



ACTIVITY COEFFICIENTS FROM EMF MEASUREMENTS USING
CATION-RESPONSIVE GLASS ELECTRODES

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ERRATA

Regrettably, some errors were located after the thesis was bound. The writer wishes to draw attention to, and apologise for the following errors:

PAGE -----	LINE -----	CORRECTION -----
3	13	Lanier ¹³ , 13 was missing
7,49	5,10	Reference <u>not</u> Preference
16	16	Tadros <u>not</u> Tadroz
37	12	was also <u>not</u> is also
38	11	them <u>not</u> then
50	22	Z. Physik <u>not</u> z. Physik
60	20	An emf <u>not</u> A emf
67	2	Phys. Chim. <u>not</u> Phys.-chim.
71	8	m_D <u>not</u> m_B
80	13	coefficients <u>not</u> coefficient
86	8	where <u>not</u> wgere
139	10	'and' missing
142	9	Equation 7-12 <u>not</u> Equation 7-11
Fig. 7-8		''
A-10	11	-8.8 <u>not</u> 08.8
C-1, C-13	19,1	(7-11) <u>not</u> (7-20)

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Summary

The cation-responsive glass electrode has been used to measure the mean molal activity coefficient of sodium chloride in water and in glycine-water mixtures at 0°, 10°, 25° and 50°. In the ternary system, the concentration range of sodium chloride was 0.01 m to about 1 m and that of glycine from 0.3 m to near saturation. The activity coefficient of potassium chloride in water and in glycine-water mixtures was also determined and then compared with literature values. Excellent agreement was obtained. Hydrogen-sensitive glass electrodes were also used to determine the mean molal activity coefficient of hydrochloric acid in water and in potassium chloride-water mixtures. Again the results were compared with literature values, where good agreement was obtained. Evidence is also produced in this work to show that the cation-responsive glass electrodes are sensitive to light.

As a preliminary of this research some silver-silver chloride electrodes were prepared and tested. The preparation and behaviour of these electrodes is discussed. The thermal-electrolytic type was found to be suitable for this research.

The activity coefficients of sodium chloride in the binary system have been fitted by the method of least squares to a semi-empirical equation of the type

$$\log \gamma_c^\circ = \frac{-A\sqrt{m_c}}{1 + B\sqrt{m_c}} + 2Cm_c + \frac{3}{2}Dm_c^2 + \frac{4}{3}Em_c^3$$

The values at 0°, 10° and 50° have been compared with literature values, where the data at these temperatures were meagre and contradictory. The activity coefficients of sodium chloride in the ternary system have also been fitted by the method of least squares to an empirical equation of the type

$$\log \frac{\gamma_c}{\gamma_c^\circ} = m_B (B_{10} + B_{11} m_c^{1/2} + B_{12} m_c + B_{13} m_c^{3/2}) + m_B^2 (B_{20} + B_{21} m_c^{1/2})$$

at 0°, 10°, 25° and 50°. Values at rounded concentrations are presented.

It was found that glycine and sodium chloride displayed mutual salting-in phenomena at all four temperatures. A correlation of the activity coefficients of sodium chloride with dielectric constants has been made in the light of the Born Equation. The dipole moment of glycine has also been determined following the method of Roberts and Kirkwood who investigated the system KCl-Glycine-Water at 25°. The value obtained from this work was comparable to literature values. Finally, important thermodynamic properties of sodium chloride in the ternary system, e.g. relative partial molal heat content, heat capacity, and relative partial molal enthalpy, free energy and entropy of transfer have been derived and discussed. For comparison, literature values for other ternary systems have also been included in the discussion.

I hereby certify that this thesis contains no material which has been accepted for the award of any other degree or diploma in any University, and to the best of my knowledge contains no material previously published or written by any other person, except where due reference is made in the text.

Sonny Phang

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Table of Important Symbols and Constants

- F Faraday $\equiv 23062 \text{ cal. volt}^{-1} \text{ equiv.}^{-1}$.
- N Avogadro number $\equiv 6.02380 \times 10^{23}$.
- R Gas constant $\equiv 1.98719 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.
- T Absolute temperature.
- k Boltzmann's constant $\equiv 1.380257 \times 10^{-16} \text{ erg. deg.}^{-1} \text{ molecule}^{-1}$.
- $\gamma_B, \gamma_B^\circ, \gamma_c, \gamma_c^\circ, \gamma_c^*$ Mean molal activity coefficient. Subscripts B and c indicate non-electrolyte and electrolyte respectively.
- Superscript $^\circ$ indicates binary systems of non-electrolyte-water and electrolyte-water. The asterisk indicates the value of γ_c in the ternary system when concentration of c equals zero.
- f_c Mean rational activity coefficient of electrolyte.
- m_B, m_c Molality in moles per 1000 gm. water as solvent. Subscripts B and c indicate non-electrolyte and electrolyte respectively.
- \bar{L}_2, \bar{L}_3 Relative partial molal heat content of electrolyte*.
- \bar{J}_2, \bar{J}_3 Relative partial molal heat capacity of electrolyte*.
- * Subscripts 2 and 3 indicate binary and ternary systems respectively.

Ice-point = 273.160° Absolute.

Values of $k = 2.303 \times \frac{RT}{F}$

$2k = 0.108394$ at 0°C .

$2k = 0.112364$ at 10°C .

$2k = 0.118316$ at 25°C .

$2k = 0.128234$ at 50°C .



Introduction

The influence of electrolytes on the behaviour of the amino acids is, perhaps, one of the most important topics in the physical chemistry of these substances.

Early methods of investigation of the interaction between amino acids and salts have been based on solubility measurements.¹ Such measurements have the disadvantage of observing the interactions between the ions and the dipolar molecules at only the saturated concentrations of the amino acids or the salts. A complete understanding of the interactions must depend upon a knowledge of the activity coefficients at every concentration of both components.

In 1934, Scatchard and Prentiss,² made some accurate freezing point measurements on systems containing glycine and sodium chloride. A year later Joseph³ reported the effect of some amino acids (including glycine) on the activity coefficient of thallos chloride and sodium chloride. Joseph had made use of the emf method using cells without liquid junction. He compared his results measured at 1.4° with those of Scatchard and Prentiss for the system, sodium chloride-glycine-water. The agreement varied between 0 and 0.7 mV. Forced by experimental difficulties, his measurements at 25° were made at high concentrations of sodium chloride between 1 m and 4 m and at glycine concentration of 0.5 m and 1 m.

By 1939 considerable interest had been built around the properties of electrolytes in aqueous solutions of amino acids

and also of electrolytes in aqueous solutions of proteins and peptides. In that year Kirkwood⁴ presented a systematic theoretical interpretation of the properties of the dipolar ions which were characteristics of their electrical structure. The dipolar ion was first treated as one of spherical shape and then as one of ellipsoidal shape. Each model was characterised by certain charge distributions.

These theoretical interpretations were applied in 1941, when together with Roberts,⁵ Kirkwood made measurements on the ternary system of potassium chloride-glycine-water using an emf method on cells with transference. They obtained the activity coefficients of potassium chloride and glycine respectively at 25° over the concentration range of 0.05 m and 0.5 m of either component. From the theoretical interpretations they calculated the dipole moment of the glycine dipolar ion. A value of 14.4 Debyes was obtained and this was in close agreement with values from other methods.

In 1965 Bower and Robinson,⁶ using the isopiestic vapour pressure measurements at 25°, studied the same ternary system as that of Roberts and Kirkwood. The concentration of sodium chloride was extended to about 1.5 m and that of glycine to about 3 m. Excellent agreement was obtained with the results of Roberts and Kirkwood within the concentration ranges common to both experiments.

It should be noted that interest in the influence of electrolytes

on the behaviour of amino acids is not confined only to activity coefficient measurements. Thus in 1966 Tonomura and Okamoto⁷ reported density, viscosity and conductance measurements for lithium chloride and for potassium chloride at concentrations from 0.05 M to 0.25 M, in aqueous urea solutions and in aqueous glycine solutions at 15°, 25° and 35°. During that year the writer⁸ made a study of the same properties of potassium chloride and of potassium iodide in 1 M aqueous solutions of the same non-electrolytes at 25°.

The influence of electrolytes on the behaviour of non-electrolytes other than the amino acids have also received considerable attention, for example, see reference 9, 10, 11, 12. Of particular interest is the work of Lanier, who in 1965 used the sodium-responsive glass electrode to measure the activity coefficients of sodium chloride in a ternary system of sodium chloride-non-electrolyte-water at 25°. The non-electrolytes were methanol, ethylene glycol, ethylene glycol diacetate, diethylene glycol monomethyl ether, dioxane, urea, and dimethylformamide.

For this research the cation-responsive glass electrode has been selected to measure the activity coefficients of sodium chloride in the ternary system of sodium chloride-glycine-water at 0°, 10°, 25° and 50°. The results are presented in Chapter 7. However, before the ternary system was measured much had to be learned about the working of these glass electrodes. Even after the publication of Lanier's

work the activity coefficients of sodium chloride and of potassium chloride in the binary system of electrolyte-water were still being investigated^{14,15,16} by means of the cation-responsive glass electrode. This is because the properties of these cation-responsive glass electrodes are as yet little understood. Thus Chapter 1 of this thesis makes a brief survey of some of the properties, applications and limitations of these electrodes.

Although the silver-silver chloride electrode has been widely used, contradictions have built up concerning their use and performance in aqueous solutions.¹⁷ Since these electrodes were to be used in this research, a careful preparation and preliminary investigation of these electrodes were made. The aim was not only to understand their behaviour but also to find a reliable type which could be easily prepared for use in this research. This work is described in Chapter 2 of this thesis. Chapters 3 and 4 show the preliminary work undertaken in order to understand the working of the cation-responsive glass electrodes. In Chapter 5, evidence is produced to show that the cation-glass electrode can be used just as successfully as other methods for the measurement of the activity coefficients of potassium chloride in glycine-water mixtures. Chapters 6 and 7 contain the results of sodium chloride in water and of sodium chloride in glycine-water mixtures at 0°, 10°, 25° and 50°. Comparison with available literature values and limitations in the binary system are discussed. In the ternary system correlations are

5.

drawn and thermodynamic properties are derived and discussed.

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Chapter 1

The Cation-Responsive Glass Electrode

- (a) Introduction
- (b) Composition of Cation-Responsive Glass Electrodes
- (c) Applications and Limitations of Cation-Responsive Glass Electrodes
- (d) References

The Cation-Responsive Glass Electrode(a) Introduction

Early in the study of pH glass electrodes it was found that errors occurred in the pH response in solutions of $\text{pH} > 9$. It was observed that these errors increased with increasing concentration of alkali metal cations in the solution, especially sodium ions. Much effort was spent trying to minimise this 'alkaline error' by incorporating in the glass varying proportions of Li_2O , Cs_2O , CaO and La_2O_3 . In 1934 Lengyel and Blum¹ showed that the 'alkaline error' increased greatly by increasing the amount of Al_2O_3 and/or B_2O_3 in the glass. Three years later Nicol'skii² (1937) gave the first equation for the glass electrode which was capable of describing not only the H^+ ion response and the initial portions of the cation errors, but also the Na^+ ion response of the glass electrode in the region when the electrodes were responding essentially to Na^+ ions alone (see Equation 3-4, Chapter 3). Then in 1957 Eisenman, Rudin and Casby³, through a systematic study of sodium aluminium silicate glass, empirically confirmed and elaborated Nicol'skii's equation. Eisenman and his co-workers showed that certain aluminosilicate glasses were capable of increasing the "alkaline error" to such an extent that these glasses could be used as sodium-ion or potassium-ion responsive glass electrodes, with interference due to H^+ ion at low pH. Since then glass electrodes responsive to cations other than H^+ ions have become commercially available.

(b) Composition of Cation-Responsive Glass Electrodes

In order to understand why glass electrodes may be sensitive to various cations one must briefly consider the structural chemistry of glass. Early theories of the structure of glass are given by Zacharisen⁴ and Warren.⁵ Recently, Burggraaf⁶ has discussed a structural model of the alkali-alumino glasses. Excellent accounts of the compositions and structures of glass responsive to H^+ and other cations have been given by Bates⁷ and Eisenman.⁸

In many common glasses, including the cation-responsive glass, the main constituents are silicon and oxygen incorporated with variable amounts of aluminium, boron, alkali and alkaline earth metals, and other metals. In pure silica glass each oxygen is shared by two silica tetrahedra, Figure 1-1(a). The difference in ionic radius between the Al^{3+} ion (0.50-0.57 Å) and the Si^{4+} ion (0.39 Å) is so small that the Al^{3+} ion can replace the Si^{4+} ion in the tetrahedral to produce a negative charge on the AlO_4 tetrahedron. The negative charge can be compensated, e.g. by an alkali metal M^+ . Thus the basic units in alumino silicate glasses are SiO_4 and AlO_4 tetrahedra, with a $-\frac{1}{4}$ charge on the oxygen shared between the two cations, Figure 1-1(b).

It must be pointed out that there is short range order around each silicon atom but there is no long range order. It is this lack

of long range order that distinguishes a glass from a crystal with the same composition. The disorder is frozen in as the glass cools.

When an alkali oxide, e.g. Na_2O is added to the alumina-silica glass the Si-O-Si bonds are broken with the formation of another type of negative centre, Figure 1-1(c). The sodium atoms become associated with oxygen atoms which are only bonded to one silicon atom.

Eisenman et al.³ have shown that small additions of Al_2O_3 to sodium silicate glass increased the response of the glass to sodium ions. Since sodium silicate glass has only Si-O^- sites, and the addition of Al_2O_3 creates $\text{Al-O-Si}^{-1/4}$ sites, it can be concluded that the sodium-ion exchange between the solution and the glass takes place only at the $\text{Al-O-Si}^{-1/4}$ sites.⁹ The influence the positive charges have on the $\text{Al-O-Si}^{-1/4}$ sites can decrease their negative force fields. This will in turn affect the cation-response of the glass.^{8,9}

As pointed out by Lyklema and Tadros,¹⁰ the assumption that the space charge density of the fixed negative groups is constant may hold for the bulk of the glass membrane but is not correct for the surface gel layer. Since the potential-determining process occurs in the vicinity of the interface a theory such as that described above would need improvement.

For practical purposes, the sodium-aluminosilicate glass used by Eisenman and his co-workers was found to be highly refractory and extremely difficult to obtain in quantity in a homogeneous and bubble free condition. As a result, efforts were directed to develop new

glasses of high Na^+ ion specificity but at the same time less refractory and viscous.

Lithium-aluminosilicate glass has the lowest melting point and the lowest viscosity among the alkali-aluminosilicates.⁶ Guha et al.¹¹ have investigated lithium-aluminosilicate as well as lithium-sodium-aluminosilicate glasses. They have claimed that the LAS(22-3) glass produced slope values very near to the ideal Nernst value and at the same time showed very little sensitivity to K^+ ion when the emf was measured in pure potassium chloride solutions. (The notation LAS 22-3 follows Eisenman's where the first figure refers to the Li_2O content and the second to that of Al_2O_3 , both in mole %.)

Lengyel and Czakvari¹² have studied a glass of composition 21.4 mole % Na_2O , 6.4 mole % CaO , and 72 mole % SiO_2 in which 12 mole % of the SiO_2 was replaced by equivalent quantities of glass forming and transition metal oxides (GeO_2 , P_2O_5 , TiO_2 , V_2O_5 , B_2O_3 , PbO , ZrO_2 , BeO , ZnO). They concluded that the strongest cation responsiveness resulted from additions of Al_2O_3 , B_2O_3 and ZrO_2 . Others who have also studied the composition of glass for cation specificity include Tandeloo et al.¹³ and Mans and Kateman¹⁴ on potassium-silicate glass containing BeO ; Covington and Lilley¹⁵ on sodium-aluminosilicate glass and its response to Ag^+ ions; and Savage and Isard^{16,17} on various glass compositions in NaCl , KCl and Li_2SO_4 solutions. Nicolskii et al.¹⁸ have given an excellent review

on glass compositions and some of their properties.

The exact compositions of commercial electrodes are not available. The GEA33 electrodes¹⁹ are made from BH104 glass which, according to Covington and Lilley,¹⁵ is of lithium-aluminosilicate composition. The Beckman 39278 and 39137 are made of lithium-aluminosilicate and sodium-aluminosilicate glass compositions respectively.^{20,21} Vail and Khalaimova²² reported the use of Soviet-made sodium-responsive electrodes of composition 24 mole % Na₂O, 3 mole % Al₂O₃, 61 mole % SiO₂, and 12 mole % B₂O₃, while Ise and Okubo²³ employed some Japanese-made sodium-responsive electrodes.

(c) Applications and Limitations of Cation-Responsive Glass Electrodes

This type of electrode has found a large number of applications, e.g. in biological and clinical studies, laboratory analytical work, industrial plants, and chemical research.^{7,8,24,25,26} A recent survey of the literature reveals further improvements and more applications of such electrodes.

Vail and Khalaimova²² have shown the feasibility of determining the amount of sodium in desulphurising plant wash liquors whilst Halliday and Wood²⁷ have described a rapid determination of salt content of cured meat products. Webber and Wilson²⁸ and Hawthorn and Ray²⁹ have carried out the determination of small amounts of sodium ion (10^{-7} M) in high purity water. The cation-responsive

electrode (Beckman 39047 and 39137) can also be used for the determination of NH_4^+ ions as shown recently by Guilbault et al.³⁰ Satake et al.³¹ have measured the counter-ion activity coefficient of sodium alkyl sulphate solutions with and without the presence of added magnesium ions. The sodium alkyl sulphate, a detergent, was of chain length from C_8 to C_{14} . Feinstein and Rozano³² using a cation-responsive electrode determined the degree of dissociation of potassium and sodium carboxylate miscelles at a constant cation concentration. Stenius and Ekwell³³ have obtained the sodium ion activity in a sodium caprylate solution using an E.I.L. GNA33 electrode.

Very little, however, is known about the performance of such electrodes in non-aqueous systems or in aprotic organic solvents. Recently, McClure and Reddy³⁴ have made some investigations using a Beckman 39047 cation electrode in aprotic organic solvents.

A main limitation of such electrodes is that they are susceptible to poisoning. Webber and Wilson²⁸ found that octadecylamine seriously affected the response of the electrodes. Fortunately, they were able to remedy the situation by washing the electrode with ethanol. Hubbard and Lucas³⁵ have shown that some glass-electrode surfaces favour the coagulation of fresh blood. However, Moore and Wilson³⁶ have shown that proteins as normally found in human plasma have no adverse effects on cation-glass electrode response. Friedman, Wong and Walton,³⁷ and Portnoy and Gurdjian^{38,39} have made their own

small electrodes from Corning NAS11-18 glass in their study of sodium content in various biological fluids. They have also reported no indication of glass poisoning by any of the constituents in the samples which they analysed.

Mattock²⁵ has pointed out that further studies concerning the resistance of these electrodes to poisoning, e.g. by adsorption, would be valuable. It is also clear that these electrodes are not exclusively selective towards any particular cation. Thus it remains to be seen if these problems could be overcome with the increased knowledge of glass chemistry.

This research represents one of the applications of these electrodes in the field of chemical research, namely, the determination of some thermodynamic properties of two and three component systems. In the process particular attention was paid to the behaviour of these electrodes under various conditions so that accurate measurements could be obtained.

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Chapter 2

Basic Theory of EMF Measurement, Preparation of Materials,
Apparatus, Technique and the Preliminary Investigations of
the Silver-Silver Chloride Electrode

- (a) Basic Theory of EMF Measurement using Cation-Responsive Electrodes
- (b) Preparation of Materials
- (c) Apparatus
- (d) Technique of EMF Measurement using Cation-Responsive Glass Electrode
 - (i) Binary System of Sodium Chloride-Water
 - (ii) Ternary System of Sodium Chloride-Glycine-Water
- (e) Preliminary Investigations of Silver-Silver Chloride Electrodes
 - (i) Introduction
 - (ii) Preparation of the Electrodes
 - (iii) Sensitivity to Artificial Light
- (f) References

Basic Theory of EMF Measurement, Preparation of Materials,
Apparatus, Technique and the Preliminary Investigations of
The Silver-Silver Chloride Electrode

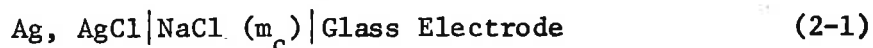
(a) Basic Theory in EMF Measurement using Cation-Responsive Electrodes

The main purpose of this research was to utilise some commercial electrodes in the accurate measurement of the mean molal activity coefficient of aqueous sodium chloride with and without the presence of glycine at various temperatures. This would then allow a thermodynamic study to be made on the ternary system of sodium chloride-glycine-water. These cation-responsive electrodes have already been used by other workers for the measurement of activity coefficients especially at 25°. ^{1,2,3} Truesdell et al. ^{4,5} appear to be the only workers who have made use of these electrodes for accurate activity coefficient measurements at temperatures as low as 10° and 15°. In this research project measurements were made at 0°, 10°, 25° and 50°.

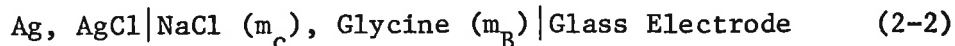
The basic theory for these measurements will now be discussed.

The electrode potential sign used in this research is that suggested by the International Union of Pure and Applied Chemistry (I.U.P.A.C.) in 1953. ^{6,7} It has become known as the Stockholm Convention.

The activity coefficient of aqueous sodium chloride can be obtained from emf measurements using the cell,



and in the presence of glycine,



The silver-silver chloride electrode and the glass electrode are reversible to the Cl^- ion and the Na^+ ion respectively. The electrode potentials are then given by,

$$E_g = E_g^{\circ} + \frac{RT}{F} \ln a_{\text{Na}} \quad (2-3)$$

and

$$E_{\text{AgCl}} = E_{\text{AgCl}}^{\circ} - \frac{RT}{F} \ln a_{\text{Cl}} \quad (2-4)$$

a_{Na} and a_{Cl} are the activities of the sodium and the chloride ion respectively. E_{AgCl}° is the standard potential of the silver-silver chloride electrode. E_g° is the standard potential of the glass electrode plus its asymmetry potential. The emf of the cell is given by,

$$\begin{aligned} E_{\text{cell}} &= E_{\text{right}} - E_{\text{left}} \\ &= E_g^{\circ} + \frac{RT}{F} \ln a_{\text{Na}} - E_{\text{AgCl}}^{\circ} + \frac{RT}{F} \ln a_{\text{Cl}} \end{aligned} \quad (2-5)$$

Equation 2-5 can be written as,

$$E_{\text{cell}} = c + \frac{RT}{F} \ln a_{\text{Na}} a_{\text{Cl}} \quad (2-6)$$

where c includes E_{AgCl}° , E_g° , and the asymmetry potential. In this work c has been assumed to be constant since most of the experiments are of short duration (about 4 or 5 hours at 25°). It may be pointed out that among some of the electrodes used, c remained constant within 0.2 mV over a 12 hour period at 25° . Equation 2-6 is the

basic equation used in this work.

If the pair of electrodes measures two different emfs E_1 and E_2 , of two different solutions m_1 and m_2 of mean molal activity coefficients γ_1 and γ_2 respectively, one obtains

$$E_1 = c + \frac{2RT}{F} \ln m_1 \gamma_1 \quad (2-7)$$

and

$$E_2 = c + \frac{2RT}{F} \ln m_2 \gamma_2 \quad (2-8)$$

Eliminating c ,

$$E_1 - E_2 = \frac{4.606 RT}{F} \log \frac{m_1 \gamma_1}{m_2 \gamma_2}$$

$$\text{i.e.} \quad \log \gamma_2 = (E_2 - E_1) + \frac{4.606 RT}{F} \log \frac{m_1 \gamma_1}{m_2} \quad (2-9)$$

It should be noted that E_1 and E_2 have positive values if the set up of the cell is as shown in Equation 2-1. Equation 2-9 is the practical equation used in this work for determining the mean molal activity coefficient of sodium chloride. By making E_1 , γ_1 and m_1 the reference quantities, γ_2 can be determined by the accurate measurement of E_2 .

(b) Preparation of MaterialsSodium Chloride

A.R. grade sodium chloride was dissolved in boiling doubly distilled water. The hot saturated solution was then filtered and the filtrate cooled with constant agitation to prevent the formation of a crust. Doubly distilled ethanol was then added and the snow-white crystals of sodium chloride were collected. The filtrate was concentrated and a further amount of doubly distilled ethanol was added. A second crop of sodium chloride was thus collected before the filtrate was discarded. It was then dried in vacuo at 107°. Fused recrystallised sodium chloride was also used in the earlier part of this research. Some samples of sodium chloride prepared in this manner showed the presence of alkali.⁸ However, no differences were obtained in the results between the two preparations.

A determination of the bromide content in the sample of sodium chloride was carried out using the method suggested by Pinching and Bates.^{9,10} The method made use of uranine, the sodium salt of fluorescein, to develop a rapid colour test for bromide in the presence of chloride. The following was the procedure: 0.2 ml. of saturated chromic acid solution was added to an equal volume of a saturated sodium chloride solution. A small piece of filter paper was dipped into the uranine dye solution and placed over the test tube mouth. The tube was heated for 6 minutes in a boiling

water bath. From an inspection of the colour developed on the filter paper, and comparison with simultaneously run tests in solutions having known amounts of bromide, the amount of bromide present in the unknown could be determined. A comparison of the colours was made under U.V. light. The method was capable of detecting the presence of 0.001% mole of bromide. The amount of bromide in the recrystallised sodium chloride was not detectable.

Potassium Chloride

The potassium chloride used was a once recrystallised sample which had been fused. The sample had been analysed before and used earlier by the author.¹¹

Glycine

B.D.H. laboratory reagent glycine was recrystallised in doubly distilled water. Precipitation of the glycine was effected by cooling in ice-salt mixture and the addition of doubly distilled ethanol to the solution. Two crops of glycine were collected before discarding the solution. The crystals were then dried in vacuo at 75°.¹²

The purity of the sample was determined. The procedure of Dunn and Loshakoff¹³ involving a formol titration was adopted.

A.R. formalin solution was treated with a minimum amount of magnesium carbonate powder and then used as a medium for the titration.

A glycine sample of known weight (about 0.6 gm.) was then dissolved in the formalin solution and titrated with sodium hydroxide solution. The titration was carried out at room temperature (about 22°) using CO₂-free 0.3202 N NaOH and a pH meter Type PHM26C (Radiometer, Copenhagen).

The formol titration indicated a purity of 99.7 ± 0.5% for the glycine. Furthermore, it was found that the sample had a melting point of 290° which was in accord with the literature melting point.¹⁴

Silver Oxide, Silver Chlorate, Silver Chloride and Hydrochloric Acid

The silver oxide was prepared by adding a solution of sodium hydroxide to a vigorously stirred solution of silver nitrate.¹⁵ The precipitate of silver oxide was collected in a sintered glass filter. It was washed with doubly distilled water until the specific conductance of the final washing was less than $3 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature. It was then stored as an aqueous paste in a dark bottle.

Silver chlorate was prepared as prescribed.¹⁶ Equal portions of concentrated sodium chlorate (10 N) and silver nitrate (10 N) solutions were heated to about 85° and then mixed and slowly cooled to 0°. The crystals of silver chlorate were collected, washed, and recrystallised once in doubly distilled water. Finally, the

crystals were dried in a vacuum oven and then stored in a dark bottle.

Silver chloride was prepared by mixing together solutions of A.R. silver nitrate and recrystallised sodium chloride. The precipitate of silver chloride was collected and washed several times with doubly distilled water until the specific conductance of the final washing was $2.5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature. It was then dried in vacuo at 100° before storage.

The constant boiling hydrochloric acid was prepared by the distillation of diluted A.R. hydrochloric acid in the manner described by Ives and Janz.¹⁶

Distilled Water

Demineralised water from a bulk supply was distilled from glass and stored in polypropylene containers. The average specific conductivity was $1.1 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$.

Preparation of the Solutions

All solutions were prepared by weight, and vacuum corrections^{17,18} were applied in the calculation of their concentrations. "Quickfit" flasks, which had previously been steam cleaned, were used. These were sealed with Parafilm, following the final weighing.

(c) The Apparatus

The apparatus for the measurement of the cell potential together with the circuit are shown in Figure 2-1.

The micro-step potentiometer which was capable of reading to 1×10^{-4} mV, was standardised using a standard cell.¹⁹ The latter was checked against other certified standard cells in the laboratory. One terminal of the potentiometer was connected to the silver-silver chloride electrode and the other was grounded. Together, they formed the low impedance side of the circuit.

The high impedance side of the circuit consisted of a Cary Model 31CV vibrating reed electrometer.²⁰ The instrument was used as a high impedance voltmeter, having an extremely high input resistance. It could measure accurately voltages from high internal resistance circuits and was adapted for measuring the voltages of easily polarised electrolytic cells, such as with glass electrodes.

The shielded lead of the glass electrode was connected to the electrometer input whilst the electrometer feedback was grounded. The shorting switch allowed a check to be made on any zero drift of the electrometer. This was done by grounding the input of the electrometer as shown by the detailed diagram of the shorting switch in Figure 2-1. The electrometer, the standard cell (attached to the potentiometer), and the potentiometer were all placed on a grounded equipotential surface.

Full scale voltages of 1, 3, 10, 30, 100 and 300 mV and 1, 3, 10

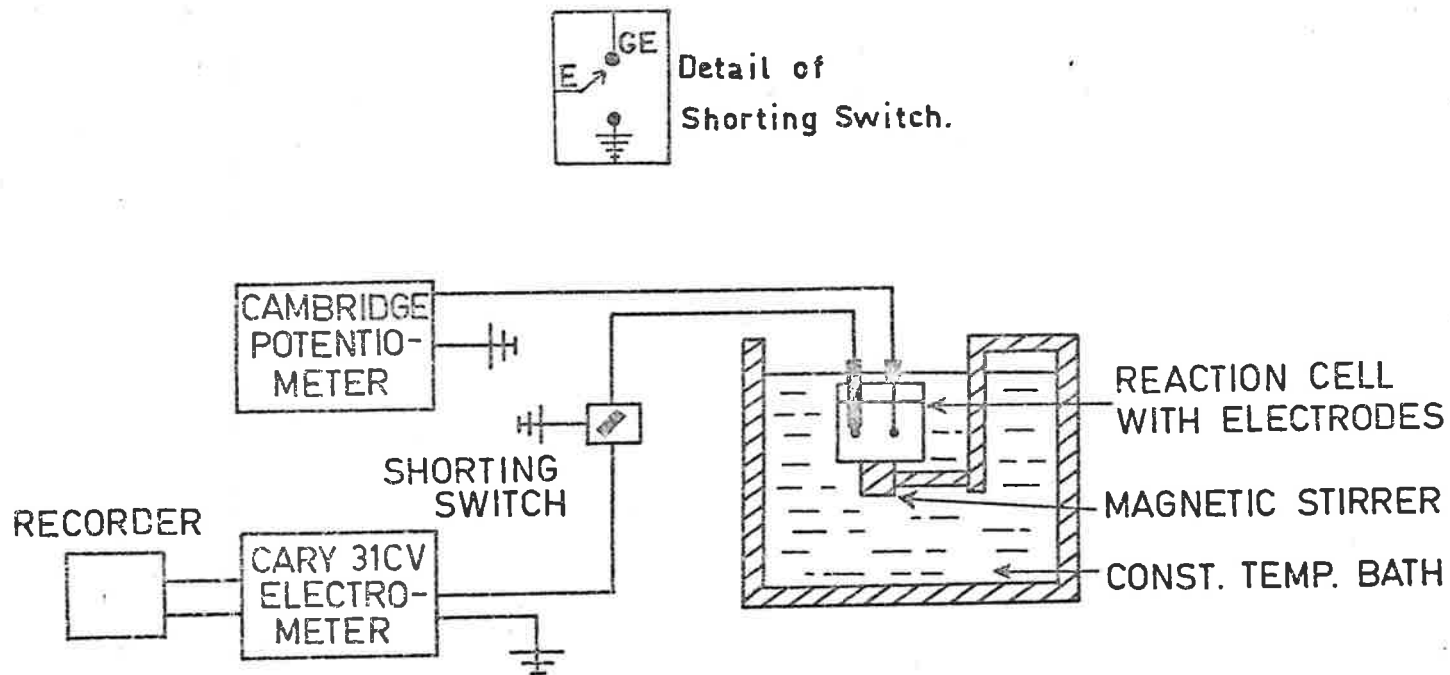
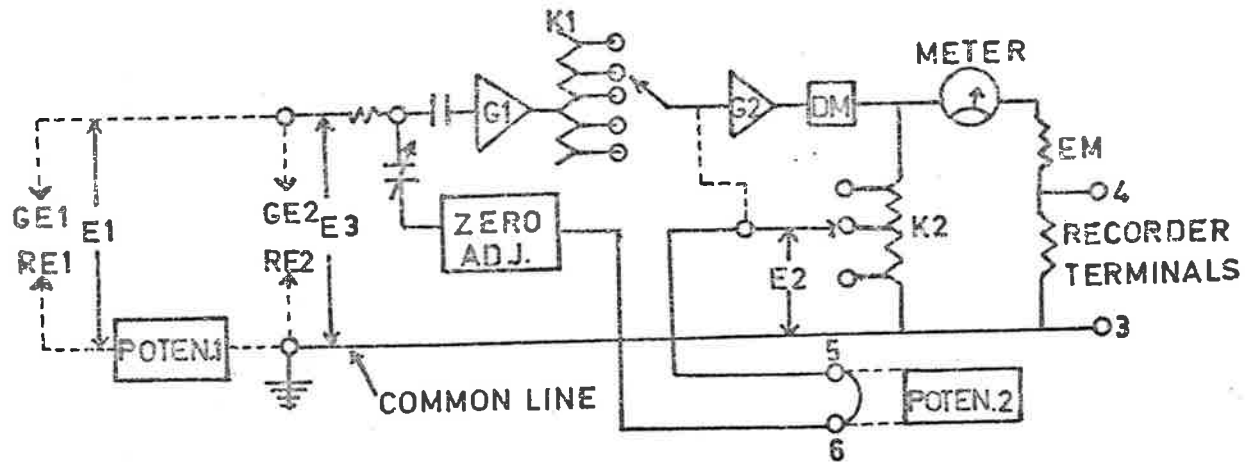


Fig. 2-1. Apparatus for measurement of the cell potential .

and 30 V were provided by a range switch on the electrometer. With the arrangement shown in Figure 2-1, the potentiometer was used as an external bias. By biasing out the cell potential in the desired range of sodium activity, the electrometer was used on its lowest range (0 to 1.0 mV). The residual voltage was either read off on the electrometer or followed on a chart recorder²¹ attached to the electrometer. The latter could, of course, be used as a null meter by completely biasing out the cell potential. The circuit is shown in Figure 2-2 and will be discussed as the first case.

Figure 2-2 shows two different circuit arrangements for measuring the cell emf. Consider the first case in which GE1, RE1, and POTEN.1 represent the glass electrode, the silver-silver chloride reference electrode, and the potentiometer, respectively. One terminal of the potentiometer is directly connected to RE1 and the other is grounded. The COMMON LINE of the electrometer is also grounded. In this set-up E1 is the emf of the cell. By completely 'bucking out' E1, the electrometer can be used as a null meter. E1 is then read off by POTEN.1.

Another arrangement is to connect the COMMON LINE directly to RE2, the silver-silver chloride electrode in this second arrangement. Here, GE2 is the glass electrode. The potentiometer, POTEN.2, is connected in series with the electrometer feedback. E3 is now the emf of the cell. E3 is balanced against E2. When the electrometer is used as a null meter, E2 is completely bucked out by POTEN.2. E3 is



$E_1, E_3 =$ Input voltage

$E_2 =$ Feedback voltage; $E_3 = E_2(1 + 1/G)$. For the normal value of G ,

$E_2 = E_3$ within 0.1%

Fig. 2-2. Circuit for 2 different arrangements of measuring the cell emf.

then read off by POTEN.2.

Using either arrangement, E1 should equal E3. Any cell electrical leakage will not affect the value of E3 but will affect the value of E1. At 25°, calibration of the glass electrodes using either arrangement produced identical results. Since no electrical cell leakage was obtained the inconvenience of using an oil-bath was avoided.

The reaction cells and the weighing vessels are shown in Figure 2-3. The reaction cells (a) and (b) were constructed from 250 ml. Pyrex beakers. They were all fitted with B19/26 'Quickfit' glass joints except for the two slant necks of (b) which were fitted with B10/14 'Quickfit' glass joints. The weighing vessel (c) was similar to a weight burette²² except that it allowed the weighing of solid materials. Vessel (d) allowed the glass capsule to be weighed with and without any solid materials. The capsule and the contents were together dropped into the reaction cell. A tiny hole blown at the bottom of the capsule prevented the trapping of air. Solutions in the reaction cell were magnetically stirred with teflon-coated magnets.

A grounded water bath was used throughout this work. At 0° and 10°, ethylene glycol was added as an anti-freeze. In order to reduce evaporation at 25° and 50°, cetyl alcohol was added. Polyethylene foam painted over with a water-insoluble resin was also used to cover the surface of the water. An opaque brass lid was used to cover the bath, and it also acted as both a light and an electrical shield.

