Een experimenteele toetsing van de theorie van Debye-Hückel

AN EXPERIMENTAL TEST
OF THE
DEBYE-HÜCKEL THEORY

WOUTER BOSCH

AN EXPERIMENTAL TEST OF THE DEBYE-HÜCKEL THEORY

AN EXPERIMENTAL TEST OF THE DEBYE-HÜCKEL THEORY

THESIS

PRESENTED TO THE FACULTY OF THE
STATE UNIVERSITY OF UTRECHT, THE
NETHERLANDS
BY

WOUTER BOSCH

IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY.

UTRECHT, JULY 9 1931.

DRUK UTR. TYPOGRAFEN-ASSOCIATIE, KEIZERSTRAAT 5, UTRECHT

Dedicated to my Parents
and to my Wife.

At the finish of my university education, I want to thank every body who has contributed to my scientific development and to the completion of my thesis.

In the very first place I would like to thank Professor I. M. Kolthoff of the University of Minnesota, not only for his thorough interest and help in our research, but also for the splendid opportunity, that he has given me to get acquainted with America and its friendly population.

Further I wish to take the opportunity of thanking Professor H. R. Kruyt of the University of Utrecht for having taken so much interest in the work. His extraordinarily stimulating personality was at all times a source of inspiration, especially when I started teaching in the United States.

I wish to thank Professor Ernst Cohen, Director of the van 't Hoff Laboratory, for his fine lectures and for his unfailing kindness and courtesy.

I also wish to thank Professor N. Schoorl and Professor W. C. de Graaff of the University of Utrecht, whose ways of education in many scientific fields will be among my most pleasant memories.

I particularly feel greatly indebted to the Authorities of the University of Minnesota, Minneapolis and of the Oklahoma Agricultural and Mechancal College, Stillwater, especially to Dean O. M. Leland, Dean C. H. McElroy, Professor S. C. Lind and Professor O. M. Smith. I want to thank them for the splendid opportunities that they have given me to perform this work and for their trouble in helping me to obtain several facilities.

My thanks are also due to Professor H. M. Trimble of the Oklahoma A. and M. College for his kindness in helping me to correct the English of this Thesis.

Finally I wish to take the opportunity of thanking the Holland—America Foundation for its stipendium.

TABLE OF CONTENTS.

Page

I. Introduction 11

II. Outline of the work 19

III. Materials used 22

IV. Description of experiments: 32

- **a.** Solubility Measurements
- **b.** pa_H Measurements
- **c.** pa_{Ag} Measurements

V. Solubility of benzoic acid and activity coefficient of the undissociated acid in aqueous salt solutions . . . 43

V. Hydrogen ion activity in benzoic acid — benzoate solutions in the presence of neutral salts 53

The activity coefficient of the benzoate ion.

VII. Solubility of silver benzoate in water and in aqueous salt solutions 63

The mean activity coefficient of the silver and benzoate ions.

VIII. Silver ion activity and benzoate ion activity 67

IX. Discussion of the results. Summary 74

AN EXPERIMENTAL TEST OF THE DEBYE-HÜCKEL THEORY. 1)

CHAPTER I.

Introduction.

The Theory of Electrolytic Dissociation of Svante Arrhenius does not give a true picture of the behaviour of strong electrolytes in solution. The crystals of strong electrolytes, to which class most salts belong, are built up from ions and it is improbable, that these ions would combine to undissociated molecules, when the salts are brought into solution (See Kolthoff's article about activity products and activity constants 2)).

In addition to this there are other objections against the Theory of Arrhenius. When NaCl dissolves in water the ionization is not complete. If we assume that there exists the equilibrium $NaCl \rightleftarrows Na^{+} + Cl^{-}$ we can apply the Mass Action Law which gives us the following equation.

$$K = \frac{[Na^{+}]\,[Cl^{-}]}{[NaCl]}$$

This K ought to be a constant, but it has been found for strong electrolytes to vary with the electrolyte concentration.

Another great objection against the theory is the fact, that the degree of dissociation "α" gives different values in the same solutions, when calculated from measurements a of the conductivity, b of the lowering of the freezing point (or the osmotic pressure) or c of the E.M.F. of concentration cells, as can be seen from the following table taken from the publication of Kolthoff. 2)

concentration of KCl	α (conduct,)	α (E.M.F.)	α (freezing point)
.001 molar	.979	.943	.985
.01 ,,	.941	.882	.969
.1 ,,	.861	.762	.932
1 ,,	.755	.558	.854

Several empirical equations have been advanced, which express

---

1) For a thermodynamical discussion of the Debye—Hückel theory we want to refer to the papers of van Veldhuizen in the Chemisch Weekblad.

2) I. M. Kolthoff Chem. Weekbl. **27** 250 (1930).

more or less satisfactorily the change of α with the concentration, but none of these provide a clue as to which of the assumptions the Arrhenius' theory need modification.

Besides these there are other points, which cannot be explained by this theory e.g. the influence of strong electrolytes upon the solubility of difficultly soluble substances or the fact that a solution of 1N HCl (containing 1.5% undissociated HCl) does not have any appreciable vapor pressure of HCl.

Many authors have held the view, that some fundamental modification of the theory was needed. J. J. van Laar[3] and O. Jahn[4] have attacked the assumption, the the mobilities of the ions are independent of the concentration, their view being, that the enormous electrostatic charges on the ions must alter the properties of the solvent and influence the ionic speeds. Van Laar expressed as early as 1900 the opinion, that in rather dilute solutions of all strong electrolytes the degree of dissociation becomes unity.

A. A. Noyes and Coolidge[5] had the idea, that the decrease of conductivity and of the calculated dissociation is due to a physical cause (probably related in some way to the electrical charges of the ions) and not to the specific chemical affinity. Noyes[6] also brought forward evidence of a change in mobilities with concentration, when he showed, that the transport numbers of the ions of HCl and HNO_3 alter with concentration.

Sutherland[7] held the opinion, that the aqueous solutions of strong electrolytes are completely ionized. Later on Milner[8] and Bjerrum[9] have also used the same hypothesis as a basis for their discussion of the behaviour of salt solutions.

---

[3] J. J. van Laar Z. physik. Chem. **15** 457 (1894), **17** 245 (1895), Arch. Teyler **7** 1 (1900), Z. anorg. allgem. Chem. **139** 108 (1924).

[4] O. Jahn ibid. **27** 354 (1898), **33** 345 (1900), **35** 1 (1900), **36** 443 (1901), **37** 490 (1901).

[5] Noyes and Coolidge J. Am. Chem. Soc. **26** 167 (1904).

[6] Noyes and Sammet ibid. **24** 944 (1902).
Noyes and Katz ibid. **30** 318 (1908).

[7] Sutherland Phil. Mag. **3** 161 (1902), **7** 1 (1906), **14** 1 (1907).

[8] Milner ibid. **23** 551 (1912), **25** 743 (1913).

[9] N. Bjerrum 7e Intern. Congres voor toegep. chem. deel **10** 59 1909). Z. Elektrochem. **24** 321 (1918) Z. anorg. Chem. **10** 275 (1920).

As a mathematical interpretation of the interionic actions was very difficult, N. Bjerrum [9]) introduced "deviation coefficients" that were determined empirically and expressed the effects of the electrostatic action of the ions upon the various properties of electrolyte solutions. These coefficients give the proportion between the observed value and those, that could be expected, if no interionic forces were active. He distinguished:

f_o: the osmotic coefficient

f_λ: the conductivity coefficient and

f_a: the activity coefficient (The latter is of special interest in our investigation).

Bjerrum's activity coefficient gives the proportion of the active mass or the activity of the ions to the total concentration or the ratio between the chemical or electrochemical activity and the total ionic concentration.

As has been pointed out above Sutherland [7]), Milner [8]) and Bjerrum [9]) have put forward the view, that strong electrolytes are completely ionized. However the theory of incomplete ionization of Arrhenius is based upon facts which demand adequate explanation. For instance the equivalent conductivity of a strong electrolyte decreases as we pass from extremely dilute solutions to more concentrated ones and so does the activity coefficient. An answer to the above question is found in the electrostatic forces, which exist between the ions. If we consider any one positively charged ion, its motion through the liquid will cause it to approach negatively charged ions and also positively charged; in the first case the attractive force between the two tend to bring them into closer proximity, and in the second case the two will repel each other. The net result will be to alter the average distribution of the ions. Each positive ion will at any moment be surrounded by more negative ions than positive ions, and visa versa. Debye and Hückel have found, that this state of affairs is capable of accounting for the decrease in the activity coëfficient.

In 1923 they have published an article [10]), in which they have derived thermodynamically the relationship between the several coefficients on the one hand and the concentration, valence and specific nature of the ions on the other hand.

---

[10]) P. Debye and E. Hückel Physik. Z. 24 185 (1923). 26 93 (1925).

Debye and Hückel's equation for the activity coefficient of an ion is

$$\ln f_{\alpha} = -\frac{e^2}{2DhT} \cdot \frac{\Sigma z_i^2}{\Sigma \nu_i} \sqrt{\frac{4\pi e^2}{DhT} \Sigma n_i z_i^2} \tag{1}$$

where

$f\alpha$ = activity coefficient of the ion
D = dielectric constant of the solvent
h = 1.37×10^{-16}
T = absolute temperature
e = charge of a univalent ion
ν_i = number of ions of kind i, formed by the dissociation of the molecule
n_i = number of such ions in 1 cc
z_i = valency of the ions.

In this derivation several simplifying assumptions are made and the equation can only be applied to very dilute solutions.

A less complicated formula, that can be derived from the preceeding one by substituting in the different values is given

$$-\log f_{\alpha} = A z_i^2 \sqrt{\mu} \tag{2}$$

A = constant and is a function of the dielectric constant, having a value of .5 at roomtemperature in aqueous medium.
z_i = valency of the ion.
μ = ionic strength, defined by Lewis [11]) as half the sum of the molar concentrations of each ion present, multiplied by its valency squared. For example the ionic strength of .01 molar bariumchloride solution is:

$$\mu = \frac{.01 \times 2^2 + .02}{2} = .03$$

It is evident from equation (2), that the activity coefficient in very dilute solutions is dependent only upon the concentration and

---

[11]) G. N. Lewis and M. Randall Thermodynamics and the free energy of chemical substances. McGraw Hill Co. New York 1923.

the valency of the ions and not upon their specific character.

If the solution is not very dilute the ionic size has to be taken in account and equation (2) goes over in Debye-Hückel's formula to

$$-\log f_\alpha = .5 z_i^2 \frac{\sqrt{\mu}}{1 + .329 \times 10^8 \times b \sqrt{\mu}} \qquad (3)$$

b = ionic diameter and has the value for KCl of 3.76×10^{-8} and for K_2SO_4 of 2.69×10^{-8} etc.

The ionic size varies with the concentration as the ions exert forces upon each other, as discussed before.

Also A in equation (2) is a function of the dielectric constant and there is practically nothing known in the field of the dielectric constants of electrolyte solutions.

Brönsted has drawn our attention to the fact, that we have to deal with a „salting out" effect in concentrated electrolytes solutions. The activity coefficient of a non-electrolyte is dependent upon the ionic strength of the solution:

$$\log f = B \mu$$

in which B is a constant, which is different for a special substance for different electrolytes.

If we assume, that the same kind of „salting out" effect is exerted upon ions equation (3) goes over into formula (4).

$$-\log f_\alpha = .5 z_i^2 \frac{\sqrt{\mu}}{1 + .329 \times 10^8 \times b \sqrt{\mu}} - B \mu \qquad (4)$$

Finally we want to mention, that we have to take into account the so-called ion-association, that is a function of the ionic size and ionic strength: Bjerrum [12]).

Gronwall, La Mer and Sandved have published a study on various terms of the Debye — Hückel equation [13]).

When we give our attention to all the above mentioned facts, it becomes quite doubtful, whether the formula No. 3 is valuable, even in dilute solutions. The question arises, whether it would not be better to find an empirical relationship between the activity coefficient and the ionic strength as Bjerrum [12]) has done.

---

[12]) N. Bjerrum Ergebn. der exakten Naturwiss. 5 125 (1926).

[13]) Gronwall, La Mer and Sandved, Physik. Z. 29 358 (1928).

He finds, that the following equation reproduces quite well the changes of the activity coefficient with the ionic strengths:

$$-\log f_a = A' \sqrt[3]{\mu} - B' \mu$$

A′ and B′ are constants, that can be derived from experimental data.

At smaller ionic strengths, the following formula gives sufficiently good results:

$$-\log f_a = .5 \sqrt{\mu} - B \mu$$

In 1927 we started our research on the influence of neutral salts on acid-salt, acid-base equilibria respectively and seven publications have been the result of a number of investigations in this field. 14)

We will give here a brief summery of the conclusions, that we have drawn from our experiments so far.

From measurements of the activity of the hydrogen ions in a dilute solution of hydrochloric acid with uni-univalent salts in our first investigation, we found in agreement with other investigators 15), that small quantities of salts cause a decrease of the activity coefficient, whilst with higher concentrations the coefficient tends to increase, reaching in the case of a .5 N solution of Lithium chloride a value greater than 1.

It was also shown, that there is a distinct cation effect in the order of the so-called lyotropic series and that the different anions used had all the same influence. It was further concluded in agreement with Scatchard 16) and Güntelberg 17), that the activity coefficients of two individual ions are not equal to the mean of their coefficients.

We found the same pronounced cation effect in our second investigation in which we studied different equilibria in citric acid

---

14) I. M. Kolthoff and Wouter Bosch Rec. Trav. Chim. **46** 430 (1927), **47** 558 (1928), **47** 819 (1928), **47** 826 (1928), **47** 861 (1928), **47** 873 (1928), **48** 37 (1929).

15) H. S. Harned J. Am. Chem. Soc. **38** 1986 (1916), **42** 1808 (1920), **48** 326 (1926).

16) G. Scatchard J. Am. Chem. Soc. **47** 641, 648, 696 (1925).

17) E. Güntelberg Z. physik. Chem. **123** 199 (1926).

solutions. An application of the Debye-Hückel equation (3) for the calculation of the p_H in mixtures of citric acid and monovalent citrate was not very succesful. It was found, that the activity coefficient of the undissociated acid becomes much larger than 1 with increasing concentration of the neutral salt; therefore we concluded, that electrolytes apparently increase the first dissociation constant of citric acid.

Only in the case of potassium chloride the influence of the salt upon the p_H of different mixtures could be approximately calculated by means of the Debye-Hückel equation. In using sodium or lithiumchloride other factors seemed to complicate the problem.

Neither was it possible to calculate quantitatively the influence of neutral salts upon the p_H of a dilute bicarbonate-carbonate mixture on the basis of the Debye-Hückel theory, as was found in the third part of our research.

The influence of neutral salts on the p_H of a very dilute mixture of ter- and quadrivalent pyrophosphate is much larger than that calculated according to the equation of Debye and Hückel. The salt effect on a dilute mixture of di- and tervalent pyrophosphate could be calculated by means of this equation accepting an average ionic size of the ions of potassium chloride equal of 3.7×10^{-8} cm. and of sodium chloride of 2.3×10^{-8} cm.

In the summary of our fifth publication about the first and second dissociationconstant of succinic acid, tartaric acid and adipinic acid and the influence of neutral salts on different equilibria we stated, that the effect of these salts upon the p_H of a weak acid and its monovalent salt is partly explained by the fact, that the salts increase the activity coefficient of the undissociated acid. There was no reason to assume, that neutral salts increase the dissociation constant of the weak acids, that were investigated.

The influence of neutral salts upon the ratio of the activity coefficients of the anions in a mixture of a mono- and divalent anion of a weak acid could not be calculated on the basis of the Debye—Hückel equation only. There seemed to be some specific interaction between the cations of the salt added and the anions of the weak acid.

The assumption, stated above has been strengthened by our sixth investigation in which we studied the dissociationconstant of acetic acid, capronic acid and benzoic acid and the influence of neutral salts upon the dissociationconstant of weak acids. We found here again, that neutral salts do not increase these constants and it also was stated in the summary, that the influence of neutral salts on the p_H of a dilute mixture of a weak acid and its salts may be calculated by using the equation of Debye and Hückel, if the influence of the salts on the activity coefficient of the undissociated acid is taken into account.

