SC

M I C R O C A L O R I M E T R I C

I N V E S T I G A T I O N S

PART I

CONSTRUCTION OF A MICROCALORIMETER FOR HEATS OF COMBUSTION

PART II

HEATS AND ENTROPIES OF IONIZATION OF SOME ANILINES

by

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P R E F A C E

This thesis consists of two parts. Part I is devoted to a description of the construction of a microcalorimeter of the Tian-Calvet type, suitable especially for the measurement of heats of combustion of substances which are difficult to prepare on a large scale. This part of the thesis consists of a general introduction, in which different types of calorimeters used in combustion studies are briefly reviewed, an experimental part in which the construction of the components of the microcalorimeter and the apparatus itself are described, and finally of a discussion of the theory of the apparatus.

Part II of the thesis deals with measurements of the heats of ionization of aniline, o-, m-, and p-toluidines and of all six xylidines. These heats were determined using an apparatus similar to that described in Part I. All reactions were performed in aqueous hydrochloric acid solutions at concentrations in the range of 10^{-3}M to 10^{-2}M. The techniques and results are described, and in a final section the results are discussed from the standpoint of modern theories of ionization reactions.

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CONTENTS

TABLES

FIGURES

P A R T I

CONSTRUCTION OF A MICROCALORIMETER FOR HEATS OF COMBUSTION.

ABSTRACT

A microcalorimeter of the Tian-Calvet type has been constructed for the purpose of measuring heats of combustion. The instrument consists of a differentially-connected system of two iron-constantan thermopiles, each being constructed of sixteen thermocouples. The recording of the heat liberated is accomplished by means of a d.c. amplifier; the areas thus recorded are integrated by an electronic integrator. The apparatus is capable of measuring heats of the order of 10^{-3}cal. The microcalorimeter is discussed from the theoretical and practical points of view.

INTRODUCTION

Heats of combustion are thermochemical quantities of the greatest importance, particularly in view of the fact that they may be used for the calculation of heats of formation. Much effort has been devoted to making accurate measurements of these heats and two main types of combustion calorimeter have been employed: these are adiabatic bomb calorimeters, and flame calorimeters.

Adiabatic bomb calorimeters, employed for the study of reactions at constant volume, have been described by many authors (see especially refs. (1) and (2)). In these calorimeters the sample is burned in a metal bomb containing oxygen at some 25 atmospheres pressure. The sample is ignited electrically by a fuse wire. The heat evolved is conducted to the bomb walls and to the water in which the bomb is immersed. The rise in temperature may be only several degrees and usually is measured by a mercury thermometer reading to hundredths of a degree, by a Beckman thermometer, or by a resistance thermometer of small thermal capacity.

The flame calorimeter measures heats of combustion at constant pressure. This calorimeter is essentially identical with the calorimeter used for measurements of heats of combustion at constant volume, except that in place of the calorimetric bomb there is used a glass reaction vessel

accommodating a flame at constant pressure, with appropriate inlet tubes for the reacting gases and an appropriate exit tube for the issuing gases. The heat is again measured by measuring the rise of temperature of water which surrounds the reaction vessel.

In both of these types of calorimeter substantial amounts of the substances must be burned in order for the elevation of the temperature caused by the heat produced during reaction to be determined accurately.

In order to be able to measure small amounts of heat liberated during combustion reactions it was decided to construct a microcalorimeter of the Tian-Calvet type, with certain modifications which would improve the apparatus. The measurement of the heat liberated in this microcalorimeter is achieved by means of a series of iron-constantan thermocouples, which are distributed symmetrically around the reaction vessel. The calorimeter still employs a bomb, which is a microbomb capable of burning only a few milligrams of the substance in question.

EXPERIMENTAL

(i) General Description of the Microcalorimeter.

The microcalorimeter constructed in our laboratory is a differential microcalorimeter of the Tian-Calvet type. It consists essentially of two reaction cells or "thimbles" made of silver each of which is surrounded by sixteen iron-constantan thermocouples. A schematic representation of such a cell and the thermocouples is shown in Fig.1. E_1 represents the silver socket around which the detector thermopile D is constructed. E_e shows part of the sixty-pound aluminum block to which the cold junctions of the thermopile are attached. The dotted line P shows the possibility of superimposing another thermopile on the already existing one. The purpose of the additional thermopile P would be to compensate heats liberated by the Peltier effect.

A top view of the differential arrangement of the two detector piles is shown in Fig. 2, where E_1 and E_2 stand for cell #1 and cell #2 respectively. Also in Fig. 2 is shown the connection of the differential system to an e.m.f. measuring device (G), which in our case consists of a d.c. amplifier with a feed back system and a Speedomax recorder manufactured by Leeds and Northrup. In addition to this the microcalorimeter is being equipped with an electronic integrator.

The central block is surrounded by five concentric aluminum cans (not shown). The innermost can is made of 2-inch thick aluminum, and the remaining four cans of quarter-inch aluminum. The four innermost cans are insulated by air spaces of about fifteen centimetres between each can. Between the outermost and the second outermost can there is insulating material (well-packed cotton). The second outermost can carries an adiabatic shield made up of several heating resistors uniformly distributed around it. The heating and controlling of the temperature is accomplished by a temperature-controlling unit manufactured by the Polytronics Company of Toronto.

The calorimeter will be enclosed in a small cabin, the temperature of which will be controlled to within 0.1°C., and the relative humidity will be kept below 5 per cent.

(ii) Construction Details.

(a) The Thermocouples.

The thermocouples are constructed of iron and constantan wires. The diameter of the iron elements is 0.4mm.; that of the constantan elements is 0.75mm. The thermocouples were welded electrically and then silver-soldered on to small silver discs. These silver discs were in turn fastened symmetrically around the reaction vessel, by means of glyptal cement. This method of attachment of the hot junctions

FIGURE 1

SCHEMATIC REPRESENTATION OF THE THIMBLE
SURROUNDED BY THE THERMOCOUPLES

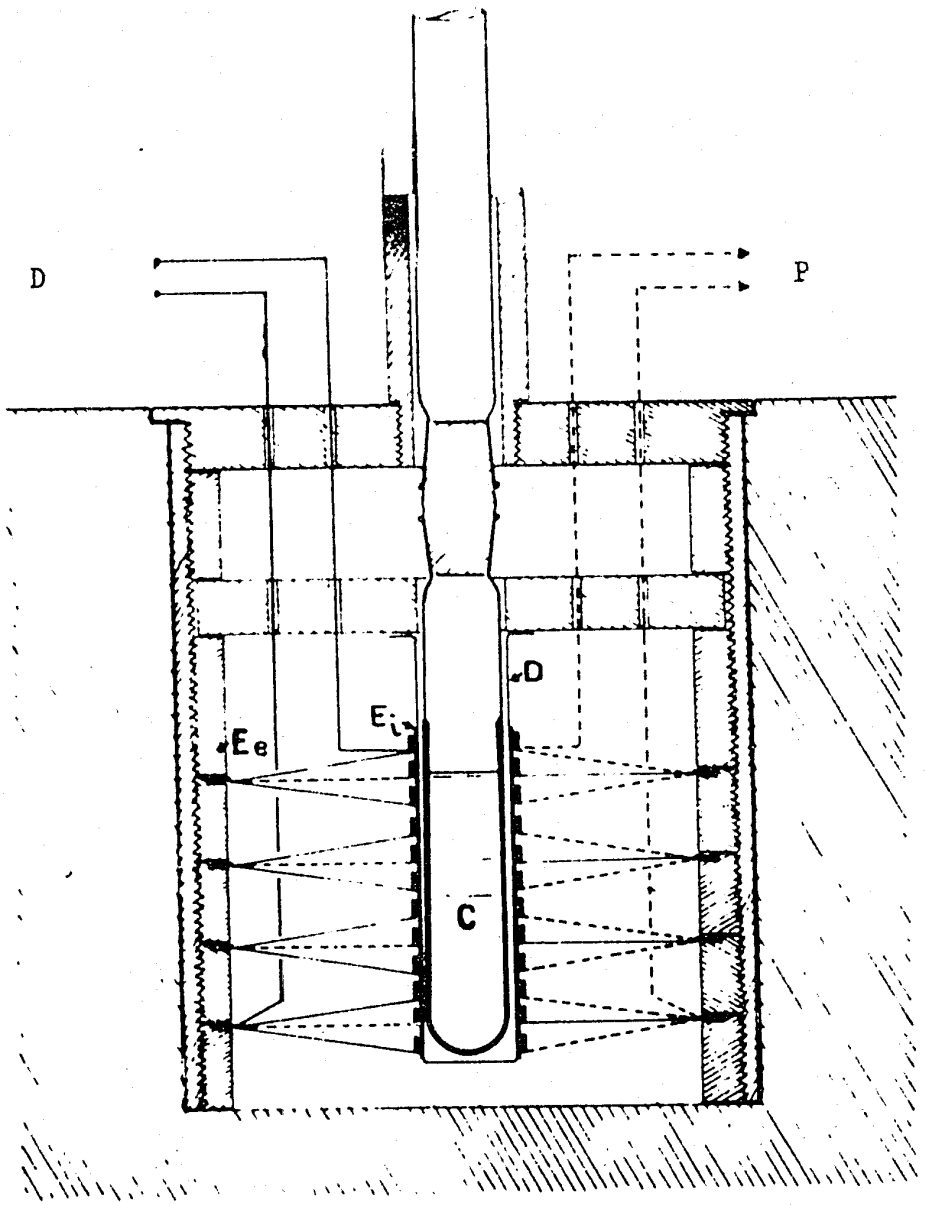
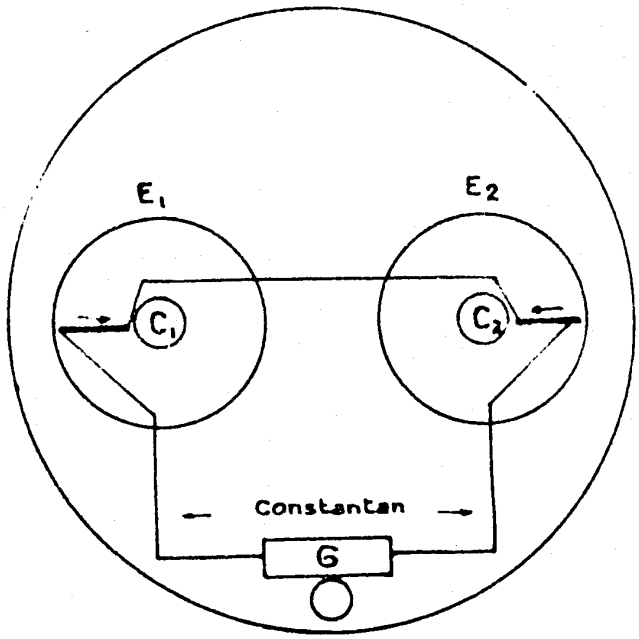


FIGURE 2

TOP VIEW OF THE DIFFERENTIAL SYSTEM



of the couples permitted very good thermal contact, and at the same time very good electrical insulation. The cold junctions of the thermopile were electrically welded and then silver-soldered to small rectangular plates and attached to the aluminum block by means of half-circular aluminum clips. Electrical insulation was insured by covering the places of contact with a thin coating of thermoplastic. All wires used in the construction of the thermocouples were previously annealed by heating to dull-redness in a helium atmosphere, this gas being used to prevent possible oxidation of the thermopile elements. All subsequent handling of the wires was performed using rubber gloves, in order to avoid as much as possible any contact with grease, etc. Two thermopiles, each of sixteen thermocouples, were mounted and connected differentially.

