce an ionization constant of a given accuracy the data in Table VIII were calculated. The reported deviations in the experimental variables are expected to be about what were obtained in practice. An important feature of this table is the calculated effect of an error in one buffer region on the neighboring K_1 's. The error in K_1 and K_2 is expected to be concentration dependent; this probably accounts for the fact that the sum of the error in Table VIII for K_2 is less than that reported experimentally for K_2 in Table VII.

Table XI is used to illustrate the overall quality of the experimental work as well as the self consistency of the data analysis. The data in the first column are the results reported by Maxwell and Partington at a constant ionic strength of 0.03 M; the second column was produced by putting their data into our program and using Equation (3.6) for the activity coefficients. The next two columns were obtained in this study by the Harned cell method and the glass-calomel assemblies, respectively. Agreement is excellent.

Mixture Analysis

A byproduct of the glass-calomel studies was the development of a method to analyze for the analytical concentrations of two dibasic-acids in solution simultaneously. α, α' -Oimethylsuccinic acid (DMSA) was used in Table XII to illustrate this method of analysis. DMSA exists

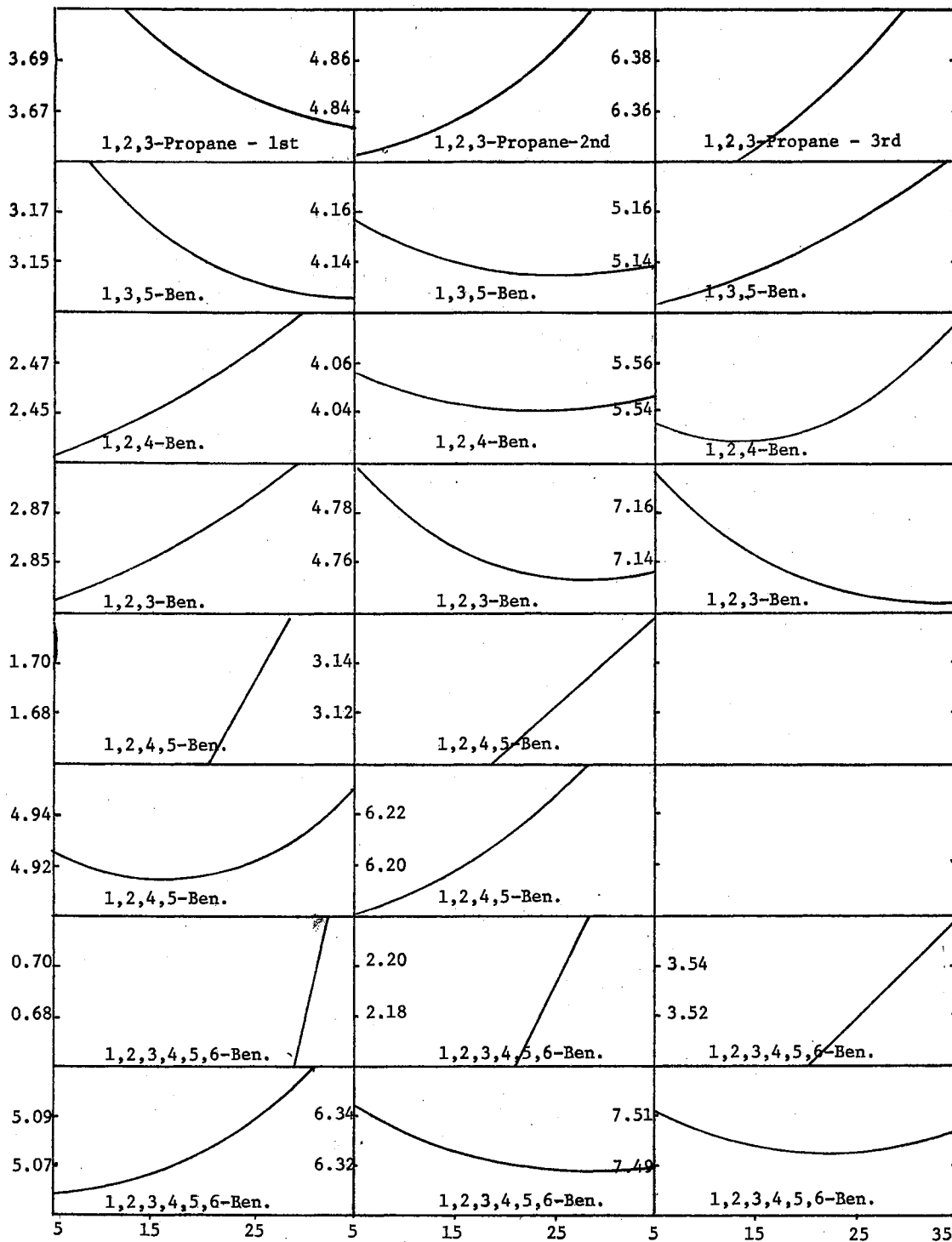


Figure 3. Graphical Representation of Data From Table X

TABLE X

THERMODYNAMICS OF IONIZATION OF CARBOXYLIC ACIDS AT 25°

Acid	pK_i	ΔG° Kcal/mole	ΔH° Kcal/mole	$-\Delta S^\circ$ eu.	$\Delta S^\circ_{st.}$ (Eq.3.16) eu.	$-\Delta C_p^\circ$ eu.	T_{max}	ΔH_c Kcal/mole	B	A	C
1,2,3- propane	3.67	5.00	0.56	14.9	17.1	27	319	1.11	35.93	-1867.2	-13.47
	4.87	6.64	-1.19	26.3	26.3	49	273	0.26	65.84	-2925.6	-24.61
	6.38	8.70	-1.81	35.2	33.0	52	263	0.34	67.78	-2964.5	-25.95
1,2,3,4- butane	3.43	4.66	0.2	15.0	17.8	--	301	0.75	---	---	---
	4.58	6.21	-0.3	21.9	22.7	--	295	0.80	---	---	---
	5.85	7.95	-0.5	28.4	27.6	--	291	1.11	---	---	---
	7.16	9.73	-1.2	36.7	33.9	--	258	1.07	---	---	---
1,3- benzene	3.50	4.74	0	15.9	17.3	--	298	0.58	---	---	---
	4.50	6.10	-0.44	22.0	18.6	--	293	0.59	---	---	---
1,2,3- benzene	2.88	3.93	-1.06	16.7	18.9	22	249	-0.37	27.95	-1175.4	-10.87
	4.75	6.49	0.21	21.1	21.1	65	301	1.25	90.64	-4283.4	-32.75
	7.13	9.72	0.37	31.4	29.2	57	305	2.22	75.81	-3760.9	-28.42
1,2,4- benzene	2.48	3.38	-1.24	15.5	17.7	32	258	-0.65	42.76	-1783.6	-15.87
	4.04	5.51	-0.09	18.5	18.5	46	296	0.74	63.24	-2977.6	-23.16
	5.54	7.56	-0.95	28.6	26.4	91	288	0.68	127.61	-5749.3	-46.02
1,3,5- benzene	3.12	4.26	0.87	11.4	13.6	53	315	1.14	74.77	-3628.9	-26.56
	4.10	5.60	-0.49	20.4	20.4	49	288	0.49	66.50	-3051.3	-24.39
	5.18	7.07	-1.17	27.7	25.5	66	280	0.39	90.75	-4052.4	-33.28

TABLE X (Continued)

Acid	$pK_{\frac{1}{2}}$	ΔG° Kcal/mole	ΔH° Kcal/mole	$-\Delta S^{\circ}$ eu.	$\Delta S^{\circ}_{st.}$	$-\Delta C_p^{\circ}$ eu.	T_{max}	ΔH_c Kcal/mole	B	A	C
1,2,4,5- benzene	1.70	2.31	-3.11	18.2	21.0	--	< 200	-2.30	2.64	385.0	-2.27
	3.12	4.26	-1.57	19.6	20.4	--	277	-0.65	-33.28	1634.2	9.97
	4.92	6.71	-0.79	25.2	24.4	86	289	0.64	120.9	-5453.7	-43.45
