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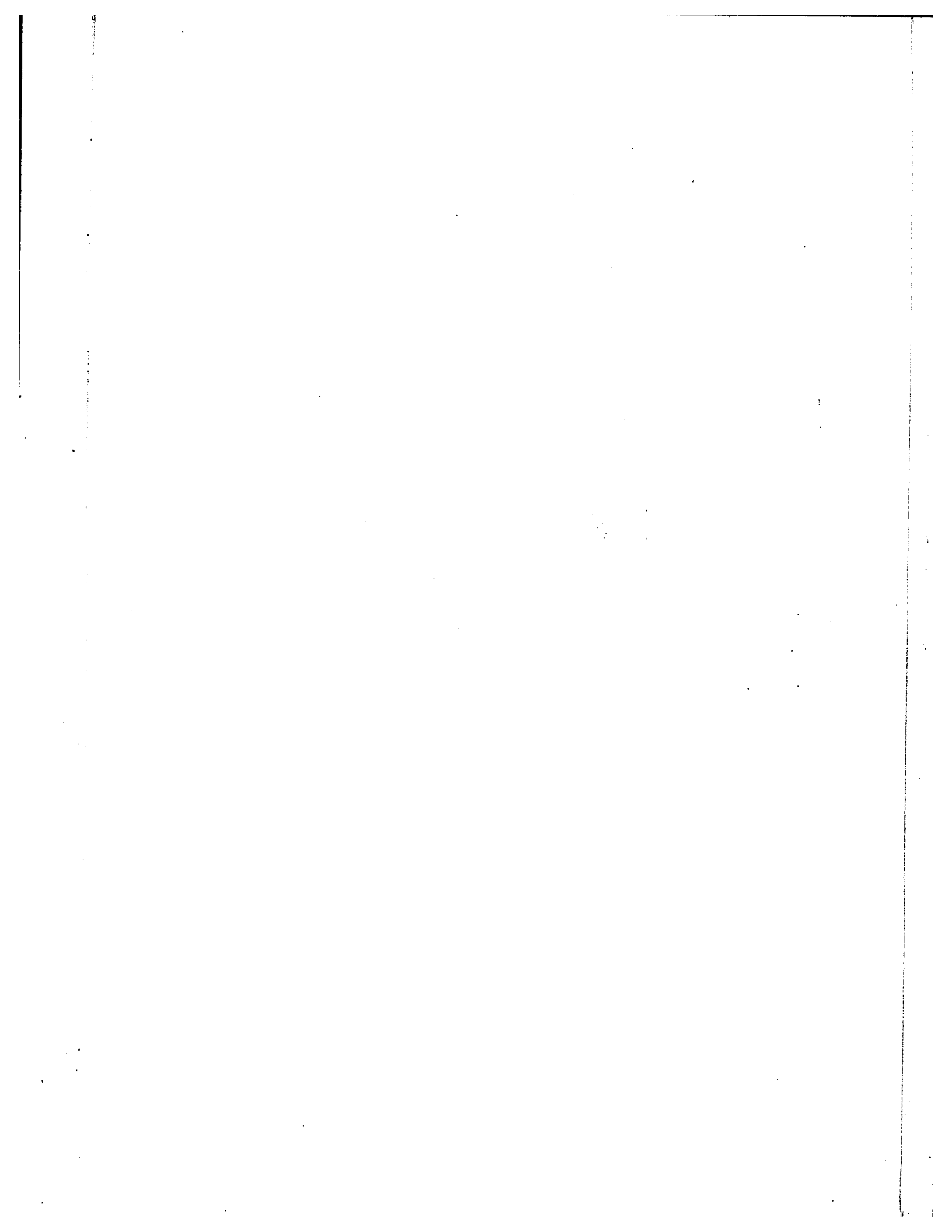
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THERMODYNAMICS
OF THE IONIZATION OF SUBSTITUTED
PHENOLS

by

DAVID T. Y. CHEN, M.Sc.

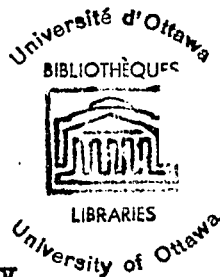
A Thesis Submitted in Partial Fulfillment
of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

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PREFACE

The object of the work described in this thesis was to study the thermodynamics of ionization processes in aqueous solutions. Since there is no satisfactory theoretical treatment on this subject, the accumulation of additional data on ionization constants and related thermodynamic properties will furnish a broad basis for the comprehensive examination of the thermodynamics of the ionization process. The compounds under investigation are phenol itself and all the mono- and di- methyl-substituted phenols. A study has also been made of how the substitution of a hydrogen atom by a methyl group at different positions on the benzene nucleus affects the heat, free energy and entropy of ionization, and an attempt has been made to separate these effects into inductive, resonance and steric contributions.

The candidate owes a great deal to his research director, Professor K. J. Laidler, and wishes to express his deepest gratitude for his kind direction and generous help in every respect. He is also indebted to Professor F. A. L. Anet for his valuable instructions and suggestions regarding the apparatus. Thanks are also due to Mr. P. Sefton and Miss O. Boshko of the computing centre for computing the parameters of the Harned and Robinson equation.

The work was supported by a grant from the National Research Council of Canada to whom grateful acknowledgment is made.

The candidate is also grateful to Dr. R. G. Bates and Mrs. H. B. Hetzer for their information regarding pK_a values of tris-(hydroxymethyl)-aminomethane at different temperatures.

TABLE OF CONTENTS

	Page
TITLE PAGE	1
PREFACE	ii
TABLE OF CONTENTS	iv
LIST OF TABLES	vi
LIST OF FIGURES	vii
ABSTRACT	viii
CHAPTER 1. GENERAL INTRODUCTION	1
1. HISTORICAL REVIEW	1
2. METHODS FOR THE DETERMINATION OF IONIZATION CONSTANTS	14
A. Conductance Method	15
B. Electromotive Force Method	16
C. Spectrophotometric Method	19
3. METHODS FOR THE DETERMINATION OF HEATS OF IONIZATION	28
A. Calorimetric Method	28
B. Ionization Constant Method	30
C. Semi-empirical Treatment of the Ionization Process	32
(1) Harned and Ehler's Equation	32
(2) Harned and Embree's Equation	33
(3) Pitzer's Equation	35
(4) Everett and Wynne-Jones's Equation	36
(5) Harned and Robinson's Equation	40
(6) Jenkins's Equation	41
(7) Discussion of the Equations	42
CHAPTER 2. GENERAL THEORY OF THE THERMODYNAMICS OF IONIZATION	46
1. INTRODUCTION	46
2. SOLUTE-SOLVENT INTERACTIONS	51
A. Interaction Between Neutral Molecules and Water	51
B. Interaction Between Ions and Water Molecules	53
C. The Situation of Ions in Water	56

	Page
3. INTERPRETATION OF PREVIOUS RESULTS BY THE SOLUTE-SOLVENT INTERACTION THEORY	59
4. FREE ENERGY OF IONIZATION	62
5. SUBSTITUENT EFFECTS ON THERMODYNAMIC FUNCTIONS AND ADDITIVITY	69
6. HEATS OF IONIZATION	73
7. ENTROPY OF IONIZATION	73
8. HEAT CAPACITY OF IONIZATION	84
9. THE TEMPERATURE OF MAXIMUM IONIZATION	90
CHAPTER 3. EXPERIMENTAL METHODS AND RESULTS	94
1. MATERIALS	94
2. APPARATUS	96
3. PROCEDURE	98
4. CALCULATION AND RESULTS	101
A. The pK Values	101
B. Analysis of Temperature Dependence	125
5. PRECAUTIONS	130
6. ESTIMATION OF ERRORS	132
CHAPTER 4. DISCUSSION	136
1. COMPARISON WITH PREVIOUS WORK	136
2. COMPARISON OF HARNED AND ROBINSON AND EVERETT AND WYNNE-JONES EQUATIONS	142
3. INTERPRETATION OF THE RESULTS	145
APPENDIXES	
I. Absolute Entropies of H_2O and H_3O^+	160
II. Statistical Methods	166
CLAIMS TO ORIGINAL RESEARCH	169
LIST OF REFERENCES	171

LIST OF TABLES

1. Melting points of phenols.	92
2. The pH' values of standard buffer solutions at various temperatures.	103
3. Correction values for pH.	104
4. Activity coefficients at different temperatures. ...	106
5. Absorptions and ionization constants of various phenols at different temperatures.	115
6. Constants for the Harned and Robinson equation.	125
7. Thermodynamic functions for the ionization of phenols at 25° C.	126
8. pK values at 25° C for various phenols by different authors.	134
9. Heats of ionization of phenols at 25° C by different authors.	136
10. Comparison of the Harned-Robinson and Everett- Wyme-Jones equations for phenol.	140
11. Additivity of the pK and ΔF values.	143
12. Test for additivity of ΔH	149
13. Test for additivity of ΔS	150
14. Test for correlation between $T\Delta S$ and ΔF for the compounds in which no substituent is in an ortho position.	154

LIST OF FIGURES

1. Absorption curves for a compound in acid, alkaline and buffer solutions. 22
2. Apparatus for the determination of ionization constants at different temperatures. 94
3. Spectra of phenol in 0.1 M NaOH solution at different temperatures. 109
4. Spectra of phenol in 0.01 M HCl solution at different temperatures. 110
5. Spectra of phenol in 0.025 M Na_2CO_3 + 0.025 M NaHCO_3 buffer solution at different temperatures. 112
6. Spectra of phenol in 0.05 M borax buffer solution at different temperatures. 113
7. Spectra of o-chlorophenol in 0.02 M "THAM" buffer solution at different temperatures. 114
8. Variation of log K with temperature for various phenols. . 123
9. Comparison of the Harned-Robinson, and Everett-Wynne-Jones equations for phenol. 141
10. Correlation between entropy and free energy of ionization. 152
11. Correlation between entropy and heat of ionization. 153

ABSTRACT

Ionization constants of phenol, the three cresols, the six xylenols and o-chlorophenol were determined at seven temperatures from 5° to 38° C using the spectrophotometric method of Robinson and Biggs. The values at 25° C agree with those of Herrington and Kynaston. The variation of the ionization constant with temperature for each compound was expressed by the semi-empirical equation of Harned and Robinson. The parameters of this equation were determined from the experimental values of K by the method of least squares. Heat, free energy, entropy and heat capacity of ionization were calculated from these constants.

It was found that the substitution of a hydrogen atom by a methyl group decreases the acidity of phenol due to an inductive and resonance effect. Steric effects were found to be unimportant. The heat of ionization does not vary much with substitution. The free energy and the absolute value of the entropy and heat capacity of ionization were increased by substitution. The pK values and the free energy of ionization are additive while the rest of the thermodynamic functions are not. The pK value of phenol is increased by 0.31, 0.08 and 0.16 units when the methyl group was substituted at the o-, m- and p- positions respectively. The corresponding changes in free energy are approximately 0.4, 0.1 and 0.3 cal. mole⁻¹. Ionization processes are discussed in terms of solute-solvent interactions.

CHAPTER 1

GENERAL INTRODUCTION

1. HISTORICAL REVIEW

Ionization processes have been studied for more than a century, but there is still no satisfactory theoretical treatment on this subject. The ionization of organic acids has been a particular object of extensive study because these acids form the greater portion of the class of weak electrolytes which obey the Ostwald dilution law.

The idea of the ionization constant was put forth by Ostwald and Arrhenius. Comparisons of the relative strengths of the different acids have been made for many years. Early in 1854 Julius Thomsen attempted to compare the "avidities" of two acids competing for a limited quantity of base in aqueous solution by a thermochemical method. Later, Ostwald (1) used various methods to compare the strength of acids. He studied, for example, the catalytic action of acids on the rate of hydrolysis of methyl acetate and acetamide and the inversion of cane sugar. His most successful method was to compare the electrical conductivities of the acids in aqueous solution using Kohlrausch's alternating current technique. He found that the relative orders of strength of the acids observed by these methods are essentially the same. He concluded that the relative order of avidity of

acids could be expressed by the relative order of their molecular conductivities.

At about the same time Arrhenius (2) formulated his theory of the ionic dissociation of electrolytes. This theory was verified by the experiments of Ostwald (3) who, within a short period of time, examined about two hundred and fifty organic acids. He developed the well-known dilution law,

$$K = \frac{\alpha^2 c}{1 - \alpha} = \frac{(\Lambda_c)^2 c}{\Lambda_0(\Lambda_0 - \Lambda_c)}, \quad (1)$$

where Λ_c and Λ_0 are the equivalent conductances at concentration c and at infinite dilution respectively, and α is the degree of dissociation. K is the ionization constant, which serves as a measure of acid strength.

By determining the ionization constant at different temperatures, the heat of ionization can be obtained. This involves the measurement of conductivity at various temperatures. It was early known that the conductances of electrolytic solutions increase with increasing temperature, whereas those of metals decrease. Ohm (4) was the first to measure the conductivity of the same electrolyte in aqueous solutions at different temperatures. Hankel (5) made a more detailed study of the variation of electrolytic conductance with temperature. The first important investigation was made by Grotrian (6), who studied the conductivity of aqueous sulfuric

acid solution at temperatures between 0° and 70° C and found a parabolic relationship. His work was extended by Kohlrausch and Grotrian (7) to other acids. They concluded that the conductivity of dilute solutions of electrolytes is a parabolic function of temperature and can be expressed by the equation

$$K_t = K_0 (1 + \alpha t + \beta t^2), \quad (2)$$

where K_t and K_0 is the conductivity at t° and 0° C respectively, and α and β are constants depending on the nature of the substance.

The effect of temperature on the ionization was first investigated by Arrhenius (8). He found that the degrees of ionization of phosphoric and hypophosphorous acids decrease with increasing temperature. This seems contradictory to the common belief at that time, to account for the increasing conductivity with temperature, that the degree of ionization should increase with temperature. He also calculated (9) heats of ionization of some organic acids and inorganic salts using van't Hoff's equation. Some later workers (10, 11) reported that temperature has no effect on the degree of ionization. They suggested that the increase in conductance with temperature is due to the decrease in ionic friction. Jahn and Schroder (11) noticed that the conductivities of some simple fatty acids between

10° and 40° C passed through a maximum. Heats of ionization for some of the acids were also calculated. In 1896 Euler (12) studied the ionization of benzoic and some substituted benzoic acids between 0° to 50° C. He noted that the variation of molecular conductivity with temperature could be expressed by the equation

$$\lambda = a + b t + c t^2. \quad (3)$$

He also calculated heats of ionization at different temperatures. Schaller (13) investigated the ionization of water and substituted benzoic acids at temperatures between 25° and 99° C. Heats of ionization were calculated from the slopes of the straight lines obtained by plotting log K against 1/T. He found that maximum dissociation occurs between 25° and 40° C. Jones and his students (14-24) investigated the ionization of a large number of organic acids, including amino acids and dibasic acids at various temperatures below 65° C. They did not, however, calculate heats of ionization. They confirmed the observation of Euler that the conductance of most organic acids is a parabolic function of temperature, but they could not find any regular relationship between degree of ionization and temperature. Noyes (25-27) also found that degree of ionization in most cases decreased with rise in temperature, but that it increased in a few other cases. Walden (28) studied the effect of solvent on heat of ionization. He found that the heats of

ionization of potassium iodide and tetraethyl ammonium iodide in a number of organic solvents are nearly the same. He therefore concluded that the heat of ionization of any binary electrolytes was independent of the solvent provided that molecules do not associate in any particular solvent and that the ions formed are the same. This statement was soon refuted by Dutoit and Dupertuis (29) who investigated the ionization constants of sodium iodide in several organic solvents and also three other inorganic salts in pyridine at temperatures from 10° to 80° C. They found that the heats of ionization of sodium iodide in different solvents are not the same. On the other hand the heats of ionization of four salts in pyridine do not differ much from one another. They therefore concluded that the heat of ionization is the difference between the heat of solvation before and after the ionization process.

Lunden (30-33) was the first to consider the ionization process from the thermodynamic point of view. He measured the heats of ionization of some weak acids and bases in aqueous solution, including phenol and p-nitrophenol at temperatures from 10° to 50° C. A general review was also given by him on this subject (31). He concluded that heat of ionization increases with temperature while free energy of ionization decreases with increasing temperature. Oliveri-Mandala (34) concluded that there is no relationship between heat of ionization and the chemical constitution of a compound. Neal (35) investigated the influence of solvent on the degree and

heat of ionization. He determined the ionization constant of picric acid in mixtures of water and acetone at 25° and 35° C, by the conductometric method. He found that the ionization constant drops considerably as the percentage of acetone increases. In anhydrous acetone picric acid behaves as a weak acid and Ostwald's dilution law is obeyed. The heat of ionization was found to vary largely with the nature of the solvent; it passes through a minimum of about 70% acetone.

The work in this field was greatly revived during 1930 to 1940 after the development, by Harned and Robinson (36) and Harned and Owen (37), of the e.m.f. method for determining ionization constants. The early conductometric data are not accurate enough for precise interpretation. Most of the accurate data on the variation of ionization constants with temperature have been derived from the e.m.f. method. The foundation was laid by Harned and his co-workers. They determined the ionization constants of weak acids, bases and ampholytes at 5° C intervals between 0° and 60° C by the precise e.m.f. method, and expressed their data as a function of temperature by empirical or semi-empirical equations from which they derived the thermodynamic functions.

Harned and Ehler (38, 39) measured the ionization constant of acetic acid and expressed their results for the variation of ionization constant with temperature by the

equation

$$\log K = \frac{a}{2.303 RT} + \frac{b}{R} \log T + \frac{c}{2.303 R} T + d \quad (4)$$

Owen (40) investigated both the acid and base ionization constants of glycine from 10° to 45° C. He used the following equations to express his results:

$$\log K = a + bt + ct^2 \quad (5)$$

and

$$\Delta H = A + Bt + Ct^2. \quad (6)$$

Harned and Embree (41) noticed that the ionization constants of most electrolytes exhibit a maximum within the temperature range investigated, and that they can be fitted to a parabolic function. They worked out an empirical formula,

$$\log K - \log K_m = -5 \times 10^{-5} (t - \theta)^2, \quad (7)$$

where K is the ionization constant at any temperature t , K_m is the maximum value of the ionization constant, and θ is the temperature at which ionization is a maximum. The heat of ionization is represented by

$$\Delta H = 2.303 \times 10^{-4} RT^2 (t - \theta). \quad (8)$$

This formula has been used by many authors (42-47) to express their experimental results. Harned et al. (48-50) also claimed that this equation can be applied to non-aqueous solutions.

Pitzer (51) investigated the heat of ionization of water, ammonium hydroxide, and phosphoric and sulfuric acids by a calorimetric method. He also calculated the thermodynamic constants for the ionization of weak acids in aqueous solutions, and found that, while the heats and free energies of ionization varied over a wide range, the entropies and heat capacities of ionization are nearly the same for different acids. For the first stage of ionization they have roughly the values -22 and -40 cal. deg.⁻¹ respectively. Using $\Delta C_p = -40$ cal. deg.⁻¹ for the ionization of all organic acids the following equation was obtained for the variation of ionization constant with temperature:

$$\log K = A + \frac{B}{T} - 20 \log T. \quad (9)$$

Pitzer claimed that this equation represents the experimental data better than that of Harned and Embree.

Gurney (52) was the first to consider the ionization process on a purely theoretical basis. He suggested that the free energy of ionization can be split into electrostatic and non-electrostatic parts. Only the former part changes with temperature. His idea was developed in a more suitable manner by Baughan (53), who arrived at the following equation for the variation of heat of ionization as a function of temperature:

$$\Delta H_T = \Delta H_X + C \frac{1}{D_T} \left(1 + T \frac{\partial \ln D}{\partial T} \right), \quad (10)$$

where ΔH_T is the heat of ionization at temperature K . ΔH_X is the heat of ionization in a medium of infinite dielectric constant where no electrical work would be involved on ionization. This quantity could also be regarded as the heat effect if there were no charge separation in the ionization process. Consequently it is temperature invariant. C is the electrical work involved in creating the electric field; according to Born, this work is equal to $\frac{\epsilon^2}{2} \left(\frac{1}{r_+} + \frac{1}{r_-} \right)$ where ϵ is the elementary electronic charge. r_+ and r_- are the radii of the cation and anion respectively, and D is the dielectric constant.

Everett and Wynne-Jones (54) gave a satisfactory semi-empirical treatment of the thermodynamics of acid-base equilibria. By assuming ΔC_p of all ionization processes to be independent of temperature but to vary with the substance, they arrived at the equation

$$\ln K = - \frac{\Delta H_o}{RT} + \frac{\Delta C_p \ln T}{T} + \frac{\Delta S_o - \Delta C_p}{R} . \quad (11)$$

Brescia, LaMer and Nachod (55) determined the heat of ionization of deuterated acetic acid by the modified conductance method of MacInnes and Shedlovsky (56) at various temperatures from 14.36° to 44.86° C. They found that the ionization constant of this acid also follows the Harned and Embree equation, but that the optimum temperature is 9° C

higher than that for ordinary acetic acid. The heat of ionization of deuterio-acetic acid decreased more slowly with rise in temperature than the corresponding functions for the non-deuterated acid. Their results verified Baughan's equation. They also showed that the universal constant p in Harned and Embree's equation has a physical significance, being given by

$$p = \left(\frac{s^2}{2.303 RTD^3} \right) \left(\frac{\partial D}{\partial T} \right)^2 \left(\frac{1}{2\theta} \right). \quad (12)$$

Harned and Robinson (57), on the basis of the observed quadratic relationship between the e.m.f. of a cell and the temperature, proposed the following equation for the ionization process:

$$\ln K = - \frac{A}{RT} - CT + D. \quad (13)$$

They tested five previously derived empirical formulae, using the data for formic acid. They claimed that equation (4) (Harned and Ehler), equation (11) (Everett and Wynne-Jones), and equation (13) (Harned and Robinson) are of the same accuracy. They all represent the experimental data within the experimental error, but equation (13) is the easiest to apply. For the sake of consistency, therefore, they recommended that this equation should be used to analyse experimental data.

Harmer, Burton and Acree (58) measured the second

ionization constant of malonic acid from 0° to 60° C by the e.m.f. method. They plotted log K against 1/T and calculated ΔH by measuring the slope of the tangent line at each temperature. They found that the variation of ΔH with temperature is best expressed by the equation

$$\Delta H = a + bT + cT^2 + dT^3, \quad (14)$$

as had been foreseen by Harned and Ehler (39). They thereby obtained the following equation to express the variation of ionization constant with temperature:

$$\ln K = -\frac{a}{RT} + \frac{b}{R} \ln T + \frac{c}{R} T + \frac{d}{R} T^2 + e. \quad (15)$$

This equation is of course even more difficult to apply, and the accuracy does not require the use of such an equation.

Harned and Dedell (59) tested Baughan's equation by investigating the ionization of propionic acid from 0° to 50° C in various mixtures of dioxane and water. They doubted whether the Born equation used by Baughan is valid, and claimed that the assumption that the non-electrostatic part of the heat of ionization, ΔH_x , is independent of temperature is certainly not correct.

In the following years, most of the studies in this field were contributed by Bates (60-68), and by Harned (69-72) and co-workers. There are also a few other investigations (73-76). All of these authors analysed their results using

the Harned and Robinson equation for computing thermodynamic functions, with the exception of Everett and his co-workers (77-79) who employed the Everett and Wynne-Jones equation. Harned and Nestler (71) had extended the temperature range to 0° to 90° C, the largest range ever covered in work of this kind, and found that Harned and Robinson's equation still holds well.

In 1944, however, Jenkins (80), on the basis of the suggestion of Gurney that energy of ionization is made up of electrostatic and non-electrostatic parts, and assuming an empirical equation for the variation of the dielectric constant of water with temperature, proposed another semi-empirical equation to express the relation of ionization constant and temperature:

$$\log K = \frac{A}{T} + \frac{B \log T}{T} + \frac{C \log^2 T}{T} + D. \quad (16)$$

He tested the above equation (81) with the experimental data of several weak acids, and found that the deviation was a little better than that derived from the equation of Harned and Robinson and of Everett and Wynne-Jones, although he himself stated that the three equations are of the same accuracy. He also noticed that a plot of ΔC_p against the number of carbon atoms of the simple fatty acids shows a good linear relationship, in striking contrast to the type of curve obtained by Everett and Wynne-Jones. Moreover, the

order of the ΔH values calculated from the Jenkins equation ((of. eq. (102)) below) agrees with the generally accepted order of acid strengths. In spite of all of these merits, little attention has subsequently been paid to Jenkins's equation. This may be because the accuracy gained is only slight, and the theoretical background is not more sound than that of the other equations.

Very recently, the method of determination of ionization constants from the e.m.f. of cells without liquid junction has been extended with considerable success to the study of equilibria of biologically important solutions. Swinehart and his co-workers (82, 83) determined ionization constants of sulfanilic and metanilic acids from 0° to 50° C. Datta and his co-workers (84-87) investigated the thermodynamic function for the ionization of some biologically important compounds. King et al. (88, 89) studied the thermodynamics of the ionization of amino acids. Harned and Robinson's equation was employed in each case.

Nagakura et al. (90, 91) have investigated the thermodynamics of the ionization of mono derivatives of methyl-, chloro-, and nitro-substituted phenols by determining the ionization constants from 5° to 40° C using the spectrophotometric method. The technique used in the present work is similar to theirs except that the pH values of their solutions were measured with a pH meter. Heats of ionization

were calculated from the slopes of the straight lines of a van't Hoff's plot. Their results were explained in terms of the inductive and resonance effects.

Ives and Pryor (92) determined the ionization constants of monohalogenoacetic acids by conductance measurements from 5° to 35° C at 5° C intervals. Thermodynamic functions were calculated by the equation

$$\ln K = a + bT + cT^2. \quad (17)$$

Feates and Ives (93) determined the ionization constants of cyanoacetic acid from 5° to 45° C by the conductance method. They used more elaborate equations to compute the thermodynamic functions. They found that heats and entropies of ionization are sigmoid functions of temperature while ΔC_p is parabolic.

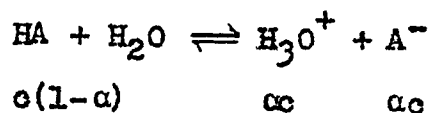
2. METHODS FOR THE DETERMINATION OF IONIZATION CONSTANTS

There are three main methods for the determination of ionization constants for weak electrolytes, namely the conductance method, the electromotive force method, and the spectrophotometric method. The conductance method is the earliest one; the electromotive force method is the most accurate and widely used; the spectrophotometric method is recently developed. In the following sections a brief account for all the three methods will be given with somewhat more detail on the spectrophotometric method which was the one used in the present investigation.

A. Conductance Method

This method was originally developed by Ostwald (1) and later modified by MacInnes and Shedlovsky (56). The principle involved is that each ion in a solution retains its own mobility; consequently the conductance of a solution depends on the number of ions present. The ratio of conductance at a certain concentration to that corresponding to complete ionization therefore gives the degree of ionization.

Consider the following equilibrium:



The equilibrium constant K_a is represented by

$$K_a = \frac{a_{\text{H}^+} a_{\text{A}^-}}{a_{\text{HA}}} = \frac{[\text{H}^+] \gamma_{\text{H}^+} [\text{A}^-] \gamma_{\text{A}^-}}{[\text{HA}] \gamma_{\text{HA}}} = \frac{\alpha^2 c}{1-\alpha} \frac{\gamma_{\text{H}^+} \gamma_{\text{A}^-}}{\gamma_{\text{HA}}} \quad (18)$$

where the a terms represent activities, square bracket terms represent stoichiometric concentrations and γ terms represent activity coefficients. The degree of ionization can be obtained by the equation

$$\alpha = \frac{\Lambda_c}{\Lambda_\infty} \quad (19)$$

where Λ_c is the equivalent conductance at concentration c measured experimentally, Λ_∞ is the equivalent conductance of a hypothetical solution of concentration c in which all of the acid molecules were completely ionized, but the mobilities of the ions were assumed to be the same as if they were in

the solution of ionic concentration c_1 ($=ac$). The value of Λ_e for a weak acid HA can be obtained by the equation

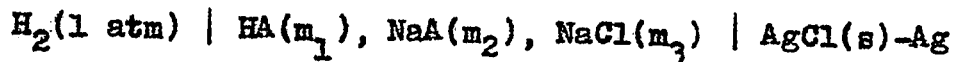
$$\Lambda_{HA} = \Lambda_{HCl} + \Lambda_{NaA} - \Lambda_{NaCl} \quad (20)$$

where Λ_{HCl} , Λ_{NaA} and Λ_{NaCl} stand for the equivalent conductances of HCl, NaA and NaCl solutions respectively all at concentration c_1 . The γ terms can be evaluated using the Debye-Hückel limiting law. They may also be eliminated by determining the classical ionization constant, which does not involve this term, at several concentrations and extrapolating to zero concentration where the activity coefficients become unity.

B. Electromotive Force Method (94, 95)

The principle of this method lies in the fact that the e.m.f. of a cell containing a weak acid depends on the hydrogen ion activity of the electrolyte, which in turn depends on the degree of ionization. There are two types of cells: cells with liquid junction and cells without liquid junction. The latter type can again be classified as buffered cells and unbuffered cells. The buffered cell technique is the one that is widely applied because of its accuracy. For the sake of conciseness only this method will be described briefly.