The last part of our previous research was carried out in the field of weak bases with an investigation which had to do with the apparently anomalous behaviour of a mixture of a weak base and its salt on dilution and on the addition of a salt. We came here to the same conclusion as before, e.g. that there is no special anion effect, but that there is a pronounced cation influence in the order K, Na, Li, which is just the reverse of that observed in the case of an acid system. An explanation was given by the assumption, that sodium- and lithium chloride increase the ionic product of water.

Finally summarizing our research, that was carried out before we started on the present problem we came to the conclusions:

a. That there is a special cation effect in the order $Li > Na > K$ for the influence of neutral salts upon the p_H of different mixtures of weak acids and their salts.

b. That there has not been observed any special anion effect upon these equilibria.

c. That the influence of neutral salts upon the p_H of a weak acid and its monovalent salt is partly explained by the fact, that salts increase the activity coefficient of the undissociated acid. If we assume this, this influence may probably be calculated by using equation Nr. 3 of Debye and Hückel.

d. That there is no evidence, that neutral salts increase the dissociation constant of weak acids.

To support and strenghten the statements, made above, and to bring more light into this important field of the behaviour of strong electrolyte solutions, we have carried out the research work that will be outlined in the following chapter.

CHAPTER II.

OUTLINE OF THE WORK.

In the present work a study has been made of the activity coefficient of the benzoate ion and of the system benzoic acid — benzoate in the presence of various neutral salts.

The advantage of this investigation over the work that has been carried out previously is, that the activity of the undissociated benzoic acid has been kept constant by working with saturated solutions.

The dissociation constant of benzoic acid was calculated from p_H measurements in solutions of benzoic acid — sodium benzoate 1 : 1 and 2 : 1 and the dilutions thereof. As the hydrogen ion concentration in the mixtures was rather high, the p_H values measured in all dilutions had to be corrected for the dissociation of the acid.

The activity coefficient f_o of the undissociated benzoic acid in solutions of various salts was calculated from the values of the solubility of the acid in water and in the salt solutions. These activity coefficients were compared with those obtained by different authors.

Along with the solubility measurements p_H determinations were carried out both with the hydrogen electrode and with the quinhydrone electrode. In a previous investigation [18]) of the system benzoic acid — benzoate we had found already, that these measurements were very troublesome. We noticed that there was a certain drift in the value of the dissociation constant; with increasing ionic strength a higher value of the constant was found. In this research we met with the same difficulties which we could not explain. Especially in the dilute solutions it was quite impossible to obtain constant E. M. F. values. However, the quinhydrone electrode proved not very satisfactorily either as will be mentioned later.

---

[18]) Kolthoff and Bosch Rec. Trav. Chim. 47 876 (1928).

The activity coefficient f_1 of the benzoate ion can be calculated in the following way:

$$K = \frac{[a_{H+}] \times [a_{benzoate^-}]}{[a_{Hbenzoate}]} = \frac{[a_{H+}] \times [c_{benzoate^-}] \times f_1}{[a_{Hbenzoate}]}$$

$$-\log f_1 = -\log K\,[a_{Hbenzoate}] - p_{aH} - p_{c_{benzoate^-}}$$

p_{aH} is the experimental value

$[c_{benzoate^-}]$ is the concentration of the benzoate ions, corrected for the dissociation of the acid.

$[a_{Hbenzoate^-}]$ is the constant value of the activity of the undissociated benzoic acid and can be extrapolated from measurements of the solubility of the acid in solutions of sodium benzoate of decreasing concentrations and paH determinations.

An objection against this type of work is that the measurement of a single activity coefficient involves an uncertainty on account of the liquid junction potential. It is possible to decrease the value of this junction potential by the use of a saturated potassium chloride solution, but this measure is not satisfactory. We also can calculate the potential, but this involves considerable uncertainty.

Therefore it is impossible to determine exactly single activity coefficients. Guggenheim [19]) even states: "The electric potential difference between two points in different media can never be measured and has not yet been defined in terms of physical realities; it is therefore a conception which has no physical significance". It is believed that the uncertainty, involved in using saturated potassium chloride as bridge solution is one of the smaller errors in this work.

It was further decided to determine the activity coefficient of the benzoate ion in quite a different way. Pure silver benzoate was prepared and its solubility in water and in various salt solutions was determined. From these values the mean activity coefficient f_0 of the silver and benzoate ions can be calculated.

Assuming that in saturated solutions in pure water $f_{Ag} = f_{benzoate}$ then

---

[19]) E. A. Guggenheim J. Phys. Chem. 33 842 (1929).

$$s_o \text{ (at } \mu = o) : \qquad s_o = s_{\text{water}} \sqrt{f_{Ag+} \times f_{\text{benzoate}^-}} = [a_{Ag+}] \cdot$$

$$[a_{\text{benzoate}^-}] = K = \sqrt{\text{true solubility product}}$$

$$f_{\text{benzoate}^-} = \frac{s_o^2}{s^2} \cdot \frac{1}{f_{Ag+}}$$

s_0 = solubility at ionic strength = 0
s = solubility at ionic strength given.

However since we were interested to know the activity coefficient of the benzoate ion, we had to know the activity coefficient of the silver ion f_{Ag+} as is evident from the above equations. This silver ion activity coefficient was determined in the saturated solutions of silver benzoate potentiometrically by means of the silver electrode. Since $f_{Ag+} \times f_{\text{benzoate}^-}$ was found from the solubility measurements and f_{Ag+} is determined, f_{benzoate^-} could be calculated.

Incidentally it may be mentioned that the determination of the f_{Ag+} involved an exact study of the silver electrode.

By working with silver benzoate solutions with the same salt and same ionic strength as in the system benzoic acid — benzoate the values of the activity coefficient of the benzoate ion found by two entirely different methods could be compared.

CHAPTER III.

MATERIALS USED.

Certain reagents were prepared or especially purified for this research.

1. Pure water.

The "pure water" was obtained from ordinary distilled water by a redistillation over $Ba(OH)_2$ and $KMnO_4$ in an all tin apparatus. Before use the excess carbon dioxide was removed by drawing through CO_2 free air for two hours.

2. Benzoic acid.

The benzoic acid was a U.S.P. product from the Research Laboratory of the Eastman Kodak Company, Rochester, N.Y.

A preliminary test showed, that the product was not very pure, so we recrystallized the acid. 200 grams of the impure material were dissolved in as little boiling 95% alcohol as possible and the solution was filtered through a Buchner funnel. Then two liters of hot distilled water were added, and after cooling the crystals were separated as thoroughly as possible from the deep yellow colored mother liquid.

A second purification was performed in a similar way with the exception, that in stead of distilled water, "pure" water was used. The upper part of the crystallized acid in the Buchner funnel was scraped off and used in the experiments, so it could not be contaminated with filter paper fibres.

After being dried to constant weight over sulphuric acid, the benzoic acid was tested for purity. 0.5 gram, dissolved in 100 cc of "pure" water used more than 10 cc. 1N $KMnO_4$ solution after boiling for five minutes and a pungent odor was evident. According to this test the purified product was no better than the original material. However we had the same experience with a U.S.P. product from Merck (recrystallized from toluene) and even with a sample of pure benzoic acid from "Kahlbaum, für kalorimetrische Bestimmungen, geprüft von Prof. Dr. P. E. Verkade, Verbrennungswärme pro Gramm in luft gewogen 6324 Kal. 15°. Aschegehalt ca. .005%." So we drew the conclusion, that there is probably a destruction of the benzoic acid, when boiled in neutral medium with permanganate solution and that the latter is not an adequate test for its purity.

Our recrystallized product did not change color in strong sulphuric acid and 1 gram of acid, dissolved in 30 cc of hot „pure" water did not use more than 1 drop of .1N permanganate solution after the addition of some sulphuric acid.

Finally we made a chlorine test as described in the Pharmacopoeia of The United States of America 1926. 0.5 gram of benzoic acid was mixed with .7 gram of pure calciumcarbonate and a little distilled water in a crucible, the mixture dried and incinerated at a low red heat. The residue was dissolved in 20 cc of dilute nitric acid, the solution filtered and the insoluble residue and filter washed with 15 cc of distilled water. To the filtrate .5 cc of .1N $AgNO_3$ was added and the solution diluted with distilled water to 50 cc. The liquid showed a slight turbidity of about the same degree as in the blank test, so we concluded, that chlorine was absent.

Further purity tests were made by comparison of our product with the benzoic acid "Kahlbaum" as described below under "standardization of NaOH, approximately .05 N" and under "solubility measurements" and as a result of these tests we concluded, that our recrystallized product was as good as the Kahlbaum preparation.

3. Sodium benzoate.

U.S.P. Sodium benzoate by Merck was used after recrystallizing from water. The solubility of this salt in water is large at room temperature and the temperature coefficient of the solubility is small. However, from data, available in the literature, it seemed to be the only possible method of purification.

Sodium benzoate was dissolved in water and a saturated solution made at boiling temperature. The boiling liquid was filtered through a Buchner funnel and the solution cooled in ice. The white voluminous mass was separated from the liquid, washed twice with small amounts of cold distilled water and once with a small volume of cold absolute ethyl alcohol. The product was dried to constant weight at 150° C.

A chlorine test was performed as described in the Pharmacopoeia of the U.S.A. 1926. 1 gram of sodium benzoate was dissolved in 10 cc of water in a separatory funnel, 10 cc of dilute sulphuric acid added and the benzoic acid shaken out with 2 successive 20 cc portions of ether. After evaporation of the solvent a test for chlorinated compounds was made as described under benzoic acid. The test was negative.

The test for alkalinity was also negative, as 2 grams of sodium benzoate, dissolved in 20 cc of distilled water did not produce a red color with phenolphthalein.

A further test for purity of our product is described under "solubility measurements of benzoic acid". We determined the solubility of benzoic acid in sodium benzoate solutions of different strengths. We made these solutions by weighing out our product or by preparing the solution by neutralization of benzoic acid with sodium hydroxide. As will be seen the checks were very satisfactory.

4. Sodium Hydroxide, Approximately .05N.

The sodium hydroxide solution was made by proper dilution with "pure" water of a stock solution of NaOH "Kahlbaum, precipitated by alcohol", according to the method of Sörensen. The concentrated base was filtered through a Jena filter crucible with a fritted glass bottom.

The standardization was done with two samples of benzoic acid, that by Kahlbaum and our own preparation (see under benzoic acid) using phenolphthalein as an indicator and neutral alcohol for solution of the acid.

To check the water content, both preparations were also used for the standardization after they had been melted for one half hour at 130° C. in a paraffin bath. From the following table it may be seen, that the material was dry.

Standardization of sodium hydroxide with benzoic acid.

	"KAHLBAUM"		"OUR PREPARATION"	
	unmelted	melted	unmelted	melted
1. weight acid	.2255 g	.2177 g	.1175 g	.2062 g
volume NaOH	37.67 cc	36.31 cc	19.66 cc	34.45 cc
norm. NaOH	.04907	.04914	.04899	.04906
2. weight acid	.1555 g	.2265 g	.1347 g	.2587 g
volume NaOH	25.97 cc	37.89 cc	22.47 cc	43.26 cc
norm. NaOH	.04908	.04900	.04917	.04902

Average normality of NaOH .04907 ± .0001

5. Chloroplatinic acid.

The chloroplatinic acid, used for the coating of the hydrogen electrodes was prepared according to a procedure of Wichers. [20])

Approximately 1 gram of platinum foil was dissolved in pure aqua regia and the solution three times evaporated to dryness with pure HCl to remove the HNO_3. The residue was dissolved in 50 cc of distilled water and the chloroplatinic acid precipitated with a 15% pure ammonium chloride solution. The precipitate was washed by decantation with a large volume of the 15% NH_4Cl solution and finally separated from the liquid in a small Buchner funnel.

The ammonium chloroplatinate was decomposed to platinum sponge in a silica crucible at 1000° C. in an electrically heated muffle furnace.

The pure platinum was then dissolved in aqua regia, the nitric acid removed as before and finally the HCl by a last evaporation to dryness. The hloroplatinic acid was dissolved in 100 cc of "pure" water and this solution, containing 1% of platinum, used for platinizing.

6. Silver benzoate.

The silver benzoate was prepared as follows: 40 grams of sodium benzoate Merck U.S.P. Quality were dissolved in 500 ml of distilled water, the solution boiled and added to a boiling solution of 45 grams of silver nitrate (Mallinckrodt C. P. Quality, Maximum impurities less than .13%) in 500 ml of distilled water. After standing over night the precipitate, which had a slight brown color was separated as thoroughly as possible from the mother liquid in a Buchner funnel and washed five times by decantation by rubbing in a mortar with distilled water. Finally the Ag-benzoate was washed with absolute ethyl alcohol and dried to constant weight at 120° C.

Tests: Inorganic substances: 5 grams of silver benzoate were dissolved in boiling distilled water, the silver precipetated with hydrochloric acid and the AgCl filtered from the solution. The filtrate was evaporated to dryness in a weighed evaporating dish and finally heated to remove all benzoic acid. As there was no

---

[20]) Edw. Wichers, J. Am. Chem. Soc. 43 1268 (1921).

residue present, we concluded that inorganic matter was absent.

Silver determination:

A further purity test was made by a gravimetric determination of the silver content:

.4013 grams of silver benzoate yielded .2500 grams of silver chloride = 46.89% of Ag. (Gooch crucible method).

.3737 grams of silver benzoate yielded .2336 grams of silver chloride = 47.05% of Ag. (Filter paper method).

The theoretical value of Ag/Ag-benzoate = 47.13%.

7. Silver nitrate.

General Chemical Company, C. P. Quality "Maximum impurities less than .022%".

Preliminary tests showed that this chemical was not as pure as was mentioned on the label. Therefore we purified it by melting in a silica dish, keeping it at the melting point for about 15 minutes. (most of the nitrates decompose at this temperature, except silver nitrate). The melt was then poured upon a porcelain plate and after cooling the crust was powdered and brought into solution with distilled water. The liquid, that showed a black precipitate of probable lead and bismuth oxides was filtered and evaporated to dryness on a water bath. The crystals were then heated until they just melted in order to remove the water.

A purity test was made by an electrometric titration with a solution of potassium chloride "Kahlbaum":

.5006 grams of silver nitrate used 29.50 ml of .1 N KCl solution = 63.75% of Ag.

.5002 grams of silver nitrate required 29.48 ml of .1 N KCl solution, = 63.58% of Ag.

The theoretical value of Ag/$AgNO_3$ = 63.50%.

Certain commercial reagents were used in this work. Their quality is set forth below.

8. Barium nitrate.

Central Scientific Company, C. P. Quality, "Maximum impurities less than .04%".

Tests: Neutrality: 5 grams, dissolved in 25 cc of water reacted neutral to phenolphtalein.

Chlorine : negative
Water : negative; 2.0082 grams did not lose any water, when left for 3 months over sulphuric acid.

9. Barium chloride.

Baker's Analyzed, C. P. Quality, "Maximum impurities less than .011%".

Tests: Neutrality: 5 grams, dissolved in 25 cc of water react ed neutral to phenolphtalein.
Water : direct determination: 2.0167 grams lost .2945 g of water, when heated to constant weight at 200° C 14.60% water
indirect determination (barium determination)
.2889 gram of salt gave .2759 g of barium sulphate 14.92% water
.4503 gram of salt gave .4297 g of barium sulphate 14.88% water.
Theoretical value for $BaCl_2.2H_2O$ 14.74%.

10. Calcium nitrate.

Riedel-de Häen, "chemically pure crystals".

Tests: Neutrality: 5 grams, dissolved in 25 cc of water used 1 drop of HCl .05N to methyl orange to neutralize.
Chlorine : negative
Water : direct determination: 2.2815 grams lost .6650 g of water, when heated to constant weight at 240° C. 29.15% water
indirect determination: (calcium determination) 1.1025 g of salt gave .2717 g of CaO 29.56% water
1.1580 g of salt gave .2785 g of CaO 29.65% water.
Theoretical value for $Ca(NO_3)_2.4H_2O$ 30.51%.

11. Calcium chloride.

Riedel-de Häen, "chemically pure crystals".