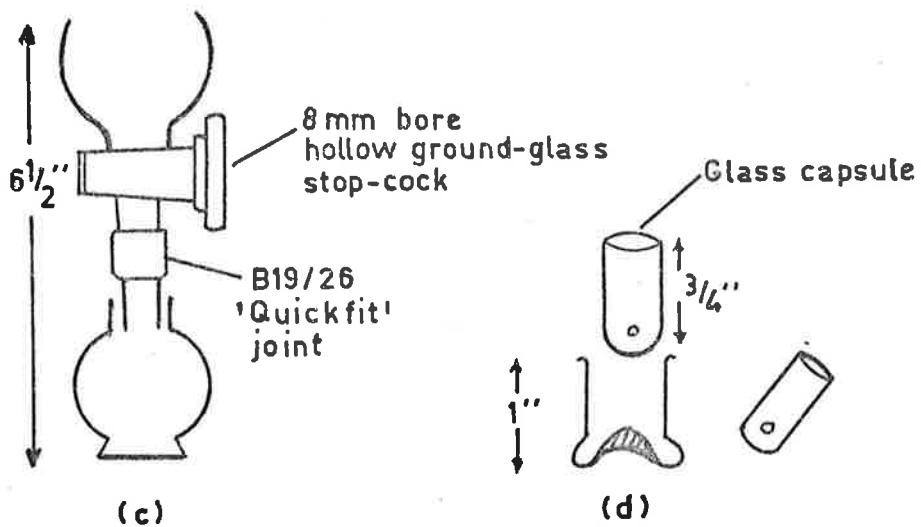
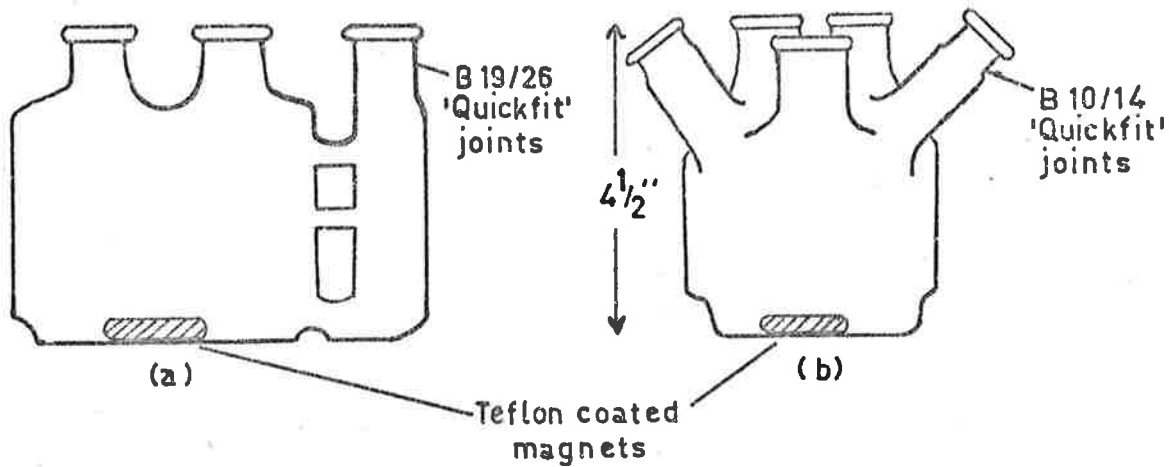


Fig. 2-3. Reaction cells and weighing vessels.

The temperature of the bath was controlled to 0.005° .

(d) Technique of EMF Measurement using Cation-Responsive Glass Electrodes

(i) Binary System of Sodium Chloride-Water

The technique involves the preparation of the reference solution whose concentration was known accurately and usually at a rounded value. About 100 ml. of it was then transferred to either the reaction cell (a) or (b), shown in Figure 2-3. Reaction cell (b) was used only when the pH of the solutions was also required, since its side-arm was specially made to fit a pH glass electrode. The reaction cell containing the electrodes and the reference solution was then placed in the water-bath. The solution was stirred magnetically.

On numerous occasions it was observed that the initial emf reading was steady only after leaving the cell in the bath for several hours (at 25° , about 4 or 5 hours depending upon the particular glass electrode). Thus it was normal to leave the cell overnight in the bath before the initial emf was recorded. With each subsequent addition of salt, the time taken to reach equilibrium or steady emf was much less. In general, it was about 1 hour and this, of course, depended upon the magnitude of the change in emf which the electrodes had to measure, or alternatively upon the amount of salt added and

again on the glass electrode. Equilibrium was assumed when the emf changed by less than 0.02 mV in 15 minutes. A large change in emf (> 50 mV) was found to give rise to errors in the reading (about 0.5 mV error) among some of the glass electrodes.

At equilibrium, the emf was practically independent of the stirring rate of the test solution. However, fluctuations of the emf occurred whenever the silver-silver chloride electrode was badly prepared or had corroded. Drifting of the emf appeared in most cases to be due to the glass electrode. The Beckman-type electrodes were more susceptible to such behaviour than the E.I.L.-type. This drift effect was remedied in most cases by soaking the offending electrodes in dilute sodium hydroxide solution (a few drops of concentrated sodium hydroxide solution in about 150 ml. of water). Otherwise, these electrodes were normally stored in sodium chloride solutions whose concentrations were close to those under investigation.

(ii) Ternary System of Sodium Chloride-Glycine-Water

The plan for the study in the ternary system at each temperature is shown schematically in Figure 2-4. The activity coefficient of sodium chloride, γ_c , measured at $m_c = m_c'$ for various values of m_B is shown by the curve ABC. B represents the activity coefficient of sodium chloride at $m_c = m_c'$ and $m_B = m_B'$. m_B and m_c are the concentrations of glycine and sodium chloride respectively. When

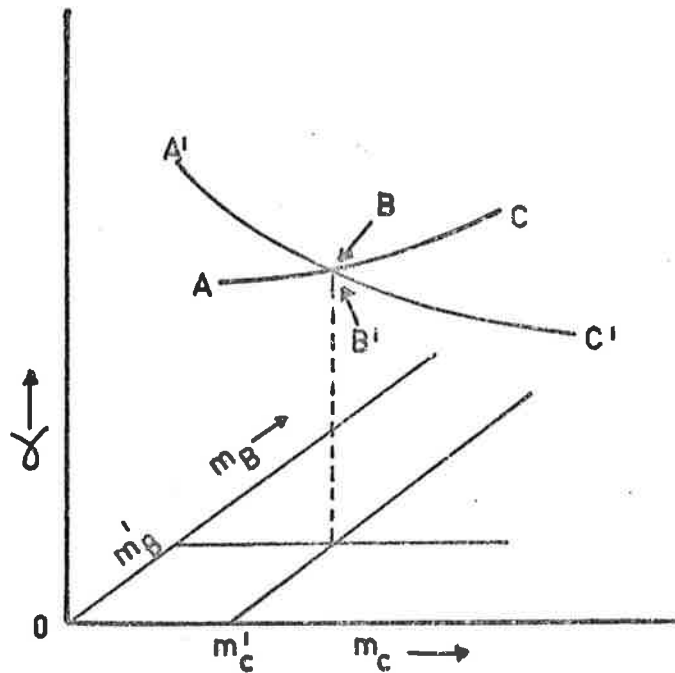


Fig. 2-4. Plan of investigation for ternary system NaCl (m_c)-
Glycine (m_B)-Water.

measured at $m_B = m_B'$ for various values of m_C , the curve A'B'C' is obtained. This time B' represents the activity coefficient of sodium chloride at $m_C = m_C'$ and $m_B = m_B'$. Thus the value of B' provides a check on the value of B obtained previously. In this way, measurements on a series of constant m_C at various m_B values and constant m_B at various m_C values, can provide numerous cross-checks on any single experiment. In the ternary system at 0°, 10°, 25°, and 50°, these cross-checks did not differ by more than 0.2 mV at each temperature. As an example, some of the data at 50° (see Appendix B, Table B-4) are shown in Figure 2-5.

The curve in Figure 2-5 is the result of an experiment in which m_B , the concentration of glycine, was held constant at $m_B = 0.53301$ while m_C , the concentration of sodium chloride, was varied. The dark squares represent the values taken from other experiments in which m_C was kept constant while m_B was varied. As shown, these cross-check values do not deviate from the curve by more than 0.1 mV.

The technique of emf measurement for the ternary system was quite similar to that in the binary system. Here, aqueous sodium chloride was again used as the reference solution whether the experiment involved m_B or m_C being kept constant. For example, in the case where m_B was kept constant, an accurately known concentration of aqueous sodium chloride was first equilibrated in the reaction cell. Then by means of the weighing vessel (c), shown in Figure 2-3, solid glycine

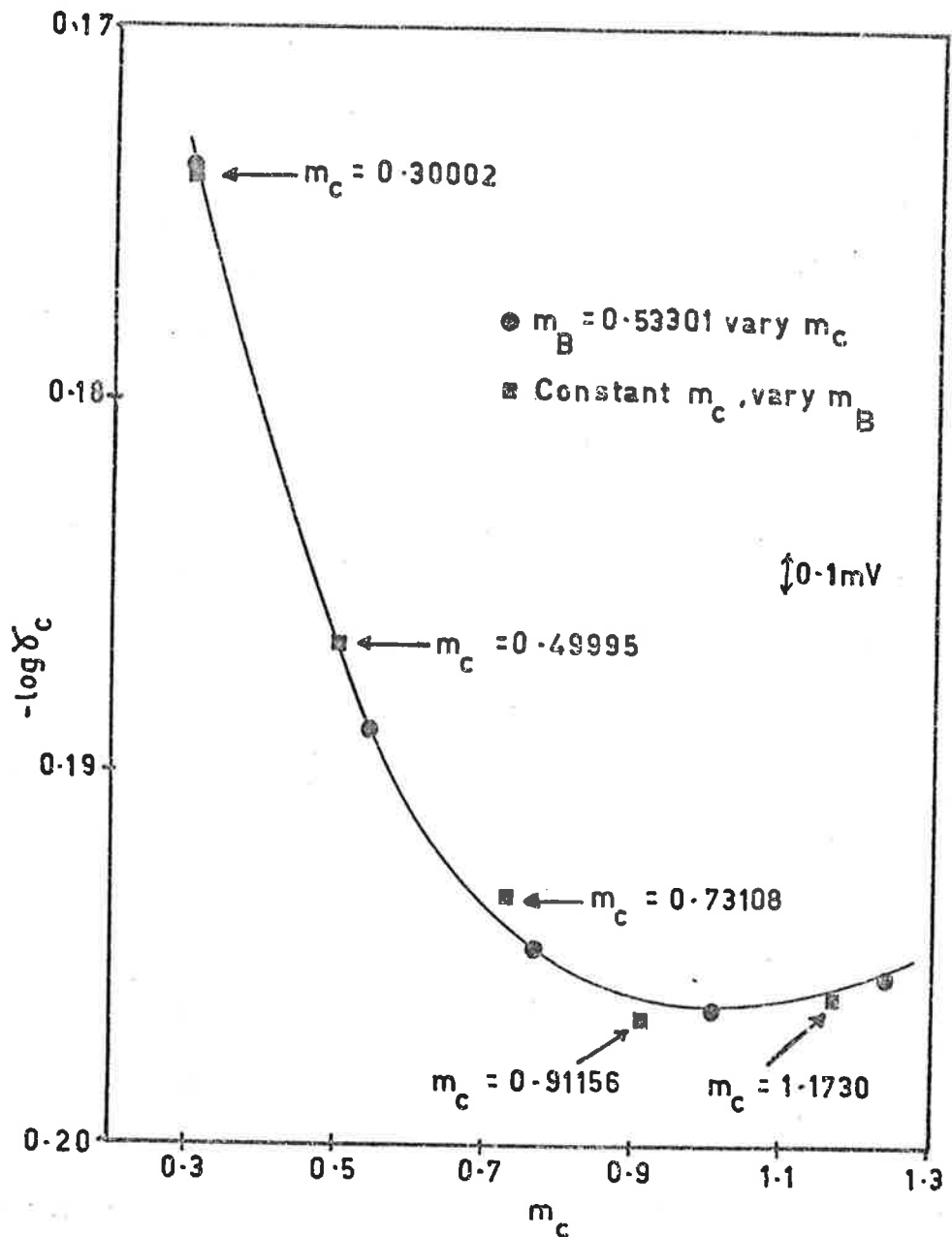


Fig. 2-5. Experiment at 50° : $m_B = 0.53301$ while m_c was varied.

■ are values read off from experiments in which m_c was constant while m_B was varied.

was added. Subsequent additions would only be that of solid sodium chloride to produce the curve A'B'C' as shown in Figure 2-4. In the dilute region ($< 0.1 \text{ m NaCl}$), direct addition of solid sodium chloride was not possible. The following procedure was therefore adopted: The reference emf was first measured at, say, $m_c = m_c'$ and $m_B = 0$. On addition of glycine, the resulting solution was $m_c = m_c'$ and $m_B = m_B'$. A concentrated solution of sodium chloride containing glycine at $m_B = m_B'$ was then made up and added to the reaction cell, using the weight burette technique.²² Such a procedure would maintain $m_B = m_B'$ whilst varying the value of m_c . In the case where m_c was kept at $m_c = m_c'$ for various values of m_B , additions to the reaction cell was made by using concentrated solutions of glycine in sodium chloride solution of molality m_c' .

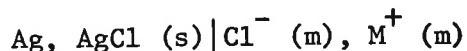
(e) Preliminary Investigation of Silver-Silver Chloride Electrode

(i) Introduction

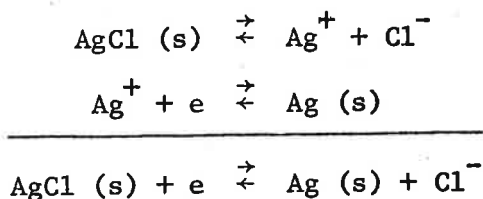
Silver-silver chloride electrodes constitute one of the most important types of reversible electrodes of the second kind. They owe their usefulness mainly to (i) their comparatively easy preparation, (ii) their inertness and consequent non-contamination of the experimental medium, and (iii) their stability and high degree of reproducibility.

The silver-silver chloride electrode consists of solid silver

chloride on silver and in contact with a solution of a soluble chloride.



The reversible electrode reaction involves the silver chloride going into solution to form silver and chloride ions and the silver ion receiving an electron to form solid silver:



As a reference electrode it has achieved importance. Its preparation, stability, reproducibility, and its standard potentials in aqueous and non-aqueous media have received extensive reviews by Janz and Taniguchi,²³ and Janz.²⁴

Recently Pal and Sengupta,²⁵ measured the intercomparison potentials (or potential bias) of silver-silver chloride electrodes in aqueous hydrochloric acid. These potentials were measured by placing a set of two or more electrodes in aqueous hydrochloric acid and then measuring the emf between any two. Usually, an aged electrode is retained for measuring the potential difference between itself and any of the electrodes being tested. The measurement of potential biases is discussed by Ives and Janz.²⁴ Pal and Sengupta found that the intercomparison potentials among electrodes prepared by the same

method had low values, being 0.05 mV for the thermal-electrolytic type and 0.2 mV for the electrolytic type. They had little success with the thermal type.

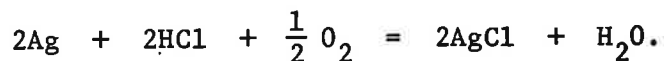
In conjunction with cation-responsive electrodes, Lanier¹ made use of thermal-type electrodes. He reported long equilibration times at low chloride concentration (below 0.1 m sodium chloride solution) and instability of the electrodes in organic-rich water mixtures. Steel²⁶ found that the thermal-electrolytic type was sluggish in response whilst working in conjunction with sodium-responsive glass electrodes. Roy and Sen,²⁷ also working with thermal-electrolytic type, have stated that the two essential requirements for obtaining good silver-silver chloride electrodes were proper washing of the silver oxide, and the use of hydrochloric acid of the highest purity.

(ii) The Preparation of Silver-Silver Chloride Electrodes

In this study the electrodes were prepared under normal lighting conditions in the laboratory. Dissolved impurities such as bromide and iodide are known to affect the electrode in the solution.²⁴ Thus such contaminations were avoided through the careful purification of the reagents used.

The solutions in which the emfs were measured were not purged of dissolved air. Smith and Taylor,^{28,29} working on electrolytic-type, thermal-type, and thermal-electrolytic type of electrodes have

found that these electrodes were unaffected by dissolved air in neutral solution. They were only affected in acidic solutions. Guntelberg³⁰ had attributed the latter disturbance to the reaction,



The intercomparison potentials were measured with a precision of ± 0.01 mV by using a micro-step potentiometer (see under the heading Apparatus) and a galvanometer. All measurements were made at room temperature with constant stirring of the solutions.

As a preliminary of this research, a number of silver-silver chloride electrodes, namely the electrolytic type, the silver-mirror type, the thermal type and the thermal-electrolytic type, were prepared and then tested in order to determine the most suitable type for this research. The following discussion will deal with the typical behaviour of some of the electrodes prepared.

Electrolytic-type electrodes:

Two electrodes labelled Q and S were prepared and the intercomparison potential was measured against an aged thermal-electrolytic type R. Q is shown in Figure 2-6(a), and S in Figure 2-6(b). The platinum was cleaned by anodising for 1 hour at 1 ma. in concentrated nitric acid. Each was then thoroughly washed in doubly distilled water and soaked overnight. Cyanide-free $\text{KAg}(\text{CN})_2$

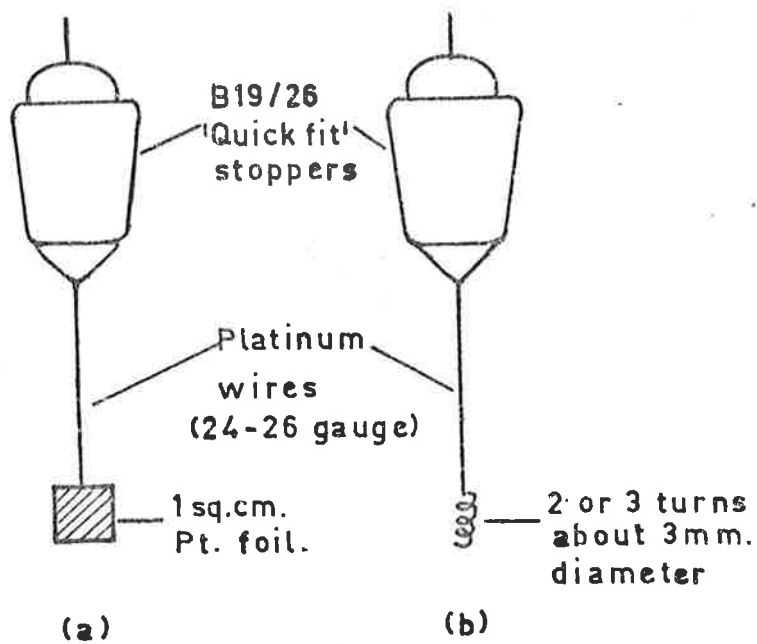


Fig. 2-6. Silver-silver chloride electrodes.

solution was used to silver-plate each electrode at 1 ma. current for 6 hours. They were then rinsed with doubly distilled water and soaked for 6 to 8 hours in 50% ammonia solution. This was followed by soaking them in doubly distilled water again for a day, and then chloridising in 0.1 N constant boiling hydrochloric acid. Assuming that the chloridising was 100% effective, about 15 to 20% of the silver was converted to silver chloride. The plum-coloured electrodes were then rinsed with doubly distilled water and stored in 0.01 m NaCl solution.

The aging process of the electrodes is shown in Table 2-1. Since electrode S was negative in polarity it was more stable than Q, and is also in a state of lower energy than Q. From Table 2-1 S was considered as having reached equilibrium, whilst Q would be discarded.

TABLE 2-1

Aging process of some electrolytic-type electrodes in 0.01 m NaCl.

Polarity of R is shown.

<u>Electrodes</u>	<u>1 day (mV)</u>	<u>2 days (mV)</u>	<u>3 days (mV)</u>	<u>4 days (mV)</u>	<u>5 days (mV)</u>
R (-ve) + Q	0.40	0.61	0.69	0.78	1.15
R (+ve) + S	0.16	0.17	0.12	0.00	0.10

Silver-Mirror Electrode:

The main features of the electrode are shown in Figure 2-6(a). Its preparation is fully described by Ives and Janz.²⁴ Two electrodes

labelled P and Q were prepared and tested. Silver was deposited on the foil by the Rochelle salt mirror process.³¹ A period of 18 hours was required to deposit about 0.003 gm. of silver on P and Q respectively. The electrodes were chloridised in dilute hydrochloric acid. About 15 to 20% of the silver was converted to silver chloride using a current of 1.2 ma. P and Q were rinsed several times in doubly distilled water before being stored in a 1 m NaCl solution together with H, an aged thermal-electrolytic type electrode. When the electrodes were 2 days old the intercomparison potentials were measured against H. Also their response time was tested by transferring then between a 1 m and a 5 m NaCl solution.

The results are shown in Table 2-2. C was another aged thermal-electrolytic type electrode stored in the 5 m NaCl solution. C and H had a negligible intercomparison potential. P and Q showed good response time. However, such electrodes were found to deteriorate rapidly especially in fresh sodium chloride solutions. Both P and Q possessed large and positive potentials when compared to the aged thermal-electrolytic type. Grunwald and Purlee^{32,33} have obtained good results using the silver-mirror electrodes in solutions of low dielectric constant.

Thermal Electrodes:

The main features are shown in Figure 2-6(b). The platinum spiral was covered with a paste consisting of 90% silver oxide and 10% silver chlorate

TABLE 2-2

Intercomparison potentials (mV) of the silver-mirror electrodes.

t (min.)	C (-ve) and P	C (-ve) and Q	H (-ve) and P	H (-ve) and Q	C (-ve) and P	C (-ve) and Q
	I		II		III	
10	0.97	0.87	0.95	0.77	0.72	0.56
15	1.00	0.89	0.94	0.73	0.73	0.57
20	1.05	0.91	0.91	0.72	0.74	0.59
30	1.08	0.90	0.90	0.70	0.76	0.61
	H (-ve) and P	H (-ve) and Q	C (-ve) and P	C (-ve) and Q	H (-ve) and P	H (-ve) and Q
	IV		V		VI	
10	0.87	0.66	0.83	0.69	0.93	0.76
15	0.84	0.65	0.83	0.69	0.94	0.75
20	0.84	0.65	0.84	0.69	0.94	0.75
30	0.86	0.69	0.84	0.71	0.94	0.75

Notes:

1. The Roman numerals indicate the sequence of transfer of the electrodes.
2. The initial intercomparison potential of the electrodes P and Q after soaking for two days with H in the 1 m sodium chloride solution were: H (-ve) and P = 0.90 mV; H (-ve) and Q = 0.75 mV.
3. Brackets indicate the polarity of the electrode.
4. t, time after transfer of the electrodes and recorded in minutes.
5. H is kept in 1 m NaCl solution and C in 5 m NaCl solution.

made up by weight. The paste was fired in the oven at 650° for about ten minutes. As a result of thermal reduction, a mixture of silver and silver chloride was left. The electrodes were snow-white in colour.

Table 2-3 shows the response time of a typical batch of electrodes which are about a week old. C and H were aged thermal-electrolytic type of negligible potential bias. The others were thermal-type. Electrodes D and E were stored with H in a 1 m NaCl solution whilst F, A and B were stored with C in a 5 m NaCl solution. It was normal practice in this study to test the response time of the freshly prepared silver-silver chloride electrodes in the concentration range in which they were to be used.

Pal and Sengupta²⁵ had reported a large potential bias (~ 10 mV) between the thermal and the thermal-electrolytic type. However, Table 2-3 shows that the potential bias was less than 0.1 mV for this particular batch of thermal electrodes. Electrodes F, A and B when transferred to the 1 m NaCl solution acquired a slightly larger potential bias which appeared to decrease with time. This was probably due to the porosity of the electrodes. D and E also displayed the same effects when transferred from the 5 m to the 1 m solution. It seemed that the electrodes responded more effectively when transferred from a lower to a higher concentration. In practice, electrodes D, E, F, A and B would be accepted for use.

TABLE 2-3

Intercomparison potentials (mV) of some thermal electrodes.

		H (-ve) and D	H (-ve) and E	C (+ve) and F	C (+ve) and A	C (+ve) and B
Potential Bias		0.00	0.08	0.01	0.07	0.03
t (min.)		C (+ve) and D	C (+ve) and E	H (-ve) and F	H (-ve) and A	H (-ve) and B
10	I	0.04	0.04	0.18	0.23	0.20
15		0.04	0.02	0.17	0.20	0.19
20		0.04	0.05	0.16	0.17	0.18
30		0.04	0.06	0.16	0.17	0.19
		H (-ve) and D	H (-ve) and E	C (+ve) and F	C (+ve) and A	C (+ve) and B
10	II	0.13	0.04	0.00	0.08	0.05
15		0.10	0.04	0.01	0.09	0.05
20		0.11	0.03	0.00	0.09	0.05
30		0.13	0.08	0.01	0.09	0.05
		C (+ve) and D	C (+ve) and E	H (-ve) and F	H (-ve) and A	H (-ve) and B
10	III	0.03	0.02	0.21	0.22	0.24
15		0.02	0.02	0.19	0.23	0.20
20		0.03	0.02	0.19	0.20	0.19
30		0.02	0.03	0.18	0.20	0.17
		H (-ve) and D	H (-ve) and E	C (+ve) and F	C (+ve) and A	C (+ve) and B
10	IV	0.27	0.16	0.01	0.06	0.06
15		0.24	0.15	0.00	0.06	0.04

(contd.)

TABLE 2-3 (contd.)

	H (-ve) and D	H (-ve) and E	C (+ve) and F	C (+ve) and A	C (+ve) and B
20	0.23	0.15	0.01	0.06	0.05
30	0.22	0.14	0.00	0.04	0.03

Notes:

1. The Roman numerals indicate the sequence of transfer of the electrodes.
2. The intercomparison potentials were measured while the solutions were stirred.
3. C kept in 5 m and H kept in 1 m sodium chloride solutions. Electrodes D, E, F, A and B were transferred between the two solutions.
4. t, time after transfer of the electrodes and recorded in minutes.

Thermal-electrolytic electrodes:

The main features are shown in Figure 2-6(b). The platinum spiral was thoroughly cleaned and then covered with a thick paste of silver oxide. After being superficially dried, the electrode was heated in an oven at 450° for about half an hour. The heating process was repeated a few times, each time with the addition of slightly thinner paste of silver oxide. When the spiral had acquired about 0.2 gm. of silver, the electrode was left in the oven at 450° for several hours. This was to ensure the complete thermal reduction of all the silver oxide.

The electrodes were then chloridised in 1 m HCl solution using a 10 ma. current. About 15 to 20% of the silver was converted to silver chloride.

A typical set of thermal-electrolytic type electrodes is shown in Tables 2-4 and 2-5. The electrodes were tested prior to being used. Electrodes A, B, D and E were freshly prepared. A, B and D were kept with an aged thermal-electrolytic type electrode H in 0.1 m NaCl solution. E was kept with another similar but aged electrode R in 0.01 m NaCl solution. Electrodes H and R possessed negligible potential bias.

Table 2-4 shows that the electrodes had very rapidly achieved equilibrium.

Table 2-5 shows the results of transferring the electrodes from one solution to another. It appeared that electrode E, although displaying a good potential bias value, was poor in response time. Electrodes

TABLE 2-4

Aging of some thermal-electrolytic type electrodes. Potential bias (mV) values measured against H (in 0.1 m NaCl) and R (in 0.01 m NaCl).

Electrodes	Age of Electrodes (days)				
	1	2	3	4	5
H (+ve) + A	0.07	0.08	0.11	0.07	0.11
H (+ve) + B	0.07	0.08	0.10	0.12	0.11
H (+ve) + D	0.09	0.10	0.11	0.12	0.12
R (+ve) + E	0.00	0.00	0.05	0.08	0.00

Note:

1. The polarity of the H and R electrodes are shown.

TABLE 2-5

Response time of some thermal-electrolytic electrodes. Electrodes were transferred between cells containing electrodes H (in 0.1 m NaCl) and R (in 0.01 m NaCl).

		H (+ve) and A	H (+ve) and B	H (+ve) and D	R (+ve) and E
Potential Bias		0.11	0.11	0.12	0.00
t (min.)		R (+ve) and A	R (+ve) and B	R (+ve) and D	H (+ve) and E
10	I	1.69	1.72	2.42	-3.36
20		0.40	0.49	0.53	-2.35
30		0.21	0.28	0.26	-1.30
40		0.14	0.16	0.17	-0.84
50		0.11	0.13	0.13	-0.46
120		0.06	0.07	0.06	0.00
	II	H (+ve) and A	H (+ve) and B	H (+ve) and D	R (+ve) and E
10		0.49	0.43	0.30	10.76
30		0.07	0.05	0.10	2.06
40		0.10	0.10	0.12	1.00
50		0.12	0.10	0.12	0.50
120		0.12	0.12	0.13	0.12

(contd.)

TABLE 2-5 (contd.)

	III	R (+ve) and A	R (+ve) and B	R (+ve) and D	H (+ve) and E
10		1.70	1.32	1.26	-5.31
20		0.42	0.37	0.39	-2.49
30		0.26	0.23	0.26	-1.32
40		0.20	0.17	0.20	-0.77
50		0.14	0.14	0.17	-0.49

Notes:

1. The Roman numerals indicate the sequence of transfer of the electrodes.
2. H kept in 0.1 m NaCl and R in 0.01 m NaCl solutions. Electrodes A, B, D and E were transferred between the two solutions.
3. t, time after transfer of the electrodes in minutes.
4. The polarity of electrodes H and R are shown in brackets.

A, B and D appeared to respond better in going from a lower to a higher concentration.

In practice, A, B and D would be accepted, whilst E would be discarded.

In this study batches of six to eight electrodes were prepared at a time. They were stored in sodium chloride solution in the concentration range in which they were to be used. All electrodes were tested for potential bias and response time before being accepted for use in an experiment.

(iii) Sensitivity to Light

Two silver-silver chloride electrodes B (a thermal type), and C (a thermal-electrolytic type) were tested for sensitivity towards light. Both were aged electrodes.

B and C were placed in an "H-shaped" cell filled with 1 m NaCl solution and equilibrated at 25° in the water-bath. Apart from an adjustable window, the cell was completely enclosed in the water-bath. A normal reading lamp (Mazda, tungsten filament, 48W, 6V bulb) was placed at the window about 15 cm. from B and C and directed at them. The potential bias was measured: $B + C (+ve) = 0.07 \text{ mV}$. It was found that the emf remained unchanged under the following conditions:

- (a) Both B and C measured in the dark.
- (b) Both B and C measured in the light.

- (c) B was exposed while C was completely shielded from the light by wrapping an aluminium foil around the arm of the "H-shaped" cell.
- (d) Repeating (c) with the positions reversed.

In each case, the observation lasted about 1 hour. It appeared that the electrodes were insensitive to artificial light of the type mentioned.

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Chapter 3

Preliminary Investigation of Cation-Responsive Glass Electrodes

- (a) Introduction
- (b) The Origin of the Glass Electrode Potential
- (c) Selectivity Constants of the Electrodes
 - (i) Experimental
 - (ii) Results and Discussion
- (d) Response of the Electrodes to pH Variations
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- (f) References

Preliminary Investigation of Cation-Responsive Glass Electrodes

(a) Introduction

In Chapter 1 the composition, applications and the limitations of the sodium-responsive glass electrode were discussed. This chapter reports the characterisation and the conditions necessary for them to be useful in the determination of activity coefficients.

Unlike the silver-silver chloride electrodes which were alphabetically labelled, the glass electrodes were numerically labelled. Only glass electrodes from two manufacturers were used throughout this study, namely the Beckman Instruments Inc. (U.S.A.), and the Electronics Instruments Ltd. (U.K.). They are listed in Table 3-1.

The GEA33, GEA33/C and the Beckman 39278 electrodes are sodium-responsive and are designed for use in routine measurements of sodium ion concentrations. On the other hand, the Beckman 39137 Cationic Electrode is meant generally for monovalent cations.

(b) The Origin of the Glass Electrode Potential

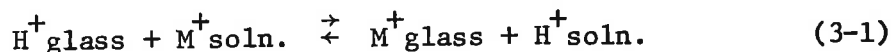
Nicolskii¹ was the first to develop the theory that the glass electrode potential was determined by the exchange of cations between the glass and the solution. He believed that a swollen layer was formed on the surface of certain glasses in contact with water or an aqueous solution. Only this layer was considered to be involved in the

TABLE 3-1Glass electrodes used in this research.

<u>Label on Electrode</u>	<u>Type</u>	<u>Manufacturer</u>
1	GEA33	E.I.L.
2	GEA33	"
3	39278	Beckman
4	39278	"
5	39137	"
6	39278	"
7	39137	"
8	GEA33	E.I.L.
9	GEA33	"
10	GEA33/C	"

ion-exchange processes. Recently, experiments by Boksay et al.² have confirmed this view.

According to Nicolskii, an equilibrium of the ion-exchange process existed between the surface layer of the glass and the solution. In the case when H^+ ions of the glass were exchanged for M^+ ions of the solution, the process could be described by the equation



The electrical-potential difference, E , between the surface layer of the glass and the solution was determined by the chemical work needed for the transfer of H^+ and M^+ ions from glass to solution. He then showed that this led to the expressions

$$E = E_1^{\circ} + \frac{RT}{F} \ln \frac{a_H}{a'_H} \quad (3-2)$$

and

$$E = E_2^{\circ} + \frac{RT}{F} \ln \frac{a_M}{a'_M} \quad (3-3)$$

where E_1° and E_2° were standard potential values. a_H and a_M were, respectively, the activities of H^+ and M^+ ions in the solution. The apostrophes indicate the activities in the glass. He then assumed that (1) the activities of H^+ and M^+ ions in the glass were equal to their total concentrations; (2) the total concentration of H^+ and M^+ ions in the glass was always constant and equal to the concentration of the fixed counterions. From these assumptions it was shown that the

glass electrode potential, E , was given by the equation

$$E = \text{Constant} + \frac{RT}{F} \ln (a_H + K_{HM} a_M) \quad (3-4)$$

where $K_{HM} = \frac{a_H a'_M}{a_M a'_H}$, the equilibrium constant for the cation exchange process described by Equation 3-1.

In 1957 Eisenman, Rudin and Casby³ gave a precise description of the glass electrode potential in mixtures of any two univalent cations. The empirical equation was

$$E = \text{Constant} + \frac{nRT}{F} \ln (a_i^{1/n} + K_{ij}^{1/n} a_j^{1/n}) \quad (3-5)$$

where K_{ij} and n were empirical constants for a given glass composition and cation pair i^+ and j^+ of activities a_i and a_j respectively, in the solution. For sodium glasses sensitive to Na^+ ions, $n = 1$ and Equation 3-5 becomes identical to Equation 3-4. However, for $\text{H}^+ - \text{K}^+$ mixtures the value of n is normally greater than 1 and approaching values as high as 3.5 for many glass compositions. K_{ij} is also known as the selectivity constant of the glass and is specific for a given glass and a pair of ions present in the solution.

The analyses of Eisenman et al.^{4,5} lead to the conclusion that K_{ij} can be analysed into contributions from the mobilities of the ions in the glass and from the cation-exchange equilibrium constant, K^0 , of the membrane and solution interfaces. They found that

$$K_{ij} = \frac{p_j}{p_i} = K^0 \left(\frac{\mu_j}{\mu_i} \right)^n \quad (3-6)$$

where p_i and p_j were the permeabilities of the cations i and j ; μ_i and μ_j were the mobilities of i and j in the glass and K^0 was the true equilibrium constant. From Equation 3-1

$$K^0 = \frac{a_{H^+} a_{M^+}'}{a_{H^+}' a_{M^+}} \quad (3-7)$$

where a indicates the activities of the ions and the apostrophe denotes those at the surface layer of the glass phase. Also in Equation 3-6 $n = 1$ for $Na^+ - H^+$ ionic mixtures when the glass is sodium-responsive. Thus the total glass electrode potential is essentially made up of a phase-boundary contribution and a diffusion potential contribution.

One would have expected the diffusion potential to vary with time as the ion exchange proceeded and as the ion concentration profiles within the glass varied. However, it has been shown⁶ that once chemical equilibrium is established between the solution and the surface layer of the glass, the diffusion potential is independent of time. Recently, Boksay et al.² have reported that although the diffusion of H^+ and Na^+ ions does occur, it does not give rise to a diffusion potential.

In this research project mixtures of cations in the solutions were limited to $Na^+ - H^+ - Ag^+$ and $K^+ - H^+ - Ag^+$. All reaction solutions were saturated with Ag^+ ions by the addition of small amounts of solid silver chloride. The pH of all the solutions was always between 6 and 7.

The Cation-Responsive Glass Electrode

They are shown in Figure 3-1. The Beckman 39278 and 39137 electrodes were identical in shape and size. They differed only in the composition of the glass bulb. Each had a silver-silver chloride internal element dipping into a buffered 0.1 m NaCl solution.⁷ They are described in the Beckman literature.⁸ The GEA33 electrodes were constructed slightly differently from the Beckman electrodes. The silver-silver chloride internal element was hidden from sight by a grounded metallic shield.

(c) Selectivity Constants of the Electrodes

The selectivity constant, K_{HNa} , for the $\text{H}^+ - \text{Na}^+$ pair was determined for some of the electrodes used in this research. The experiments were carried out at 25°. The value of K_{HNa} shows how effective an electrode 'sees' the Na^+ ions relative to the H^+ ions. For example, when $K_{\text{HNa}} = 10$, the Na^+ ions are ten times as effective as the H^+ ions on a mole-for-mole basis in determining the electrode potential.