According to this method, the ionization constant of a weak acid HA can be determined by measuring the e.m.f. of the cell



where NaA acts as a buffer. The e.m.f. of this cell is given by the equation

$$E = E^\circ - \frac{RT}{F} \ln a_{\text{H}^+} a_{\text{Cl}^-} \quad (21)$$

where E° is the standard e.m.f. of the hydrogen silver chloride cell. Since

$$K_a = \frac{a_{\text{H}^+} a_{\text{A}^-}}{a_{\text{HA}}}, \quad (22)$$

$$a_{\text{H}^+} = \frac{K_a a_{\text{HA}}}{a_{\text{A}^-}}, \quad (23)$$

and therefore

$$E = E^\circ - \frac{RT}{F} \ln \frac{K_a a_{\text{HA}} a_{\text{Cl}^-}}{a_{\text{A}^-}} \quad (24)$$

$$= E^\circ - \frac{RT}{F} \ln K_a - \frac{RT}{F} \ln \frac{m_{\text{HA}} m_{\text{Cl}^-}}{m_{\text{A}^-}} - \frac{RT}{F} \ln \frac{\gamma_{\text{HA}} \gamma_{\text{Cl}^-}}{\gamma_{\text{A}^-}} \quad (25)$$

$$\frac{F(E - E^\circ)}{2.303 RT} + \log \frac{m_{\text{HA}} m_{\text{Cl}^-}}{m_{\text{A}^-}} = \text{p}K_a - \log \frac{\gamma_{\text{HA}} \gamma_{\text{Cl}^-}}{\gamma_{\text{A}^-}} \quad (26)$$

In order to evaluate the ionization constant by the above equation it is necessary to relate m_{HA} , m_{Cl^-} and m_{A^-} to the known values of m_1 , m_2 and m_3 , which are the stoichiometric molalities of HA, NaA and NaCl respectively. For moderately weak acids whose ionization constants are of the order of 10^{-3} to 10^{-5} this can be done as follows. In dilute solutions

NaCl is considered to be completely ionized, so that $m_{\text{Cl}^-} = m_3$. NaA is also considered as completely ionized into Na^+ and A^- . HA is only partly ionized into H^+ and A^- . Let m_{H^+} be the molality of the hydrogen ions resulting from the ionization of HA; then the molality of A^- resulting from this ionization will also be m_{H^+} and the molality of the unionized acid will be $m_{\text{HA}} = m_1 - m_{\text{H}^+}$. Since A^- is also produced from the complete ionization of NaA, $m_{\text{A}^-} = m_2 + m_{\text{H}^+}$, and equation (26) can be rewritten as

$$\frac{F(E - E^0)}{2.303 RT} + \log \frac{(m_1 - m_{\text{H}^+})m_3}{m_2 + m_{\text{H}^+}} = pK_a - \log \frac{\gamma_{\text{HA}} \gamma_{\text{Cl}^-}}{\gamma_{\text{A}^-}} \quad (27)$$

Therefore if m_{H^+} is known, the left side of equation (27) can be evaluated since E is the measured e.m.f. of the cell under investigation. The evaluation of m_{H^+} involves a series of approximations. First, HA is assumed to be completely unionized, so that $m_{\text{HA}} = m_1$, $m_{\text{A}^-} = m_2$ and $m_{\text{Cl}^-} = m_3$. Substitution of these values into equation (26), together with the γ terms evaluated by the limiting law, gives $(K_a)_{\text{app}}$, the apparent ionization constant. Then m_{H^+} is calculated by the equation

$$(K_a)_{\text{app}} = \frac{m_{\text{H}^+} m_{\text{A}^-}}{m_{\text{HA}}} \frac{\gamma_{\text{H}^+} \gamma_{\text{A}^-}}{\gamma_{\text{HA}}} = \frac{m_{\text{H}^+} (m_2 + m_{\text{H}^+})}{m_1 - m_{\text{H}^+}} (\gamma_{\pm})^2 \quad (28)$$

Using the values of m_{H^+} thus obtained, the left hand side of equation (27) can be evaluated. Let this be designated as K'_a . A series of K'_a values is obtained by varying the concentration of the solutions. The usual practice is to keep m_1/m_2 constant, approximately unity, and to vary the ionic strength by using different concentrations of sodium chloride.

If K_a' is plotted against the ionic strength and extrapolated to zero, the value obtained represents the thermodynamic ionization constant K_a .

C. Spectrophotometric Method

The ionization constant of an acid, K_a , is expressed by the equation

$$K_a = \frac{a_{H^+} a_{A^-}}{a_{HA}} = a_{H^+} \frac{m_{A^-}}{m_{HA}} \frac{\gamma_{A^-}}{\gamma_{HA}} \quad (29)$$

In dilute solutions, γ_{HA} can be taken as unity at all temperatures. Taking logarithms of equation (29) gives

$$\log K_a = \log a_{H^+} + \log \frac{m_{A^-}}{m_{HA}} + \log \gamma_{A^-} \quad (30)$$

or

$$pK_a = pH + \log \frac{m_{HA}}{m_{A^-}} - \log \gamma_{A^-} \quad (31)$$

The activity coefficient term can be eliminated by extrapolation when K_a is measured in solutions of different ionic strengths. It can also be calculated from the Debye-Hückel equation

$$\log \gamma_{A^-} = \frac{-A\sqrt{\mu}}{1+\alpha B\sqrt{\mu}} + C\mu, \quad (32)$$

where μ is the ionic strength and A and C are constants. A depends on temperature, but the dependence of C on temperature is neglected since it is a small term. The pH of the

solution can be measured by pH meter or by cells with liquid junction. A buffer of known pH may also be used; this is the procedure in the present work. The only term left on the right hand side of equation (31) is $\log \frac{m_{HA}}{m_{A^-}}$; if this term is evaluated, the pK_a of the acid can be calculated.

The concentration of the ionized and unionized species of the acid can be determined by visual colorimetry if they exhibit different absorption spectra in the visible region. If the two species exhibit different absorption spectra in the near ultraviolet region, as they do in most cases, the spectrophotometric method can be used. The principle involved is the same, both methods making use of the Beer-Lambert law, which can be expressed by the equation

$$\log \frac{I_0}{I} = \epsilon c d. \quad (33)$$

Here I_0 is the intensity of the incident monochromatic light; I , the intensity of absorbed light; c , the concentration of the solution; d , the length of the light path. ϵ is a characteristic constant called the extinction coefficient; its value depends on the nature and temperature of the solution and the wave length of the light. It is called the molar extinction coefficient if c is expressed in moles liter⁻¹, and d in cm. The quantity $\log \frac{I_0}{I}$ is generally referred to as the absorbance of the sample and is designated by A . It is sometimes called the optical density D or extinction E .

According to the Beer-Lambert law it is seen that if a solute is dissolved in a solvent the absorbance at certain wavelengths is directly proportional to the concentration. For a multicomponent system, the total absorbance is equal to the sum of the absorbances due to individual components if they do not interact with each other; in other words, the absorbance is additive. Expressed mathematically,

$$\log \frac{I_0}{I} = A = (\epsilon_1 c_1 + \epsilon_2 c_2 \dots) d \quad (34)$$

$$= A_1 + A_2 + \dots \quad (35)$$

where c_1, c_2 etc. are the concentrations of the non-interacting components having molar extinction coefficients of ϵ_1, ϵ_2 etc. A_1, A_2 etc. are the absorbances of these components.

In the acid-base equilibria there are two main species in solution, the unionized molecules HA and the acid anions A^- . The latter usually have sharper bands and absorb more strongly than the former in the ultraviolet region. A particular wavelength can be chosen at which the absorbances of the two species are greatly different; the concentrations of the individual species in a mixture can then be determined by measuring the absorbance of the latter. This is illustrated in Figure 1. Curve A is the absorption curve for the unionized species HA, curve B that of the ionized species A^- and curve C that of a mixture (partially ionized solution). From

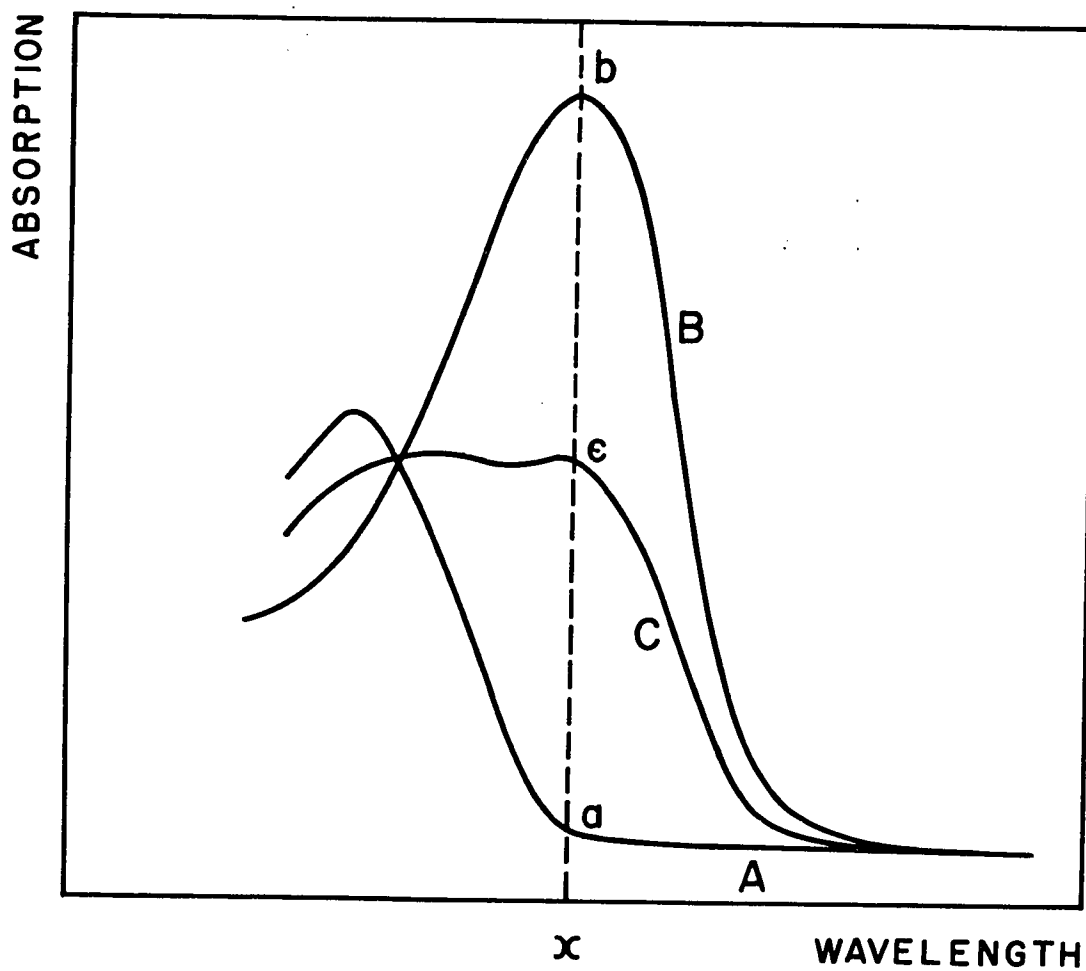


Figure 1. Absorption curves for a compound in acid (A), alkaline (B) and buffer (C) solutions.

the figure it is seen that curves A and B have maximum separations at wavelength x .

Let a be the absorbance of the unionized species HA of concentration c at this wavelength; b be that of the ionized species A^- of same concentration, and ϵ that of the partially ionized solution of the same total concentration. This last quantity is composed of a part of a and a part of b .

Let x = fraction of acid present as anion

$1-x$ = fraction of acid present as unionized molecule

then

$$\epsilon = b x + a (1-x) = b x + a - a x \quad (36)$$

From this

$$x = \frac{\epsilon - a}{b - a} \quad (37)$$

and

$$1-x = \frac{b - \epsilon}{b - a} \quad (38)$$

Therefore

$$\frac{m_{HA}}{m_{A^-}} = \frac{1-x}{x} = \frac{b-\epsilon}{\epsilon-a} \quad (39)$$

Substitution into equation (31) gives

$$pK = pH + \log \frac{b-\epsilon}{\epsilon-a} - \log \gamma_{A^-} \quad (40)$$

Therefore by measuring the absorbances of equal concentrations of the completely ionized, completely unionized and partially ionized solutions of known pH at a chosen wavelength, it is possible to calculate the ionization constant

of the acid. In actual practice a certain amount of the sample is first dissolved in a certain volume of slightly acidic solution to suppress its ionization and to measure the absorbance a . The same amount of the sample is next dissolved in the same volume of alkaline solution and the absorbance b measured. Finally, the same quantity of sample is dissolved in a buffer solution of known pH and the absorbance c is measured. Maximum accuracy is assured when the pH of the buffer solution is the same as the pK of the acid.

The determination of ionization constants by the spectrophotometric method is the extension of the colorimetric method from the visible to the ultraviolet regions. The usual visual colorimetric method is not accurate enough for this purpose. However, the method of photoelectric colorimetry, in which the color is measured by a photoelectric cell, is adequate. Halban and Ebert (96) first applied the technique developed by Halban and Siedentopf (97) to determine the ionization constant of picric acid. The validity of the Beer-Lambert law was thoroughly examined by Halban and his co-workers (98-104). The application of this method to the ultraviolet region seems to have been initiated by Stenström. In 1925, Stenström and Reinhard (105) noticed that the absorption curves for phenol and tyrosine and some other cyclic compounds change as the pH of the solution is changed. They

explained that this is due to the fact that the absorption curve of the ionized and non-ionized molecules are different. They suggested that this fact could be utilized to determine the "affinity constant" with respect to the OH group for phenol and tyrosine by measuring the absorbance in the ultraviolet region. This was confirmed by the work of Stenström and Goldsmith (106) in the following year, in a determination of the ionization constants of phenol and tyrosine. Morton and Topping (107) determined the ionization constants of some weak acids by the same principle. Flexer, Hammett and Dingwall (108) made a thorough study on this subject. Hughes, Jellinek and Ambrose (109), and Herrington (110), determined the ionization constants of pyridine and its derivatives. In those early days, the absorption was measured by means of a spectrograph and photometer. The invention of the spectrophotometer made this method more convenient in practice. Sager and Siewers (111) determined the ionization constant of 4-aminobenzophenone from 10° to 40° C using a Beckman DU spectrophotometer. Andon, Cox and Herrington (112) also determined the ionization constants of pyridine and its derivatives. Thamer and a co-worker (113, 114) have extended the method to the ionization constant of dibasic acids. Kieffer and Rumpf (115) determined the ionization constants of phenol and methyl-substituted phenols and some related substances by using both the e.m.f. and spectrophotometric methods.

Minegishi and Nagakura (91) determined the ionization constants of phenol, and the monomethyl-, chloro- and nitro-substituted phenols, from 15° to 40° C. Nigakura (90) also investigated the hydrogen bonding power between these phenols and methyl acetate in n-heptane by measuring the equilibrium constant from 5° to 35° C. All of these authors measured the pH of their solution directly. Edward (116), however, determined the ionization constants of acetyl salicylic acid and salicylamide by using acetate buffers, the pH values of which were calculated from the ionization constant of acetic acid that had been determined accurately. Robinson and Biggs (117) further improved their technique by employing buffer solutions of known pH, thus simplifying the experimental procedure. Since then the modified methods were widely adopted. Robinson and Kiang determined the ionization constants of vanillin and its isomers (118) and also of the vanillyl ammonium ion as a dibasic acid (119). Biggs (120) determined the ionization constants of phenol and some substituted phenols. Robinson and Biggs (121) determined the ionization constants of benzoic acid, p-amino benzoic acid and its esters. Herrington and Kynaston (122) determined the ionization constants of phenol, cresols and xylenols. In the present work, their procedure was followed directly except that measurements were made at various temperatures.

This method is capable of being very accurate and is

much easier than the conductance and electromotive force method. Because the quantity measured is the relative concentration of the ionized and non-ionized species, and since the absorbances of the substances are additive, this method is not subject to appreciable error by small amounts of impurities, nor does the actual concentration of the solution matter. Andon, Cox and Herrington (112) have shown theoretically that if the sample contains 2% of impurity, the error introduced into the pK is less than 0.01 unit. But this method also has its limitations. The absorption spectra of the ionized and non-ionized species must be different. Another requirement is that in order to acquire maximum accuracy, the buffer solution employed has to have a pH value approximately equal to the pK of the acid under examination, and this buffer solution must not absorb strongly at the particular wavelength chosen.

The spectrophotometric method has also been found useful for studying the ionization constants of complex ions (123-129). It is particularly useful for determining the ionization constants of very weak electrolytes which can not be determined by other methods. Thus Hall, DeVries and Gantz (130) have succeeded in determining the ionization constants of two very weak bases, nitroguanidine and nitroaminoguanidine by measuring the spectra in concentrate hydrochloric acid solution.

3. METHODS FOR THE DETERMINATION OF HEATS OF IONIZATION

Heats of ionization can be obtained in two ways; the direct calorimetric method and the ionization constant method.

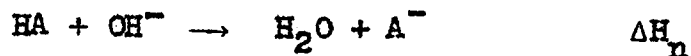
A. Calorimetric Method

This method can be used to measure the amount of heat evolved in any chemical reaction. In simple calorimeters the amount of heat evolved is calculated from the rise in temperature of the water surrounding the reaction system:

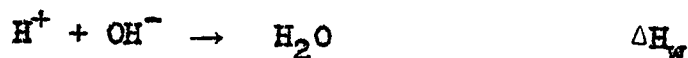
$$\text{Heat evolved} = C_p \Delta T, \quad (41)$$

where C_p is the heat capacity of the system and ΔT is the rise in temperature. C_p can be determined by introducing a known quantity of heat into the system either from a reaction of known ΔH or from electrical energy.

The heat of ionization of a weak acid HA may be obtained from its heat of neutralization, which is the enthalpy change ΔH_n in the following reaction:



This is the sum of the following two reactions:



Therefore

$$\Delta H_1 = \Delta H_n - \Delta H_w, \quad (42)$$

where ΔH_1 is the heat of ionization; ΔH_n is the heat of

neutralization and ΔH_w the heat of ionization of water.

Calorimeters can be classified into two main types; isothermal and adiabatic calorimeters. Isothermal calorimeters were used by J. Thomson in 1854. In this type the water in the outer jacket is kept at constant temperature by thermostat so that there is a steady rate of heat loss from the water that surrounds the reaction system; this rate is evaluated and the heat loss corrected. The adiabatic calorimeter was developed by T. W. Richards in 1905. In this type the water in the outer jacket is kept at the same temperature as that of the water in the calorimeter itself by an automatic heating device. The heat loss is therefore eliminated.

For measuring small amounts of heat a microcalorimeter (131, 132) is used. One type was invented by Tian (133) and later modified by Calvet (134). It consists of two similar silver reaction thimbles placed in a large aluminum block, one for the sample and the other for a blank. Each thimble is completely surrounded by the same number of uniformly distributed thermocouples, the cold junctions of which are attached to the aluminum block. The two thermopiles are connected in opposition. The instrument is kept in a room of constant temperature. Part of the heat evolved by the reaction is transmitted by conductivity through the thermopile and causes the generation of an electromotive force

which is then amplified and recorded. When the two thermopiles are connected in opposition, the e.m.f. generated is directly proportional to the temperature difference between the two reaction thimbles. When the e.m.f. is plotted against time the area underneath the curve will be directly proportional to the total heat produced in the sample reaction thimble. This can be written as:

$$\text{heat evolved} = a \iint dT dt = b \iint dE dt = c A \quad (43)$$

where a, b, and c are proportionality constants. E is the e.m.f. generated in the thermopile; t is the time and T the temperature. A is the area underneath the curve. The constant c can be evaluated by calibration usually with electric energy of an amount approximately equal to the heat of the reaction under investigation.

Many microcalorimeters are very sensitive. The amount of heat measured is usually of the order of one hundredth to one-tenth of a calorie. Because of its extreme sensitiveness, it is very easily subject to errors. For example, the breaking of a glass cell to bring two solutions into contact and the agitation of the solution to ensure complete mixing will affect the result greatly.

B. The Ionization Constant Method

The equilibrium constant is related to the temperature by van't Hoff's equation

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H}{RT^2} . \quad (44)$$

In an ionization process K is the ionization constant and ΔH is the heat of ionization. If ΔH is independent of temperature equation (44) can be integrated to give

$$\ln K = - \frac{\Delta H}{RT} + C . \quad (45)$$

A plot of $\ln K$ against $1/T$ will therefore give a straight line with slope of $-\Delta H/R$. If H varies with temperature, the plot of $\ln K$ against $1/T$ will show curvature. The heat of ionization at each temperature may be obtained from the slope of the tangent line at that temperature. An alternative procedure which has been applied by Lunden is to plot $\log \frac{K}{K_w}$ against $1/T$. This usually gives a straight line. The heat of reaction thus obtained is the difference between the heat of ionization of the substance under investigation and that of water. In other words it is the heat of neutralization of that substance, ΔH_n . The heat of ionization ΔH_i can then be obtained from equation (42).

The methods for the determination of ionization constant have already been discussed. The variation of ionization constant with temperature has been expressed by many semi-empirical equations involving several parameters which are evaluated in each case from the experimental data. Heats of ionization and other thermodynamic functions for the ionization

process are then calculated from these parameters. These semi-empirical treatments will now be discussed.

C. Semi-empirical Treatment of the Ionization Process

There are a number of theoretical treatments of the ionization process, most of them being concerned with the effects of substituents on the ionization constant. Only a few (52, 53, 135-137) deal with the heat and other thermodynamic functions. In view of the unsatisfactoriness of the purely theoretical treatments, semi-empirical equations are frequently used for analysing the experimental data and computing thermodynamic functions. There are at least six semi-empirical equations available, as has already been mentioned in the previous section. A more detailed discussion of them in the order of their appearance, will now be given.

(1) Harned and Ehler's Equation (39)

If $\ln K$ is plotted against $1/T$, and the heat of ionization evaluated at each temperature from the slope of the tangent line at each point, it is found that the heat of ionization varies approximately linearly with temperature and can be expressed in a power series. No experimental results are sufficiently accurate to require terms higher than the second power of T . Therefore one can write:

$$\Delta H = A - BT - CT^2 \quad (46)$$

$$\Delta C_p = \left(\frac{\partial \Delta H}{\partial T} \right)_p = -B - 2CT \quad (47)$$

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad (48)$$

$$\ln K = \int \frac{\Delta H}{RT^2} dT = -\frac{A}{RT} - \frac{B}{R} \ln T - \frac{C}{R} T + D \quad (49)$$

where all the thermodynamic functions are referred to the standard condition. If the experimental values of K at each temperature T are substituted into equation (49), a set of equations is obtained. The constants A, B, C and D can be computed from these equations by the method of least squares. The values of ΔH and ΔC_p can be calculated from equations (46) and (47). The other thermodynamic functions are obtained as follows:

$$\Delta F = -RT \ln K = A + BT \ln T + CT^2 - RDT \quad (50)$$

$$\Delta S = \frac{-d\Delta F}{dT} = -B \ln T - B - 2CT + RD \quad (51)$$

(2) Harned and Embree's Equation (41)

It is a well-known fact that the ionization constants of weak electrolytes first increase, then pass through a maximum, and finally decrease with increasing temperature. If $\log K$ is plotted against t , the temperature on the centigrade scale,

a parabolic curve is obtained. Harned and Embree noticed that such curves are superposable for all of the weak electrolytes investigated. If $(\log K - \log K_m)$ were plotted against $(t-\theta)$, where K_m is the maximum ionization constant and θ the temperature of maximum ionization, all points representing this function fall on the same curve. This curve is almost exactly parabolic in the region of the maximum and for a considerable distance away from it. They therefore employ the following equation:

$$\log K - \log K_m = -p (t-\theta)^2 \quad (52)$$

where p is a universal constant having the value of 5.0×10^{-5} . This equation may also be written as

$$\log K = (\log K_m - p\theta^2) + 2p\theta t - pt^2 \quad (53)$$

where K_m and θ are constants characteristic of the electrolyte. They can be determined in the following way. Rearrangement of equation (53) gives

$$\log K + pt^2 = \log K_m - p\theta^2 + 2p\theta t. \quad (54)$$

From equation (54) it is apparent that if $(\log K + pt^2)$ is plotted against t , a straight line should be obtained with slope equal to $2p\theta$, and an intercept at 0°C of $\log K_m - p\theta^2$. From these values the values of K_m and θ can be deduced. The thermodynamic functions can be derived as follows: Equation

(52) can be written as

$$\ln K = \ln K_m - 2.303 p(t - \theta)^2 \quad (55)$$

and

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} = -2.303 \times 2p(t - \theta) \quad (56)$$

Using p as 5×10^{-5} one obtains

$$\Delta H = -2.303 \times 10^{-4} RT^2 (t - \theta) \quad (57)$$

$$\Delta C_p = \left(\frac{\partial \Delta H}{\partial T}\right)_p = -2.303 \times 10^{-4} RT [2(t - \theta) + T] \quad (58)$$

$$\Delta F = -RT \ln K = -RT \ln K_m + 2.303 \times 5 \times 10^{-5} RT (t - \theta)^2 \quad (59)$$

$$\Delta S = -\left(\frac{\partial \Delta F}{\partial T}\right)_p = R \ln K_m - 2.303 \times 10^{-4} RT (t - \theta) - 2.303 \times 5 \times 10^{-5} R (t - \theta)^2 \quad (60)$$

(3) Pitzer's Equation (51)

Pitzer, after collecting some thermodynamic data for ionization processes, noticed that for the first ionization ΔC_p is approximately $-40 \text{ cal. deg.}^{-1}$ for all fatty acids. He assumed that ΔC_p is independent of temperature, so that

$$\Delta H = \Delta H_o + \Delta C_p T \quad (61)$$

$$\Delta S = \Delta S_o + \Delta C_p \ln T \quad (62)$$

where ΔH_o and ΔS_o refer to the standard heat and entropy of

ionization at 0° K. Also,

$$\Delta F = -RT \ln K = \Delta H - T\Delta S = \Delta H_0 - T\Delta S_0 + \Delta C_p(T - T \ln T) \quad (63)$$

$$= \Delta H_0 + T(\Delta C_p - \Delta S_0) - \Delta C_p T \ln T \quad (64)$$

$$\ln K = \frac{-\Delta H_0}{RT} + \frac{\Delta C_p}{R} \ln T - (\Delta C_p - \Delta S_0)/R \quad (65)$$

The use of $\Delta C_p = -40 \text{ cal. deg.}^{-1}$, $R = 2$, gives

$$\log K = A + \frac{B}{T} - 20 \log T. \quad (66)$$

(4) Everett and Wynne-Jones's Equation (54)

These authors also assumed that ΔC_p is independent of temperature. But instead of assigning an universal value to all organic acids they suggested that it varies from acid to acid. Its value can be determined by a graphical method in the following way.

The ionization constant is related to the heat of ionization by the van't Hoff equation

$$\frac{d \ln K}{d T} = \frac{\Delta H}{RT^2} \quad (67)$$

Since ΔH varies with temperature this equation cannot be integrated unless ΔH is expressed as a function of temperature.

In general

$$\frac{d\Delta H}{d T} = \Delta C_p, \quad (68)$$

and if ΔC_p is assumed to be independent of T, equation (68) can be integrated to give

$$\Delta H = \int \Delta C_p dT = \Delta C_p T + a \quad (69)$$

where a is a constant. Substitution of equation (69) into equation (67) and integration gives

$$\ln K = \frac{A}{T} + \frac{\Delta C_p}{R} \ln T + B \quad (70)$$

where B is a constant. A, equal to a/R , is also a constant. They can be evaluated from the experimental data in the following way:

Since ΔC_p is regarded as temperature invariant, one may write

$$\Delta H = \Delta H_0 + \Delta C_p T \quad (71)$$

$$\Delta S = \Delta S_0 + \Delta C_p \ln T \quad (72)$$

or

$$T \Delta S = T \Delta S_0 + T \Delta C_p \ln T. \quad (73)$$

Subtraction of equation (73) from equation (71) gives rise to

$$\Delta H - T \Delta S = \Delta H_0 + T(\Delta C_p - \Delta S_0) - T \Delta C_p \ln T \quad (74)$$

$$= \Delta F = -RT \ln K \quad (75)$$

Therefore

$$\ln K = - \frac{\Delta H_o}{RT} + \frac{\Delta C_p}{R} \ln T + \frac{\Delta S_o - \Delta C_p}{R} \quad (76)$$

Comparison of (76) and (70) shows that

$$A = - \frac{\Delta H_o}{R} \quad (77)$$

$$B = \frac{\Delta S_o - \Delta C_p}{R} \quad (78)$$

Equation (70) can also be written as

$$T \log K = A' + \frac{\Delta C_p}{R} T \log T + B'T \quad (79)$$

where A' is equal to $A/2.303$, and B' is equal to $B/2.303$.