Tests: Neutrality: 5 grams, dissolved in 25 cc of water reacted neutral to phenolphtalein.

Water : direct determination: 2.4738 grams lost 1.2057 g of water, when heated to constant weight at 200° C. 48.74% water

indirect determination (chlorine determination)

.3057 g of salt used 28.05 ml .1007N silver nitrate solution for the Mohr's chloride titration: 48.74% water

.3674 g of salt used 33.66 ml .1007N silver nitrate solution for the Mohr's titration: 48.80% water.

Theoretical value for $CaCl_2.6H_2O$ 49.34%.

12. Lithium nitrate.

Baker's Analyzed, C. P. Quality, "Maximum impurities less than .054%".

Tests: Neutrality: 5 g dissolved in 25 cc water reacted neutral to phenolphtalein.

Chlorine : negative

Water : 1.0954 g of salt lost .0522 g of water, when heated to constant weight at 105° C.: 4.77%

1.1117 g of salt lost. 0543 g of water, when heated to constant weight at 105° C.: 4.88%.

13. Lithium chloride.

Power's Weightmann Rosengarten, "Maximum impurities less than .08%".

Tests: Neutrality: 5 g dissolved in 25 cc of water used 1 drop HCl .05N to phenolphtalein.

Water : 1.0318 g of salt lost .0395 g of water, when heated to constant weight at 105° C.: 3.83%

1.0159 g of salt lost .0392 g of water, when heated to constant weight at 105° C.: 3.86%.

14. Magnesium nitrate.

Riedel-de Häen, "chemically pure crystals".

Tests: Neutrality: 5 g dissolved in 25 cc of water reacted neutral to phenolphtalein.
Chlorine : negative
Water : a direct water determination seemed to be impossible, as magnesium nitrate decomposed already at 130° C.
indirect water determination (magnesium determ.) .7202 g of salt gave .3114 g of $Mg_2P_2O_7$: 42.42% of water.
Theoretical value: 42.14% for $Mg(NO_3)_2 . 6H_2O$.

15. Potassium nitrate.

Baker's Analyzed, C. P. Quality, "Maximum impurities less than .004%".

Tests: Neutrality: 5 g dissolved in 25 cc of water reacted neutral to phenolphtalein.
Chlorine : negative
Water : 2.0356 g of salt did not change in weight, when left for 3 months over sulphuric acid.

16. Potassium chloride.

Sterling, C. P. Quality, "Analysis certified for maximum impurities, less than .036%".

Tests: Neutrality: 5 g dissolved in 25 cc of water reacted neutral to phenolphtalein.
Water : 3.5486 g of salt did not lose in weight, when left for 3 months over sulphuric acid.

17. Potassium bromide.

Mallinckrodt, C. P. Quality, "Maximum impurities less than 1%".

Tests: Neutrality: 5 g dissolved in 25 cc of water used less than 1 drop of .05N HCl to phenolphtalein.

18. Potassium sulphate.

Central Scientific Company, C. P. Quality, "Maximum impurities less than .04%".

Tests: Neutrality: 5 g of the salt, dissolved in 25 cc of water reacted neutral to phenolphtalein.

19. Sodium nitrate.

Baker's Analyzed, C. P. Quality, "Maximum impurities less than .006%".

Tests: Neutrality: 5 g of the salt, dissolved in 25 cc of water reacted neutral to phenolphtalein.
Chlorine : negative
Water : 2.0254 g of the salt lost .0008 g of water, by drying for 3 months over sulphuric acid.

20. Sodium chloride.

Central Scientific Company, C. P. Quality, "Maximum impurities less than .033%".

Tests: Neutrality: 5 g of the salt, dissolved in 25 cc of water reacted neutral to phenolphtalein.
Water : 2.874 g of the salt did not loose any water, when left for 3 months over sulphuric acid.

21. Strontium nitrate.

Powers Weightmann Rosengarten, Maximum impurities less than .11%.

Tests: Neutrality: 5 g of the salt, dissolved in 25 cc of water used less than 2 drops of .05N NaOH to phenolphtalein.
Chlorine : negative
Water : 2.0016 g of the salt lost .0053 g of water, when left for 3 months over sulphuric acid. .25% water.
3.5297 g of the salt lost .0104 g of water, when heated to constant weight at 130° C. .30% water.

22. Strontium chloride.

Baker's Analyzed, C. P. Quality, Maximum impurities less than .022%.

Tests: Neutrality: 5 g of the salt, dissolved in 25 cc of water reacted neutral to phenolphtalein.

Water : direct determination: 2.0330 g of the salt lost .8067 g of water, during a drying period of 3 months over sulphuric acid. 39.68% water

indirect determination (chlorine det.) .4074g salt used 30.88 ml $AgNO_3$ sol. .1007N 39.50% water

.4004 g salt used 30.36 ml $AgNO_3$ sol. .1007N 39.49% water.

23. Potassium thiocyanate.

Baker's Analyzed, C. P. Quality, "Maximum impurities less than .022%.

In this investigation three solutions of KCNS approximately .01, .03 and .1 N respectively were used. The first two were made by a proper dilution of the strongest and all solutions were standardized potentiometrically against the purified silver nitrate.

CHAPTER IV.

DESCRIPTION OF EXPERIMENTS.

a. Solubility measurements.

1. Benzoic acid.

All the solubility measurements were carried out in an electrically heated water thermostat made by the "Central Scientific Company", Chicago. Since the temperature fluctuations, using the mercury thermoregulator, furnished with the thermostat, were too large, it was replaced by a toluene-mercury regulator of 300 cc volume. The heating capacity of the two electrical knife type heaters was reduced by a set of light bulbs, connected in series with the heaters, thus securing a better distribution of the heat. A two blade brass stirrer, driven by an electrical stirring motor gave the necessary movement of the water. With these improvements the temperature of the bath was kept constant at 25° C. ± .01°.

The different saturated solutions were made in 250 cc Pyrex glass bottles, closed with cork stoppers (impregnated with paraffin in a vacuum dessicator) and wired in with copper wire.

As a shaking device the apparatus was used illustrated in fig. No. 1. It is similar to that in use at the van 't Hoff laboratory of the State University at Utrecht. The great advantage of this shaker is, that it can be immersed under water without the trouble of making connections through the walls of the thermostat. The bottles are fastened to the rod ab by means of the clamps c, d, e and f and are rotated in this way end over end producing a very thorough mixing.

After saturation had been obtained the solution was drawn out into a (25 of 50 ml) pipett by means of a suction pump. The tip of the pipett was closed with a piece of glass tubing, that was drawn out in the middle and filled with a piece of absorbent cotton in order to filter the solution. The pipett was then delivered into 10 ml of distilled water as to prevent crystallization of the acid from the saturated solution.

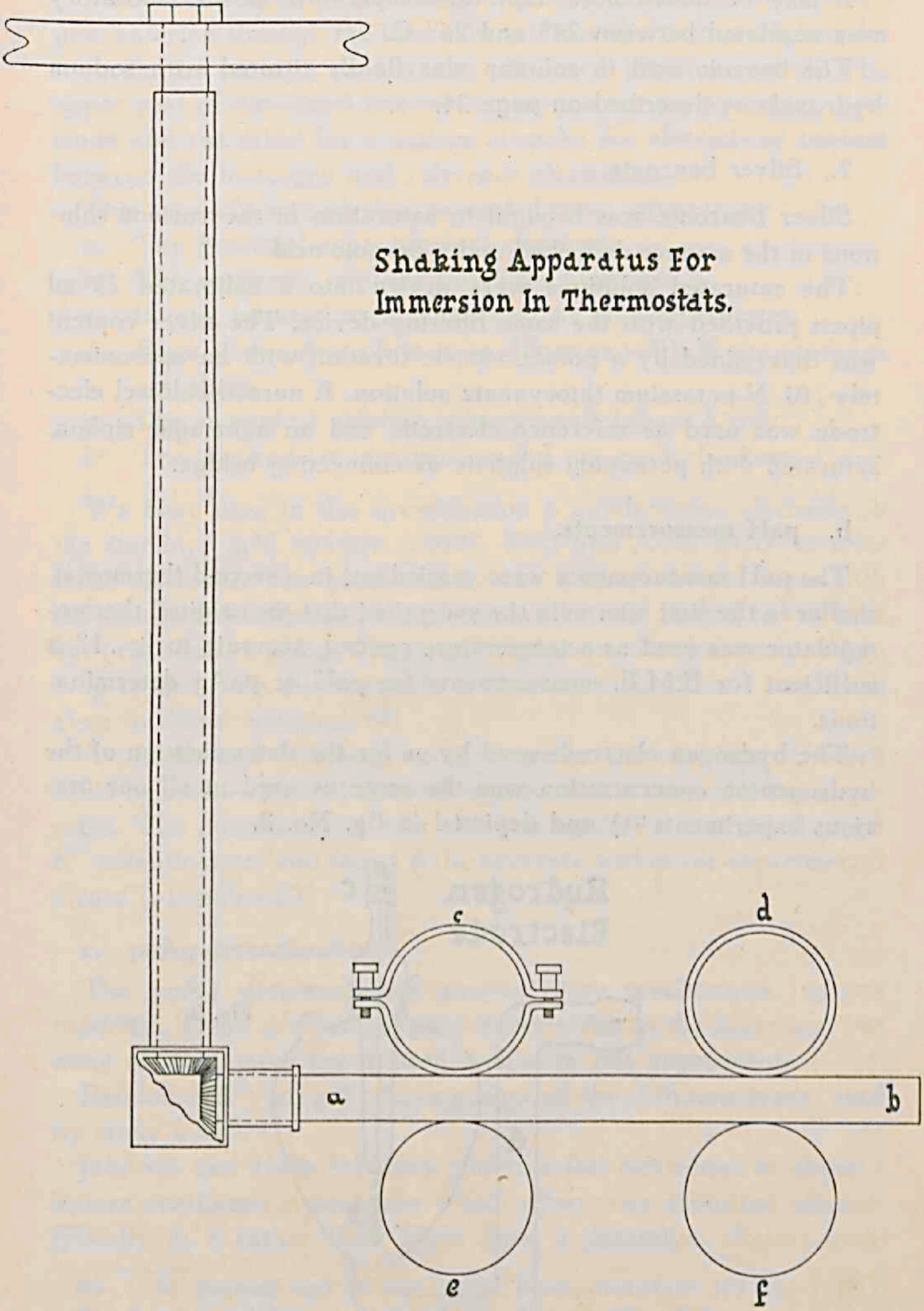


Fig. 1

It may be added here, that the temperature in the laboratory was regulated between 24° and 26° C.

The benzoic acid in solution was finally titrated with sodium hydroxide as described on page 24.

2. Silver benzoate.

Silver benzoate was brought to saturation in the various solutions in the manner described under benzoic acid.

The saturated solutions were drawn into a calibrated 25 ml pipett provided with the same filtering device. The silver content was determined by a potentiometric titration with an approximately .01 N potassium thiocyanate solution. A normal calomel electrode was used as reference electrode and an agar-agar siphon, saturated with potassium sulphate as connecting bridge.

b. paH measurements.

The paH measurements were carried out in a second thermostat, similar to the first one, with the exception, that the original thermoregulator was used as a temperature control, accurate to ± .1° is sufficient for E.M.F. measurements for paH or paAg determinations.

The hydrogen electrode used by us for the determination of the hydrogenion concentration was the same as used in all our previous experiments [21]) and depicted in fig. No. 2.

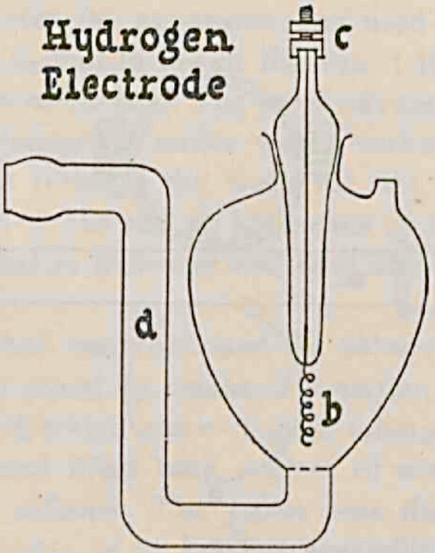


Fig. 2

---

[21]) I. M. Kolthoff and Wouter Bosch. Rec. Trav. Chim. 46 434 (1927).

The glass bottom of the vessel is perforated so that the hydrogen, entering through the bent tube **a** is devided into small bubbles in order to saturate rapidly the platinized platinum spiral. The upper part of the vessel has two holes, one for the hydrogen electrode and the other for a siphon to make the electrolytic contact between the hydrogen and reference electrodes.

This type of electrode has several distinct advantages:

a. The potential soon becomes constant.
b. The electrode requires but little hydrogen.
c. It may be used in a thermostat at all temperatures.
d. Even if the electrolyte is as dilute as .001 N the readings are sharp.
e. The amount of solution is very small (about 5 cc).
f. The electrode is inexpensive and not easily broken.

We have used in this investigation a quinhydrone electrode in the standard acid mixture (.01N HCl and .09N KCl) as reference electrode. The quinhydrone was washed several times with the standard solution and the platinum electrode heated to red heat each time before using. The liquid was renewed twice a day. Working in this way the electrode is reproducible within .1 millivolt even in dilute solutions. [22])

A „Leeds and Northrup" potentiometer, the readings of which could be made within .1 millivolt was used as a compensation apparatus. The potentiometer was checked against a calibrated „type K" potentiometer and found te be accurate within the experimental errors (.1 millivolt).

c. paAg determinations.

The paAg determinations proved very troublesome, as we expected. There are several procedures given in the literature, but none of them gave the desired results in our experiments.

Randall and Young [23]) have compared the different types, used by many authors.

Jahn [24]) and Halla [25]) used platinum foil electrodes of about 1 square centimeter area, upon which silver was deposited electrolytically in a rather thick layer from a potassium silvercyanide

---

[22]) I. M. Kolthoff und Wouter Bosch, Bioch. Zeitschrift **183** 441 (1927).
[23]) Randall and Young J. Am. Chem. Soc. **50** 990 (1928).
[24]) Jahn Z. phys. Chem. **33** 545 (1900).
[25]) Halla Z. Elektrochem. **17** 179 (1911).

solution. After washing for a couple of days the electrodes were coated with $AgCl$ by electrolysis, making them anodes in a 25% HCl solution, using a current of small amperage. The current was reversed after two hours, until a weak hydrogen evolution took place at the cathode. After washing for some days with a dilute $NaCl$ solution, the electrodes showed a potential difference of .1 to 2 millivolt.

Lewis, Brighton and Sebastian [27]) and Güntelberg [28]) prepared several electrodes in this manner, which showed a maximum difference between themselves of .9 millivolt.

Also Brönsted's [28]) silver plated platinum foil electrodes gave poor results, that were usually too high.

Since this type of electrode has proved too inaccurate we decided not to use it.

Randall and Young also studied the various forms of silver crystals, made by electrolysis. Large crystals produced by electrolysis with a low current density from silver nitrate solutions are far from reproducible.

Crystals deposited electrolytically from a molar solution of silver nitrate by the method of Linhart [29]) proved more satisfactory. The deposition was carried out at 90—100° C. using a point electrode of platinum wire with a current of about 6 amperes (Randall and Young [23])). More finely divided crystals were made in the same manner from a .1 molar $AgNO_3$ solution. This form of silver was readily reproduced and electrodes made from it never varied by more than .4 mV, when checked against each other.

Although this type of electrodes seemed to be satisfactory, we did not use this method as we wished to use the same set of electrodes in all our experiments and we were afraid, that the electrodes made from these crystals could not be used for different determinations with varying concentrations because of the difficulty of washing them. Another disadvantage was, that equilibrium was reached only after 3-4 days.

Another type of electrode was that used by Brester [30]). The first part of the method, which he used in preparing them was the

---

[26]) Lewis, Brighton and Sebastian J. Am. Chem. Soc. **39** 2245 (1917).

[27]) Güntelberg Z. phys. Chem. **123** 199 (1926).

[28]) Brönsted ibid. **50** 481 (1904).

[29]) Linhart Z. phys. Chem. **41** 1175 (1919).