(b) The Adiabatic Shield.

The adiabatic shield was constructed of resistors connected in series and in parallel and placed around the outside of the second outermost aluminum can. The resistors were so connected as to give uniform heating of the whole can. Previous to installment they were "aged" to constant resistance. The temperature of the can is controlled by a temperature controlling instrument furnished by the Polytronics Company of Toronto. By means of this arrangement the temperature of the inside of the microcalorimeter can be

controlled to within one hundredth of a degree. On the inside of the aluminum can that carries the adiabatic shield provisions were made for installation of thermocouples which would be able to detect any differences of temperature in the different parts of the can, in case the adiabatic shield should fail.

(c) The Commutators.

All of the commutators serving in changing sensitivities and control of the apparatus are thermoelectric-free multiposition switches.

(iii) Results.

The thermopiles and the adiabatic shield were successfully tried out. The piles were tested by producing a known amount of heat inside the calorimetric cell and by measuring the e.m.f. generated with a precise thermoelectric-free potentiometer, and also by recording the amplified e.m.f. on an electronic recorder. It was found that the thermopiles give reproducible results which agreed within the uncertainties of the measuring instruments.

The adiabatic shield was also tested at several temperatures between 25°C and 50°C. It was found that the temperature within the microcalorimeter could be controlled to within 10^{-2}° C. in the indicated range of temperatures. The temperature measurements inside the calorimeter were made

with a standardized platinum thermometer.

The electronic integrator is being installed at this time and unfortunately nothing can as yet be said as to its accuracy.

DISCUSSION

(i) Theory of the Microcalorimeter.

A brief discussion of the theory of the microcalorimeter, as developed originally by Tian (1,7), will now be presented. The reaction heat is transmitted by conductivity to the wires of the thermocouples. It can be shown that in the case of a cell completely surrounded by the junctions of the thermocouples, which are uniformly distributed, there is a direct proportionality between the total rate of heat flow from the cell and the electromotive force generated by the thermoelectric pile. This may be proved as follows.

The rate of flow of heat through the j-th thermocouple element is given by

$$\frac{d\,Q'_j}{d\,t} = k\,\Delta T_j \qquad (1)$$

where $\frac{d\,Q'_j}{d\,t}$ is the rate of heat flow conducted by the element of the thermocouple wire, and ΔT_j is the difference between the temperature T_j of the j-th silver socket (internal chamber) and the uniform temperature T_o of the aluminum block (external chamber). The thermocouples are practically identical so that the total rate of flow of heat $Q'(=\sum_{j=1}^{n} \Delta Q'_j)$ due to conduction by n thermocouples is

$$\frac{d\,Q'}{d\,t} = k \cdot \sum_{j=1}^{n} \Delta T_j \qquad (2)$$

The electromotive force E_j appearing in each thermocouple is

$$E_j = L\,\Delta T_j \qquad (3)$$

L being the thermoelectric power of an element for one degree difference between the hot and the cold junctions. The total electromotive force E generated by n elements in series is therefore

$$E = L \sum_{j=1}^{n} \Delta T_j \qquad (4)$$

Combination of equations (2) and (4) gives

$$E = \frac{L}{k} \frac{d\,Q'}{d\,t} \qquad (5)$$

There is therefore a direct proportionality between the total electromotive force generated by the thermopile and the total rate of heat flow through the n thermocouples.

In practice the thermocouple junctions do not cover the entire surface of the cylindrical silver socket, and through the free space heat is lost by radiation and convection. It is reasonable to assume that the rates by

which this heat is lost are also proportional to the difference in temperature ΔT existing between the inner chamber of the microcalorimeter and the outer chamber of the apparatus, and if such is the case the expression for the rate of heat loss due to radiation and convection is similar to equation (2) and may be written as

$$\frac{d\,Q''}{d\,t} = h \sum_{j=1}^{n} \Delta T_j \qquad (6)$$

Also if the losses in wires by conductivity are given by

$$\frac{d\,Q'}{d\,t} = k \sum_{j=1}^{n} \Delta T_j \qquad (7)$$

The total rate of heat loss is

$$\frac{d\,Q}{d\,t} = \frac{d\,Q'}{d\,t} + \frac{d\,Q''}{d\,t} \qquad (8)$$

and therefore

$$E = \frac{L}{k+h} \frac{d\,Q}{d\,t} \qquad (9)$$

From equation (9) it can be readily seen that the electromotive force is less than if the entire heat were conducted by the thermocouple wires. It is therefore advantageous to

weld the wires to small circular silver discs, which are placed in thermal contact with the surface of the cylinder. Electrical insulation between the plates and the cylinder is assured by covering the latter with a thin film of thermoplastic (approximately 1/100mm. thick).

The upper part of the thimble must be closed by a stopper, through which the control rods of the apparatus pass. Consequently there are losses of heat in the upper part of the thimble. These losses may be reduced considerably by using a long thimble of small diameter. With thimble of $2cm.^2$ section by 8cm. long, the stopper only occupies about four per cent of the total surface area. In order for such a loss to be taken into account, it may be represented by a known small fraction K of the total loss, so that direct proportionality between E and $\frac{d\,Q}{d\,t}$ is always preserved. The resulting relationship is

$$E = (1 - K)\,\frac{L}{k+h}\,\frac{d\,Q}{d\,t} \qquad (10)$$

Also, in order for this to be the case the thermal contact between the reaction bomb and the silver cylinder carrying the thermopile junctions has to be as perfect as possible.

In practice it is usually satisfactory to employ a simplified theory of the apparatus, based on the assumption of complete thermal uniformity of the cell and its contents.

The external chamber (thermostatted aluminum block) is supposed to be at constant temperature. As previously pointed out, the temperature of the internal chamber is not usually uniform. However, it is possible to define an average temperature T_j of this internal chamber by the equation

$$T_j = T_o + \Delta T_j \qquad (11)$$

where ΔT_j is the same quantity as used in equation (4).

Let $\dot{Q}$ be the total amount of heat energy released inside the reaction cell at time t. The total amount of heat given off during the time interval dt will then be represented by $\dot{Q}dt$. Some of this heat quantity will be lost by conduction through the thermocouple wires, and this loss may be represented by $p(T_o - T_j)$ where p is the rate of heat loss for a $1^oC.$ difference in temperature between the thimble and the aluminum block; the rest of the heat will be used to raise the temperature of the reaction cell by dT. This quantity of heat may be represented by μdT where μ is the heat capacity of the reaction cell and its contents. The total heat energy liberated during a time interval dt may then be written in the form of the equation

$$\dot{Q}dt = p(\Delta T)dt + \mu dT \qquad (12)$$

whence

$$\dot{Q} = p\,\Delta T + \mu \frac{d\,T}{d\,t} \tag{13}$$

Also the deviation Δ of the recorder pen is proportional to the electromotive force generated by the detector thermopile, and hence, using equation (4), it is possible to write

$$\Delta = g(T_o - T_j) \tag{14}$$

and

$$\frac{d\Delta}{d\,t} = g\left(\frac{d\,T}{d\,t}\right) \tag{15}$$

Upon inserting equation (14) and (15) into the equation (13) we obtain

$$\dot{Q} = \frac{p}{g}\Delta + \frac{\mu}{g}\,\frac{d\Delta}{d\,t} \tag{16}$$

This is the fundamental equation of the microcalorimeter, and is known as Tian's equation (3 - 7).

Relation (16) may somewhat be simplified for very fast reactions, and the simplification leads to the result that the heat generated in the internal chamber is proportional to the area obtained on the recorder. For such fast reactions we can employ the apparatus as a "ballistic" one.

During a very short time the heating effect is produced in the reaction cell (without compensating by Peltier effect). The curve O A B C D in Fig.3 is recorded, in which A B is corresponding to the heating period. Tian's fundamental equation may now be written as

$$\dot{Q}dt = \frac{p}{g}\Delta dt + \frac{\mu}{g} d\Delta \qquad (17)$$

Integration of equation (17) between t=0 and t=∞ gives

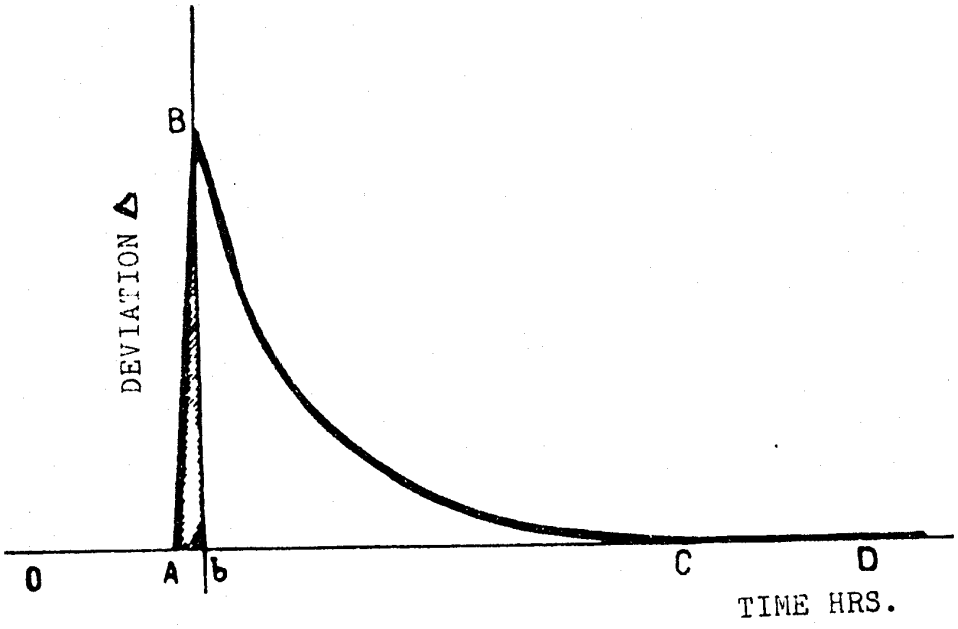
$$\int_{t=0}^{t=\infty} \dot{Q}dt = \frac{p}{g}\int_{t=0}^{t=\infty} \Delta dt + \frac{\mu_o}{g}\int_{i}^{f} d\Delta \qquad (18)$$

where μ_o represents the same value as μ in equation (17) but for a very short period of heating. The left-hand-side of equation (18) is equal to the total heat given off during a fast reaction, and the right-hand-side of the equation is proportional to the area A B C represented in Fig.3. Measurement of heats of reactions of short duration reduces, therefore, to the measurement of an area obtained by the deflection registered on the recorder. The apparatus must be calibrated, and in the present work this was done using the Joule effect, the calibration being made over the range of the scale used.