	6.23	8.49	-1.60	33.9	31.1	73	276	0.55	99.45	-4406.2	-36.73
1,2,3,4, 5,6- benzene	0.68	0.99	-7	27	23	--	< 100	-4.5	1183.3	-5134.3	-408.9
	2.21	3.01	-3.56	21.9	23.7	--	< 200	-2.43	-34.0	2071.3	10.0
	3.52	4.80	-2.75	25.3	25.9	64	255	-1.38	87.87	-3557.1	-32.1
	5.09	6.94	-1.13	27.1	26.5	58	278	0.38	78.24	-3498.9	-28.9
	6.32	8.62	0.05	28.7	26.9	48	299	1.69	63.36	-3110.0	-24.0
7.49	10.34	-0.27	35.5	31.9	61	293	1.90	80.92	-3887.6	-30.5	
formic*		5.12	0.	17.2		41					
acetic*	4.76	6.48	-0.10	22.1		37	296	1.01	----	----	----
succinic*	4.21	5.74	0.76	16.7	18.1	32	326	1.45	----	----	----
	5.64	7.69	0.04	25.7	24.3	52	296	1.44	----	----	----
maleic*	1.91	2.60	0.08	8.5	9.9	--	296	0.12	----	----	----
	6.33	8.64	-0.83	31.5	30.1	--	285	1.03	----	----	----
fumaric*	3.19	4.22	0.11	13.8	15.2	--	299	0.57	----	----	----
	4.60	6.28	-0.68	23.3	21.9	--	266	0.53	----	----	----
citric*	3.13	4.27	1.00	11.0	13.2	--	327	1.24	----	----	----
	4.76	6.49	0.58	19.8	19.8	45	310	1.51	----	----	----
	6.40	8.73	-0.80	32.0	29.8	60	285	1.10	----	----	----
benzoic	4.20	5.73	0.10	18.9		37	296	0.96	----	----	----

TABLE X (Continued)

Acid	pK_i	ΔG° Kcal/mole	ΔH° Kcal/mole	$-\Delta S^\circ$ eu.	$\Delta S^\circ_{st.}$	$-\Delta C_p^\circ$ eu.	T_{max}	ΔH_c Kcal/mole	B	A	C
1,2-	2.95	4.02	-0.64	15.6	17.0	22	266	-0.04	---	---	---
benzene*	5.41	7.38	-0.50	26.4	25.0	70	291	0.95	---	---	---

*This data was taken from Reference 44.

TABLE XI
IONIZATION CONSTANTS FOR 1,2,3,4,5,6-
BENZENEHEXACARBOXYLIC ACID

	Ref. 45 Q.H.-Calomel	Ref. 45 Recalculated	Present Work Harned Cells	Present Work Glass-Calomel
pK ₁	1.40	1.31	0.68	1.21
pK ₂	2.19	2.39	2.21	2.19
pK ₃	3.31	3.57	3.52	3.53
pK ₄	4.78	5.08	5.09	5.09
pK ₅	5.89	6.31	6.32	6.31
pK ₆	6.96	7.46	7.49	7.45

in a dl and a meso form. In Table XII, column 1 is the titration curve for the pure meso form and column 2 contains the data from the titration of the pure dl form. The isomer compositions indicated in the next three columns were made by mixing known amounts of the pure forms. The last columns were made by mixing known amounts of the pure forms. The last column contains the results from the titration of the commercially available sample. From the data in columns 1 and 2 the ionization constants for the pure meso and dl forms were obtained. Then, based upon these ionization constants, 11 titration curves were calculated for a given total acid concentration by varying the fraction of the forms by 0.1 from one curve to another (Figure 5). For each of the 11 curves the absolute value of the difference between the experimental and the calculated emf for each data point was computed and summed.

$$\text{SUM} = \sum_{\text{all pts.}} | \text{emf}_{\text{calc}} - \text{emf}_{\text{exp}} | = \sum_{\text{all pts.}} | \Delta E_i \text{ mV.} | \quad (4.1)$$

The idea being that, if the correct composition were used to obtain SUM, that SUM would be a minimum. Figure 4 is a plot of SUM vs. mole-fraction of meso isomer for all six columns in Table VII. For the first five columns the calculated minimum in SUM vs. mole-fraction occurs within 1% of the true composition. The commercially obtained mixture was, therefore, determined to be 78% meso and 22% dl DMSA.