For two different temperatures, T_1 and T_2 , one can write

$$T_1 \log K_1 = A' + \frac{\Delta C_p}{R} T_1 \log T_1 + B'T_1 \quad (80)$$

$$T_2 \log K_2 = A' + \frac{\Delta C_p}{R} T_2 \log T_2 + B'T_2 \quad (81)$$

Subtraction of equations (81) from (80) gives

$$\begin{aligned} T_1 \log K_1 - T_2 \log K_2 \\ = \frac{\Delta C_p}{R} (T_1 \log T_1 - T_2 \log T_2) + B' (T_1 - T_2) \end{aligned} \quad (82)$$

or

$$\frac{T_1 \log K_1 - T_2 \log K_2}{T_1 - T_2} = \frac{\Delta C_p}{R} \frac{T_1 \log T_1 - T_2 \log T_2}{T_1 - T_2} + B' \quad (83)$$

According to equation (83) it is evident that a plot of

$$\frac{T_1 \log K_1 - T_2 \log K_2}{T_1 - T_2} \text{ against } \frac{T_1 \log T_1 - T_2 \log T_2}{T_1 - T_2} \text{ will}$$

give a straight line. From its slope, which equals $\Delta C_p/R$, the value of ΔC_p can be evaluated. Equation (79) can be transformed into the following:

$$\log K - \frac{\Delta C_p}{R} \log T = \frac{A'}{T} + B'. \quad (84)$$

This shows that a plot of $(\log K - \frac{\Delta C_p}{R} \log T)$ against $1/T$ should be a straight line of slope A' equal to $\Delta H_0/2.303R$, and hence ΔH_0 can be evaluated. From ΔH_0 , ΔC_p and K , all the other thermodynamic functions can be calculated. The value of T_m can be obtained as follows:

At the maximum point

$$\frac{d \ln K}{d T} = \frac{\Delta H}{RT^2} = 0 \quad (85)$$

According to equation (71)

$$\Delta H_m = \Delta H_0 + \Delta C_p T_m = 0 \quad (86)$$

whence

$$T_m = - \frac{\Delta H_0}{\Delta C_p}. \quad (87)$$

(5) Harned and Robinson's Equation (57)

These authors observed that the e.m.f. of a cell for measuring the ionization constant is a quadratic function of the temperature. Since the change of e.m.f. is directly related to the free energy of ionization, the latter is also expected to vary quadratically with temperature. Hence the following equations arise:

$$\Delta F = A' - D'T + C'T^2 = - RT \ln K \quad (88)$$

$$\ln K = - \frac{A'}{RT} + \frac{D'}{R} - \frac{C'}{R} T \quad (89)$$

$$\log K = - \frac{A^*}{T} + D^* - C^*T \quad (90)$$

$$\frac{\Delta H}{RT^2} = \frac{d \ln K}{dT} = \frac{A'}{RT^2} - \frac{C'}{R} \quad (91)$$

$$\Delta H = A' - C'T^2 \quad (92)$$

$$\Delta S = - \frac{d \Delta F}{dT} = D' - 2C'T \quad (93)$$

$$\Delta C_p = \frac{d \Delta H}{dT} = - 2C'. \quad (94)$$

To find the temperature of maximum ionization, equation (92) can be used

$$\Delta H_m = A' - C'T_m^2 = 0 \quad (95)$$

$$T_m = \sqrt{\frac{A'}{C'}} = \sqrt{\frac{A^*}{C^*}} \quad (96)$$

Substitution of (96) into (90) gives

$$\log K_m = D^* - 2C^*A^* \quad (97)$$

(6) Jenkins's Equation (80)

Gurney (52) suggested that the energy of ionization is made up of two terms, a non-electrostatic term and an electrostatic term. The latter is represented by Born's equation. Jenkins assumed an empirical equation for the variation of the dielectric constant with temperature and arrived at the equation

$$\Delta H = (a + b \log T) (\log \theta - \log T) \quad (98)$$

where a and b are constants and θ is the temperature for maximum ionization. Division of equation (98) by RT^2 and integration gives

$$\ln K = \frac{A}{T} + \frac{B \log T}{T} + \frac{C \log^2 T}{T} + D \quad (99)$$

$$\Delta F = - RT \ln K = - RA - RB \log T - RC \log^2 T - RDT \quad (100)$$

$$\Delta S = - \left(\frac{\partial \Delta F}{\partial T} \right)_p = - \frac{RB}{2.303 T} - \frac{2RC}{2.303} \frac{\log T}{T} - RD. \quad (101)$$

Equation (98) can be written as

$$\begin{aligned} \Delta H = (RB - 2.303 RA) + 2.303 \log T \left(\frac{2RC}{2.303} - RD \right) \\ - 2.303 RC \log^2 T. \end{aligned} \quad (102)$$

From this we get

$$\Delta C_p = \left(\frac{\partial \Delta H}{\partial T} \right)_p = \frac{2RC - 2.303 RB}{2.303 T} - \frac{2RC \log T}{T} . \quad (103)$$

(7) Discussion of the Equations

The above equations have been tested by Harned and Robinson (57), and by Jenkins (81), with the ionization data of fatty acids obtained by Harned et al. It was found that Harned and Embree's equation and Pitzer's equation are only first-order approximations; they do not represent the experimental data very well. The equations of Harned and Ehler, Harned and Robinson, Everett and Wynne-Jones, and Jenkins are of the same order of accuracy. They all represent the experimental data well within the experimental error. The ΔH values computed from Harned and Ehler's equation are a little higher than those computed from the equation of Everett and Wynne-Jones. The results computed from Harned and Robinson's equation lie in between. Harned and Ehler's equation and Jenkins's equation have four constants that have to be evaluated by the method of least squares. It is easier to use Harned and Robinson's equation, which has only three constants. Harned and Robinson claimed that their equation represents the experimental results for the ionization constant of water at high temperatures ((results obtained by Noyes and Kato (138)) better than did that of Everett and Wynne-Jones and Harned and Ehler.

Another point of contrast between Harned and Robinson's equation and that of Everett and Wynne-Jones relates to the ΔC_p values. Thermodynamic functions derived from different equations do not differ much except in this quantity. This is because different equations involve different functions for the variation of ΔC_p with temperature. The equations of Pitzer and of Everett and Wynne-Jones imply the invariance of ΔC_p with temperature, while all of the other equations imply a temperature-dependent ΔC_p . Harned and Ehler, and Harned and Robinson assumed that ΔC_p increases linearly with temperature. Harned and Embree's equation implies a quadratic relationship. Jenkins's equation implies that ΔC_p decreases with temperature. Since all of these equations except those of Pitzer and of Harned and Embree represent the experimental data very well, it is not possible to decide experimentally how ΔC_p actually varies with temperature. In order to do this it would be necessary to employ a wide temperature range, which involves serious experimental difficulties. A theoretical treatment needs a satisfactory representation of the variation of dielectric constant of the solvent with temperature. At the present moment, this is still unavailable. The temperature invariance of ΔC_p in chemical reactions has not been proved, but many instances of reactions are known in which ΔC_p varies linearly or even quadratically with temperature (139). Moelwyn-Hughes (140) has also shown, from the

kinetic point of view, that ΔC_p for ionization processes is a linear function of temperature. For these reasons, most workers prefer to use Harned and Robinson's equation for computing the thermodynamic functions. For the sake of consistency with the majority of the authors in this field, Harned and Robinson's equation is adopted in present work.

Very recently Feates and Ives (93) found that $-\Delta C_p$ for the ionization of cyanoacetic acid from 5° to 45° C passes through a minimum at about 30° C. They also tested nine different empirical equations which include all of the equations mentioned above. Deviations from experimental values were examined on a statistical basis for randomness. They claimed that none of the above-mentioned equations is "capable of expressing the observed values of $\ln K$ as a function of temperature with fully random deviations not exceeding those to be expected from the standard error in the ionization constant determinations." Three equations which they found satisfactory are:

$$pK = a + bT + cT^2 + dT^3 + eT^4 \quad (104)$$

$$pK = a + bT + cT^2 + dT^3 + eT^4 + fT^5 \quad (105)$$

$$pK = \frac{A}{T} + B + CT + DT^2 + ET^3 + FT^4 \quad (106)$$

These equations include five to six parameters, and an extremely laborious computation procedure is to be expected.

The standard deviation in pK they assigned is 0.00021 unit or 0.005%. The experimental accuracy in present work is about ± 0.01 units in pK. It is therefore not worth while to employ such complicated equations.

CHAPTER 2

GENERAL THEORY OF THE THERMODYNAMICS OF IONIZATION

1. INTRODUCTION

Ionization processes in solution have been a subject of considerable study in the past years. Most of the investigations have been devoted to ionization constants at ordinary temperature, and studies have been made of how they are affected by chemical constituents, the dielectric constant of the medium, and so forth. Much effort has also been made to study the thermodynamics of ionization processes, as has been mentioned previously. Many thermodynamic functions are available and have been listed by Harned and Owen (141) and Everett and Wynne-Jones (54). The theory, however, is still not clear, and it is not possible, at present, to interpret the thermodynamic functions quantitatively. In the present chapter a review is given of the general theoretical treatment of ionization processes.

Ionization processes always involve a creation or transfer of charge. The degree of ionization is greater in polar solvents than in non-polar solvents. It is therefore evident that electrostatic energy is involved in the ionization processes. But since no simple relationship between the ionization constant of an electrolyte and the dielectric constant of the medium can be found ((plots of $\log K$ against

1/D show curvature (142)), it would not be correct to conclude that the free energy of ionization is purely electrostatic; some non-electrostatic factors must also be involved.

For an ionization process involving the creation of two ions from a neutral molecule the electrostatic energy originates from the coulombic forces between the two charges created. The energy is given by the Born equation

$$W = - \frac{Ne^2}{2D} \left(\frac{1}{r_+} + \frac{1}{r_-} \right) \quad (107)$$

where W is the electrostatic energy, N is Avogadro's number, e, the electric charge, D, the dielectric constant of the medium, and r_+ and r_- are the radii of the positive and negative ions respectively. The non-electrostatic energy is due to exchange forces between the two separated atoms. Gurney (52) assumed that only the electrostatic energy is temperature dependent; this involves the dielectric constant, which varies with temperature. The non-electrostatic energy he assumed to be temperature independent. This is concluded from the fact that the heats of ionization of anilinium and o-chloro-anilinium ions (143) are independent of temperature; these processes only involve non-electrostatic energy as there is no creation of charge.

The following equations therefore apply:

$$\Delta F^\circ = \Delta F^\circ_{n.e.} + \Delta F^\circ_e. \quad (108)$$

$$-RT \ln K = -RT \ln K_{n.e.} + \frac{Ne^2}{2D} \left(\frac{1}{r_+} + \frac{1}{r_-} \right) \quad (109)$$

$$- \ln K = - \ln K_{n.e.} + \frac{Ne^2}{2DRT} \left(\frac{1}{r_+} + \frac{1}{r_-} \right) \quad (110)$$

Differentiation of equation (110) with respect to T, setting

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H^{\circ}}{RT^2} \quad (111)$$

and

$$\frac{\partial \ln K_{n.e.}}{\partial T} = \frac{\Delta H^{\circ}_{n.e.}}{RT^2} \quad (112)$$

gives

$$\Delta H^{\circ} = \Delta H^{\circ}_{n.e.} + \frac{Ne^2}{2} \left(\frac{1}{r_+} + \frac{1}{r_-} \right) \frac{1}{D} \left(1 + T \frac{\partial \ln D}{\partial T} \right) \quad (113)$$

This equation was first obtained by Baughan (53). From this equation it can be seen that a plot of the heat of ionization against

$$\frac{1}{D} \left(1 + T \frac{\partial \ln D}{\partial T} \right)$$

will give a straight line of slope equal to

$$\frac{Ne^2}{2} \left(\frac{1}{r_+} + \frac{1}{r_-} \right) ;$$

from this the mean radius r can be evaluated, where r is defined by

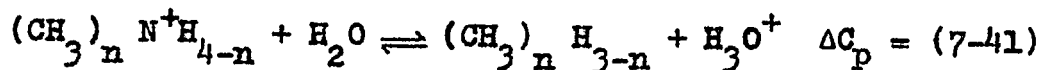
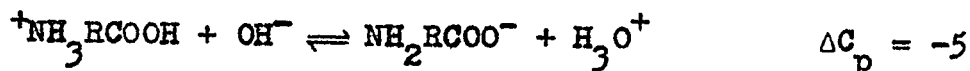
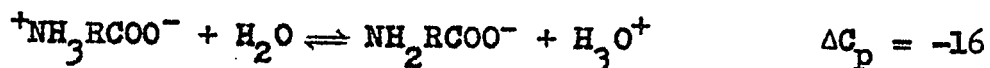
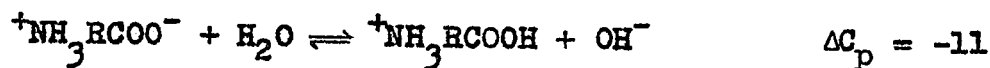
$$\frac{2}{r} = \frac{1}{r_+} + \frac{1}{r_-} . \quad (114)$$

Baughan has obtained this value from experimental data, with the right order of magnitude.

In spite of this success, the above treatment can be criticized along the following lines:

(1) The plot of ΔH° against $\frac{1}{D} (1 + T \frac{\partial \ln D}{\partial T})$ for water and acetic acid shows distinct curvature (144).

(2) ΔC_p values for most isoelectric ionization processes are not zero, for example (145);



(3) Although the values of r are of the right order of magnitude they are not convincing. They seem too small in pure water and too large in 70% dioxane-water mixture. It is also difficult to explain why the value should change with the solvent.

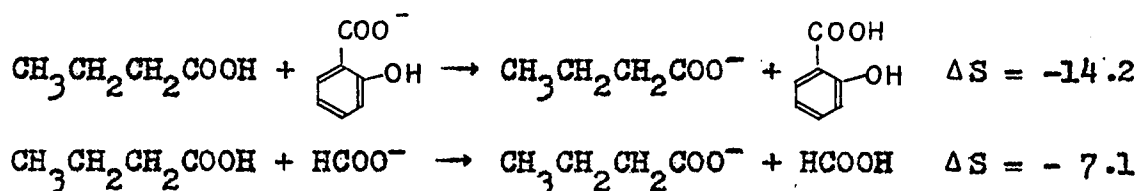
(4) ΔS° is related to free energy by

$$\Delta S^\circ = - \frac{\partial \Delta F^\circ}{\partial T} = - \frac{\partial \Delta F}{\partial T} \frac{n.e.}{e} + \frac{\partial \Delta F}{\partial T} e \quad (115)$$

Since, according to Gurney, the non-electrostatic part does not vary with the temperature, the above equation reduces to

$$\Delta S^{\circ} = - \frac{\partial \Delta F_e^{\circ}}{\partial T} \quad (116)$$

This means that the entropy of ionization has solely an electrostatic origin. There are, however, cases of non-ionic and isoelectric dissociation processes which have large values of ΔS° . For example Bodenstein (146) found that ΔS° for the dissociation of HI in the gas phase is 13.6 e.u., while that for H_2Se is 4 e.u. ΔS° values for the following isoelectric reactions are (54):



(5) The dependence of ΔS° upon the dielectric constant of the solvent suggests that only a part of the entropy is electrostatic. This can be shown from Harned and Kazajum's (50) results for the ionization of acetic acid in dioxane-water mixtures. The plot of ΔS° against $1/D$ at $25^{\circ} C$ is a straight line, and the intercept at $1/D = 0$ is about -18 e.u. which represents the non-electrostatic entropy change.

(6) ΔS° for the dissociation of trimethylaniline (54) is very small, only -3.3 e.u., and it becomes positive at

temperatures below 15° C. This phenomenon can not be explained by Gurney's suggestion.

2. SOLUTE-SOLVENT INTERACTIONS

It is clear from the above discussion that consideration of the interaction energies between the solutes alone is not sufficient; one must, in addition, take into account the solute-solvent interactions. As pointed out by Everett, Landsman and Pinsent (79), these interactions should include the interactions between ions and the solvent molecules, as well as those between the latter and the unionized acid molecules. This makes the situation more difficult, and it is not possible at the present time to give a quantitative interpretation.

A. Interactions Between Neutral Molecules And Water

There are three kinds of interactions between an acid molecule and water molecules:

(1) "Iceberg" effect. Frank and Evans (147) studied the entropy of solution of various substances. They found that the entropy loss for the solution of noble and non-polar gases in non-polar liquids is about 10-15 e.u., and that it varies little with temperature. The entropy of solution of these gases in water is about -25 to -40 e.u., and its value decreases rapidly with increasing temperature. Since entropy represents degree of disorder, the extra entropy lost in the

formation of an aqueous solution over that for the formation of a non-aqueous solution would imply that the water structure becomes more ordered through the influence of the dissolved molecules. They suggested that water molecules build up a microscopic iceberg round the non-polar molecule, which can "rattle" in its cage. Other evidence for hydration of non-polar solutes is also convincing. The clathrate nature of inert gas hydrates, suggested by Claussen (148), has been confirmed by the X-ray structure determination of Stackelburg and Miller (149) and has a clear relation with the iceberg of Frank and Evans (147). The forces involved in the iceberg formation probably consist of dipole-induced dipole interactions, London dispersion forces, and repulsive forces if the non-polar molecule becomes too close to the water molecule. In the hydrocarbon part of the acid molecule one would therefore expect this kind of interaction to exist.

(2) Hydrogen bonding. Hydrogen bonding occurs when two electronegative elements approach sufficiently close with a hydrogen atom in between, e.g., $O - H \dots O$, $F - H \dots F$, $N - H \dots O$ etc. The energy arises from electrostatic, delocalization, dispersion and repulsive forces (150). These energies are very small and the resultant bond strength is much smaller than in an ordinary covalent bond; it still, however affects many properties of a compound. Its value depends not only on the two end elements involved, but also on other conditions, e.g. groups attached to them. For example the energy of the

O - H...O bond varies from 3 to 6 kcal mole⁻¹ while that of the N - H...N bond varies from 3 to 5 kcal mole⁻¹ (151). If there are some electronegative elements in the acid molecule, they will certainly form hydrogen bonds with water molecules.

(3) Dipole-dipole interactions. The water molecule is a dipole, which will interact with any polar group present in the acid molecule. This is purely an electrostatic term and can be evaluated by Coulomb's law if the dielectric constant involved is known accurately. This, however, presents a difficulty since the bulk dielectric constant is only applicable to a macroscopic system, and the application of the theory of dielectric saturation is not very successful.

B. Interaction Between Ions And Water Molecules

The interaction between an ion and water molecules involves, in addition to the three types of interactions mentioned above, the ion-dipole interaction. This is also purely electrostatic. Its value is equal to $124 \cos \theta / r^2$ kcal mole⁻¹, if an isolated water molecule and an ion were placed in a vacuum, where r is the distance from the ion to the centre of the dipole in Å and θ is the angle of orientation. The calculation, however, becomes difficult in solution owing to the uncertainty of the dielectric constant of water at short distances from ions. Nevertheless it is reasonable to conclude that all of the water molecules in

the first layer around any monoatomic ion are bonded to the latter with an energy greater than the thermal energy, kT ; i.e. they lose their rotational and translational freedom. Considering the water molecules as being absorbed, using the modified Brunauer-Emmett-Teller adsorption isotherm Anderson (152) has calculated the energy of adsorption by an ion of the first layer of water molecules to be about 1.3 to 2.4 kcal mole⁻¹ higher than the latent heat of vaporization. The fact that water molecules are bound to ions is also indicated by the hydration numbers determined in various ways. Although the values obtained by different methods are not consistent, nevertheless they do show hydration phenomena.

Certain facts about the structure of water are relevant in this connection. The water molecule, because of its lone-pair electrons on the oxygen atom, possesses high hydrogen bonding power. In ice a water molecule is bound tetrahedrally to four nearest neighbours: that is, each oxygen atom is surrounded tetrahedrally by four other oxygen atoms 2.76 Å away. Four hydrogen atoms lie on the O...O line, two of them being 1.01 Å apart, the other two 1.75 Å apart. The two closer H atoms belonging to the central oxygen atom, form a molecule; the other two hydrogen atoms belong to two other water molecules. Ice is therefore a molecular crystal. When ice melts to form water the O-H bond shortens to 0.97 Å. Because molecules of liquid are in continuous motion, hydrogen

bonds must be continuously breaking and reforming. These processes are much faster than the thermal motion but are slower than corresponds to the infrared and Raman frequencies. Hydrogen bonding in liquid water is thus still detectable by infrared and Raman spectra. The average distance between two oxygen atoms is about 3.10 \AA so that hydrogen bonds in liquid water are longer than in ice and are consequently weaker and more flexible. They can be bent independently, which is not the case in ice. The bending of a hydrogen bond absorbs energy, and this accounts for the high heat capacity of liquid water (153). The average structure of liquid water is cubic with all oxygen atoms occupying the lattice positions (154). Each water molecule has six nearest neighbours, so that the structure of liquid water is more compact than that of ice. There is still, however, some tetrahedral structure in liquid water at low temperatures. Thus Ginnings and Eurakawa (155) found that the heat capacity of liquid water at constant pressure shows a minimum near 35° C , although this effect is small compared with the total heat capacity ($\approx 1\%$). This indicates that there are two types of structure in liquid water; the heat capacity of the tetrahedral structure decreases with rising temperature while that of the cubic structure increases with temperature, and these two tendencies nearly balance at 35° C . The effect of pressure on the viscosity of water is more convincing (156). The viscosity-

pressure isotherm at 0° C shows a marked minimum at above 1000 kg. cm⁻². This is the well-known evidence for the existence of an ice-like structure which is broken by compression above this pressure. As the temperature increases, this minimum becomes shallower and finally disappears at about 30° C, which might imply that the open tetrahedral structure of ice no longer exists.

C. The Situation Of Ions In Water

The situation of an ion in water has been picturized by Frank and Wen (157), based on the idea of Frank and Evans (147). Immediately outside the ion there is a region called the hydration shell, in which all of the water molecules are bound firmly to the ion. This region may further be divided into two zones. The inner one is called the primary hydration shell, and in it the water molecules are attached to the ion with loss of rotational and translational freedom. For univalent ions, this shell usually contains four water molecules. The outer shell is called the secondary hydration shell; a water molecule in this shell retains some translation freedom but has lost its rotational freedom owing to dielectric orientation by the ionic field. All of the water molecules in both the primary and secondary hydration shells can exchange actively with the rest of the water molecules (158). The orientation effect of the ionic field is spherically symmetrical. Around

a positive ion the water molecules are oriented with their oxygen atoms inward and hydrogen atoms outward. The orientation about a negative ion is the opposite. Outside the hydration shell there is a region of disorder in which the water molecules are in a state of great randomness. Beyond this disorder zone is the ordinary water structure. In ordinary water the molecules are oriented tetrahedrally or cubically by hydrogen bonding forces. In the hydration shell, water molecules are oriented spherically symmetrically by the ionic field. In the disorder zone, these two forces are approximately balanced, and the water molecules have more freedom. The evidence for this zone is as follows:

(1) Frank and Evans (147) compared the entropy of hydration and the entropy loss when gas ions dissolve in water. The former value is the difference between the molal entropy of gas ions computed from statistical thermodynamics (this will be discussed in somewhat more detail later) and the experimental value of the molal entropy of the salt. The latter value is estimated as due to the free volume effect and hydration only. When they did this they found that the estimated entropy loss when an ion dissolves in water is numerically much bigger than the actual entropy of hydration, i.e. the ion lost too little entropy when dissolved in water. They attributed this to formation of the disorder zone.

(11) Entropies of solution of alkali halides in absolute methanol (159) are, on the average, about 15 e.u. more negative than the corresponding entropies of hydration. Frank and Evans estimated that about 5-10 e.u. is due to the fact that no disorder zone is formed in methanol solution.

(111) Frank and Robinson (160) concluded from the study of entropies of dilution of alkali halides that the structure of water has been broken by some electrolytes.

The distance from the centre of the ion to the end of the disorder zone is about 5 \AA (79), but the relative thickness of the hydration zone and disorder zone depends on the individual ion. Small polyvalent ions have strong ionic fields. They create a hydration zone more than a disorder zone, and are called "structure promoters". Large univalent ions create more disorder zone than hydration zone, and are called "structure breakers". "Structure promoters", therefore, decrease the entropy of water while "structure breakers" increase it. Since structure affects viscosity and the viscosity will decrease with increase in size of the disorder zone, one would expect some sort of relationship between entropy and viscosity. Gurney (161) showed that ionic entropy decreased linearly with the viscosity B-coefficient of Jones and Dole (162). This supplies strong support for the general theory discussed above.

3. INTERPRETATION OF PREVIOUS RESULTS BY THE SOLUTE-SOLVENT INTERACTION THEORY

The solvent interaction theory of ionization process is capable of explaining a number of previous results. The ionization of fatty acids produces charge, while the ionization of α -amino acid hydrochlorides creates no new charge. The entropy of ionization in the former case is much more negative than in the latter. This is because the charged ammonium group binds water both to the unionized and to the ionized forms, so that less water can be influenced by the carboxylate ion. Polar groups will also bind water molecules. Their presence in acid molecule will therefore decrease the absolute value of the entropy of ionization. For example, entropies of ionization of chloroacetic acid (42), glycolic acid (45-b), acetyl glycine (89) and propionyl glycine (89) are all about -17 e.u., which is about 5 e.u. less negative than the entropy of ionization of normal fatty acids. The entropy of ionization of d-tartaric acid (-11.4 e.u.) (66) is about 5 e.u. less negative than that of succinic acid (-16.7 e.u.) (65-b). Another factor, restricted rotation, may also play a role in determining the entropy of ionization (79). According to electrostatic theory, groups of low dielectric constant embedded in a medium of high dielectric constant are repelled from the neighbourhood of a charge or polar group. Because of this, the hydrocarbon chain of the acid molecule is stiffened after ionization. The presence of polar groups

in the acid molecule stiffens the hydrocarbon chain before ionization, so that less decrease in entropy results on ionization.

It is instructive to examine the entropy of ionization of two different series of weak electrolytes: the normal fatty acids and the alkyl-substituted ammonium ions. In the former series one goes from a neutral molecule to an ion, while in the latter series one goes from an ion to a neutral molecule: yet in both cases the entropy of ionization decreases when a hydrogen atom is substituted by a methyl group. The explanation of the fact that the effect of substitution by an alkyl group in the apparently two different types of reaction are the same must be based on the above discussed model.

Because of the distribution of the negative charge between two oxygen atoms, the ionic field in the carboxylate ion is weak. The hydration shell is therefore small, only extending to the back of the carbon atom. The hydrogen atom of the HCOO^- ion is embedded in the disorder zone. Replacement of a hydrogen atom by a methyl group displaces the high entropy water molecule. The entropy of the hydrated CH_3COO^- ion is thus more negative than that of the hydrated HCOO^- ; consequently the entropy of ionization of the former is also more negative than that of the latter. Increasing the chain length increases this effect.

The nearly spherical NH_4^+ ion and all the methyl substituted ammonium ions are all within the range of influence of the ionic field. It has been pointed out by Everett (163) that the iceberg around an inert molecule and the hydration shell around an ion have different properties. The water structure around an inert molecule or inert part of a molecule or ion is more close-packed and less stable. Under the influence of an ionic field it is converted into a hydration shell. Moreover the formation of an iceberg increases the heat capacity of the solution, while the formation of a hydration shell decreases the heat capacity, although they both lower the entropy. Since the iceberg is more order-packed than a hydration shell, it has a larger entropy-lowering effect than the latter. The entropy of ionization of these ions are all negative (54), but if the absolute entropy of the hydrogen ion is taken into account it is noticed that the entropy of the NH_4^+ ion is less than that of NH_3 by about 5 e.u., that of $\text{CH}_3\text{N}^+\text{H}_3$ is less than that of CH_3NH_2 by about 0.8 e.u., that of $(\text{CH}_3)_2\text{N}^+\text{H}_2$ is more than that of $(\text{CH}_3)_2\text{NH}$ by about 4 e.u., that of $(\text{CH}_3)_3\text{N}^+\text{H}$ is more than that of $(\text{CH}_3)_3\text{N}$ by about 10 e.u. That the entropy of NH_4^+ is less than that of NH_3 is understandable because of the formation of the hydration shell by the positive charge. The fact that the entropies of the last two ions are higher than those of their corresponding molecules seems a little puzzling. But

if it is considered that the entropy of the iceberg is lower than that of the hydration shell, this puzzling feature is immediately cleared up. Besides, the disorder zone makes the entropy of the ion higher. Therefore the more methyl groups the smaller will be the entropy of the molecule compared with that of the ion, and the entropy of ionization will be more negative.

The effect of chain branching is also to make the entropy of ionization slightly more negative, as in the pairs: glycolic acid (-17.2) (45-b), lactic acid (-18.2) (46), glycine (-7.3) (40), α -alanine (-8.1) (47), propionic acid (-22.9) (39-b), isobutyric acid (-25) (79). This can be explained in the same way as the chain lengthening discussed above. When chain branching and lengthening occur beyond 5 Å from the carboxylate group, they produce little or no effect, because of the limited influence of the ionic field.

4. FREE ENERGY OF IONIZATION

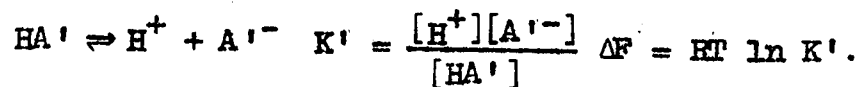
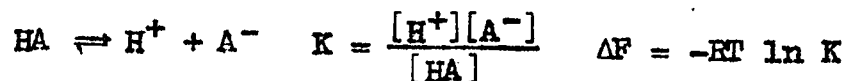
The free energy change of a reaction is related to the equilibrium constant K by the equation

$$\Delta F = -RT \ln K. \quad (117)$$

In some case plots of log K for one reaction for different substituted compounds against log K for another reaction for the corresponding substituted compounds (e.g. log K values

for the ionization of various substituted benzoic acids against those for corresponding substituted phenylacetic acids) show points falling on a straight line. This is referred to as a linear free-energy relationship.

Consider the ionization of the unsubstituted acid HA and the substituted acid HA':



The change of ionization constant by substitution may be expressed by another constant K_r ,

$$K_r = \frac{K'}{K} = \frac{[\text{HA}][\text{A}'^-]}{[\text{HA}'][\text{A}^-]} \quad (118)$$

which is the equilibrium constant of the reaction



The change of ΔF due to substitution is

$$\Delta \Delta F = \Delta F' - \Delta F = -RT \ln K_r . \quad (119)$$

The free energy change ΔF can be separated into a potential-energy change ΔE_p and a kinetic energy change ΔE_k . Kinetic energy includes vibrational, rotational and translational energies.