A major improvement to Tian's original microcalorimeter

FIGURE 3

TYPICAL CURVE RECORDED DURING AN EXPERIMENT



was introduced by E.Calvet, who employed a differential system (8,1,7). This improvement brings about the result that, should a change in temperature of the thermostatted aluminum block occur, there is no effect on the experimental results. Such a failure in the microcalorimeter without the differential arrangements results in very large errors, since in fact the electromotive force e produced by the detector thermopile is

$$e = k\,(T_1 - T_o), \tag{19}$$

k being the proportionality constant, T_1 the temperature of the reaction cell (inner chamber) and T_o temperature of the aluminum block (outer chamber). It is seen therefore from equation (3) that variations in T_o considerably affect the electromotive force e; this is translated in the recorded curve as variations of the experimental zero. Consider the differential arrangement of identical calorimetric units represented in Fig.2. If the aluminum block is well designed, its temperature is uniform near the calorimetric units. The temperature T_o varies only slightly, and it is the same at all times in the outer chamber around the two calorimetric units. Calling the temperatures of the two cells T_1 and T_2 respectively we obtain for the electromotive forces e_1 and e_2

$$e_1 = k\,(T_1 - T_o) \tag{20}$$

$$e_2 = k\,(T_2 - T_o) \tag{21}$$

These thermopiles being in opposition, the resulting electromotive force is

$$E = e_1 - e_2 = k\,(T_1 - T_2) \tag{22}$$

It is seen from equation (22) that E does not depend any longer on the variations of T_o with respect to time. The variations of T_o in the course of time cause variations in the temperature of the two cells, but these variations are identical and have no effect on E as is shown by equation (22). This arrangement is of remarkable reliability.

One final comment may now be made regarding a difficulty arising during calibration of the microcalorimeter. The calibration is performed by means of the Joule effect, and therefore consists essentially of the passage of a known amount of electricity through a standard resistance immersed in the silver thimble. If there is a large temperature difference between the thimble and the outside of the instrument, the losses of heat due to conduction will be large. These losses can be reduced by passing the connecting wires

through the heavy aluminum block. In practice this is accomplished by winding the wires several times around the block. As mentioned previously the block is thermostatted, and since the rise of temperature in the microcalorimetric cell is very small, there will be no appreciable difference between the temperatures of the thimble and of the aluminum block.

(ii) Advantages of Electronic Recording.

If an amplifier is used instead of galvanometers as in the original Calvet apparatus the number of thermocouples is greatly reduced. The electromotive force generated by the detector thermopile is amplified to the desired extent and then the signal is recorded by a Speedomax recorder. The advantage of the electronic arrangement lies in the fact that at least the same sensitivity can be achieved with only 16 thermocouples per pile instead of 128 as is the case in the Calvet type of microcalorimeter. The following equation is obeyed,

$$\frac{d\dot{Q}}{dt} = \alpha \Delta T = \beta E \qquad (23)$$

whence

$$\dot{Q} = \beta \int E dt \qquad (24)$$

The right-hand-side of equation (24) is proportional to the area registered by the recorder, and measurements of heat generated in the reaction bomb therefore reduce to an estimation of the area. In future it is intended to employ an electronic integrator for this purpose.

P A R T I I

HEATS AND ENTROPIES OF IONIZATION OF SOME ANILINES

ABSTRACT

Heats of ionization of a number of anilines in aqueous solutions of hydrochloric acid have been determined, using a microcalorimeter of the Tian-Calvet type. The range of concentrations was 10^{-3}M to 10^{-2}M, which is sufficiently low to permit an accurate extrapolation to be made to infinite dilution. The substances investigated were: aniline, o-, m-, and p-toluidines, and all six dimethyl substituted anilines (xylidines). The heats were found to vary markedly with concentration, but no systematic effects could be recognized. With the aid of the heat of the process $RNH_2 + H_3^+O \rightleftharpoons RNH_3^+ + H_2O$ and the dissociation constants, the entropies of ionization have been computed. The results are discussed from the standpoint of the effects of solvent and structural factors on the ionization processes.

INTRODUCTION

Most previous studies of ionization processes in solution have been limited to the determination of the ionization constants, from which the free energies of ionization can be calculated. Few investigations have been concerned with heats and entropies of ionization, quantities that will undoubtedly throw much light on the details of ionization processes and on ionic processes in general. Everett and Wynne-Jones (9), and Harned and Owen (10), have listed some heats and entropies of ionization calculated from electrochemical data, and these have led to conclusions of considerable interest. There are, however, few values available for members of homologous series, and such values would be useful in providing information about the effects of substituents. Considerable knowledge might, for example, be expected to be gained on the nature of steric hindrance by investigations of this type. The program of work, the results of which will be described, was designed with a view to providing information of this type. The procedure has been to make direct determinations of heats of ionization of aniline, the three monomethyl substituted anilines, and all the six dimethyl substituted anilines (xylidines) using a microcalorimeter of the Tian-Calvet type. This instrument enabled measurements to be made of heats of ionization at concentrations as low as 10^{-3} M, and a reliable

extrapolation to infinite dilution was therefore possible. The heat measured directly is the heat for the process

$$RNH_2 + H_3O^+ \rightleftharpoons RNH_3^+ + H_2O.$$

The neutralization was carried out by the addition of a sufficient excess of hydrochloric acid.

(i) Heats of Neutralization of Weak Acids.

Many studies of ionization processes in solution have been limited to the dissociation constants, from which the free energies of ionization may be calculated. Relatively few investigations have been concerned with such thermodynamic properties of weak electrolytes as heats and entropies of ionization. This is quite surprising, since a knowledge of these quantities may throw much light on ionic reactions in general.

Recently Canady, Papée and Laidler (11) carried out microcalorimetric measurements of heats of neutralization and ionization of some weak acids in highly dilute aqueous solutions. The work was concerned with some of the lower members of the aliphatic acid series and with benzoic acid. The results obtained by the above investigators will now be considered in some detail.

From the results obtained by Canady and al. (11), it is

observed that for formic, acetic, propionic, and butyric acids the heats of neutralization are not strongly dependent on concentration. In the case of isobutyric and benzoic acids, however, the influence of the ionic strength on the heats of neutralization is a very marked one. Direct tests in which the concentration of the acid was kept constant, and only the sodium hydroxide concentration was varied, indicated that this variation depends entirely on the alkali concentration. Moreover it was found that the conventional Debye-Hückel theory of the effect of ionic strengths on the heats of dilution is incapable of explaining the results obtained, the heat changes observed over the range of concentrations studied being much larger than those predicted by the theory. Thus the theory predicts a heat of dilution of 0.05k-cal. per mole in diluting from 10^{-2}M to zero concentration, while heat changes were obtained which are much larger for isobutyric and benzoic acids. It was pointed out that these large heat changes occur in compounds when a large group is adjacent to the carbon atom attached to the functional group; it is also possible that the smearing of charges on the aromatic ring (as in the case of benzoic acid) produces effects that are not predicted by the Debye-Hückel theory, and the present work will be concerned with the further investigation of this problem as applied to aniline and its analogues.

(ii) Theories Related to Entropies of Ionization.

The difference between the change in heat content and the change in free energy is the entropy term $T\Delta S$, which is related to the temperature coefficient of the free energy change by the equation

$$\Delta S = - \frac{\partial (\Delta F)}{\partial T} \qquad (25)$$

Eley and Evans (12) considered the orientation of the solvent molecules around ions of the particular type under investigation, and have arrived at entropy values which are in fairly good agreement with the experimental data. More recently heats and entropies of ionization of some weak organic acids in highly dilute aqueous solutions were obtained experimentally by Laidler and coworkers (11,13,14) and the results could be satisfactorily explained in terms of the concept of electrostriction of water molecules.

Gurney (15) laid particular stress on the temperature dependence of the dissociation constants of weak acids, and showed that, if the dissociation energy is split into an electrostatic and non-electrostatic term, it is possible to give a qualitative explanation of the maximum which occurs when dissociation constants of weak acids are plotted as a function of temperature. His theory is based on the assump-

tion that, while the non-electrostatic energy required for dissociation does not depend on temperature, the electrostatic energy increases as temperature increases. The position of the maximum in the above-mentioned dependence should vary, according to Gurney, as the relative importance of the electrostatic free energy contribution to the total free energy increases or decreases.

Everett and Wynne-Jones (9) pointed out that in a complete treatment of entropies of ionization one must take into account non-electrostatic factors, and in support of this they mentioned the following three pieces of evidence:

(a) Non-ionic and isoelectric equilibria often have large values of ΔS.

(b) The dependence of ΔS upon the dielectric constant of the solvent suggests that only a part of the entropy is purely electrostatic.

(c) For one ionic equilibrium, Everett and Wynne-Jones (9) found an extremely small value of ΔS which, moreover, changed sign within the experimental range.

The evidence for the first statement is given on the one hand by such gaseous equilibria as the dissociation of gaseous hydrogen iodide and hydrogen selenide, and on the other hand by the values of isoelectric equilibrium constants which may be calculated from other experimental data.

The second point mentioned by Everett is supported by the results obtained by Harned and Kaznajian (16). If their values of ΔS are plotted against the reciprocal of the dielectric constant, a linearity is obtained, but there is no apparent proportionality between these quantities since the entropy is still quite large (approximately 18 e.u.) even when $\frac{1}{D}$ is zero.

The third argument is mainly based on the results obtained by Everett and coworkers themselves (9), in connection with studies of dissociation constants of mono-, di- and tri-methylamines. From this work it seems obvious that the sign of ΔS is not characteristic of ionic reactions, and that the separation of an electrostatic energy of ionization is not sufficient to give a complete explanation.

In view of the difficulty in interpreting the origin of entropies of ionization, more investigations of this problem are required to further clarify the situation.

(iii) Theories on the Effects of Structure on Protonic Acids and Bases.

The following part of the introduction is largely based on the discussion of the subject by H.C.Brown, D.H.McDaniel, and O.Hafliger (19). This discussion of the behaviour of acids will be limited to those species which are relevant to the compounds studied in this work. Thus the factors affecting primarily the ionization of aliphatic and aromatic amines will be considered; the ioni-

zation of an organic base may be represented by the reaction

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

and the strength of the base may be represented in terms of either the equilibrium constant, K_b, or in terms of its negative logarithm, pK_b

$$K_b = \frac{[BH^+][OH^-]}{[B]} \cdot \frac{f_{BH^+} f_{OH^-}}{f_B} \simeq \frac{[BH^+][OH^-]}{[B]} \quad (26)$$

The strength of the base may also be expressed in a different fashion, namely, in terms of the acidity of the BH^+ ion

$$BH^+ + H_2O \rightleftharpoons B + H_3O^+$$

$$K_a = \frac{[H_3O^+][B]}{[BH^+]} \quad (27)$$

The two dissociation constants, K_b for B and K_a for BH^+ are related through the expression

$$K_a \cdot K_b = K_w \quad (28)$$

where K_w is the ionic product of water, 1.0×10^{-14} at 25°C. Expressed in more convenient form this relation becomes

$$pK_a + pK_b = 14 \quad (29)$$

In view of the simplicity of this relationship, it has become increasingly common to report the strengths of bases in terms of pK_a values. Moreover it is highly convenient to consider bases from the standpoint of ionization of their conjugate acids. Thus the identical factors which affect the acidity of the substituted homologues will be expressed in terms of the pK_a values in this work.

(a) Polar Effects.