TABLE XII

DATA FOR THE ANALYSIS OF A MIXTURE OF DIBASIC ACIDS (DMSA)

	0.01173	0.00924	0.01023	0.01072	0.01121	0.01168						
Acid (M)	0.01173	0.00924	0.01023	0.01072	0.01121	0.01168						
Base (M)	0.1033	0.1033	0.1033	0.1033	0.1033	0.1033						
Temp (°C)	25.3	25.3	25.3	25.3	25.3	25.3						
Initial Vol. of Acid (ml.)	25.00	25.00	25.00	25.00	25.00	25.00						
Emf. -4.01	0.1852	0.1852	0.1852	0.1852	0.1852	0.1852						
Emf. -9.18	-0.1198	-0.1198	-0.1198	-0.1198	-0.1198	-0.1198						
meso %	100	0.00	45.8	65.5	83.6	?						
dl %	0.00	100.00	54.2	34.5	16.3	?						
	ml.	Emf.	ml.	Emf.	ml.	Emf.	ml.	Emf.	ml.	Emf.	ml.	Emf.
	0.00	0.2533	0.00	0.2453	0.00	0.2492	0.00	0.2506	0.00	0.2518	0.00	0.2523
	1.00	0.2165	1.00	0.1978	0.50	0.2264	0.50	0.2293	0.50	0.2314	0.50	0.2322
	1.50	0.2009	1.50	0.1766	1.00	0.2070	1.00	0.2104	1.00	0.2135	1.00	0.2145
	2.00	0.1860	2.00	0.1506	1.50	0.1888	1.50	0.1935	1.50	0.1973	1.50	0.1987
	3.50	0.1365	2.50	0.11715	2.00	0.1694	2.00	0.1757	2.00	0.1811	2.00	0.1830
	4.00	0.12075	3.00	0.0898	2.50	0.1470	2.50	0.1561	2.50	0.1643	2.50	0.1662
	4.50	0.1045	3.25	0.0783	3.00	0.1235	3.00	0.1352	3.00	0.1448	3.00	0.1481
	5.60	0.0226	3.50	0.0669	3.50	0.1015	3.50	0.1155	3.50	0.1270	3.50	0.1304
	5.65	-0.0062	3.74	0.0548	4.00	0.1783	4.00	0.0953	4.00	0.1097	4.00	0.1135
	5.70	-0.1069	4.00	0.0403	4.50	0.1493	4.50	0.0716	4.50	0.0905	4.50	0.0956
	5.75	-0.1506	4.25	0.0180	4.85	0.0045	5.00	0.0293	5.00	0.0631	5.00	0.0725
			4.30	0.0111	4.90	-0.0135	5.10	0.0092	5.35	0.0165	5.50	0.0256
			4.35	0.0018	4.95	-0.0656	5.15	-0.0127	5.40	-0.0061	5.55	0.0129
			4.40	-0.0120	5.00	-0.1397	5.20	-0.0818	5.45	-0.1161	5.60	-0.0084
			4.45	-0.0422	5.05	-0.1709	5.25	-0.1450			5.65	-0.0926
			4.50	-0.1177							5.70	-0.1428
			4.55	-0.1602								