[30]) Brester Rec. Trav. Chim. **46** 328 (1927).

same as used by Noyes and Ellis [31]). The spiral electrodes, made from .6 mm. platinum wire were silverplated, properly washed and then coated with a paste of pure silver oxide (prepared from a silver nitrate solution by the addition of sodium hydroxide) and then heated during a period of 4-6 hours at a temperature of 400—500° C. to decompose the oxide to metallic silver. As Brester found, his deviations in E.M.F. were not larger than .3 mV. However our results with this type of electrode were very poor as the following figures, taken from a large number will show:

a. E.M.F. of silver electrode in .1 N silver nitrate solution, measured against quinhydrone electrode in Sörensen standard mixture after ½ hour . . . . .1603 Volt
b. electrode refilled with same solution . . . . .1632 „
c. „ „ „ „ „ . . . . . .1647 „
d. electrode washed with boiling distilled water and heated at 500° for 3 hours (cleaning method, as prescribed by Brester) in same solution as under c
E. M. F. after 5 hours . . . . .1617 Volt

Better results were obtained by us, using the method of Walter R. Carmody [32]).

This author notes, that the following factors influence the potential of the silver electrode:

a. cyanide ion, absorbed in the silver plated electrode
b. light
c. time of electrolyzing
d. concentration of the chloride solution

We want to add to this as fifth very important factor

e. influence of air

as will be discussed later.

As we got fair results with Carmody's procedure, we have adopted his method of preparing the electrodes, which will now be described.

d. Preparation of silver electrodes and their use in silver nitrate and silver benzoate solutions.

The platinum gauze electrodes were of cylindrical shape with a diameter of .5 cm. and a height of 1 cm. and the mesh was 52

---

[31]) Noyes and Ellis J. Am. Chem. Soc. 39 2533 (1917).
[32]) Carmody J. Am. Chem. Soc. 51 2901 (1929).

to the inch. The wire had a diameter of .01 mm. They were cleaned with boiling nitric acid and after washing and heating to red heat plated with silver from an approximately 1N solution of potassium silver cyanide. This solution was prepared by the addition of 13 grams of KCN, dissolved in 100 cc of distilled water to a solution of 18 grams of silver nitrate in 100 cc of water.

The electroplating was carried out in a H-shaped, black painted vessel with a current of 1 milli ampere during 18 hours, using a strip of pure silver as anode. After boiling with distilled water, that was changed three times, the electrodes were covered with a thin layer of silver chloride by using them as anodes during 20 minutes in 1N hydrochloric acid with a current strength of 3.5 milli amperes.

Finally the electrodes were washed with a very dilute NaCl solution. They were kept in the dark at all times during preparation and during the measurements.

Although this method of preparation gave by far better results than any of our previous measurements, the checks were not good enough, especially not in the more dilute solutions.

As already mentioned we had noticed in our experiments the great influence of air upon the electrodes. Some values, that will illustrate this point, are given below.

One electrode vessel was filled with .1N $AgNO_3$ solution and the E.M.F. measured against the quinhydrone electrode in the Sörensen standard mixture:

E.M.F. after ½ hour	.1542 Volt
after passing air for 1 hour	.1542 „
„ „ „ „ 2 hours	.1549 „
„ „ „ „ 3 „	.1551 „
„ „ „ „ 12 „	.1571 „

This change in voltage was not due to an increase of concentration, as evaporation was prevented by passing the air through water before sending it through the cells.

Then we tried to obtain better results by removing the air with an indifferent gas e.g. nitrogen. However our trials failed also here, as may be seen from the following figures:

E.M.F. of Ag-electrode in .1N $AgNO_3$, measured against the

quinh. electrode in the standard solution .1566 Volt
after passing nitrogen, washed
through water for one half hour .1540 ,,
for one hour .1542 ,,
for 12 hours .1640 ,,

When we purified the nitrogen by passing it over glowing copper and then through wash bottles, containing sulphuric acid, sodium hydroxide and water the results did not improve, as shown by the following results:

E.M.F. after 15 minutes .1528 Volt
,, ,, 75 ,, .1520 ,,

The values using N_2 purified by passing through alkaline pyrogallic acid, sulphuric acid, sodium hydroxide and water in turn are the following:

E.M.F. after 5 minutes .1567 Volt
,, ,, 10 ,, .1558 ,,
,, ,, 15 ,, .1550 ,,

Also the checks of the different electrodes among each other were terrible, as the following values measured with three different electrodes in the same solution, will show:

E.M.F. electr. No. 1 after 5 minutes .1568 Volt
,, ,, ,, 2 ,, ,, ,, .1567 ,,
,, ,, ,, 3 ,, ,, ,, .1554 ,,

E.M.F. electr. No. 1 after 10 minutes .1561 ,,
,, ,, ,, 2 ,, ,, ,, .1558 ,,
,, ,, ,, 3 ,, ,, ,, .1541 ,,

E.M.F. electr. No. 1 after 15 minutes .1560 ,,
,, ,, ,, 2 ,, ,, ,, .1550 ,,
,, ,, ,, 3 ,, ,, ,, .1530 ,,

Since it seems from these experiments, that the influence of air, and even of nitrogen, which is probably indifferent, is very large, we thought it worthwhile to try the effect of removing all gases as much as possible by evacuating the electrode vessel and the liquid in the same way as Brester (l.c.) has done. This, as will be seen, made it possible to get results, which were satisfactorily constant and reproducible.

The final design of the apparatus, as we used it in all our experiments, is pictured in fig. 3 and the method of using the silver electrodes — prepared as given at page 38 — in these vessels will be described.

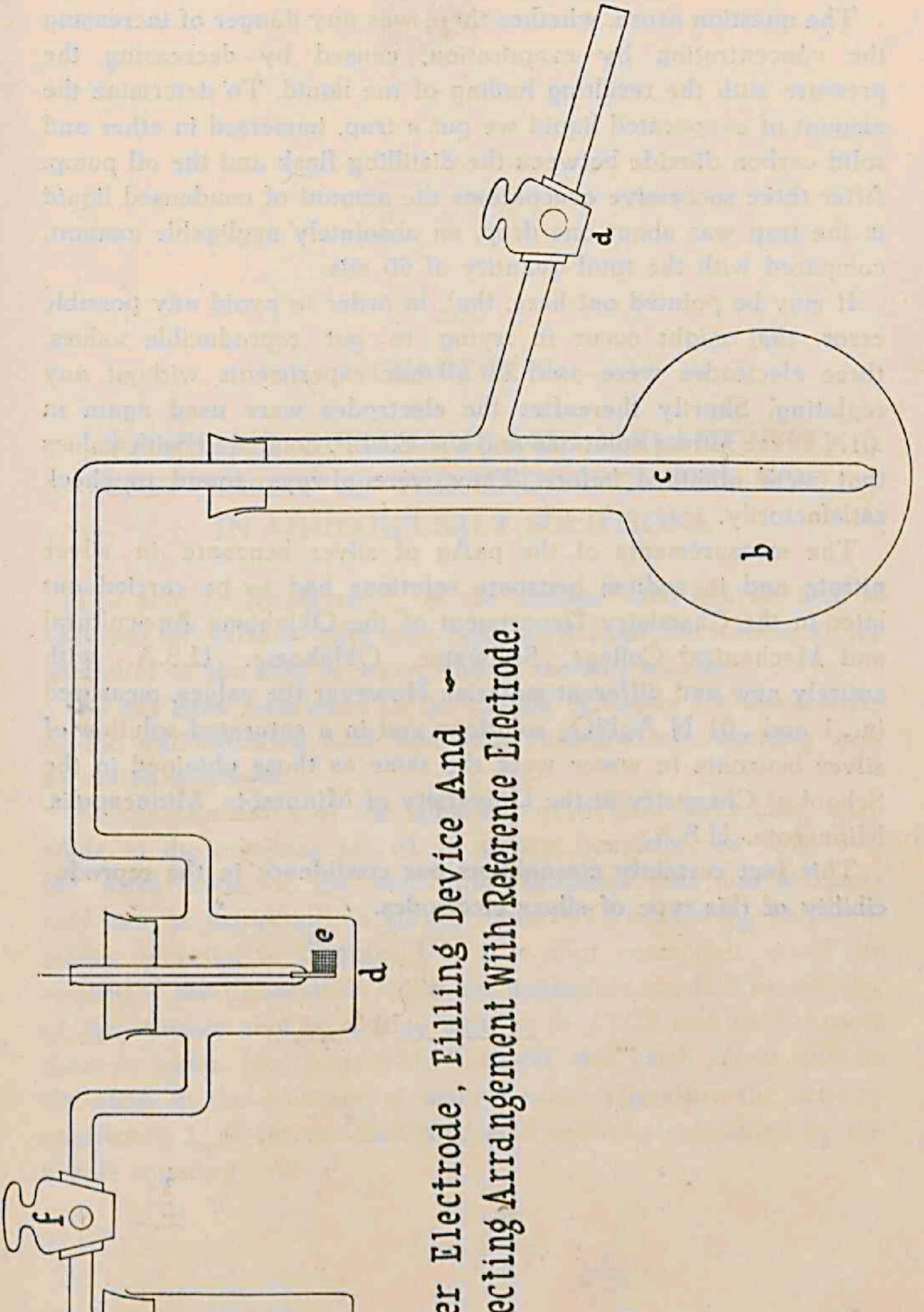
The apparatus consists of a vessel **d** in which the silverplated and silver coated platinum gauze electrode **e** is fixed by means of an one hole rubber stopper. The long tube **c** sticks into the distilling flask **b**. At the left side is a wide tube, which is fitted with a glass stopcock **f** of 3 mm. bore, which in turn leads into the vessel **g**.

This end was closed by means of a piece of rubber tubing with a screw clamp, the distilling flask filled with a suitable amount of the liquid to be measured and the apparatus put together as shown in the illustration, with the exception of the vial **g**, which was connected later.

After opening of the stopcock **f** a suction was applied at the tube **a** by means of an oil vacuum pump. The air was then admitted through he tube, filling the entire apparatus with liquid. This operation was repeated three times, decreasing the pressure each time until the liquid in the vessel started boiling. This was necessary to remove air bubbles sticking to the electrode and to the walls of the vessel as thoroughly as possible. The distilling flask was then removed and the electrode vessel closed at both sides **c** and **g** and immersed in the thermostat over night. The next morning the tap **f** was closed and the tubes **c** and **g** opened. The latter was then connected with the vial **g** which had been filled with a concentrated potassium chloride solution, while the other end **c** was attached to a Kipp apparatus, filled with air.

By the pressure it was possible to make fresh contact in the tube **g** between the silver solution and chloride solution. There was a small turbidity at the end of this tube, but as it was wide (4 mm. inside diameter) there was no danger of stopping up. The necessary contact with the reference electrode (quinhydrone in standard mixture) was made with a 2% agar bridge, saturated with KCl at 25° C. (approximately 3.5 N).

With this setup the E.M.F. readings checked readilly within .1 millivolt, even in the most dilute solutions, e.g. .001 N and the values were also reproducible.



Silver Electrode, Filling Device And ~ Connecting Arrangement With Reference Electrode.

Fig. 3

The question arose, whether there was any danger of increasing the concentration by evaporation, caused by decreasing the pressure with the resulting boiling of the liquid. To determine the amount of evaporated liquid we put a trap, immersed in ether and solid carbon dioxide between the distilling flask and the oil pump. After three successive evacuations the amount of condensed liquid in the trap was about one drop, an absolutely negligable amount, compared with the total quantity of 50 mls.

It may be pointed out here, that, in order to avoid any possible error, that might occur in trying to get reproducible values, three electrodes were used in all our experiments without any replating. Shortly thereafter the electrodes were used again in .01N silver nitrate solutions and the E.M.F. compared with values that were obtained before. They were always found to check satisfactorily.

The measurements of the paAg of silver benzoate in silver nitrate and in sodium benzoate solutions had to be carried out later in the Chemistry Department of the Oklahoma Agricultural and Mechanical College, Stillwater, Oklahoma, U.S.A. with entirely new and different material. However the values, measured in .1 and .01 N $AgNO_3$ solutions and in a saturated solution of silver benzoate in water were the same as those obtained in the School of Chemistry at the University of Minnesota, Minneapolis, Minnesota. U.S.A.

This fact certainly strenghtens our confidence in the reproducibility of this type of silver electrodes.

CHAPTER V.

SOLUBILITY OF BENZOIC ACID AND ACTIVITY COEFFICIENT OF THE UNDISSOCIATED ACID IN AQUEOUS SALT SOLUTIONS.

The activity coefficient f_o of the undissociated benzoic acid in solutions of various salts was calculated from the values of the solubility of the acid in water and in the salt solution.

As has been mentioned in the outline (Chapter II) the activity of the undissociated acid was kept constant by working with saturated solutions.

All measurements of the solubility of benzoic acid have been made in the presence of .01 N sodium benzoate. In this way the dissociation of the acid into hydrogen ions and benzoate ions can be neglected, as may be inferred from all p_H measurements, reported in Chapter VI, or a sligt correction could be applied if the dissociation were not neglegibly small. The activity of the benzoic acid is sligthly smaller in .01 N sodium benzoate than in water (see page 57); however this small effect will be the same in the presence of neutral salts .Therefore the activity coefficient f_o of the undissociated acid could be calculated by the simple equation

$$f_o = \frac{s_o}{s}$$

where s_o is the solubility of benzoic acid in .01 N sodium benzoate
s ,, ,, ,, ,, ,, ,, ,, the salt solution.

In Table 1 we give the values of f_o in the different salt solutions.

TABLE 1.

Activity coefficient f_o of undissociated benzoic acid in salt solutions

Salt added	ionic strength salt	normality salt	normality benzoic acid	f_o	$-\log f_0$
------			.02676		
KCl	.09	.09	.02588	1.033	-.0142
,,	.25	.25	.02456	1.089	-.0371
,,	.50	.50	.02266	1.180	-.0718
,,	1.00	1.00	.01938	1.380	-.1398
NaCl	.09	.09	.02568	1.042	-.0179
,,	.25	.25	.02408	1.111	-.0457
,,	.50	.50	.02170	1.232	-.0906
LiCl	.09	.09	.02558	1.045	-.0192
,,	.25	.25	.02394	1.127	-.0480
,,	.50	.50	.02160	1.238	-.0928
KNO_3	.05	.05	.02658	1.006	-.0027
,,	.09	.09	.02640	1.013	-.0058
,,	.25	.25	.02610	1.022	-.0095
,,	.50	.50	.02558	1.045	-.0192
,,	1.00	1.00	.02432	1.097	-.0402
$NaNO_3$	.05	.05	.02648	1.010	-.0042
,,	.09	.09	.02634	1.025	-.0066
,,	.25	.25	.02658	1.041	-.0176
,,	.50	.50	.02452	1.091	-.0378
$LiNO_3$	.05	.05	.02642	1.012	-.0053
,,	.09	.09	.02618	1.022	-.0094
,,	.25	.25	.02552	1.048	-.0204
,,	.50	.50	.02470	1.083	-.0345
KBr	.09	.09	.02608	1.025	-.0108
,,	.25	.25	.02562	1.068	-.0285
,,	.50	.50	.02364	1.132	-.0537
KI	.09	.09	.02642	1.012	-.0053
,,	.50	.50	.02528	1.058	-.0244
K_2SO_4	.09	.060	.02620	1.021	-.0090
,,	.50	.333	.02412	1.119	-.0450
$NaClO_4$	.09	.09	.02630	1.027	-.0072
,,	.25	.25	.02590	1.033	-.0141
,,	.50	.50	.02554	1.060	-.0253
$BaCl_2$	.09	.060	.02614	1.023	-.0098
,,	.50	.333	.02376	1.126	-.0516

Salt added	ionic strength salt	normality salt	normality benzoic acid	f_0	$-\log f_0$
$CaCl_2$	.091	.061	.02608	1.025	-.0108
"	.506	.337	.02348	1.139	-.0564
$SrCl_2$	.0914	.061	.02604	1.026	-.0113
"	.508	.339	.02346	1.140	-.0568
$Ba(NO_3)_2$	.09	.06	.02650	1.009	-.0040
"	.25	.168	.02608	1.025	-.0110
	.50	.333	.02564	1.043	-.0182
$Ca(NO_3)_2$	.0912	.0608	.02646	1.010	-.0045
"	.253	.169	.02624	1.019	-.0084
"	.507	.338	.02582	1.036	-.0154
$Sr(NO_3)_2$	.120	.080	.02640	1.013	-.0058
"	.334	.223	.02580	1.037	-.0157
"	.668	.445	.02506	1.067	-.0283
$Mg(NO_3)_2$	.0896	.0597	.02646	1.010	-.0045
"	.249	.166	.02594	1.031	-.0131
"	.498	.333	.02534	1.055	-.0234

The first column gives the kind of salt added, the second and third columns the ionic strength (Chapter I note 11) and the normality respectively. The normality of the benzoic acid, found by the titration with the standard alkali is given in the fourth, and in the fifth and sixth column the values of f_o and $-\log f_o$ are recorded.