The introduction of a methyl group into formic acid (pK_a 3.77) to give acetic acid (pK_a 4.76) results in a considerable decrease in the acid strength. Increase in the length of the chain beyond acetic acid and branching of the chain have relatively little further effects upon the ionization constant. In the same way, the introduction of the first methyl group into the ammonia molecule (pK_a 9.25) to form methylamine (pK_a 10.64) results in a considerable increase in the basic strength, but further lengthening of the chain or branching of the chain does not affect significantly the ionization constant of the base.

The introduction of a substituent carrying an electrical charge greatly affects the acidic and basic strengths. Thus a positive charge markedly increases the ease with which the proton is removed i.e. favors the acidic properties of the compound. A negative charge has the opposite effect.

The change in the acid strength is attributed to the effect of the group on the work required to transfer a proton to and from the acid-base center within a molecule. Two distinct mechanisms have been proposed for the transmission of the effect of a group to the acid-base center (17,18). In the first the group is considered to produce a shift of electrons within the molecule, and such a shift of electrons is referred to as resulting from the inductive effect of the group. In the second it is considered that the electrostatic influence of the group is transmitted directly through space or solvent to the acid-base center; this is known as a direct or field effect.

At the present time there is no general agreement as to the relative importance of these two mechanisms for the transmission of the electrostatic effects from the group itself to the acid-base center in the molecule. Although the question is of importance to theory, it is not so vital in interpreting the experimental results on the effect of substituents on acid and base strength. By either mechanism the presence of an electron-attracting group in the molecule should greatly increase the acid strength, whereas an electron-repelling group should have the opposite effect. The effect of the substituent on the ionization constant decreases rapidly as the distance from the reaction center increases. The effect of a positive group has been examined

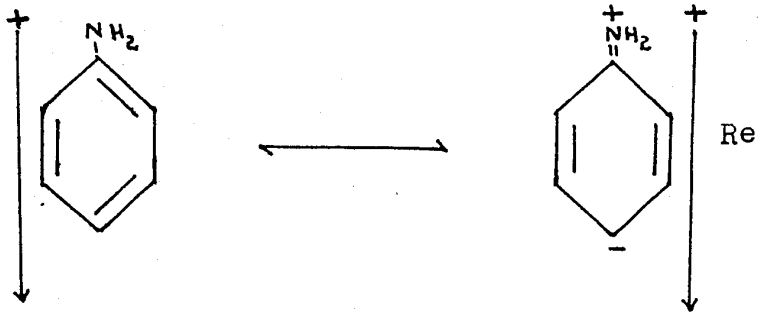
in benzoic acid and aniline molecules. Here also the effect is larger in the nearer meta position than in the more distant para position. These effects can be illustrated using Cl and $-NH_3^+$, for example, as the electron-repelling and the electron-attracting groups respectively.

The introduction of a single alkyl group to the ammonia molecule results in an increase in the base strength. The increase is attributed to the inductive effect of the alkyl group, which results in the increase of the electron density on the nitrogen atom. A second alkyl group causes a further increase in the basic strength, as would be expected. The third alkyl group, however, results in a decrease of the basic strength. Tertiary aliphatic amines are uniformly weaker than the corresponding primary and secondary amines. It seems that some new factor is inhibiting the ability of the nitrogen atom to add a proton. This is probably due to steric effect and will be discussed in a later section.

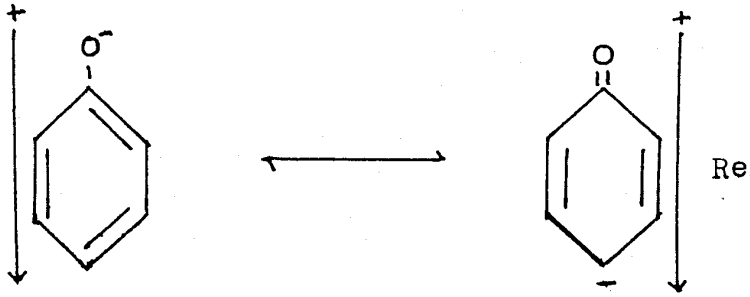
(b) Resonance Effects.

Aniline (pK_a 4.58) is a much weaker base than its saturated analogue, cyclohexylamine (pK_a 10.64). Similarly phenol (pK_a 9.95) is a much stronger acid than cyclohexanol ($pK_a \sim 18$). These marked changes resulting from the presence of the benzene ring may be attributed to the resonance interaction and the inductive effect of the aromatic ring, both

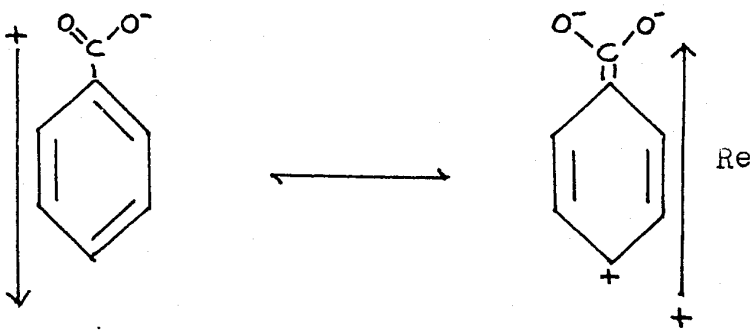
effects operating in the same direction, namely to increase the acid strength or to reduce the base strength. The effects may be represented more clearly using such forms of the compounds as

Inductive  Resonance

and

Inductive  Resonance

The slight effect of the benzene ring in case of the benzoic acid (pK_a 4.17) as compared with the cyclohexacarboxylic acid (pK_a 4.90), may, probably, be attributed to the fact that the inductive and the resonance effects work in opposite directions. The opposing effects may be illustrated by considering such forms of benzoic acid as

Inductive  Resonance

There is some evidence (19) that approximately half of the decrease in base strength observed in aniline arises from the inductive effect, with resonance accounting for the other half. In the case of the acid, therefore, we can assume that the resonance and inductive effects are of the same order of magnitude but act in opposite directions. The effect of the substituents, particularly in the ortho and para position to the base or acid center, will also depend on the resonance effect. The effects of the ortho-substituents will in addition depend on the steric requirements. Hence at present only para- and meta-substituents will be considered while ortho-substituents will be dealt with in the sub-section concerned with steric effects. In cases where one deals with such substituents as $-N(CH_3)_3^+$ on the ring of benzoic acid and aniline, the substituents in the meta-position have a larger effect on the acid or base center than in the para-position. This of course may be accounted for by the theories of inductive effects discussed previously. In consideration of the substituents in aromatic acids and bases, difficulties often arise when it comes to the interpretation of results. Thus an electron-repelling group normally decreases acid strength and increases basic strength.

Summarizing the effects discussed on mono substitution products of benzoic acid, phenol, and aniline the following generalizations can be made. Electropositive substituents,

such as alkyl groups, in the meta- and para-positions weaken aromatic acids and strengthen bases. Electronegative substituents, such as nitro, nitrile, hydroxyl, methoxyl, halogen, etc., uniformly strengthen acids and weaken bases when in the meta-position. In the case of groups possessing unpaired electrons which can interact with the ring (-OH, $-OCH_3$, -X), there is usually observed a smaller electron-withdrawing effect from the para-, than from the meta-position. Since in some cases the opposite holds, the difference between the pK_a values for the meta- and para-compounds should give a measure of the importance of resonance interaction.

(c) Steric Effects.

There are two main types of steric effects to be considered with reference to this work:

(1) Steric inhibition of resonance in unsaturated and aromatic compounds.

(2) Steric strains resulting from conflicting steric requirements at the reaction center.

The methyl group is an electron-releasing group and accordingly if it is substituted in the meta- or para-position in an aromatic acid such as phenol it will decrease its acidic strength. In the ortho-position, however, the

effect is quite opposite to those encountered in the meta- and para-positions. This suggests that some other factors, other than purely inductive ones, play an important role here. If the bulky tertiary butyl group is considered, then in the para- and meta-positions it has an effect of comparable magnitude to that of the methyl group, on the one hand, and a much stronger effect in the ortho-position, than that caused by the CH_3 group on the other hand. Brown (19) gave a satisfactory explanation of these effects in terms of steric requirements of the two functional groups of different compounds and the difference in bulk of the two alkyl groups. The resonance structures for benzoic acid and benzoate ion require the carboxylate group to be coplanar with the aromatic ring. A large substituent in the ortho-position would interfere with the coplanar carboxylate group. The crowding could be released at the expense of the resonance energy by twisting of the carboxylate group out of the plane of the ring. There would then result a decrease in resonance contribution and consequently a decrease in the acid strength. Such effect is known as a steric inhibition to resonance. In the case of phenol where the functional -OH group has small steric requirements, this effect may be negligible. In case of anilines, where the steric requirements of $-NH_3^+$ are larger, the effect becomes more important and, therefore cannot be negligible, even with the methyl group as substituent. The introduction

of a methyl group in the ortho-position of such a compound as dimethylaniline results in an increase in base strength, an increase which is generally attributed to steric inhibition of resonance. A second methyl group in the remaining ortho-position, instead of increasing the base strength still further, decreases it. This decrease is assigned to an increase in steric strain accompanying the addition of the proton to the base center. In view of these two opposing effects, as in the series methyl, ethyl, isopropyl, and t-butyl, the base strength should first increase as the resonance is increasingly inhibited, but should then decrease. The decrease should be more marked as the larger steric requirements of the ortho-substituents result in larger steric strain effects. There is some evidence now available to support this point of view (18). Steric strain appears to be of importance even in primary aniline bases where a methyl group in the meta- or para-position of aniline increases its base strength, and a methyl group in the ortho-position causes decrease in the base strength. Again it appears reasonable that the greater steric requirements of an $-NH_3^+$ group as compared to the $-NH_2$ group should result in an increased tendency to favor the free amine in compounds containing bulky substituents in ortho-positions. In these compounds there is steric inhibition to resonance strain effect, and this would explain a regular decrease in base strength with increasing steric requirements of the ortho-substituents.

(d) Solvent Effects.

There are great difficulties which are at present encountered in attempting a complete analysis of the effects of solvent interactions on acid-base behavior. At the present moment the effect of the solvent on the transmission of polar effects may be considered. It has been pointed out that polar or dipolar substituents may have large effects on the strengths of acids and bases. The substituent produces its effect at the reaction center by modifying the electrostatic environment of the functional group. In part this modification must result from a shift in the electrons of the intervening bonds under the influence of the substituent. From a low polarizability of the electrons in a single bond, the inductive effect should drop off rapidly with increasing length of the chain. Bjerrum (18) realized that the effect of a substituent did not decrease as rapidly as may be expected from the inductive effect. To explain this he suggested that a substituent could alter the electrostatic surroundings of the functional group by a direct action through the solvent. If such is the case then the two effects would vary in their relative contributions depending on the solvent. In general, however, more work will perhaps enlighten many problems which arise when the influences of solvent on the acid-base systems are considered. At the present moment the situation is not clear as yet.

Recent investigations (13) showed that electrostriction of water molecules around phenolate ions is responsible for large negative values of entropies of ionization of phenols on the one hand; on the other hand in the present work the electrostriction of water molecules around the anilinium ions did not seem to be as pronounced. It appears therefore that clustering of solvent molecules around ions has a large influence on the ionization process particularly where the functional groups are not very large. The extent of electrostriction of the solvent molecules around the ions in question will also depend on the nature of the solvent. Thus for strongly polar solvents more electrostriction would be expected than for less polar solvents.