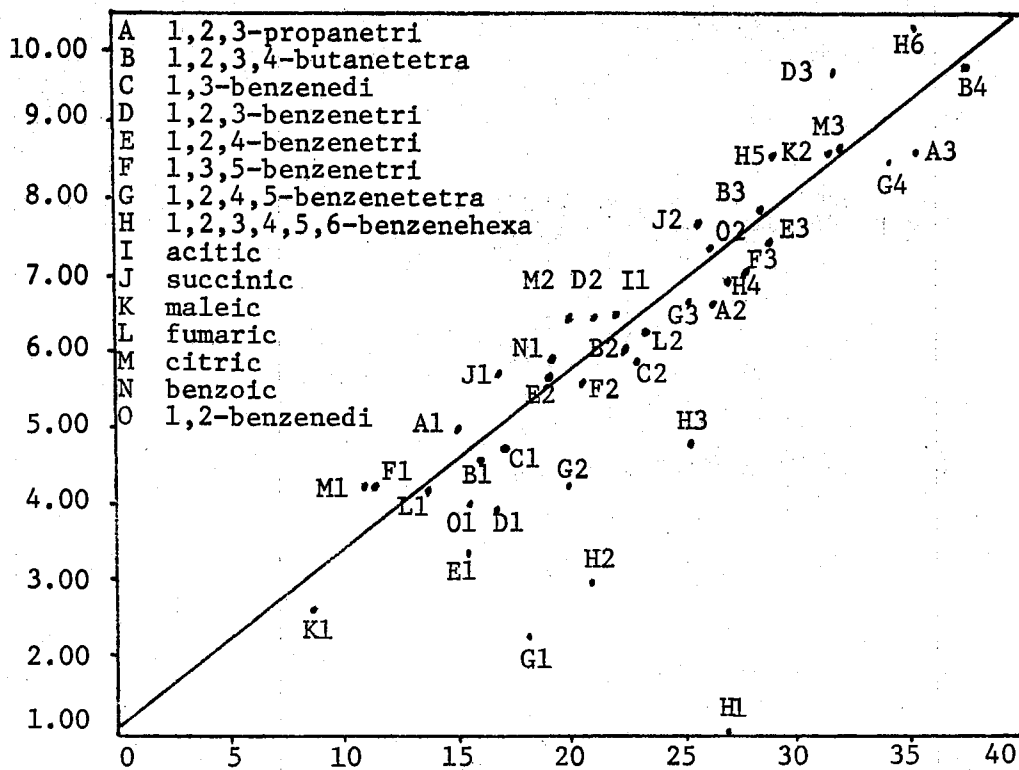


Figure 4. Test of Electrostatic Model

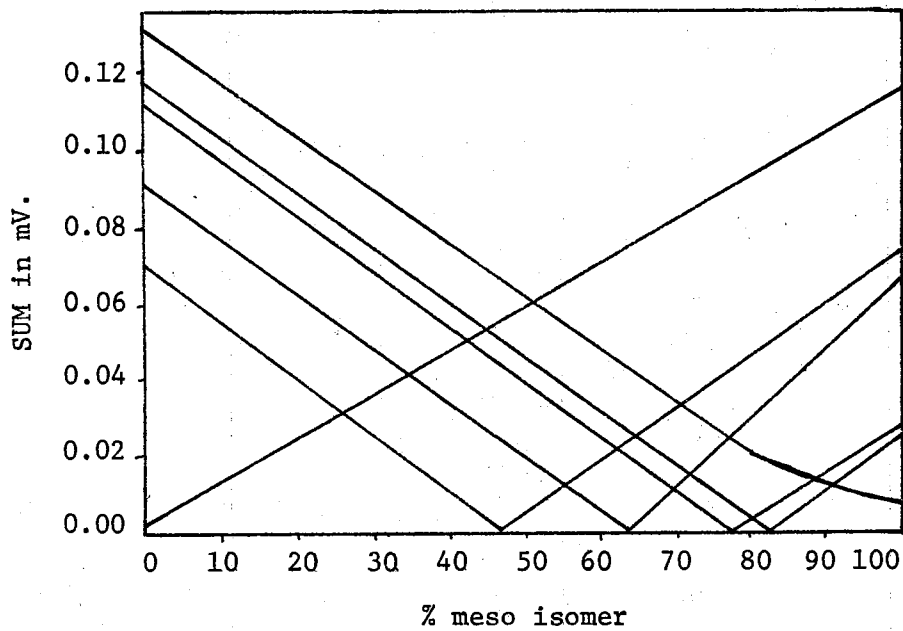


Figure 5. Plot of SUM (Eq. 4.1) Vs. Mole % of Meso Isomer

CHAPTER V

DISCUSSION

Evaluation of the Calculation Procedure

A program was written (see Appendix for a summary of program) to solve for the n ionization constants in Equation (3.7) by the use of n data points measured as a function of degree of neutralization (46). The data points were chosen from the approximate n buffer regions, which corresponded with the n ionization steps, by a random number generator subroutine. Using these n data points the coefficients of an n by $n+1$ matrix were calculated and the n ionization constants obtained by elimination and back-substitution. The calculation required reiteration around the matrix coefficients using as a criterion for convergence the variation in γ_i in successive cycles, $\text{dif} = |\gamma_{i,x+1} - \gamma_{i,x}|$. To initiate the calculation the first coefficients were calculated using estimated γ_i values. Termination occurred when $\text{dif} < 0.0001$. Convergence was generally accomplished within three or four cycles.

Besides the random error mentioned in the results, the uncertainty of the true functional form for the activity coefficient as a function of concentration for multiply charged ions is a source of systematic error. Citric acid (12) is the only polybasic organic acid with $n > 2$ for which thermodynamic ionization constants have been calculated, and this was done by extrapolation to infinite dilution (this procedure makes a knowledge of the true activity coefficient functional form much

less critical). In our laboratory citric acid was titrated at $T_a = 0.01$ M and its ionization constants obtained by using Equation (3.6) for the activity coefficients.

	pK_1	pK_2	pK_3
Extrapolated to $T = 0$ M	3.13	4.76	6.40
This work Equation 3.6	3.13	4.78	6.43

Agreement is within experimental error in all pK_i 's. Even if Equation (3.5) does produce a systematic error in pK_i as i increases, the relative error in adjacent ionization constants is expected to be small and of about the same size and sign for similarly charged analogous acids. This source of error will be even less important when pK_i at one T is compared with the same pK_i at other T 's, which is pertinent to the calculation of the entropy and the enthalpy change.

Interpretation of the Thermodynamics of Polybasic Acids

Before proceeding it should be noted that in all cases the ΔH_i° data is the most accurate. This follows from the fact that what is actually calculated from experimental data is the ionization constant or pK at a given temperature. This data is then curve fitted by Equation (3.12) and differentiated to obtain ΔH_i° . Therefore, to the extent that an error is temperature independent, this error will be eliminated. For example: if due to an incorrect activity coefficient equation, the pK data at every temperature is 0.3 in pK too large (which corresponds to 0.4 kcal./mol in ΔG°) the resultant ΔH° data will not be affected,

rather, the error will occur in the calculated TAS° term.

This elimination of temperature-independent systematic error in ΔH° is extremely fortunate, because ΔH° is used extensively to understand trends in the data. To a large extent the dichotomized approach of Gurney will be used. Often, the data is not accurate enough to produce reliable T_{\max} data needed in Equation (3.26). Harned and Embree (47) showed that all of the available pK data, at that time, could be fitted to a two parameter equation

$$pK = pK_{\max} + P(T - T_{\max}) \quad (5.1)$$

where P was a constant (5×10^{-5}) and pK_{\max} was the value of the ionization constant at the temperature of maximum ionization, T_{\max} . It follows that for a number of acids T_{\max} varies linearly with ΔH° , at a given T. From these arguments Equation (3.26), which states that $T_{\max} \propto \Delta G_{\text{non}}^\circ / \Delta G_{\text{el}}^\circ$, can be written as

$$\Delta H_{25^\circ\text{C}}^\circ \propto \Delta G_{\text{non}}^\circ / \Delta G_{\text{el}}^\circ \quad (5.2)$$

All of the ΔH° trends in the multiple ionizations of the individual acids studied appear to be consistent with Equation (5.2), although anomalies will be seen to exist if detailed comparisons are made between the ΔH° data of one acid with the ΔH° data of another acid.