ΔE_k can be evaluated statistically from partition functions,

$$\Delta E_k = RT \ln (\pi Q), \quad (120)$$

where (πQ) is the ratio of the product of partition functions of the products to that for the reactants. These partition functions are based upon the energy levels of all forms of motions including zero-point vibration and solute-solvent interaction. However, the last term is difficult to evaluate.

ΔE_p involves the energy of the bond that is broken and the solute-solvent interaction energy. According to Taft (164) these energies arise from three contributions:

(1) Polar energy; the coulombic energy which results from charge separation between the functional group and the rest of the molecule.

(2) Resonance energy; if a compound can be written in two or more valence bond structures involving the bond to be broken, then there is a resonance energy contribution to the bond.

(3) Steric interaction, which may involve (i) the repulsive forces between non-bonded atoms in the functional group and in the rest of the molecules, and (ii) angle strain energy.

$\Delta \Delta F$, i.e. the effect of the substituent on the free energy of ionization, can also have these contributions.

Since the substituent changes the kinetic energy to approximately the same extent before and after ionization, $\Delta\Delta E_k$ is very small and $\Delta\Delta F$ is largely determined by $\Delta\Delta E_p$. In the case of meta and para substituted compounds the steric effect is not important and $\Delta\Delta F$ involves polar and resonance energy only, due to changes in the electron density at the reaction center. The effect of a substituent is, therefore, governed by two factors. One factor, designated by σ , is related to the ability of the substituent to change the electron density. The other is related to the susceptibility of the reaction to a change of electron density; this factor is designated by ρ . Since $\log \frac{K'}{K}$ is proportional to $\Delta\Delta F$, the following equation applies:

$$\log \frac{K'}{K} = \rho\sigma. \quad (121)$$

This is known as the Hammett equation (165). By arbitrarily assigning ρ and σ as unity for the ionization of benzoic acid and the hydrogen atom respectively, Hammett has succeeded in obtaining values of ρ and σ for various reactions and substituent groups, from which the equilibrium constant of an unknown reaction can be predicted. Positive values of ρ mean that the reaction is accompanied by a release of electron density at the reaction centre, while negative values of ρ indicates attraction of electrons. The higher the value of ρ the more sensitive is the reaction to the change of electron

density, and vice versa. A positive value of σ means that the group withdraws electrons, while a negative value of σ indicates electron donation. This σ value of Hammett is not a simple quantity. It can be resolved into σ_I , due to the inductive effect, and σ_R , due to the resonance. The σ value for a meta substituent is given by $\sigma_m = \sigma_I + \frac{1}{3}\sigma_R$, and that for a para substituent by $\sigma_p = \sigma_I + \sigma_R$. σ_I is equal to the σ' value of Roberts (166), which is the substituent constant for the ionization of bicyclo - (2,2,2) - octane-1-carboxylic acid substituted at the 4-position; no resonance can occur in this compound. From σ_p and σ' , the value of σ_R can be obtained by difference.

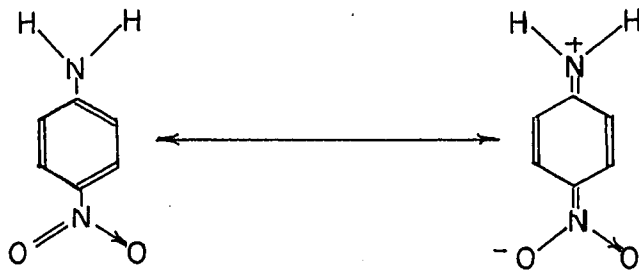
The ionization of acids is accompanied by a release of electrons. Electron-withdrawing groups thus facilitate ionization, and increase acid strength. Halogen and nitro substituted phenols, for example, are considerably stronger than phenol itself. Electron-donating groups decrease acid strength; thus the methyl group in the meta and para positions reduces the strength of phenol and benzoic acid. These polar effects are transmitted both through the bond as an inductive effect and through space as a field effect. The effect should therefore decrease with increasing distance between the substituent and the functional group. MacInnes (167) plotted the ionization constants of the hydroxyl and halogen substituted aliphatic acids against the reciprocals of distances d along the

carbon chain, taking d as 1,2,3,4 for the α , β , γ , δ positions respectively. Straight lines were obtained which can be represented by the equation

$$\log K = C + s \frac{1}{D}, \quad (122)$$

where C and s are constants depending on the nature of the substituent. An application of this formula will be made later. Branch and Calvin (168) assumed that the effect of a substituent on the acid strength decreases by a factor of 2.8 for each CH_2 group introduced between the substituent and the functional acid group.

Resonance within the substituent does not affect ionization. If resonance involves the functional group, however, an effect is observed; for example, the nitro group reduces the basicity of aniline by the following resonance:



Groups attached to the ortho position facilitate the ionization of benzoic acid; this effect has previously been known as the ortho effect and later classified as the steric effect. Thus all ortho-substituted benzoic acids have higher ionization constants than benzoic acid itself, even with those

substituents, such as alkyl groups, which generally decrease acid strength. This is because the ortho groups cause strain to the $-\text{COOH}$ group. This type of steric effect does not apply to phenol because there is no overlap between the hydroxyl and the alkyl group at the ortho position. Thus the ortho-substituted methyl phenol is weaker than the meta and para substituted ones.

The steric effect may hinder resonance and indirectly affect the pK. For example (169), 3,5-dimethylation decreases the acidity of phenol by 0.18 pK units and that of p-cyanophenol by 0.26 pK units; but it greatly reduces the acidity of p-nitrophenol by 1.09 pK units. (The pK values are p-cyanophenol 7.95; 3,5-dimethyl p-cyanophenol 8.21; p-nitrophenol 7.16; 3,5-dimethyl p-nitrophenol 8.25). This is because the nitro group cannot lie in the same plane as the ring, which is a necessary condition for resonance that stabilizes the anion. The resonance of the linear cyano group with the ring is not hindered. A similar explanation can be given to the fact that N,N-dimethyl-2,4,6-trinitroaniline is much more basic than 2,4,6-trinitroaniline (170), while N,N-dimethylaniline is only slightly more basic than aniline.

The relative magnitudes of the steric effects of different groups are represented by the E_s values of Taft (171):

$$E_s = \log \left(\frac{k}{k_0} \right)_A \quad (123)$$

where k is the rate of hydrolysis of substituted acetates or ortho-substituted benzoates, k_0 is the rate of hydrolysis of acetates or of ortho-methyl-substituted benzoates. The subscript A refers to acid hydrolysis. The assumption is made that the rate of acid hydrolysis of esters is independent of polar effects because the p value of these reactions are very small.

σ values are additive but E_s values are not. Therefore if the steric effect is not important, the free-energy change of a series of such reactions will be additive. Consequently pK values will be additive.

5. SUBSTITUENT EFFECTS ON THERMODYNAMIC FUNCTIONS AND ADDITIVITY

The above mentioned constituents of the free energy, together with solvent-solute interactions, affect the thermodynamic functions of ionization. Some general conclusions relative to these functions are as follows:

(1) The kinetic energy terms for the substituent usually remain the same before and after ionization. They therefore do not affect any thermodynamic function.

(11) On the basis of the analysis of thermochemical data for a number of ionization processes in aqueous solution it has been concluded (172) that polar and resonance effects affect ΔH_0 but not ΔS_0 and ΔC_p . They must therefore affect ΔH and ΔF in a parallel manner and leave $T\Delta S$ unchanged. Their effects are additive; if these effects are

predominant, ΔH and ΔF will be additive and ΔS and ΔC_p do not change. There will be linear free-energy relationships between different series.

(iii) Steric effects influence ΔH_o , ΔS_o and ΔC_p , and therefore affect ΔH , ΔF and ΔS in a complicated manner. If steric effects play an important role in the ionization process, these thermodynamic functions will not be additive and linear free-energy relationships between different series would not be found. However, under certain circumstances the steric effects on ΔH and ΔS may be of such a character that the magnitudes of ΔH and $T \Delta S$ are roughly equal; the free energy will still be additive and the linear free-energy relationships will remain.

(iv) Solvent effects also influence ΔH_o , ΔS_o and ΔC_p , and they also destroy the additivity and linear free-energy relationship. But sometimes the solvent-solute interactions are also additive. If this is the case, and also steric effects are not important, all of the thermodynamic quantities will be additive.

Very recently Laidler et al. (173-176) made a study of the thermodynamics of ionization process in aqueous solutions. They measured the heats of ionization of four series of methyl substituted compounds, namely pyridines, phenols, anilines and benzoic acids. In each series, good additivity was found for ΔF , but not for ΔH and ΔS . They also observed compensation

between ΔH and $T \Delta S$. They noticed that a rough linear free-energy relationship exists between the pyridines and the phenols and between the anilines and benzoic acids. No such relationship can be observed between the pyridines and the benzoic acids or between the pyridines and the anilines. It appears that the ionizations of pyridines and phenols constitute a fairly closely related pair of reaction types and that the anilines and the benzoic acid ionizations are another related pair. Probably the steric effects are insignificant in the former pair owing to the smaller functional group, but is important in the latter pair in which the functional groups are much bigger. These steric effects are apparently sufficiently important to affect the free energies, but not sufficiently great to destroy additivity. The compensation between ΔH and $T \Delta S$ is not complete. It is therefore seen that the existence of linear free-energy relationships requires two conditions: the existence of additivity relationships in free energy, and negligibly small steric effects.

Compensation of ΔH and $T \Delta S$ has been frequently observed (177) for reactions in solution. It arises from changes in the nature of the interaction between solute and solvent molecules. This subject has been discussed by Laidler (172). Three aspects may be considered:

(1) Longuet-Higgins (178) has shown theoretically that for a variety of "conformal" solutions the ratio of $T \Delta S$ to

ΔH of mixing is of the order of 0.5, indicating partial compensation. Therefore this compensation is independent of the exact nature of the solution or of the intermolecular forces.

(ii) The substituents may, through inductive, resonance and steric effects, influence the binding power of solute molecules to solvent molecules, and this in turn changes the vibrational frequency between them. The plot of E/T against S calculated from the vibrational partition functions showed that when $\nu/T > 5$ (where ν is the frequency of vibration in cm^{-1}), the slope of the curve approaches unity, i.e. there is complete compensation between E and TS . If the PV term remains unchanged there will be compensation between H and TS .

(iii) The substituent may also modify the frequency of restricted rotation of the solvent molecules. Everett, Landsman and Pinsent (79) pointed out that this modification may under certain circumstances change the heat capacity in the opposite direction to that of the entropy and free energy. This also gives rise to the compensation between H and TS .

It follows that a study of the free energy of ionization only provides information about polar and resonance effects. In order to study steric and solvent effects, it is necessary to measure other thermodynamic functions, especially heats and entropies of ionization.

6. HEATS OF IONIZATION

The heat of ionization is the total energy change during the ionization process. It is related to the variation of ionization constant with temperature. Unlike other thermodynamic quantities, this quantity varies considerably from reaction to reaction. It may have large positive values (e.g., ΔH for water is 13,500 cal. mole⁻¹) or large negative values (e.g., ΔH for orthonitro benzoic acid is -3,355 cal. mole⁻¹). In general, however, these values are small, and the ionization constants of weak acids do not change greatly with temperature.

Heats of ionization vary with temperature, as represented by the equation

$$\Delta H_T = \Delta H_0 + \int_0^T \Delta C_p dT \quad (124)$$

ΔH_0 is the heat of ionization at the absolute zero, and is equal to ΔF_0 , the standard free energy of ionization at the same temperature. This quantity has been suggested by Everett and Wynne-Jones (54) to be the measure of the intrinsic acid strength; but an alternative view was taken by Dippy and Jenkins (179).

7. ENTROPY OF IONIZATION

The entropy of ionization is the difference in entropy of the system before and after the ionization process. Consider

the ionization process



The entropy of ionization of this process is the difference between the sum of the entropies of H_3O^+ and A^- in solution and that of HA and H_2O in solution. Since entropy is an extensive property, and its value is independent of path, it can also be considered in the following way. An HA and an H_2O molecule are first vaporized from the solution. The HA and H_2O molecules in the gas phase are then dissociated into H_3O^+ and A^- ions. These ions are then dissolved in water. Since there is no change in the number of particles before and after the dissociation process, the "cratic term" (180) is zero. The entropy of ionization would be the entropy of dissociation in the gas phase, which may be termed the "intrinsic entropy change", plus the difference between the entropies of solution and the entropies of vaporization.

A. Intrinsic Entropy Change

According to statistical thermodynamics, the entropy of a substance arises from electronic, translational, rotational and vibrational contributions:

$$S = S_{\text{el}} + S_{\text{tr}} + S_{\text{rot}} + S_{\text{vib}}. \quad (125)$$

The electronic contribution to the entropy is equal to $R \ln G_0$, where G_0 is the degeneracy of the ground electronic energy state. In most cases there is only one ground state, so that S_{el} is zero. The translational contribution to entropy is

represented by the equation

$$S_{tr} = 4.576 \left(\frac{3}{2} \log M + \frac{5}{2} \log T - \log P - 0.505 \right) \quad (126)$$

where M is the molecular weight, T the absolute temperature, and P the pressure in atmospheres. The rotational contribution to entropy is represented by the equation

$$S_{rot} = 4.576 \left(\frac{1}{2} \log I_A I_B I_C + \frac{3}{2} \log T - \log \sigma + 58.51 \right) \quad (127)$$

where I_A , I_B and I_C are the moments of inertia in three principal axes respectively; σ is the symmetry number. The entropy corresponding to each normal mode of vibration is given by the equation

$$S_{vib} = \frac{Rx}{e^x - 1} - R \ln (1 - e^{-x}) \quad (128)$$

where $x = h\nu/kT$, and h is Planck's constant; k is the Boltzmann constant and ν the vibrational frequency of that particular mode.

The absolute entropy of a molecule therefore depends on its mass, temperature, volume, moment of inertia, symmetry number and vibrational frequencies of various modes, and the intrinsic entropy change can thus be considered on this basis. The intrinsic entropy change can again be computed from two parts. One is the difference in absolute entropy between the H_3O^+ gas ion and the gas H_2O molecule; the other is the difference in entropy between A^- and HA . The former is about

+ 1 e.u. as shown in Appendix II. The latter has been discussed by Pitzer (51). His considerations applied to the present case would be as follows:

(1) A^- is one mass unit lighter than HA; this causes the entropy of a gas ion A^- to be about 0.1 e.u. less than that of HA.

(2) If the A^- ion is non-linear, A^- and HA have the same rotational degrees of freedom and there will be no loss of entropy due to rotational contributions. However, if A^- is linear, HA is non-linear, and A^- will have one degree of rotational freedom less than HA. This makes the entropy of A^- about 5 e.u. less than that of HA at 25° C.

(3) There will be a loss of 3 e.u. in going from HA to A^- because of the loss of a vibrational mode of torsional character. The entropy difference due to loss of the other two modes of vibration is very small.

(4) The entropy loss due to the difference in symmetry number accounts for about 1 e.u.

In the present case, all anions are non-linear, so that the difference in entropies of A^- and HA is about -4 e.u. The intrinsic entropy change is, therefore, about -3 e.u.

B. Entropies of Dissolution

The entropies of dissolution of the four gaseous species in water are best considered separately.

(1) Entropy of dissolution of HA

(a) Free volume effect. A molecule can move freely in the gas phase. But when it enters into solution it is confined by the surrounding solvent molecules. The volume within which the solute molecule can move freely without collision with the solvent molecules is known as its free volume. This confinement of translational motion in a free volume box causes a decrease in entropy. According to Frank and Evans (147) this amount is about 3 to 4 e.u. less than the entropy of condensation of the solvent which for water is -28.3 e.u. at 25° C (see below). So the free volume contribution to the entropy of dissolution of HA molecule is roughly -25 e.u.

(b) Formation of H-bonding. There is H-bonding between the OH group of phenol and a water molecule. The entropy change due to the formation of an H-bond can be roughly estimated by the difference in the entropies of solution of alcohol and of the corresponding hydrocarbon in water which is about -5 e.u. (147).

(c) Formation of iceberg. It has been noted in a previous section that the water molecules around an inert solute molecule form an iceberg; the ring part of phenol molecule is, therefore, surrounded by an iceberg. Frank and Evans (147) showed that the differences in the entropies of solution of methane, ethane, ethylene and acetylene in water and in inert solvent are about -18, -20, -15 and -7 e.u. respectively, each of which can be

taken as the entropy loss due to the formation of an iceberg. It seems that the magnitude of this entropy loss increases with the size of the molecule and decreases with unsaturation. If we take 2 e.u. as the increase in entropy loss due to formation of an iceberg for each increase of CH_2 or CH_3 group, and 5 e.u. as the decrease in entropy loss for each double bond present, then the entropy loss due to the formation of an iceberg around a substituted benzene molecule would be -20 e.u.

(2) Entropy of condensation of H_2O

The heat of condensation of water vapor at 25°C is $-10481.4 \text{ cal mole}^{-1}$. The free energy change for condensing one mole of water vapor at a pressure of one atmosphere (standard state) to one mole of liquid water is equal to the free energy change when one mole of water vapor is expanded from a pressure of one atmosphere to the pressure of the saturated vapor, i.e., 23.69 mm Hg at 25°C .

$$\Delta F = RT \ln \frac{23.69}{760} = -2054.1 \text{ cal mole}^{-1}$$

$$\Delta S = \frac{\Delta H - \Delta F}{T} = \frac{-10481.4 + 2054.1}{298} = -28.3 \text{ e.u.}$$

(3) Entropy of dissolution of H_3O^+ and A^- ions

The entropy change when the gaseous H_3O^+ and A^- ions enter into water arises from the following contributions.

(a) Free volume effect. This is due to the same reason as has been mentioned above; but the amount is taken as -30 e.u.

owing to the large forces between the ion and its water neighbours.

(b) Restriction of rotation of H_3O^+ ion. Molecules or ions in gas phase have complete freedom of rotation. When they go to solute state, their rotation is restricted by the surrounding solvent molecules and becomes some sort of libration. The entropy of the latter may be represented in terms of some effective free angle ratio; but it is not easy to calculate. Everett and Coulson (183) suggested that the libration of water molecules contribute $2 \text{ cal deg}^{-1} \text{ mole}^{-1}$ to the heat capacity of liquid water. If we take entropy and heat capacity to be of the same magnitude, since the rotational entropy of H_3O^+ in gas phase is 11 e.u., the entropy loss due to restriction of rotation would be approximately 9 e.u. The entropy of dissolution of HA and A^- due to restriction of rotation should be nearly equal and need not be taken into consideration.

(c) Immobilization of the first-layer water molecule. The number of water molecules frozen by a univalent ion is usually four. This freezing is not as strong as in ice (147). The entropy of fusion of ice at 25° C is about 6 e.u. Frank and Evans assumed that the entropy loss due to the freezing of each water molecule by an ion is 3 e.u. The entropy loss due to the formation of the first hydration shell around a H_3O^+ ion is, therefore, $3 \times 4 = 12$ e.u. In the case of the phenolate ion, the number of the nearest-neighbour water is cut down by one.

Neglecting the complications that might arise from the "low dielectric constant" of the phenyl group, this term would be $3 \times 3 = 9$ e.u.

(d) Dielectric polarization of water molecules in the second hydration shell. This can be estimated by the use of Latimer's equation (181)

$$\Delta S = - \frac{22z^2}{r} \quad (129)$$

where z is the valency of the ion and r is the radius of the ion in Å. The value of ΔS is calculated for r between the outside radius of the first hydration shell and the limit of influence of the ionic field (5 Å from the surface of the ion). The loss of entropy of water molecules beyond this limit is estimated by the Born charging term. The outside radius of the hydration shell is the radius of the ion plus the diameter of a water molecule. In the case of the anion, the charged atom is oxygen and its ionic radius is taken as 1.4 Å. Taking the O-O distance as the diameter of a water molecule which is about 2.8 Å, this term is about -5 e.u. In the case of the cation, the diameter of a proton is very small in comparison with that of a water molecule. If the former is neglected and the size of an H_3O^+ ion is taken as equal to that of a water molecule, this term is also -5 e.u. Now taking r equal to 6.4 Å, (limit of influence of the ionic field) this term would be -3.5 e.u. Therefore the loss of entropy due to

dielectric polarization of water molecules in the second hydration shell of each type of ion is 1.5 e.u.

(e) Entropy due to the formation of the disorder zone.

This is the structure-breaking entropy of Frank and Evans. Its value varies with the size of the ion; the larger the ion, the greater is the structure-breaking entropy. There is no reliable theoretical way of estimating it. The structure-breaking entropy of the smallest ion listed by Frank and Evans, the F^- ion, is + 3.5 e.u. and this means that the ion is structure-forming. It does not mean that there is no disorder zone around the fluoride ion, because this zone is a necessary consequence of the existence of the hydration zone. A positive value of the structure entropy might mean that the disorder zone is very thin. The entropy change for its formation is so small that it is overcome by the errors involved in estimating the first two terms. The O^- , H_3O^+ and the F^- ions are approximately the same size, and this term is, therefore, expected to be of the same magnitude, i.e., 3.5 e.u.

(f) Entropy arises from the Born charging term in the water molecules outside the disorder zone. This is due to the change of dielectric constant with temperature. This term can be evaluated as follows. According to the Born equation

$$\Delta F = \frac{z^2 e^2}{2r} \left(\frac{1}{D} - 1 \right) \quad (130)$$

where ΔF is the free energy of transfer of an ion from vacuum to a medium of dielectric constant D , z is the valence of the ion, e is the electronic charge and r is the radius of the ion. The entropy change is then given by

$$\Delta S = - \frac{d \Delta F}{dT} = - \frac{z^2 e^2}{2r} \frac{d}{dT} \left(\frac{1}{D} \right). \quad (131)$$

To evaluate ΔS due to Born's charging term, the variation of the dielectric constant with temperature is required. Use is made of the Abegg equation (182)

$$\log D = A - b T \quad (132)$$

where A and b are constants. This equation may also be written as

$$D = e^{A' - b'T} \quad (133)$$

where $A' = 2.303 A$ and $b' = 2.303 b$. From this equation

$$\frac{d}{dT} \left(\frac{1}{D} \right) = b' e^{(-A' + B'T)} = \frac{b'}{D} \quad (134)$$

and substitution into (131) gives

$$\Delta S = - \frac{z^2 e^2}{2r} \frac{2.303 b}{D} \quad (135)$$

With $b = 0.002 \text{ deg}^{-1}$, $z = 1$, $D = 78.5$, $r = 6.4 \text{ \AA}$, equation (135) gives a value of -2 e.u. for each type of ion.

The above statement can be summarized as following:

Items	Contribution to ΔS
Intrinsic entropy change (in the gas phase)	- 3 e.u.
Entropy of removal of HA from solution	
free volume term	+25 e.u.
breaking of H-bonding	+ 5 e.u.
melting of iceberg	+20 e.u.
Entropy of vaporization of H_2O	+28 e.u.
Entropy of solution of H_3O^+ and A^- ions	
free volume term (-30×2)	-60 e.u.
restriction of rotation of H_3O^+	- 9 e.u.
formation of first hydration shell $(-12 - 9)$	-21 e.u.
formation of second hydration shell (-1.5×2)	- 3 e.u.
correction for disorder zone (-3.5×2)	- 7 e.u.
Born charging term (-2×2)	- 4 e.u.
	<hr/>
Total	-29 e.u.

The experimental values for phenol and methyl substituted phenols lie between -27 and -30 e.u. In view of the crudeness involved in the estimation of various terms, the agreement is very satisfactory.

8. HEAT CAPACITY OF IONIZATION

The large negative partial molar heat capacities of ions in solution are related to the loss of kinetic freedom of solvent molecules under the influence of the ionic field. The high heat capacity of water is due to its hydrogen bonded structure. Ions break the structure of water and reduce the heat capacity, and this makes the partial molar heat capacity of ions more negative.

The heat capacity of ionization is the main point of controversy. Everett and Wynne-Jones (54) claimed that this quantity is independent of temperature, while other authors regard it as temperature dependent. It is difficult to test experimentally which statement is true because the data available are limited to a small temperature range within which the change in this quantity is very small.

To estimate the heat capacity of ionization one must consider the effect on the heat capacity of water by the unionized acid molecules as well as that by the ions; the heat capacity of ionization is of course the difference between them. Everett and Coulson (183) have tried to treat this problem quantitatively, but unfortunately their treatment was not entirely successful owing to a number of complications. Their

treatment, in terms of a more recent picture of ions in solution, can be summarized as follows.

The heat capacity of ionization of weak acid arises from the following contributions:

- (1) Loss of kinetic freedom of water molecules in the hydration shell.
- (2) Breaking of the structure of water in the disorder zone.
- (3) Born's charging term.
- (4) Effect of free volumes.

It has been mentioned that water molecules in the first hydration shell have lost their rotational and translational freedom, whereas those in the second hydration shell have lost their rotational freedom but retain part of their translational freedom. Water molecules in the first hydration shell can still librate. Each water molecule can have three modes of rotation according to three main axes. The first axis is the one that joins the centre of the water molecule and the ion; rotation about this axis is called "spinning". The second axis lies in the plane of the average position of the water molecule, passes through its centre and is perpendicular to the first axis. The third axis passes through the centre of the water molecule and is perpendicular to both of the other

two axes. Restricted rotations about the last two axes are called "librations". Spinning rotation is not greatly affected by the presence of an ion; its contribution to the heat capacity of ionization can, therefore, be neglected. The contribution to the heat capacity of an ion by the two librational motions can be evaluated from the forces exerted on the motion by the ionic field. Its value depends greatly on the charge and radius of the ion and slightly on the temperature. In liquid water, the rotations of some of the molecules are also restricted. It is difficult to know what is the proportion of molecules undergoing restricted rotation, and which degree of rotation is restricted; their contribution to the heat capacity of water thus cannot be evaluated. Everett and Coulson simply assumed that the two librations contribute $2 \text{ cal deg}^{-1} \text{ mole}^{-1}$. The heat capacity of ionization due to the orientation of the water molecules is the difference between these two terms. They considered the hydration number of the first hydration shell to be four, for both cations and anions. The contribution to the heat capacity of ionization for an anion of radius 1 \AA at 25° C is about $14 \text{ cal deg}^{-1} \text{ mole}^{-1}$; for a cation of radius 1 \AA it is about $6 \text{ cal deg}^{-1} \text{ mole}^{-1}$ at the same temperature.

The change of heat capacity due to the orientation of water molecules in the second hydration shell and disorder zone is very complicated; a treatment of it requires a knowledge of the mutual interaction of the oriented molecules in

each layer and the extent to which the structure of water is broken. Even the structure of ordinary water is not known very accurately. Everett and Coulson include them in the Born charging term.

Born's charging term arises because of the change of dielectric constant of water with temperature, which in turn charges the free energy to charge the ions.

From equation (135) it follows that

$$(\Delta C_p)_{B.C.} = \frac{d\Delta H}{dT} = \frac{d\Delta F}{dT} + \Delta S + T \frac{d\Delta S}{dT} \quad (136)$$

$$= T \frac{d\Delta S}{dT} = - \frac{z^2 e^2}{2r} T \frac{d^2}{dT^2} \left(\frac{1}{D} \right) \quad (137)$$

Here $(\Delta C_p)_{B.C.}$ represents the change of heat capacity due to Born's charging term. Using Abegg's equation (182) for the variation of the dielectric constant with temperature,

$$(\Delta C_p)_{B.C.} = - \frac{z^2 e^2}{2r} T \frac{(b')^2}{D} = - \frac{z^2 e^2}{2r} T \frac{(2.303b)^2}{D} \quad (138)$$

Taking $b = 0.002 \text{ deg}^{-1}$, $r = 3.8 \text{ \AA}$ (radius of ion 1 \AA + diameter of water molecule, 2.8 \AA), $z = 1$, $D = 78.5$, $T = 298.16$, this gives a value for $(\Delta C_p)_{B.C.}$ of $-7 \text{ cal deg}^{-1} \text{ mole}^{-1}$ for both the cation and anion at 25° C .

The free volume arises from the restricted translation of the molecule. According to current theories of liquid structure, any molecule can be considered as moving in a

"cage" of uniform potential field made for it by the surrounding molecules. The molecule is confined in this cage for a certain length of time, and collides a number of times with its neighbours before it escapes from it. The time it spends in the cage is considerably longer than the period of vibration. The molecule can move freely inside this cage, and the effective volume it occupies is termed its free volume. The contribution of the free volume to the heat capacity of the liquid depends on how the volume varies with temperature. When an ion is present, the free volume of the liquid is decreased and the way it varies with temperature is also altered; this results in a change of the heat capacity. Again, the free volume for the undissociated molecule and that for the ion are different from one another, and the same is true of their temperature dependence. This will again contribute to the heat capacity of ionization. Because of the lack of knowledge in this field it is impossible to make a quantitative estimation. This effect probably takes care of the rest of the heat capacity of ionization.

With regard to the change of heat capacity of ionization with temperature, it is necessary to discuss the above mentioned contributions separately. The last term cannot be considered because even its contribution is not known, not to mention its temperature variation. The absolute value of Born's charging term increases with increasing temperature, while that due to

the first hydration shell decrease with rising temperature. These two terms almost cancel each other as shown from Everett and Coulson's calculation. This, of course, should not be considered as proof for the temperature invariant heat capacity of ionization because of two reasons. Firstly, Born's charging term should not include the change in heat capacity due to the second hydration shell and the disorder zone. Secondly, the free volume effect has been neglected. If it is considered from the point of view of the solvent solute interaction a qualitative conclusion might be reached.