EXPERIMENTAL

(i) Description of the Apparatus.

The microcalorimeter employed was of the type originally designed by Tian and later modified by Calvet (5,8) by the introduction of a differential system that increased the sensitivity. The instrument consists essentially of a central aluminum block containing four cells, to each of which 144 iron-constantan thermocouples are attached. These are connected differentially to a high sensitivity galvanometer and a switching arrangement which provides three sensitivities. The instrument was used at its highest sensitivity when heats of 0.01 to 0.4 calories were being measured, at medium sensitivity for heats of 0.4 to 2.0 calories, and at low sensitivity for heats of over 2 calories. This calorimeter being of the conduction type, the results are independent of the specific heat of the solutions involved. The microcalorimeter is kept in a specially built isolated room maintained at 25.0 ± 0.1°C. and a relative humidity of about 5%.

(ii) Calibration of the Apparatus.

Calibration of the microcalorimeter was carried out from 5×10^{-3}cal to approximately 10^{-1}cal. The calibration was performed by passing a known number of joules of electri-

city through a manganin resistor. The resistance of the resistor was previously measured by means of a Wheatstone Bridge. It was also ensured that the resistance of the resistor did not change with time during calibration by previously "tiring" the resistor. Two resistors were used in the calibration process; one of 989.32 Ω for great sensitivity calibration, and one of 73 Ω for medium and small sensitivities with a current of 6.774×10^{-4} amp. to 11.71×10^{-4} amp. passing through it for a three-hour period.

The variation of current was used in order to cover the whole scale of the photoelectric recorder. The average of three calibrations per sensitivity was taken and it was found that the three calibrations were reproducible to the third significant figure.

In case of medium sensitivity and small sensitivity a similar procedure was followed, with resistances so chosen as to cover the whole scale of the recorder. During calibration the resistances were immersed totally in paraffin oil and identical experimental cells as used for heat measurements were used (c.f. description of the cell). Absolute joules of electricity were then converted into calories by means of the factor 4.1840 joules per calorie, and the calories quoted in this work are therefore the "thermochemical" calories employed by the U.S. National Bureau of Standards.

(iii) The Microcalorimetric Cells.

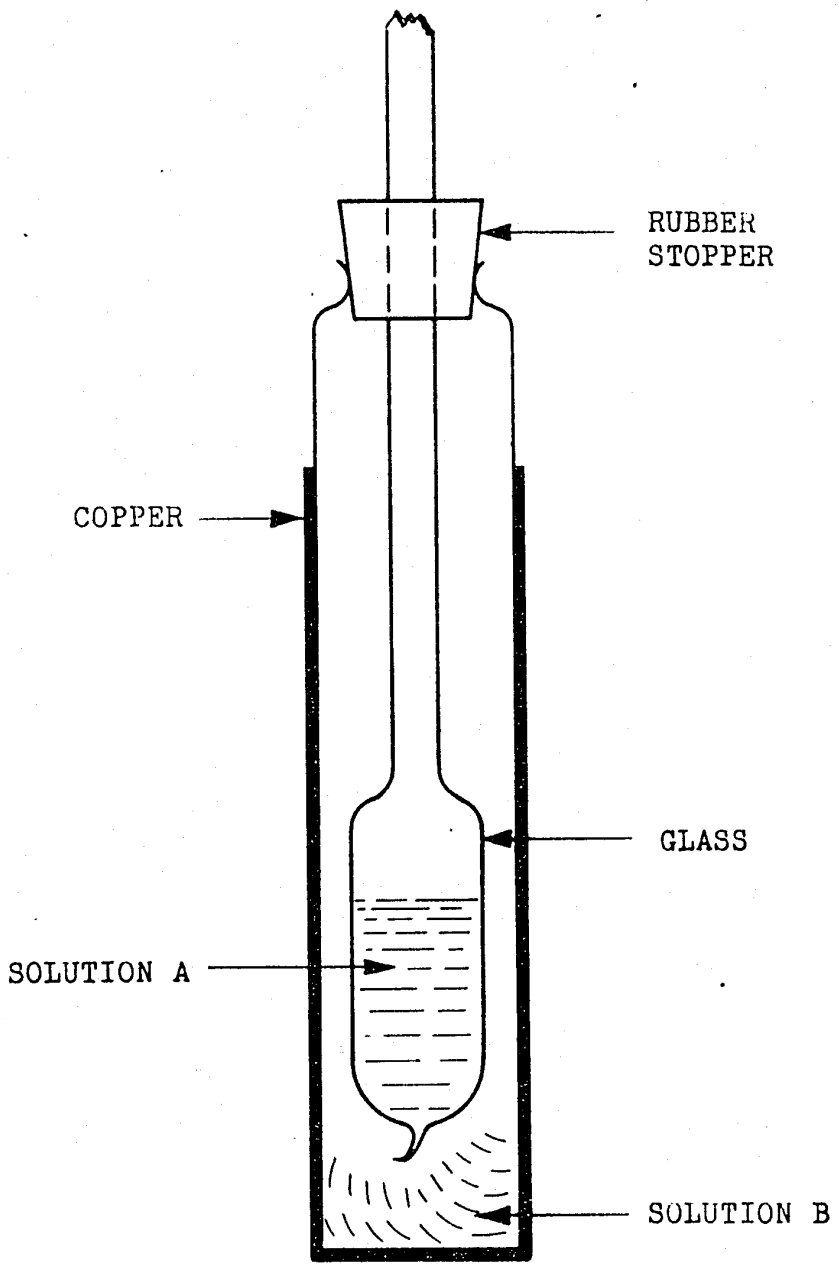
The cell used in the experiments is represented in Fig.4. The outer cell is made of thin glass (0.5mm.). It is 10.5cm. high and 1.5cm. in outside diameter. The cell was first covered with a silver mirror and then copper-plated electrochemically from acidic copper sulphate solution. The inner cell was made of pyrex glass at the lower end of which there was a brittle capillary. The upper end of it was attached to a long glass tube, passing through a rubber stopper on top of the outer cell. In most of the cases Solution A of Fig.4 was the solution of the aniline under investigation, while Solution B was the acid solution of concentration ten times that of the aniline.

(iv) Purification of the Compounds and Preparation of Solutions.

The compounds used were of the highest purity commercially available, and were purified further by vacuum distillation. The melting point of the middle fraction was then determined and compared with the value recorded in the literature. After the distillation, the compounds were handled as much as possible in a dry nitrogen atmosphere. This was achieved by letting dry nitrogen into the vacuum circuit after distillation was completed, and then by introducing the

FIGURE 4

SCHEMATIC REPRESENTATION OF THE EXPERIMENTAL CELLS AND THEIR CONTENTS.



particular aniline into a dry box. The weighing of the compound was performed in a closed weighing bottle which was loaded in the dry box. The weighed compound was then introduced into a volumetric flask, and then diluted with redistilled water to give a solution of the desired concentration. All measurements were made in triplicate, for each of which a different starting solution was used. The concentrations were chosen in such a way as to assure complete solution of the compound; this was achieved on the basis of solubility data of the anilines, available in literature. The original stock solutions were then diluted, as heats of ionization were measured at different concentrations. The hydrochloric acid solution was prepared by diluting C.P. grade concentrated acid to a desired concentration. The acid was then titrated five times with sodium hydroxide solution of known normality; the first three titrations were performed using phenolphthalein as indicator, while the last two titrations were performed using methyl orange as indicator. The average of the five titrations was taken as final concentration of the acid. The sodium hydroxide solution was prepared by the usual analytical methods and its concentration was determined by titration with potassium phthalate using phenolphthalein as indicator. In this case the average of five titrations was also taken.

(v) <u>The Mixing Technique.</u>

The procedure was to mix, in the cell of the calorimeter,

0.5ml. of a solution of the aromatic base with 9.5ml. of a hydrochloric acid solution. The aniline concentration was varied over such a range that the final concentration of the aniline in the mixture (before the reaction) was from 5×10^{-4}M to 3×10^{-2}M. The hydrochloric acid concentration was adjusted so as always to be in considerable excess. It was found by direct test that the heat evolved was dependent only on the concentration of the hydrochloric acid. The hydrochloric acid solution (Solution B, Fig.4) was placed in the main cell of the calorimeter, which was coppered on the outside to assure good heat conduction to the block. The aniline solution (Solution A, Fig.4) delivered from a micropipette capable of an accuracy of 0.02%, was contained in a small glass bulb with a thin capillary at its base, Before being mixed the solutions were allowed to come to thermal equilibrium (approximately 3 hours). Mixing was achieved by breaking the projection on the bulb, and complete mixing brought about by the manipulation of a rubber bulb connected to the bulb. In all cases a blank was run simultaneously in another cell of the microcalorimeter connected in opposition to the experimental cell. This allows for the effects of dilution (actually negligible at these concentrations) and for the heat developed in the mixing operations.

(vi) Results.

The heats evolved for the various anilines are shown plotted as a function of the ionic strength in Figs.5 to 7. The plots are all linear within the experimental error. The slopes and intercepts, and the corresponding probable errors, were determined by the method of least squares, and are shown in Table 2. In Table 3 free energies, enthalpies and entropies of ionization are tabulated.

FIGURE 5

PLOT OF HEAT OF IONIZATION AGAINST IONIC STRENGTH FOR ANILINE (H), O-TOLUIDINE (o), M-TOLUIDINE (m) AND P-TOLUIDINE (p).