Since the glass electrodes are sodium-responsive and only $\text{H}^+ - \text{Na}^+$ ionic mixtures are considered, Equation 3-5 is taken as

$$E = \text{Constant} + \frac{RT}{F} \ln (a_{\text{H}} + K_{\text{HNa}} a_{\text{Na}}) \quad (3-8)$$

where a_{H} and a_{Na} are the activities of the H^+ and Na^+ ions respectively. Now one considers a cell of the type,

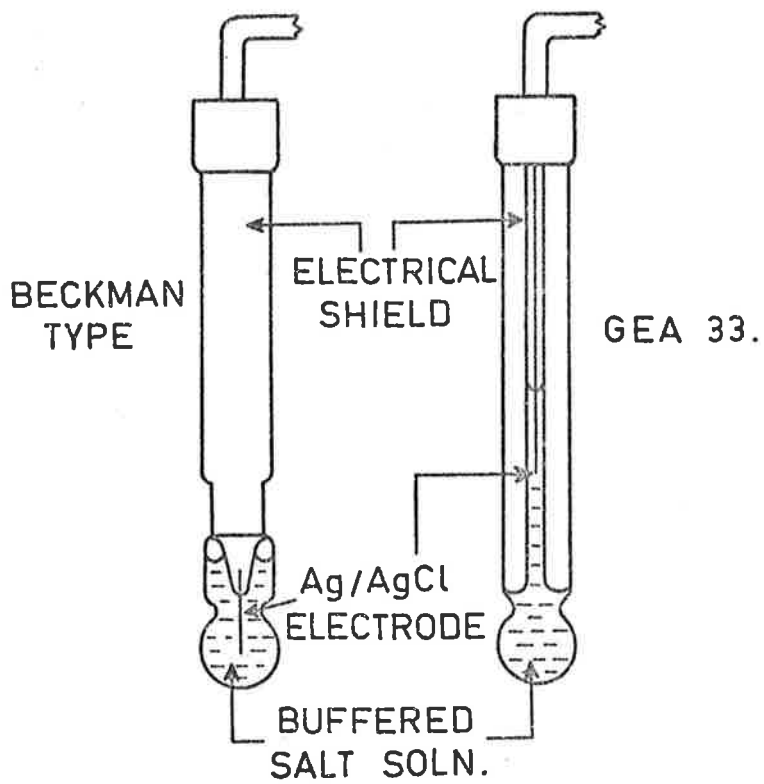
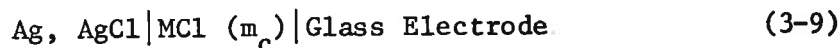


Fig.3-1. Cation-sensitive glass electrodes.



The emf of the cell in 0.1 m NaCl solution in the limit as H^+ ions $\rightarrow 0$ is given by

$$E_1 = \text{Constant} + \frac{RT}{F} \ln K_{\text{HNa}} a_{\text{Na}} - E_{\text{AgCl}}^{\circ} + \frac{RT}{F} \ln a'_{\text{Cl}} \quad (3-10)$$

where E_{AgCl}° is the standard potential of the silver-silver chloride electrode and a'_{Cl} is the ionic activity of the chloride ions in the sodium chloride solution.

The emf of the cell in 0.1 m HCl solution is given by,

$$E_2 = \text{Constant} + \frac{RT}{F} \ln a_{\text{H}} - E_{\text{AgCl}}^{\circ} + \frac{RT}{F} \ln a''_{\text{Cl}} \quad (3-11)$$

where a''_{Cl} is the ionic activity of the chloride ions in the hydrochloric acid solution.

Subtracting Equation 3-11 from Equation 3-10 one obtains,

$$E_1 - E_2 = \frac{RT}{F} \ln \frac{K_{\text{HNa}} \cdot a_{\text{Na}} \cdot a'_{\text{Cl}}}{a_{\text{H}} \cdot a''_{\text{Cl}}} \quad (3-12)$$

which according to Eisenman⁹ can be approximated to

$$E_1 - E_2 = \frac{RT}{F} \ln K_{\text{HNa}} \quad (3-13)$$

by taking the activity coefficient ratios of the ions as unity.

Equation 3-13 is then the basic equation for the determination of selectivity constant in this work by simply measuring the cell emfs E_1 and E_2 .

(i) Experimental

Electrodes 1, 3, 4 and 5 were chosen for the experiment to determine their selectivity constants. Two cells, one containing exactly 0.1 m NaCl solution (adjusted to pH = 9 using sodium hydroxide solution) and the other, 0.1 m HCl solution, were set up in a water bath kept at 25°. Each cell was magnetically stirred and contained aged silver-silver chloride electrodes of the thermal-electrolytic type. The glass electrodes were transferred from one cell to the other and each time the electrodes were rinsed with the solution in which it was to be immersed.

(ii) Results and Discussion

The final emf values were recorded in Table 3-2 together with the K_{HNa} values. Table 3-2 also shows the steps taken in measuring the emfs. For example, 1 and 3 were first measured in 0.1 m HCl solution and then transferred to the 0.1 m NaCl solution. A record was made of the average emf arrived at in each solution and later used in the calculation of K_{HNa} .

All the electrodes responded to within a few millivolts of the equilibrium value in less than 1 hour. However, each took several hours to reach the equilibrium value. A emf change of less than 0.02 mV in 15 minutes was considered as having reached the equilibrium state.

TABLE 3-2

Selectivity constants of some glass electrodes.

Electrode	emf of the cells (mV)		K_{HNa}	K_{HNa} (literature)
	0.1 m HCl	0.1 m NaCl pH = 9.0		
1	31.68	2.69		
3	311.91	139.08		
1	35.38	2.16		
3	310.55	136.19		
Ave. emf 1	33.52	2.43	0.546	
Ave. emf 3	311.23	137.64	0.034	0.06 ^a
4	235.00	83.98		
5	174.97	101.64		
4	235.95	108.01*		
5	175.66	102.64		
Ave. emf 4	235.48			
Ave. emf 5	175.32	102.14	0.241	0.65 ^b

Notes:

* Non-equilibrium value after 4 days.

a NAS 11-18 glass¹⁰b NAS 27-4 glass¹⁰

Electrode 1 (GEA 33) appeared to equilibrate much faster than the others. Such an experiment appeared to impose a considerable strain on the glass electrodes. Electrodes 3 and 4 (both Beckman 39137), showed the symptom of 'flaking', i.e. flakes of glass appeared to peel off at the bulb towards the end of the experiment. Electrode 4 became erratic and drifted with time without reaching the equilibrium state even after 4 days in the sodium chloride solution. Presumably, as a result of this experiment Electrode 4 never completely recovered and soon had to be discarded.

The values of K_{HNa} were compared with Eisenman's NAS 11-18 sodium-responsive glass.¹⁰ All the K_{HNa} values indicate that the electrodes responded more towards H^+ ions than Na^+ ions. Among the electrodes tested, Electrode 1 was apparently the best sodium-responsive electrode.

It is of interest to note that Savage and Isard^{11,12} have shown that glass of compositions $\text{Na}_2\text{O} \cdot 0.4\text{Al}_2\text{O}_3 \cdot 6.3\text{SiO}_2$, $\text{Na}_2\text{O} \cdot 0.75\text{Al}_2\text{O}_3 \cdot 6.5\text{SiO}_2$, and $\text{Li}_2\text{O} \cdot 0.5\text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$ have K_{HNa} values slightly greater than 1. K_{HNa} values for commercial electrodes do not appear to be readily available for a useful comparison to be made with those from this work.

(d) Response of the Electrodes to pH Variations

This experiment followed part (c) and Electrodes 1, 3 and 5 were chosen for the experiment.

The medium was 0.5 m NaCl solution in a reaction cell (see Figure 2-3(b), Chapter 2) kept at 25° in a water-bath.

Specially prepared nitric acid, hydrochloric acid and sodium hydroxide solutions were made up in order that the pH could be changed with a minimum number of drops of the acid or base. The pH was measured using a conventional pH meter.

The results are shown in Table 3-3.

Of the three electrodes tested, 1 appeared to be the least affected by pH variations, followed by 5 and then 3. Such a behaviour was consistent with the K_{HNa} values, where $K_{\text{HNa}} = 0.546$ for 1, 0.241 for 5 and 0.034 for 3.

Mattock¹³ has shown that above 0.01 M Na^+ ion concentration and for pH > 5, the effects of pH changes would become unimportant for BH68, BH104, and NAS 11-18 glasses. His measurements were carried out using a conventional pH meter and the background medium of his solutions was ethanolamine hydrochloride. Since Electrode 1 (GEA 33) is known to be made from BH104 glass,¹⁴ the findings here are in accord with Mattock's.

(e) Response of Electrodes to Light Variations

Electrodes 6, 7, 8 and 10 (see Table 3-1 for the type) were tested using a Mazda incandescent tungsten-filament lamp (60 watt, 240 V). The electrodes were placed in a reaction cell containing 0.1 m NaCl solution and magnetically stirred in a water-bath at 25°.

TABLE 3-3

Response of electrodes to pH changes in 0.5 m NaCl solution.

(i) pH adjusted using hydrochloric acid.

emf of Electrodes (mV)		pH
1	3	
74.18	196.50	9.00
74.09	196.61	7.12
74.03	197.19	6.27
74.06	219.71	4.22
1	5	
73.64	173.75	8.72
73.44	173.68	6.22
73.56	173.54	4.52

(ii) pH adjusted using nitric acid.

emf of Electrodes (mV)		pH
1	3	
72.76	189.48	7.10
72.60	188.25	8.15*
72.53	188.63	7.25
72.60	205.80	5.05

(contd.)

TABLE 3-3 (contd.)

emf of Electrodes (mV)		pH
1	5	
72.23	169.30	9.63
72.27	169.79	7.06
72.32	170.28	6.30
72.70	170.99	5.40

Note:

* NaOH was used to increase the pH.

The silver-silver chloride electrode was not shielded because it had been shown earlier that they were not affected by light emitted from this type of lamp (see Chapter 2).

A glass window in the bath allowed the electrodes to be exposed to the lamp which was held about 20 cm. away. All the electrodes were affected by the light. In Figure 3-2(a) and (b), A represents the time when the light was switched on, and B when the light was switched off. The emf at zero time was taken as the reference value. The emf was showing a steady value before the light was switched on. The subsequent increase in emf was more pronounced for the Beckman than for the GEA electrodes. In fact, for Electrode 7 the emf was still increasing after the light was switched off. Electrode 8 (GEA 33) was the least affected.

Very recently, Milward¹⁵ also observed some effects of light on glass pH electrodes but no photo effects on the silver-silver chloride electrodes. He reported a decrease in the pH when the glass electrodes were illuminated with an Osram mercury vapour lamp, a Desaga Heidelberg T.L. illuminator, a Mazda infrared lamp, and sunlight. He attributed the effect to a possible formation of F-centres in the glass.

As a result of this finding all emf measurements were made with the reaction cell in darkness throughout this study with cation-responsive glass electrodes.

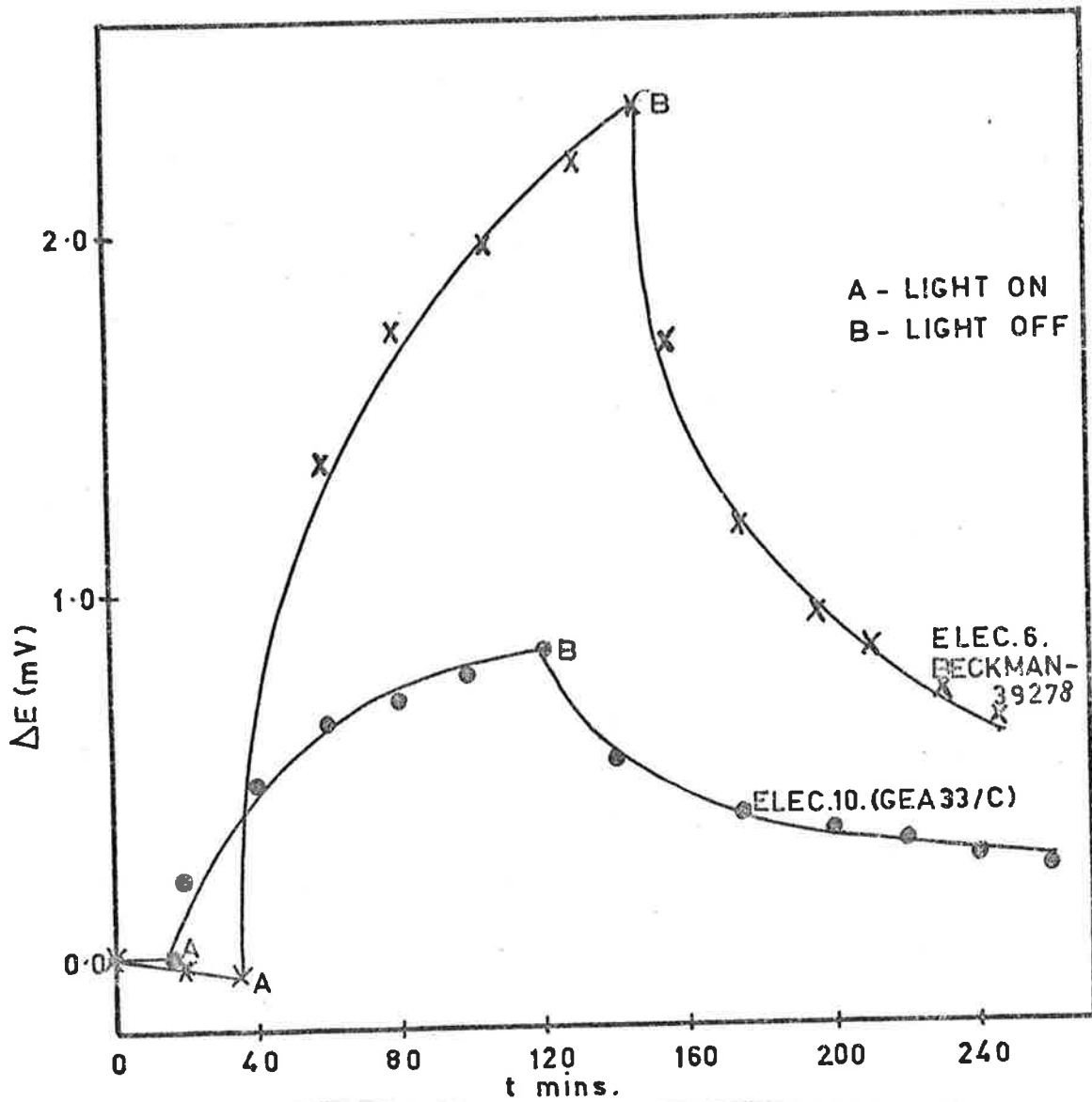


Fig. 3-2(a). Photo-electric effects on cation-responsive glass electrodes.

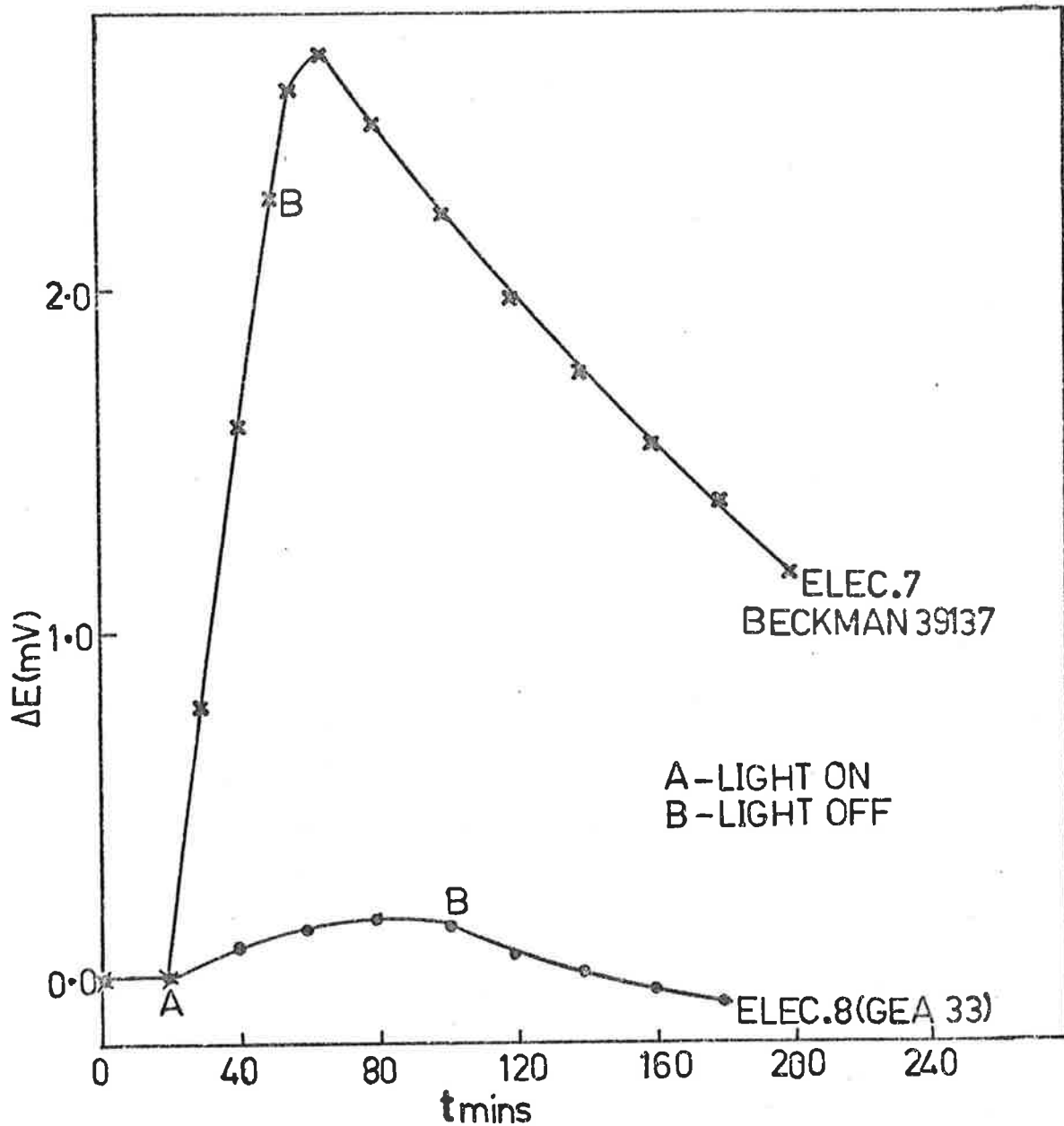


Fig. 3-2(b). Photo-electric effects on cation-responsive glass electrodes.

(f) References

1. Nicol'skii, B.P., Acta Phys.-chim. URSS, 7, 597 (1937).
2. Boksay, Z. et al., Chem. Abs., 70 (22), 99963W (1969).
3. Eisenman, G., Rudin, D.O., and Casby, J.U., Science, 126, 831 (1957).
4. Eisenman, G. et al., "The Glass Electrode", Interscience Publishers, John Wiley and Sons (New York) 1962, p. 307.
5. Karreman, G., and Eisenman, G., Bull. Math. Biophys., 24, 413 (1962).
6. Conti, F., and Eisenman, G., J. Biophys., 5, 247 (1965).
7. Lanier, R.D., J. Phys. Chem., 69, 2697 (1965).
8. Beckman Instructions 1154-B and 1155-B, Beckman Instruments Inc., Scientific and Process Instruments Division, Fullerton, Calif. (March 1963 13TW184 81154) and (August 1964 14TW467 81155).
9. Reference 4, p. 232.
10. Eisenman, G., Ed., "Glass Electrodes for Hydrogen and Other Cations", Marcel Dekker (New York) 1967, p. 426.
11. Savage, J.A., and Isard, J.O., Phys. Chem. Glasses, 3, 147 (1962).
12. idem., ibid., 7, 60 (1966).
13. Mattock, G., Chimia, 21, 209 (1967).
14. Covington, A.K., and Lilley, T.H., Phys. Chem. Glasses, 8, 88 (1967).
15. Milward, A.F., Analyst, 94, 154 (1969).

Chapter 4The Activity Coefficient of Hydrogen Chloride in Water and in
Potassium Chloride-Water Mixtures at 25°.

- (a) Introduction
- (b) Theory
- (c) Experimental
- (d) Results and Discussion
 - (i) HCl-H₂O System
 - (ii) HCl-KCl-H₂O System
- (e) References

The Activity Coefficient of Hydrogen Chloride in Water and in
Potassium Chloride-Water Mixtures at 25°.

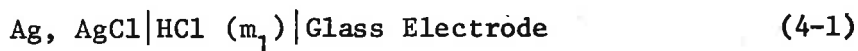
(a) Introduction

The purpose of this experiment was to acquaint the writer with the use of glass electrodes for the measurement of activity coefficients and to show the feasibility of using such electrodes in aqueous hydrochloric acid and in hydrochloric acid in potassium chloride-water mixtures.

(b) Theory

The basic theory in emf measurements using cation-responsive glass electrodes which was discussed in Chapter 2, is equally applicable here.

The cell may be represented as

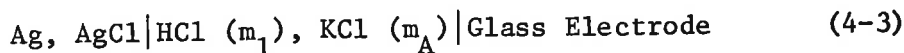


Thus, if the cell measures the emf of two different solutions of hydrochloric acid of molalities m_1 and m_2 and of mean molal activity coefficients γ_1 and γ_2 respectively, one obtains

$$\log \gamma_2 = (E_2 - E_1) + \frac{4.606 RT}{F} \log \frac{m_1 \gamma_1}{m_2} \quad (4-2)$$

E_1 and E_2 are the measured emfs. Using E_1 , m_1 and γ_1 as the reference, γ_2 can therefore be determined experimentally.

For a mixture of hydrochloric acid and potassium chloride, the cell may be represented by



where m_A is the molality of the potassium chloride. The emf of the cell is given by¹

$$E_1 = E_{\text{Total}} + \frac{RT}{F} \ln \gamma_1^2 m_1 (m_A + m_1) \quad (4-4)$$

E_{Total} is similar to C in Equation 2-6 in Chapter 2, and γ_1 is the mean molal activity coefficient of hydrochloric acid in the HCl-KCl-H₂O mixture.

On changing the concentration of potassium chloride from m_A to m_D and keeping m_1 constant,

$$E_2 = E_{\text{Total}} + \frac{RT}{F} \ln \gamma_2^2 m_1 (m_D + m_1) \quad (4-5)$$

γ_2 is now the new mean molal activity coefficient of hydrochloric acid.

E_{Total} is constant since it is assumed that the asymmetry potential of the glass electrode has not changed. Subtracting Equation 4-5 from Equation 4-4,

$$E_1 - E_2 = \frac{RT}{F} \ln \frac{\gamma_1^2 (m_A + m_1)}{\gamma_2^2 (m_D + m_1)} \quad (4-6)$$

In this study the initial emf was measured in aqueous hydrochloric acid without potassium chloride. Subsequent emfs were then measured by

the addition of potassium chloride while keeping the concentration of the acid unchanged. Hence, by Equation 4-6 one obtains

$$E_1 - E_2 = \frac{RT}{F} \ln \frac{\gamma_1^2 m_1}{\gamma_2^2 (m_1 + m_D)} \quad (4-7)$$

γ_2 and γ_1 are the mean molal activity coefficients of hydrochloric acid with and without potassium chloride respectively. E_2 and E_1 are the measured emfs with and without potassium chloride respectively. Thus, making γ_1 , E_1 and m_1 as the reference values, γ_2 can be determined at various values of m_D . Equation 4-7 is, therefore, the basic equation in this study of the activity coefficient of hydrochloric acid in potassium chloride-water mixtures.

(c) Experimental

For the system HCl-H₂O, a reaction cell containing a known concentration of hydrochloric acid, two silver-silver chloride electrodes and a Titron hydrogen-responsive glass electrode,² were set up in a water-bath at 25°. The silver-silver chloride electrodes were of the thermal-electrolytic type of negligible potential bias. The solution was magnetically stirred. The concentration of the acid in the reaction cell was increased by the addition of a more concentrated solution of hydrochloric acid by means of a weight burette.

The experimental set-up for the system HCl-KCl-H₂O was similar to that in the HCl-H₂O system. Two silver-silver chloride electrodes

were used in conjunction with the glass electrode. The emf of the reaction cell containing the hydrochloric acid solution was first recorded and then used as the reference emf. A solution of potassium chloride was then made up using hydrochloric acid of the same molality as that in the reaction cell. This solution was added to the reaction cell by means of the weight burette. In this way, the concentration of the acid was kept constant whilst that of the potassium chloride was increased.

In both the binary and the ternary system, the emf measured between the glass electrode and any of the two silver-silver chloride electrodes never differed by more than 0.05 mV. The average value was taken.

(d) Results and Discussion

Table 4-1 shows the results for the HCl-H₂O system and Table 4-2, those of HCl-KCl-H₂O system.

(i) HCl-H₂O System

Covington and Prue,³ and Annino,⁴ have also reported the use of glass electrodes for the measurement of the mean molal activity coefficient of hydrochloric acid. Covington and Prue employed special low resistance glass (0.3-0.6 megohm) and measured the potentials directly using a conventional potentiometer without an amplifier.

Their values over the range 0.005 to 0.1 m were in good agreement with those of Hills and Ives⁵ whose work was based on the hydrogen-calomel cell. However, it appeared that the electrodes of Covington and Prue were not at equilibrium when the emf was measured. They had to employ an extrapolation technique in order to determine the correct emf. In this work, no extrapolations were necessary since the electrodes were at equilibrium when the emfs were recorded. Equilibrium was assumed when an emf change of less than 0.02 mV in 15 minutes was obtained.

Annino⁴ used "General Purpose" glass electrodes (Beckman No. 41293) and silver-silver chloride electrodes (Beckman No. 1281) to obtain activity coefficients which did not deviate by more than 0.5% from those reported by Covington and Prue.³ He covered the concentration range of 0.01 to 0.1 m.

In this work the concentration range studied was from 0.001 to about 1 m. The technique differed slightly from those of Covington and Prue, and of Annino. Their work involved the setting up of a reference solution (0.1 m HCl) in a reaction cell whose emf was measured each time a new solution was measured. This meant that the glass electrodes were rinsed and transferred from cell to cell. In this work, the initial solution was used as the reference and the electrodes were left in the reaction cell until the end of the experiment.

As shown in Table 4-1, the values obtained from this work were

TABLE 4-1

Mean molal activity coefficients of aqueous hydrochloric acid at 25°
 using a hydrogen-ion sensitive glass electrode.²

m_{HCl}	-E (Volts)	$-\log \gamma$	$-\log \gamma$ (Liter)
0.0018764	0.15982	0.0200	0.0200*
0.0064415	0.22125	0.0365	0.0360
0.0098055	0.24207	0.0428	0.0430
0.028487	0.29425	0.0651	0.0665
0.060339	0.33055	0.0842	0.0855
0.089488	0.34949	0.0955	0.0958
0.22124	0.38845	0.1170	0.1170*
0.31778	0.40654	0.1214	0.1216
0.38800	0.41666	0.1226	0.1223
0.52693	0.43282	0.1190	0.1200
0.64753	0.44400	0.1139	0.1155
0.74124	0.45150	0.1092	0.1103
0.82644	0.45773	0.1037	0.1045
0.93503	0.46503	0.0957	0.0965
1.0636	0.47281	0.0858	0.0868
0.13663	0.36622	0.1065	0.1065*
0.29548	0.40415	0.1209	0.1210
0.51074	0.43234	0.1205	0.1205
0.60393	0.44135	0.1170	0.1177
0.87958	0.46254	0.1010	0.1008

Notes:

1. * Reference points.
2. $\gamma \equiv$ mean molal activity coefficient.
3. $-\log \gamma$ (Liter) are interpolated values from a large-scale plot of $-\log \gamma$ against the square root of molality of aqueous hydrochloric acid taken from Robinson and Stokes⁶ and Harned and Owen.⁷

in good agreement with the values recorded by Robinson and Stokes⁶ and Harned and Owen.⁷

(ii) HCl-KCl-H₂O System

Table 4-2 shows the mean molal activity coefficients of 0.010186 m HCl in various concentrations of potassium chloride. Two experiments were performed and the results were plotted as $\log \gamma$ versus m , where γ was the mean molal activity coefficient of the hydrochloric acid when the molality of potassium chloride was m . The values of $\log \gamma$ from either experiment did not differ by more than 0.002 from the best line drawn through the points. The plots are shown in Figures 4-1(a) and 4-1(b).

The values from Harned and Owen⁸ for the activity coefficients of 0.01 m HCl at various concentrations of potassium chloride were also included in the graphs. All their values appeared to fall on the drawn curves except at 0.5 m where a difference of 0.004 in $\log \gamma$ was obtained. Exact agreement in $\log \gamma$ values was not expected in view of the slight difference in the molality of the hydrochloric acid.

From this work, it seems that the glass electrode can be used quite successfully to determine the activity coefficients of hydrochloric acid in aqueous and in mixed electrolyte solutions so long as other ions do not interfere with the hydrogen-ion response of the glass.

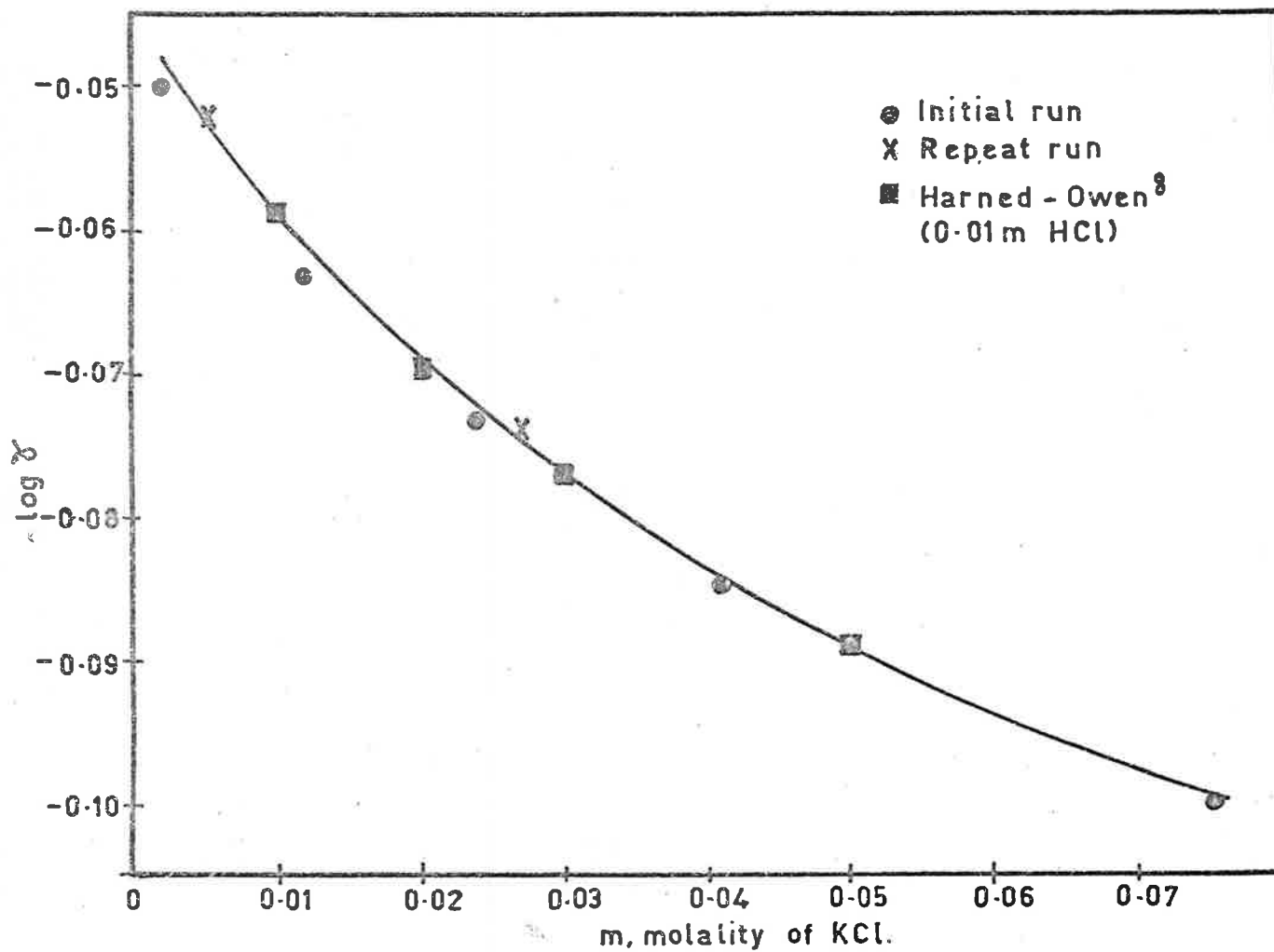


Fig. 4-1(a). The mean molal activity coefficients of 0.010186 m HCl in KCl solution (as $\log \gamma$) plotted against the molality of KCl.

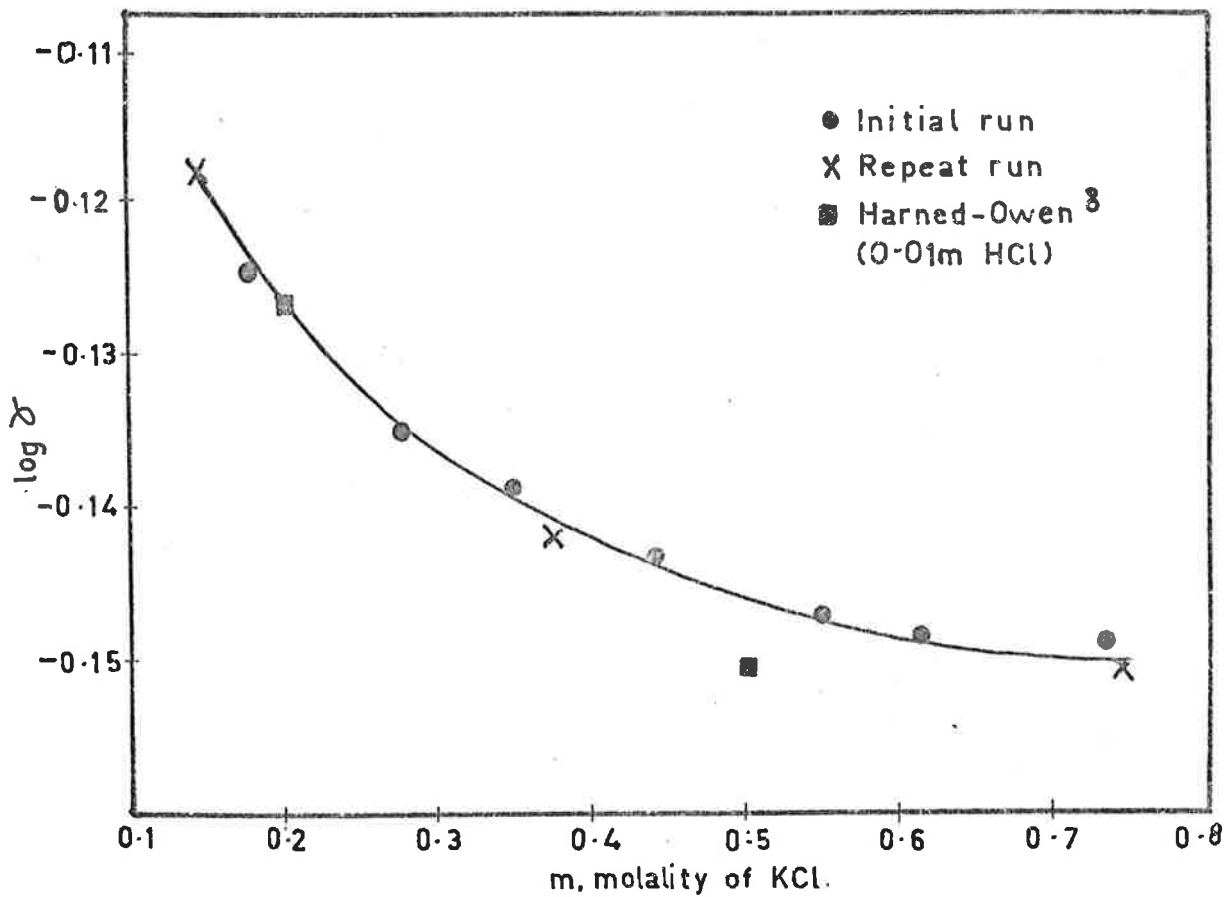


Fig. 4-1(b). The mean molal activity coefficients of 0.010186 m HCl in KCl solution (as $\log \gamma$) plotted against the molality of KCl.

TABLE 4-2

Mean molal activity coefficients of 0.010186 m hydrochloric acid in potassium chloride solution at 25°, using a hydrogen-responsive glass electrode.²

m_{KCl}	-E (Volts)	$-\log \gamma$
0.00000	0.24472	0.0440*
0.0020767	0.24879	0.0500
0.012046	0.26251	0.0635
0.023893	0.27222	0.0738
0.041273	0.28152	0.0848
0.075603	0.29285	0.1000
0.18255	0.31074	0.1245
0.28713	0.31985	0.1349
0.34850	0.32502	0.1387
0.44245	0.33046	0.1433
0.54955	0.33546	0.1470
0.61644	0.33828	0.1478
0.73322	0.34257	0.1487
<u>Repeat Run</u>		
0.00000	0.24755	0.0440*
0.0054395	0.25759	0.0521
0.026847	0.27715	0.0741
0.14628	0.30898	0.1180
0.37361	0.32918	0.1421
0.74575	0.34563	0.1504

Note:

1. * Reference points taken from a large-scale plot of $\log \gamma$ versus $m_{\text{HCl}}^{1/2}$ of aqueous hydrochloric acid.^{6,7}

$\gamma \equiv$ mean molal activity coefficient of hydrochloric acid.