By examining the aliphatic dicarboxylic acids it is observed that in nearly all cases ΔH_2° is less endothermic than ΔH_1° . This is surprising because ΔG_2° must be greater than ΔG_1° . It is noted that this ΔH_i° dependence is consistent with a constant $\Delta G_{\text{non}}^\circ$ and an increasing $\Delta G_{\text{el}}^\circ$ due to the already present charge. The same behavior was observed for

the only tribasic acid, citric acid.

Most of the aliphatic acids studied had the COOH groups close together and free to rotate and possibly even for the COO⁻ and the COOH to interact. To understand the importance of this proximity effect two acids with distant carboxyl groups were studied, 1,3-benzenedi and 1,3,5-benzenetricarboxylic acid. Two points in the comparison of citric and trimesic acid are worthy of comment: The first is that ΔS_1° is nearly the same in both cases and the second is that, although there are significant differences in ΔH_1° , ΔH_1° in both cases becomes more exothermic with ionization. The overall decrease in ΔH_1° is consistent with an ever increasing ΔG_{el}° in Equation (5.2) with ΔG_{non}° constant. The 1.1 kcal. difference in the ΔH_1° values together with constant ΔS_1° values would indicate an inductive effect (Laidler's arguments) possibly due to the presence of the OH group in citric acid. But there is no clear cut difference in the trends that could be identified with a proximity effect in the aliphatic di-or tri-carboxylic acids.

To better understand the importance of the OH group in citric acid 1,2,3-propanetricarboxylic acid, tricarbollylic acid, was studied. Again, a monotonic decrease in ΔH_1° was observed (Table IX). In each ionization both ΔH_1° and ΔS_1° are more negative than in citric acid yielding partial compensation in ΔG_1° and nearly complete compensation in ΔG_2° and ΔG_3° , relative to citric acid. Then, based upon Laidler's arguments on compensation, it appears that the OH group basically changes the solvation in citric relative to tricarbollylic. No attempt will be made in general to further rationalize such subtle differences in individual thermodynamic values.

On the other hand, the data for O-phthalic acid (Table IX) is anoma-

lous relative to the "normal" dibasic aliphatic acids. This is rather surprising because both 1,3 and 1,3,5 benzene acids were found to be "normal" when compared to the aliphatic acids.

Acid	ΔG_1°	ΔG_2°	ΔH_1°	ΔH_2°	ΔS_1°	ΔS_2°
O-Phthalic	4.02	7.38	-0.64	-0.50	16	26

The most striking feature of the data is that ΔH_2° is more endothermic than ΔH_1° . This means that $T_{\max,1} < T_{\max,2}$. Yet, ΔS_1° and ΔS_2° are comparable to those for dibasic acids. In an attempt to see if this was a general result for ortho-ionization pairs, most of the polybasic benzene acids were studied. Indeed, it was found that for every ortho pair there was one reversal in the ΔH_1° data relative to the aliphatic case (see Table IX).

Of the numerous ways that this ortho effect could be accounted for by use of Equation (5.2) it is believed to be due to an unusually small $\Delta G_{\text{non}}^{\circ}$. This is consistent with and supported by the following arguments:

1) The entropies, which are associated with the electrostriction about a charge and related to ΔG_{e1}° , are similar to those observed for aliphatic dicarboxylic acids in which proximity effects have been shown to be unimportant.

2) By Laidler's arguments based upon statistical mechanics, if ΔS_1° is unchanged and ΔH_1° changes significantly, the observed difference is quantum mechanical in origin, e.g., induction or resonance. This is just what is observed.

3) As argued in Chapter III, if electrostatics is the origin of the difference in the ionizations, a plot of ΔG° vs. ΔS° should be a

straight line of slope -219°K . When the $\Delta G_1^{\circ} - \Delta S_1^{\circ}$ data from Table IX is plotted only the first ionization of each ortho pair is off the line, and in every case below the line drawn through the remaining data (Figure 4). Consequently, the second ionization of each ortho pair can be considered to be electrostatic in origin.

4) If the $\Delta H_{\text{non}}^{\circ}$ values (Equation (3.27)) are considered for every ortho ionization pair, only the first $\Delta H_{\text{non}}^{\circ}$ of each pair is negative. For all other aliphatic and aromatic acids studied $\Delta H_{\text{non}}^{\circ}$ is positive.

5) From molecular models it is observed that the two COOH groups of *o*-phthalic acid are sterically crowded. This steric crowding can be relieved if one of the COOH groups rotates out of the plane of the benzene ring. This rotation, though, destroys the resonance stabilization of the acid thus making it a stronger acid. Since only one COOH group need be rotated; the other member of the pair can behave "normally", as is observed. This allows one to better understand the fact that 1,2,3-benzenetricarboxylic acid appears to have only one ortho-type ionization: if the middle COOH group rotates out of the plane of the ring, then the two remaining COOH groups can be accommodated in the plane of the ring and therefore resonance stabilized as the 1,3; 1,3,5; or the second ionization of *o*-phthalic acid.

Hammett Linear Free Energy Relationship for Tribasic Acids

The Hammett Equation (3.29) gives excellent results for polysubstituted benzoic acids (see Table V). A problem arises in the application of Equation (3.29), or its equivalent free energy form to tribasic acids like 1,2,4-benzenetricarboxylic acid (48). The first ionization may occur via proton release from position 1, 2, or 4. Release from each

position has a characteristic free energy ΔG_1^1 determined by the σ constants for the remaining 2 groups. In reality all three positions ionize to some extent and the observed free energy, $\langle G_1^0 \rangle$, is a Boltzmann weighted average of the three. Defining Q as

$$Q = e^{-\Delta G_1^1/RT} + e^{-\Delta G_1^2/RT} + e^{-\Delta G_1^4/RT} \quad (5.3)$$

the average free energy, $\langle G_1^0 \rangle$, becomes

$$\langle G_1^0 \rangle = 1/Q \{ \Delta G_1^1 e^{-\Delta G_1^1/RT} + \Delta G_1^2 e^{-\Delta G_1^2/RT} + \Delta G_1^4 e^{-\Delta G_1^4/RT} \} \quad (5.4)$$

$$= \sum_{i=\text{all sites}} P_1^i \Delta G_1^i \quad (5.5)$$

where P_1^1 represents the probability of the first ionization being from position 1, and P_1^2 , P_1^4 have similar meanings. It should be noted that the sum of P_1^i 's is one.