It has been mentioned that there are three main kinds of interactions in the ionization system:

(1) Short-range hydrogen-bonding forces which produce the quasi-crystalline structure of water.

(2) Short-range forces of molecule-solvent interactions which produce iceberg.

(3) Long-range forces of ion-solvent interaction which produce the hydration shell.

Of these three, the first one is more easily destroyed by temperature and the last one is more widespread in effect. As the temperature increases, the tetrahedral orienting effect of the hydrogen bonding forces becomes weaker, but the strength of the ionic field is not affected by temperature. As a result the disorder zone becomes bigger. Since this zone reduces heat capacity, the heat capacity of the final product

will decrease as the temperature increases. In other words, the heat capacity of ionization will be more negative. The second term acts on the inert part of the molecule. Since the heat capacity of ice increases with increasing temperature, the heat capacity of the unionized molecules which are surrounded by icebergs will be bigger at higher temperatures; the heat capacity of ionization will also be more negative. Hence the absolute value of the heat capacity of ionization is very likely to increase with temperature unless the free volume term acts in the opposite direction and overcomes it.

9. THE TEMPERATURE OF MAXIMUM IONIZATION

The ionization constants of weak acids have an optimum temperature, at which the ionization is a maximum. Roughly speaking, the higher this temperature, the weaker the acid. Thus water is the weakest of all acids and has the highest optimum temperature (about 291° C). The optimum temperatures of fatty acids lie between 0° to 60° C, and those of phenol and methyl substituted phenols are around 170° and 180° C. For strong acids like mineral acids and halogen-substituted carboxylic acids, the optimum temperatures are below 0° C. There is, however, no exact relationship between this quantity and the acid strength. The optimum temperature can be related to the heat of ionization in the following way. According to Harned and Robinson's equation,

$$\Delta H = A' - C'T^2 . \quad (139)$$

When $T = T_m$ (optimum temperature in absolute scale), $\Delta H = 0$; therefore

$$A' = C'T_m^2 . \quad (140)$$

Substitution into equation (139) gives

$$\Delta H = C' (T_m^2 - T^2) . \quad (141)$$

Therefore

$$T_m^2 = \frac{\Delta H}{C'} + T^2 . \quad (142)$$

C' is a parameter in Harned and Robinson's equation and is related to ΔC_p according to equation (94). Since C' does not vary much from acid to acid, at any specified temperature T , say 298.16 K, there should be a corresponding tendency of variation of T_m and of $\Delta H_{298.16}$ among acids.

Gurney proposed that the work required to separate a proton from the acid molecules can be divided into a non-electrostatic part $\Delta F_{n.e.}$ and an electrostatic part ΔF_e as has been mentioned previously. From this idea he developed the expression

$$\theta = \frac{1}{b} \left[1 + \frac{\Delta F_{n.e.}}{\Delta F_e(\theta)} \right], \quad (143)$$

where θ is the optimum temperature in centigrade scale, $\Delta F_e(\theta)$ is the electrostatic part of the free energy at the

optimum temperature (this part of the free energy is temperature dependent), and b is a constant characteristic of the solvent which relates the change of dielectric constant with temperature given in Abegg equation. From this expression it is seen that the value of θ depends neither on the total ΔF nor on either $\Delta F_{n.e.}$ or ΔF_e alone, but depends on the relative magnitude of $\Delta F_{n.e.}$ and ΔF_e . Therefore one can not expect a relationship between θ and the degree of ionization because the latter quantity depends on ΔF . This expression is quite successful for explaining the behaviour of different types of acids, but is not very good applied to similar acids. For example, the introduction of a methyl group to the α -carbon atom of fatty acids and acyl-amino acids decreases the value of θ by 15° to 20° C, while the difference in θ between fatty acids and amino acids is only about 30° . Again, if θ depends on the ratio of ΔF_e and $\Delta F_{n.e.}$, and since ΔF_e varies greatly with the dielectric constant of the solvent, so should the value of θ . But this is not found to be the case. The difference between this value for fatty acids in dioxane-water mixtures containing 20% dioxane and 70% dioxane is only 3° C in the case of propionic acid (59) and 25° C in the case of formic acid (69). This difference between the behaviour of formic acid and propionic acid is also difficult to explain. Furthermore the optimum temperature for the ionization of acetic

acid in mixtures of methanol (48) and water, and for the basic ionization of glycine in dioxane-water mixtures (72), increases as the percentage of organic solvent increases. This is also contrary to Gurney's expression because it predicts a decrease in θ with decreasing dielectric constant. For ionization processes it is more adequate to base a treatment upon the solvent-solute interactions, including the chain-stiffening effect, rather than on the simple electrostatic theory which treats the water as a structureless dielectric medium. The importance of solvent-solute interactions can be demonstrated by the work of Brescia, LaMer and Nachod (184). These authors found that the difference in θ between acetic acid in water and deuterio acetic acid in heavy water is 9° C, the same as the difference in the temperature of maximum density of water and heavy water. This difference is due to differences in binding power of the molecules of the two solvents.

CHAPTER 3

EXPERIMENTAL METHODS AND RESULTS

1. MATERIALS

The chemicals used were of highest purity. Phenol, the cresols and the xylenols were purified either by vacuum distillation or recrystallization from water and their melting points checked. Their values are listed in Table 1. With the exception of 3,5-xyleneol the observed values agree well with the accepted values (185).

The water used was redistilled from an all-glass apparatus, out of contact with rubber or plastic tubing, reboiled to expel carbon dioxide and cooled under the protection of a soda-lime tube. It was found that rubber and plastics (except lucite) in contact with water show absorption. The sodium hydroxide and hydrochloric acid were of the highest grade obtained commercially, and were used without further purification. Saturated sodium hydroxide solution was prepared and stocked in a paraffin-lined bottle which was then used to prepare the desired reagent free from carbonate. The sodium carbonate had been heated to 270-300° C for half an hour. The sodium bicarbonate was dried in a desiccator over phosphorus pentoxide for two or three days. The borax was recrystallized from water and left to dry in air carefully with occasional stirring until it just began to show fluorescence; and its formula was taken as $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$. "THAM"

Table 1
Melting Point of Phenols

Materials	Method of purification	m.p. observed	m.p. accepted (185)
phenol	vacuum distillation	40.5-41.5°C	42°C
o-cresol	vacuum distillation	30-31°C	31°C
m-cresol	vacuum distillation	11.2°C	12°C
p-cresol	vacuum distillation	35-36°C	36°C
2,3-xyleneol	vacuum distillation	73.5-74°C	75°C
2,4-xyleneol	vacuum distillation	24-25°C	26°C
2,5-xyleneol	recrystallization	74-75°C	74°C
2,6-xyleneol	recrystallization	47-48°C	49°C
3,4-xyleneol	recrystallization	63.5-64.5°C	63°C
3,5-xyleneol	recrystallization	61.5-62.5°C (constant)	68°C

(tris hydroxymethyl aminomethane) was a crystallized commercial preparation. All the solutions were stocked under an atmosphere of nitrogen.

2. APPARATUS

The apparatus used for the determination of ionization constants at different temperatures is shown in Figure 2. A is a pyrex glass cell with quartz windows at the ends; the distance between the windows was about 8 cm. The quartz windows, about 1.2 cm. in diameter, were cemented to the pyrex glass cell with Hysol epoxy-adhesive cement. This cement is suitable for present purposes because it does not increase the absorption of the solvents (0.1 M NaOH, 0.01 M HCl, 0.01 M and 0.025 M buffers). B is a two-litre beaker used as a water bath. C is a glass container of about 150 ml. capacity. D is a pump also made of glass; it was driven by a small motor not shown in the figure. The outlet tube O, at the bottom of C is tangential to the periphery, so that when D rotates, the solution in C is pumped to circulate through the cell A. The pump D has a mercury seal to prevent the contact of solution with air and also to prevent evaporation. All the connections were made of ground-glass joints and clamped tightly. This is of primary importance as rubber or tygon tubing contaminate the solution.

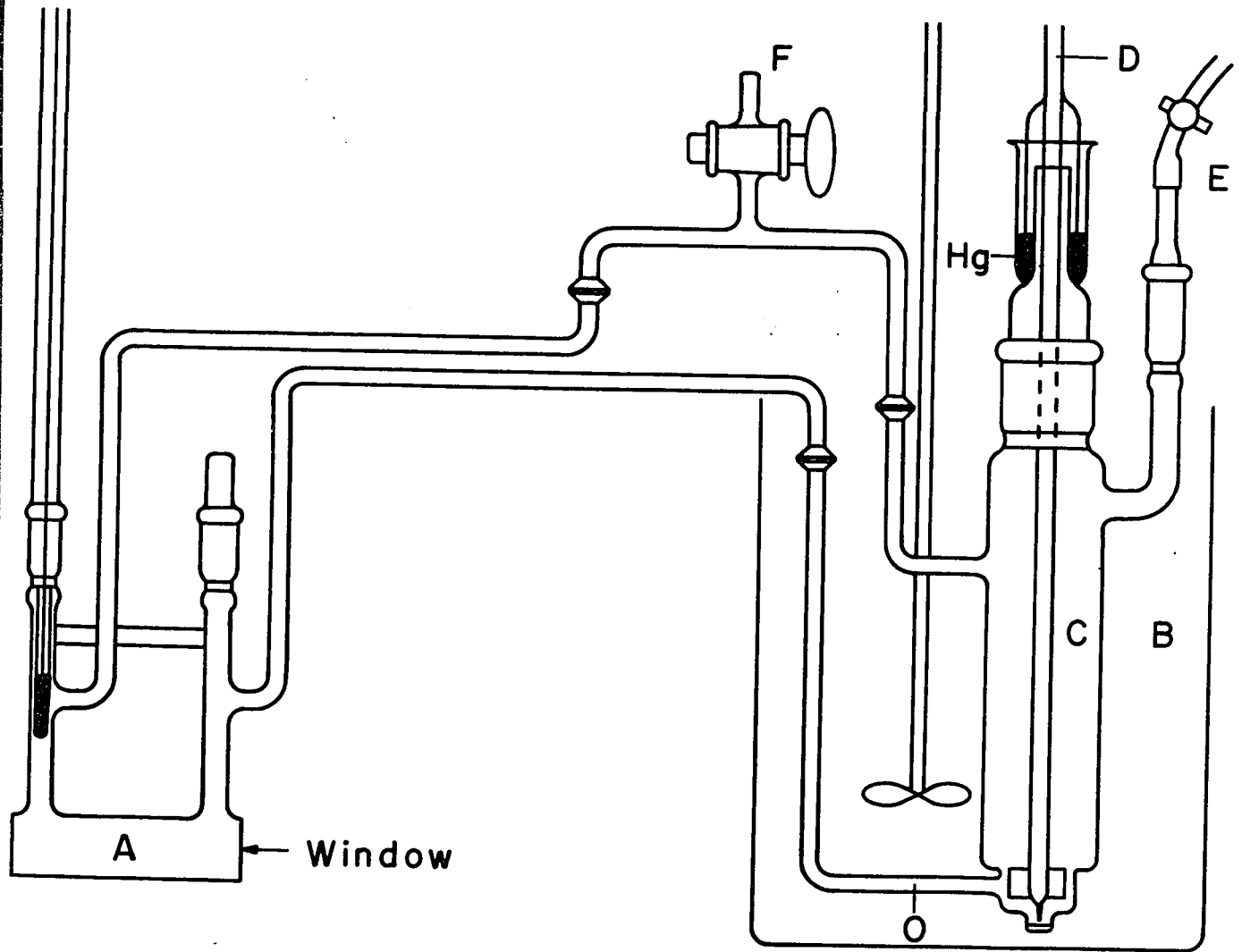


Figure 2. Apparatus for the determination of ionization constants at different temperatures.

3. PROCEDURE

About 0.1 g. of the sample was weighed out accurately in a stoppered bottle and dissolved in water. It was then diluted to about 0.0009 molar. 10 ml. of the solution was then diluted to 250 ml. with standard sodium hydroxide, hydrochloric acid and buffer solutions respectively so that the resulting solution was 0.1 M in NaOH, 0.01 M in HCl and 0.01 or 0.025 M in buffer. The concentration of the phenols in the final solution was about 0.000036 M. This gives an absorbance in the sodium hydroxide solution between 90 and 95, which gives maximum accuracy. To reduce error, the same volumetric flask and pipette were used. The air in the volumetric flask was displaced with nitrogen before dilution so that there was no danger of a change in pH owing to absorption of carbon dioxide. The spectrum was taken with a Beckman DK-2 ratio-recording spectrophotometer. The apparatus was set up as shown in Figure 2, with cell A placed in the cell compartment. After sweeping out all of the air in the system by a stream of nitrogen passing in from tube E, the solution was poured into C which then fills the cell A. To fill the connecting tubes with solution, gentle suction was applied through the tube F, with the stopcock open. As soon as the connecting tubes were filled with solution, the stopcock was closed. The glass rod D which has propellers at the lower end was then rotated by a small motor not shown in the diagram; this

keeps the solution in circulation through the cell. The cell compartment was then covered with a wooden cover specially made to fit the cell. It has six holes, four for the outlet tubes of the cell, one for rubber tubing to pass in dry nitrogen, the other one for exit. Dry nitrogen was then passed in to sweep out all the air in the compartment, in order to prevent the condensation of moisture on the surface of the cell windows when the solution was cooled below the dew point. The cell compartment was again covered with black cloth to keep out light. The temperature was adjusted manually by cooling with crushed ice or heating with an electric heater. The temperature of the solution was taken by a mercury thermometer which had been calibrated indirectly with a platinum resistance thermometer. The temperatures of the solution at the two ends of the cell were found to be the same. The instrument was run at a time constant of 0.1, absorption range of 0-1, sensitivity of 0-10. The scanning time was not the same for the whole spectral range. Owing to a delay in the response of the recording pen, the absorption occurs at a slightly lower value when a higher scanning speed is used; the difference is larger when there is a high peak of absorption. Because of the difficulty of keeping the temperature constant, the scanning time was set at 3 (the lowest scanning speed) only 10 millimicrons before and after the chosen wavelength. For the rest of the region the scanning time was set at 2 or even 1 (the highest

speed). The spectrum was taken at 25° C at first, then at 5° C, 10° C, 15° C, 20° C and then checked at 25° C; then at 38° C, then at 30° C and finally 25° C again. The spectra were taken twice at each temperature one descending and one rising. If the instrument was in good condition the two spectral curves coincided and the three checks at 25° C differed by less than 0.2 absorption.

Ionization constants at different temperatures were determined for phenol, the three cresols and the six xylenols. For phenol and meta cresol, 0.025 M sodium carbonate and 0.025 M sodium bicarbonate buffer solution was used; for the other phenols 0.01 M sodium carbonate and 0.01 M sodium bicarbonate buffer solution was used. This was done to obtain maximum accuracy, the pH of the buffer solution used being closest to the pK of the compound. The determinations were done in duplicate for each compound. The pK values for phenol and the ortho and meta cresols were also investigated by using 0.05 M borax buffer solution. The pK values of the rest of the compounds are far from the pH value of this buffer solution; this makes the method not applicable because the absorbances at different temperatures are too close together to be read accurately. In addition a measurement was made of the heat of ionization of ortho-chlorophenol using 0.01 M THAM buffer solution. The measurements were also done in duplicate. One was with THAM theoretically half neutralized by standard hydrochloric acid

obtained from the constant boiling mixture, and the other with THAM neutralized by hydrochloric acid so that the pH of the solution is equal to its pK; this was done using a pH meter.

4. CALCULATIONS AND RESULTS

A. The pK Values

It has been shown that the ionization constant can be determined by the spectrophotometric method according to the equation

$$pK = pH + \log \frac{b - \epsilon}{\epsilon - a} - \log \gamma . \quad (144)$$

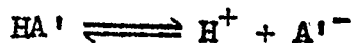
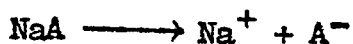
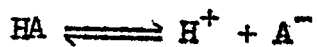
The pH values for the sodium carbonate and sodium bicarbonate buffer solutions at various temperatures were obtained from Bates, Pinching and Smith (186). That for 0.05 M borax buffer was taken from Manov, Delollis, Lindvall and Acree (187). The pH values at intermediate temperatures were interpolated from plots of pH against $1/T$. The pH of the THAM buffer was calculated from the pK_a of THAM recently determined by Hetzer and Bates (188).

The pH values of all the above-mentioned standard buffer solutions at different temperatures are listed in Table 2.

The pH of the buffer will change after the addition of a small amount of phenol. This problem has been treated by Robinson and Kiang (118) as follows. Let K be the ionization constant of the weak acid of the buffer HA, (HCO_3^- in the

present case of NaHCO_3 and Na_2CO_3 buffer), and K' be the ionization constant of the weak acid HA' (phenol in the present case) which is being added to the buffer to produce a change of pH of the latter. Let m_1 , m_2 , and m_3 be the stoichiometric concentrations of HA , NaA and HA' respectively.

Owing to the equilibria



the following species are in the solution: H^+ , A^- , Na^+ , A'^- , HA , HA' . If their respective concentration be represented using square brackets, the following equations may be written down:

$$m_1 = [\text{HA}] + [\text{A}^-] - m_2 \quad (145)$$

$$m_3 = [\text{HA}'] + [\text{A}'^-] \quad (146)$$

$$K = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (147)$$

$$K' = \frac{[\text{H}^+][\text{A}'^-]}{[\text{HA}']} \quad (148)$$

Since the solutions must be electrically neutral, the sum of the positive charges must equal to that of the negative charges, i.e.,

$$[\text{Na}^+] + [\text{H}^+] = [\text{A}^-] + [\text{A}'^-] \quad (149)$$

or

$$m_2 + [\text{H}^+] = [\text{A}^-] + [\text{A}'^-] \quad (150)$$

Solution of equations (145) and (147) gives

$$[\text{A}^-] = \frac{m_1 K + m_2 K}{K + [\text{H}^+]} \quad (151)$$

From equations (146) and (148) one obtains

$$[\text{A}'^-] = \frac{m_3 K'}{K' + [\text{H}^+]} \quad (152)$$

Substitution of (151) and (152) in (150) gives

$$[\text{H}^+] = \frac{m_1 K - m_2 [\text{H}^+]}{K + [\text{H}^+]} + \frac{m_3 K'}{K' + [\text{H}^+]} \quad (153)$$

Let the hydrogen ion concentration of the buffer in the absence of HA' be $[\text{H}^+]'$; by an analogous treatment it can be shown that

$$[\text{H}^+]' = \frac{m_1 K - m_2 [\text{H}^+]'}{K + [\text{H}^+]' } \quad (154)$$

Therefore

$$[\text{H}^+] - [\text{H}^+]' = \frac{m_1 K - m_2 [\text{H}^+]}{K + [\text{H}^+]} - \frac{m_1 K - m_2 [\text{H}^+]' }{K + [\text{H}^+]' } + \frac{m_3 K'}{K' + [\text{H}^+]} \quad (155)$$

$$= \frac{K([\text{H}^+]' - [\text{H}^+]) (m_1 + m_2)}{(K + [\text{H}^+]) (K + [\text{H}^+]')} + \frac{m_3 K'}{K' + [\text{H}^+]} \quad (156)$$

Rearrangement of equation (156)

$$[H^+] - [H^+]' = \frac{\frac{m_3 K'}{K' + [H^+]}}{1 + \frac{K(m_1 + m_2)}{(K + [H^+]) (K + [H^+]')}} \quad (157)$$

$$= \frac{m_3 K' (K + [H^+]')}{K^2 + K [H^+] + K [H^+] + [H^+] [H^+] + K(m_1 + m_2)} \quad (158)$$

Because K , K' , $[H^+]$, $[H^+]'$ are approximately equal, m_1 and m_2 are also approximately equal, and are much greater than the preceding quantities. Those terms that involve the square or product of two smaller quantities can be neglected, equation (158) then, reduces to

$$[H^+] - [H^+] = \frac{2m_3 K [H^+]'}{2m_1 K} = \frac{m_3}{m_1} [H^+]'. \quad (159)$$

Therefore

$$\frac{[H^+]}{[H^+]'} = \frac{m_3}{m_1} + 1 = \frac{m_1 + m_3}{m_1} \quad (160)$$

and

$$pH - pH' = - \log \frac{m_1 + m_3}{m_1} = \Delta pH. \quad (161)$$

The pH' values, which are the hydrogen ion exponents of pure buffer solutions, are given in Table 2. The values that

must be used in equation (144) are the actual hydrogen ion exponents for the solution under investigation; these have been designated as pH values and are equal to $\text{pH}' + \Delta\text{pH}$. The correction terms, ΔpH , for different solutions are listed in Table 3.

There are many equations, based on the Debye-Hückel interionic attraction theory, which relate activity coefficient to ionic strength. The one employed in the present work was that originally suggested by Gugenheim (189).

$$\log \gamma = \frac{-A \sqrt{\mu}}{1 + \sqrt{\mu}} + C \mu . \quad (162)$$

Here μ is the ionic strength, equal to $\frac{1}{2} \sum z_i^2 m_i$, in which z is the valence of the ion and m is the molarity; the summation is taken over all of the cations and anions present. A is a constant which takes into account the long-range coulombic forces between ions, and its value varies with the dielectric constant of the solvent and also with the temperature. For aqueous solutions values of A at different temperatures are given by Robinson and Stokes (190). C is the solution parameter which takes into account the short-range interactions between ions and solvent molecules. Its value varies with the solvent and solute and is determined empirically to fit the experimental data. Davies (191) pointed out that in the absence of experimental data, C in aqueous solution can be

Table 2
 pH' Values of Standard Buffer Solutions
 at Various Temperatures

t°C	0	5	10	15	20	25	30	38
0.01M ($\text{HCO}_3^- + \text{CO}_3^{=}$) (ref.186)	10.421	10.348	10.280	10.222	10.164	10.112	10.065	9.996
0.025M ($\text{HCO}_3^- + \text{CO}_3^{=}$) (ref.186)	10.325	10.249	10.184	10.125	10.068	10.018	9.972	9.907
0.05 $\text{Na}_2\text{B}_4\text{O}_7$ (ref.187)	9.512	9.434	9.362	9.305	9.247	9.196	9.152	9.085
0.01 (THAM) ⁺ (ref.188)	pK	8.678	8.516	8.362	8.214	8.075	7.935	7.727
	pH	8.720	8.559	8.406	8.258	8.119	7.980	7.773

Table 3
Correction Values for pH

Compound	m_1	m_3	$\frac{m_1}{m_1 + m_3}$	$\log \frac{m_1}{m_1 + m_3}$	ΔpH
phenol	0.025	0.00003800	0.9984	$\bar{1}.9993(-0.0007)$	-0.001
o-cresol	0.01	0.00003329	0.9966	$\bar{1}.9985(-0.0015)$	-0.002
m-cresol	0.025	0.00003579	0.9985	$\bar{1}.9993(-0.0007)$	-0.001
p-cresol	0.01	0.00004140	0.9958	$\bar{1}.9981(-0.0019)$	-0.002
2,3-xyleneol	0.01	0.00003405	0.9966	$\bar{1}.9985(-0.0015)$	-0.002
2,4-xyleneol	0.01	0.00003234	0.9967	$\bar{1}.9986(-0.0014)$	-0.001
2,5-xyleneol	0.01	0.00002616	0.9973	$\bar{1}.9988(-0.0012)$	-0.001
2,6-xyleneol	0.01	0.00002800	0.9972	$\bar{1}.9989(-0.0011)$	-0.001
3,4-xyleneol	0.01	0.00003618	0.9963	$\bar{1}.9988(-0.0013)$	-0.001
3,5-xyleneol	0.01	0.00003800	0.9962	$\bar{1}.9984(-0.0016)$	-0.002
o-Cl-phenol	0.01	0.00002692	0.9970	$\bar{1}.9987(-0.0013)$	-0.001

taken as equal to $0.1 |z_1 z_2|$. Biggs (120) took C to be 0.2, which has also been employed by Herrington and Kynaston (122). This value is twice as big as would be given by Davies. At first sight C is expected to be temperature dependent, but there is no theoretical relationship. Since this term is small compared to the square-root term of μ , its temperature dependence was neglected, and C is taken as equal to 0.2 for all temperatures. More rigorously the following equation should be used:

$$\log \gamma = \frac{-A \sqrt{\mu}}{1 + \alpha B \sqrt{\mu}} + C \mu, \quad (163)$$

where α is the closest distance the ions can approach, and B is a constant which also depends on temperature. Its values at different temperatures are also given by Robinson and Stokes (190). Its small temperature dependence was again neglected as compared to that of A , and αB was taken as equal to unity for all temperatures. This was proved to be satisfactory for monovalent ions by Gimblett and Monk (125). The equation used to calculate $\log \gamma$ is therefore

$$\log \gamma = \frac{-A \sqrt{\mu}}{1 + \sqrt{\mu}} + 0.2 \mu. \quad (164)$$

The values of $-\log \gamma$ for various buffer solutions at different temperatures were calculated and are listed in Table 4.

To evaluate the relative concentration term, the absorbances of the sample in acidic, alkaline, and buffer solutions

Table 4
Activity Coefficients at Different Temperatures

Temperature deg.C	5	10	15	20	25	30	38
A	0.495	0.499	0.503	0.507	0.512	0.516	0.524
0.025M (Na ₂ CO ₃ +NaHCO ₃) μ = 0.1	0.099	0.100	0.101	0.102	0.103	0.104	0.106
0.01M (Na ₂ CO ₃ +NaHCO ₃) μ = 0.04	0.075	0.075	0.076	0.077	0.077	0.078	0.079
0.01M THAM μ = 0.01	0.043	0.043	0.044	0.044	0.045	0.045	0.046
0.05M Borax μ = 0.15	0.108	0.109	0.110	0.112	0.113	0.114	0.116

were measured using the Beckman DK-2 Ratio-Recording Spectrophotometer. This instrument can record the absorbance of a solution in comparison with the solvent, i.e., the absorbance of the solute. But because of the difficulty of making two cells exactly the same length only one cell was used. This means that the absorbance of the solution is measured in comparison with air. The absorbance of the solvent against the air should also be measured and subtracted from that of the solution to get the absorbance of the solute. It has been found that the absorbance of the solvent, i.e., 0.1 M sodium hydroxide, 0.01 M hydrochloric acid and 0.01 M or 0.025 M buffer, does not change with temperature between 5° to 38° C within the instrumental error. The absorbance of the solvent is therefore measured at room temperature in each case. The absorbance of the completely ionized solution varies slightly with temperature. The spectra shift to longer wavelength with increase in temperature. The shift is not very much, only about 2 millimicrons from 5° to 38° C. The spectra at different temperatures intersect at two points, known as isosbestic points*. The isosbestic point is the point where all the spectra meet; there are two absorbing species in the solution and the absorbances of the two species are equal at this wavelength. Therefore no matter how their relative concentration is varied, the absorption remains

* Commonly, but incorrectly, referred to as "isobestic points."

unchanged. The existence of the isosbestic point is of great significance in studies of this kind. The non-existence of the isosbestic point implies that: (1) the solution contains more than two absorbing species, (2) the absorbance of the pure species changes with condition, the so-called "medium effect", (3) failure of the instrument, e.g., change of zero point during measurement.

Figure 3 shows the absorption curves of phenol in 0.1 M sodium hydroxide solution at different temperatures. Two isosbestic points can easily be detected. It seems that there are two species of hydrated anions (192). If the wavelength of the isosbestic point of the hydrated anions is chosen as the reference wavelength then the absorbance of the phenols in 0.1 M sodium hydroxide solution will be independent of temperature. The spectra of the phenol in 0.01 M acid solutions also change with temperature and exhibit isosbestic points (Fig. 4). This might also be due to the existence of two species of hydrated molecules. Since the change in spectra in the same temperature range is not as great as that of the anions, it appears that the difference in hydration between two species is greater in the latter case. The wavelengths of the isosbestic points of the undissociated molecules and anion do not coincide; therefore at the chosen reference wavelength the absorbance of the phenols in acid solution still varies with temperature. However, the

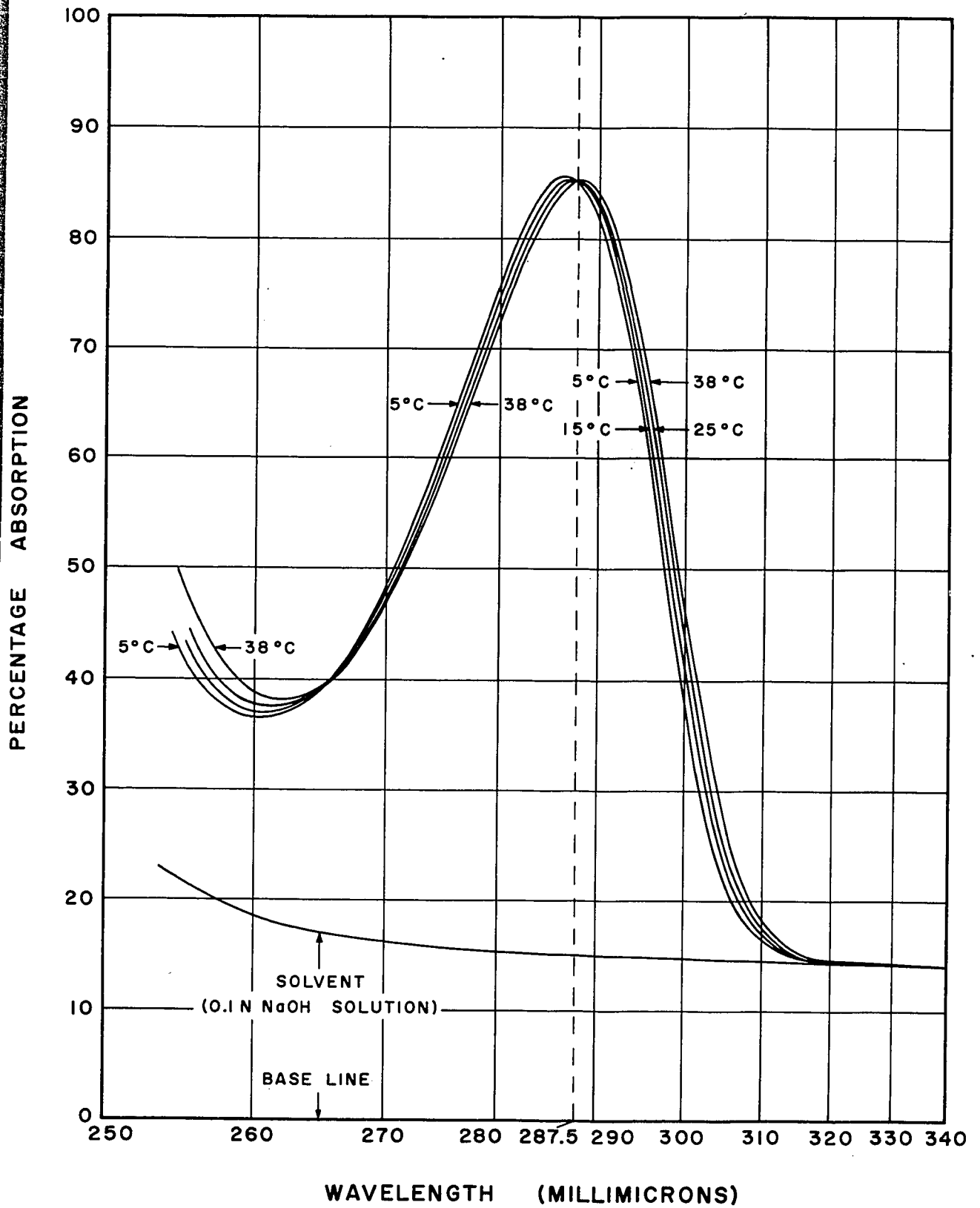


Figure 3. Spectra of phenol in 0.1 N NaOH solution at different temperatures.