(e) References

1. Harned, H.S., and Owen, B.B., "The Physical Chemistry of Electrolytic Solutions", Reinhold Book Corporation (New York), 3rd Ed., 1958, p. 591.
2. Titron 106 APS made by Titron Instruments, Sandringham, Victoria, Australia.
3. Covington, A.K., and Prue, J.E., J. Chem. Soc., 3696 (1955).
4. Annino, R., J. Chem. Ed., 39, 240 (1962).
5. Hills, G.J., and Ives, D.J.G., J. Chem. Soc., 318 (1951).
6. Robinson, R.A., and Stokes, R.H., "Electrolyte Solutions", Butterworths (London), 2nd. Ed., 1965, p. 491 for $m \geq 0.1$.
7. Reference 1, p. 484 for $m < 0.1$.
8. Reference 1, p. 748.

Chapter 5

The Activity Coefficient of Potassium Chloride in Water and in
Glycine-Water Mixtures at 25°

- (a) Introduction
- (b) Experimental
- (c) Results and Discussion
- (d) References

The Activity Coefficient of Potassium Chloride in Water and in
Glycine-Water Mixtures at 25°

(a) Introduction

The purpose of this experiment was to test the accuracy of using the glass electrode in the determination of the activity coefficient of potassium chloride in water and in glycine-water mixtures. The results were compared with those obtained by other standard methods.

(b) Experimental

Electrode 7 (Beckman 39137), a cation-responsive glass electrode was chosen for this work. The apparatus and the experimental technique were previously discussed in Chapter 2.

(c) Results and Discussion

The activity coefficients of potassium chloride in water have recently been determined at 10°, 18°, 25°, 38° and 50° by Hostetler et al.¹ over the concentration range of 0.01 m to 1 m. They also made use of a Beckman 39137 cation-responsive glass electrode. Their values at 25° were in good agreement with those tabulated by Robinson and Stokes.² Figure 5-1 shows the activity coefficient of potassium chloride (as $\log \gamma_c$) being plotted against m_c , its molality. In drawing the curve, the values of Robinson and Stokes were used. The values of Hostetler et al.¹, and those from this work were also included for comparison. Those from this work were in good agreement

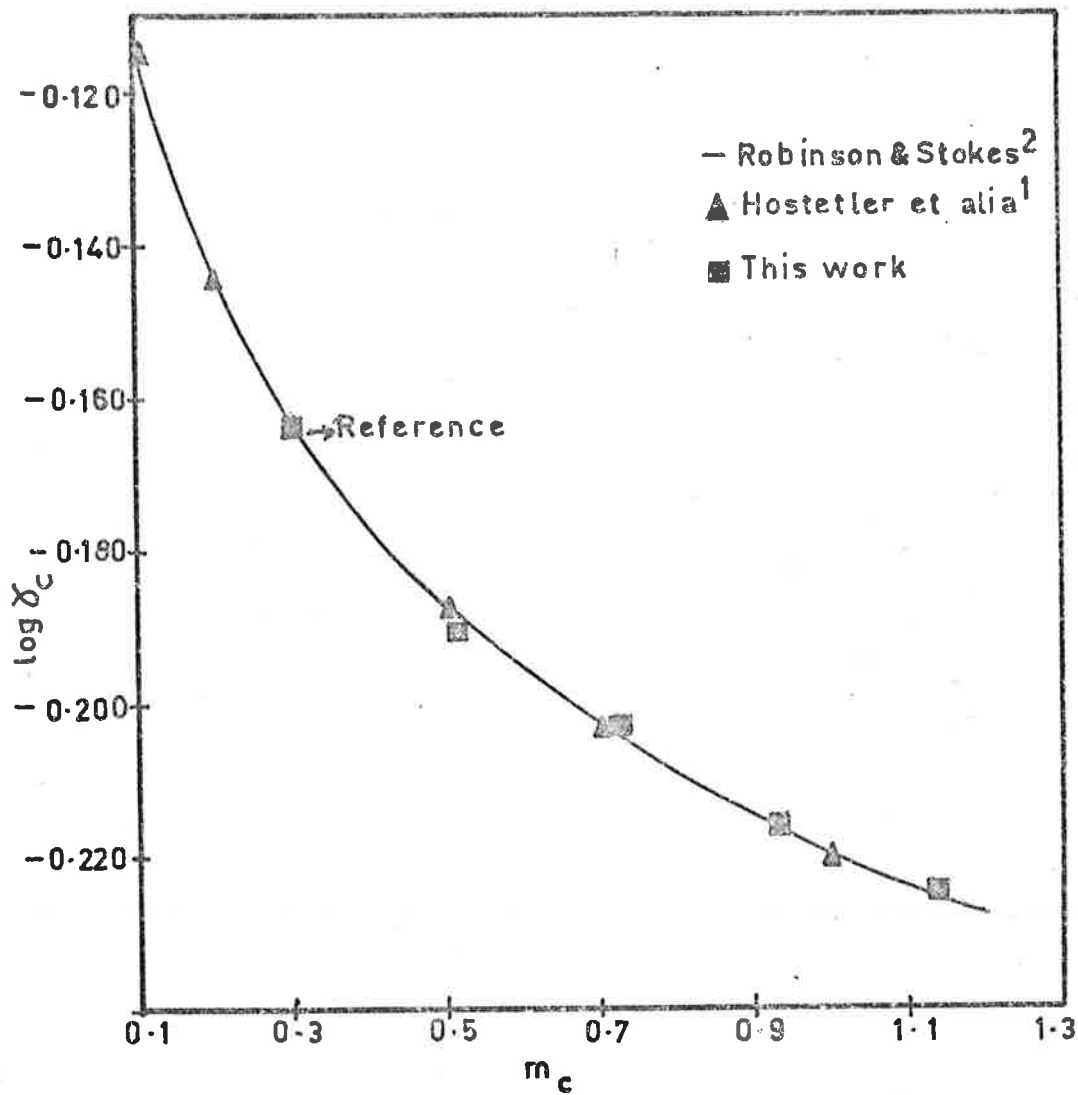
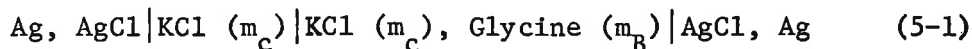


Fig. 5-1. The mean molal activity coefficients of aqueous KCl (as $\log \gamma_c$) plotted against its molality at 25°.

with the literature values.

In Table 5-1 are the tabulated results of this work for the mean molal activity coefficients of potassium chloride in water and in glycine-water mixtures. In the system potassium chloride-glycine-water, the results obtained were compared with those of Roberts and Kirkwood.³ Their work was based on the emf measurements on concentration cells with transference of the type



together with the accurate transference data of Longworth.⁴

They have expressed their results by the equation,

$$\log \frac{\gamma_c}{\gamma_c^\circ} = \frac{1}{2.303} (-0.2059 m_B + 0.2824 m_c^{1/2} m_B + 0.0247 m_B^2 - 0.1446 m_B m_c) \quad (5-2)$$

γ_c and γ_c° were the mean molal activity coefficient of potassium chloride of molality m_c with and without glycine respectively. m_B and m_c were the molalities of glycine and potassium chloride respectively. Equation 5-2 was valid for $m_B \leq 0.5$ and $m_c \leq 0.5$.

In Table 5-1 the results of this work are shown in column 4. They were compared with those of Roberts and Kirkwood, shown in column 5. It can be seen that an excellent agreement was obtained. Eisenman⁵ has reported that glasses of certain compositions were less selective towards the dipolar ions of the amino acids than to K^+ ions. The amino

TABLE 5-1

Mean molal activity coefficients of potassium chloride (as $-\log \gamma_c$)
in water and in glycine-water mixture at 25°.

m_c	m_B	E (Volts)	$-\log \gamma_c$	$-\log \gamma_c$ (Liter.)
0.30000	0	0.19065	0.1627*	0.1627
0.51057	0	0.21469	0.1904	0.1890
0.71778	0	0.23067	0.2033	0.2045
0.93303	0	0.24270	0.2155	0.2160
1.1438	0	0.25212	0.2245	0.2245
0.30000	0	0.19110	0.1627*	0.1627
"	0.19172	0.19027	0.1697	0.1702
"	0.37582	0.18945	0.1766	0.1766
"	0.55889	0.18875	0.1826	0.1826
0.50000	0	0.22161	0.1876*	0.1876
"	0.15942	0.22107	0.1922	0.1927
"	0.34439	0.22047	0.1972	0.1980
"	0.57369	0.21974	0.2034	0.2037

Notes:

- * Reference point.
- $-\log \gamma_c$ (Liter.) are literature values. At $m_B = 0$, they were obtained from the interpolation of the values tabulated by Robinson and Stokes.² At $m_B \neq 0$, they were calculated from Equation 5-2.

acids included glycine. The cation-responsive glass electrode used here was unaffected by glycine. It was therefore capable of measuring accurate activity coefficients of potassium chloride in glycine-water mixtures. This experiment was indicative of the possibility of measuring accurate activity coefficients of sodium chloride in glycine-water mixtures. Indeed it was later found (see Chapter 7) that not only Electrode 7, but also others, were capable of such measurements. Results from the others were just as good as those obtained by using Electrode 7.

(d) References

1. Hostetler, P.D., Truesdell, A.H., and Christ, C.L., Science, 155, 1537 (1967).
2. Robinson, R.A., and Stokes, R.H., "Electrolyte Solutions", 2nd. Ed., Butterworth and Co. Ltd., (London) 1965, p. 476.
3. Roberts, R.M., and Kirkwood, J.G., J. Am. Chem. Soc., 63, 1373 (1941).
4. Longworth, L.G., J. Am. Chem. Soc., 54, 2741 (1932).
5. Eisenman, G. et al., "The Glass Electrode", Interscience Publishers (N.Y.) 1962, p. 294.

Chapter 6The Activity Coefficients of Aqueous Sodium Chloride at 0°, 10°, 25°
and 50°

(a) Introduction

(b) Experimental and Treatment of Results

(i) NaCl-H₂O at 0°, 10° and 50°

(ii) Treatment of Data at 0°, 10° and 50°

(iii) NaCl-H₂O at 25°

(iv) Treatment of Data at 25°

(c) Discussion

(d) References

The Activity Coefficients of Aqueous Sodium Chloride at 0°, 10°, 25°
and 50°

(a) Introduction

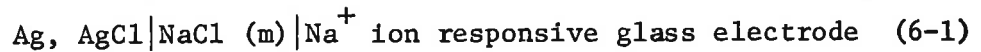
The mean molal activity coefficients of aqueous sodium chloride have been determined by many workers, especially at 25°, using various methods. For example, Harned and Nims¹ made use of sodium-amalgam cells between 0° and 40°; Smith² used the elevation of boiling point method between 60° and 100°; Robinson³ used the isopiestic method between 0° and 50°; Caramazza⁴ used concentration cells between 0° and 50°, and very recently, Truesdell⁵, using sodium-responsive glass electrodes, also covered the temperature range between 0° and 50°.

In this study the mean molal activity coefficients of sodium chloride were determined at 0°, 10°, 25° and 50° from 0.01 m to 1 m. At 25° the study was extended to near saturation of the sodium chloride solution.

The purpose of this work was to demonstrate the accuracy of the experimental arrangement in the determination of the mean molal activity coefficient of sodium chloride; to test the sodium ion response properties of the glass electrode especially at 25° where there was a wealth of data from other standard methods, and to supplement the data at other temperatures where they were meagre.

(b) Experimental and Treatment of Results

The experimental techniques have already been discussed in Chapter 2. It will thus suffice to point out that the cell employed may be represented by



The resulting emf of the cell was

$$E = C + S \log m^2 \gamma^2 \quad (6-2)$$

where C was a constant, $S = \frac{2.303 RT}{F}$ or the Nernst slope. Details of Equation 6-2 have already been discussed in Chapter 2. For two measurements of sodium chloride solutions at molalities m_1 and m_2 of mean activity coefficients γ_1 and γ_2 respectively, the value of γ_2 may be determined with the elimination of C;

$$\log \gamma_2 = \log \gamma_1 + \frac{E_2 - E_1}{2S} + \log \frac{m_1}{m_2} \quad (6-3)$$

m_1 and γ_1 were the molality and the mean molal activity coefficient, respectively, of the reference solution.

It should be noted that since only the binary system of NaCl-water is considered in this chapter, m and γ will represent the molality and the mean molal activity coefficient of sodium chloride respectively. The subscript c and superscript ° will be dropped.

(i) NaCl-H₂O at 0°, 10° and 50°

The study was divided into two concentration ranges, namely between 0.01 m and 0.1 m and between 0.1 m and 1 m. Each range contained its own reference solutions. This method was undertaken to avoid errors arising from emf drifts of the glass electrodes which could occur as a result of C in Equation 6-2 not remaining constant for long periods, or over a wide range of solution concentrations. C could be treated accurately as a constant only in successive measurements of potential on solutions of relatively small incremental differences in concentrations. The constancy of C depended on the glass electrode itself and varied with electrodes (see Chapter 2). Hostetler, Truesdell and Christ⁶ have also recognised this fact when they measured the activity coefficients of aqueous potassium chloride with a potassium-responsive glass electrode.

(ii) Treatment of Data at 0°, 10° and 50°

The raw data at these temperatures are shown in Tables A-1, A-2 and A-4 in Appendix A.

Lietzke and Stoughton⁷ have proposed an equation to describe the concentration dependence of the activity coefficient of aqueous sodium chloride at 25° and at 100°. The equation was of the form

$$\log \gamma = - \frac{A_m^{1/2}}{1 + B_m} + 2C_m + \frac{3}{2} D_m^2 + \frac{4}{3} E_m^3 \quad (6-4)$$

A was the Debye-Huckel limiting slope and was taken as 0.5089 at 25°. Values of the parameters B, C, D and E have been obtained by them for aqueous sodium chloride at 25° by using the osmotic coefficient data tabulated by Robinson and Stokes.⁸ The activity coefficients calculated using Equation 6-4 and those tabulated by Robinson and Stokes⁹ are compared in Table 6-1. It can be seen that the equation expresses the experimental values quite adequately.

In this work, Equation 6-4 was employed at 0°, 10°, 25° and 50° as a semi-empirical equation to fit the data. Thus at 0°, 10° and 50° the activity coefficients in the concentration range of 0.1 m to 1 m were fitted to Equation 6-4 by the method of least squares. Values of the A coefficient were given by Robinson and Stokes.¹⁴ Values of the coefficients B, C, D and E were obtained from the least square fit. Having obtained the parameters for Equation 6-4 at this concentration range, the reference activity coefficients for that between 0.01 m and 0.1 m were calculated. As shown in the tables in Appendix A, those with concentrations near to 0.1 m were always chosen as reference solutions. In this way Equation 6-4 was never extrapolated to concentrations outside those with which the initial fit was made.

Finally, all the data at each temperature, e.g. all the data in Table A-1 in Appendix A, were fitted to Equation 6-4. The fit was again made by the method of least squares. The parameters obtained from this final fit are shown in Table 6-2. The standard deviation

TABLE 6-1Values of $-\log \gamma$ at 25°.

The mean molal activity coefficient of aqueous sodium chloride (as $-\log \gamma$) at 25°. Experimental (RS) versus Calculated (LS).

m	RS	LS	m	RS	LS
0.01	0.0447	0.0442	1.00	0.1825	0.1822
0.02	0.0602	0.0593	2.00	0.1755	0.1749
0.05	0.0866	0.0849	3.00	0.1463	0.1461
0.10	0.1088	0.1082	4.00	0.1061	0.1057
0.20	0.1339	0.1338	5.00	0.0585	0.0578
0.50	0.1668	0.1662	6.00	0.0060	0.0056

Notes:

1. RS, Robinson and Stokes.^{16,21}
2. LS, Lietzke and Stoughton⁷ using Equation 6-4 and the parameters quoted by them (Table 6-2, fourth column).

and the number of points used to fit Equation 6-4 are also shown. From the parameters, the activity coefficients at rounded concentrations have been calculated. The results are presented in Table 6-3. The least square computer program for Equation 6-4 is shown in Appendix C.

(iii) NaCl-H₂O at 25°

As shown in Appendix A, the amount of data at 25° exceeded those at other temperatures. This was due to the preliminary investigations of this research being carried out at 25°. The work at this temperature was essentially that of finding the optimum conditions for measuring accurate activity coefficients and the calibration of new glass electrodes.

(iv) Treatment of Data at 25°

Results at this temperature are shown in Appendix A in which Table A-3(a) contains those between 0.01 m and 0.1 m; Table A-3(b), those between 0.1 m and 2 m; Table A-3(c), those between 1 m and 5 m by the 'multi-step' method; and Table A-3(d), those between 1 m and 5 m by the 'single-step' method.

The 'multi-step' method involved the changing of the concentration in small increments so that a few separate experiments had to be carried out in order to cover the concentration range of 1 m to 5 m. However, the 'single-step' method would cover the same concentration

range in a single experiment. This was done by measuring the reference emf at 1 m and then after large additions of the salt. The tables in Appendix A will assist the explanation.

Unlike the results obtained at 0°, 10° and 50°, those obtained at 25° were not least squared because deviations from the values tabulated by Robinson and Stokes⁹ were considered as departures from ideality of the glass electrode measurements. Instead, Equation 6-4 and the parameters quoted by Lietzke and Stoughton at 25° were used to calculate the activity coefficients at the various molalities. Differences between these calculated values and those obtained from this work were considered as the deviations. The parameters quoted by Lietzke and Stoughton are shown in Table 6-2. Also shown are the parameters from the 'single-step' experiments.

(c) Discussion

The results at 0°, 10° and 50° will be discussed first. The mean molal activity coefficients at these temperatures will be compared with literature values. They are shown in Tables 6-4, 6-5 and 6-6. Also shown in the tables are values calculated using the Davies equation,¹⁰

$$-\log f = A \left(\frac{m^{1/2}}{1 + m} - 0.2 m \right) \quad (6-5)$$

A is the temperature dependent Debye-Huckel coefficient. f is the mean rational activity coefficient of sodium chloride and was replaced by γ , the mean molal activity coefficient, when calculating the activity

TABLE 6-2

Parameters describing the concentration dependence of the activity coefficients of aqueous sodium chloride between 0.01-1 m.

Coefficients	0°	10°	25° ^a	50°	25° ^b
A	0.4918	0.4989	0.5089	0.5373	0.5089
B	1.40009	1.44183	1.45397	1.86484	1.34767
C x 10 ³	-2.0054	3.7882	9.7075	-24.6254	15.6479
D x 10 ³	12.1489	6.2119	4.0418	56.9774	2.0116
E x 10 ³	-3.7461	-0.7558	-0.2328	-24.762	0.0218
Std.Dev. x 10 ³	1.4	0.9	0.3	0.8	1.5
No. of points	41	30		32	37

Notes:

1. The parameters are for the Equation 6-4. Values of A at 0°, 10° and 50° are taken from Robinson and Stokes.¹⁴
2. a, these are parameters quoted by Lietzke and Stoughton⁷ for the concentration range 0.006-6.0 m.
3. b, parameters for 'single-step' experiment over the concentration range 1 m to 5 m.

TABLE 6-3

Activity coefficients of aqueous sodium chloride (as $-\log \gamma$) at 0° ,
 10° , 25° and 50° using Equation 6-4,

$$\log \gamma = - \frac{A_m^{1/2}}{1 + B_m^{1/2}} + 2C_m + \frac{3}{2} D_m^2 + \frac{4}{3} E_m^3.$$

m	0°	10°	25°	50°
0.01	0.0432	0.0435	0.0442	0.0458
0.02	0.0581	0.0585	0.0593	0.0611
0.03	0.0687	0.0689	0.0698	0.0717
0.04	0.0770	0.0771	0.0781	0.0801
0.05	0.0839	0.0840	0.0849	0.0870
0.06	0.0899	0.0898	0.0907	0.0930
0.07	0.0951	0.0950	0.0959	0.0982
0.08	0.0999	0.0996	0.1004	0.1029
0.09	0.1041	0.1037	0.1045	0.1071
0.10	0.1080	0.1075	0.1082	0.1110
0.20	0.1354	0.1338	0.1338	0.1377
0.30	0.1522	0.1496	0.1488	0.1536
0.40	0.1640	0.1606	0.1590	0.1641
0.50	0.1728	0.1687	0.1662	0.1712
0.60	0.1797	0.1749	0.1716	0.1762
0.70	0.1851	0.1797	0.1756	0.1795
0.80	0.1894	0.1834	0.1786	0.1817
0.90	0.1929	0.1863	0.1808	0.1832
1.00	0.1957	0.1884	0.1822	0.1844

Note:

- Parameters used in the above calculations are found in Table 6-2.

TABLE 6-4

Values of γ at 0°.

Comparison of the mean molal activity coefficient of aqueous sodium chloride at 0°. C = Caramazza,⁴ HN = Harned and Nims,¹ HC = Harned and Cook.¹¹

m	References				
	This work	C	HN	Eqn. 6-5	HC
0.01	0.905	0.904		0.904	
0.03	0.854			0.852	
0.05	0.824	0.822	0.823		0.825
0.07	0.803				
0.10	0.780	0.772	0.773		0.781
0.20	0.732	0.723	0.724		0.731
0.50	0.672	0.664	0.664		0.671
0.70	0.653				
1.00	0.637	0.631	0.631		0.638

TABLE 6-5Values of γ at 10°.

Comparison of the mean molal activity coefficient of aqueous sodium chloride at 10°. HR = Harned and Robinson.¹²

m	References		
	This work	HR	Eqn. 6-5
0.01	0.905		0.903
0.03	0.853		0.850
0.05	0.824		
0.07	0.803 ₅		
0.10	0.781	0.781	
0.20	0.735	0.734	
0.50	0.678	0.677	
0.70	0.661		
1.00	0.648	0.649	

TABLE 6-6

Values of γ at 50°.

Comparison of the mean molal activity coefficient of aqueous sodium chloride at 50°. C = Caramazza,⁴ HR = Harned and Robinson,¹² R = Robinson,³ T = Truesdell.⁵

m	References				
	This work	C	HR	R	T
0.01	0.900	0.896			(0.898)
0.03	0.848				
0.05	0.818 ₅	0.820			0.816
0.07	0.798				
0.10	0.774 ₅	0.768	0.770	0.772	0.770
0.20	0.728	0.721	(0.725)	0.729	0.726
0.50	0.674	0.668	(0.675)	0.678	0.677
0.70	0.661 ₅			0.666	0.668
1.00	0.654	0.649	(0.656)	0.660	0.661 ₅

Note:

1. Values in parentheses under HR were read from plots of the emf and boiling point results. That under T was Truesdell's reference activity coefficient.

coefficients in Tables 6-4, 6-5 and 6-6. Equation 6-5 is known to be useful only at low concentrations.

As shown in Table 6-4, the results from this work at 0° were in good agreement with those of Harned and Cook.¹¹ The recent data of Caramazza,⁴ however, agreed with those of Harned and Nims,¹ but Harned and Cook have shown that the values of Harned and Nims were in slight error and the recalculated values were in better agreement with results from other measurements. Unfortunately, Caramazza made no mention of the results of Harned and Cook. Values calculated from the Davies equation are shown in the fifth column for 0.01 m and 0.03 m. Literature values of the activity coefficients of sodium chloride at this temperature appear to be scanty. A graphical comparison of γ values is shown in Figure 6-1. The curve was drawn using the values from this work.

The results from this work at 10° are shown in Table 6-5. They showed good agreement with those tabulated by Harned and Robinson.^{12,13} The values calculated using Equation 6-5 were slightly smaller than the experimental values.

At 50° (see Table 6-6), the results were compared with those obtained by a number of workers. Measurements by Truesdell⁵ were made using a cation-responsive glass electrode (NAS 11-18 glass composition). It was not stated if the electrode was available commercially. He used 0.01 m NaCl as the reference solution and calculated the reference

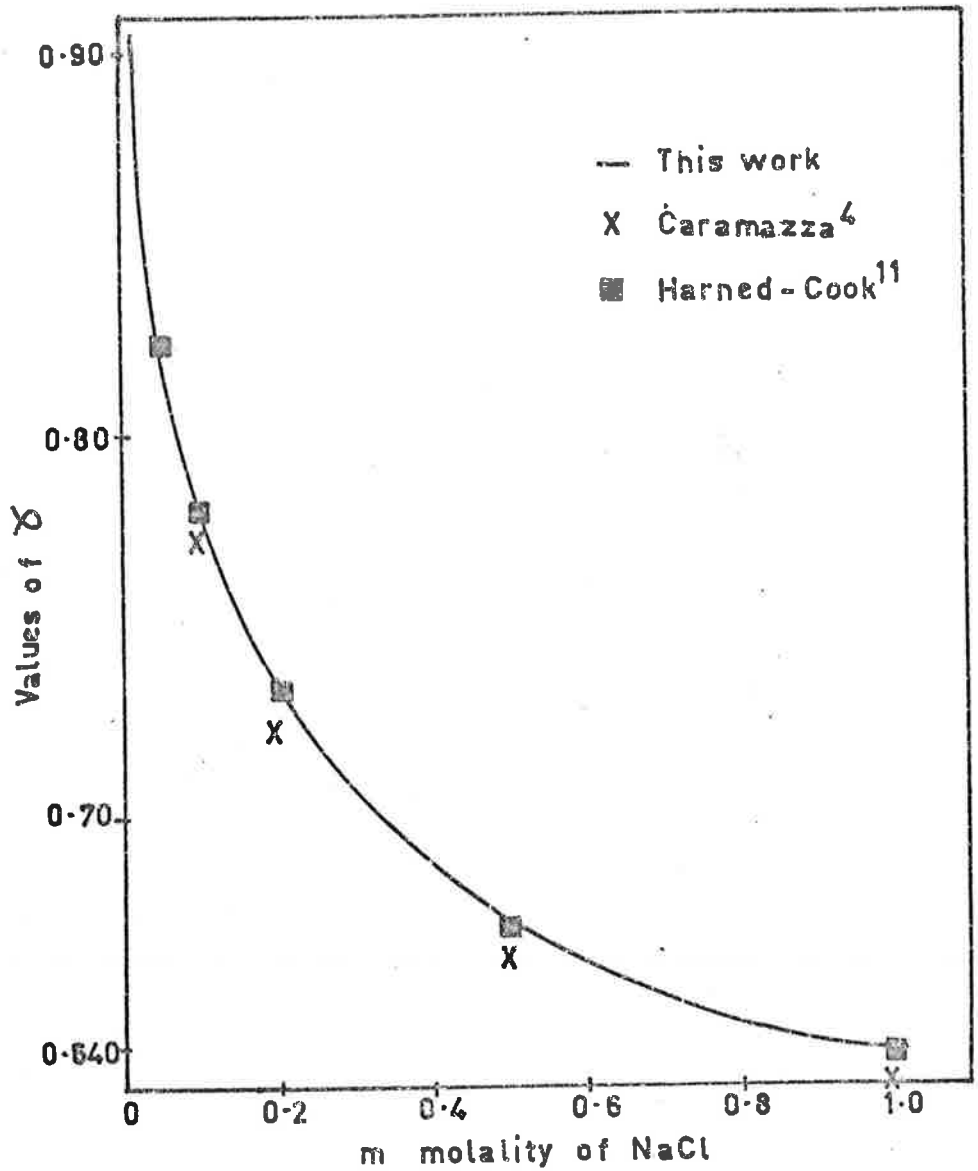


Fig. 6-1. A comparison of the mean molal activity coefficient of aqueous NaCl at 0°.

activity coefficient using Equation 6-5 by replacing f with γ , the mean molal activity coefficient. The A coefficient was taken as 0.524, whereas the value recorded by Robinson and Stokes¹⁴ was 0.537 at 50°. Truesdell's reference activity coefficient of $\gamma = 0.8983$ would be altered to $\gamma = 0.8960$ if the A value was 0.537. This would produce a lowering of about 0.002 in all his γ values at 50°. The dielectric constant of water calculated from his A value at this temperature was 71.14 whilst that given by Robinson and Stokes yielded a value of 69.91. Kay et al.²³ recently reinvestigated the dielectric constant of water and gave an equation expressing the dielectric constant as a function of temperature. From the equation a value of 69.91 was obtained. No reason could be found for the discrepancy of the A values quoted by Truesdell.²⁴ Caramazza's activity coefficients were again smaller than those from this work except at 0.05 m. The values of Harned and Robinson¹² and the isopiestic results of Robinson³ were also recorded in Table 6-6. It can be seen that serious disagreement among the different sources exist in view of the importance of the activity coefficients of sodium chloride at this temperature.¹⁵ The graphical comparison is shown in Figure 6-2 where the curve was drawn using the values from this work.

In a manner similar to that adopted in this study, Schindler and Wälti¹⁷ confirmed the ideality of their glass electrodes by comparing the activity coefficient of sodium chloride at 25° in the range of 0.1 m to about 2 m with that tabulated by Robinson and Stokes. Table 6-7

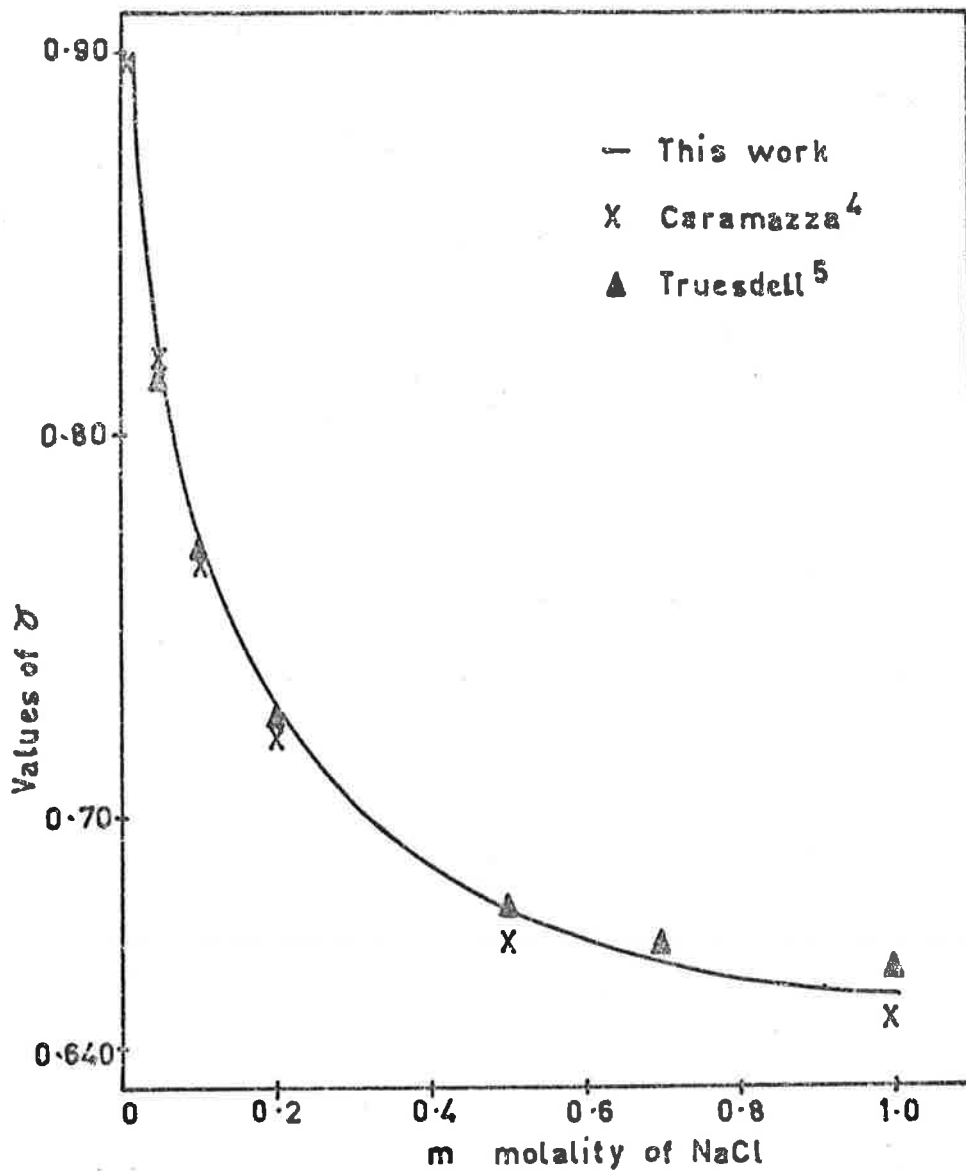


Fig. 6-2. A comparison of the mean molal activity coefficients of aqueous NaCl at 50°.

shows Robinson and Stokes' values compared with those of Caramazza,⁴ Truesdell,⁵ and Harned and Cook.¹¹ The work of these workers have already been discussed at other temperatures. At 25°, the results of Harned and Cook¹¹ are in good agreement with those of Robinson and Stokes.⁹ Of particular interest are the results of Truesdell since he measured the activity coefficients using cation-responsive glass electrodes. His results show about 0.3 mV disagreement at 0.05 m, 0.5 m, 0.7 m and 1.0 m. The results of Caramazza above 0.01 m show deviations in excess of 0.4 mV.

Most of the electrodes used in this work were calibrated at 25°. As shown in Table A-3(a) in Appendix A, electrodes 5, 6, 7 and 9 show excellent response to sodium ions in the concentration range of 0.01 m to 0.1 m. It was normal practice to recalibrate the electrodes after a series of investigations in the ternary system. Thus Table A-3(b) shows that electrodes 1 and 3 have been calibrated more than once between 0.1 m and 2 m. In general, all the electrodes when freshly procured exhibited long stability and good response with drift rates of less than 0.1 mV/hr.

In Appendix A, Tables A-3(c) and A-3(d) show the results from the 'single-step' and the 'multi-step' methods respectively. Their techniques were already discussed earlier (see section (b)(iv) of this chapter). At 25°, and between 1 m and 5 m NaCl, the 'single-step' method resulted in deviations of the activity coefficients from those

TABLE 6-7

Values of γ at 25°.

Comparison of the mean molal activity coefficient of aqueous sodium chloride at 25°. RS = Robinson and Stokes,⁹ HC = Harned and Cook,¹¹ T = Truesdell,⁵ C = Caramazza.⁴

m	RS	HC	T	C
0.01	0.902		(0.902 ₇)	0.901
0.02	0.871		0.872	
0.05	0.819	0.821	0.822	0.823
0.10	0.778	0.779	0.778	0.774
0.20	0.735	0.733	0.733	0.729
0.30	0.710		0.709	
0.50	0.681	0.681	0.683 ₅	0.676
0.70	0.667		0.672 ₅	
1.00	0.657	0.658	0.664	0.653

Note:

- The value in parentheses under T was Truesdell's reference activity coefficient.



recorded by Robinson and Stokes.¹⁶ In the 'single-step' method the pH of the solutions were also determined to ensure that the deviations were not due to pH changes. During the experiment it was observed that the silver-silver chloride electrodes were corroded very rapidly, although the solution was already kept saturated with silver chloride by the presence of added solid silver chloride. This was probably due to the salting-in of silver chloride by sodium chloride solution. The solubility of silver chloride in 1 N NaCl is 0.1×10^{-3} N and increases to 6×10^{-3} N in 5 N NaCl.^{19,20} The plum coloured silver-silver chloride electrodes generally became pale pink or white at the end of such an experiment, and the emf showed slight sensitivity to the stirring rate. However, the emfs recorded were reproducible within a few tenths of a millivolt. The results have been fitted to Equation 6-4 by the method of least squares. The parameters are presented in Table 6-2 (column 6) and the average deviation of the fit was about 0.15 mV. Activity coefficients at rounded concentrations have been calculated and presented in Table 6-8, where they were compared with those tabulated by Robinson and Stokes.²¹ A graphical comparison in Figure 6-3 shows that the deviations increased with concentration so that at 5 m, the deviation was about 1 mV.