The second ionization constant can occur in six different ways with six different microscopic free energies, G_2^i 's. The probability of each second ionization must be multiplied by the probability of the corresponding first ionization.

$$\langle \Delta G_2^0 \rangle = \sum_{i=\text{all sites}} \sum_{\substack{j=\text{all sites} \\ j \neq i}} P_1^i P_2^{ij} G_2^{ij} \quad (5.6)$$

$$\sum_i \sum_j P_1^i P_2^{ij} = 1 \quad (5.7)$$

For each second ionization, there is only one way for the third proton to ionize (i.e., each P_3^{ijk} is one). For the sake of generality $\langle G_3^0 \rangle$ can be written as

$$\langle G_3^0 \rangle = \sum_j \sum_{\substack{\text{all} \\ k \neq i}} \sum_{\substack{i \neq j \\ k \neq j}} \sum_{\substack{k \neq j \\ k \neq i}} P_1^i P_2^{ij} P_3^{ijk} G_3^{ijk} \quad (5.8)$$

To evaluate Equations (5.4-8) for the overall calculated free energy the first and second ionizations of 1,2; 1,3; 1,4-benzenedicarboxylic acids (49) were used to obtain the variation in the free energy relative to benzoic acid, induced by substituting a COOH or a COO⁻ group in the o, m, or p position.

TABLE XIII(A)

SIGMA PARAMETERS FOR BENZENEDICARBOXYLIC ACIDS

$$(\Delta G_0^0 = 5.73 \text{ kcal.})$$

	o	m	p
$(\Delta G_0^0 - \Delta G_1^0)^*$	1.28	0.26	0.47
$(\Delta G_0^0 - \Delta G_2^0)^*$	-1.29	-0.17	0.02

* These ΔG^0 values are statistically corrected relative to monobasic acid by Equation (3.18).

TABLE XIII(B)

IONIZATION DATA FOR 1,2,4-BENZENETRICARBOXYLIC ACID

Ionization Sequence (i)	$\Delta G_i^{(i)}$	$P_1^{(i)}$	Ionization Sequence (ij)	$\Delta G_2^{(ij)}$	$P_2^{(ij)}$	Ionization Sequence (ijk)	$\Delta G_3^{(ijk)}$	$P_3^{(ijk)}$
1	3.98	0.48	12	6.65	0.048	124	5.88	0.104
			14	5.34	0.432			
2	4.08	0.41	24	5.43	0.355	241	7.02	0.400
			21	6.55	0.056			
4	4.89	0.11	41	4.43	0.062	412	7.19	0.494
			42	4.62	0.045			

TABLE XIII(C)
TABULATED DATA

	ΔG_1° (Eq. 5.4)	ΔG_2° (Eq. 5.6)	ΔG_3° (Eq. 5.8)
Calculated	4.12	5.42	6.97
Experimental	4.04	5.51	6.90

If the symmetrical 1,3,5-benzenetricarboxylic acid is examined, only one ionization sequence is possible. The calculated and the observed free energy data are:

Ionization	ΔG_{cal}°	Sigma Values	ΔG_{obs}°
1	4.97	$2\sigma_{COOH}^m$	4.92
2	5.52	$\sigma_{COOH}^m + \sigma_{COO^-}^m$	5.60
3	6.40	$2\sigma_{COO^-}^m$	6.02

The third ionization is the only one outside of the expected experimental error; no explanation is offered for the difference because the data is very difficult to obtain and the error is not certain.

If the σ constants of Table XIII(A) are used for 1,2,3-ben. agreement with experiment is poor. This is explained by the fact that none of the dibasic acids have a group on both sides of the ionizing COOH group; similar results are observed for 2,6-dimethylbenzoic acid in Table V.

Although the dibasic acid ΔH_1° and ΔS_1° are not available, it is suggested that the additivity of these variables be weighted in a manner

consistent with that done for the ΔG_1^0 data.

Analysis of a Mixture of Acids

If Equations (3.1) through (3.6) are modified to simultaneously refer to a solution with more than one polybasic acid (50), an equation can be derived which reduces to Equation (3.7) in the limit of only one acid in solution

$$L = \sum_{p=1}^{N_a} \alpha_p T_{ap} \quad (5.9)$$

with

$$\alpha_p = \frac{\sum_{i=0}^{N_p} i a_{H^+}^{-i} \gamma_i^{-1} \prod_{j=0}^{N_p} K_{p,j}}{\sum_{i=0}^{N_p} a_{H^+}^{-i} \gamma_i^{-1} \prod_{j=0}^{N_p} K_{p,j}} \quad (5.10)$$

and where N_a is the number of acids in solution of concentration T_{ap} and N_p is the number of ionization constants of the p -th acid, $K_{p,j}$ refers to the j -th ionization of the p -th acid, and $L = (H) + (T_b) - (OH)$.

Equation (5.9) was used to analyze a mixture of the dl and meso isomers of DMSA. Only a mixture of the isomers, of unknown composition, could be purchased commercially. The mixture was separated by recrystallization from concentrated HCl. The ionization constants of the separated isomers were determined by use of Equation (3.7).

		This Work	Ref. (51)	Ref. (52)
meso	pK_1	3.726 ± 0.005	3.77	3.77
	pK_2	5.370 ± 0.001	5.28	5.92
dl	pK_1	3.867 ± 0.005	3.92	3.95
	pK_2	5.947 ± 0.005	5.96	6.19

Based upon these ionization constants and a titration of the mixture from Aldrich the composition of the commercially available sample was determined to be $78 \pm 1\%$ meso acid. This contradicts some reports on the isomer ratio (53), which is related to stability, but knowledge of the synthesis mechanism was not available, therefore, no definitive conclusion could be made.