The results are further represented graphically in figures 4 and 5; the abcissae giving the ionic strength and the ordinates the corresponding $-\log f_o$. These graphs in which the effects of the monovalent and divalent salts have been plotted separately show very nicely the salting-out effect, giving straight lines in every case. A slight curvature of the lines is found in the case of the nitrates.

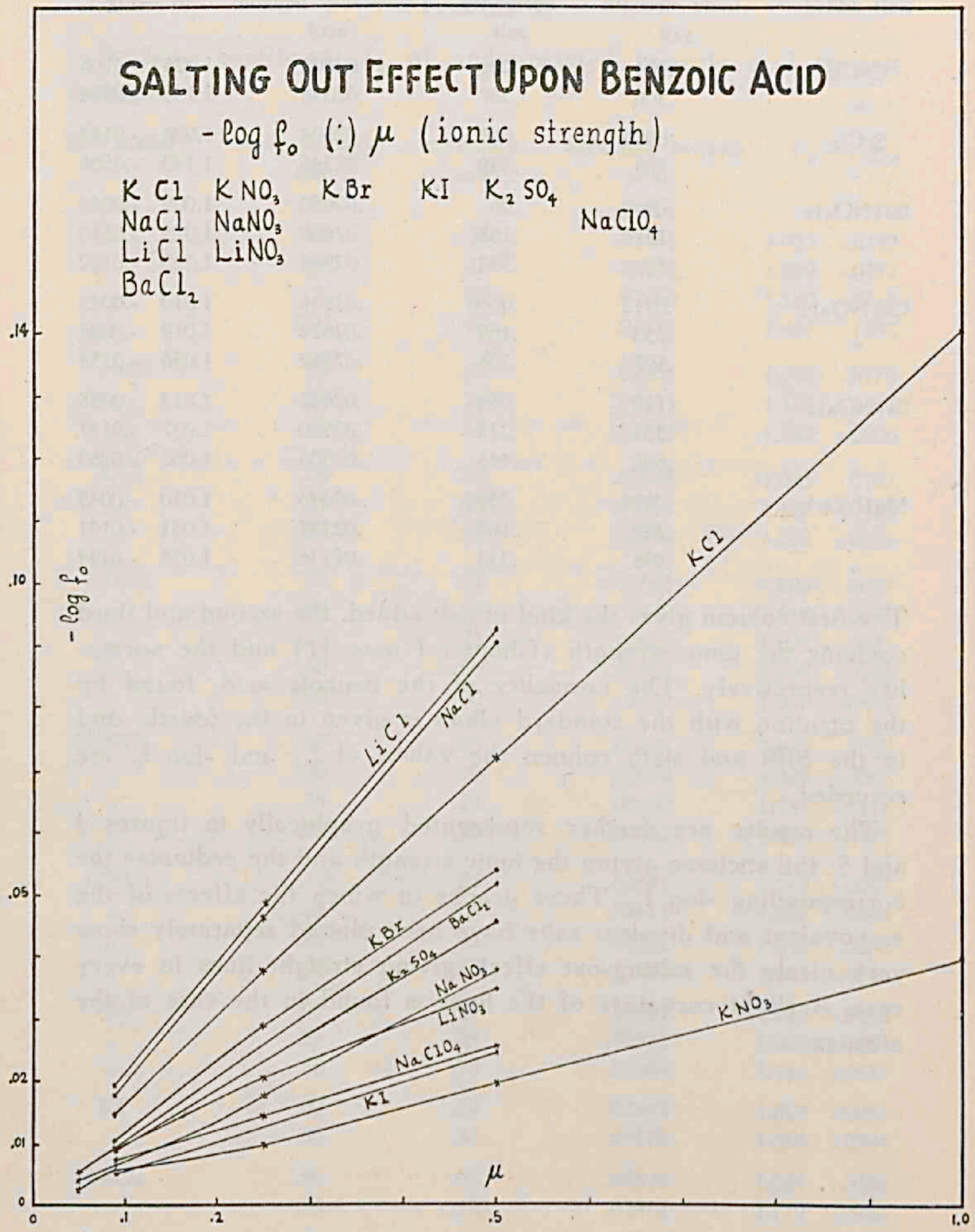

SALTING OUT EFFECT UPON BENZOIC ACID
- log f₀ (:) μ (ionic strength)
K Cl K NO₃ K Br KI K₂ SO₄
NaCl NaNO₃ NaClO₄
LiCl LiNO₃
BaCl₂
- log f₀
μ
.14
.10
.05
.02
.01
0
0
.1
.2
.5
1.0
KCl
LiCl
NaCl
KBr
BaCl₂
K₂SO₄
NaNO₃
LiNO₃
NaClO₄
KI
KNO₃

Fig. 4

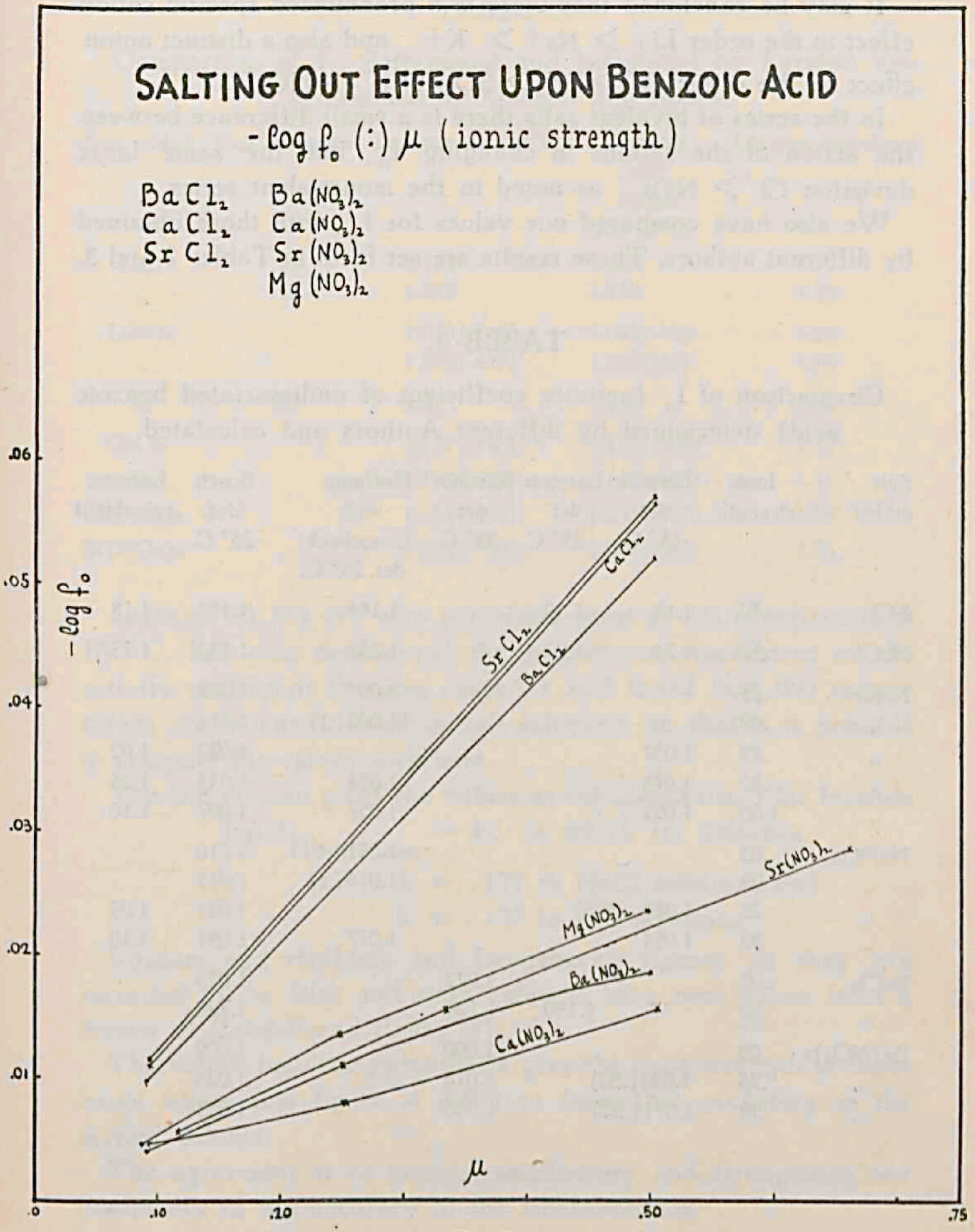

SALTING OUT EFFECT UPON BENZOIC ACID
- log f₀ (:) μ (ionic strength)
BaCl₂
CaCl₂
SrCl₂
Ba(NO₃)₂
Ca(NO₃)₂
Sr(NO₃)₂
Mg(NO₃)₂
-log f₀
.06
.05
.04
.03
.02
.01
CaCl₂
SrCl₂
BaCl₂
Sr(NO₃)₂
Mg(NO₃)₂
Ba(NO₃)₂
Ca(NO₃)₂
μ
.0
.10
.20
.50
.75

Fig. 5

It may be concluded that there is a pronounced specific cation effect in the order $Li^+ > Na^+ > K^+$ and also a distinct anion effect in the order $Cl^- > Br^- > SO_4^= > I^- > NO_3^-$.

In the series of bivalent salts there is a small difference between the action of the cations in changing f_o, but the same large deviation $Cl^- > NO_3^-$ as noted in the monovalent series.

We also have compared our values for f_o, with those obtained by different authors. These results are set forth in Tables 2 and 3.

TABLE 2.

Comparison of f_0 (activity coefficient of undissociated benzoic acid) determined by different Authors and calculated.

Salt added	Ionic strength	Larsson det. 18° C.	Larsson det. 25° C.	Rördam det. 25° C.	Hoffman and Langebeck det. 25° C.	Bosch det. 25° C.	Larsson calculated
KCl	.50	1.18	1.19		1.164	1.180	1.18
NaCl	.50	1.24	1.23		1.231	1.232	1.23
KNO_3	.05				1.007	1.006	
"	.09				1.008 (.1)	1.013	
"	.25	1.031				1.022	1.02
"	.50	1.048			1.028	1.045	1.05
"	1.00	1.092			1.057	1.097	1.10
$NaNO_3$	.05				1.011	1.010	
"	.09				1.016 (.1)	1.015	
"	.25	1.049				1.041	1.05
"	.50	1.084			1.077	1.091	1.10
$BaCl_2$	.09			1.022		1.023	
"	.50		1.140	1.124		1.126	
$Ba(NO_3)_2$	.09			1.000		1.009	
"	.25	1.024 (.30)		1.018		1.025	
"	.50	1.071 (.90)		1.036		1.043	

TABLE 3.

Comparison of f_0, determined and calculated by Larsson and determined by Kolthoff and Bosch.

Salt added	Ionic strength	Larsson det. 18°C	Kolthoff and Bosch det. 25°C	Larsson calculated
LiCl	.25	1.138	1.117	1.12
"	.50	1.255	1.238	1.25
$LiNO_3$		1.053(.208)	1.048(.25)	1.04
"		1.083(.417)	1.083(.50)	1.08
Ki	.50	1.07	1.058	1.06
$CaCl_2$		1.147(.450)	1.139(.506)	1.12
$SrCl_2$		1.172(.600)	1.140(.508)	1.17
$Ca(No_3)_2$		1.054(.495)	1.036(.507)	1.05
$Sr(NO_3)_2$		1.058(.750)	1.067(.668)	1.06

Larsson [33] [34] [35] who performed most of his experiments at 18° C. has also determined the temperature coefficient of the activity coefficient in some cases [35] and found that this temperature coefficient is small in salt solutions, so that it is possible to compare his values with ours.

The last column gives the values as calculated using his formula

$\log f_{\text{Hbenzoate}} = kc$, in which for instance

k = .177 in NaCl solutions and
k = .137 in KCl solutions.

Rördam and Hoffman and Langebeck's figures as they are recorded in the fifth and sixth columns have been taken from a review of Randall and Failey [36].

The values between parenthesis give the ionic strength in those cases where this figure is different from that occurring in the second column.

The agreement is in general satisfactory and strengthens our confidence in the accuracy of the measurements.

In a second series of measurements we have determined the f_0

---

[33] E. Larsson Z. Physik. Chem. **148** A 307 (1930).
[34] E. Larsson ibid **153** 299 (1931).
[35] E. Larsson ibid **153** 466 (1931).
[36] M. Randall and C. F. Failey Chem. Rev. **4** 295 (1927).

values of benzoic acid in sodium benzoate solutions of various concentrations. These determinations, together with p_H measurements were necessary in order to calculate the constant value of the activity of the undissociated acid in water as will be described in the following Chapter.

Many measurements have been made in order to check the four following factors that influence the solubility:

- **a.** different preparations of benzoic acid
- **b.** size of acid crystals
- **c.** amount of benzoic acid
- **d.** time of shaking

a. and **b.**: As described in Chapter III 2 we have compared our preparation of benzoic acid with a product "Kahlbaum" in two ways, first by using them as standard substance in the titration of NaOH and second by the determination of the solubility of both products, the results of which are given in Table 4.

TABLE 4.

Solubility of benzoic acid in water.

Kind of benzoic acid	amount per 200 cc of water	time of shaking	normality of saturated solution 1.	2.
"Kahlbaum"	.8 g	5 hours	.02775	.02777
	.8 g	22 hours	.02775	.02775
	1.5 g	5 hours	.02773	.02775
	1.5 g	22 hours	.02777	.02775
"Kahlbaum" melted	1.5 g	6 hours	.02777	
	1.5 g	18 hours	.02775	.02777
"our preparation"	.8 g	5 hours	.02773	.02775
	.8 g	22 hours	.02773	.02775
	1.5 g	5 hours	.02781	.02780
	1.5 g	22 hours	.02781	.02777
"our preparation" melted	1.5 g	6 hours	.02780	
	1.5 g	18 hours	.02779	
	2.0 g	6 hours	.02778	
	2.0 g	18 hours	.02779	.02776
	3.0 g	6 hours	.02783	
	3.0 g	18 hours	.02778	.02777

In the first column the kind of acid used is recorded: both preparations also have been used after they had been kept at the melting point for one half hour. The crust was then powdered, so that there was a great difference in the size of the crystals before and after melting.

c.: Different amounts of benzoic acid from .8—3 grams were shaked with 200 ml of water (Table 4 column 2)

d.: The time of shaking varied from 5—22 hours: column 3. As we found, saturation was obtained in the case benzoic acid — water already after 5 hours; the figures for the solubility for a shaking period of 22 hours do not differ from the „5 hour" values by more than the experimental error, so that it was not necessary to extend the shaking time for longer thans 22 hours.

Kilpatrick and Chase [37]) have used a shaking time of even 217 hours and did not find any increase in solubility after 5 hours of shaking.

The values of the benzoic acid normalities are set forth in the fourth column; the agreement between the figures is very good and we have taken therefore as an average normality of a saturated aqueous solution of benzoic acid of .02778 at 25° C. Table 5 gives the values obtained by other workers.

TABLE 5.

Some previous determinations of the solubility of benzoic acid in water at 25° C.