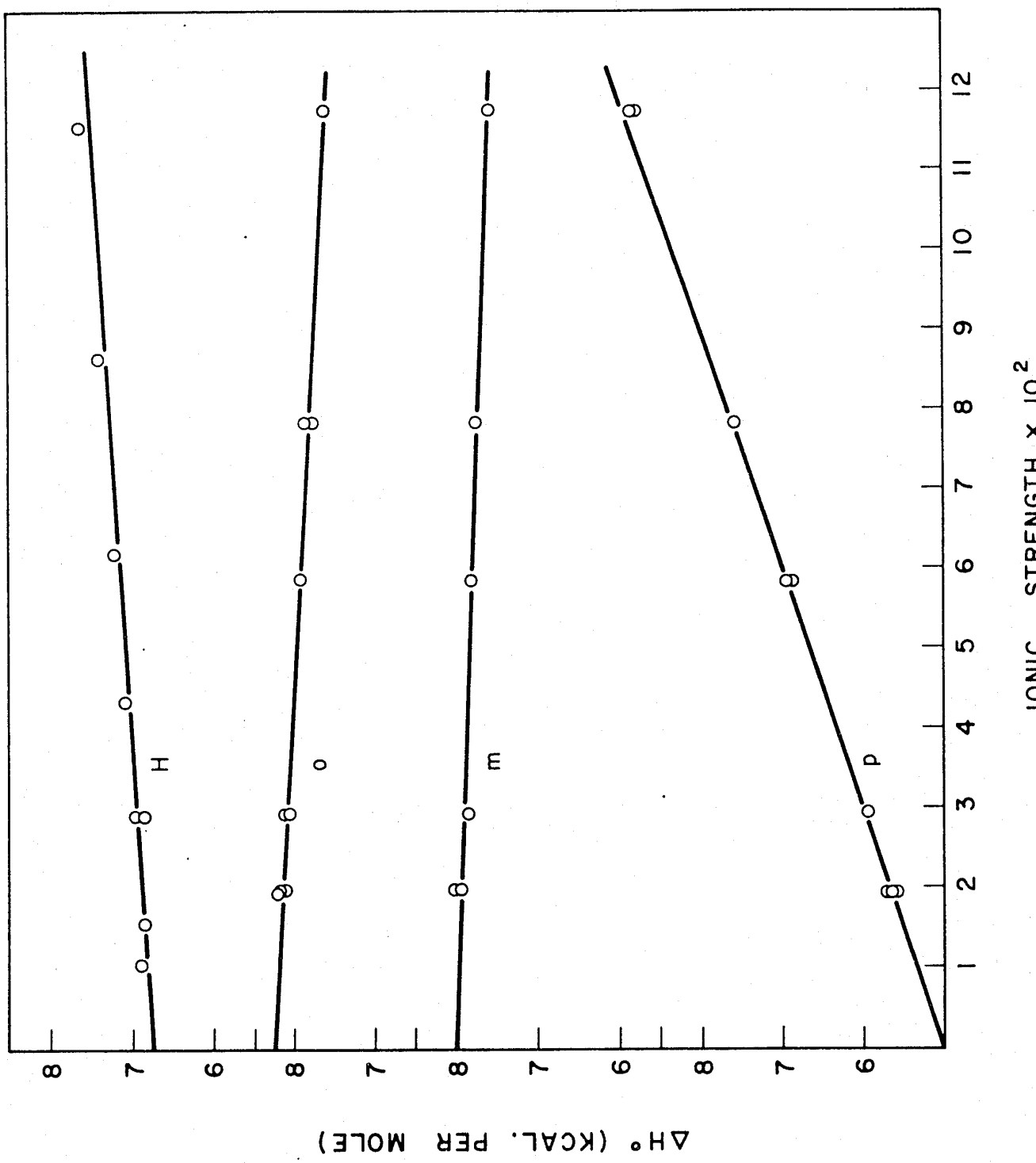


FIGURE 6

PLOT OF HEAT OF IONIZATION AGAINST IONIC STRENGTH FOR 2,4-XYLIDINE, 2,5-XYLIDINE AND 2,6-XYLIDINE.

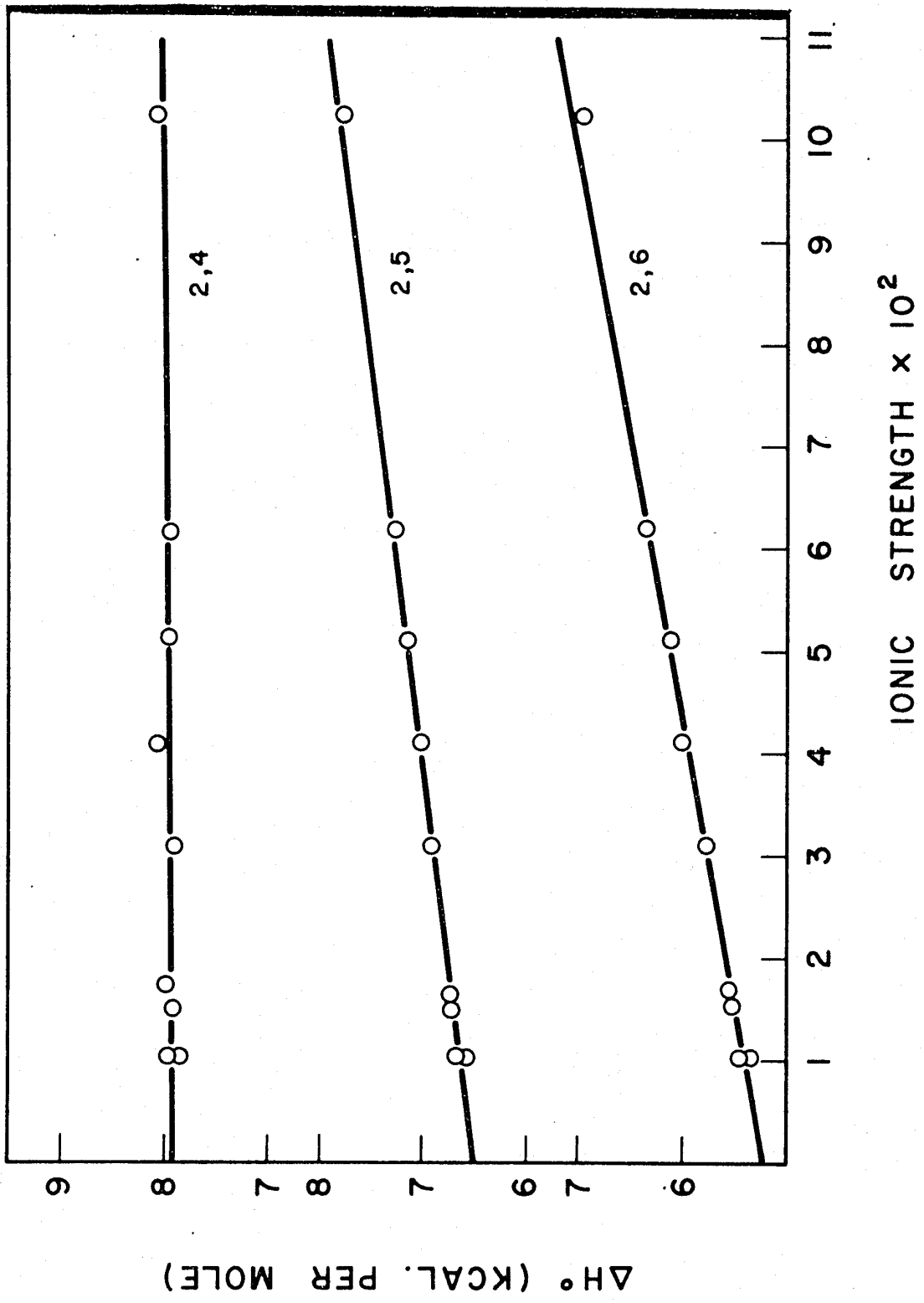


FIGURE 7

PLOT OF HEAT OF IONIZATION AGAINST IONIC STRENGTH FOR 3,5-XYLIDINE, 3,4-XYLIDINE AND 2,3-XYLIDINE.

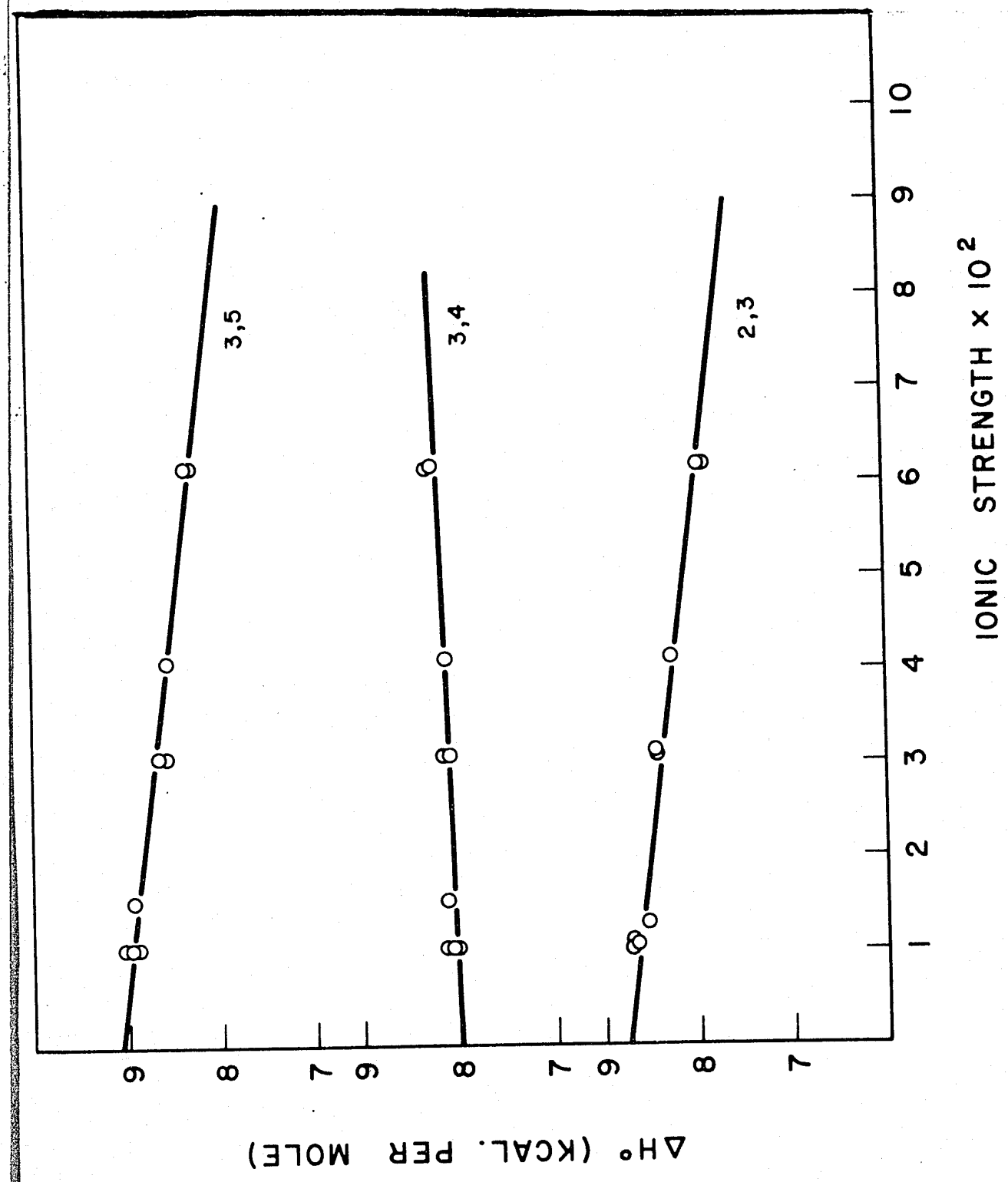


TABLE 1

RANGE OF CONCENTRATIONS USED

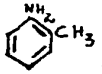
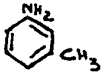
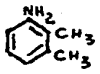
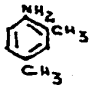
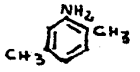
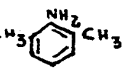
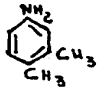
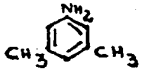
COMPOUND	FORMULA	pK_a	AMINE MAX.	AMINE MIN.	HCl MAX.	HCl MIN.
ANILINE		4.58	6.730×10^{-3}M	3.175×10^{-3}M	11.52×10^{-2}M	1.030×10^{-2}M
O-TOLUIDINE		4.39	3.163×10^{-3}M	5.270×10^{-4}M	11.74×10^{-2}M	1.957×10^{-2}M
M-TOLUIDINE		4.66	2.464×10^{-3}M	4.106×10^{-4}M	11.74×10^{-2}M	1.957×10^{-2}M
P-TOLUIDINE		5.07	2.357×10^{-3}M	4.175×10^{-4}M	11.74×10^{-2}M	1.957×10^{-2}M
2,3-XYLIDINE		4.57	9.350×10^{-3}M	1.356×10^{-3}M	6.18×10^{-2}M	1.030×10^{-2}M
2,4-XYLIDINE		5.00	9.057×10^{-3}M	1.697×10^{-3}M	10.25×10^{-2}M	1.030×10^{-2}M
2,5-XYLIDINE		4.60	1.486×10^{-2}M	1.337×10^{-3}M	10.25×10^{-2}M	1.030×10^{-2}M
2,6-XYLIDINE		4.20	5.028×10^{-3}M	7.914×10^{-4}M	10.25×10^{-2}M	1.030×10^{-2}M
3,4-XYLIDINE		5.15	7.775×10^{-3}M	1.296×10^{-3}M	6.18×10^{-2}M	1.030×10^{-2}M
3,5-XYLIDINE		4.74	8.138×10^{-3}M	1.357×10^{-3}M	6.18×10^{-2}M	1.030×10^{-2}M