It has been shown by Lanier¹⁸ that his measured activity coefficients at 25° differed from those recorded by Robinson and Stokes by as much as 1 mV near 5 m. A proper study of his work was impossible through the absence of numerical data in his paper. However, judging from the

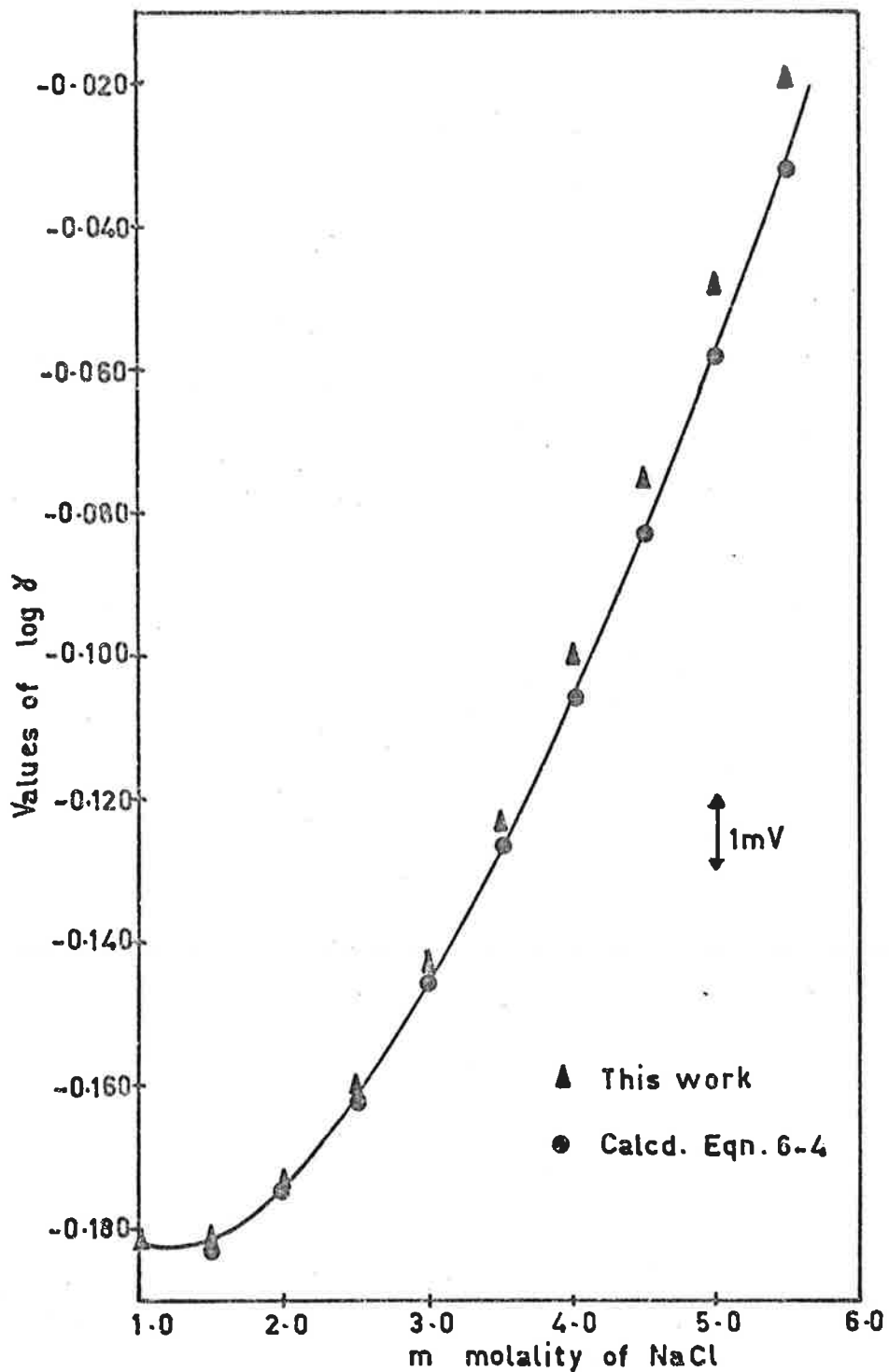


Fig. 6-3. The mean molal activity coefficients of aqueous NaCl obtained from the 'single-step' experiments compared with the literature values. ● Values calculated from Equation 6-4.

TABLE 6-8

Values of $-\log \gamma$.

Mean molal activity coefficients (as $-\log \gamma$) from the 'one-step' experiment (1 m to 5 m).

m	This work	RS
1.0	0.1824	0.1822
1.5	0.1813	0.1824
2.0	0.1728	0.1749
2.5	0.1595	0.1623
3.0	0.1425	0.1461
3.5	0.1226	0.1270
4.0	0.1001	0.1057
4.5	0.0752	0.0825
5.0	0.0480	0.0578
5.5	0.0186	0.0321

Note:

1. RS \equiv Robinson and Stokes.²¹ The values are calculated from Equation 6-4 using the parameters shown in the fourth column of Table 6-2.

graphical data provided, the deviation from Robinson and Stokes' values was similar to that which was obtained in the 'single-step' experiments.

The possibility that the deviations were due to the shortcomings of the 'single-step' method resulted in the initiation of the 'multi-step' method. The results of the 'multi-step' method are shown in Table A-3(c) in Appendix A. Good agreement was obtained with the activity coefficients of Robinson and Stokes. Although the deviations were in the same direction as those in the 'single-step' experiments, they were less than about 0.2 mV. It must be pointed out that the results from the 'multi-step' method do not prove that those obtained from the 'single-step' method were incorrect. This is because all the reference activity coefficients in the 'multi-step' method were taken from the curve describing the data of Robinson and Stokes. However, it does show that agreement with Robinson and Stokes' values can be obtained by working in steps over the concentration range of 1 m to 5 m. Also, it does present the possibility that the 'single-step' method could have shortcomings. Recently, Scatchard et al.²² reported emf measurements for the systems $\text{NaCl-MgSO}_4\text{-H}_2\text{O}$ and $\text{Na}_2\text{SO}_4\text{-MgCl}_2\text{-H}_2\text{O}$ using some Beckman 39137 cation-responsive glass electrodes at 25°. They tested the accuracy of their procedure with a series of sodium chloride solutions in the range 1.0-6.16 m and found that the deviations from the activity coefficients given by Robinson and Stokes were less than 0.4 mV. Unfortunately, no data was given for any

useful comparison with this study.

Finally, the activity coefficients of sodium chloride between 0° and 100° have been plotted versus temperature for 0.1 m, 0.2 m, 0.5 m and 1.0 m using the data of Harned and Robinson.²¹ Results from this work have also been included, and they are shown in Figure 6-4.

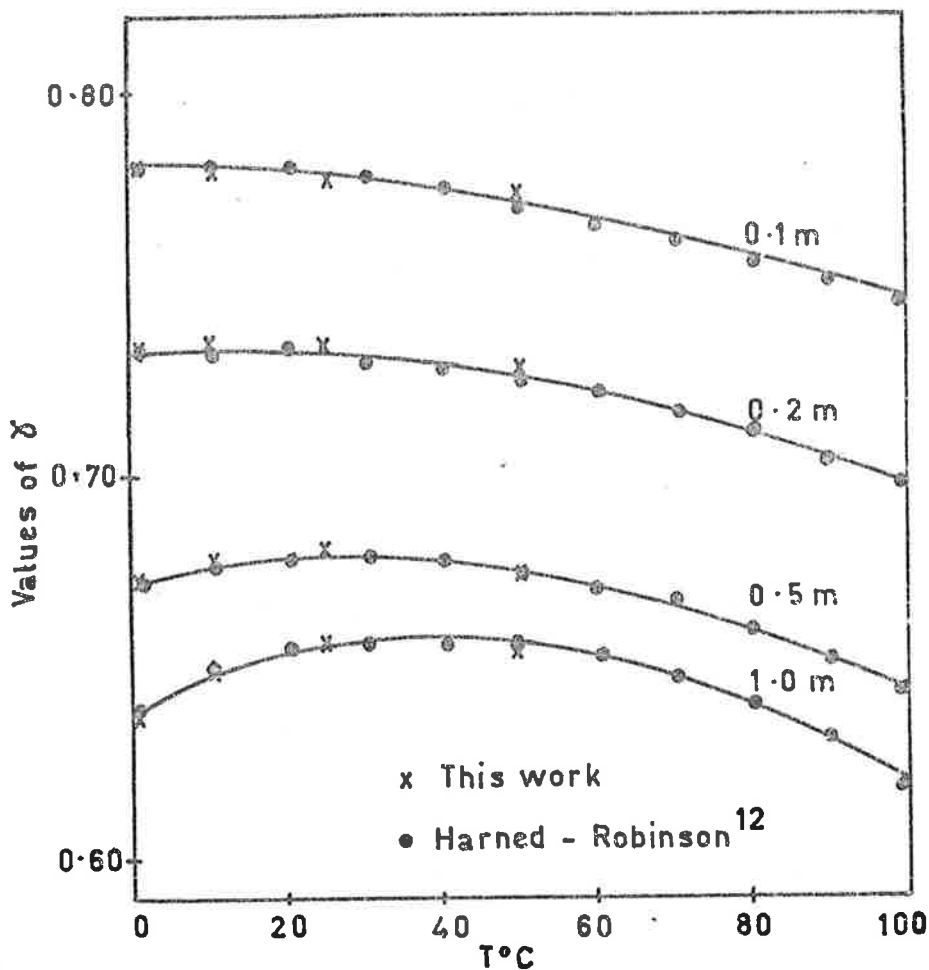


Fig. 6-4. The mean molal activity coefficients of NaCl as a function of temperature.

(d) References

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24. The values of A at 15°, 25° and 38° were also in disagreement with those of Robinson and Stokes (reference 14).

Chapter 7Activity Coefficients in the Ternary System: Sodium Chloride-Glycine-
Water at 0°, 10°, 25° and 50°

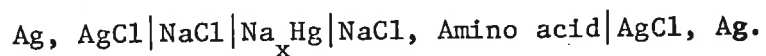
- (a) Introduction
- (b) Experimental
- (c) Results
- (d) Discussion
 - (i) Activity Coefficient of Sodium Chloride as a Function of Temperature
 - (ii) A Comparison with Literature Values
 - (iii) Effects of Electrolytes on Aqueous Non-Electrolyte Solutions and Vice Versa.
 - (iv) The Dipole Moment of the Glycine Molecule
 - (v) Salting-in and Salting-out
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Activity Coefficients in the Ternary System: Sodium Chloride-Glycine-
Water at 0°, 10°, 25° and 50°

(a) Introduction

The effects of aqueous salt solutions on the activity coefficients of non-electrolytes was reviewed in 1952 by Long and McDevit.¹ Later, a summary of developments up to 1964, together with an extension of the theories, was published by Conway, Desnoyers and Smith.² These reviews were more concerned with salting-out effects than with salting-in since the latter phenomenon was not so common, especially with the simpler 1-1 salts.³

The problems, where the non-electrolyte happens to be an amino acid, a protein, or a peptide, are of sufficient importance to merit an extensive consideration in the book edited by Cohn and Edsall.⁴ The early methods of studying non-electrolytes in aqueous salt solutions were based on solubility methods. This was replaced by emf methods which had an added advantage over the solubility methods because the concentration of more than one of the components could be independently varied. Thus Joseph⁵, using emf cells without liquid junctions, determined the activity coefficients of sodium chloride in aqueous glycine solutions. Glycine, which is a non-electrolyte, is best described as a dipolar amino acid. The results were then used to calculate the activity coefficient of glycine in the salt solutions. Joseph used a cell of the type:



The use of sodium amalgam electrodes in solutions containing amino acids creates a number of experimental difficulties. For example, Joseph found that when sodium amalgam was brought into contact with a solution of glycine, there was an evolution of hydrogen. In spite of these experimental difficulties he was able to measure the activity coefficients at 25° and at 1.4° \pm 0.2°. Thus at 1.4° he was able to derive values at low concentrations of sodium chloride and glycine (0.01 m to 0.1 m NaCl and 0.1 m to 0.4 m glycine); at 25° he was limited to working at higher concentrations (1 m to 4 m NaCl and 0.5 m to 1 m glycine).

Scatchard and Prentiss⁶ have also measured the activity coefficient of sodium chloride in glycine-water mixtures using the depression of freezing point method. The chief disadvantage of this method for thermodynamic calculation is that the temperature at which the chemical potential of the solvent is measured varies with the composition.

The cation-responsive glass electrode has been used by Lanier⁷ to measure the activity coefficient of sodium chloride in water-organic solvent mixtures at 25°. Apart from being used in biological fluids (see Chapter 1) there seem to be no instances of such electrodes being used in a medium containing an amino acid.

In this section of the research, various cation-responsive glass electrodes were used to investigate the sodium chloride-glycine-water system at 0°, 10°, 25° and 50°. The activity coefficients of sodium

chloride were calculated from these experiments and then using Equation 7-4, those of glycine were calculated.

(b) Experimental

The experimental techniques and procedures have already been discussed in Chapter 2.

(c) Results

All the results regarding the system NaCl (m_c)-Glycine (m_B)-Water are tabulated in Appendix B. The investigations were carried out at 25°, 50°, 0° and 10° and in that order. The large amount of data at 25° was again due to the preliminary investigations of this ternary system being carried out at this temperature and also, most of the experiments were repeated more than once. In the earlier part of this work (i.e. at 25°), solutions of glycine containing known concentrations of sodium chloride were made up and used as reference solutions (e.g. see Table B-3, Appendix B for electrodes 5 + G, $m_B = 0.098888$, $m_c = 0.095656$). In such cases the reference activity coefficient relied upon the accuracy of an earlier experiment. Thus in the example mentioned, the reference activity coefficient was taken from an experiment in which the values of m_c were varied at $m_B = 0.1$. This technique was later discarded and pure sodium chloride solution was used as the reference (e.g. see Table B-3, Appendix B for electrodes 9 + C and 9 + G, $m_B = 0.028669$, $m_c = 1.4928$). Glycine was then added after which only the concentration of the sodium chloride (m_c) was

varied. Such a technique was adopted at 0°, 10° and 50°. The sources from which the reference activity coefficients were taken are indicated in the Notes at the end of each table.

From the investigations at 25°, it was found that the GEA type electrodes showed a superior performance to the others (e.g. see Chapter 3). Hence, at other temperatures it was decided to use only the GEA type electrodes.

The system KCl (m_c)-Glycine (m_B)-Water has been investigated by Roberts and Kirkwood⁸ and by Robinson and Bower.⁹ Roberts and Kirkwood have expressed the activity coefficient of potassium chloride as a power series of m_B and m_c :

$$\log \frac{\gamma_c}{\gamma_c^\circ} = m_B (B_{10} + B_{11} m_c^{1/2} + B_{12} m_c) + B_{20} m_B^2 \quad (7-1)$$

γ_c and γ_c° are the activity coefficients of potassium chloride in water with and without glycine respectively.

Robinson and Bower, in extending the system over larger concentrations, have expressed the activity coefficient of potassium chloride in the form,

$$\begin{aligned} \log \frac{\gamma_c}{\gamma_c^\circ} = & B_{10} m_B + B_{20} m_B^2 + B_{30} m_B^3 + B_{12} m_B m_c \\ & + B_{14} m_B m_c^2 + B_{24} m_B^2 m_c^2 \end{aligned} \quad (7-2)$$

Joseph⁵ has expressed the data of Scatchard and Prentiss⁶ in the form,

$$\log \frac{\gamma_c}{\gamma_c^\circ} = m_B (B_{10} + B_{11} m_c^{1/2} + B_{12} m_c + B_{13} m_c^{3/2}) + m_B^2 (B_{20} + B_{21} m_c^{1/2}) \quad (7-3)$$

where γ_c and γ_c° were the activity coefficients of sodium chloride in water with and without glycine respectively. Equation 7-3 is an extended form of Equation 7-1.

The results from this work at 25° were fitted to a number of empirical equations, including Equation 7-2, by the method of least squares. It was found that Equation 7-3 expressed the data within the experimental errors not only at 25° but also at 0°, 10° and 50°. The parameters are tabulated in Table 7-1 together with the average deviations of $\log \gamma_c / \gamma_c^\circ$ in making the fit. The last row of Table 7-1 shows the number of points actually used in the least square calculation. They also represent the total number of experimentally determined values at each temperature. The computer programs written for the least square of Equations 7-1 and 7-3 are presented in Appendix C.

The data at 25° in the concentration range of $m_B \leq 0.5$ and $m_c \leq 0.5$, were also fitted by the method of least squares to Equation 7-1. The parameters are shown in the last column of Table 7-1. Activity coefficients of sodium chloride at rounded concentrations in the NaCl-glycine-water mixtures were then calculated. They are shown in Tables 7-2 and 7-3 for the four temperatures. Since the solubility of glycine is limited by temperature, for $m_B > 1.5$ the activity coefficient

TABLE 7-1

Parameters for Equation (7-1) and Equation (7-3).

Equation	(7-3)				(7-1)
Temperature	0°	10°	25°	50°	25°
$B_{10} \times 10^3$	-109.646	-95.4397	-88.2207	-72.4392	-95.8745
$B_{20} \times 10^3$	17.4372	13.1255	11.5182	6.8650	16.4936
$B_{11} \times 10^3$	138.491	118.034	117.323	94.6560	117.728
$B_{12} \times 10^3$	-105.773	-81.7807	-74.9969	-66.6301	-52.4754
$B_{13} \times 10^3$	43.6589	30.1798	22.9092	23.8390	
$B_{21} \times 10^3$	-13.1407	-10.1482	-10.0574	-5.2654	
Ave. Dev.	8.6×10^{-4}	9.4×10^{-4}	1.06×10^{-3}	1.49×10^{-3}	5.8×10^{-4}
No. Pts.	50	44	167	70	34

Notes:

1. Ave. Dev. \equiv Mean deviation.
2. No. Pts. \equiv Number of points least squared.
3. Values in which $m_B \leq 0.5$ and $m_C \leq 0.5$ were used in the least square calculation, when deriving the parameters of Equation 7-1.

TABLE 7-2

The effect of glycine on the activity coefficient of sodium chloride in aqueous solution at 0°, 10°, 25° and 50°.

Tabulated values of $-\log \frac{\gamma_c}{\gamma_c^0}$ at rounded concentrations.

m_B	Temp. °C	m_c				
		0.01	0.05	0.07	0.10	0.20
0.5	0	0.0444	0.0381	0.0363	0.0342	0.0296
	10	0.0392	0.0337	0.0321	0.0302	0.0260
	25	0.0360	0.0304	0.0288	0.0269	0.0226
	50	0.0302	0.0257	0.0244	0.0229	0.0195
0.7	0	0.0599	0.0513	0.0489	0.0460	0.0398
	10	0.0532	0.0456	0.0434	0.0409	0.0352
	25	0.0489	0.0413	0.0391	0.0364	0.0307
	50	0.0414	0.0352	0.0335	0.0313	0.0267
1.0	0	0.0807	0.0690	0.0656	0.0618	0.0534
	10	0.0723	0.0619	0.0589	0.0554	0.0477
	25	0.0667	0.0562	0.0531	0.0496	0.0417
	50	0.0573	0.0487	0.0461	0.0432	0.0368
1.5	0	0.1089	0.0926	0.0880	0.0827	0.0714
	10	0.0994	0.0848	0.0806	0.0757	0.0651
	25	0.0922	0.0774	0.0731	0.0681	0.0573
	50	0.0812	0.0687	0.0651	0.0609	0.0518
2.0	10	0.1204	0.1022	0.0970	0.0910	0.0783
	25	0.1124	0.0939	0.0886	0.0824	0.0693
	50	0.1019	0.0859	0.0813	0.0760	0.0646
2.5	25	0.1273	0.1058	0.0997	0.0926	0.0779
	50	0.1194	0.1003	0.0948	0.0885	0.0751
3.0	25	0.1370	0.1130	0.1063	0.0986	0.0829
	50	0.1338	0.1118	0.1056	0.0984	0.0833
4.0	50	0.1530	0.1264	0.1189	0.1105	0.0930

TABLE 7-3

The effect of glycine on the activity coefficient of sodium chloride in aqueous solution at 0°, 10°, 25° and 50°.

Tabulated values of $-\log \frac{\gamma_c}{\gamma_c^\circ}$ at rounded concentrations.

m_B	Temp. °C	m_c				
		0.30	0.50	0.70	1.00	1.10
0.5	0	0.0266	0.0225	0.0195	0.0156	0.0143
	10	0.0233	0.0196	0.0170	0.0138	0.0128
	25	0.0198	0.0162	0.0138	0.0111	0.0104
	50	0.0173	0.0144	0.0123	0.0099	0.0091
0.7	0	0.0358	0.0304	0.0264	0.0212	0.0195
	10	0.0315	0.0266	0.0231	0.0188	0.0175
	25	0.0269	0.0221	0.0189	0.0154	0.0144
	50	0.0237	0.0197	0.0169	0.0136	0.0126
1.0	0	0.0481	0.0410	0.0358	0.0290	0.0267
	10	0.0428	0.0362	0.0316	0.0260	0.0243
	25	0.0367	0.0303	0.0260	0.0215	0.0203
	50	0.0327	0.0273	0.0235	0.0190	0.0176
1.5	0	0.0645	0.0554	0.0489	0.0402	0.0373
	10	0.0585	0.0499	0.0440	0.0368	0.0346
	25	0.0505	0.0421	0.0367	0.0312	0.0297
	50	0.0460	0.0385	0.0334	0.0273	0.0254
2.0	10	0.0705	0.0606	0.0540	0.0461	0.0436
	25	0.0614	0.0517	0.0459	0.0401	0.0386
	50	0.0574	0.0482	0.0420	0.0347	0.0325
2.5	25	0.0692	0.0591	0.0535	0.0483	0.0470
	50	0.0668	0.0563	0.0494	0.0414	0.0390
3.0	25	0.0740	0.0643	0.0595	0.0558	0.0550
	50	0.0742	0.0629	0.0556	0.0473	0.0448
4.0	50	0.0830	0.0713	0.0643	0.0567	0.0543

of sodium chloride at 0° can no longer be represented in the tables.

In a separate experiment at 25°, the parameters in Table 7-1 were tested by using them to predict some experimental values. The results are shown in Table 7-4. The test shows that the results at 25° are reproducible to within 0.2 mV and that the parameters given for Equation 7-3 are reliable.

In Figure 7-1 the concentration range in which the activity coefficients in this research were measured are shown for each temperature. Those of Joseph,⁵ and Scatchard and Prentiss⁶ are also included. Scatchard and Prentiss made measurements using compositions of $2/3$ sodium chloride and $1/3$ glycine, and $1/3$ sodium chloride and $2/3$ glycine, in terms of their molalities. The actual compositions used are shown by black dots in Figure 7-1. Those from this research are enclosed in the rectangles where the m_B values indicate near or at saturation of the glycine solutions. The shaded rectangle represents Joseph's work at 1.4°.

By applying the cross-differentiation relationship,¹³

$$2 \left(\frac{\partial \log \gamma_c}{\partial m_B} \right)_{m_c} = \left(\frac{\partial \log \gamma_B}{\partial m_c} \right)_{m_c} \quad (7-4)$$

one can also express the activity coefficient of glycine as a power series of m_B and m_c . Thus Equation 7-3 is transformed into

$$\log \left(\frac{\gamma_B}{\gamma_B^0} \right) = m_c \left(2B_{10} + \frac{4}{3} B_{11} m_c^{1/2} + B_{12} m_c + \frac{4}{5} B_{13} m_c^{3/2} \right) + 4m_B m_c \left(B_{20} + \frac{2}{3} B_{21} m_c^{1/2} \right) \quad (7-5)$$

TABLE 7-4

Experimental test on Equation 7-3 for sodium chloride-glycine-water at 25° using the parameters shown in Table 7-1.

Electrode	m_c	m_B	E_{volts}	$-\log \gamma_c$	$-\log \gamma_c$ (Calc.)
4 + G	0.29937	0.53833	0.14215	0.1700 ^a	0.1700
	0.44862	"	0.16159	0.1813	0.1810
	0.62170	"	0.17749	0.1886	0.1883
	0.77919	"	0.18863	0.1925	0.1921
	0.92586	"	0.19728	0.1943	0.1938
	1.0903	"	0.20559	0.1952	0.1942
5 + G	0.29937	0.53833	0.14739	0.1700 ^a	0.1700
	0.44102	"	0.16601	0.1808	0.1805
	0.78693	"	0.19438	0.1926	0.1922
	1.1470	"	0.21345	0.1950	0.1942
	1.2925	"	0.21962	0.1947	0.1932
4 + G	0.29938	0.75993	0.14080	0.1777 ^a	0.1777
	0.43528	"	0.15892	0.1871	0.1870
	0.59284	"	0.17403	0.1936	0.1934
	0.80314	"	0.18912	0.1978	0.1976
	1.0568	"	0.20304	0.1994	0.1988
	1.3291	"	0.21502	0.1978	0.1968

Note:

1. a represents the reference activity coefficient and the reference point. Values of a and $-\log \gamma_c$ (Calc.) are calculated from Equation 7-3 using the 25° parameters shown in Table 7-1.

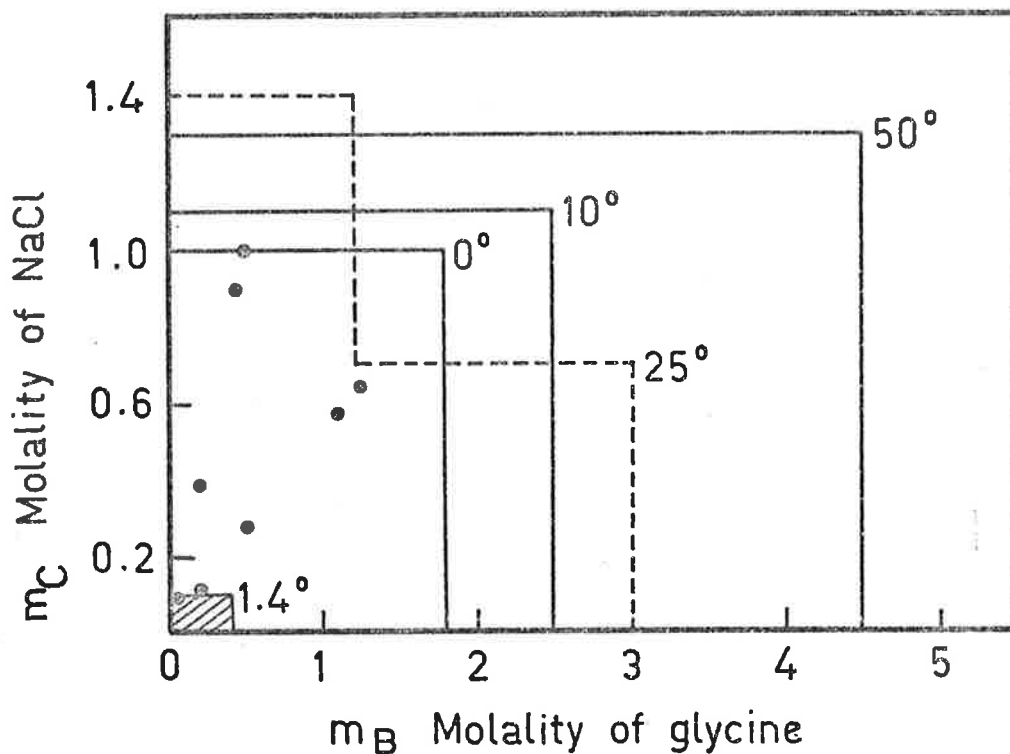


Fig. 7-1. Concentration range investigated. The black dots represent the work of Scatchard and Prentiss.⁶ The shaded rectangle is that of Joseph⁵ at 1.4° . The concentration ranges covered in this work are enclosed in the other rectangles. The concentration range enclosed by the broken lines represents the work at 25° .

From the parameters tabulated in Table 7-1, values of $\log \left(\frac{\gamma_B}{\gamma_B^\circ} \right)$ at rounded concentrations of glycine and sodium chloride are calculated. They are shown in Tables 7-5 and 7-6 for the four temperatures.

(d) Discussion

In the following discussion, unless otherwise stated, m_B and m_C will represent the molality of the non-electrolyte and electrolyte respectively. γ_B , γ_C , γ_B° , and γ_C° will represent the mean molal activity coefficients. The subscripts B and c indicate the non-electrolyte and electrolyte respectively. The superscript $^\circ$ indicates the value in the binary system, e.g. γ_B and γ_B° indicate the mean molal activity coefficient of the non-electrolyte at molality m_B with and without the presence of the electrolyte respectively. Similarly, γ_C and γ_C° represent the mean molal activity coefficient of the electrolyte at molality m_C with and without the presence of the non-electrolyte respectively.

(i) The Activity Coefficient of Sodium Chloride as a Function of Temperature

The behaviour of the mean molal activity coefficient of aqueous sodium chloride with and without added glycine and also as a function of temperature is shown in Figure 7-2. Curves P and Q show the activity coefficients of 0.5 m and 1.0 m NaCl solutions as a function of temperature. On adding glycine to these two solutions

TABLE 7-5

The effect of sodium chloride on the activity coefficient of glycine in aqueous solution at 0°, 10°, 25° and 50°.

Tabulated values of $-\log \frac{\gamma_B}{\gamma_B^\circ}$ at rounded concentrations.

m_B	Temp. °C	m_c				
		0.01	0.05	0.07	0.10	0.20
0.5	0	0.0017	0.0076	0.0103	0.0141	0.0255
	10	0.0015	0.0068	0.0092	0.0127	0.0229
	25	0.0014	0.0062	0.0084	0.0115	0.0206
	50	0.0012	0.0054	0.0073	0.0100	0.0179
0.7	0	0.0016	0.0070	0.0094	0.0129	0.0234
	10	0.0014	0.0063	0.0086	0.0118	0.0213
	25	0.0013	0.0058	0.0079	0.0108	0.0192
	50	0.0011	0.0051	0.0069	0.0095	0.0170
1.0	0	0.0014	0.0060	0.0082	0.0112	0.0201
	10	0.0013	0.0057	0.0076	0.0105	0.0189
	25	0.0012	0.0052	0.0071	0.0096	0.0172
	50	0.0011	0.0048	0.0064	0.0088	0.0158
1.5	0	0.0010	0.0045	0.0061	0.0082	0.0147
	10	0.0010	0.0045	0.0061	0.0083	0.0148
	25	0.0010	0.0042	0.0057	0.0078	0.0137
	50	0.0009	0.0042	0.0056	0.0076	0.0137
2.0	10	0.0008	0.0033	0.0045	0.0061	0.0108
	25	0.0007	0.0032	0.0043	0.0059	0.0103
	50	0.0008	0.0036	0.0048	0.0065	0.0115
2.5	25	0.0005	0.0022	0.0030	0.0040	0.0069
	50	0.0007	0.0029	0.0040	0.0053	0.0094

(contd.)

TABLE 7-5 (contd.)

m_B	Temp. °C	m_c				
		0.01	0.05	0.07	0.10	0.20
3.0	25	0.0003	0.0012	0.0016	0.0021	0.0035
	50	0.0005	0.0023	0.0031	0.0042	0.0073
4.0	50	0.0003	0.0011	0.0015	0.0019	0.0031

Note:

$$1. \quad \log \left(\frac{\gamma_B}{\gamma_B^\circ} \right) = m_c \left(2B_{10} + \frac{4}{3} B_{11} m_c^{1/2} + B_{12} m_c + \frac{4}{5} B_{13} m_c^{3/2} \right) \\ + 4m_B m_c \left(B_{20} + \frac{2}{3} B_{21} m_c^{1/2} \right) \quad (7-5)$$

γ_B and γ_B° are the activity coefficients of glycine with and without sodium chloride respectively.

TABLE 7-6

The effect of sodium chloride on the activity coefficient of glycine in
aqueous solution at 0°, 10°, 25° and 50°.

Tabulated values of $-\log \frac{\gamma_B}{\gamma_B^\circ}$ at rounded concentrations.

m_B	Temp. °C	m_c				
		0.30	0.50	0.70	1.00	1.10
0.5	0	0.0357	0.0534	0.0687	0.0881	0.0937
	10	0.0319	0.0476	0.0612	0.0784	0.0835
	25	0.0284	0.0416	0.0529	0.0671	0.0712
	50	0.0248	0.0367	0.0468	0.0595	0.0632
0.7	0	0.0326	0.0489	0.0631	0.0812	0.0864
	10	0.0297	0.0443	0.0570	0.0733	0.0781
	25	0.0265	0.0389	0.0495	0.0632	0.0673
	50	0.0236	0.0350	0.0446	0.0568	0.0604
1.0	0	0.0281	0.0421	0.0546	0.0708	0.0756
	10	0.0263	0.0393	0.0507	0.0657	0.0702
	25	0.0237	0.0349	0.0446	0.0574	0.0614
	50	0.0219	0.0323	0.0413	0.0528	0.0562
1.5	0	0.0205	0.0309	0.0404	0.0534	0.0574
	10	0.0206	0.0310	0.0403	0.0530	0.0569
	25	0.0190	0.0281	0.0363	0.0478	0.0515
	50	0.0189	0.0280	0.0358	0.0461	0.0492
2.0	10	0.0150	0.0226	0.0298	0.0403	0.0437
	25	0.0142	0.0213	0.0280	0.0382	0.0416
	50	0.0159	0.0236	0.0303	0.0394	0.0422
2.5	25	0.0095	0.0145	0.0198	0.0285	0.0318
	50	0.0130	0.0192	0.0248	0.0327	0.0352

(contd.)

TABLE 7-6 (contd.)

m_B	Temp. °C	m_c				
		0.30	0.50	0.70	1.00	1.10
3.0	25	0.0048	0.0078	0.0115	0.0189	0.0219
	50	0.0100	0.0148	0.0193	0.0260	0.0282
4.0	50	0.0041	0.0060	0.0083	0.0125	0.0141

Note:

$$1. \quad \log \frac{\gamma_B}{\gamma_B^\circ} = m_c \left(2B_{10} + \frac{4}{3} B_{11} m_c^{1/2} + B_{12} m_c + \frac{4}{5} B_{13} m_c^{3/2} \right) + 4m_B m_c \left(B_{20} + \frac{2}{3} B_{21} m_c^{1/2} \right) \quad (7-5)$$

γ_B and γ_B° are the activity coefficients of glycine with and without sodium chloride respectively.

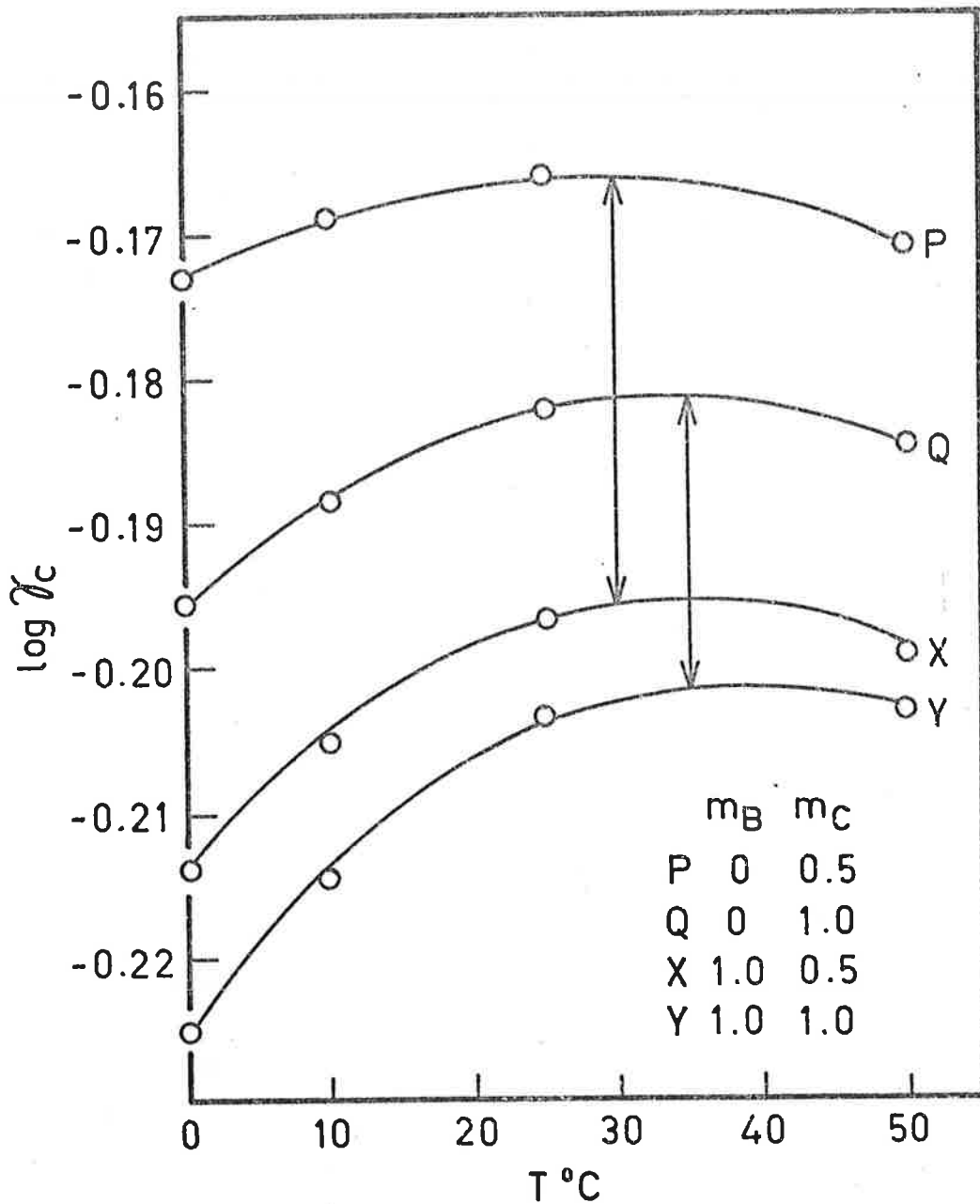


Fig. 7-2. The mean molal activity coefficient of NaCl (as $\log \gamma_c$) with and without glycine plotted as a function of temperature.

($m_B = 0 \rightarrow m_B = 1$), the chemical potential of sodium chloride decreases. This is shown by the decrease in $\log \gamma_c$ and the result is represented by curves X and Y. The decrease appears larger at 0° than at the other temperatures studied. By keeping m_B constant (at $m_B = 1.0$) and increasing m_c from 0.5 to 1.0, the activity coefficient of sodium chloride is again decreased. This is shown by the difference in the curves X and Y. By considering the pairs of curves P and Q, and X and Y, it can be seen that the decrease in $\log \gamma_c$ values (when m_c increases from 0.5 to 1.0) is larger in the absence of glycine. It is of interest to note that the addition of glycine appears to have shifted the maxima of $\log \gamma_c$ towards a higher temperature.

Figure 7-3 shows the activity coefficient of sodium chloride in 1 m glycine solution at 0° , 10° , 25° and 50° plotted as a function of its concentration. For the purpose of comparison, similar graphs have been plotted but this time without glycine. They are shown in Figure 7-4.

The lowering of the activity coefficients of sodium chloride by glycine and vice versa will be discussed in a later section under 'Salting-in and Salting-out'.