Solubility moles per liter	Observer	
.02808	Paul	Z. physik. Chem. **14** 105 (1894)
.02793	Noyes and Chapin	J. Am. Chem. Soc. **20** 751 (1898)
.02796	Hoffmann and Langebeck	Z. physik. Chem. **51** 385 (1905)
.02799	Freundlich and Seal	Kolloid Z. **11** 257 (1912)
.02791	Rördam	Thesis Copenhagen (1925)
02781	Larsson	Z. Anorg. Chem. 155 247 (1926).
.02781 (25.15° C.)	Kilpatrick and Chase	J. Am. Chem. Soc. **53** 1734 (1931)

---

[37]) Kilpatrick and Chase J. Am. Chem. Soc. **53** 1734 (1931).

The solubilities and f_0 values of benzoic acid in sodium benzoate solutions of various concentrations are given in Table 6. The calculation of f_0 was carried out in the same way as described before. As will be seen from the figures in the fourth column the f_0 values are all smaller than 1 in contradiction with those obtained before in the neutral salt solutions.

TABLE 6.

Activity coefficient f_0 of undissociated benzoic acid in sodium benzoate solutions.

Normality sodium benzoate	nomality benzoic acid	fo	-log f_0
	.02635		
.01	.02676	.985	.007
.02	.02674	.985	.007
.03	.02684	.982	.008
.05	.02706	.973	.012
.10	.02759	.955	.020
.25	.02936	.898	.047
.50	.03398	.776	.110
.75	.03933	.670	.174
1.00	.04623	.570	.244

Also Larsson 35) has found that the activity coefficient of benzoic acid in sodium benzoate solutions is smaller than 1 in concentrations from .01—1.0 N at 18° C.

In a 1 N solution Larssen's value for f_0 at 18° C. is .61, whereas we have found .60 at 25° C. at this concentration. 38)

Larsson tries to explain this anomalous behaviour by the assumption, that the benzoate ions have a special action (relative to the dipole character of the ions) upon the activity of the benzoic acid molecules, besides their free electric charge. He also thinks it possible, that there exist acid benzoate ions, which are in equilibrium with the benzoic acid molecules and benzoate ions. The temperature may possibly have an influence upon this equilibrium and this will account for the large temperature coefficient of f_0.

---

38) E. Larsson Z. physik. Chem. **148** A 148 (1930).

CHAPTER VI.

Hydrogen ion activity in benzoic acid — benzoate solutions in the presence of neutral salts.

The activity coefficient of the benzoate ion.

As mentioned in the outline (Chapter II) it was planned to determine the activity coefficient f_1 of the benzoate ion in the presence of various neutral salts.

Application of the Mass Action Law for the ionization of benzoic acid gives us the following equation:

$$K = \frac{[{}^{a}H^{+}] \times [{}^{a}\text{benzoate}^{-}]}{[{}^{a}\text{Hbenzoate}]} = \frac{[{}^{a}H^{+}] \times [{}^{c}\text{benzoate}^{-}] \times f_1}{[{}^{a}\text{Hbenzoate}]} \quad (1)$$

From this we find for the activity coefficient f_1 of the benzoate ion

$$-\log f_1 = -\log \left\{ K \times [{}^{a}\text{Hbenzoate}] \right\} - p{}^{a}H^{+} - p{}^{c}\text{benzoate}^{-} \quad (2)$$

1. Determination of K.

For the calculation of the ionization constant of benzoic acid we have carried out pH determinations in two series of solutions, containing sodium benzoate : benzoic acid in ratio's of 1 : 1 and 2 : 1.

The dissociation of the acid is so large that a correction has to be applied. For instance:

We measured in a solution, that was .005 N to benzoic acid and .005 N to sodium benzoate a pH of 4.124. This is equal to a hydrogen ion concentration of 7.516×10^{-5}. The corrected benzoate ion concentration is then 507.5×10^{-5} and the corrected concentration of the benzoic acid 492.5×10^{-5}.

We calculate then for K'

$$K' = \frac{[{}^{a}H+] \times [{}^{c}\text{benzoate}^{-}]}{[{}^{c}\text{Hbenzoate}]} = 7.516 \times 10^{-5} \times \frac{507.5}{492.5} =$$

7.745×10^{-5} or $p_K' = 4.111$

The results of the dilution series 1 : 1 are reported in Table 1.

TABLE 1.

p_H and p_K values of .25 normal benzoic acid and .25 normal sodium benzoate and its successive dilutions at 25° C.

concentration benzoate	p_H	$p_{K'}$	p_{Ko}	p_K
.25	4.092	4.089	(4.169)	
.01	4.107	4.101	4.151	4.188
.005	4.124	4.111	4.146	4.183
.0025	4.140	4.115	4.140	4.177
.001	4.172	4.114	(4.130)	

By application of the simple Debye-Hückel equation $-\log f_1 = .5 \sqrt{\mu}$, in the different solutions, we find at infinite dilution

$$p_{Ko} = p_{K'} + .5 \sqrt{.01} = 4.151$$

These values are set forth in the fourth column. If we correct for the difference between p_H and p_{aH} we find

$$p_{aH} \text{ infinite} = p_K = 4.177 — 4.188 \text{ or}$$

$K = (6.66 \text{ to } 6.50) \times 10^{-5}$ or an average of 6.60×10^{-5}.

The results of the second dilution series 2 : 1 are given in Table 2.

TABLE 2.

p_H and p_K values of .25 normal benzoic acid and .50 normal sodium benzoate and its successive dilutions at 25° C.

concentration benzoate	p_H	$p_{K'}$	p_{Ko}	p_K
.05	4.349	4.047	(4.172)	
.025	4.365	4.062	4.141	4.178
.01	4.400	4.094	4.144	4.181
.005	4.414	4.103	4.138	4.175
.0025	4.431	4.111	4.136	4.173
.001	4.474	4.143	(4.159)	

$p_K = 4.173 — 4.181$ or $K = (6.71 — 6.59) \times 10^{-5}$ or an average of 6.65×10^{-5}.

In a previous investigation 39) we found a value of 7.0×10^{-5}, whereas Jones and collaborators 40) calculated from conductivity measurements a value of 6.8×10^{-5} at 25° C.

---

39) Kolthoff and Bosch Rec. Trav. Chim. 47 876 (1928).

40) Jones Am. Chem. Journ. 44 159 (1910); 46 56 (1912).

The agreement is quite good, especially when we consider the difficulties, that are connected with p_H determinations in these solutions.

When we started our p_H measurements in this investigation it was quite impossible to get constant E.M.F. values; there was a certain drift in the E.M.F. that could not be explained. The following table, taken from a large number of experiments may illustrate this:

Influence of time upon the E.M.F. between the hydrogen electrode in a solution of .025 N sodium benzoate and .025 N benzoic acid and the quinhydrone electrode in the Sörensen standard solution.

Time		E.M.F.	
5	minutes	.6722	Volt
10	„	.6748	„
15	„	.6760	„
25	„	.6772	„
40	„	.6785	„
1½	hours	.6818	„
14	„	.7000	„
19	„	.7020	„

These facts could not be explained by an oxygen content of the hydrogen used; in a first series of measurements the gas was passed through an alkaline pyrogallol solution and then through washbottles containing sulphuric acid and water. In a second series we passed the hydrogen over the above reagents and then over red hot copper wire, but this did not give any better results.

An explanation of this irregular behavior was then sought in the method of platinizing. It was found, that the rate of increase of the E.M.F. was proportional to the thickness of the layer of platinum black on the electrode.

Therefore we came to the conclusion, and the experiments proved it, that it was advantageous to platinize the electrodes as lightly as possible. For platinizing we used a current of 20 milli amperes during 5 minutes. After using the electrode as a cathode in a 1 N sulphuric acid solution with a current of 20 milli amperes for 5 minutes the spiral electrode had a slight grayish color.

Using this procedure in platinizing, the potentials usually became constant after 10—15 minutes and stayed constant for several hours. However it happened once in a while, that it still was impossible to get constant values. Replating of the electrode helped sometimes but because of the uncertainties the p_H values in sodium benzoate solutions with concentrations larger then .25 N may be considerably in error.

We have not been able to find any explanation for these irregularities. When we measured p_H values in solutions that contained nitrates a possible explanation could be found in the formation of ammonia. In a solution, containing .002 N hydrochloric acid and .5N sodium nitrate the p_H measured with the quinhydrone electrode was 2.698 and the value, determined with the hydrogen electrode after one half hour of H_2 passing through was 3.015. When this latter solution was compared with the original solution, the former showed a more alkaline reaction (p_H of about 3) to thymolblue as an indicator. It was also possible to make a positive test for ammonia with Nessler's reagent. We have not been able to find such a reduction in the case of sodium benzoate.

2. Activity of undissociated benzoic acid: $[a_{H\,\text{benzoate}}]$

The activity of undissociated benzoic acid is constant in saturated solutions and its value, as it occurs in equation 2 Chapter VI was extrapolated from the values in sodium benzoate solutions of various concentrations.

As it is not permissable to consider benzoic acid as completely undissociated we had to correct the normality values of benzoic acid for this dissociation. For instance: we measured in a .01 N sodium benzoate solution a solubility of benzoic acid of .02663 moles per liter and a p_H of 3.668 or a hydrogen ion concentration of 2.148×10^{-4}. The corrected value for $[c_{H\,\text{benzoate}}]$ is then $2.663 \times 10^{-2}. - .021 \times 10^{-2} = 2.642 \times 10^{-2}$.

The different results are given in table 3. In columns 1 and 2 the sodium benzoate and benzoic acid normalities are given respectively, whereas we have reported in the third and fourth column the p_H and hydrogen ion concentration. The last column gives the value of the concentration of undissociated benzoic acid, corrected for dissociation.

In order to extrapolate we have plotted the results from Table 3 in figure 6, the abscissae giving the sodium benzoate concentrations and the ordinates the corresponding concentration values. The graph shows a straight line relationship except in the most dilute solution and we therefore felt confident in accepting an extrapolated value of 2.635 × 10^{-2} for $[{}^{a}\text{Hbenzoate}]$ in aqueous solutions at 25° C.

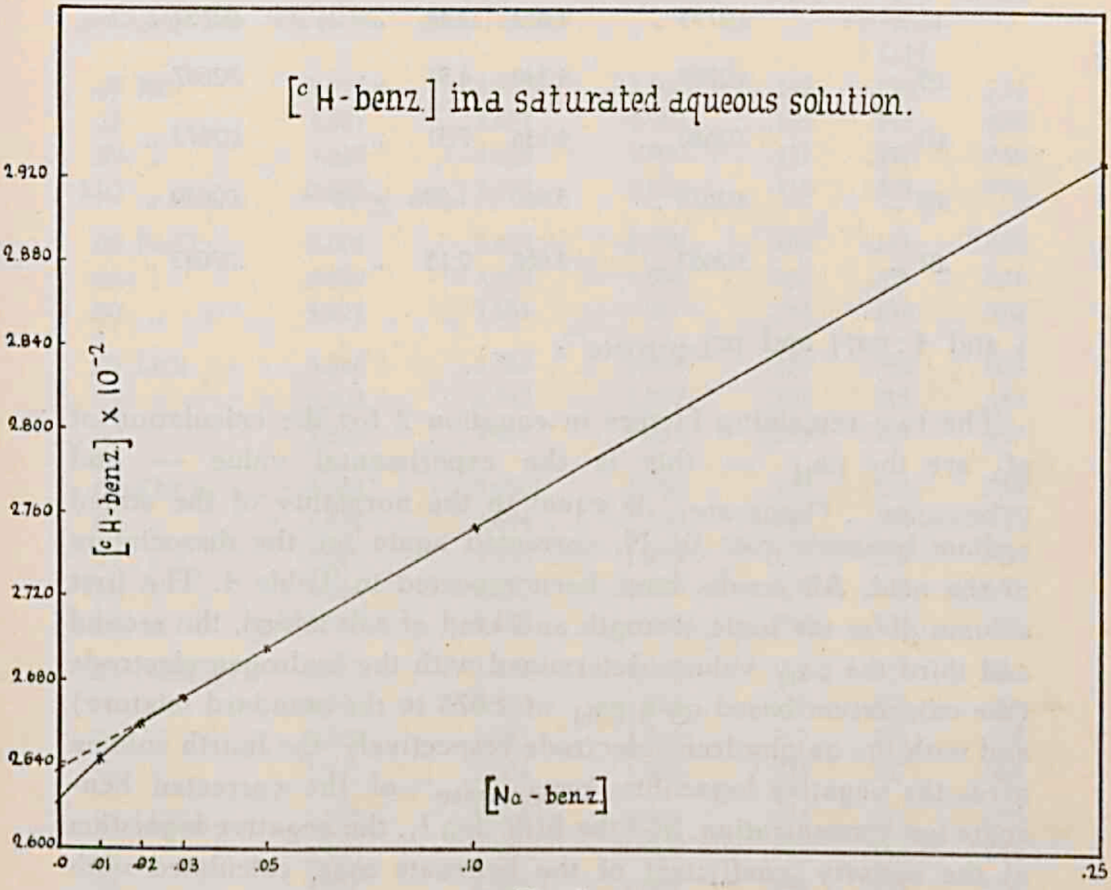


Fig. 6

TABLE 3.

$[c_{\text{Hbenzoate}}]$ values in .25 N sodium benzoate and its successive dilutions at 25° C.

Sodium benzoate	benzoic acid	p_H	a_{H^+}	$[c_{\text{Hbenzoate}}]$ corr.
.25 N	.02932 N	4.914	1.22×10^{-5}	.02931 N
.1 „	.02755 „	4.613	2.44 „	.02752 „
.05 „	.02702 „	4.340	4.57 „	.02697 „
.03 „	.02680 „	4.136	7.31 „	.02673 „
.02 „	.02670 „	3.960	1.096×10^{-4}	.02659 „
.01 „	.02663 „	3.668	2.15 „	.02642 „

3 and 4 : pa_H and pc_{benzoate^-}.

The two remaining factors in equation 2 for the calculation of pf_1 are the pa_H — this is the experimental value — and pc_{benzoate^-}. c_{benzoate^-} is equal to the normality of the added sodium benzoate e.g. .01 N, corrected again for the dissociation of the acid. All results have been reported in Table 4. The first column gives the ionic strength and kind of salt added, the second and third the pa_H values, determined with the hydrogen electrode (the calculation based on a pa_H of 2.075 in the standard mixture) and with the quinhydrone electrode respectively; the fourth column gives the negative logarithm pc_{benzoate^-} of the corrected benzoate ion concentration, and the fifth -log f_1, the negative logarithm of the activity coefficient of the benzoate ions, calculated with equation 2. For example we calculate for -log f_1 in .5 N KCl solution:

$$-\log f_1 = -\log K - \log [{}^{a}_{\text{Hbenzoate}}] - pa_H - pc_{\text{benzoate}^-} =$$

$$= -\log K - \log [{}^{a}_{\text{Hbenzoate}}] - pa_H - \log [{}^{c}_{\text{benzoate}^-} + {}^{c}_{H^+}] =$$

$$= 4.175 + 1.579 - 3.627 - \log (.01 + .0003) = .137$$

We also have applied the simple Debye—Hückel equation $-\log f = .5 \sqrt{\mu}$ the results of which are given in the next (sixth) column. The last column gives the f_1 values, corresponding to the -log f_1 values occurring in the fifth column.

TABLE 4.

Activity coefficient f_1 of the benzoate ion in salt solutions.