TABLE 2

HEATS OF IONIZATION AT INFINITE DILUTION AND THE VARIATION OF THE HEATS WITH IONIC STRENGTH FOR SOME AROMATIC AMINES

COMPOUND	ΔH^{o} ion. (kcal/mole)	ΔH ion./$\Delta\mu$
ANILINE	6.74 ± 0.09	7.3 ± 0.4
O-TOLUIDINE	8.25 ± 0.03	-5.5 ± 0.4
M-TOLUIDINE	8.00 ± 0.04	-3.7 ± 0.4
P-TOLUIDINE	4.98 ± 0.02	32.9 ± 0.3
2,3-XYLIDINE	8.79 ± 0.07	-13.3 ± 0.7
2,4-XYLIDINE	7.90 ± 0.03	1.6 ± 0.7
2,5-XYLIDINE	6.53 ± 0.03	11.8 ± 0.1
2,6-XYLIDINE	5.24 ± 0.02	17.0 ± 0.4
3,4-XYLIDINE	8.04 ± 0.04	2.7 ± 0.7
3,5-XYLIDINE	9.07 ± 0.06	-12.6 ± 0.9

TABLE 3

THERMODYNAMICAL QUANTITIES FOR THE IONIZATION PROCESSES FOR SOME AROMATIC AMINES

COMPOUND	ΔF^{o} (kcal/mole)	ΔH^{o} (kcal/mole)	ΔS^{o} (e.u./mole)
ANILINE	6.24	6.74 ± 0.09	1.66
O-TOLUIDINE	5.98	8.25 ± 0.03	7.60
M-TOLUIDINE	6.35	8.00 ± 0.04	5.53
P-TOLUIDINE	6.91	4.98 ± 0.02	-6.48
2,3-XYLIDINE	6.23	8.79 ± 0.07	8.59
2,4-XYLIDINE	6.81	7.90 ± 0.03	3.63
2,5-XYLIDINE	6.27	6.53 ± 0.03	0.87
2,6-XYLIDINE	5.73	5.24 ± 0.02	-1.63
3,4-XYLIDINE	7.02	8.04 ± 0.04	3.42
3,5-XYLIDINE	6.46	9.07 ± 0.06	8.75

DISCUSSION

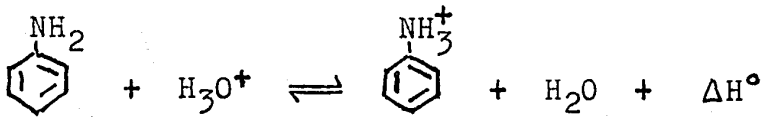
(i) The Influence of Concentration.

The values plotted in Figs.5 to 7 show that there is a very significant variation of the heat of ionization with the concentration. Direct tests in which the concentration of the aniline was maintained constant, and only the hydrochloric acid concentration was varied, showed this variation to depend entirely on HCl concentration. It is planned to investigate this effect in some detail, by making studies of the heats of dilution of the anilines and their chloride salts over a range of concentrations, but some comments can be made at the present time. In the first place the conventional Debye-Hückel theory of the effect of ionic strength on heats of dilution is incapable of explaining the results, for two reasons: (1) the theory predicts a dependence of heat on the square root of the concentration (5), whereas the results definitely show a first-power dependence, and (2) the heat changes observed over the range of concentrations investigated are much larger than the theory predicts. Thus the theory predicts a ΔH of dilution from concentration c to zero concentration of $-500\sqrt{c}$ cal/mole, or a heat of 0.05 kcal. per mole in diluting from 10^{-2}M to infinite dilution. Figs.5 to 7 and Table 2 actually show that the heat changes are very much greater than this. Another

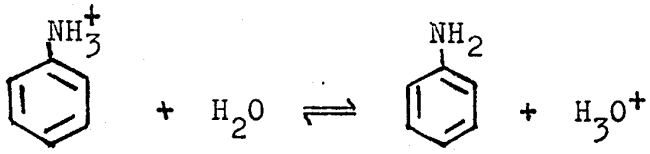
interesting point about the results relates to the sign of the effects; some are positive and some negative, and there is no obvious correlation with structural factors. In the investigations so far of heats of neutralization and of heats of ionization it was observed that the large concentration effects such as found in the present work are observed when an aromatic ring is in such a position that resonance involving the charge group is possible. The effects are, for example, found with anilines, phenols (13), substituted benzoic acids (14) and pyridines (20); they are not found with aliphatic acids (11) and aliphatic amines (21). It is suggested that the smearing of the charge over the aromatic ring produces effects that are not predicted by the simple Debye-Hückel theory, and it would be interesting to investigate the problem in more detail.

(ii) Heats and Entropies of Ionization at Infinite Dilution.

The heats listed in Table 2 are the heats evolved in processes such as



occuring at infinite dilution; the heats are therefore the ΔH° of ionization of the conjugate acid



The ΔH° value is the heat of ionization of the anilinium ion at infinite dilution. These heats are listed in Tables 2 and 3. Also shown in Table 3 are the free energies ΔF° of ionization, obtained from the pK_a's (14) of these compounds, and the entropies of ionization ΔS°.

(iii) Additivity of ΔF° and ΔS° for the Ionization Processes.

It is found that the ΔF° values are quite additive, whereas the ΔH° and ΔS° values are not. The additivity of the ΔF° values can be demonstrated by employing the values for aniline and the toluidines to estimate the values for the xylidines. The values for aniline and the toluidines lead to the following increments for groups in the three positions:

o-methyl	-0.26
m-methyl	+0.11
p-methyl	+0.67

The use of these values leads to predictions for the ΔF° values of the xylidines that are shown in Table 4. The agreement with experiment is fairly satisfactory, although

TABLE 4

COMPARISON OF ESTIMATED (ON THE BASIS OF ADDITIVITY) AND OBSERVED VALUES OF ΔF° FOR SOME AROMATIC AMINES

COMPOUND	ΔF° kcal/mole ESTIMATED	OBSERVED	DIFF.
2,3-XYLIDINE	6.09	6.23	0.14
2,4-XYLIDINE	6.65	6.81	0.16
2,5-XYLIDINE	6.09	6.27	0.18
2,6-XYLIDINE	5.72	5.73	0.01
3,4-XYLIDINE	7.02	7.02	0.00
3,5-XYLIDINE	6.46	6.46	0.00

in the case of the 2,3, 2,4, 2,5 compounds the observed values are significantly higher than the estimated, Previously, Shorter and Stubbs (22) and Stubbs and Hinshelwood (23) have demonstrated the additivity of free energies of ionization and of free energies of activation. There is only very approximate additivity for ΔS° values for the 2,3, 2,4, 3,4, and 3,5 substituted compounds, and a complete lack of additivity for the 2,5 and 2,6 compounds.

(iv) Relationship between ΔH° and ΔS° for the Ionization Processes.

It is evident from the values obtained for the ΔF° and ΔS° of ionization of the various anilines that the influence of substituents is a somewhat complicated one. The variations of $T\Delta S^\circ$ are very much greater than those of ΔF°; so that there is a considerable degree of compensation between $T\Delta S^\circ$ and ΔH°. That is to say, certain factors that influence $T\Delta S^\circ$ influence ΔH° to almost exactly the same extent. The compensation is demonstrated in Fig.8, in which $T\Delta S^\circ$ has been plotted against ΔH°; the correlation is seen to be quite significant. It is of interest that similar correlation between heats and entropies of solution have been observed previously (24 - 27). It follows that studies of the variation of ΔS° and ΔH° provide much more information about the factors involved than do studies of the variation of ΔF°.

(v) Influence of Methyl Substituents on the ΔF° and ΔS° for the Ionization Process.

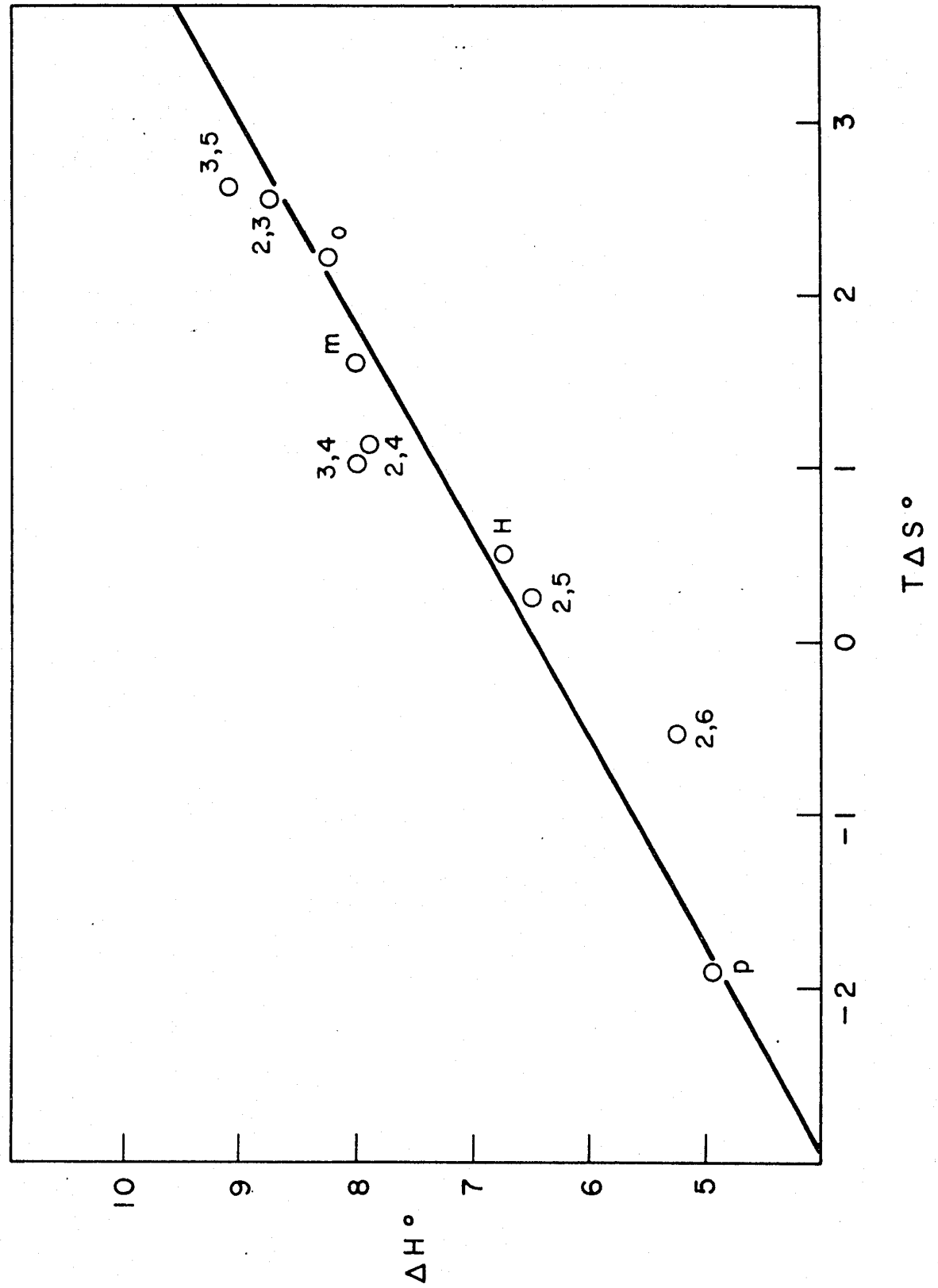
A complete explanation of the substituents effects cannot be given at the present time, but in what follows an attempt will be made to discuss some of the regularities that are observed.