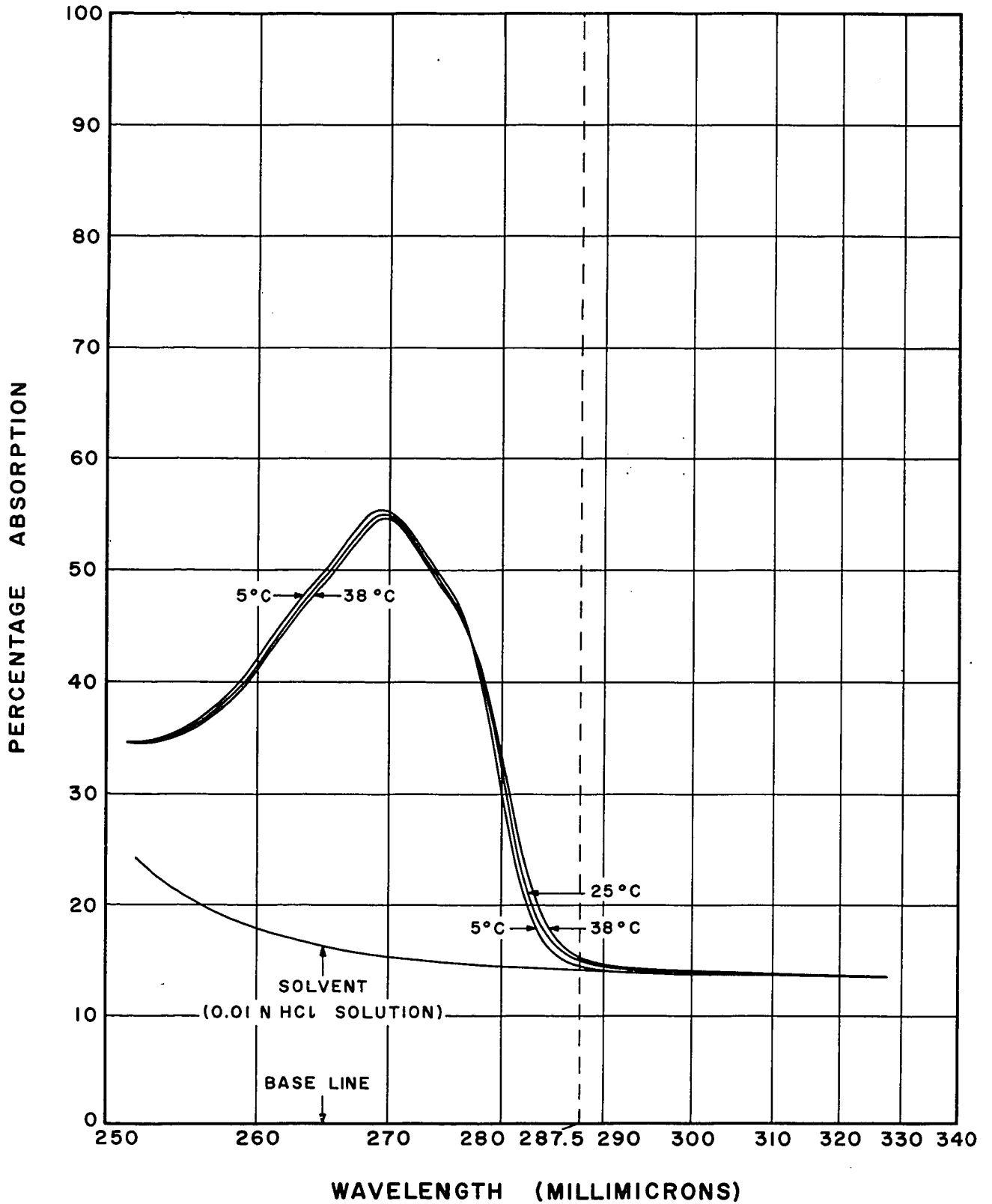


Figure 4. Spectra of phenol in 0.01 N HCl solution at different temperatures.

temperature variation is small and the procedure was to take spectra at three temperatures and to estimate the absorbance at intermediate temperatures by linear interpolation. The spectra of phenols in buffer solutions change greatly with temperature. This is due to the change in concentration of the ionized and unionized species as a result of the shifting of equilibrium. The shape of the spectra depends on the buffer solution used. The closer is the pH of the buffer to the pK of the phenol, the greater will be the separation of the spectra at different temperatures. This is shown in Figs. 5, 6 and 7 which represent the absorption spectra, at different temperatures, of phenol in carbonate buffer, phenol in borax buffer and ortho-chlorophenol in THAM buffer respectively.

The absorbance of the sample in acid solution minus that of the acid gives the value of a . The values of b in alkaline solution and of c in buffer solution are obtained in a similar way. They are listed in Table 5. Substitution of them together with pH and $\log \gamma$ values into equation (144) gives the pK values at each temperature.

It is instructive to take the pK value of phenol at 25° C as an illustrative example.

$$pK_{25} = pH_{25} + \log \left(\frac{b-c}{c-a} \right)_{25} - \log \gamma_{25} + \Delta pH. \quad (165)$$

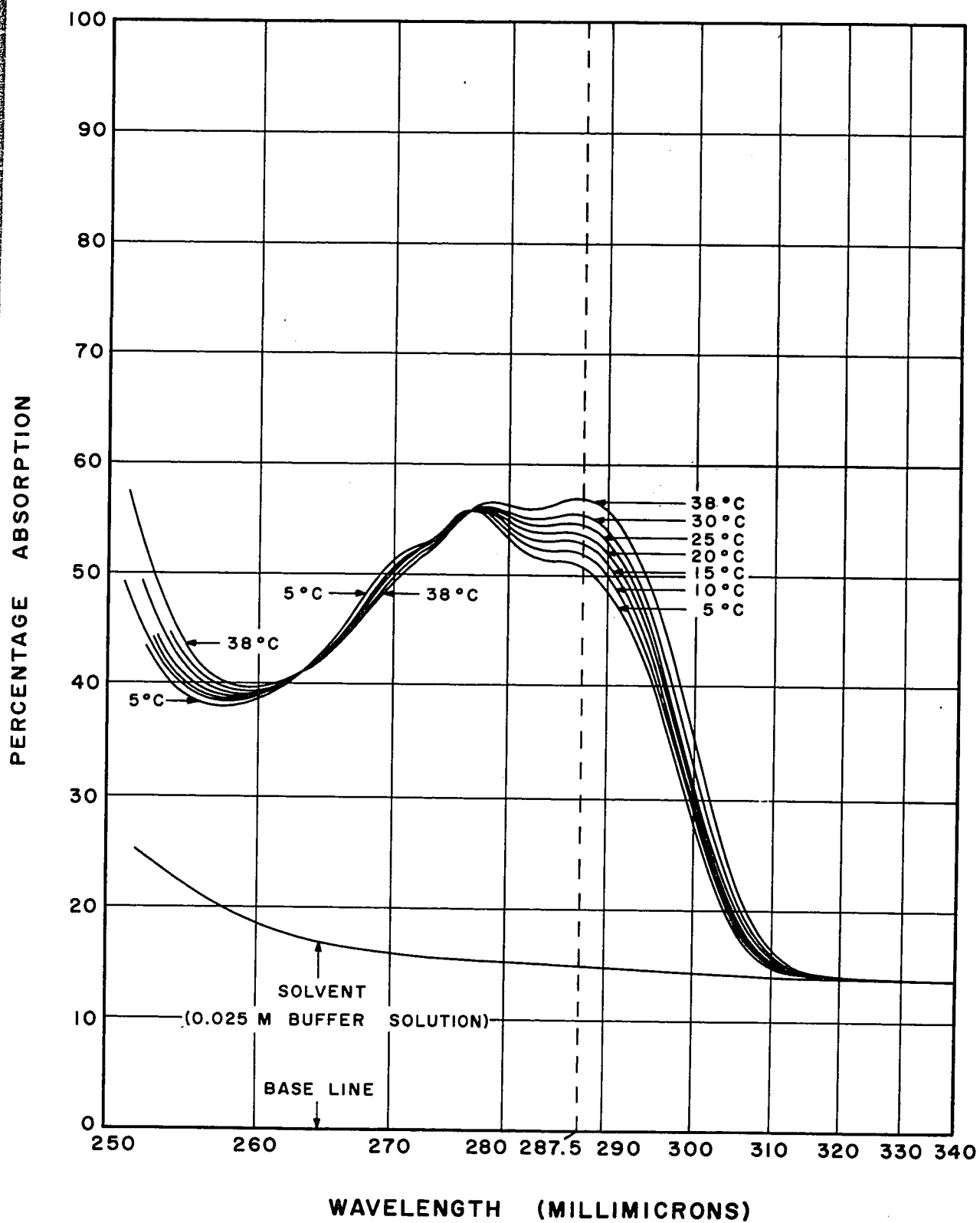


Figure 5. Spectra of phenol in 0.025 M Na_2CO_3 + 0.025 M NaHCO_3 buffer solution at different temperatures.

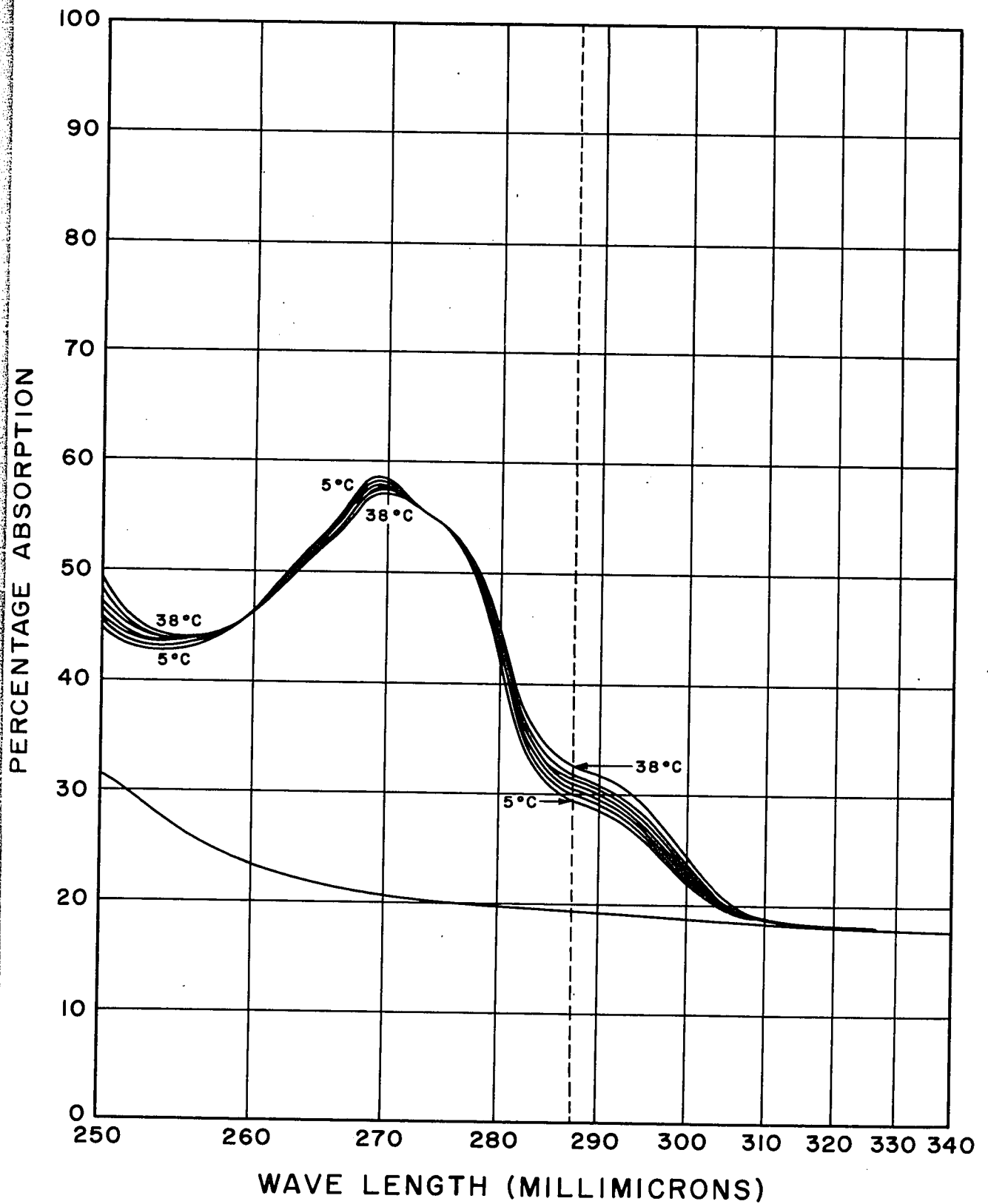


Figure 6. Spectra of phenol in 0.05 M borax buffer solution at different temperatures.

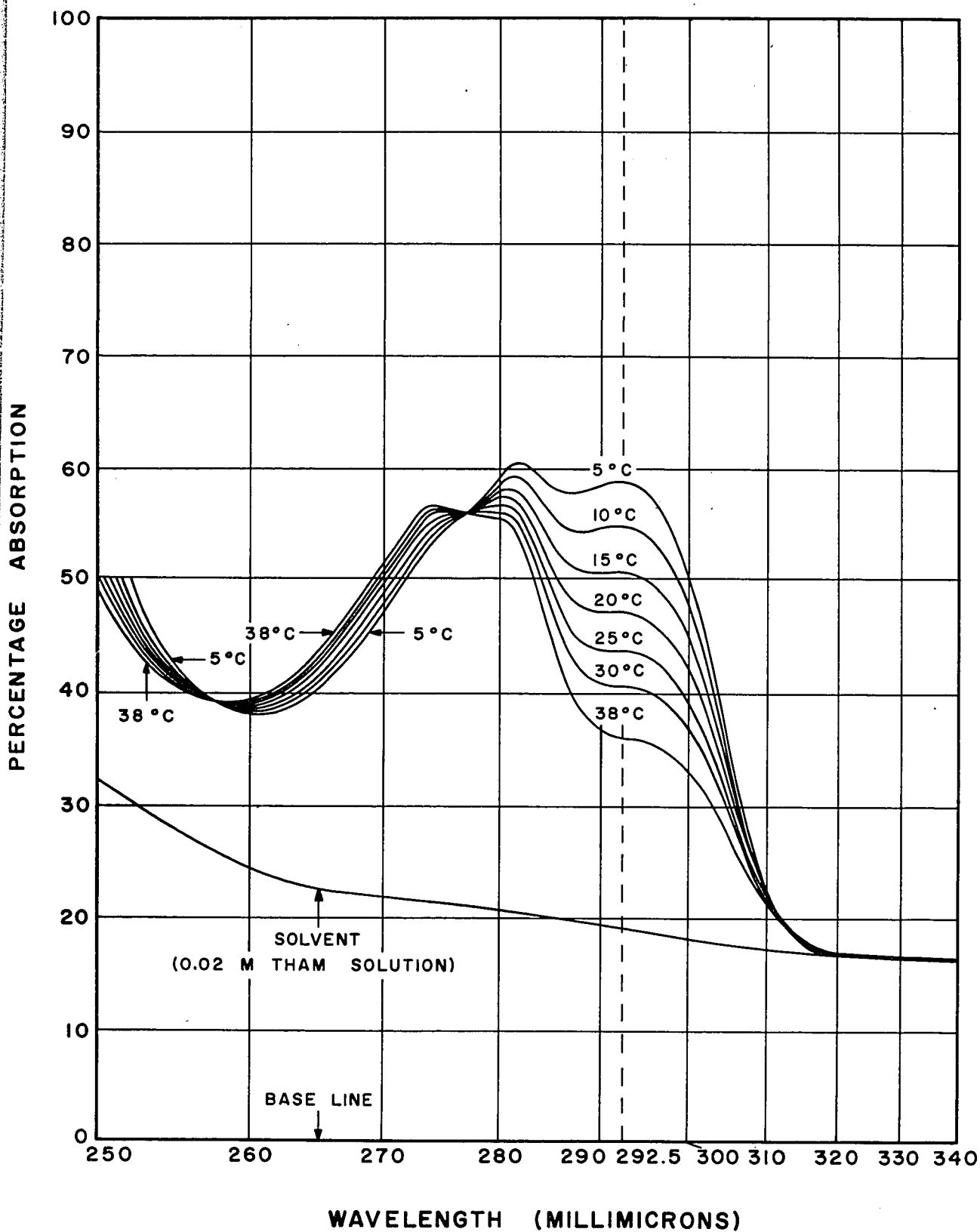


Figure 7. Spectra of o-chlorophenol in 0.02 M "THAM" buffer solutions at different temperatures.

Table 5

Absorptions and Ionization Constants of Various Phenols at Different Temperatures

(1) Phenol, measured at $\lambda = 287.5 \text{ m}\mu$, $b = 70.1$

$t^{\circ}\text{C}$		5	10	15	20	25	30	38
a		0.3	0.4	0.5	0.6	0.7	0.8	0.9
e	(1)	35.8	36.7	37.7	38.5	39.4	40.2	41.6
	(2)	35.6	36.6	37.6	38.4	39.4	40.4	41.9
pK	(1)	10.332	10.247	10.165	10.090	10.020	9.955	9.857
	(2)	10.337	10.249	10.168	10.093	10.020	9.950	9.850
	Av.	10.334	10.248	10.167	10.091	10.020	9.952	9.853

(2) o-cresol, measured at $\lambda = 288.7 \text{ m}\mu$, $b = 80.7$, $a = 0.7$

$t^{\circ}\text{C}$		5	10	15	20	25	30	38
e	(1)	30.3	31.1	32.0	33.1	34.1	34.9	36.4
	(2)	30.0	31.1	32.0	32.9	34.0	34.9	36.2
pK	(1)	10.652	10.566	10.488	10.406	10.332	10.268	10.167
	(2)	10.659	10.566	10.488	10.411	10.334	10.268	10.171
	Av.	10.655	10.566	10.488	10.409	10.333	10.268	10.169

(3) m-cresol, measured at $\lambda = 289.0 \text{ m}\mu$, $b = 67.0$

t°C		5	10	15	20	25	30	38
a		0.4	0.5	0.6	0.7	0.8	0.9	1.1
ε	(1)	31.3	32.3	33.2	33.9	34.7	35.6	36.9
	(2)	31.6	32.4	33.3	34.1	34.8	35.6	37.0
pK	(1)	10.410	10.321	10.241	10.168	10.099	10.032	9.937
	(2)	10.402	10.319	10.238	10.162	10.096	10.032	9.934
	Av.	10.406	10.320	10.240	10.165	10.098	10.032	9.936

(4) p-cresol, measured at $\lambda = 295.0 \text{ m}\mu$, $b = 80.2$, $a = 1.4$

t°C		5	10	15	20	25	30	38
ε	(1)	32.8	34.0	35.0	35.8	36.7	37.5	38.6
	(2)	33.1	34.3	35.2	35.9	36.8	37.5	38.9
pK	(1)	10.600	10.504	10.425	10.350	10.278	10.214	10.121
	(2)	10.593	10.498	10.420	10.348	10.275	10.214	10.115
	Av.	10.597	10.501	10.423	10.349	10.276	10.214	10.118

(5) 2,3-xyleneol, measured at $\lambda = 288.0 \text{ m}\mu$,
 $b_1 = 74.8$, $b_2 = 73.1$, $a = 1.1$

$t^{\circ}\text{C}$		5	10	15	20	25	30	38
ϵ	(1)	20.4	21.1	22.0	23.0	23.6	24.3	25.6
	(2)	20.5	21.3	21.9	22.5	23.1	23.9	25.0
pK	(1)	10.871	10.782	10.698	10.613	10.544	10.479	10.376
	(2)	10.854	10.762	10.687	10.612	10.544	10.475	10.377
	Av.	10.863	10.772	10.693	10.613	10.544	10.477	10.376

(6) 2,4-xyleneol, measured at $\lambda = 296.0 \text{ m}\mu$, $b = 74.9$, $a = 1.0$

$t^{\circ}\text{C}$		5	10	15	20	25	30	38
ϵ	(1)	18.9	19.6	20.4	21.1	21.9	22.6	23.8
	(2)	19.0	19.8	20.3	21.1	21.7	22.4	23.8
pK	(1)	10.917	10.827	10.748	10.668	10.592	10.526	10.424
	(2)	10.914	10.821	10.749	10.668	10.598	10.532	10.424
	Av.	10.916	10.824	10.748	10.668	10.595	10.529	10.424

(7) 2,5-xyleneol, measured at $\lambda = 291.5 \text{ m}\mu$, $b = 63.4$

$t^{\circ}\text{C}$		5	10	15	20	25	30	38
a		0.5	0.6	0.7	0.8	1.0	1.1	1.2
e	(1)	21.9	22.6	23.2	23.8	24.5	25.4	26.5
	(2)	21.8	22.5	23.2	24.1	24.7	25.3	26.2
pK	(1)	10.710	10.622	10.549	10.476	10.407	10.334	10.231
	(2)	10.713	10.625	10.549	10.467	10.401	10.337	10.240
	Av.	10.712	10.623	10.549	10.472	10.404	10.335	10.235

(8) 2,6-xyleneol, measured at $\lambda = 285.5 \text{ m}\mu$, $b = 72.3$, $a = 1.0$

$t^{\circ}\text{C}$		5	10	15	20	25	30	38
e	(1)	18.3	18.9	19.5	19.8	20.5	21.2	22.1
	(2)	18.1	18.6	19.2	19.9	20.3	20.9	21.7
pK	(1)	10.916	10.829	10.752	10.686	10.612	10.545	10.450
	(2)	10.923	10.838	10.762	10.683	10.619	10.554	10.462
	Av.	10.920	10.835	10.757	10.684	10.615	10.549	10.456

(9) 3,4-xylenol, measured at $\lambda = 294.0 \text{ m}\mu$, $b = 72.3$, $a = 1.5$

$t^{\circ}\text{C}$		5	10	15	20	25	30	38
ϵ	(1)	27.5	28.3	28.9	29.5	30.3	31.0	32.0
	(2)	27.7	28.4	28.8	29.3	30.0	30.8	31.9
pK	(1)	10.658	10.569	10.497	10.424	10.352	10.288	10.195
	(2)	10.654	10.570	10.499	10.420	10.360	10.293	10.198
	Av.	10.656	10.569	10.498	10.422	10.356	10.291	10.197

(10) 3,5-xylenol, measured at $\lambda = 290.0 \text{ m}\mu$, $b = 71.1$

$t^{\circ}\text{C}$		5	10	15	20	25	30	38
a		0.3	0.4	0.5	0.6	0.7	0.8	0.9
ϵ	(1)	32.5	33.2	33.9	34.6	35.2	36.0	37.2
	(2)	32.5	33.2	33.9	34.6	35.3	36.0	37.1
pK	(1)	10.500	10.416	10.343	10.270	10.204	10.140	10.043
	(2)	10.500	10.416	10.343	10.270	10.202	10.140	10.045
	Av.	10.500	10.416	10.343	10.270	10.203	10.140	10.044

(11) o-cl-phenol, measured at $\lambda = 288.7 \text{ m}\mu$, $b = 79.3$, $a = 0.8$

$t^{\circ}\text{C}$		5	10	15	20	25	30	38
e	(1)	41.4	37.5	33.5	29.6	26.0	23.1	18.6
	(2)	39.7	35.7	31.8	28.2	24.5	21.4	17.0
pK	(1)	8.732	8.658	8.595	8.538	8.488	8.425	8.351
	(2)	8.770	8.698	8.634	8.572	8.527	8.473	8.404

(12) Phenol in borax buffer, measured at $\lambda = 287.5 \text{ m}\mu$, $b = 70.3$

$t^{\circ}\text{C}$	5	10	15	20	25	30	38
a	0.3	0.4	0.5	0.6	0.7	0.8	0.9
e	10.2	10.8	11.3	11.7	12.0	12.4	13.4
pK	10.325	10.229	10.152	10.082	10.022	9.964	9.859

(13) o-cresol in borax, measured at $\lambda = 288.7 \text{ m}\mu$,
 $b = 64.4$, $a = 0.6$

$t^{\circ}\text{C}$	5	15	25	30	38
ϵ	5.2	5.7	6.2	6.4	6.9
pK	10.649	10.476	10.326	10.266	10.160

(14) m-cresol in borax, measured at $\lambda = 289 \text{ m}\mu$,
 $b = 79.0$

$t^{\circ}\text{C}$	5	15	25	30	38
a	0.5	0.7	0.9	1.0	1.2
ϵ	9.9	10.8	11.7	12.1	13.0
pK	10.408	10.244	10.104	10.046	9.949

The buffer solutions employed were 0.025 sodium bicarbonate +0.025 sodium carbonate; the pH at 25° C was found from Table 2 to be 10.018; $-\log \gamma$ was found from Table 4 to be 0.103 and ΔpH was found from Table 3 to be -0.001; and from Table 5(1), b was found to be 70.1; e, 39.4; a, 0.7. Substitution into equation (165) gives

$$\begin{aligned} \text{pK}_{25} &= 10.018 + \log \frac{70.1 - 39.4}{39.4 - 0.7} + 0.103 - 0.001 \\ &= 10.120 + \log \frac{70.1 - 39.4}{39.4 - 0.7} = 10.020 \end{aligned}$$

pK values at other temperatures are obtained in an analogous way.

The pK values for the various compounds investigated are also listed in Table 5. The values of log K corresponding to average pK values at different temperatures are plotted in Fig. 8. The lines have approximately the same curvature. It is a well-known fact that curves of this sort for weak acids exhibit maxima near room temperature. Obviously these curves do not have maxima in the range investigated, their maximum points are at much higher temperatures.