Ionic strength and added salt	pa_H H_2 electr.	pa_H quinh. electr.	$pc_{benzoate}$	-log.f_1	-log.f_1 equation I D.H.	f_1 exp.
.09 KCl	3.622	3.642	1.990	.142	.158	.721
.25 ,,	3.601	3.627	1.989	.164	.255	.686
.50 ,,	3.627	3.654	1.990	.137	.357	.730
1.00 ,,	3.652	3.698	1.990	.112	.503	.773
.09 NaCl	3.601	3.625	1.989	.164	.158	.686
.25 ,,	3.559	3.583	1.988	.207	.255	.621
.50 ,,	3.524	3.561	1.987	.243	.357	.572
.09 LiCl	3.546	3.567	1.988	.220	.158	.603
.25 ,,	3.502	3.532	1.987	.265	.255	.543
.50 ,,	3.420	3.461	1.984	.350	.357	.447
.05 KNO_3	3.664	3.656	1.990	.120	.123	.759
.09 ,,	3.639	3.644	1.990	.125	.158	.750
.25 ,,	3.610	3.650	1.989	.155	.255	.700
.50 ,,	3.586	3.650	1.989	.179	.357	.662
1.00 ,,	3.568	3.689	1.988	.198	.503	.634
.05 $NaNO_3$	3.610	3.617	1.989	.155	.123	.700
.09 ,,	3.598	3.622	1.989	.167	.158	.681
.25 ,,	3.549	3.590	1.988	.217	.255	.607
.50 ,,	3.541	3.603	1.988	.225	.357	.596
.05 $LiNO_3$	3.591	3.600	1.989	.174	.123	.670
.09 ,,	3.575	3.590	1.988	.191	.158	.644
.25 ,,	3.527	3.563	1.987	.240	.255	.576
.50 ,,	3.468	3.529	1.985	.301	.357	.500
.09 KBr	3.615	3.650	1.989	.150	.158	.708
.25 ,,	3.622	3.649	1.989	.143	.255	.720
.50 ,,	3.561	3.661	1.988	.205	.357	.624
.09 KI	3.610	3.639	1.989	.155	.158	.716
.09 K_2SO_4	3.627	3.625	1.988	.139	.158	.726
.50 ,,	3.657	3.617	1.990	.107	.357	.782
.09 $BaCl_2$	3.578	3.593	1.989	.187	.158	.650
.50 ,,	3.427	3.427	1.984	.343	.357	.454
091 $CaCl_2$	3.557	3.574	1.988	.209	.159	.618
.506 ,,	3.380	3.414	1.982	.392	.359	4.06

Ionic strength and added salt	pa_H H_2 electr.	pa_H quinh. electr.	$pc_{benzoate}$	-log.f_1	-log.f_1 equation I D.H.	f_1 exp.
.091 $SrCl_2$	3.516	3.590	1.988	.205	.160	.624
.508 „	3.407	3.444	1.983	.364	.360	.433
.09 $Ba(NO_3)_2$	3.554	3.563	1.988	.212	.158	.614
.25 „	3.497	3.508	1.986	.271	.255	.536
.50 „	3.478	3.507	1.986	.290	.357	.513
.091 $Ca(NO_3)_2$	3.495	3.503	1.986	.273	.159	.533
.253 „	3.454	3.461	1.985	.315	.257	.484
.507 „	3.314	3.349	1.980	.460	.360	.347
.12 $Sr(NO_3)_2$	3.576	3.563	1.988	.190	.181	.646
.334 „	3.466	3.476	1.985	.303	.294	.498
.668 „	3.422	3.476	1.984	.348	.412	.449
.09 $Mg(NO_3)_2$	3.563	3.541	1.988	.203	.158	.695
.249 „	3.461	3.469	1.985	.308	.255	.556
.498 „	3.420	3.451	1.984	.350	.357	.440

Comparing the —log f_1 values in the fifth and sixth columns it is evident that the agreement between the values, calculated from experimental data and calculated with the simple Debye-Hückel equation is very poor and that it is not permissible to use this equation for the calculation of activity coefficients in more than very dilute solutions.

Therefore we have also applied the more complicated Debye—Hückel equation Chapter 1 equation 3

$$-\log f = \frac{.5\sqrt{\mu}}{1 + .329 \times a \times 10^{8}\sqrt{\mu}} \qquad (3)$$

in which a is the ionic size of the ions and has an average value of 3.76 A¨.U. for KCl and of 2.35 A ¨ U. for NaCl 41). If we calculate —log f_1 with these values we find the figures given in Table 5.

---

41) E. Hückel Physik. Z. 26 93 (1925).

TABLE 5.

Kind of salt	Total ionic strength	-log f_1 calculated from experimental data	-log f_1 calculated with D.H. equation (3)
KCl	.1002	.142	.144
,,	.2603	.164	.156
,,	.5102	.137	.190
,,	1.0102	.112	.240
NaCl	.1003	.164	.127
,,	.2603	.207	.183
,,	.5103	.243	.230

Since the agreement is not good at all, we can not draw a conclusion from these values about the validity of the D. H. equation as the —log f_1 values in the third column of Table 5 seem to be irregular.

As these values seem to be normal in the cases of KNO_3 and $NaNO_3$ we have calculated an A value ($= .329 \times a \times 10^{-8}$), using the —log f_1 value from the fifth colmn Table 4 for the .25 N solutions.

This A figure we have used in calculating —log f_1 values in the other concentrations of potassium and sodium nitrate as they occur in the first column of Table 4. 42)

The results are given in Table 6.

TABLE 6.

Application of the Debye—Hückel equation (3) in potassium and sodium nitrate solutions.

Kind of salt	Total ionic strength	A value	-log f_1 calculated from experimental data	-log f_1 calculated with D.H. equation (3)
KNO_3	.2602	1.266	.155	.155
,,	.0602	,,	.120	.094
,,	.1002	,,	.125	.113
,,	.5103	,,	.179	.188
,,	1.0103	,,	.198	.221
$NaNO_3$	.2603	.340	.217	.217
,,	.0602	,,	.155	.113
,,	.1003	,,	.167	.147
,,	.5103	,,	.225	.287

---

42) F. H. Mc Dougall J. Am. Chem. Soc. 52 1392 (1930) calculated from solubility measurements of silver acetate A values varying from 1.408—1.479 in KNO_3 solutions up to an ionic strength of 1.

From these figures we draw the conclusion that the more complicated Debye—Hückel equation can not be applied successfully for the calculation of activity coefficients in these solutions either.

Finally we have calculated the activity coefficient f_1 of benzoate ion in solutions of sodium benzoate of different concentrations saturated with benzoic acid. These results are reported in table 7.

The first column gives the normality of sodium benzoate, the second the paH as determined experimentally, the third the benzoate ion concentration, corrected for the dissociation of benzoic acid, whereas we have reported in the fourth column the —log f_1 values as calculated in a way similar to this calculation in the case of the system benzoic acid - sodium benzoate and salts (page 58).

We also have applied the simple D. H. equation in calculating —log f_1 and these results occur in the fifth column. The f_1 values as they belong to the —log f_1 values from the fourth column are found in the last row of figures of Table 7. It seems, that this equation holds approximately up to an ionic strength of .1 in these solutions.

TABLE 7.

Activity coefficient f_1 of benzoate ion in 1.00 N sodium benzoate, saturated with benzoic acid, and successive dilutions.

Concentration	$p^{a}{}_{H}$ H_2-electrode	$c_{benzoate}$ corrected	-log f_1 exp.	-log f_1 equation I D.H.	f_1 exp.
1.00 N	5.495	1.0000	.259	.500	.551
.75 „	5.369	.7500	.260	.433	.549
.50 „	5.327	.5000	.126	.353	.748
.25 „	4.951	.2500	.101	.250	.792
.10 „	4.650	.1000	.104	.158	.787
.05 „	4.377	.05005	.086	.112	.820
.03 „	4.173	.03007	.059	.087	.873
.02 „	3.997	.02011	.060	.070	.871
.01 „	3.725	.01020	.058	.050	.875

CHAPTER VII.

Solubility of silver benzoate in water and in aqueous salt solutions.

The mean activity coefficient of silver and benzoate ions.

The mean activity coefficient of the silver and benzoate ions f_0 has been calculated from solubility measurements of silver benzoate in water and in salt solutions. The relationship between this activity coefficient and the solubility is given by the following equation:

$$f_o = \sqrt{f_{Ag^+} \times f_{benzoate^-}} = \frac{s_o}{s} \qquad (1)$$

in which s is the solubility of silver benzoate in the salt solution and s_o is the solubility if $f_o = f_{Ag^+} = f_{benzoate^-} = 1$

Assuming that in a saturated solution of silver benzoate in water $f_{Ag^+} = f_{benzoate^-}$ then s_o at an ionic strength o =

$$s_o = s_{water} \sqrt{f_{Ag^+} \times f_{benzoate^-}} = \sqrt{a_{Ag^+} \times a_{benzoate^-}} =$$
$$= \sqrt{\text{true solubility product}} \qquad (2)$$

The solubility of silver benzoate in water has been determined several times and the influence of the shaking period has been checked. As an average of 12 values we find a normality of a saturated aqueous solution of silver benzoate of .01162. The largest and smallest figures found are .01166 and .01156 respectively.

The solutions were saturated after 3 days of shaking. Accidentally we were able to determine the solubility of a solution, that had been rotating for 25 days continiously and we found a figure of .01156.

Assuming that the simple Debye—Hückel equation —lof f = $.5\sqrt{\mu}$ holds in this dilute solution we find for —log f = $.5 \times \sqrt{.01162}$ = .054 or f_o = .883.

When we insert this value in the equation for s_o we calculate

$$s_o = .01162 \times .883 = .01026.$$

All results have been recorded in Table 1. The first column gives the kind of salt added and its analytical strength, the second the solubility of silver benzoate in moles per liter, the third the total *ionic strength*, whereas we have given in the two last columns the $-\log f_o$ and f_o values respectively as calculated by means of equation (1).

TABLE 1.

Mean activity coefficient f_o of silver and benzoate ions in salt solutions.

Ionic strength and added salt	Solubility silverbenzoate	Total ionic strength	$-\log f_o$	f_o
water	.01162 N			
s_o	.01026 „			
.05 N KNO_3	.01298 „	.06298	.1021	.791
.09 „ „	.01369 „	.10369	.1253	.749
.10 „ „	.01366 „	.11366	.1243	.751
.25 „ „	.01483 „	.26483	.1600	.692
.50 „ „	.01590 „	.51590	.1903	.645
.50 „ $NaNO_3$	.01628 „	.51628	.2005	.630
.50 „ $LiNO_3$	.01648 „	.51648	.2058	.623
.50 „ $Ba(NO_3)_2$	.01697 „	.51697	.2185	.605
.498 „ $Mg(NO_3)_2$	.01759 „	.51559	.2341	.583
.668 „ $Sr(NO_3)_2$	.01784 „	.68584	.2402	.575
.253 „ $Ca(NO_3)_2$	.01633 „	.26933	.2018	.628
.507 „ „	.01834 „	.52534	.2523	.559
1.013 „ „	.02079 „	1.0338	.3067	.494

An application again has been made of the two Debye — Hückel equations

$$-\log f = .5\sqrt{\mu}\ (1) \quad \text{and} \quad -\log f = \frac{.5\sqrt{\mu}}{1 + A\sqrt{\mu}} \qquad (2)$$

and the results can be found in Table 2.

TABLE 2.

Application of the Debye — Hückel equations (1) and (2) for the calculation of the mean activity coefficient f_0 of the silver- and benzoate ions in salt solutions.

Kind of salt	Total ionic strength	$-\log f_0$ calculated from experimental data	$-\log f_0$ calculated with D. H. equation (1)	A	$-\log f_0$ calculated with D.H. equation (2)
KNO_3	.06298	.1021	.1255	1.182	.0968
,,	.10369	.1253	.1610	,,	
,,	.11366	.1243	.1686	,,	.121
,,	.26483	.1600	.2573	,,	.1600
,,	.51590	.1903	.3591	,,	.194
$NaNO_3$	.51628	.2005	.3592		
$LiNO_3$	.51648	.2058	.3594		
$Ba(NO_3)_2$	.51697	.2185	.3595		
$Mg(NO_3)_2$	.51559	.2341	.3590		
$Sr(NO_3)_2$	.68584	.2402	.4140		
$Ca(NO_3)_2$	.26933	.2018	.2594	.551	.2018
,,	.52534	.2523	.3624	,,	.2590
,,	1.0338	.3067	.508	,,	.3259

In the first and second column the kind of salt and the total ionic strength respectively are given. The values of $-\log f_0$ in the third row are those occurring in the fourth one of table 1. The fourth column of Table 2 gives the —lof f_0 figures calculated with the D. H. equation (1).

The A value in the cases potassium and calcium nitrate has been calculated in the .25 N solutions with the second D. H. equation, taking the $-\log f_0$ values from column 3 table 2. This A value finally has been used to calculate the figures of the negative logarithm of the activity coefficient in the remaining concentrations of KNO_3 and $Ca(NO_3)_2$ and are reported in the last column of this Table.

As can be seen is the agreement between the values of the columns 3 and 4 very poor and is it not permissable to use this simple equation in solutions of an ionic strength higher than .05.

In contrast to this, the application of the second D. H. equation in some cases is more fruitful, as can be seen from a comparison of the figures for -lof f_o from the third and sixth rows in Table 2.

CHAPTER VIII.

Silver ion activity and benzoate ion activity.

As was mentioned in the Outline (Chapter II) it was our aim to determine the activity coefficient f_1 of the benzoate ion in quite a different way, i.e. with the silver electrode.

In the preceding Chapter we have calculated from solubility measurements the mean activity coefficient f_o of the silver and benzoate ions. For the calculation of f_1 we had to know the activity coefficient f_{Ag^+} of the silver ions. The difficulties which we had to overcome in the measurements of the silver electrode potentials have been fully discussed in Chapter IV, to which we refer.

In order to calculate the normal potential of the silver electrode we measured the potentials in .05 N silver nitrate and successive dilutions.

For the calculation we applied the well known Nernst's equation

$$E_o = E + \frac{RT}{nF} \text{In} \frac{1}{{}^aAg^+}$$

At 25° C. and using monovalent salts the above equation becomes

$$E_o = E + .0591 \log \frac{1}{{}^aAg^+} = E + .0591 \log \frac{1}{{}^cAg^+ \times {}^fAg^+}$$

The f_{Ag^+} values have been calculated by means of the simple Debye—Hückel equation $-\log f = .5 \sqrt{\mu}$. All results are reported in Table 1.

TABLE 1.

The normal potential of the silver electrode.

Normality $= c_{Ag}$	$-\log f_{Ag}$ calculated with D.H. equation (1)	f_{Ag}	a_{Ag}	E.M.F.	E_o
.0504	.1123	.772	.03891	.1443 V	.2276
.0402	.1002	.794	.03192	.1386 ,,	.2270
.0202	.071	.849	.01715	.1223 ,,	.2267
.0101	.050	.891	.00891	.1056 ,,	.2268
.0050	.035	.923	.00461	.0891 ,,	.2272
.0030	.027	.940	.00282	.0752 ,,	.2268
.0020	.022	.951	.00190	.0658 ,,	.2266
.0010	.016	.964	.00096	.0480 ,,	.2263
				Average	.2269

The first column gives the analytical concentration of the silver nitrate solution, the second the $-\log f_{Ag}$ values as calculated with the D, H. equation (1), the third the corresponding f_{Ag} figures, the fourth the activity of the silver ions and in the fifth column the potentials (measured against the quinhydrone electrode in the Sörensen standard mixture: .01 N HCl-.09 N KCl). Finally the E_o values have been recorded in the last column.

For instance we calculate in the .0402 N silver nitrate solution for $-\log f_{Ag} = .5 \times \sqrt{.0402} = .1002$, with a corresponding value for $f_{Ag} = .794$. With $c_{Ag} = .0402$ the activity of the silver ions $a_{Ag} = .0402 \times .794 = .03192$.

Inserting these values, together with the measured E.M.F. of .1386 Volt, in the equation for E_o we calculate

$$E_o = .1386 + .0591 \log \frac{1}{.03192} = .2270$$

The check between the E_o values is quite good and we therefore feel condifent in taking an average of .2269 as the zero potential of the silver electrode.

Considering the good checks of the E_o numbers in Table 1 we draw the conclusion that the D. H. equation (1) can be used satisfactorily for the calculation of the activity coefficient of the silver ion in silver nitrate solutions up to an ionic strength of .05.

In order to calculate the activity coefficient of the silver ions in a saturated aqueous solution of silver benzoate we have determined the E.M.F. a large number of times. The measurements were quite difficult and it was not easy to obtain a good check. The values varied from .1068—.1081 Volt and as an average of seven we find an E.M.F. of .1073 V, corresponding to a silver ion activity of .009462. From Table 1 Chapter VII we take the solubility figure of silver benzoate in water of .01162. Then we calculate

$$f_{Ag+} = \frac{.009462}{0.1162} = .813 \text{ (Chapter VIII, Table 3)}$$

The next Table No. 2 gives the f_{Ag} values in salt solutions, saturated with silver benzoate. The first column gives the kind of salt added and its ionic strength, the second the measured potential and the third the values of the activity of the silver ions calculated by means of the Nerst' equation

$$-\log a_{Ag} = \frac{E_o - E}{.0591} \qquad \text{(25° C., monovalent salts),}$$

in which E_o is the normal potential of the silver electrode (Chapter VII) and E is the measured potential.