The effects found with the single methyl groups will be considered first. The introduction of a methyl group into either the meta- or para-position is seen to increase ΔF°; and this is attributed to the +I effect of the substituent, which decreases the ease with which a proton is lost. In the case of a methyl group in the para-position there is a decrease in ΔS°; and this is most readily explained in terms of the inductive effects of the $-CH_3$ and $-NH_2$ or $-NH_3^+$ groups. In the cation the +I effect of $-CH_3$ and the -I of $-NH_3^+$ cooperate with one another in causing a displacement of electrons in the molecule; this may contribute to a raising of the entropy of the cationic form. Conversely, in the neutral molecule the +I effects of the $-CH_3$ and $-NH_2$ groups are in opposition, and the entropy will be low.

In the case of a meta-methyl group the behavior as regards ΔS° is different, there being an increase in ΔS°. Evidence to be referred to later suggests that there is some steric interference between the $-NH_3^+$ group and a meta-methyl

FIGURE 8

PLOT OF $T\Delta S^{o}$ FOR THE IONIZATIONS AGAINST HEAT OF IONIZATION.



group, and this will cause a lowering of the entropy of the cationic form. In the neutral molecule, however, there will be little such interference since the non-planar $-NH_2$ group can orient itself so as to avoid contact with the $-CH_3$ group.

In the case of an ortho-methyl substituent this interference will be greatly intensified, and a further increase in $\Delta S°$ would be expected; this is actually found. The extent of the interference is now sufficient to cause the proton to leave more readily (i.e. $\Delta F°$ is smaller) than in aniline and in the meta- and para-substituted anilines; in other words, the steric effect is now more important than the inductive effect.

As was seen in Table 4, there is good additivity for all the disubstituted compounds as far as $\Delta F°$ is concerned. For $\Delta S°$ there is very approximate additivity for the 2,3, 2,4, 3,4, 3,5 substituted compounds, but a complete lack of additivity for the 2,5 and 2,6 compounds (Table 5). The much greater degree of additivity for $\Delta F°$ as compared with $\Delta S°$ is a further indication that $\Delta F°$ is much less sensitive to certain factors, in that certain factors affect $\Delta H°$ and $T\Delta S°$ in practically the same way. Both solvent (electrostriction) and steric effects may be expected to affect $\Delta S°$ much more than $\Delta F°$. The result that the additivity is only approximate as far as $\Delta S°$ is concerned is understandable in view of the fact that steric interference could not be expected

TABLE 5

COMPARISON OF ESTIMATED (ON THE BASIS OF ADDITIVITY) AND OBSERVED VALUES OF ΔH° AND ΔS° FOR SOME AROMATIC AMINES

COMPOUND	ΔH° kcal/mole ESTIMATED	ΔH° kcal/mole OBSERVED	ΔS° e.u./mole ESTIMATED	ΔS° e.u./mole OBSERVED
2,3-XYLIDINE	9.51	8.79	11.47	8.59
2,4-XYLIDINE	6.50	7.90	-0.54	3.63
2,5-XYLIDINE	9.51	6.53	11.47	0.87
2,6-XYLIDINE	9.76	5.24	13.54	-1.63
3,4-XYLIDINE	6.25	8.04	-2.61	3.42
3,5-XYLIDINE	9.26	9.07	9.40	8.75

to be additive.

The complete lack of ΔS° additivity with the 2,6 and 2,5 compounds does, however, call for further explanation. There is additivity with respect to ΔF°, which is lower than with the ortho-compound, and the additional lowering is attributed to the additional steric effect. The ΔS° is, however, abnormally low for the 2,5 and 2,6 compounds, and this implies that the entropies of the cations are abnormally high. The explanation of this may well be that in the cations the methyl groups are forced away from the $-NH_3^+$ group, which is then able to rotate freely; the cationic form is therefore of high energy and high entropy. In the neutral form, on the other hand, the non-planar $-NH_2$ group will tend to be prevented from rotating by the neighbouring methyl groups, and these will therefore not be forced apart; the neutral forms will therefore be of low energy and low entropy. It is of interest that, as expected, this effect is much more pronounced in the 2,6 compound than in the 2,5.

The results for this group of compounds lead one to conclude that effects due to electrostriction do not play a prominent part; this is in contrast to the situation with the phenols (8). For example, on the basis of electrostriction one would predict for the ortho-substituted compound an abnormally high entropy as a result of the interference by the methyl group of the binding of water; no such effect

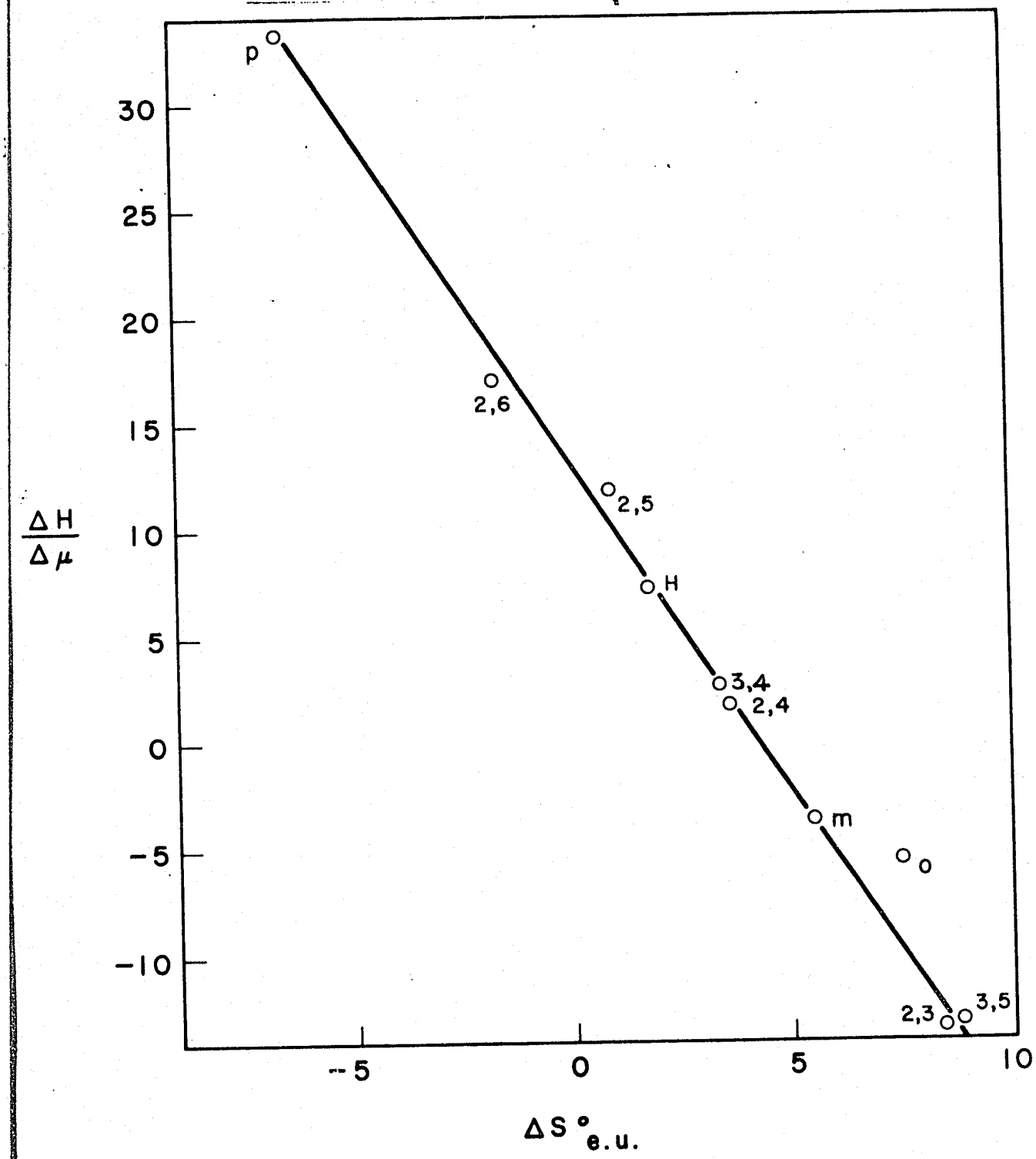
is found, however. This result is no doubt due to the large size of the $-NH_3^+$ group, making electrostriction much less important than with the $-O^-$ ion.

One other observation that may be of considerable interest and significance is the fact that if the slopes (i.e. the $\frac{\Delta H}{\Delta \mu}$) for the various anilines are plotted as a function of $\Delta S°$ a very good straight line results; this is shown in Fig.9. The slopes may probably be identified with some important factor in ionic interaction, and if so it is not surprising that these are dependent on the entropies of ionization. The real significance of this correlation, however, is still not clear.

The formulation of a completely quantitative interpretation of the results obtained for the heats and entropies of ionization has not as yet been successful. This is not surprising in view of the fact that the problem is evidently a very complicated one; at least three important factors are involved and these by no means work in the same directions. The results, however, lead to some interesting observations about the details of these ionization processes, observations that were not revealed by pK_a studies alone, owing to the cancellation of certain heat and entropy terms. Further investigations in this field should throw some light on these problems.

FIGURE 9

PLOT OF ΔS° FOR THE IONIZATIONS AGAINST $\Delta H/\Delta \mu$.



CLAIM TO ORIGINAL RESEARCH

(1) The construction of a modified microcalorimeter of the Tian-Calvet type, described above, has been carried out (the same construction was carried out simultaneously by the Atomic Energy of Canada (28)).

(2) Direct measurements of the heats of ionization of aniline, o-, m-, p-toluidines and of all six xylidines, in hydrochloric acid, have been determined at concentrations which permitted accurate extrapolation to infinite dilution.

(3) Entropies of ionization at infinite dilution, for the above mentioned compounds, have been calculated on the basis of the heats of ionization determined experimentally and the dissociation constants reported in the literature.

(4) A possible explanation of the results obtained is given.

(5) It has been discovered that the Debye-Hückel limiting law is not obeyed by the compounds used.

(6) It has been discovered that $T\Delta S^{\circ}$ varies linearly with ΔH°. This variation was found to be comparable with what was observed previously with regard to heats and entropies of activation (25-27).

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