B. Analysis Of Temperature Dependence

The ionization constants at different temperatures were substituted into the Harned and Robinson equation. The parameters A*, C* and D* were evaluated from the resulting

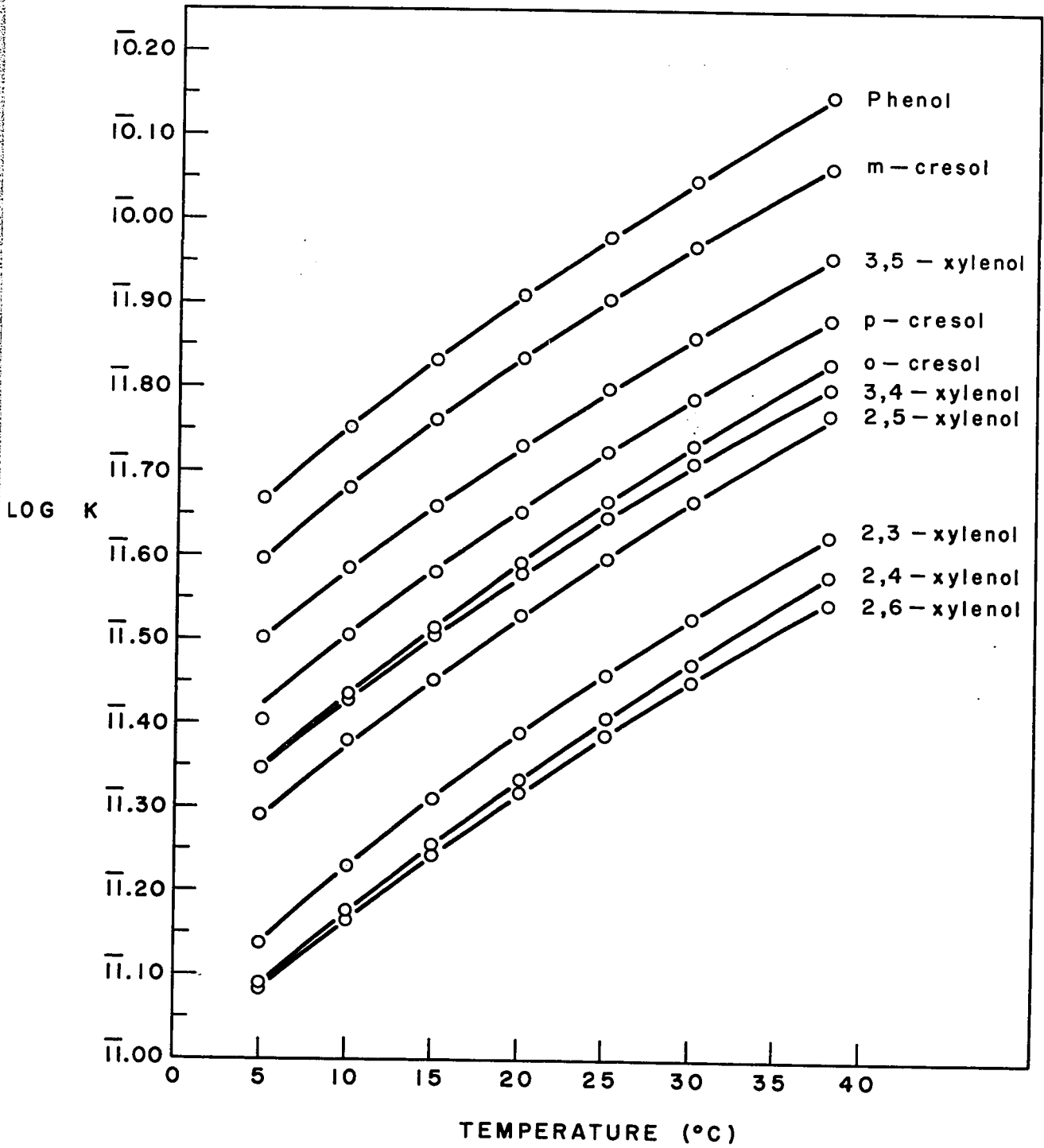


Figure 8. Variation of log K with temperature for various phenols.

equations by the least-squares method. They are listed together with A', C' and D' in Table 6. The thermodynamic functions ΔH , ΔF , ΔS , ΔC_p , θ and pK_m were calculated from these parameters by means of equations (88)(92)(93)(94)(96) and (97). They are tabulated in Table 7. As an illustrative example the analysis of data for phenol was taken.

The average pK values for phenol at 5°, 10°, 15°, 20°, 25°, 30° and 38° C are found from Table 5(1) to be 10.334, 10.248, 10.167, 10.091, 10.020, 9.952 and 9.852 respectively. Substitution of these values into the Harned and Robinson equation gives the following seven equations:

$$D^* - 0.0035951A^* - 278.16C^* = - 10.334$$

$$D^* - 0.0035316A^* - 283.16C^* = - 10.248$$

$$D^* - 0.0034703A^* - 288.16C^* = - 10.167$$

$$D^* - 0.0034111A^* - 292.16C^* = - 10.091$$

$$D^* - 0.0033539A^* - 298.16C^* = - 10.020$$

$$D^* - 0.0032986A^* - 303.16C^* = - 9.952$$

$$D^* - 0.0032138A^* - 311.16C^* = - 9.853$$

By means of the least-squares method, the constants A*, C*, D*, A', C' and D' were found to be:

$$A^* = 2119.8145$$

$$A' = 4.576A^* = 9700.27$$

$$C^* = 0.00991837$$

$$C' = 4.576C^* = 0.0453865$$

$$D^* = 0.04681$$

$$D' = 4.576D^* = 0.214203$$

Table 6

Constants for the Harned and Robinson Equation

Compounds	A*	D*	C*	A'	D'	C'
Phenol	2119.815	0.04681	0.00991837	9700.27	0.2142	0.0453865
o-cresol	2180.866	0.09325	0.0104490	9979.64	0.4267	0.0478145
m-cresol	2127.243	0.12797	0.0103673	9734.26	0.5856	0.0474408
p-cresol	2127.400	-0.04043	0.0104094	9734.98	-0.1850	0.0476334
2,3-xyleneol	2205.574	0.07068	0.0107906	10092.71	0.3234	0.0493778
2,4-xyleneol	2213.171	0.03112	0.0107457	10127.47	0.1424	0.0491723
2,5-xyleneol	2159.324	-0.007419	0.0105714	9881.07	-0.0339	0.0483747
2,6-xyleneol	2190.368	0.08498	0.0112486	10023.12	0.3889	0.0514736
3,4-xyleneol	2140.128	0.06355	0.0108702	9793.23	0.2908	0.0497420
3,5-xyleneol	2105.822	0.01157	0.0105696	9636.24	0.0529	0.0483665
o-Cl-phenol	1758.471	0.05717	0.00885824	8046.76	0.2616	0.0405353

Table 7
 Thermodynamic Functions for the Ionization
 of Phenols at 25° C

Compounds	ΔH kcal.	ΔF kcal.	ΔS e.u.	ΔC_p cal.	θ °C	pK_m
Phenol	5.66	13.67	-26.9	-27.1	189.1	9.123
o-cresol	5.73	14.10	-28.1	-28.5	183.7	9.455
m-cresol	5.52	13.78	-27.7	-28.3	180.0	9.299
p-cresol	5.50	14.02	-28.6	-28.4	179.0	9.452
2,3-xyleneol	5.70	14.39	-29.1	-29.4	178.9	9.686
2,4-xyleneol	5.76	14.46	-29.2	-29.3	180.6	9.723
2,5-xyleneol	5.58	14.19	-28.9	-28.8	178.8	9.563
2,6-xyleneol	5.46	14.49	-30.3	-30.7	168.1	9.843
3,4-xyleneol	5.37	14.13	-29.4	-29.7	170.5	9.582
3,5-xyleneol	5.34	13.92	-28.8	-28.8	173.2	9.424
o-Cl-phenol	4.44	11.57	-23.9	-24.2	172.3	7.837

Thence at 25° C:

$$\Delta H = A' - C'T^2 = 5665.45 \text{ cal. mole}^{-1}$$

$$\Delta F = A' - D'T + C'T^2 = 13671.2 \text{ cal. mole}^{-1}$$

$$\Delta C_p = -2C'T = -27.06 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta S = D' - 2C'T = -26.9 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_M = \sqrt{\frac{A^*}{C^*}} = 462.3^\circ \text{ K}$$

$$\theta = 462.3 - 273.2 = 189^\circ \text{ C}$$

$$pK_M = -D^* + 2\sqrt{C^*A^*} = 9.123$$

5. PRECAUTIONS

In carrying out the experiments precautions must be taken in view of the following factors:

(1) Change of the pH of the buffer solution during storage. This might be due to the absorption of carbon dioxide from the air and the attacking of glass by the alkaline buffer solution. In the early work the individual pK values at the same temperature differed by from 0.02 to 0.03 units. Fresh prepared buffer solutions were used each time in later work, and this gave satisfactory results.

(2) Deterioration of phenols. Phenols are easily oxidized to form quinones which impart a light yellow colour to the

compound. The colour may deepen by the formation of additional products with phenol. The oxidation not only occurs in the pure state but also in solution. The absorption of phenol in alkaline solution decrease about 2% during a week's storage. Therefore, if the determination should last more than a couple of days, the absorbance of the completely ionized form should be remeasured.

(3) Change of zero point of the instrument. The measurement of the absorption of the sample in buffer solution at various temperatures usually takes three hours. The zero point of the instrument might change during this time interval. This can be shown from the difference in absorbance at 25° C when the solution has been cooled down to 5° C and warmed up again. It can also be judged from the blurring of the isosbestic point. If the difference in absorbance at 25° C is less than 0.3% some corrections could be applied without producing any appreciable error.

(4) Change of the absorption of the solvent due to the absorption of carbon dioxide. The absorption of the solvent, especially the alkaline solutions, does not give reproducible spectral lines; it increases gradually with successive measurements. The lines are almost of the same curvature. This phenomenon also occurs when the solvent is allowed to stand in the cell in contact with air. If the air in the cell has been swept out by nitrogen gas prior to the introduction of

the solvent, the reproducibility is greatly improved. In some cases it is found that the flat part of the spectrum of the solution does not coincide with that of the solvent, as it should do if the absorption of the latter does not change. Therefore, in order to obtain the net absorption of the solute by subtracting that of the solvent from that of the solution, the difference between the flat part of the two spectra should also be taken into account.

6. ESTIMATION OF ERRORS

A. Maximum Error in pK

The experiments were carried out carefully to eliminate experimental errors as thoroughly as possible. All the solutions were adjusted to 25° C before dilution. The same pipette and volumetric flask were used to prepare the solutions in acid, alkaline and buffer media. The possible errors involved are in the reading of the absorbances of different species, the reproducibility of the instrument, the impurities contained in the sample and the error due to temperature variation. They are discussed separately, taking phenol at 25° C as an example.

(1) Error introduced in reading the absorbances of different species and the reproducibility of the instrument.

These two items can be evaluated together. The absorbances were read with the help of a magnifying glass, but there may still be an error of 0.1%. The reproducibility of the instrument

is also assumed to be 0.1%, so that the total error in the absorbances is 0.2. The equation used to calculate pK is

$$pK = pH + \log \frac{b - \epsilon}{\epsilon - a} - \log \gamma \quad (166)$$

The change of pK due to change of b, ϵ and a is given by

$$dpK = \frac{\partial}{\partial b} \left(\log \frac{b - \epsilon}{\epsilon - a} \right) db + \frac{\partial}{\partial \epsilon} \left(\log \frac{b - \epsilon}{\epsilon - a} \right) d\epsilon + \frac{\partial}{\partial a} \left(\log \frac{b - \epsilon}{\epsilon - a} \right) da \quad (167)$$

$$= \frac{1}{2.303} \left[\frac{db}{b - \epsilon} + \frac{(a - b)d\epsilon}{(b - \epsilon)(\epsilon - a)} + \frac{da}{\epsilon - a} \right] \quad (168)$$

The second term in the bracket is negative since a is smaller than b. But for evaluating the maximum error, only the absolute value is taken. In the case of phenol at 25° C, b = 70.1, $\epsilon = 39.4$, a = 0.7, $db = d\epsilon = da = 0.2$. Substitution into the above equation gives

$$dpK = \frac{1}{2.303} \left[\frac{0.2}{70.1 - 39.4} + \frac{(70.1 - 0.7) \times 0.2}{(70.1 - 39.4)(39.4 - 0.7)} + \frac{0.2}{39.4 - 0.7} \right] \\ = 0.0102.$$

(2) Error due to impurities present in the sample. It has been shown by Andon, Cox and Herrington (112) that the error in pK produced by X mole % of impurity is given by

$$\Delta pK = \left(\frac{0.868 X}{1 + X} \right) \left(\frac{J - 1}{J + 1} \right) \left(\frac{\epsilon_1' - \epsilon_3'}{\epsilon_1 - \epsilon_3} \right) \quad (169)$$

where $\log J = pK' - pK$; pK is the ionization constant exponent

for the sample and pK' is that for the impurity. ϵ_1 and ϵ_3 are the extinction coefficients of the sample in acid and alkaline solutions respectively; ϵ_1' and ϵ_3' are the corresponding values for the impurity at the same wavelength. In the present case the purity of the sample was greater than 99.9%, i.e., the maximum value of x is 0.001. The most likely impurities are the homologues. The corresponding extinction coefficients in acid and alkaline solutions of the homologues are approximately equal, i.e., $\frac{\epsilon_1' - \epsilon_3'}{\epsilon_1 - \epsilon_3} = 1$. The maximum difference in pK among them is 0.6 unit. This gives $J = 4$, and the error introduced in pK would be

$$\frac{0.868 \times 0.001}{1.001} \times \frac{4 - 1}{4 + 1} = 0.0005 \text{ units.}$$

(3) Error due to temperature variation. The thermometer is read with the help of a magnifying glass attached to it and the parallax error is reduced to a minimum. But because of the difficulty of maintaining the bath temperature constant, the temperature of the solution is only accurate to $\pm 0.1^\circ \text{C}$. From Table 5(1) it is seen that 5°C difference in temperature results in about 0.075 units difference in pK . Hence the error caused by $\pm 0.1^\circ \text{C}$ is $0.075 \times \frac{0.1}{5} = \pm 0.0015$ units.

Therefore the total maximum error in pK is $0.0102 + 0.0005 + 0.0015 = \pm 0.0122$ units.

This is the maximum error. The chance of having this error is rather small, because here all the errors are counted in the same direction. In practice some of the errors might occur in the opposite direction and cancel each other. Thus if the second term of equation (168) is taken to be negative, then the error introduced in the reading of absorbances will be

$$\begin{aligned} dpK &= \frac{1}{2.303} \left[\frac{0.2}{70.1-39.4} + \frac{(0.7-70.1) \times 0.2}{(70.1-39.4)(39.4-0.7)} + \frac{0.2}{39.4-0.7} \right] \\ &= 0.00009 \end{aligned}$$

and the total error would be

$$0.00009 + 0.0005 + 0.0015 = \pm 0.002 \text{ units.}$$

B. Errors for Other Thermodynamic Functions

Errors for other thermodynamic functions were estimated by inserting + ΔpK to pK values at three temperatures and $-\Delta pK$ to those at other three temperatures and recalculating the thermodynamic values by the least squares method. The differences between the new set of thermodynamic functions and the corresponding original values were taken as the maximum errors. It was found that the error in ΔH is about $\pm 0.35 \text{ kcal mole}^{-1}$, the error in ΔF is about $\pm 0.016 \text{ kcal mole}^{-1}$ and the error in ΔS is $\pm 1.2 \text{ e.u.}$

The errors in ΔC_p and θ can not be estimated because these values, using the Harned and Robinson equation, are not certain.

CHAPTER 4

DISCUSSION

1. COMPARISON WITH PREVIOUS WORK

The ionization constants of phenol and substituted phenols have been measured by many authors (105, 106, 193-209), but few temperature data are available. Ionization constants at 25° C in the present work agree very well with those of Herrington and Kynaston (122), which are about 0.1 to 0.2 pK units higher than those of Kieffer and Rumph (115), who used both the e.m.f. and spectrophotometric methods. All these values are listed in Table 8 for comparison, together with those of Minegishi and Nagakura (91).

Heats of ionization of phenols have not been determined by many authors. Berthelot (210) determined the heat of ionization of phenol by the calorimetric method to be 6100 cal. Lunden (32) determined the ionization constant of phenol and m-nitrophenol from 10° to 50° C by the conductometric method, and the heat of ionization was calculated by the van't Hoff equation. The heat of ionization of phenol was found to be $-7095 + 43.5 t$ cal. mole⁻¹, where t is the temperature in degrees centigrade; this gives the heat of ionization at 25° C to be 6008 cal. mole⁻¹. Minegishi and Nagakura (91) determined the ionization constant of phenol and methyl, chloro and nitro phenols from 15° to 40° C by nearly the same technique as that used in the present work except that they used different buffer

Table 8
pK Values at 25° C for Various Phenols by Different Authors

Compounds	Present work	Herrington & Kynaston (122)	Kieffer & Rumpf (115)	Minegishi & Nagakura (91)
phenol	10.02	10.02	9.87	
o-cresol	10.33	10.32	10.14	10.14
m-cresol	10.10	10.09	9.96	9.99
p-cresol	10.28	10.27	10.11	10.14
2,3-xyleneol	10.54	10.54	10.37	
2,4-xyleneol	10.60	10.60	10.45	
2,5-xyleneol	10.40	10.41	10.19	
2,6-xyleneol	10.62	10.63		
3,4-xyleneol	10.36	10.36	10.22	
3,5-xyleneol	10.20	10.19	10.03	
o-Cl-phenol	8.48			8.36

solutions. Apparently the pH values of their buffers were adjusted to the pK's of the compound under investigation, and the actual pH values at different temperatures were measured by a Beckman pH meter; this, of course, is not sufficiently accurate. In addition, they neglected the activity coefficient term. Their pK values differ greatly from those of the present work for the three cresols and o-chloro phenol. They claimed that the van't Hoff plot was linear, and their heats of ionization, derived from the slopes also differ from those of the present work; these are listed in Table 9. Very recently Binns (211) determined the ionization constants of phenol by the e.m.f. method from 25° to 60° C. His values at 25° C and 30° C are 9.97 and 9.90 respectively, which are lower than those of the present work by 0.05 unit. Binns did not calculate the heat of ionization, but only stated that the plot of pK against t is not linear. From his data we calculated the heat of ionization of phenol to be 6.29 kcal. at 25° C, closer to that obtained by Lunden and Berthelot than to the values of the present work.

Heats of ionization of all the methyl substituted phenols were determined in our laboratory by Papee, Canady, Zawidzki and Laidler (174) using a microcalorimeter. Their values are also listed in Table 9 for comparison. It can be noted that the values obtained by the two different methods are entirely different. According to them the heat of ionization of these

Table 9
Heats of Ionization of Phenols at 25° C by Different Authors

Compounds	Present work		Papee et al.* (174)	Minegishi & Nagakura (91)	Fernandez & Hepler (212)
	Carbonate	Borax			
phenol	5.66	5.34	4.3	6.29	5.650
o-cresol	5.73	5.68	6.3	6.5	
m-cresol	5.52	5.32	4.4	5.2	
p-cresol	5.50		4.7	6.3	
2,3-xyleneol	5.70		6.8		
2,4-xyleneol	5.76		8.2		
2,5-xyleneol	5.58		4.6		
2,6-xyleneol	5.46		5.1		
3,4-xyleneol	5.37		8.0		
3,5-xyleneol	5.34		4.6		
o-Cl-phenol	4.44			3.8	4.630

*Note: The values quoted here have been converted to the same ionic strength as in the present work, from the authors' original plot. They are, therefore, different from their published values which are supposed to be the heat of ionization at zero ionic strength.

substances varies with ionic strength and the values reported by Papee et al. (174) were extrapolated to zero ionic strength; the values listed in Table 9 refer to the same ionic strength as in the present work. The exact composition of the buffer solution employed by Minegishi and Nagakura is not known. Assuming that it is composed of equal mixtures of 0.1 N NaOH and 0.05 M Na_3BO_3 , the ionic strength would be approximately 20×10^{-2} moles liter⁻¹. Their values for the three cresols do not agree with those of Papee's, or with the present work. In Papee's results the difference in heat of ionization among the members is of the order of 2 or 3 keals. This difference between meta and other cresols reported by Minegishi and Nagakura is about 1.2 kcal. But the differences in present work is only 0.2 to 0.3 kcal, ten times as small as that of Papee's. A check was made on the heat of ionization of phenol, and the ortho and meta cresols by using 0.05 M borax buffer. The values obtained are also listed in Table 9 for comparison. It can be seen that they agree reasonably well with those obtained by using carbonate buffer.

Very recently Fernandez and Hepler (212) determined heats of ionization of phenol and the chloro and nitro phenols by the calorimetric method. Their value of 5650 cal. mole⁻¹ for phenol agrees with the present work. Ortho-chlorophenol has been chosen as a check for the determination of heat of ionization by the calorimetric and the ionization constant method,

because its value differs from that of phenol by approximately 1 kcal. as reported by the above authors. It turned out that the results are quite satisfactory. They are also listed in Table 9 together with the value obtained by Minegishi and Nagakura which is about 0.7 kcal. smaller.

The heat of ionization of 3,4-xyleneol has been checked by Mr. E. Lovering in our laboratory using the microcalorimeter. This compound was chosen because the difference between present work and that of Papee's is the biggest. His value of 5.1 ± 0.3 kcal. mole⁻¹ agrees with the present work within experimental error. He also used different concentrations of sodium hydroxide solution and found that heat of neutralization varies linearly with ionic strength but the slope is almost zero, whereas in Papee's data the heat of neutralization of this compound decreased with decreasing ionic strength. The effect of ionic strength on the heat of ionization has also been studied by the present author. According to Papee et al. ortho-cresol exhibits a large slope on the heat against ionic strength plot. It was found that the difference in the heat of ionization of this compound in 0.01 M and in 0.025 M carbonate-bicarbonate buffer solutions is only 0.16 kcal. mole⁻¹, practically the same within experimental error, whereas according to Papee's work this difference should be as much as 1.4 kcal. mole⁻¹. Also the ionic strength of borax buffer is 0.15 greater than that of the carbonate-bicarbonate buffer,

yet the heats of ionization of phenol, ortho and meta cresols in these buffers do not change appreciably. Therefore it is apparent that the heat of ionization of these compounds does not vary much with ionic strength.

The ionization constants of o-cresol has been determined recently by Louise (213) from 30° to 70° C using the e.m.f. method. His pK value at 30° C is about 0.12 unit lower than that of the present work. The heat of ionization calculated from his data, however, is 5.50 kcal mole⁻¹ which agrees with that of the present work within experimental error.

2. COMPARISON OF HARNED AND ROBINSON AND EVERETT AND WYNNE-JONES EQUATIONS

The data for phenol have been tested by the methods of both Everett and Wynne-Jones and of Harned and Robinson. The results are compared in Table 10. It is seen that they are of the same order of accuracy. The values of ΔF computed by the two methods are practically the same. The differences in ΔH and ΔS values also lie within the limits of experimental error. The ΔC_p and θ values, however, differ considerably and it is difficult to decide which are the true values. The curves representing the two different equations for phenol are shown in Figure 9, in which $\log K$ has been plotted against T . It is seen that the two curves coincide in the temperature range from 200° K to 400° K. At high temperatures they differ greatly. The data for the narrow temperature range employed

Table 10

Comparison of Data for Phenol Derived from the Equations of Harned and Robinson and of Everett and Wynne-Jones

Equation	Harned and Robinson		Everett and Wynne-Jones	Experimental data
	(1)	(2)		
Parameters	D* = 0.04681 A* = 2119.815 C* = 0.00991837	D* = 1.5140 A* = 2339.350 C* = 0.012458	A' = -3266.7 $\frac{\Delta C_p}{R}$ = -15.833 B' = 40.1137	
ΔH	5665.45	5636.89	5568.3	
ΔF	13671.2	13670.4	13671.1	
ΔS	-26.9	-26.9	-27.2	
ΔC_p	-27.1	-34.0	-31.5	
θ	189.1	160.1	201.9	
pK_m	9.123	9.267	9.144	
pK_5	10.333	10.334	10.331	10.334
pK_{10}	10.247	10.249	10.246	10.248
pK_{15}	10.167	10.167	10.165	10.167
pK_{20}	10.092	10.091	10.091	10.091
pK_{25}	10.020	10.019	10.020	10.020
pK_{30}	9.952	9.953	9.953	9.952
pK_{38}	9.852	9.853	9.855	9.853

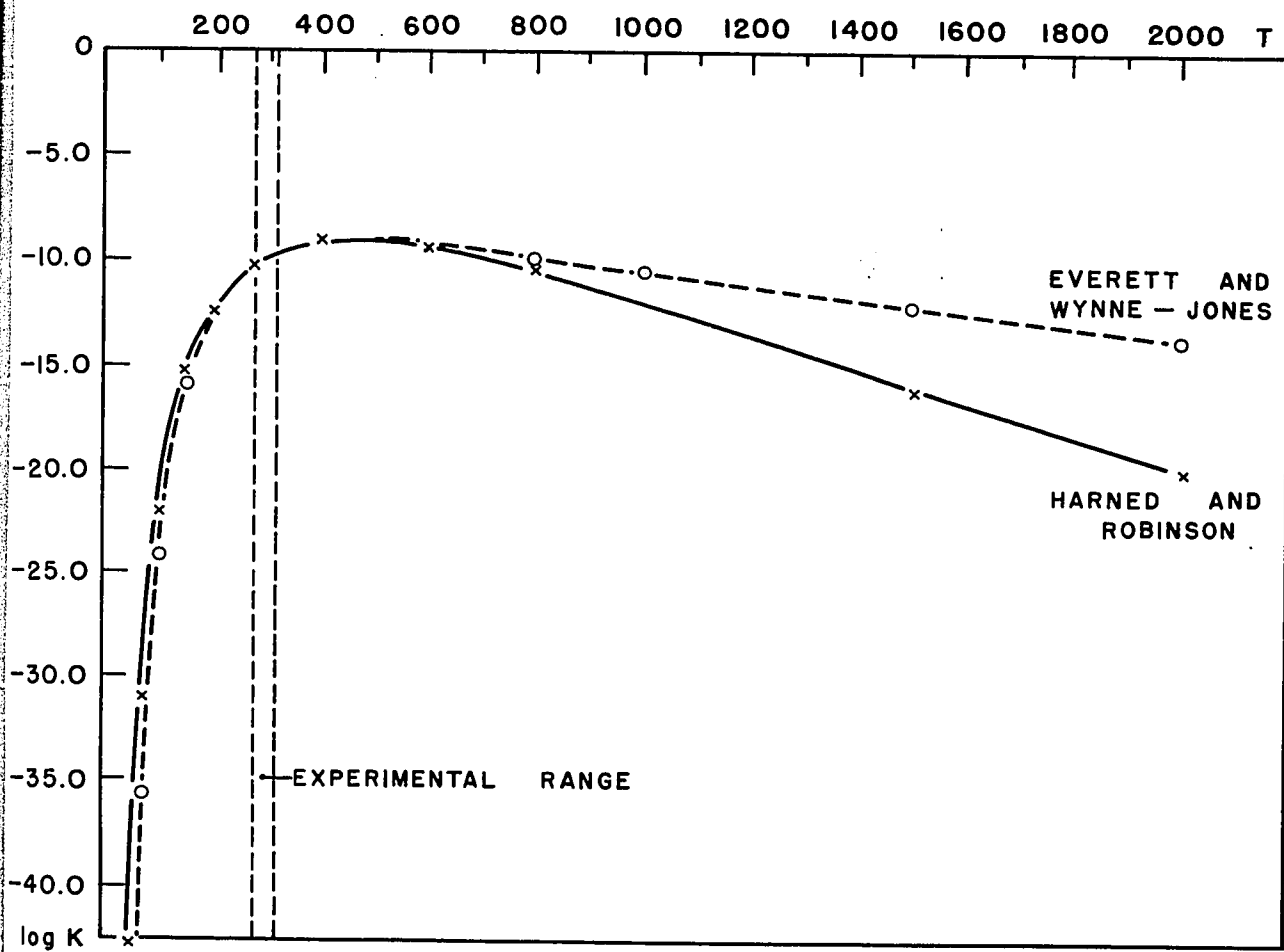


Figure 9. Comparison of the Harned and Robinson, and Everett and Wynne-Jones equations for phenol.

can fit into many equations. Even using the Harned and Robinson equation alone, many different combinations of parameters can be chosen to fit the data, and the resulting different Harned and Robinson equations yield different values of thermodynamic functions, two examples of which are shown in Table 10. Those functions like ΔH , ΔF and ΔS that contain more than one parameter do not vary much with the parameter. They also agree with those derived from the Everett and Wynne-Jones treatment. On the other hand, the functions ΔC_p , θ and K_m change considerably. These are also the ones that do not agree with those obtained by the Everett and Wynne-Jones equation. It is apparent that only ΔH , ΔF and ΔS are of significance, and in the interpretation of data only these will be discussed.

3. INTERPRETATION OF THE RESULTS

A. The ΔF Values. It has previously been pointed out (174) that the free energies and pK values for the ionizations of substituted phenols are additive. This is shown for the present data in Table 11. The ΔF values for phenol and the three cresols lead to the following increments for groups in the three positions:

o-methyl 0.43 m-methyl 0.11 p-methyl 0.35

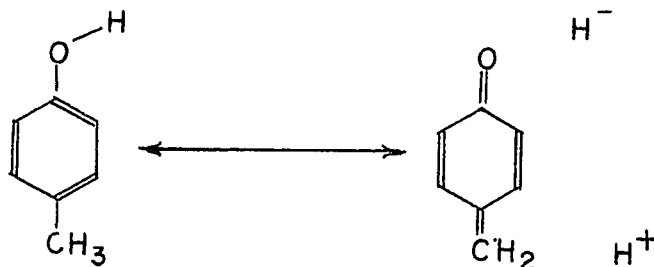
The use of these values leads to predictions for the ΔF values of the xylenols that are shown in Table 11, and the agreement

Table 11
Additivity of the pK and ΔF Values

Compound	pK		ΔF	
	Experimental values	Estimated assuming additivity	Experimental values	Estimated assuming additivity
phenol	10.02	-	13.67	-
o-cresol	10.33	-	14.10	-
m-cresol	10.10	-	13.78	-
p-cresol	10.28	-	14.02	-
2,3-xyleneol	10.54	10.41	14.39	14.21
2,4-xyleneol	10.60	10.59	14.46	14.45
2,5-xyleneol	10.40	10.41	14.19	14.21
2,6-xyleneol	10.62	10.64	14.49	14.53
3,4-xyleneol	10.36	10.36	14.13	14.13
3,5-xyleneol	10.20	10.18	13.92	13.89

with the experimental values is very satisfactory. This additivity is to be contrasted with the lack of additivity in the case of the entropies and heats of ionization; this will be discussed below.