With the figures for the total concentration of the silver ions in the fourth column (taken from Table 1 Chapter VII) we calculate the f_{Ag} and corresponding $-\log f_{Ag}$ values in the fifth and sixth solumns respectively from the E.M.F. measurements.

The f_{Ag} values have also been determined in a .01 N silver nitrate solution in the presence of neutral salts. These results are reported in Table 3 and are calculated in exactly the same way as in the preceding case of silver benzoate.

It was expected that the values of f_{Ag} in the fifth column of Table 2 and those occurring in the fourth row of Table 3 would be the same at corresponding ionic strengths. However comparing these figures shows that all f_{Ag} values in the case of silver benzoate are smaller than the corresponding values in silver nitrate solutions. An explanation for this difference will be given in the next Chapter.

With the known values for the mean activity coefficient f_o of the silver and benzoate ions and for f_{Ag}, the activity coefficient of the silver ions we are able to calculate the activity coefficient f_1 of the benzoate ions.

TABLE 2.

Influence of salts upon the activity coefficient f_{Ag} of the silver ions in a saturated solution of silver benzoate.

Ionic strength and added salt		E.M.F.	a_{Ag}	c_{Ag}	f_{Ag}	$-\log f_{Ag}$
Water		.1073 V	.00946	.01162	.813	.090
KNO_3	.05	.1052 ,,	.00873	.01298	.673	.172
,,	.10	.1048 ,,	.00859	.01366	.629	.201
,,	.25	.1039 ,,	.00850	.01483	.560	.252
,,	.50	.1047 ,,	.00815	.01590	.538	.269
$NaNO_3$	.50	.1077 ,,	.00962	.01628	.591	.228
$LiNO_3$	.50	.1097 ,,	.01040	.01648	.631	.200
$Ba(NO_3)_2$	.50	.1100 ,,	.01052	.01697	.620	.208
$Mg(NO_3)_2$	.498	.1110 ,,	.01094	.01759	.622	.206
$Sr(NO_3)_2$	.668	.1114 ,,	.01112	.01784	.623	.206
$Ca(NO_3)_2$	.253	.1098 ,,	.01045	.01633	.640	.194
,,	.507	.1115 ,,	.01114	.01834	.608	.216
,,	1.013	.1136 ,,	.01211	.02079	.583	.234

TABLE 3.

Influence of salts upon the activity coefficient f_{Ag} of the silver ions in a .01 N silver nitrate solution.

Ionic strength and added salt		E.M.F.	a_{Ag}	f_{Ag}	$-\log f_{Ag}$
KNO_3	.05	.0998 V	.00706	.699	.155
,,	.10	.0982 ,,	.00664	.657	.182
,,	.25	.0954 ,,	.00596	.591	.228
,,	.50	.0941 ,,	.00566	.560	.252
$NaNO_3$	.50	0.975 ,,	.00647	.641	.193
$LiNO_3$	.50	.0992 ,,	.00690	.683	.166
$Ba(NO_3)_2$	.50	.0980 ,,	.00659	.653	.185
$Ca(NO_3)_2$	.507	.0986 ,,	.00675	.668	.175
$Sr(NO_3)_2$	.668	.0987 ,,	.00678	.671	.173
$Mg(NO_3)_2$	.498	.0992 ,,	.00690	.683	.166

With the equation $-\log \sqrt{f_{Ag^+} \times f_1} = -\log f_o$ we find that $-\log f_1 = -2\log f_o + \log f_{Ag}$.

The results from these calculations can be found in Table 4. The first column again gives the kind of salt added and its ionic strength; in the three following columns we haxe reported the values of $-\log f_o$ as they are taken from Table 1 Chapter VII, the doubled values of the negative logarithms of these coefficients, and the $-\log f_{Ag}$ figures, taken from Table 2 respectively. In the fifth and sixth columns the values for $-\log f_1$ and for f_1 are given.

A discussion of all results will be taken up in the next Chapter.

TABLE 4.

Activity coefficient f_1 of the benzoate ion in salt solutions, saturated with silver benzoate.

Added salt and ionic strength		$-\log f_o$	$-2\log f_o$	$-\log f_{Ag}$	$-\log f_1$	f_1
KNO_3	.05	.1021	.2042	.172	.032	.929
,,	.10	.1243	.2486	.201	.048	.895
,,	.25	.1600	.3200	.252	.068	.855
,,	.50	.1903	.3806	.269	.112	.772
$NaNO_3$	.50	.2005	.4010	.228	.173	.671
$LiNO_3$	.50	.2058	.4116	.200	.212	.613
$Ba(NO_3)_2$	.50	.2185	.4370	.208	.229	.590
$Mg(NO_3)_2$	.498	.2341	.4682	.206	.262	.547
$Sr(NO_3)_2$	.668	.2402	.4804	.206	.274	.532
$Ca(NO_3)_2$	.253	.2018	.4036	.194	.210	.616
,,	.507	.2523	.5046	.216	.289	.514
,,	1.013	.3067	.6134	.234	.379	.417

Finally we determined the solubility of silver benzoate in silver nitrate and sodium benzoate solutions of various concentrations and calculated the mean activity coefficient f_o of the silver and benzoate ions by means of the equation

$$f_o = \sqrt{\frac{S_o^{\,2}}{[c_{Ag^+}] \times [c_{\text{benzoate}^+}]}}$$

We also measured the silver ion activity with the silver electrode and calculated the activity coefficient of the silver ions in the way as described before. The activity coefficient f_1 of the benzoate ions was computed by means of the following equation

$$f_{\text{benzoate}^-} = \frac{s_0{}^2}{[{}^a\text{Ag}^+] \times [{}^c\text{benzoate}^-]}$$

All results are given in tables 5 and 6. The first column gives the concentration of the silver nitrate and sodium benzoate solutions respectively, the second the solubility of silver benzoate, the third the measured E.M.F. against the quinhydrone electrode in the standard mixture, the fourth and fifth the silver ion concentration and silver ion activity respectively. In the sixth column we have reported the activity coefficient of the silver ions with the corresponding negative logarithm values in the seventh column. The eigtht gives the concentration of the benzoate ion, the ninth the activity coefficient of this ion and finally we have reported in the eleventh column the mean activity coefficient f_0. The expressions f'_{benzoate} and f'_0 will be discussed in the next Chapter.

A comparison of the f_0 values in both tables shows that these figures are in good agreement at corresponding concentrations. The measurements of the potential of the silver electrode in presence of an excess benzoate caused many difficulties, they are hard to reproduce and are not considered as very reliable. Therefore we do not attach much significance to the values of f_{Ag} and f_{benzoate} in table 6. On the other hand the figures of f_0 are accurate within 1%.

TABLE 5.

Solubility of silver benzoate in silver nitrate solutions of various concentrations. Activity coefficients of silver- and benzoate ions.

Silver nitrate	Silver benzoate	E.M.F.	c_{Ag}	a_{Ag}	f_{Ag} exp.	$-\log f_{Ag}$ exp.	$c_{benzoate}$	$f_{benzoate}$	$f'_{benzoate}$	f_o	f'_o
.00 N	.01162 N	.1073 V	.01162	.00946	.813	.090					
.01 „	.00786 „	.1128 „	.01786	.01476	.827	.082	.00786 N	.907	.771	.866	.798
.02 „	.00576 „	.1272 „	.02576	.02056	.798	.098	.00576 „	.889	.755	.842	.777
.03 „	.00447 „	.1346 „	.03447	.02742	.796	.099	.00447 „	.859	.730	.827	.760
.04 „	.00392 „	.1412 „	.04392	.03548	.808	.093	.00392 „	.757	.643	.782	.721
.05 „	.00328 „	.1456 „	.05328	.04207	.790	.102	.00382 „	.763	.648	.777	.716
.10 „	.00248 „	.1605 „	.10248	.07534	.752	.124	.00248 „	.563	.480	.644	.593

TABLE 6.

Solubility of silver benzoate in sodium benzoate solutions of various concentrations. Activity coefficients of silver- and benzoate ions.

Sodium benzoate	Silver benzoate	E.M.F.	c_{Ag}	a_{Ag}	f_{Ag} exp.	$-\log f_{Ag}$ exp.	$c_{benzoate}$	$f_{benzoate}$	$f'_{benzoate}$	f_o	f'_o
.00 N	.01162 N	.1073 V	.01162	.00946	.813	.090					
.01 „	.00816 „	.0910 „	.00816	.00501	.614	.212	.01816 N	1.157	.983	.843	.777
.02 „	.00585 „	.0818 „	.00585	.00351	.600	.222	.02585 „	1.161	.987	.834	.769
.03 „	.00477 „	.0742 „	.00477	.00261	.546	.263	.03477 „	1.162	.987	.797	.734
.04 „	.00396 „	.0680 „	.00396	.00205	.517	.287	.04396 „	1.171	.995	.778	.717
.05 „	.00347 „	.0630 „	.00347	.00169	.486	.313	.05347 „	1.167	.992	.753	.694
.10 „	.00240 „	.0470 „	.00240	.00090	.377	.424	.10240 „	1.137	.966	.655	.603

CHAPTER IX.

Discussion of the results.

As has been mentioned we have determined the activity coefficient f_1 of the benzoate ion in salt solutions in two different ways, i.e. from acid — base equilibrium and from solubility equilibrium of silver benzoate. The results are given in Table 1.

The first column gives the kind of salt added and its ionic strength, the second the $-\log f_1$ values determined with the hydrogen electrode (taken from Table 4 Chapter VI) and the third the corresponding figures derived from measurements with the silver electrode (table 4 Chapter VIII).

A comparison of these two sets of figures shows that there is an average difference between these two of .08 ± .01 as shown in the fourth column. This difference is much larger than can be accounted for by experimental errors.

We want to emphasize that the values of f_{Ag} and of f_1 for the computation of s_o have been calculated on the assumption thay the simple Debye—Hückel equation holds; correspondingly in the saturated solution of silver benzoate in water a value of $f_{Ag} = f_1$ was found equal to .883 (page 1 Chapter VII). These figures have been used throughout in all further calculations (compare previous Chapter).

Experimentally however we found for the activity coefficient of the silver ion a value of .813 (Chapter VIII page---). If this value is correct it indicates that silver benzoate is not a strong electrolyte. Therefore if we recalculate all data on the basis of an activity coefficient of .813 of the silver ion in a saturated solution of silver benzoate which is experimental and assume that in such a dilute solution $f_1 = f_{Ag}$, all figures of the activity coefficients of the benzoate ion become

$\left(\frac{.883}{.814}\right)^2$ times larger, and the s_o values of silver benzoate

$\frac{.814}{.883}$ times smaller than was assumed in the calculations in Chapter VIII.

On the basis of the experimental figures $f'_{benzoate}$ has been calculated and these values are given in the fifth column of Table 1. As is shown in the sixth column the difference (Δ) between the values based on measurements with the silver electrode and those with the hydrogen electrode becomes so small as to come within the experimental error.

TABLE 1.

Comparison of the activity coefficient f_1 of the benzoate ion, calculated from measurements with the hydrogen electrode and the silver electrode respectively.

Kind of salt	Ionic strength	$-\log f_1$ H_2—electr.	$-\log f_1$ Ag—electr.	Δ $\log f_1$	$-\log f_1$ corrected	Δ
KNO_3	.05	.120	.032	.088	.104	.016
,,	.25	.155	.068	.087	.140	.015
,,	.50	.179	.112	.067	.184	.005
$NaNO_3$	.50	.225	.173	.052	.245	.020
$LiNO_3$	.50	.301	.212	.089	.284	.017
$Ba(NO_3)_2$	.50	.290	.229	.061	.301	.011
$Mg(NO_3)_2$	.498	.350	.262	.088	.334	.016
$Sr(NO_3)_2$	.668	.348	.274	.074	.346	.002
$Ca(NO_3)_2$	.253	.315	.210	.105	.282	.033

The conclusion that silver benzoate does not behave as an ideal strong electrolyte is entirely new and may have far reaching consequences. Therefore it was desirable to show in a more independent way the justification of this conclusion. The conductivities of silver- and sodium benzoate solutions have been determined and the degree of dissociation, i.e. $\frac{\Lambda c}{\Lambda \infty}$ calculated.

The results are reported in Table 2. The first column of the two sections gives the analytical concentrations of the sodium- and silver benzoate solutions respectively, the second the aequivalent conductivity and the third the degree of dissociation (or better the conductivity coefficient) as calculated by means of the equation

$$\alpha = \frac{\Lambda c}{\Lambda \infty}.$$

Plotting Λ agaist $\sqrt{\mu}$ we extrapolate for the conductivity at infinite dilute solution a value of 84.0 in the case of sodium benzoate and of 97.0 in the case of silver benzoate. Using an ionic conductivity of 50.8 of the sodium ion and a value of 63.4 of the silver ion (Landolt—Börnstein, Physikalisch-Chemische Tabellen, Erster Ergänzungs Band 1927 page 622) we calculate from measurements for the ionic conductivity of the benzoate ion figures of 33.2 and 33.6 respectively, whereas Landolt—Börnstein page 621 reports a value of 33.5 at 25° C.

Comparing the α figures from Table 2 proves also that silver benzoate is not an ideal strong electrolyte. We find an α value of .910 in a .01 N sodium benzoate solution and of .872 in a .0116 N silver benzoate solution.

As it seems that the f_{Ag} value in an aqueous saturated solution of silver benzoate = .813 we have corrected the f_1 and f_0 figures in tables 5 and 6 Chapter VIII for this incomplete dissociation. The new values can be found in the tenth ($f'_{benzoate}$) and twelfth column (f_0') of tables 5 and 6 respectively. The f_1 (uncorrected) values in the ninth column of table 6 are larger than 1, which is improbable; the corrected values are somewhat better, although we expected a value of approximately .90 in the .01 N sodium benzoate solution. However we have mentioned that we do not attach much significance to these figures as the measurements of the potential of the silver electrode in the presence of excess benzoate caused many difficulties.

TABLE 2.

Conductivity coefficients at 25° C. in

(a) Sodium benzoate solutions (b) Silver benzoate solutions

Normality	Λ_c	α	Normality	Λ_c	α
.01	76.7	.910	.01162	84.6	.872
.005	78.6	.932	.00581	88.6	.913
.0025	79.8	.947	.00291	91.6	.944
.00166	80.8	.959	.00145	93.8	.967
.00125	81.1	.962	.00116	94.8	.977
.001	82.2	.975			
.000	84.0	1.000	.000	97.0	1.000

Summary:

The activity coefficient f_0 of undissociated benzoic acid was calculated in a large number of cases from solubility measurements of benzoic acid in the presence of various neutral salts. These values were compared with those obtained by different Authors and the check was in general quite good. Furthermore the activity of the hydrogen ions has been measured in benzoic acid-benzoate solutions in the presence of neutral salts and the activity coefficient of the benzoate ions calculated.

In the second part of this investigation the mean activity coefficient f_0 of the silver and benzoate ions was calculated from solubility measurements in solutions of neutral salts. In addition the activity coefficient of the silver ions was measured in these solutions by means of the silver electrode and from the latter and the mean activity coefficient we computed the activity coefficient f_1 of the benzoate ions.

These values were compared with the figures that we have determined in the system benzoic acid — benzoate. There was a constant difference of .08 ± .01 between both and we therefore concluded that the dissociation of silver benzoate is not complete. This conclusion was supported experimentally by the determination of the f_{Ag} value of .814 in a saturated aqueous solution of silver benzoate, whereas originally we used a value of .883 (computed with the simple Debye—Hückel equation) in our calculations.

A third proof for the incomplete ionization of silver benzoate was found from conductivity measurements. The values of the so-called degree of dissociation of silver benzoate were smaller thans those of sodium benzoate at corresponding concentrations.