(ii) A Comparison with Literature Values

A comparison of the results obtained from this work with those of Joseph,⁵ and Scatchard and Prentiss⁶ is shown in Figure 7-5. Curves

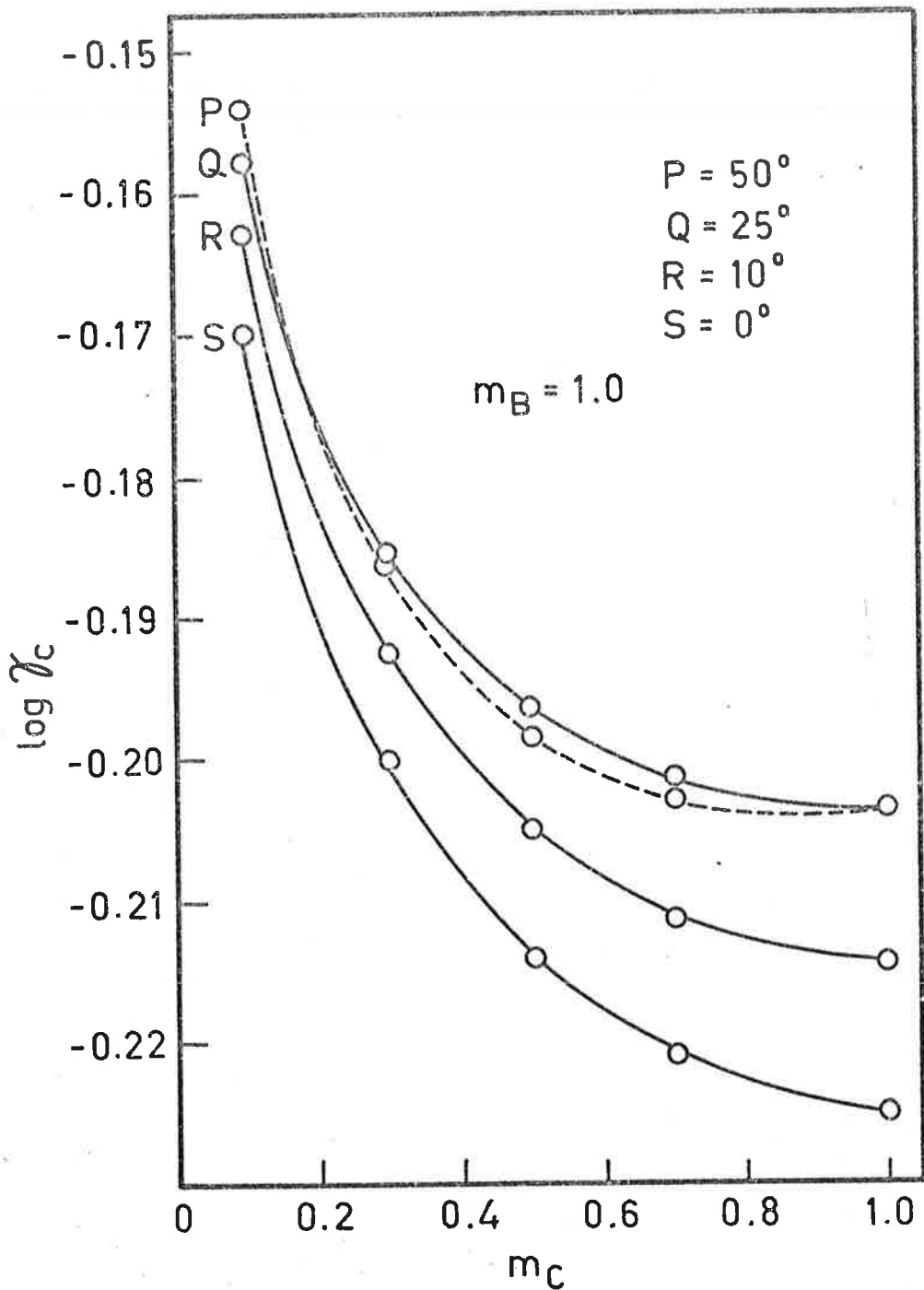


Fig. 7-3. The mean molal activity coefficient of NaCl (as $\log \gamma_c$) in Glycine-Water mixtures at various temperatures and at $m_B = 1.0$.

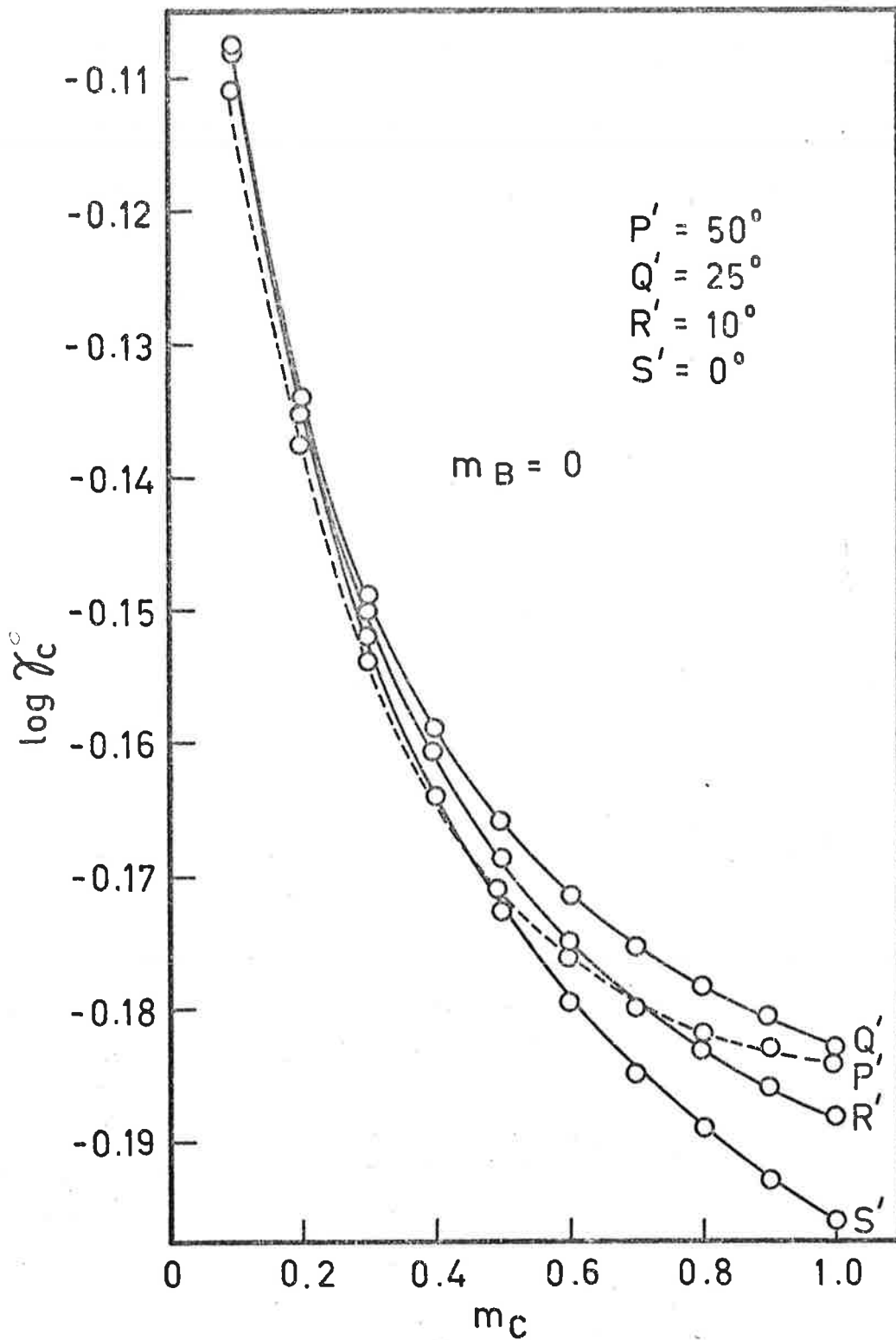


Fig. 7-4. The mean molal activity coefficient NaCl (as $\log \gamma_c^\circ$) in water at various temperatures.

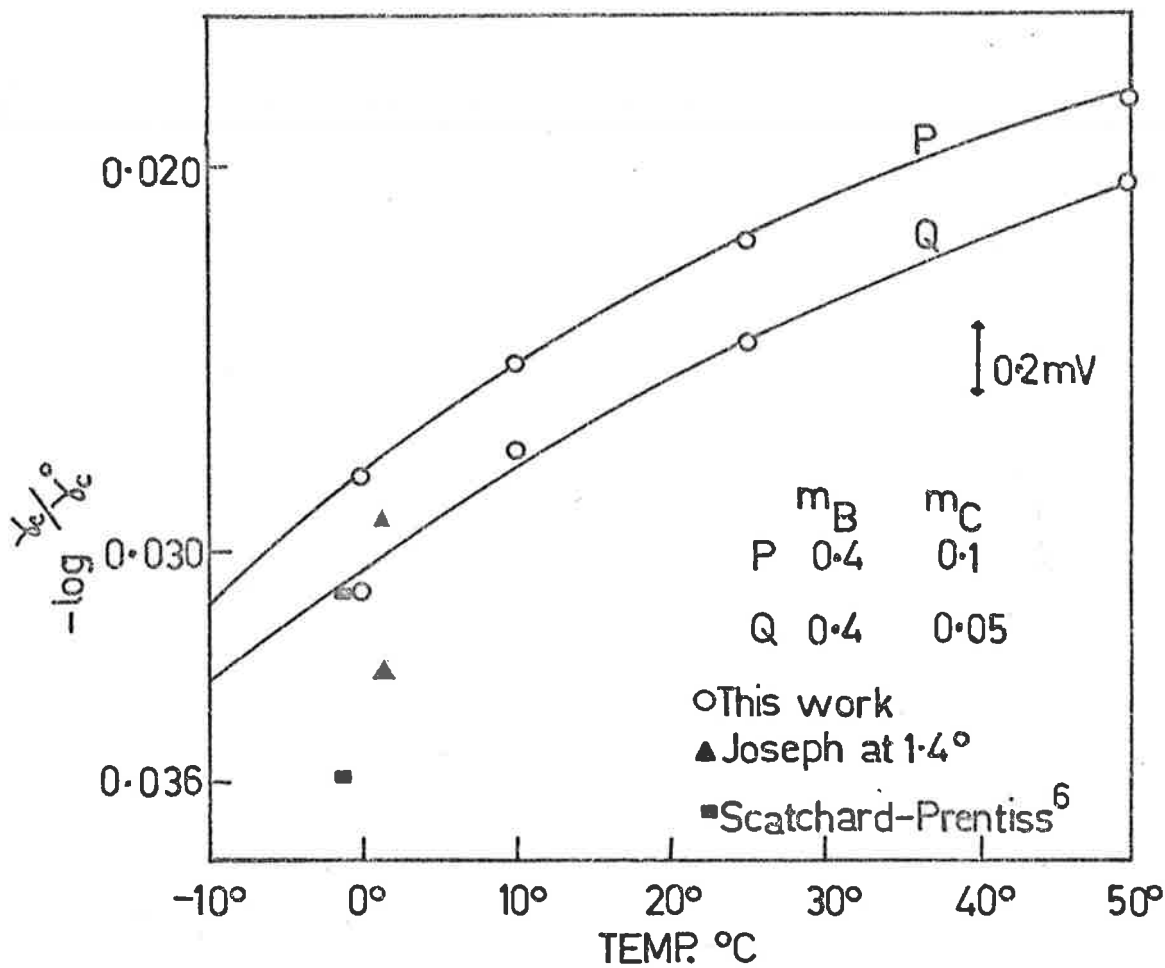


Fig. 7-5. A comparison of the results from this work with those of Joseph, and Scatchard and Prentiss.

P and Q are drawn using the results from this work for solutions of compositions $m_B = 0.4$, $m_c = 0.1$ and $m_B = 0.4$, $m_c = 0.05$. The subscripts B and c represent glycine and sodium chloride respectively.

Regarding the results of Scatchard and Prentiss, the depression of freezing point of water by glycine and sodium chloride was estimated by assuming ideal solute in water. The molal lowering of freezing point for water as solvent was taken as 1.86 and the estimated lowering of the freezing point was about 1° for both compositions. As shown in Figure 7-5, the values obtained by Joseph, and Scatchard and Prentiss were lower than those of this work. Joseph's results indicate deviations of about 0.15 mV from the curves P and about 0.3 mV from Q. Scatchard and Prentiss' results indicate deviations of about 0.3 mV from the curves P and about 0.5 mV from Q.

At 25° comparison with Joseph's work was only possible at one composition, namely, at $m_B = 0.5$ and $m_c = 1.0$. For the value of $\log \frac{\gamma_c}{\gamma_c^\circ}$ he obtained 0.006 as compared to -0.011 from this work, a difference of about 1.7 mV. At this composition his results, therefore, indicate slight salting-out of sodium chloride by glycine, whereas this work indicates salting-in. However, considering the experimental difficulties of his method (see Introduction) the results from this work should be more reliable. Joseph's other compositions at this temperature contained sodium chloride at 2 m, 3 m and 4 m - all of which were above the concentration covered in this work. It is interesting to

note that his results at 2 m, 3 m and 4 m NaCl indicated salting-out of sodium chloride by glycine and the salting-out increased with the concentration of NaCl. The results from this work shown in Table 7-3 for $m_B = 0.5$ at 25° shows the decrease in salting-in of NaCl as the value of m_c , the molality of NaCl increases. Such a trend is similar to that of Joseph's and it may well be that at 2 m, 3 m and 4 m NaCl, sodium chloride is salted-out by glycine.

(iii) The Effects of Electrolytes on Non-electrolytes in Aqueous Solutions and Vice Versa

The thermodynamics of the ternary system, Electrolyte (c) - Non-electrolyte (B) - Water at 25° , have been investigated for $c = \text{NaCl}$ with $B = \text{mannitol}$,¹⁰ sorbitol ,¹¹ and urea ¹² and also for $c = \text{KCl}$ with $B = \text{glycine}$.⁹ The influence of the electrolytes on the non-electrolytes are described by the values of $\log \frac{\gamma_B}{\gamma_B^\circ}$ and that of the non-electrolytes on the electrolytes by $\log \frac{\gamma_c}{\gamma_c^\circ}$. These values are presented in Table 7-7 for $m_B = m_c = 1$ and from them interesting comparisons can be obtained for the different systems.

As shown, the influence of NaCl on glycine at 25° is more than five times that of NaCl on urea and greater than that of KCl on glycine. At the same time, the influence of glycine on NaCl at 25° is more than five times that of urea on NaCl and greater than that of glycine on KCl. It is also shown that for the system NaCl-Glycine- H_2O , a decrease in

TABLE 7-7

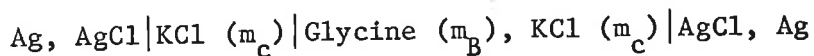
Values of $(-\log \frac{\gamma_B}{\gamma_B^\circ})$ and $(-\log \frac{\gamma_C}{\gamma_C^\circ})$ at $m_B = m_C = 1$.

Systems		$-\log \frac{\gamma_B}{\gamma_B^\circ}$	$-\log \frac{\gamma_C}{\gamma_C^\circ}$
NaCl-Glycine-H ₂ O	0°	0.0708	0.0290
"	10°	0.0657	0.0260
"	25°	0.0574	0.0215
"	50°	0.0528	0.0190
Sorbitol-NaCl-H ₂ O	25° ¹¹	0.0171	0.0101
Mannitol-NaCl-H ₂ O	25° ¹⁰	0.0048	0.0029
Urea-NaCl-H ₂ O	25° ¹²	0.0113	0.0043
Glycine-KCl-H ₂ O	25° ⁹	0.0471	0.0170

the temperature increases the magnitude of $\log \frac{\gamma_B}{\gamma_B^\circ}$ and $\log \frac{\gamma_c}{\gamma_c^\circ}$.

(iv) The Dipole Moment of the Glycine Molecule

Roberts and Kirkwood⁸ measured the emf of the cell,



and calculated therefrom the effect of glycine on the activity coefficient of potassium chloride. They expressed the activity coefficient of potassium chloride as a power series of m_B and m_c . The expression is represented by Equation 7-1.

By applying the cross-differentiation relationship (given by Equation 7-4) on Equation 7-1, one can also express the activity coefficient of glycine as a power series of m_B and m_c . Thus, Equation 7-1 is transformed into

$$\log \left(\frac{\gamma_B}{\gamma_B^\circ} \right) = m_c (2B_{10} + \frac{4}{3} B_{11} m_c^{1/2} + B_{12} m_c + 4B_{20} m_B) \quad (7-5)$$

which is equivalent to

$$\log \gamma_B = 2B_{10} m_c + \frac{4}{3} B_{11} m_c^{3/2} + B_{12} m_c^2 \quad (7-6)$$

when $m_B = 0$.

According to Kirkwood,¹⁴ the limiting slope of Equation 7-6, $2B_{10}$, can be used to calculate the dipole moment of the glycine dipolar ion. Using a spherical model of the glycine dipolar ion, he had obtained

a theoretical expression for the value of $2B_{10}$. Replacing the universal constants in the expression by their numerical values for water at 25°, one obtains⁸

$$2B_{10} = -5.48 \times 10^{-3} \mu^2/a + 4.66 \times 10^{-3} V_B/a \times \alpha(\rho) \quad (7-7)$$

where μ is the dipole moment of the dipolar ion in Debye units and V_B is the partial molal volume of the dipolar ion component. $a = b + r$, where b is the radius of the dipolar ion and r is the radius of the real ion. $\alpha(\rho)$ is a tabulated function¹⁴ where $\rho = b/a$. a , b and r are in Å units. For the glycine molecule $b = 2.82$ Å, and $V_B = 57$ ml.¹⁵

The first term on the right side of Equation 7-7 is due to the ion-dipole interaction and represents the 'salting-in' effect. This term gives rise to a decrease in the chemical potential of the dipolar ion by the electrolyte. The second term is due to the repulsion between the real ion and its image distribution in the cavity created by the dipolar ion in the solvent. This term represents the 'salting-out' effect and it gives rise to the increase in the chemical potential of the dipolar ion by the electrolyte.

Roberts and Kirkwood⁸ extrapolated their results to $m_B = 0$ and using Equation 7-7 calculated a value of 14.4 Debyes for the dipole moment of the glycine molecule. They had used $r = 1.38$ Å, where r was the arithmetic mean of the radii of the potassium and chloride ions. Recalculating with $r = 1.57$ Å (a value given by Gourary and Adrian¹⁶), $\mu = 14.3$ Debyes was obtained.

Subjecting the data at 25° of this research to a similar calculation, $\mu = 14.5$ Debyes was obtained. Equation 7-7 was used in the calculation. The value of $\alpha(\rho)$, taken from a graphical plot of ρ versus $\alpha(\rho)$, was found to be 1.285. The value of B_{10} , recorded in column six of Table 7-1, was used.

Other methods for calculating the dipole moment of the glycine molecule have also been made.

Eyring¹⁷ on statistical grounds developed an equation for the mean square distance between the ends of a straight chain molecule in which there was free rotation about all the valence bonds. Using this equation, Greenstein and Winitz¹⁸ have calculated the dipole moment of glycine in water at 25°. The value was 16 Debyes.

Buckingham¹⁹ has developed equations from the theoretical consideration of the dielectric properties in polar solvent solutions. The equations developed allowed the calculation of dipole moments of molecules in polar solvents. For glycine in water he obtained a value of 13.3 Debyes.

The result, calculated by multiplying the electronic charge (4.802×10^{-10} e.s.u.) by the charge separation (2.95×10^{-8} cm.), was 14.2 Debyes.

From a theoretical consideration, in which the glycine molecule was treated as spherical, and from the results of the solubility of glycine in alcohol-water mixtures at 25°, Kirkwood²⁰ calculated a value

of 15.0 Debyes as the dipole moment of the glycine molecule.

Thus the value obtained from this work for the dipole moment of glycine is reasonable and is in good agreement with literature values. Table 7-8 summarises the values obtained from the various methods.

(v) Salting-in and Salting-out

When an electrolyte or a non-electrolyte is dissolved in water, it shows its solvent properties in terms of the salting-in or the salting-out of the other components already present in the solution. For example, when component c is dissolved in a solution containing a component B, the solution which is formed can increase the solubility of B (salting-in of B) or it can decrease the solubility of B (salting-out of B).²¹

Apart from the measurement of solubility to interpret the type of behaviour, one can also measure the chemical potential of B with and without the presence of c. If the activity coefficient of B is decreased by adding c, then B is salted-in, and if it is increased then B is salted-out. The ternary system of sodium chloride-glycine-water will now be discussed along these lines.

From the activity coefficients recorded in Tables 7-2 and 7-3, it can be seen that sodium chloride is salted-in by glycine at 0°, 10°, 25° and 50°. The activity coefficient of sodium chloride is decreased when the concentration of glycine (m_B) is increased at fixed values of

TABLE 7-8

The dipole moment of the glycine molecule.

μ (Debyes)	Reference
14.4	Roberts and Kirkwood, ⁸ $r = 1.38 \text{ \AA}$
14.3	" $r = 1.57 \text{ \AA}$
14.5	This work $r = 1.57 \text{ \AA}$
16	Eyring Equation, ¹⁷ calculated by Greenstein and Winitz ¹⁸
13.3	Theoretical estimation by Buckingham ¹⁹
14.2	Electronic charge X Charge separation
15.0	Kirkwood, ²⁰ solubility of glycine in alcohol-water mixtures at 25°

m_c and temperature. This behaviour is shown in Figure 7-6 where the activity coefficients of sodium chloride at 25° and 50° are plotted as $(\log \frac{\gamma_c}{\gamma_c^o})$ versus m_B , the molality of glycine. The limiting slope of each curve measures the salting-in coefficient of sodium chloride. Figure 7-6 shows that at a higher salt concentration sodium chloride becomes less salted-in. Also, the salting-in of sodium chloride is decreased with an increase in temperature. An examination of Tables 7-2 and 7-3 indicate that the latter behaviour exists at every given value of m_c .

The activity coefficients of glycine recorded in Tables 7-5 and 7-6 show that glycine is salted-in by sodium chloride at 0°, 10°, 25° and 50°. In Figure 7-7 the activity coefficients of glycine (as $\log \frac{\gamma_B}{\gamma_B^o}$) at 25° and 50° are plotted against m_c , the molality of sodium chloride. At a given temperature, the salting-in of glycine is decreased with an increase in the value of m_B , the molality of glycine. At a lower value of m_B , an increase in temperature decreases the salting-in of glycine by sodium chloride. This is shown in Figure 7-7 by the R curves. However, at a higher value of m_B an increase in temperature increases the salting-in of glycine. This is shown by the curves P and Q. Until more is known about salting-in and salting-out of electrolytes and non-electrolytes as a function of temperature, any explanation given here is speculative.

Recently, Erlander⁴⁷ using the solubility data of Pfeiffer and

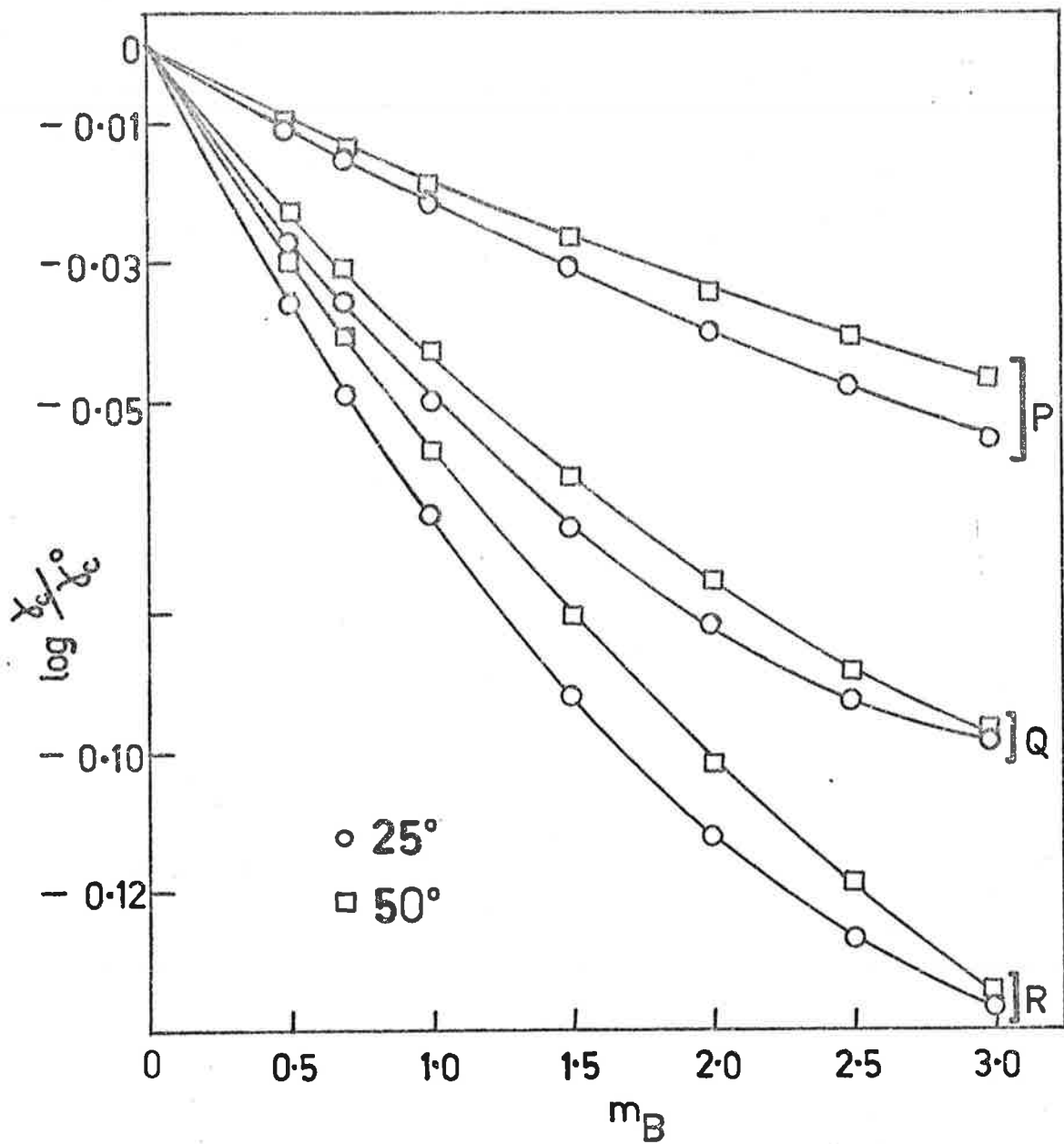


Fig. 7-6. Salting-in of sodium chloride by glycine at 25° and 50°. Curves enclosed by P represent $m_c = 1.0$; that by Q represent $m_c = 0.1$; and that by R represent $m_c = 0.01$.

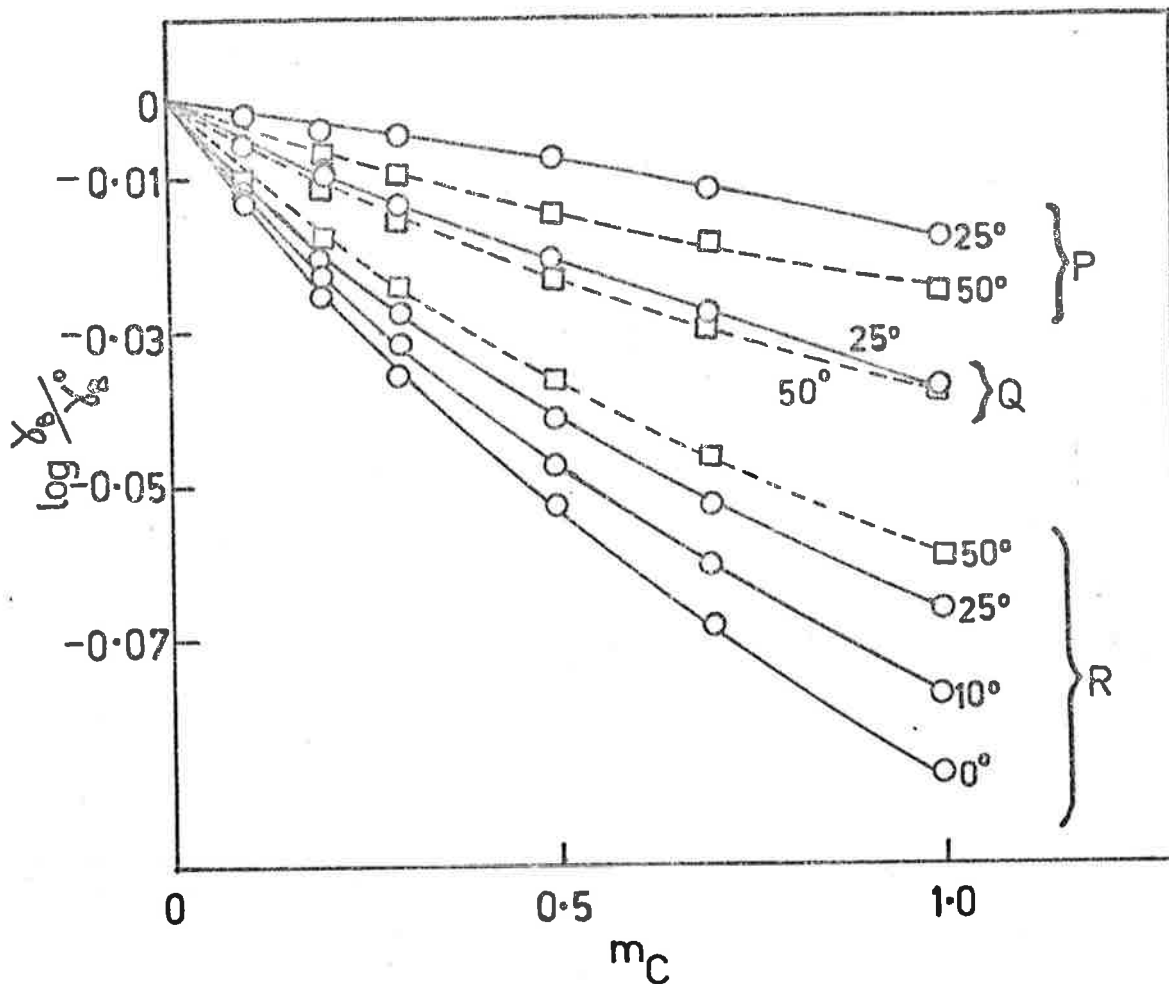
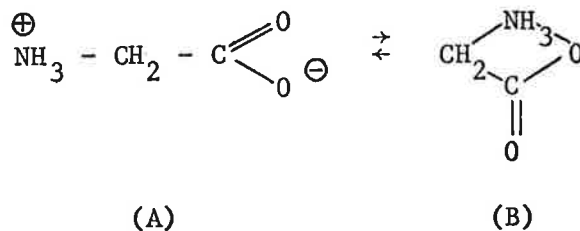
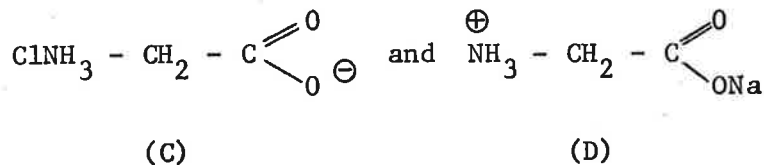


Fig. 7-7. Salting-in of glycine by sodium chloride. Curves enclosed by P represent $m_B = 3.0$; those by Q represent $m_B = 2.0$; and those by R represent $m_B = 0.5$.

Würgler,⁴⁸ has proposed an explanation for the salting-in of glycine by the alkali and alkaline earth halides. Glycine in water was considered as a dipolar ion in which the negatively charged carboxylate group and the positively charged amino group were continually forming ion-ion bonds.



The process was considered to be in dynamic equilibrium. On addition of a salt, MX, one of its ions forms an insoluble complex with either the carboxylate or the amino group. This results in the amino acid forming a permanent electrostatic charge and hence increasing its solubility in the solution. If both the anion and cation of the added salt form ion-ion complex with the molecule (A) which is more insoluble than the ion-ion complex of the amino acid, (B), then the amino acid is salted-out. Such an explanation when applied to the salting-in of glycine by sodium chloride presupposes the existence of complexes such as



At present there appears to be no direct experimental evidence for the existence of complexes (C) and (D). It is of interest to note that Davies and Waind⁴⁹ assumed that sodium glycinate was fully dissociated when they determined the dissociation constants of calcium amino acid and calcium dipeptide complexes. Lewis and co-workers⁵⁰ have measured the molecular weight of glycine in water with and without the presence of sodium chloride using the depression of freezing point method. In the absence of sodium chloride, they ascribed the increase in the apparent molecular weight of glycine to actual polymerisation of the zwitterions. In the presence of sodium chloride a further increase in the apparent molecular weight of glycine was obtained. They showed that the increased osmotic abnormality could not be ascribed to further polymerisation. More important to this discussion, they showed that the extent of complex formation between glycine and chloride ion was probably too small to account for more than a part of the abnormality. The type of explanation given by Erlander⁴⁷ may therefore need more experimental evidence.

(vi) Correlation of Activity Coefficients with Dielectric Constants

Lanier⁷ has examined $\log \gamma_c^*$ at $m_c = 0$ in the light of the Born equation. γ_c^* is the activity coefficient of sodium chloride in the limit when $m_c = 0$. A convenient form of the equation for sodium chloride in water-organic mixtures was obtained by Lanier from an

equation first derived by Scatchard.²⁷ The ions were considered as charged rigid spheres, all with the same distance of closest approach and the solvent was a continuum characterised only by its dielectric constant. Accordingly, the equation can be represented by

$$\log \gamma_c^* - \log X = \frac{\epsilon^2}{4.606 DkT} \left(\frac{1 - \rho}{\rho b} \right) \quad (7-8)$$

X is the mole fraction of water; ϵ , the charge of the electron; D, the dielectric constant of water. D° , the dielectric constant of the water-organic phase; $\rho = \left(\frac{D^\circ}{D} \right)$; T, the absolute temperature; k, the Boltzmann constant and b, the radius of the ions in water, such that for sodium chloride

$$\frac{1}{b} \equiv \frac{1}{2} \left(\frac{1}{b_+} + \frac{1}{b_-} \right) \quad (7-9)$$

If the left side of Equation 7-8 is plotted against $(1 - \rho)/\rho$, a straight line, whose slope is proportional to $\frac{1}{b}$, should be obtained.

The data at 25°, 50°, 10° and 0° of this research have been examined, similar to the manner in which Lanier⁷ examined his results. Since the densities of glycine-water mixtures are not available at temperatures other than at 25°, an assumption was made in which the densities of the glycine-water mixtures at 50°, 10° and 0° were equivalent to that at 25°. This meant that the molarities at 50°, 10° and 0° equalled that at 25° when used in the calculation of D° . The results of the calculations are shown in Table 7-9.

Figure 7-8 shows a plot of $\Delta = (\log \gamma_c^* - \log X)$ versus $\left(\frac{1 - \rho}{\rho} \right)$.

TABLE 7-9

Correlation of activity coefficients with dielectric constants for
NaCl-Glycine-Water at 25° and 50°.

	m_B					
	0.5	1.0	1.5	2.0	2.5	3.0
25°						
$-\log \gamma_c^*$	0.0412	0.0767	0.1064	0.1303	0.1486	0.1610
$-\log X$	0.0039	0.0078	0.0117	0.0154	0.0191	0.0228
Δ	-0.0373	-0.0689	-0.0947	-0.1149	-0.1295	-0.1382
D°	89.69	100.4	110.6	120.4	129.7	138.7
$\frac{1-\rho}{\rho}$	-0.126	-0.219	-0.291	-0.349	-0.396	-0.435
50°						
$-\log \gamma_c^*$	0.0345	0.0655	0.0933	0.1174	0.1382	0.1555
$-\log X$	0.0039	0.0078	0.0117	0.0154	0.0191	0.0228
Δ	-0.0306	-0.0577	-0.0816	-0.1020	-0.1191	-0.1327
D°	79.49	88.64	97.40	105.8	113.8	121.5
$\frac{1-\rho}{\rho}$	-0.120	-0.211	-0.282	-0.339	-0.385	-0.424

(contd.)

TABLE 7-9 (contd.)

	m_B					
	0.5	1.0	1.5	2.0	2.5	3.0
10°						
$-\log \gamma_c^*$	0.0444	0.0823	0.1136	0.1384		
$-\log X$	0.0039	0.0078	0.0117	0.0154		
Δ	-0.0405	-0.0745	-0.1019	-0.1230		
D°	96.15	107.8	119.0	129.7		
$\frac{1-\rho}{\rho}$	-0.127	-0.221	-0.294	-0.352		
0°						
$-\log \gamma_c^*$	0.0505	0.0922	0.1253			
$-\log X$	0.0039	0.0078	0.0117			
Δ	-0.0466	-0.0844	-0.1136			
D°	100.7	113.1	124.8			
$\frac{1-\rho}{\rho}$	-0.127	-0.222	-0.295			

(contd.)

TABLE 7-9 (contd.)

Notes:

1. In the limit when $m_c = 0$

$$\log \gamma_c^* = -0.08822 m_B + 0.011518 m_B^2 \text{ at } 25^\circ$$

$$\log \gamma_c^* = -0.07244 m_B + 0.006865 m_B^2 \text{ at } 50^\circ$$

$$\log \gamma_c^* = -0.09544 m_B + 0.013126 m_B^2 \text{ at } 10^\circ$$

$$\log \gamma_c^* = -0.10965 m_B + 0.017437 m_B^2 \text{ at } 0^\circ$$

γ_c^* is the mean molal activity coefficient of NaCl in the limit when $m_c = 0$. The parameters of Equation 7-3 (shown in Table 7-1) were used.

2. $\Delta = \log \gamma_c^* - \log X$.