The free energies of ionization are simply explained in terms of the usual theory of the effect of the methyl group. This group makes it more difficult for the O-H bond to ionize, and its effect is exerted most strongly in the ortho and the para positions. It was seen above that in the cresols the free energy of ionization is raised 0.43 kcal. by a methyl group in the ortho position and 0.35 kcal. by one in the para position. In the meta position the increase is much smaller, 0.11 kcal. If the influence were due to the inductive effect alone, the ΔF values would be in the order: o > m > p > phenol. In fact ΔF for p-cresol is greater than that for m-cresol, and this implies that there is some resonance of the following type:



The steric effect enhances ionization and decreases ΔF . Since ΔF for o-cresol is greater than that for the unsubstituted phenol the steric effect probably does not contribute much to

the ΔF value. To separate the inductive and resonance contributions use may be made of an equation due to MacInnes (167), but with some modifications. The MacInnes equation states that

$$\log K_s = \log K_o - \frac{I}{d} . \quad (170)$$

Here K_s is the ionization constant of a substituted acid and K_o is the ionization constant of an acid whose substituent is removed to infinity; its value is taken to be equal to the ionization constant of the unsubstituted acid, K_u . I is a constant characteristic of the substituent; it is a measure of the inductive power of that substituent. d is the distance between the substituent and the functional group; it is equal to the number of bonds separating these groups, and is 1, 2, 3, etc. for the α , β , γ , etc. positions respectively*.

Since in general

$$\Delta F = -2.303 RT \log K, \quad (171)$$

$$\Delta F_s = -2.303 RT \log K_s \quad (172)$$

and using equation (170) it follows that

$$\Delta F_s = \Delta F_u - \frac{I}{d} \quad (173)$$

*Greenstein (214) proposed a similar equation in which l^2 is used instead of d , l being the distance in Å from the centre of the substituent dipole to the reaction centre. He found that l^2 for β substitution is about twice and for γ substitution is about three times that for α substitution, so that the two equations are very similar.

ΔF_u is the free energy of ionization of the unsubstituted acid and I' is a constant equal to $-2.303 RTI$. In the present case it is assumed that the polar effect is solely transmitted through the bond, not through space; in other words, the field effect is neglected. The reaction centre is the O-H bond; the ortho position is two bonds from the oxygen atom and the meta and para positions are three and four bonds apart from the oxygen atom respectively. The following equations thus result:

$$\Delta F_o = \Delta F_u - \frac{I'}{2} \quad (174)$$

$$\Delta F_m = \Delta F_u - \frac{I'}{3} \quad (175)$$

$$\Delta F_p = \Delta F_u - \frac{I'}{4} \quad (176)$$

where ΔF_u , ΔF_o , ΔF_m and ΔF_p are the free energies of ionization of the phenol, o-cresol, m-cresol and p-cresol respectively due to the inductive effect alone.

Therefore

$$I_o = \Delta F_o - \Delta F_u = -\frac{I'}{2} \quad (177)$$

$$I_m = \Delta F_m - \Delta F_u = -\frac{I'}{3} \quad (178)$$

$$I_p = \Delta F_p - \Delta F_u = -\frac{I'}{4} \quad (179)$$

where I_o , I_m and I_p are the inductive effects in the ortho, meta and para positions respectively. From these equations

it is found that

$$I_o = \frac{3}{2} I_m \quad (180)$$

$$I_p = \frac{3}{4} I_m \quad (181)$$

The substituent effect in the ortho position is due to the inductive effect in the ortho position I_o and the resonance effect R ; the substituent effect in the meta position is due to the inductive effect in the meta position I_m alone; the substituent effect in the para position is due to the inductive effect in the para position I_p and the resonance effect. From the experimental data:

$$\Delta F_o = I_o + R = 14.10 - 13.67 = 0.43 \quad (182)$$

$$\Delta F_m = I_m = 13.38 - 13.67 = 0.11 \quad (183)$$

$$\Delta F_p = I_p + R = 14.02 - 13.67 = 0.35. \quad (184)$$

From (181) one obtains

$$I_p = \frac{3}{4} I_m = \frac{3}{4} \times 0.11 = 0.08 \quad (185)$$

and substitution into (184) gives

$$R = 0.35 - I_p = 0.35 - 0.08 = 0.27. \quad (186)$$

Substitution into (182) gives

$$I_o = 0.43 - R = 0.43 - 0.27 = 0.16. \quad (187)$$

This value is about $\frac{3}{2}$ times as large as I_m , and this confirms the previous assumptions.

Chlorine is a strong electron-withdrawing substituent and has a large - I effect. It helps the bonded hydrogen atom to release electrons and therefore increases the acidity of the phenol.

B. The Heats and Entropies of Ionization. In contrast to the situation with the free energies of ionization, the heats and entropies show no additivity. Owing to the relatively small spread in the values of these quantities this conclusion is not immediately apparent, and has been arrived at on the basis of a statistical treatment. Table 12 shows the experimental heats of ionization for the xylenols, together with the values calculated on the assumption of additivity, using the increments obtained in the series of cresols. Using the statistical treatment outlined in the Appendix the coefficient of correlation between the two series of numbers is found to be 0.3. This corresponds to a value for 'Student's t' of 0.7, which with six values leads to the conclusion that the correlation is not significant.

A similar treatment with the entropies of ionization for which the results are shown in Table 13, leads to a correlation coefficient of 0.5, and a 'Student's t' of 1.1; this again is not a significant correlation.

Correlations between heats and entropies of ionization

Table 12
Test for Additivity of ΔH

Compound	ΔH (Experimental values)	ΔH (Estimated assuming additivity)
2,3-xyleneol	5.7	5.5
2,4-xyleneol	5.8	5.5
2,5-xyleneol	5.7	5.5
2,6-xyleneol	5.5	5.7
3,4-xyleneol	5.4	5.3
3,5-xyleneol	5.3	5.3

Correlation coefficient = 0.3

'Student's t' = 0.7

Correlation not significant;
no evidence for additivity.

Table 13
Test for Additivity of ΔS

Compound	ΔS (Experimental value)	ΔS (Estimated assuming additivity)
2,3-xyleneol	29.1	28.9
2,4-xyleneol	29.2	29.8
2,5-xyleneol	28.9	28.9
2,6-xyleneol	30.3	29.3
3,4-xyleneol	29.4	29.4
3,5-xyleneol	28.8	28.5

Correlation coefficient = 0.5

'Student's t' = 1.1

Correlation not significant;
no evidence for additivity.

in other chemical processes have frequently been found; a discussion, particularly relating to heats of ionization, has recently been presented (172). In Figure 10 is shown a plot of entropy of ionization against free energy of ionization, and in Figure 11 is shown $T\Delta S$ plotted against ΔH . In these two figures a distinction has been made between the compounds in which no substituent is in an ortho position, and those in which one or more is in an ortho position. Inspection of these figures leads to the suggestion that there is something of a correlation between ΔF and $T\Delta S$, and between $T\Delta S$ and ΔH , and that the correlation is stronger when the ortho compounds are omitted from consideration. This conclusion is confirmed by calculations of correlation coefficients, as will now be seen.

Table 14 shows the relevant results, for the non-ortho compounds, as far as the correlation between entropy and free energy is concerned. The coefficient of correlation for these values is 0.9, and 'Student's t' is 3.8, which with five values leads to the result that the correlation is highly significant. The regression equation to which these statistical calculations lead is

$$T\Delta S = -1.60 \Delta F + \text{const.} \quad (188)$$

When the calculations are made including the ortho compounds the correlation coefficient is lower, 0.83, and

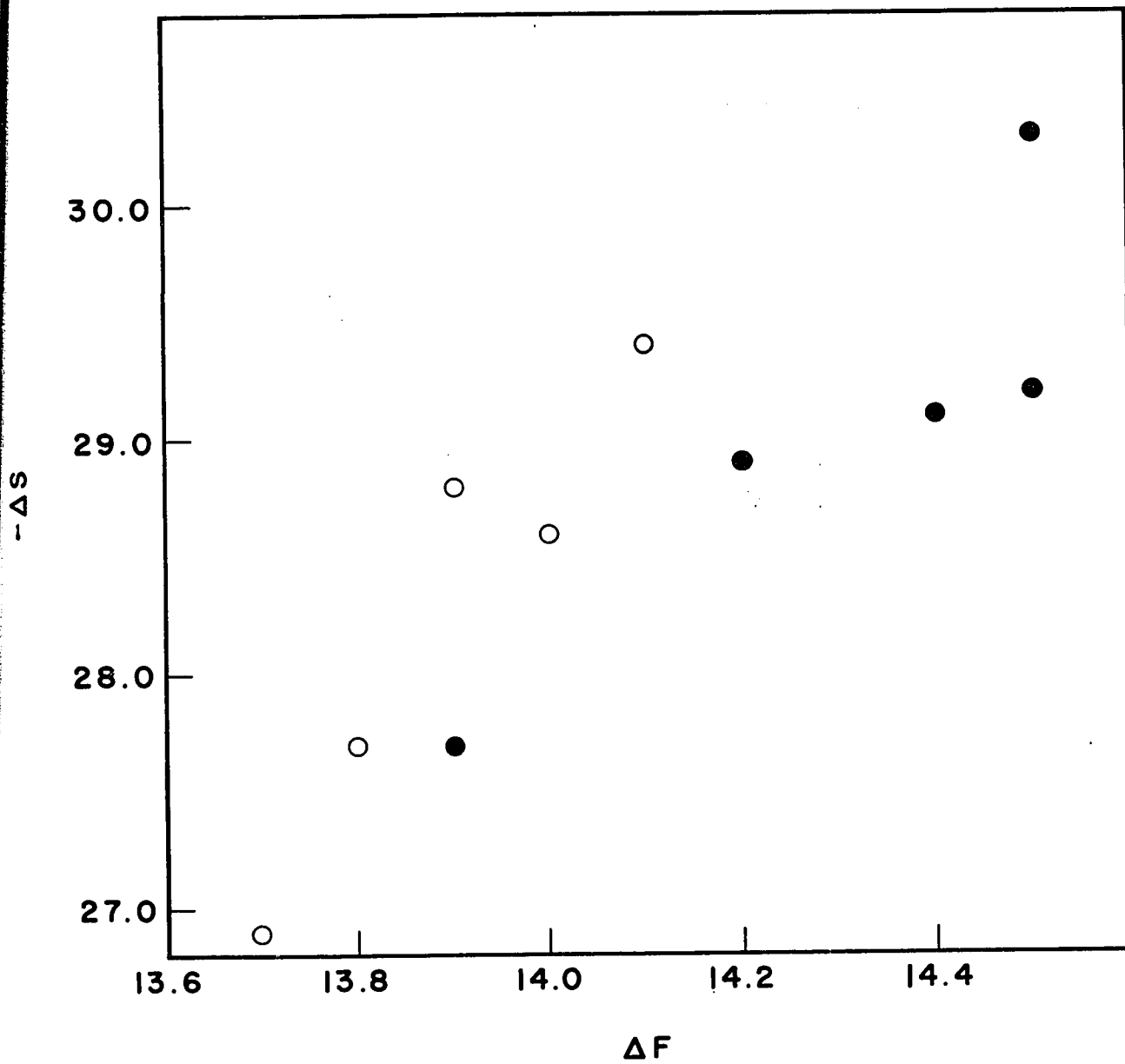


Figure 10. Correlation between entropy and free energy of ionization; the open circles are for compounds in which no substituent is in an ortho position, the closed circles for the remaining compounds.

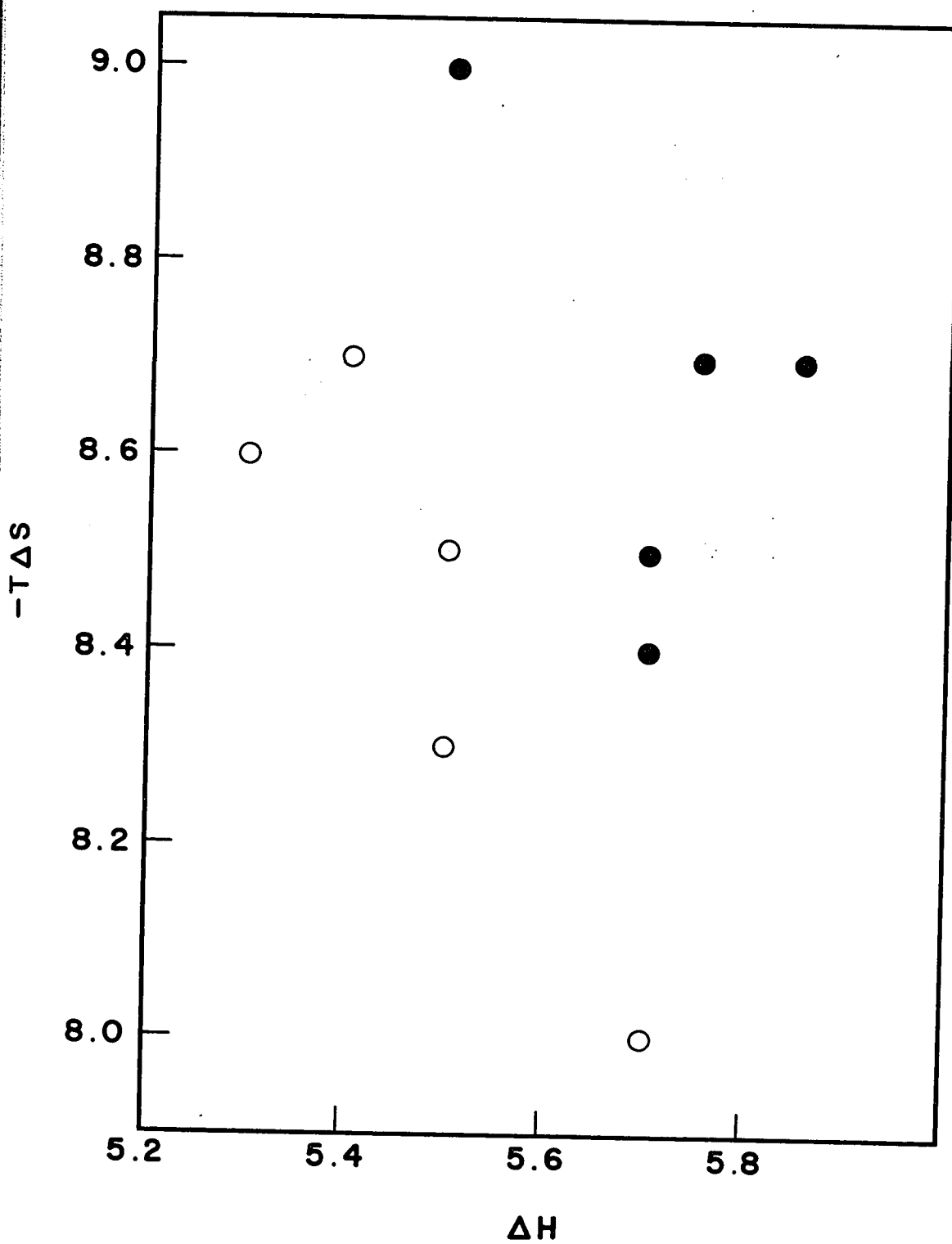


Figure 11. Correlation between entropy and heat of ionization; the open circles are for compounds in which no substituent is in an ortho position, the closed circles for the remaining compounds.

Table 14

Test for Correlation Between $T\Delta S$ and ΔF for the
Compounds in Which no Substituent is in an Ortho
Position

Compound	$-T\Delta S$	ΔF
phenol	8.0	13.7
m-cresol	8.3	13.8
p-cresol	8.5	14.0
3,4-xyleneol	8.7	14.1
3,5-xyleneol	8.6	13.9

Correlation coefficient = 0.9

'Student's t' = 3.8

Correlation significant at the 1% level

Regression equation $-T\Delta S = 1.60 \Delta F + \text{const.}$

'Student's t' is 4.21. This corresponds to a significant correlation, although the degree of significance is much less than when the ortho compounds are neglected. The regression line that results from the inclusion of the ortho compounds is

$$T\Delta S = -1.22 \Delta F + \text{const.} \quad (189)$$

Since correlations are found between ΔS and ΔF , and since ΔF is equal to $\Delta H - T\Delta S$, it follows that there must be a correlation between the heats and entropies of ionization. This can, in fact, be found by a direct statistical treatment using the same methods as above. The regression lines that result when the ortho compounds are excluded is

$$T\Delta S = 2.67 \Delta H + \text{const.} \quad (190)$$

and when all compounds are included the equation is

$$T\Delta S = 5.5 \Delta H + \text{const.} \quad (191)$$

The existence of these correlations between heats, entropies and free energies throws considerable light on the interpretation of the entropies and heats obtained. In a broad way it can be said that factors which tend to cause an increase in the free energy of ionization tend to cause a decrease in the entropy of ionization and also a decrease in the heat of ionization. In other words, heats and free energies of ionization for the most part change in opposite

directions. This result is somewhat unexpected, and previous discussion of free energies of ionization have frequently involved the assumption that they change in the same sense as the heats. The present result strengthens the conclusion (172) that certain effects, probably solvent and steric effects, influence heats and entropies of ionization in a compensating manner, so that no effect on the free energy of ionization is observed. In other words, there are certain effects on the heats and entropies of ionization that do not make themselves felt in the free energies of ionization. As far as the non-ortho compounds are concerned, these factors are probably the solvent interactions; when the ortho compounds are considered the steric factors also become important.

APPENDIX 1

Absolute Entropies of H₂O and H₃O⁺

I. Absolute Entropy of H₂O

1. Translational contribution

$$\begin{aligned} S_{tr} &= 4.576 \left(\frac{3}{2} \log M + \frac{5}{2} \log T - \log P - 0.505 \right) \\ &= 4.576 \left(\frac{3}{2} \log 18 + \frac{5}{2} \log 298 - \log 1 - 0.505 \right) \\ &= 34.613 \text{ e.u.} \end{aligned}$$

2. Rotational contribution

Moments of inertia of H₂O are (215)

$$I_A = 1.024 \times 10^{-40} \text{ g-cm}^2$$

$$I_B = 1.920 \times 10^{-40} \text{ g-cm}^2$$

$$I_C = 2.947 \times 10^{-40} \text{ g-cm}^2$$

$$\begin{aligned} S_{rot} &= 4.576 \left(\frac{1}{2} \log I_A I_B I_C + \frac{3}{2} \log T - \log \sigma + 58.51 \right) \\ &= 4.576 \left(\frac{1}{2} \log 1.024 \times 1.920 \times 2.947 \times 10^{-120} \right. \\ &\quad \left. + \frac{3}{2} \log 298 - \log 2 + 58.51 \right) \\ &= 10.544 \text{ e.u.} \end{aligned}$$

3. Vibrational contributions

H₂O is a triatomic molecule. It has three degrees of vibrational freedom. The frequencies of these three modes of vibration are (216)

$$\text{Symmetrical stretch, } \omega_1 = 3654.5 \text{ cm}^{-1}$$

$$\text{Symmetrical bend, } \omega_2 = 1595.0 \text{ cm}^{-1}$$

$$\text{Antisymmetrical stretch, } \omega_3 = 3755.8 \text{ cm}^{-1}$$

The contributions to entropy due to these three modes of vibration are evaluated separately as following

(1) Due to ω_1

$$x = \frac{h\nu}{kT} = \frac{hc\omega}{kT} = \frac{1.439\omega}{T}$$

Where ν is the frequency in sec^{-1} , ω is the frequency in wave number (cm^{-1}), c is the velocity of light.

$$x_1 = \frac{1.439\omega_1}{T} = \frac{1.439 \times 3654.5}{298} = 17.65$$

From the Einstein Functions (217) it is found that

$$\frac{Rx}{e^x - 1} = 0$$

$$-R \ln(1 - e^{-x}) = 0$$

Therefore the contribution of this mode of vibration to the absolute entropy of water molecule is zero.

(2) Due to ω_2

$$x_2 = \frac{1.439\omega_2}{T} = \frac{1.439 \times 1595}{298} = 7.70$$

$$\frac{Rx}{e^x - 1} = \frac{1}{3} (0.0208) = 0.007 \text{ e.u.}$$

$$-R \ln(1 - e^{-x}) = 0 \text{ e.u.}$$

The contribution to entropy due to this vibration is 0.007 e.u.

(3) Due to ω_3

$$x_3 = \frac{1.439\omega_3}{T} = \frac{1.439 \times 3755.8}{298} = 18.14$$

The contribution of this mode of vibration to the entropy of water is also zero.

Therefore $S_{\text{vib}} = 0.007 \text{ e.u.}$

II. Absolute Entropy of H_3O^+

1. Translational contribution

$$\begin{aligned} S_{\text{tr}} &= 4.576 \left(\frac{3}{2} \log 19 + \frac{5}{2} \log 298 - \log 1 - 0.505 \right) \\ &= 34.777 \text{ e.u.} \end{aligned}$$

2. Rotational contribution

In order to find out the rotational contribution it is necessary to know the moments of inertia which in turn needs the knowledge about the structure of the molecule. The H_3O^+ ion has the same shape as that of NH_3 (218) because they both have the same electronic configuration. The NH_3 molecule is a pyramid (219) with NH distance equals 1.016 Å and the height of pyramid equals 0.36 Å. Since the H_3O^+ ion and the NH_3 molecule are isoelectronic it is reasonable to assume that they have the same pyramid angle; but the O-H distance would be expected to remain the same as that in water, i.e., 0.96 Å, because a deficiency of electrons has little effect on the covalent radii (220). Therefore the height of the H_3O^+ pyramid is 0.34 Å. The center of gravity lies on the line which links the oxygen atom and the center of the hydrogen triangle; it is about 0.05 Å away from the oxygen atom. Take the line which links the oxygen atom and the center of the hydrogen triangle as axis A; the line which passes through the center of gravity, parallel to the hydrogen plane and whose projection on that plane passes one of the hydrogen atoms, as axis B; the line which passes through the center of gravity and perpendicular to both

A and B axes, as axis C; the moments of inertia about these three axes are calculated as follows:

$$I_A = \frac{3 \times 1.008}{6.023 \times 10^{23}} \times (0.90 \times 10^{-8})^2 = 4.034 \times 10^{-40} \text{ g-cm}^2$$

$$I_B = \frac{16}{6.023 \times 10^{23}} (0.05 \times 10^{-8})^2 + \frac{1.008}{6.023 \times 10^{23}} (0.29 \times 10^{-8})^2 \\ + \frac{2 \times 1.008}{6.023 \times 10^{23}} (0.83 \times 10^{-8})^2 = 2.505 \times 10^{-40} \text{ g-cm}^2$$

$$I_C = \frac{16}{6.023 \times 10^{23}} (0.05 \times 10^{-8})^2 + \frac{1.008}{6.023 \times 10^{23}} (0.95 \times 10^{-8})^2 \\ + \frac{2 \times 1.008}{6.023 \times 10^{23}} (0.54 \times 10^{-8})^2 = 2.505 \times 10^{-40} \text{ g-cm}^2$$

The rotational contribution to the absolute entropy of H_3O^+ is

$$S_{\text{rot}} = 4.576 \left(\frac{1}{2} \log I_A I_B I_C + \frac{3}{2} \log T - \log \sigma + 58.51 \right) \\ = 4.576 \left(\frac{1}{2} \log 4.034 \times 2.505 \times 2.505 \times 10^{-120} \right. \\ \left. + \frac{3}{2} \log 298 - \log 3 + 58.51 \right) \\ = 11.192 \text{ e.u.}$$

3. Vibrational contribution

H_3O^+ has six degrees of vibrational freedom ($3 \times 4 - 6 = 6$). There should be six modes of vibration. But two modes are degenerate, hence there are only four modes of vibration. The frequencies of these four vibrations are as follows (218):

- Symmetrical OH stretch, $\omega_1 = 3235 \text{ cm}^{-1}$
Symmetrical OH bend, $\omega_2 = 1150 \text{ cm}^{-1}$
Antisymmetrical OH stretch, $\omega_3 = 2590 \text{ cm}^{-1}$ (double degenerate)
Perpendicular bending, $\omega_4 = 1700 \text{ cm}^{-1}$ (double degenerate)

Their contribution to absolute entropy are evaluated separately:

(1) Due to ω_1

$$x_1 = \frac{1.439\omega_1}{T} = \frac{1.439 \times 3235}{298} = 15.62$$

The contribution to entropy due to this vibration is zero.

(2) Due to ω_2

$$x_2 = \frac{1.439\omega_2}{T} = \frac{1.439 \times 1150}{298} = 5.55$$

$$\frac{Rx}{e^x - 1} = 0.043 \text{ e.u.}$$

$$-R \ln(1 - e^{-x}) = 0.007$$

The contribution to entropy due to this vibration is $0.043 + 0.007$
 $= 0.05 \text{ e.u.}$

(3) Due to ω_3

$$x_3 = \frac{1.439\omega_3}{T} = \frac{1.439 \times 2590}{298} = 12.5$$

$$\frac{Rx}{e^x - 1} = 0.0001 \text{ e.u.}$$

$$-R \ln(1 - e^{-x}) = 0.$$

The contribution to entropy due to this vibration is 0.0001 e.u.
Since it is a double degenerate vibration, the total contribution

would be twice as much, i.e., 0.0002 e.u.

(4) Due to ω_4

$$x_4 = \frac{1.439\omega_4}{T} = \frac{1.439 \times 1700}{298} = 8.21$$

$$\frac{Rx}{e^x - 1} = 0.0045 \text{ e.u.}$$

$$-R \ln(1 - e^{-x}) = 0.$$

The contribution to entropy due to this double degenerate vibration is $2 \times 0.0045 = 0.009$ e.u.

The total contribution to entropy due to all the vibrations is

$$S_{\text{vib}} = 0.05 + 0.009 + 0.0002 = 0.0592 \text{ e.u.}$$

The absolute entropies of H_2O and H_3O^+ are compared as following

	<u>H_2O</u>	<u>H_3O^+</u>
S_{tr}	34.613 e.u.	34.777 e.u.
S_{rot}	10.544 e.u.	11.192 e.u.
S_{vib}	0.007 e.u.	0.059 e.u.
Total	<u>45.164 e.u.</u>	<u>46.028 e.u.</u>

APPENDIX II

Statistical Methods

In the discussion of the experimental results several references are made to statistical calculations related to coefficients of correlation and to the question of whether correlations are statistically significant. These procedures have been applied to determining whether additivity applies, in which case a correlation has been sought between experimental values and those calculated on the assumption of additivity. In addition, correlations between such quantities as entropies and free energies of ionization have been investigated.

The procedures are best explained with reference to an example. Table 14 shows values of ΔF and $T\Delta S$ for the non-ortho compounds. These are transformed for convenience as follows:

$$u = 10(\Delta F - 14.0)$$

$$v = 10(-T\Delta S - 8.5)$$

This leads to the following table, in which values of uv , u^2 and v^2 have been calculated:

	u	v	uv	u^2	v^2
phenol	-3	-5	15	9	25
m-cresol	-2	-2	4	4	4
p-cresol	0	0	0	0	0
3,4-xyleneol	1	2	2	1	4
3,5-xyleneol	-1	1	-1	1	1
Sums	-5	-4	20	15	34

One now calculates

$$\bar{u} = \frac{\sum u}{N} = -\frac{5}{5} = -1$$

$$\bar{v} = \frac{\sum v}{N} = -\frac{4}{5} = -0.8$$

$$\bar{u}\bar{v} = (-1)(-0.8) = 0.8$$

$$\frac{\sum uv}{N} = \frac{20}{5} = 4$$

$$\sigma_u^2 = \frac{\sum u^2}{N} - (\bar{u})^2 = \frac{15}{5} - 1 = 2 \quad \sigma_u = 1.414$$

$$\sigma_v^2 = \frac{\sum v^2}{N} - (\bar{v})^2 = \frac{34}{5} - 0.64 = 6.16 \quad \sigma_v = 2.482$$

The correlation coefficient is then given by

$$r = \frac{\frac{1}{N}\sum uv - \bar{u}\bar{v}}{\sigma_u \sigma_v} = \frac{4 - 0.8}{1.414 \times 2.482} = 0.91$$

This is a fairly high degree of correlation; to determine its significance one calculates 'Student's t' as follows:

$$t = \frac{r\sqrt{N-2}}{\sqrt{1-r^2}} = \frac{0.91\sqrt{3}}{\sqrt{1-(0.91)^2}} = 3.8$$

Tables are available (221) which show the significance of a particular value of t for a particular value of N. In the present case the conclusion is that the correlation is

significant at the 1% level.

The regression equation, which shows the relationship between u and v , and hence between $T\Delta S$ and ΔF , is obtained as follows:

The equation is

$$v - \bar{v} = r \left(\frac{\sigma_v}{\sigma_u} \right) (u - \bar{u})$$

whence

$$v = 1.60 u + \text{constant}.$$

From this it follows that

$$-T\Delta S = 1.60 \Delta F + \text{constant}.$$

CLAIMS TO ORIGINAL RESEARCH

1. Ionization constants for various methyl substituted phenols and o-chlorophenol, have been measured for the first time by the spectrophotometric method at more than one temperature.
2. Ionization constants for these compounds as a function of temperature have been analyzed by the Harned and Robinson's equation.
3. The significance of the Harned and Robinson's equation has been discussed and it is found that the value of ΔC_p has no significance.
4. The Harned and Robinson, and Everett and Wynne-Jones equations for phenol have been compared for a wide range of temperatures. It is found that they represent the data equally well at ordinary temperatures but shows great differences at higher temperatures.
5. Thermodynamic functions of ionization for these compounds have been calculated. The ΔF values were found to fit into a simple additivity scheme at all temperatures.
6. Substituent effects to the free energy of ionization have been separated into inductive and resonance contributions.
7. Correlations between ΔS , ΔF and ΔH values have been found.

8. The moments of inertia of H_3O^+ ion in gas phase have been calculated for the first time.
9. Absolute entropies of H_2O and H_3O^+ in the gas phase have been calculated on the basis of statistical thermodynamics.

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