The theoretical limit of the accuracy of this method is determined by the maximum ratio of the isomers' corresponding ionization constants. For DMSA $K_{1,\text{meso}}/K_{1,\text{dl}} = 1.64$ and $K_{2,\text{meso}}/K_{2,\text{dl}} = 3.84$. At the midpoint of the second buffer region the calculated $|\text{emf}_{\text{meso}} - \text{emf}_{\text{dl}}|$ is 30 mV.; with an emf readability of 0.1 mV. the limit of this analysis is 1 part in 300. In practice this accuracy was never achieved because the ionization constants themselves were in error by $\pm 1\%$.

In principle it should be possible to determine both all ionization constants, $K_{i,p}$, and all analytical acid concentrations, T_{ap} , from a single titration of the mixture. This problem was not pursued experimentally of theoretically.

The major advantage of this method of analysis is that it can easily and accurately be done in situ. This avoids the problems in separating the isomers analytically by recrystallization, etc. Also, because the analysis is done in situ, there is less chance for the acid to rearrange upon separation and analysis.

The Value of n at Which the Monomers Approach the Polymer Properties

As to the final question of when the thermodynamic data for monomeric polybasic acids and polymeric acids converge, this situation does

not appear to have been reached through 1,2,3,4-butanetetracarboxylic acid. Values of ΔH° and ΔS° for polymeric acids are (54) typically -0.2 kcal./mole and -21 cal./mole $^\circ\text{K}$, respectively. It should be emphasized that these values are weighted averages; and presumably for the first few ionizations, the ΔH_1° and ΔS_1° values are distinctly different by analogy with the monomeric acids. Convergence may have been reached as early as six carboxylic groups, however, if one compares ΔH_5° and ΔH_6° for the totally substituted benzene acid.

BIBLIOGRAPHY

1. Dippy, F. J. F., Chem. Rev., 25, 151 (1939).
2. Ostwald, W., J. Prakt. Chem., 30, 93, 225 (1884).
3. Arrhenius, S., Bihang der Stockholm Akad., 8 Nos 13 and 14 (1883).
4. Ostwald, S., op. cit., 3, 418 (1889).
5. Debye, P. and E. Huckel, Phys. Z., 24, 185, 305 (1923).
6. Harned, H. S. and R. W. Ehlers, J. Amer. Chem. Soc., 54, 1350 (1932).
7. MacInnes, D. A. and T. Schedlovsky, J. Amer. Chem. Soc., 54, 1429 (1932).
8. Christensen, T. J., R. M. Izatt, and L. D. Hansen, The Rev. of Sc. Inst., 36, 779 (1965).
9. Monk, C. B., "Electrolytic Dissociation", Academic Press, Inc., London, 1961, p. 166.
10. Bates, R. G., J. Amer. Chem. Soc., 70, 1579 (1948).
11. Bolton, P. D. and L. G. Hepler, Quart. Rev. (London), 25, 521 (1971).
12. Bates, R. G. and G. D. Pinching, J. Amer. Chem. Soc., 71, 1274 (1949).
13. Morawetz, H., "High Polymers", Vol. 21, Interscience Publishers, New York, N. Y., 1965, p. 369 ff.
14. Bates, R. G., "Electrometric pH Determinations; Theory and Practice", John Wiley and Sons, Inc., New York, N. Y., 1954, p. 184 ff.
15. Bates, R. G., Ibid., p. 165.
16. Brown, A. S., J. Amer. Chem. Soc., 56, 646 (1934).
17. Bates, R. G., "Electrometric pH Determinations; Theory and Practice", John Wiley and Sons, Inc., New York, N. Y., 1954, p. 166.

18. Vogel, A. I., "Quantitative Inorganic Analysis", Longmans Inc., London, 3rd. edition, 1961, p. 239 ff.
19. Bates, R. G. and G. D. Pinching, J. Res. Nat. Bur. Stand., A., 37, 311 (1946).
20. e. g. Ricci, J. E., "Hydrogen Ion Concentration", Princeton University Press, Princeton, N. J., 1952.
21. Davies, C. W., "Ion Association", Butterworths, London, 1962, p. 122.
22. King, E. J., "Acid-Base Equilibria", Pergamon Press, New York, N. Y., 1965.
23. Everett, D. H. and W. F. K. Wynne-Jones, Trans. Faraday Soc., 35, 1380 (1939).
24. King, E. J., "Acid-Base Equilibria", Pergamon Press, New York, N. Y., p. 194.
25. Dippy, J. F. J., Chem. Rev., 1939, 151.
26. Beetlestone, J. G. and D. H. Irvine, Proc. Roy. Soc., 277A, 401, 414 (1963).
27. Robinson, R. A. and R. H. Stokes, "Electrolyte Solutions", 2nd ed. (revised), Butterworths Inc., London, 1970, p. 348.
28. Tanford, C., "Physical Chemistry of Macromolecules", John Wiley and Sons, Inc., New York, N. Y., 1961, p. 532.
29. Bjerrum, N., Z. Physik. Chem., 106, 219 (1923).
30. Kirkwood, J. G. and F. H. Westheimer, J. Chem. Phys., 6, 506, 513 (1938).
31. Westheimer, F. H. and M. W. Shookhoff, J. Amer. Chem. Soc., 61, 555 (1939).
32. Gurney, R. W., "Ionic Processes in Solution", McGraw-Hill, New York, N. Y., 1953.
33. Hepler, L. G. and J. W. Larson in "Solute-Solvent Interactions", ed., J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York, N. Y., 1969.
34. King, E. J., "Acid-Base Equilibria", Pergamon Press, New York, N. Y., 1965, p. 211.
35. Degischer, G. and G. H. Nancollas, J. Chem. Soc. (A), 1970, 1125.
36. Hammett, L. P., "Physical Organic Chemistry", 2nd ed., McGraw-Hill Publishing Co., New York, N. Y., 1970.