3. $\rho = D^\circ/D$ where D , the dielectric constant of water, equals 78.34 at 25° , 69.91 at 50° , 83.98 at 10° and 87.92 at 0° .²⁶ D° is the dielectric constant of the glycine solution. $D^\circ = \delta \times \text{Molarity} + D$, where δ is the dielectric increment of glycine in water.

$$\delta = 22.85 \text{ at } 25^\circ, 19.58 \text{ at } 50^\circ, 24.94 \text{ at } 10^\circ \text{ and } 26.28 \text{ at } 0^\circ. \text{ }^{31}$$

4. The molarity, c , was calculated by the method of successive approximation of the equation

$$c = m(D^\circ - \frac{cM}{1000})$$

where $M \equiv$ Molecular weight of glycine (75.07), $D^\circ \equiv$ Density of glycine solution at 25° given by Dunlop et al.³⁰

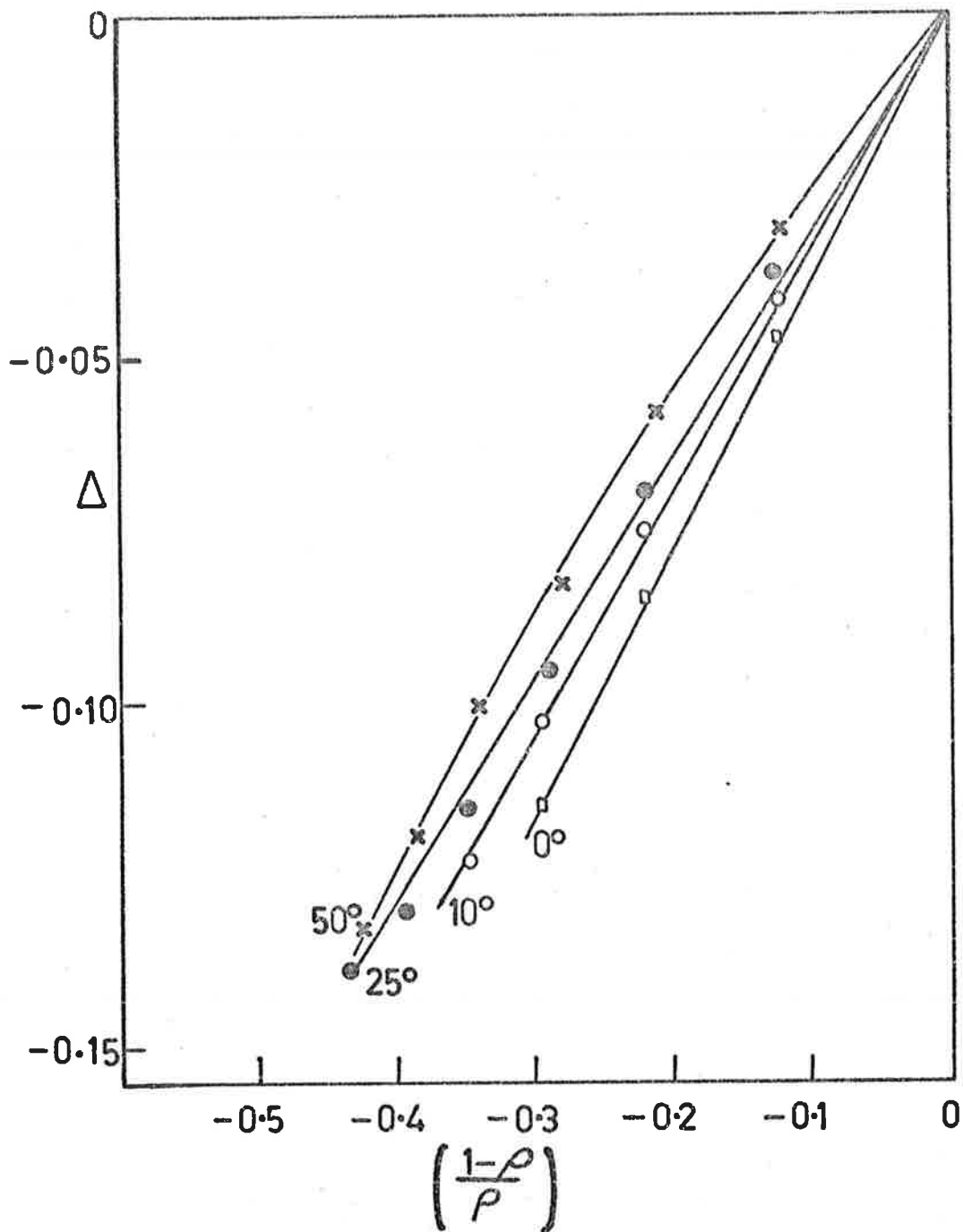


Fig. 7-8. Plotting of Equation 7-11: Δ versus $\left(\frac{1-\rho}{\rho}\right)$ at 0° , 10° , 25° and 50° .

Straight lines were obtained at 25°, 10° and 0°, whereas at 50° the line was slightly concave. Lanier⁷ had studied the ternary system of NaCl-organic compound-H₂O, where the organic compounds were methanol, ethylene glycol, diethylene glycol monoethyl ether, dioxane, urea, and dimethylformamide. In a graphical plot similar to that shown in Figure 7-8, he obtained slight concavity for all his systems. All except urea decreased the dielectric constant of water. Glycine, which was used in this research, increases the dielectric constant of water.

The slope of the 25° graph was found to be 0.32 and by Equation 7-8

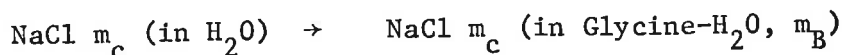
$$0.32 = \frac{\epsilon^2}{4.606 DkTb} \quad (7-10)$$

Substituting numerical values for the universal constants in Equation 7-10, b, the ionic radius of sodium chloride was found to be 4.8 Å. The estimated ionic radius for sodium chloride in water at 25° from transport experiments gave a value of 5.1 Å.²⁸ Considering the simplicity and limitations of the Born model such an agreement was good.

(vii) Free Energies of Transfer and the Primary Medium Effect

The free energies of transfer of sodium chloride, ΔG_t , from water to the mixed solvent, glycine-water, have been calculated and the results are presented in Table 7-9. The transfer can be considered

as



ΔG_t is calculated from the equation,

$$\Delta G_t = 2RT \ln \frac{f}{f^\circ} \quad (7-11)$$

f and f° are activity coefficients of sodium chloride in the mole fraction scale in the glycine-water mixture and in water respectively. The conversion from molal to mole fraction scale involving mixed solvents is given by Harned and Owen.²²

For comparison, the values calculated from other systems have also been included in Table 7-10. Those of Methanol-NaCl-H₂O Ethylene glycol-NaCl-H₂O were taken from the emf measurements of Gladden and Fanning.²⁴ They have also measured the transfer of KCl from ethylene glycol and from methanol to water, but these values have not been included for comparison. For the Mannitol-NaCl-H₂O system, the value was taken from the isopiestic measurements of Kelly, Robinson and Stokes.¹⁰ For the Glycine-KCl-H₂O system, both the results of Bower and Robinson,⁹ and Roberts and Kirkwood⁸ have been included, although in the experiments of the latter authors the concentration of glycine did not exceed 0.5 m. Recently, Wen and Chen⁴⁶ measured the activity coefficients of urea and tetraalkyl ammonium bromide at 25° for the ternary systems, Urea-Tetramethylammonium Bromide (Me₄NBr)-H₂O and Urea-Tetrabutylammonium Bromide (Bu₄NBr)-H₂O. They employed the

TABLE 7-10

Free energies of transfer, ΔG_t cal. mole⁻¹ of electrolyte from water to non-electrolyte-water mixtures.

m_c	System	m_B		
		1	2	3
0	0°	-211	-	-
0	10°	-193	-319	-
0	25°	-188	-314	-377
0	50°	-171	-298	-390
1	0°	-70.5	-	-
1	10°	-65.3	-115	-
1	25°	-56.5	-105	-143
1	50°	-53.8	-98	-133
0	Methanol-NaCl ^{24,*}	4700		
0	Mannitol-NaCl ^{10,*}	13.6		
0	Glycine-KCl ^{9,*}	-110		
0	Glycine-KCl ^{8,*}	-194		
0	Ethylene glycol-NaCl ^{24,*}	1380		
0	Urea-NaCl ^{12,*}	-2.2	1.1	
0	Urea-Me ₄ NBr ^{46,*}	-117	-214	-296
0	Urea-Bu ₄ NBr ^{46,*}	-133	-247	-345
1	Urea-NaCl ^{26,*}	11	22	
1	Urea-Me ₄ NBr ^{46,*}	-63	-120	-165
1	Urea-Bu ₄ NBr ^{46,*}	-107	-202	-287

Notes:

- Where only temperatures are indicated in the second column, the results represent those of this work for the system Glycine-NaCl-H₂O.
- * The third component is water and the experiments were carried out at 25°.
- $\Delta G_t = 4.606 RT \log \frac{f}{f^\circ}$.

isopiestic vapour pressure method for their measurements. They have calculated the free energies of transfer of R_4NBr from water to urea solution and compared the values with those of Bower and Robinson²⁶ for the transfer of sodium chloride from water to urea-water mixtures. Bower and Robinson had also employed the isopiestic vapour pressure method. Values from these two sources have also been included in Table 7-10.

The ΔG_t values of this work are all negative. Because of the limited solubility of glycine at lower temperatures, ΔG_t at $m_B = 2$ and 3 could not be calculated at 0°. Similarly, no values are given for $m_B = 3$ at 10°.

ΔG_t values at $m_c = 0$ is of considerable interest. The quantity is a measure of the primary medium effect²³ since at infinite dilution in either medium, interionic effects are absent. One is therefore measuring only the effects due to ion-solvent interactions. ΔG_t in this instance can be imagined as the free energy change in the transfer of a pair of ions from water to the non-electrolyte-water mixture. ΔG_t values at $m_c = 0$ have been calculated for other systems by Robinson and Stokes²⁵ and by Bower and Robinson.²⁶

(viii) Some Thermodynamic Properties from the Dependence of Activity Coefficients on Temperature

The variation of the activity coefficient with temperature can yield important thermodynamic data such as partial molal heat content and

partial molal heat capacity. An equation relating the activity coefficient to these thermodynamic terms will now be derived and then used in the discussion.

Consider the binary system of NaCl-H₂O. By definition, the mean molal activity coefficient γ_c° of sodium chloride of molality m_c is given by

$$\mu_c = \mu_c^\ddagger + 2RT \ln m_c \gamma_c^\circ \quad (7-12)$$

μ_c is the chemical potential and μ_c^\ddagger is that at the standard state. Rearranging Equation 7-11 and differentiating at constant pressure and composition one obtains

$$\begin{aligned} \frac{\partial}{\partial T} \left(\frac{\mu_c^\ddagger}{T} \right)_{p,m} &= \frac{\partial}{\partial T} \left(\frac{\mu_c}{T} \right)_{p,m} - 2R \frac{\partial}{\partial T} (\ln \gamma_c^\circ)_{p,m} \\ &= \left(-\frac{\bar{H}_c}{T^2} \right) - 2R \frac{\partial}{\partial T} (\ln \gamma_c^\circ)_{p,m} \end{aligned} \quad (7-13)$$

\bar{H}_c is the partial molal heat content of sodium chloride in the solution under discussion. Since $\gamma_c^\circ \rightarrow 1$ as $m_c \rightarrow 0$, then by Equation 7-13,

$$\frac{\partial}{\partial T} \left(\frac{\mu_c^\circ}{T} \right)_{p,m} = \left(-\frac{\bar{H}_c^\circ}{T^2} \right) \quad (7-14)$$

\bar{H}_c° is the partial molal heat content at infinite dilution.

Combining Equations 7-13 and 7-14,

$$\frac{\partial}{\partial T} (\ln \gamma_c^\circ)_{p,m} = \left(\frac{\bar{H}_c^\circ - \bar{H}_c}{2RT^2} \right) \quad (7-15)$$

By writing $\bar{L}_2 = (\bar{H}_c - \bar{H}_c^\circ)$ one obtains from Equation 7-15

$$\frac{\partial}{\partial T} (\ln \gamma_c^\circ)_{p,m} = - \frac{\bar{L}_2}{2RT^2} \quad (7-16)$$

Also,

$$\frac{\partial}{\partial T} (\bar{L}_2)_{p,m} = \bar{J}_2 \quad (7-17)$$

\bar{L}_2 and \bar{J}_2 denote the relative partial molal heat content and the relative partial molal heat capacity respectively of sodium chloride in the binary system of NaCl-H₂O. Both \bar{L}_2 and \bar{J}_2 are relative to infinite dilution in water at which $\bar{L}_2 = 0$ and $\bar{J}_2 = 0$.

Robinson and Harned³² have shown that the activity coefficient of sodium chloride in water can be expressed as a function of temperature in the form:

$$\log \gamma_c^\circ = I - \frac{A}{T} - B \log T \quad (7-18)$$

where I, A and B are empirical coefficients in the equation. By substituting Equation 7-18 into Equation 7-16 and 7-17 it can be shown that

$$\bar{L}_2 = 2BRT - 4.606 AR \quad (7-19)$$

and

$$\bar{J}_2 = 2BR \quad (7-20)$$

The values of γ_c° for the binary system, NaCl-H₂O, taken from this research have been used to calculate the values of \bar{L}_2 and \bar{J}_2 at 25°.

For a given concentration, the γ_c° values at 0° , 10° , 25° and 50° were fitted to Equation 7-18 by the method of least squares in order to obtain the best values for the coefficients I, A and B. A computer program written for the least square calculations is given in Appendix C. Equations 7-19 and 7-20 were then used to calculate values of \bar{L}_2 and \bar{J}_2 at 25° . The results are presented in Table 7-11 in the column under TW. They are then compared with literature values. Values under R were taken from the isopiestic results of Robinson.³³ Those under G were taken from the calorimetric results of Gulbransen and Robinson^{34,35} (the values at 0.3, 0.5, and 0.7 m by graphical interpolation). Those under Y were the calorimetric results of Young and Vogel.³⁶ A graphical comparison was made with the results of Gulbransen and Robinson and is shown in Figure 7-9. The disagreement is largest (about 45 cal.) at 0.1 m. As shown in Table 7-11, the disagreement in \bar{J}_2 with literature values is also significant.

In calculating \bar{L}_2 and \bar{J}_2 by the emf method, the original data are subjected to a very severe test since these determinations involve the first and second differential coefficients of the original data. For this reason, as pointed out by Harned and Owen,³⁷ the calorimetric determinations should yield the better result except in cases where the emfs can be measured with extreme accuracy. However, the emf method will permit a comprehensive view of the behaviour of \bar{L}_2 and \bar{J}_2 . It has been calculated that an error of 0.001 mV/deg. in the temperature

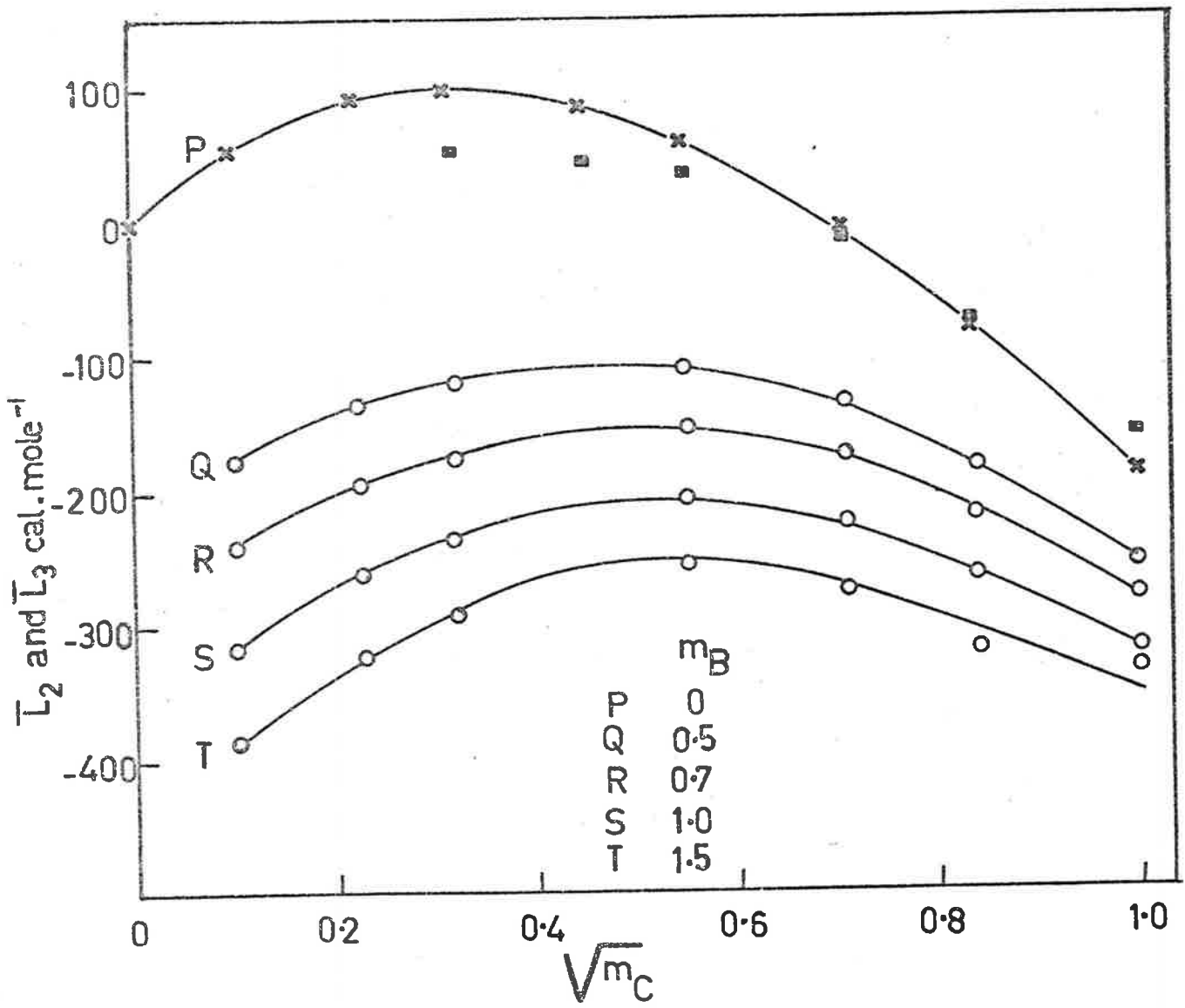
TABLE 7-11

\bar{L}_2 (cal. mole⁻¹) and \bar{J}_2 (cal. mole⁻¹ deg.⁻¹) of NaCl in binary system,
NaCl-H₂O at 25°.

m_c	\bar{L}_2				\bar{J}_2		
	TW	R	G	Y	TW	R	G
0.1	54	95	99.6	94	3.9	4.5	5
0.2	47	70	85.0	78	7.6	5.7	7.1
0.3	36	35	62	50	10.9	7.4	
0.5	-9	-31	-4	-19	14.8	10.3	11.2
0.7	-73	-117	-87	-85	16.6	11.9	
1.0	-162	-191	-188	-186	18.9	14.1	15.6

Notes:1. TW \equiv This workR \equiv Robinson³³G \equiv Gulbransen and Robinson^{34,35}Y \equiv Young and Vogel³⁶

Fig. 7-9. The relative partial molal heat content of aqueous sodium chloride (\bar{L}_2) and of sodium chloride in glycine-water mixtures (\bar{L}_3) at 25°. X represents NaCl-H₂O values of Gulbransen and Robinson.^{34,35} ■ NaCl-H₂O, values from this work. (TW) shown in Table 7-11.



coefficient will result in an error of 7 calories for \bar{L}_2 . Thus according to Harned and Cook³⁸ and White,³⁹ an error of ± 30 calories was the order of magnitude to be expected from emf measurements.

The activity coefficients of sodium chloride in the ternary system of NaCl-Glycine-H₂O were also subjected to a similar calculation for the relative partial molal heat content and heat capacity. In this system \bar{L}_3 and \bar{J}_3 denote the relative partial molal heat content and the relative partial molal heat capacity respectively, of sodium chloride in the glycine-water mixture. Like \bar{L}_2 and \bar{J}_2 , \bar{L}_3 and \bar{J}_3 are relative to infinite dilution in water. The activity coefficients were first fitted to Equation 7-18 by the method of least squares. Then using Equations 7-19 and 7-20, \bar{L}_3 and \bar{J}_3 were calculated at 25°. The results are presented in Table 7-12 together with the parameters for Equation 7-18. It was found that all the values of \bar{L}_3 were negative and all those of \bar{J}_3 were positive. In Figure 7-9 values of \bar{L}_2 and \bar{L}_3 were plotted against $m_c^{1/2}$. Curve P represents the values of \bar{L}_2 . Curves Q, R, S and T are those of \bar{L}_3 and they include values at $m_c = 0.01$ and $m_c = 0.05$.

Consider $m_c = 0.1$ in the binary system. \bar{L}_2 is then the heat change when a mole of sodium chloride is transferred from infinite dilution to the concentration at which $m_c = 0.1$. If one considers for example, $m_c = 0.1$ and $m_b = 0.5$ in the ternary system, then \bar{L}_3 is the heat change when a mole of sodium chloride is transferred from

TABLE 7-12

\bar{L}_3 (cal. mole⁻¹) and \bar{J}_3 (cal. mole⁻¹ deg.⁻¹) of NaCl in ternary system, NaCl-Glycine-H₂O at 25°. I, A and B are parameters for Equation 7-18.

m_B	Parameters	m_C				
		0.1	0.3	0.5	0.7	1.0
0.5	I	5.3699	11.1586	14.1307	15.1776	16.1222
	A	256.11	514.09	649.46	700.98	749.41
	B	1.8775	3.8809	4.9042	5.2603	5.5780
	\bar{L}_3	-121	-109	-136	-186	-253
	\bar{J}_3	7	15	20	21	22
0.7	I	6.2569	12.2524	15.2033	16.1744	16.6315
	A	300.97	567.13	701.24	748.91	775.05
	B	2.1790	4.2539	5.2698	5.6002	5.7508
	\bar{L}_3	-174	-153	-177	-222	-283
	\bar{J}_3	9	17	21	22	23
1.0	I	7.2391	13.4666	16.5522	17.5020	17.2624
	A	350.92	626.50	766.04	812.46	807.02
	B	2.5135	4.6681	5.7305	6.0535	5.9649
	\bar{L}_3	-235	-206	-225	-267	-322
	\bar{J}_3	10	19	23	24	24
1.5	I	8.1435	14.8268	17.8207	18.4759	13.6391
	A	396.97	692.43	827.96	861.19	647.64
	B	2.8242	5.1341	6.1641	6.3855	4.7208
	\bar{L}_3	-289	-257	-278	-320	-337
	\bar{J}_3	11	20	25	25	19

infinite dilution in water to the concentration at which $m_c = 0.1$ and $m_B = 0.5$. The difference in the values of \bar{L}_2 and \bar{L}_3 represents a heat change due only to the presence of glycine. It can be considered as the heat change in the transfer of a mole of sodium chloride from a solution in which $m_c = 0.1$ and $m_B = 0$ to one in which $m_c = 0.1$ and $m_B = 0.5$. The partial molal enthalpy of transfer of sodium chloride from water to the glycine-water mixture, $\bar{\Delta H}_t$, is therefore represented by the difference between the curve P and the others in Figure 7-9. In general,

$$\bar{\Delta H}_t = \bar{L}_3 - \bar{L}_2 \quad (7-21)$$

The enthalpies of transfer in combination with free energies of transfer, $\bar{\Delta G}_t$, where

$$\bar{\Delta G}_t = 4.606 RT \log \frac{\gamma_c}{\gamma_c^\circ} \quad (7-22)$$

yield the partial molal entropies of transfer, $\bar{\Delta S}_t$, where

$$\bar{\Delta S}_t = \frac{\bar{\Delta H}_t - \bar{\Delta G}_t}{T} \quad (7-23)$$

It should be noted that $\bar{\Delta G}_t$ calculated using Equation 7-22 is different from that using Equation 7-11. For the composition $m_B = 1$, $m_c = 1$, $\bar{\Delta G}_t = -58.7 \text{ cal. mole}^{-1}$, whereas ΔG_t from Equation 7-11 yields $-56.5 \text{ cal. mole}^{-1}$ at 25° . Table 7-13 shows the calculated values of $\bar{\Delta H}_t$, $\bar{\Delta G}_t$ and $T\bar{\Delta S}_t$. In calculating $\bar{\Delta H}_t$ from Equation 7-21,

TABLE 7-13

The partial molal free energy, enthalpy, and entropy of transfer at 25°.

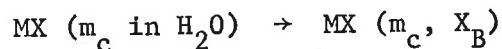
m_B	Thermo- dynamic quantities	0.1	0.3	m_c 0.5	0.7	1.0
0	\bar{L}_2	99.6	62	-4	-87	-188
0.5	\bar{L}_3	-121	-109	-136	-186	-253
	$\overline{\Delta H}_t$	-221	-171	-132	-99	-65
	$\overline{\Delta G}_t$	-73.4	-54.0	-44.2	-37.7	-30.3
	$T\overline{\Delta S}_t$	-148	-117	-88	-61	-35
0.7	\bar{L}_3	-174	-153	-177	-222	-283
	$\overline{\Delta H}_t$	-274	-215	-173	-135	-95
	$\overline{\Delta G}_t$	-99.3	-73.4	-60.3	-51.6	-42.0
	$T\overline{\Delta S}_t$	-175	-142	-113	-83	-53
1.0	\bar{L}_3	-235	-206	-225	-267	-322
	$\overline{\Delta H}_t$	-335	-268	-221	-180	-134
	$\overline{\Delta G}_t$	-135	-100	-82.7	-70.9	-58.7
	$T\overline{\Delta S}_t$	-200	-168	-138	-109	-75
1.5	\bar{L}_3	-289	-257	-278	-320	-337
	$\overline{\Delta H}_t$	-389	-319	-274	-233	-149
	$\overline{\Delta G}_t$	-186	-138	-115	-100	-85.1
	$T\overline{\Delta S}_t$	-203	-181	-159	-133	-64

Notes:

- \bar{L}_3 and \bar{L}_2 are relative partial molal enthalpies of NaCl with and without the presence of glycine respectively. \bar{L}_2 are values taken from the calorimetric data of Gulbransen and Robinson.^{34,35}
- $\overline{\Delta H}_t = \bar{L}_3 - \bar{L}_2$, $\overline{\Delta G}_t = 4.606 RT \log \gamma_c / \gamma_c^\circ$, $T\overline{\Delta S}_t = \overline{\Delta H}_t - \overline{\Delta G}_t$.
- $\overline{\Delta H}_t$ and $\overline{\Delta G}_t$ are in cal. mole⁻¹.

\bar{L}_2 values of Gulbransen and Robinson^{34,35} were used. In Figures 7-10 and 7-11 $\bar{\Delta G}_t$, $\bar{\Delta H}_t$ and $T\bar{\Delta S}_t$ are plotted versus m_B (the molality of glycine) for $m_c = 0.5$ and $m_c = 1.0$ respectively. $\bar{\Delta G}_t$, $\bar{\Delta H}_t$ and $\bar{\Delta S}_t$ were all found to be negative. Because of the negative values of $\bar{\Delta S}_t$, sodium chloride in glycine-water mixtures may find itself in a more 'structured' environment than in pure water. Frank and Evans,⁴⁰ and Stern⁴¹ have made some attempts to relate $\bar{\Delta S}_t$ to structural changes in the solutions. Since there is a lack of such data in the literature and because of the complex nature of the interactions no attempts will be made here.

Stern and co-workers have investigated the heat of transfer of ethyl acetate,⁴⁰ nitromethane,³ and acetic acid⁴² from pure water to various aqueous electrolyte solutions via calorimetry. Using similar methods they have also investigated the heat of transfer of an electrolyte from pure water to non-electrolyte solutions, e.g. HCl to acetic acid,⁴³ LiCl, LiBr, KCl, KBr to acetic acid, and KCl to CH_3NO_2 ,⁴⁴ and NaCl to urea.⁴⁵ The enthalpies of transfer were for the process



where MX was the electrolyte at molality m_c and X_B was the mole fraction of the non-electrolyte. The value of m_c was always small, i.e. between 0.002 and about 0.01. Stern and Kulluk,⁴⁵ have shown

that at $m_c = 0.01$ the enthalpy of transfer of sodium chloride from water to urea-water mixtures can be understood as applying to infinite dilution. It is of interest to compare the enthalpy of transfer of sodium chloride at infinite dilution in water to infinite dilution in 1 m urea solution with that of the transfer of sodium chloride from infinite dilution in water to infinite dilution in 1 m glycine solution. From the graphical data provided by Stern and Kulluk it was estimated that the enthalpy of transfer was about $-180 \text{ cal. mole}^{-1}$ for the system in which X_B was equivalent to 1 m urea solution. For the system containing glycine an estimation of the enthalpy of transfer was made by extrapolating curve S in Figure 7-9 to $\sqrt{m_c} = 0$. The enthalpy of transfer was about $-400 \text{ cal. mole}^{-1}$ for the transfer of NaCl from infinite dilution in water to infinite dilution in 1 m glycine solution. It is worth noting that the enthalpy of transfer of NaCl from infinite dilution in water to infinite dilution in urea-water mixtures or glycine-water mixtures is always negative and the magnitude increases with the concentration of the organic-water mixture.

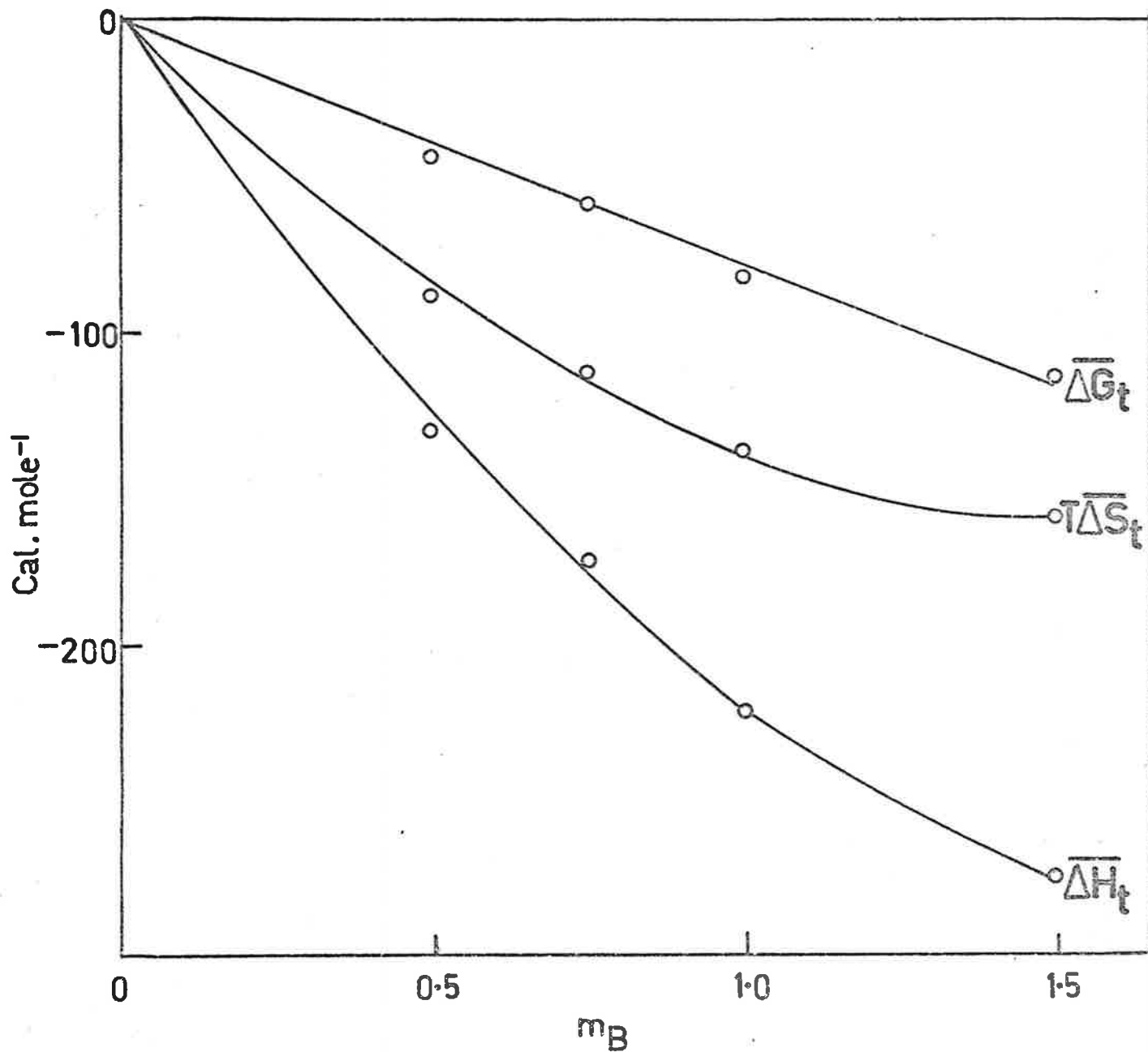


Fig. 7-10. The variation of $\overline{\Delta G}_t$, $\overline{\Delta H}_t$, and $T\overline{\Delta S}_t$ with m_B at $m_c = 0.5$.

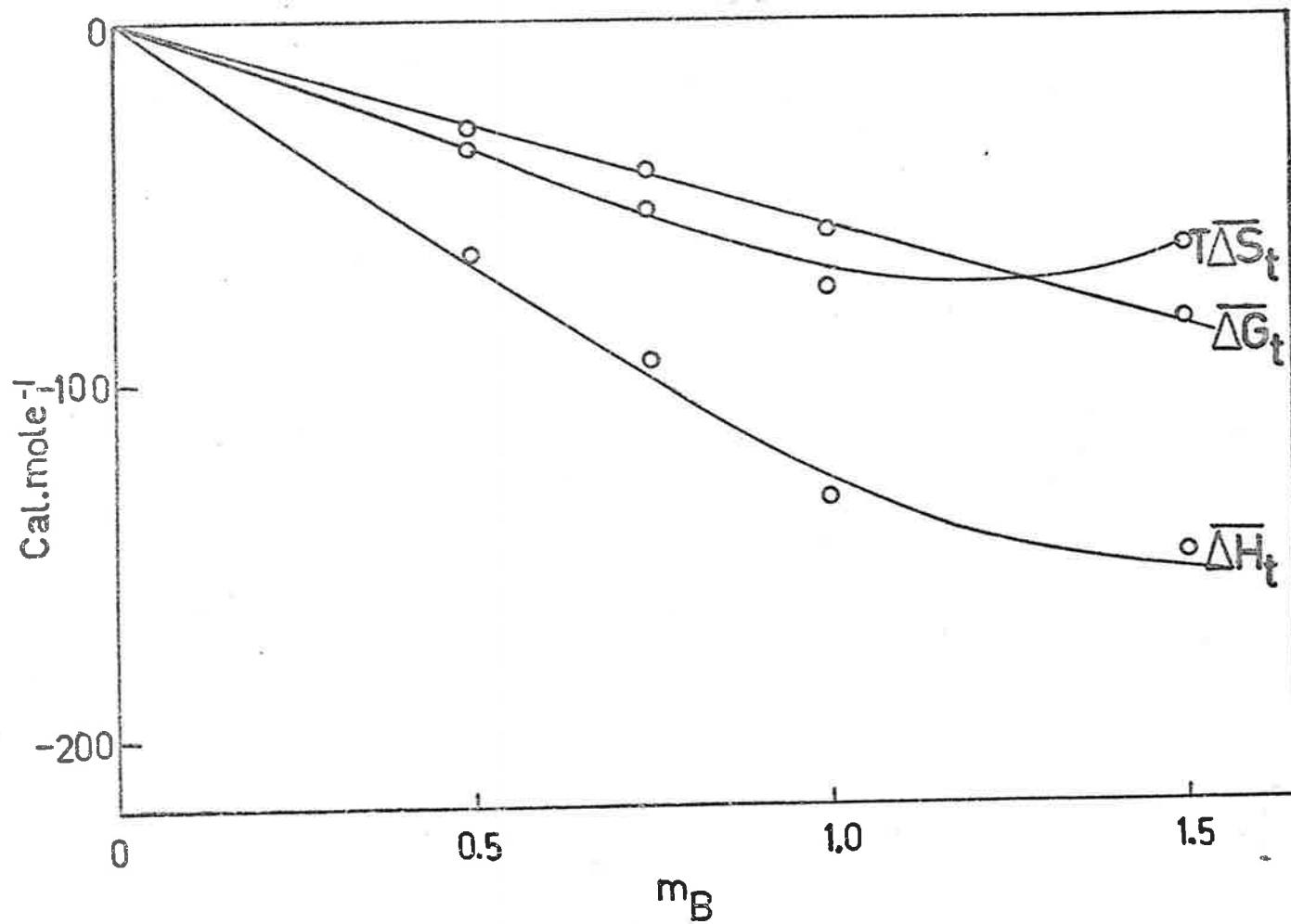


Fig. 7-11. The variation of $\overline{\Delta G}_t$, $\overline{\Delta H}_t$, and $T\overline{\Delta S}_t$ with m_B at $m_c = 1$.