37. Taft, R. W. in "Steric Effects in Organic Chemistry", ed. M. S. Newman, Wiley Publishing Co., New York, N. Y., 1956.
38. Wilson, J. M., et al., J. Chem. Soc. (B), 1967, 852.
39. Charton, M., Progress in Phys. Org. Chem., 8, 235 (1971).
40. Laidler, K. J., et al., Trans. Faraday Soc., 55, 1725-1743 (1959).
41. van Eijck, B. P., Recueil, 85, 1129 (1966).
42. Hepler, L. G. and J. W. Larson in "Solute-Solvent Interactions", ed. J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York, N. Y., 1969, p. 8.
43. Pitzer, K. S., J. Amer. Chem. Soc., 59, 2365 (1937).
44. Hepler, L. G. and J. W. Larson in "Solute-Solvent Interactions", ed., J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York, N. Y., 1969, pp.8-12.
45. Maxwell, W. R. and J. R. Partington, Trans. Faraday Soc., 33, 670 (1937).
46. Litchinsky, D., N. Purdie, M. B. Tomson, and W. D. White, Anal. Chem., 41, 1726 (1969).
47. Harned, H. S. and N. D. Embree, J. Amer. Chem. Soc., 56, 1050 (1934).
48. Purdie, N. and M. B. Tomson, J. Sol. Chem., submitted.
49. Robinson, R. A. and R. H. Stokes, "Electrolyte Solutions", 2nd ed. (revised), Butterworths Inc., London, 1970, p. 529.
50. Cook, G., N. Purdie, and M. B. Tomson, Anal. Chem., in press.
51. Dippy, J. F. J., S. R. C. Hughes, and A. Rozanski, J. Chem. Soc., 1952, 2492.
52. Gane, R. and C. K. Ingold, Ibid., 1931, 2158.
53. Sniegowski, P. J., J. Org. Chem., 36, 2200 (1971).
54. Felber, B. J. and N. Purdie, J. Phys. Chem., 75, 1136 (1971).
55. Kuo, S. S., "Numerical Methods and Computers", Addison-Wesley Publishing Co., Reading, Massachusetts, 1965.

APPENDIX

OUTLINE OF PROGRAM TO CALCULATE K_i

The object of the program is to solve n equations like (3.7) for n K_i 's.

$$-L = \sum_{i=1}^n (L - iT_a) a_{H^+}^{-1} \gamma_i^{-1} \frac{1}{i} K_j \quad (3.7)$$

From each data point, k , an equation like (3.7) can be written

$$L_k = \sum_{i=1}^n a_{k,i} B_i \quad (3.7a)$$

where $B_i = \frac{1}{i} K_j$ and $a_{k,i} = (L_k - iT_{a,k}) a_{H^+}^{-1} \gamma_{k,i}^{-1}$ or for n data points:

$$\begin{aligned} L_1 &= a_{1,1} B_1 + a_{1,2} B_2 + \dots + a_{1,n} B_n \\ &\vdots \\ L_n &= a_{n,1} B_1 + a_{n,2} B_2 + \dots + a_{n,n} B_n \end{aligned} \quad (3.7b)$$

This system of n equations and n unknowns can be solved in many ways; no attempt was made to find and use the "best" method of solution; rather, a "convenient" method was used. Once the overall plan of solution is clear, the details of the programming follow immediately from the most basic Fortran and experimental data. Therefore, only an outline and explanation of the steps will be presented herein:

1. To calculate the $a_{k,i}$ coefficients in Equation (3.7b) the following must be available for each of the n data points: T_a , T_b , γ_i , a_{H^+} , (H_i^+) , and (OH_i^-) . To start the calculation a reasonable set of n γ_i 's

must be guessed; $\gamma_1 = 0.9$ is a reasonable guess. All quantities which are dependent upon the T only are least squares curve fitted to a polynomial in T and calculated from the single parameter, T.

2. Once the coefficients are calculated, the system of n equations and n unknowns is solved for the B_i 's. The method used in this study to solve the n equations was the elementary and systematic elimination and substitution procedure found in most texts on numerical analysis (55). Cramer's rule, used by Maxwell and Partington (45), found in most basic algebra texts, would also have worked well. Both of the above methods, and others as well, are available continuously in core on most computers and can be used by simply sending the coefficients to the program in core; the resulting solutions, B_i 's, are returned automatically.

3. From the n B_i 's the concentration of each ionic species for each data point can be calculated:

$$(H_{N-1}A^{-i}) = (H_N A) B_i \frac{a_{H^+}^{-i} \gamma_1^{-1}}{H^+}$$

and put into Equation (3.5) for the ionic strength, which is used in Equation (3.6) to calculate the activity coefficients, for each point.

4. These new γ_i 's calculated in step 3 are compared with those used in step 1, $\gamma_{i,old}$. If any difference, $|\gamma_i - \gamma_{i,old}| > 0.0001$, the new γ_i 's are used in step 1 and a new set of $a_{k,i}$ calculated, etc. This repetition of steps 1, 2, and 3 until convergence is obtained for all of the γ_i 's is called the Gauss-Seidel iterative method of solving equations; generally convergence for these equations is obtained in 3-4 cycles.

5. Then the K_i 's are calculated, a new set of data points chosen, and steps 2, 3, and 4 repeated. For a titration as in Table VI, general-

ly, about 50 sets of ionization constants are calculated: the 50 sets of n data points are chosen by a random number generator, the i -th data point being chosen from the i -th buffer region; the first half of the first and the last half of the last buffer regions are neglected because the pH changes too rapidly with base volume in these regions.

6. Various statistical tests were then performed on the K_i 's. Basically the mean, median, and standard deviation were used.

VITA

Mason Butler Tomson

Candidate for the Degree of

Doctor of Philosophy

Thesis: THERMODYNAMICS OF THE IONIZATION OF POLYBASIC ORGANIC ACIDS IN WATER

Major Field: Chemistry

Biographical:

Personal Data: Born in Syracuse, Kansas, November 18, 1946; the son of Clifford J. and Mary W. Tomson.

Education: Graduated from Syracuse High School in 1964, Southwestern State College in 1967, and completed the Doctor of Philosophy degree May, 1972.

Military: ROTC graduate in 1969; commissioned 2Lt. Chemical Corp.; presently in the Army Reserves.