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Equation 7-11 in the text was obtained from Equation 8 by dropping terms involving concentrations of NaCl and distance from interfaces.
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APPENDIX A

DATA FOR THE BINARY SYSTEM OF SODIUM CHLORIDE-WATER

at 0° (TABLE A-1)

at 10° (TABLE A-2)

at 25° (TABLE A-3(a)) for 0.01 m to 0.1 m

at 25° (TABLE A-3(b)) for 0.1 m to 2 m

at 25° (TABLE A-3(c)) for 1 m to 5 m ('multi-step' method)

at 25° (TABLE A-3(d)) for 1 m to 5 m ('single-step' method)

at 50° (TABLE A-4)

Notations used in Appendix A

1. In the first column of each table (under Electrode), the number and the letter represent the cation-responsive glass electrode and the silver-silver chloride electrode respectively. The numbers correspond to those given in Table 3-1 (Chapter 3) for the type of glass electrode.
2. γ is the mean molal activity coefficient of sodium chloride in water.
3. m_c is the molality of sodium chloride.
4. E is the emf of the cell,
$$\text{Ag, AgCl} \mid \text{NaCl} (m_c) \mid \text{Glass Electrode.}$$
5. Notes are provided at the end of each table.

TABLE A-1

The activity coefficients (as $-\log \gamma$) of aqueous sodium chloride at 0°.

Electrode	m_c	E volts	$-\log \gamma$	$-\log \gamma$ (Calc.)	$\Delta \times 10^3$
9 + E	0.010000	-0.09825	0.0418	0.0432	-1.4
	0.027533	-0.05341	0.0679	0.0663	1.6
	0.047328	-0.02962	0.0838	0.0822	1.6
	0.072535	-0.01103	0.0976	0.0964	1.2
	0.094857	0.00066	0.1064 ^a	0.1061	0.3
9 + F	0.010000	-0.09741	0.0416	0.0432	-1.6
	0.032547	-0.04509	0.0714	0.0709	0.5
	0.062782	-0.01635	0.0916	0.0914	0.2
	0.080348	-0.00569	0.1005	0.1000	0.5
	0.094661	0.00138	0.1064 ^a	0.1060	0.4
8 + E	0.010000	-0.10054	0.0392	0.0432	-4.0
	0.038867	-0.04047	0.0745	0.0761	-1.6
	0.071327	-0.01412	0.0953	0.0958	-0.5
	0.087862	-0.00514	0.1028	0.1032	-0.4
	0.10312	0.00167	0.1095 ^a	0.1092	0.3
8 + S	0.010000	-0.10064	0.0393	0.0432	-3.9
	0.047955	-0.03141	0.0814	0.0826	-1.2
	0.075000	-0.01207	0.0973	0.0976	-0.3
	0.093904	-0.00245	0.1061 ^a	0.1057	0.4
9 + Q	0.20000	0.03210	0.1361 ^b	0.1353	0.8
	0.42049	0.06387	0.1657	0.1660	-0.3
	0.65603	0.08302	0.1821	0.1829	-0.8
	0.91087	0.09732	0.1928	0.1932	-0.4
9 + E	0.40000	0.06181	0.1648 ^b	0.1640	0.8
	0.61063	0.07995	0.1811	0.1803	0.8
	0.82502	0.09297	0.1918	0.1903	1.5
	1.0322	0.10292	0.1973	0.1965	0.8

(contd.)

TABLE A-1 (contd.)

Electrode	m_c	E volts	$-\log \gamma$	$-\log \gamma$ (Calc.)	$\Delta \times 10^3$
8 + F	0.20000	0.03351	0.1361 ^b	0.1354	0.7
	0.44860	0.06805	0.1682	0.1686	-0.4
	0.72265	0.08858	0.1859	0.1862	-0.3
	0.95736	0.10121	0.1916	0.1946	-3.0
8 + F	0.20000	0.03561	0.1361 ^b	0.1354	0.7
	0.42236	0.06754	0.1647	0.1662	-1.5
	0.66431	0.08701	0.1832	0.1833	-0.1
	0.92146	0.10132	0.1932	0.1935	-0.3
	1.1880	0.11267	0.1988	0.1996	-0.8
10 + F	0.10000	-0.01289	0.1073 ^b	0.1080	-0.7
	0.34965	0.04059	0.1575	0.1585	-1.0
	0.57888	0.06204	0.1787	0.1784	0.3
	0.79923	0.07603	0.1896	0.1894	0.2
	1.0277	0.08685	0.1991	0.1964	2.7

Note:

1. a and b are the reference activity coefficients. b is taken from Harned and Robinson (Reference 12 in Chapter 6). a is the predicted reference point (see Treatment of Data in Chapter 6).
2. $-\log \gamma$ (Calc.) are values calculated from Equation 6-4, where $A = 0.4918$, $B = 1.40009$, $C = -2.0054 \times 10^{-3}$, $D = 12.1489 \times 10^{-3}$, $E = -3.7461 \times 10^{-3}$.
3. $\Delta = -\log \gamma + \log \gamma$ (Calc.).

TABLE A-2

The activity coefficients (as $-\log \gamma$) of aqueous sodium chloride at 10° .

Electrode	m_c	E volts	$-\log \gamma$	$-\log \gamma$ (Calc.)	$\Delta \times 10^3$
9 + E	0.023663	-0.06307	0.0636	0.0626	1.0
	0.071807	-0.01271	0.0975	0.0958	1.7
	0.094905	0.00006	0.1049	0.1056	-0.7
	0.11787	0.00964	0.1137 ^a	0.1135	0.2
10 + Q	0.031550	-0.06622	0.0687	0.0703	-1.6
	0.060484	-0.03685	0.0902	0.0901	0.1
	0.070335	-0.03005	0.0950	0.0951	-0.1
	0.10161	-0.01359	0.1082 ^a	0.1081	0.1
10 + Q	0.036509	-0.05943	0.0735	0.0744	-0.9
	0.060546	-0.03659	0.0900	0.0901	-0.1
	0.083365	-0.02221	0.1008	0.1010	-0.2
	0.12377	-0.00457	0.1155 ^a	0.1154	0.1
8 + H	0.20000	0.03368	0.1343 ^b	0.1338	0.5
	0.48582	0.07311	0.1688	0.1677	1.1
	0.78198	0.09462	0.1842	0.1828	1.4
	1.0470	0.10810	0.1910	0.1892	1.8
10 + Q	0.20000	0.01683	0.1343 ^b	0.1338	0.5
	0.45092	0.05302	0.1652	0.1650	0.2
	0.70293	0.07301	0.1802	0.1798	0.4
	0.92410	0.08560	0.1867	0.1868	-0.1
10 + C	0.10000	-0.01481	0.1073 ^b	0.1075	-0.2
	0.35223	0.04133	0.1546	0.1558	-1.2
	0.61711	0.06646	0.1743	0.1758	-1.5
	0.83757	0.08041	0.1829	0.1846	-1.7

(contd.)

TABLE A-2 (contd.)

Electrode	m_c	E volts	$-\log \gamma$	$-\log \gamma$ (Calc.)	$\Delta \times 10^3$
10 + F	0.10000	-0.01388	0.1073 ^b	0.1075	-0.2
	0.29471	0.03419	0.1490	0.1489	0.1
	0.51085	0.05873	0.1696	0.1694	0.2
	0.74433	0.07577	0.1813	0.1814	-0.1
	0.98823	0.08886	0.1878	0.1882	-0.4
	1.1747	0.09703	0.1902	0.1909	-0.7

Note:

1. a and b are the reference points. b is taken from Harned and Robinson (Reference 12 in Chapter 6). a is the predicted reference point (see Treatment of Data in Chapter 6).
2. $-\log \gamma$ (Calc.) are values calculated from Equation 6-4, where $A = 0.4989$, $B = 1.44183$, $C = 3.7882 \times 10^{-3}$, $D = 6.2119 \times 10^{-3}$, $E = -0.7558 \times 10^{-3}$.
3. $\Delta = -\log \gamma + \log \gamma$ (Calc.).

TABLE A-3(a)

The activity coefficients of aqueous sodium chloride (as $-\log \gamma$) at 25°.

(a) 0.01 m to 0.1 m.

Electrode	m_c	E volts	$-\log \gamma$	$-\log \gamma$ (Calc.)	$\Delta \times 10^3$
5 + B	0.010027	-0.02765	0.0445	0.0443	0.2
	0.036942	0.03565	0.0758	0.0757	0.1
	0.065271	0.06275	0.0940	0.0935	0.5
	0.079958	0.07241	0.1005	0.1004	0.1
	0.10329	0.08451	0.1094	0.1094*	0
5 + A	0.010649	-0.02283	0.0448	0.0455	-0.7
	0.036922	0.03745	0.0753	0.0757	-0.4
	0.073930	0.07040	0.0983	0.0977	0.6
	0.10326	0.08626	0.1094	0.1094*	0
6 + C	0.029998	0.04673	0.0689	0.0698	-0.9
	0.046978	0.06820	0.0822	0.0830	-0.8
	0.067257	0.08523	0.0941	0.0945	-0.4
	0.085897	0.09679	0.1026	0.1029	-0.3
	0.10916	0.10807	0.1114	0.1114*	0
7 + B	0.010902	-0.00562	0.0439	0.0459	-2.0
	0.040621	0.05807	0.0768	0.0785	-1.7
	0.067102	0.08191	0.0933	0.0944	-1.1
	0.088838	0.09515	0.1033	0.1041	-0.8
	0.11637	0.10779	0.1137	0.1137*	0
9 + A	0.029998	-0.05798	0.0688	0.0698	-1.0
	0.050688	-0.03291	0.0847	0.0853	-0.6
	0.073774	-0.01510	0.0972	0.0976	-0.4
	0.094939	-0.00319	0.1060	0.1064	-0.4
	0.11231	0.00469	0.1124	0.1124*	0

TABLE A-3(b)

The activity coefficient of aqueous sodium chloride (as $-\log \gamma$) at 25°.

(b) 0.1 m to 2m.

Electrode	m_c	E volts	$-\log \gamma$	$-\log \gamma$ (Calc.)	$\Delta \times 10^3$
1 + C	0.093860	-0.00690	0.1060	0.1060*	0
	0.31277	0.04971	0.1503	0.1503	0.0
	0.53379	0.07498	0.1688	0.1682	0.6
	0.69828	0.08800	0.1754	0.1756	-0.2
	0.81585	0.09564	0.1785	0.1790	-0.5
	0.95215	0.10311	0.1824	0.1816	0.8
	1.1075	0.11070	0.1839	0.1832	0.7
1 + D	0.91555	0.10192	0.1810	0.1810*	0
	1.1178	0.11201	0.1824	0.1832	-0.8
	1.3233	0.12052	0.1838	0.1835	0.3
	1.4562	0.12546	0.1836	0.1828	0.8
	1.5946	0.13023	0.1827	0.1815	1.2
	1.7413	0.13500	0.1806	0.1795	1.1
1 + E	0.93572	0.10117	0.1813	0.1813*	0
	1.1169	0.11012	0.1826	0.1832	-0.6
	1.2952	0.11781	0.1819	0.1835	-1.6
	1.4105	0.12222	0.1817	0.1831	-1.4
	1.6932	0.13168	0.1811	0.1802	0.9
	1.8205	0.13599	0.1761	0.1783	2.2
1 + C	0.14567	0.01227	0.1220	0.1220*	0
	0.33390	0.05108	0.1542	0.1527	1.5
	0.50353	0.07047	0.1687	0.1665	2.2
	0.73862	0.08890	0.1793	0.1769	2.4
	1.0273	0.10528	0.1842	0.1825	1.7
	1.2198	0.11393	0.1857	0.1836	2.1
	1.6307	0.12916	0.1830	0.1811	1.9
2 + A	0.23057	0.00761	0.1391	0.1391*	0
	0.36368	0.02870	0.1588	0.1557	3.1
	0.47080	0.04137	0.1638	0.1643	-0.5
	0.55237	0.04895	0.1691	0.1693	-0.2
	0.65978	0.05734	0.1754	0.1742	1.2

(contd.)

TABLE A-3(b) (contd.)

Electrode	m_c	E volts	$-\log \gamma$	$-\log \gamma$ (Calc.)	$\Delta \times 10^3$
3 + D	0.098268	0.13031	0.1076	0.1076*	0
	0.35928	0.19125	0.1556	0.1552	0.4
	0.67002	0.22102	0.1746	0.1746	0.0
	0.81975	0.23086	0.1790	0.1791	-0.1
	0.96125	0.23876	0.1814	0.1817	-0.3
	1.0928	0.24522	0.1825	0.1831	-0.6
3 + D	0.92462	0.23660	0.1812	0.1812*	0
	1.1782	0.24877	0.1836	0.1835	0.1
	1.4295	0.25881	0.1827	0.1830	-0.3
	1.5946	0.26463	0.1810	0.1815	-0.5
	1.7553	0.26984	0.1786	0.1793	-0.7
	1.9049	0.27437	0.1758	0.1768	-1.0
3 + D	0.099959	0.12446	0.1082	0.1082*	0
	0.25315	0.16810	0.1429	0.1426	0.3
	0.40882	0.19074	0.1597	0.1597	0.0
	0.56437	0.20610	0.1700	0.1699	0.1
	0.73917	0.21915	0.1768	0.1769	-0.1
	0.95674	0.23190	0.1811	0.1817	-0.6
	1.4931	0.25480	0.1809	0.1825	-1.6
3 + A	0.34369	0.16243	0.1537	0.1537*	0
	0.60146	0.18889	0.1731	0.1717	1.4
	0.83778	0.20490	0.1817	0.1795	2.2
	1.0965	0.21826	0.1857	0.1831	2.6
	1.3190	0.22767	0.1864	0.1835	2.9
	1.6024	0.23789	0.1845	0.1814	3.1
5 + E	0.22353	0.13190	0.1379	0.1379*	0
	0.62867	0.18101	0.1720	0.1729	-0.9
	0.91236	0.19923	0.1797	0.1810	-1.3
	1.3308	0.21844	0.1813	0.1834	-2.1

TABLE A-3(c)

The activity coefficients of aqueous sodium chloride (as $-\log \gamma$) at 25°.

(c) 1 m to 5 m ('multi-step' method)

Electrode	m_c	E volts	$-\log \gamma$	$-\log \gamma$ (Calc.)	$\Delta \times 10^3$
6 + Q	0.99243	0.21185	0.1821	0.1821*	0
	1.3359	0.22709	0.1824	0.1834	-1.0
	1.7030	0.23999	0.1788	0.1801	-1.3
	2.0668	0.25080	0.1715	0.1735	-2.0
6 + B	0.99243	0.21074	0.1821	0.1821*	0
	1.3098	0.22488	0.1831	0.1835	-0.4
	1.6269	0.23632	0.1806	0.1811	-0.5
	1.9509	0.24630	0.1751	0.1759	-0.8
	2.2883	0.25544	0.1671	0.1682	-1.1
6 + B	2.0069	0.24739	0.1747	0.1747*	0
	2.3613	0.25677	0.1661	0.1662	-0.1
	2.7158	0.26523	0.1553	0.1557	-0.4
	3.0590	0.27272	0.1437	0.1440	-0.3
	3.4430	0.28054	0.1290	0.1293	-0.3
6 + D	2.9066	0.26765	0.1494	0.1494*	0
	3.3341	0.27660	0.1333	0.1336	-0.3
	3.7665	0.28502	0.1151	0.1159	-0.8
	4.2266	0.29340	0.0943	0.0953	-1.0
6 + D	2.9066	0.26586	0.1494	0.1494*	0
	3.2426	0.27294	0.1370	0.1372	-0.2
	3.6267	0.28050	0.1218	0.1218	0.0
	4.0146	0.28775	0.1046	0.1050	-0.4
	4.4134	0.29488	0.0855	0.0866	-1.1
	4.8230	0.30187	0.0650	0.0667	-1.7
	5.1716	0.30737	0.0488	0.0491	-0.3

(contd.)

TABLE A-3(c) (contd.)

Electrode	m_c	E volts	$-\log \gamma$	$-\log \gamma$ (Calc.)	$\Delta \times 10^3$
6 + A	2.9066	0.26541	0.1494	0.1494*	0
	3.2664	0.27303	0.1357	0.1362	-0.5
	3.6768	0.28114	0.1185	0.1197	-1.2
	4.0801	0.28864	0.1003	0.1021	-1.8
5 + D	2.0069	0.22994	0.1747	0.1747*	0
	2.3476	0.23908	0.1656	0.1666	-1.0
	2.7395	0.24838	0.1540	0.1550	-1.0
	3.1017	0.25626	0.1414	0.1424	-1.0
	3.4502	0.26311	0.1297	0.1290	0.7
	3.8589	0.27094	0.1122	0.1119	0.3
	4.2634	0.27827	0.0935	0.0936	-0.1
5 + E	*3.9649	0.27985	0.1072	0.1072*	0
	4.8232	0.29469	0.0669	0.0667	0.2
	5.2543	0.30152	0.0463	0.0449	1.4
4 + E	3.9649	0.25472	0.1072	0.1072*	0
	4.2950	0.26068	0.0916	0.0922	-0.6
	4.6295	0.26647	0.0752	0.0762	-1.0
	5.0358	0.27326	0.0544	0.0560	-1.6
	5.4460	0.27976	0.0334	0.0349	-1.5

TABLE A-3(d)

The activity coefficients of aqueous sodium chloride (as $-\log \gamma$) at 25°.

Concentration range: 1 m to 5 m ('single-step' method).

Electrode	m_c	E volts	$-\log \gamma$	$-\log \gamma$ (Calc.)	$\Delta \times 10^3$	pH
5 + G	1.0208	0.20896	0.1824	0.1824*	0	6.8
	1.7942	0.23862	0.1767	0.1787	-2.0	6.7
	2.9644	0.26855	0.1418	0.1474	-5.6	6.1
	3.6729	0.28287	0.1138	0.1199	-6.1	7.2
	4.6953	0.30136	0.0642	0.0730	08.8	7.8
5 + D	1.0208	0.20718	0.1824	0.1824*	0	7.2
	1.6556	0.23218	0.1812	0.1807	0.5	7.7
	2.5298	0.25636	0.1609	0.1615	-0.6	7.7
	3.4980	0.27730	0.1247	0.1271	-2.4	6.8
	4.4136	0.29420	0.0828	0.0866	-3.8	7.4
5 + E	1.0193	0.20714	0.1824	0.1824*	0	5.6
	2.0654	0.24489	0.1701	0.1735	-3.4	5.4
	3.0949	0.26962	0.1367	0.1427	-6.0	5.3
	4.1605	0.29029	0.0905	0.0984	-7.9	5.3
	5.2134	0.30841	0.0353	0.0470	-11.7	5.2
4 + E	1.0208	0.19795	0.1824	0.1824*	0	7.0
	1.8631	0.22952	0.1769	0.1775	-0.6	7.3
	2.8325	0.25447	0.1480	0.1519	-3.9	7.2
	3.8251	0.27489	0.1059	0.1134	-7.5	6.5
	4.9533	0.29499	0.0482	0.0602	-12.0	7.0
	5.6436	0.30647	0.0079	0.0246	-16.7	6.0
4 + A	1.0193	0.19909	0.1824	0.1824*	0	
	2.0548	0.23639	0.1716	0.1737	-2.1	
	3.1027	0.26152	0.1382	0.1424	-4.2	
	4.0755	0.28054	0.0959	0.1023	-6.4	
	5.3656	0.30268	0.0282	0.0391	-10.9	

(contd.)

TABLE A-3(d) (contd.)

Electrode	m_c	E volts	$-\log \gamma$	$-\log \gamma$ (Calc.)	$\Delta \times 10^3$	pH
1 + B	1.0193	0.10821	0.1824	0.1824*	0	
	2.0840	0.14619	0.1720	0.1731	-1.1	
	2.9450	0.16707	0.1457	0.1480	-2.3	
	4.1681	0.19115	0.0931	0.0980	-4.9	
	5.2021	0.20922	0.0366	0.0476	-11.0	
1 + E	1.0212	0.10793	0.1824	0.1824*	0	6.7
	1.8739	0.14008	0.1744	0.1773	-2.9	7.4
	2.8362	0.16447	0.1482	0.1518	-3.6	8.0
	3.8299	0.18449	0.1094	0.1131	-3.5	6.6
	4.6964	0.19994	0.0674	0.0729	-5.5	7.9
	5.6105	0.21556	0.0127	0.0263	-13.6	7.3

Note:

- * They indicate the reference activity coefficients which are calculated from Equation 6-4, using parameters which are shown in Table 6-2 in Chapter 6.
- pH is adjusted by using drops of constant boiling HCl. Sodium chloride which was recrystallised and then fused was used in some of these experiments. Sodium chloride prepared by such a method was alkaline in solution, normally about pH = 9.
- $\Delta = -\log \gamma + \log \gamma(\text{Calc.})$.
- $-\log \gamma$ (Calc.) are values calculated from Equation 6-4. The parameters used are shown in the fourth column of Table 6-2 in Chapter 6.

TABLE A-4

The activity coefficients (as $-\log \gamma$) of aqueous sodium chloride at 50°.

Electrode	m_c	E volts	$-\log \gamma$	$-\log \gamma$ (Calc.)	$\Delta \times 10^3$
8 + Q	0.030000	-0.06288	0.0700	0.0717	-1.7
	0.053371	-0.03329	0.0895	0.0891	0.4
	0.068527	-0.02051	0.0984	0.0975	0.9
	0.086783	-0.00845	0.1069 ^a	0.1058	1.1
8 + Q	0.030000	-0.06294	0.0689	0.0717	-2.8
	0.064530	-0.02363	0.0951	0.0954	-0.3
	0.092143	-0.00546	0.1081	0.1080	0.1
	0.11703	0.00671	0.1170 ^a	0.1169	0.1
8 + G	0.29925	0.05257	0.1535 ^b	0.1535	0.0
	0.52776	0.08173	0.1725	0.1728	-0.3
	0.75429	0.10054	0.1810	0.1808	0.2
	0.98560	0.11505	0.1840	0.1842	-0.2
9 + S	0.29466	0.05029	0.1530 ^b	0.1529	0.1
	0.44537	0.07142	0.1675	0.1677	-0.2
	0.59994	0.08694	0.1760	0.1762	-0.2
	0.76652	0.09994	0.1809	0.1811	-0.2
	0.94889	0.11150	0.1836	0.1838	-0.2
9 + D	0.17640	0.02457	0.1335 ^b	0.1328	0.7
	0.39584	0.06573	0.1636	0.1637	-0.1
	0.65849	0.09223	0.1779	0.1783	-0.4
9 + D	0.29466	0.05023	0.1530 ^b	0.1529	0.1
	0.51461	0.07883	0.1722	0.1721	0.1
	0.75107	0.09870	0.1814	0.1808	0.6
	0.97914	0.11296	0.1853	0.1841	1.2
9 + G	0.30000	0.05136	0.1537 ^b	0.1536	0.1
	0.57221	0.08464	0.1747	0.1750	-0.3
	0.83270	0.10451	0.1827	0.1823	0.4
	1.1230	0.12085	0.1858	0.1856	0.2
9 + G	0.30000	0.05124	0.1537 ^b	0.1536	0.1
	0.55445	0.08295	0.1733	0.1742	-0.9
	0.82460	0.10392	0.1822	0.1822	0.0
	1.1010	0.11974	0.1845	0.1854	-0.9

(contd.)

TABLE A-4 (contd.)

Note:

1. a and b are the reference points. b values are estimated graphically from the activity coefficients given by Robinson (Reference 3 in Chapter 6). a is the predicted reference point (see Treatment of Data in Chapter 6).
2. $-\log \gamma$ (Calc.) are values from Equation 6-4, where
A = 0.5373; B = 1.86484; C = 24.6254×10^{-3} ; D = 56.9774×10^{-3} ;
E = -24.762×10^{-3} .
3. $\Delta = -\log \gamma + \log \gamma$ (Calc.).

APPENDIX B

DATA FOR THE TERNARY SYSTEM OF SODIUM CHLORIDE-GLYCINE-WATER

at 0° (TABLE B-1)

at 10° (TABLE B-2)

at 25° (TABLE B-3)

at 50° (TABLE B-4)

The following notations are used in Appendix B

1. In the first column of each Table (under Electrode), the number and the letter represent the cation-responsive glass electrode and the silver-silver chloride electrode respectively. The numbers correspond to those given in Table 3-1 (Chapter 3) for the type of glass electrode.
2. γ_c , γ_c° , are the mean molal activity coefficients of sodium chloride in water, with and without glycine, respectively.
3. m_B , m_c , are the molalities of glycine and sodium chloride respectively.
4. E represents the emf of the cell,
$$\text{Ag,AgCl}|\text{NaCl} (m_c), \text{Glycine} (m_B)|\text{Glass Electrode.}$$
5. Notes are provided at the end of each table.

TABLE B-1

The activity coefficients of sodium chloride in glycine-water mixtures.

NaCl-Glycine-Water at 0°.

Electrode	m_c	m_B	E volts	$-\log \gamma_c$	$-\log \gamma_c^\circ$	$-\log \frac{\gamma_c}{\gamma_c^\circ}$
8 + E	0.010000	0	-0.10053	0.0432 ^a	0.0432	0
	"	0.34894	-0.10417	0.0768	"	0.0336
	"	0.72641	-0.10732	0.1058	"	0.0626
	"	1.0616	-0.10967	0.1275	"	0.0843
	"	1.4874	-0.11227	0.1515	"	0.1083
8 + E	0.050000	0	-0.02915	0.0839 ^a	0.0839	0
	"	0.36547	-0.03229	0.1129	"	0.0290
	"	0.70931	-0.03473	0.1354	"	0.0515
	"	1.0420	-0.03680	0.1545	"	0.0706
	"	1.3995	-0.3868	0.1718	"	0.0879
	"	Satd.	-0.04090	0.1923	"	0.1084
8 + E	0.10000	0	0.00058	0.1080 ^a	0.1080	0
	"	0.35018	-0.00211	0.1328	"	0.0248
	"	0.66602	-0.00415	0.1516	"	0.0436
	"	1.0036	-0.00604	0.1691	"	0.0611
	"	1.4716	-0.00827	0.1896	"	0.0816
8 + G	0.20000	0	0.03052	0.1354 ^a	0.1354	0
	"	0.33464	0.02822	0.1566	"	0.0212
	"	0.72319	0.02604	0.1767	"	0.0413
	"	1.0472	0.02447	0.1912	"	0.0558
	"	1.4747	0.02264	0.2081	"	0.0727
9 + S	0.20000	0	0.03348	0.1354 ^a	0.1354	0
	"	0.50687	0.03007	0.1669	"	0.0315
9 + F	0.20000	0	0.03166	0.1354 ^a	0.1354	0
	"	0.20364	0.03022	0.1487	"	0.0133
	"	0.61079	0.02781	0.1709	"	0.0355
	"	1.1968	0.02520	0.1950	"	0.0596
	"	1.8136	0.02298	0.2155	"	0.0801
	"	Satd.	0.02259	0.2191	"	0.0837

(contd.)

TABLE B-1 (contd.)

Electrode	m_c	m_B	E volts	$-\log \gamma_c$	$-\log \gamma_c^\circ$	$-\log \frac{\gamma_c}{\gamma_c^\circ}$
9 + F	0.40000	0	0.06205	0.1640 ^a	0.1640	0
	"	0.23963	0.06073	0.1762	"	0.0122
	"	0.74919	0.05841	0.1976	"	0.0336
	"	1.4335	0.05587	0.2210	"	0.0570
	"	Satd.	0.05436	0.2349	"	0.0709
8 + F	0.60000	0	0.08258	0.1797 ^a	0.1797	0
	"	0.23026	0.08153	0.1894	"	0.0097
	"	0.61497	0.07994	0.2041	"	0.0244
	"	1.0836	0.07831	0.2191	"	0.0394
	"	1.6112	0.07668	0.2341	"	0.0544
"	Satd.	0.07582	0.2421	"	0.0624	
8 + E	0.60000	0	0.07711	0.1797 ^a	0.1797	0
	"	0.37094	0.07357	0.1958	"	0.0161
	"	0.73038	0.07392	0.2091	"	0.0294
	"	1.1825	0.07233	0.2238	"	0.0441
	"	1.5409	0.07120	0.2342	"	0.0545
9 + B	0.60000	0	0.07905	0.1797 ^a	0.1797	0
	"	0.53220	0.07689	0.1996	"	0.0199
8 + F	1.0000	0	0.10435	0.1957 ^a	0.1957	0
	"	0.25051	0.10345	0.2040	"	0.0083
	"	0.60780	0.10226	0.2150	"	0.0193
	"	1.1742	0.10062	0.2301	"	0.0344
	"	1.7414	0.09927	0.2426	"	0.0469
"	Satd.	0.09846	0.2500	"	0.0543	
8 + F	1.0000	0	0.10352	0.1957 ^a	0.1957	0
	"	0.41588	0.10219	0.2080	"	0.0123
	"	0.84955	0.10092	0.2197	"	0.0240
	"	1.2268	0.09982	0.2298	"	0.0341
	"	1.6380	0.09888	0.2385	"	0.0428
"	Satd.	0.09815	0.2452	"	0.0495	

(contd.)

TABLE B-1 (contd.)

Electrode	m_c	m_B	E volts	$-\log \gamma_c$	$-\log \gamma_c^\circ$	$-\log \frac{\gamma_c}{\gamma_c^\circ}$
9 + E	1.0000	0	0.10140	0.1957 ^a	0.1957	0
	"	0.28525	0.10043	0.2047	"	0.0090
	"	0.68839	0.09917	0.2163	"	0.0206
	"	1.1174	0.09807	0.2264	"	0.0307
	"	1.5323	0.09731	0.2334	"	0.0377
8 + H	0.10000	0	0.00162	0.1080 ^a	0.1080	0
	0.10000	0.49899	-0.00205	0.1419	0.1080	0.0339
	0.30023	"	0.04573	0.1785	0.1522	0.0263
	0.52340	"	0.06982	0.1976	0.1746	0.0230
	0.77890	"	0.08725	0.2095	0.1886	0.0209
	1.0532	"	0.10075	0.2161	0.1970	0.0191

Note:

1. a, reference solution and reference activity coefficient.
2. γ_c° is the activity coefficient of sodium chloride in water.
3. $-\log \gamma_c^\circ$ values are calculated from Equation 6-4:

$$\log \gamma_c^\circ = - \frac{Am_c^{1/2}}{1 + Bm_c} + 2Cm_c + \frac{3}{2} Dm_c^2 + \frac{4}{3} Em_c^3 \quad (6-4)$$

where $A = 0.4918$; $B = 1.40009$; $C = -2.0054 \times 10^{-3}$;
 $D = 12.1489 \times 10^{-3}$; $E = -3.7461 \times 10^{-3}$.

4. Satd. indicate saturation.

TABLE B-2

The activity coefficients of sodium chloride in glycine-water mixtures.

NaCl-Glycine-Water at 10°.

Electrode	m_c	m_B	E volts	$-\log \gamma_c$	$-\log \gamma_c^\circ$	$-\log \frac{\gamma_c}{\gamma_c^\circ}$
10 + Q	0.010000	0	-0.11883	0.0435 ^a	0.0435	0
"	"	0.39158	-0.12282	0.0790	"	0.0355
"	"	0.81111	-0.12594	0.1068	"	0.0633
"	"	1.2529	-0.12868	0.1319	"	0.0877
"	"	1.8594	-0.13166	0.1577	"	0.1142
"	"	Satd.	-0.13375	0.1696	"	0.1261
10 + F	0.050000	0	-0.04559	0.0840 ^a	0.0840	0
"	"	0.34557	-0.04844	0.1094	"	0.0254
"	"	0.67916	-0.05059	0.1285	"	0.0445
"	"	1.1030	-0.05299	0.1499	"	0.0659
"	"	1.4956	-0.05486	0.1665	"	0.0825
"	"	1.8958	-0.05651	0.1812	"	0.0972
8 + Q	0.10000	0	0.00224	0.1075 ^a	0.1075	0
"	"	0.32076	-0.00014	0.1287	"	0.0212
"	"	0.62860	-0.00203	0.1455	"	0.0380
"	"	1.0907	-0.00443	0.1669	"	0.0594
"	"	1.6091	-0.00667	0.1868	"	0.0793
"	"	2.1065	-0.00850	0.2031	"	0.0956
10 + C	0.10000	0	-0.01430	0.1075 ^a	0.1075	0
	0.10000	0.99029	-0.02023	0.1603	0.1075	0.0528
	0.38815	"	0.04159	0.1991	0.1595	0.0396
	0.63159	"	0.06421	0.2092	0.1765	0.0327
	0.83443	"	0.07733	0.2134	0.1845	0.0289
	1.0491	"	0.08831	0.2151	0.1893	0.0258
10 + C	0.10000	0	-0.01432	0.1075 ^a	0.1075	0
	0.10000	1.5218	-0.02265	0.1816	0.1075	0.0741
	0.33388	"	0.03291	0.2108	0.1537	0.0571
	0.61632	"	0.06156	0.2220	0.1757	0.0463
	0.89744	"	0.07952	0.2254	0.1862	0.0392
	1.1266	"	0.09065	0.2251	0.1904	0.0347

(contd.)

TABLE B-2 (contd.)

Electrode	m_c	m_B	E volts	$-\log \gamma_c$	$-\log \gamma_c^\circ$	$-\log \frac{\gamma_c}{\gamma_c^\circ}$
8 + C	0.20000	0	0.03217	0.1338 ^a	0.1338	0
	"	0.29798	0.03032	0.1503	"	0.0165
	"	0.66421	0.02839	0.1674	"	0.0336
	"	1.2933	0.02563	0.1920	"	0.0582
	"	1.8182	0.02379	0.2084	"	0.0746
	"	2.2390	0.02250	0.2199	"	0.0861
10 + Q	0.50000	0	0.05761	0.1687 ^a	0.1687	0
	"	0.32788	0.05618	0.1814	"	0.0127
	"	0.72536	0.05459	0.1956	"	0.0269
	"	1.1785	0.05308	0.2090	"	0.0403
	"	1.7907	0.05139	0.2241	"	0.0554
	"	2.3640	0.05012	0.2354	"	0.0667
10 + Q	0.70000	0	0.07284	0.1797 ^a	0.1797	0
	"	0.34098	0.07143	0.1922	"	0.0125
	"	0.72641	0.07011	0.2040	"	0.0243
	"	1.2563	0.06856	0.2178	"	0.0381
	"	1.8787	0.06707	0.2311	"	0.0514
	"	2.5347	0.06579	0.2424	"	0.0627
10 + Q	1.0000	0	0.08891	0.1884 ^a	0.1884	0
	"	0.36403	0.08764	0.1997	"	0.0113
	"	0.74337	0.08655	0.2094	"	0.0210
	"	1.2794	0.08523	0.2212	"	0.0328
	"	1.7796	0.08420	0.2303	"	0.0419
	"	2.3096	0.08327	0.2386	"	0.0502

(contd.)

TABLE B-2 (contd.)

Note:

1. a, reference solution and reference activity coefficient.
2. γ_c° is the activity coefficient of sodium chloride in water.
3. $-\log \gamma_c^\circ$ values were calculated from Equation 6-4:

$$\log \gamma_c^\circ = - \frac{Am_c^{1/2}}{1 + Bm_c^{1/2}} + 2Cm_c + \frac{3}{2} Dm_c^2 + \frac{4}{3} Em_c^3 \quad (6-4)$$

where $A = 0.4989$; $B = 1.44183$; $C = 3.7882 \times 10^{-3}$;
 $D = 6.2119 \times 10^{-3}$; $E = -0.7558 \times 10^{-3}$.

4. Satd. indicate saturation.

TABLE B-3

The activity coefficients of sodium chloride in glycine-water mixtures.

NaCl-Glycine-Water at 25°.

Electrode	m_c	m_B	E volts	$-\log \gamma_c$	$-\log \gamma_c^\circ$	$-\log \frac{\gamma_c}{\gamma_c^\circ}$
7 + C	0.010902	0	-0.00489	0.0459 ^a	0.0459	0
	"	0.45054	-0.00908	0.0813	"	0.0354
	"	0.90785	-0.01244	0.1097	"	0.0638
	"	1.4933	-0.01577	0.1379	"	0.0920
	"	2.0213	-0.01818	0.1582	"	0.1123
	"	2.6189	-0.02038	0.1768	"	0.1309
	"	Satd.	-0.02231	0.1931	"	0.1472
5 + C	0.010902	0	-0.02197	0.0459 ^a	0.0459	0
	"	0.32048	-0.02506	0.0720	"	0.0261
	"	0.72227	-0.02822	0.0987	"	0.0528
	"	1.1561	-0.03103	0.1225	"	0.0766
	"	1.6757	-0.03376	0.1455	"	0.0996
	"	2.2069	-0.03596	0.1641	"	0.1182
	"	2.4253	-0.03672	0.1706	"	0.1247
	"	2.7613	-0.03778	0.1795	"	0.1336
"	Satd.	-0.03940	0.1932	"	0.1473	
5 + C	0.030000	0	0.02630	0.0698 ^a	0.0698	0
	"	0.36638	0.02331	0.0951	"	0.0253
	"	0.76426	0.02064	0.1176	"	0.0478
	"	1.2014	0.01800	0.1400	"	0.0702
	"	1.7449	0.01579	0.1586	"	0.0888
	"	2.2261	0.01399	0.1738	"	0.1040
	"	2.7748	0.01224	0.1886	"	0.1188
	"	Satd.	0.01082	0.2007	"	0.1309
7 + B	0.030000	0	0.04480	0.0698 ^a	0.0698	0
	"	0.36034	0.04184	0.0948	"	0.0250
	"	0.84996	0.03856	0.1226	"	0.0528
	"	1.3291	0.03601	0.1441	"	0.0743
	"	1.8198	0.03386	0.1623	"	0.0925
	"	2.6252	0.03106	0.1859	"	0.1161
	"	Satd.	0.02913	0.2023	"	0.1325

(contd.)

TABLE B-3 (contd.)

Electrode	m_c	m_B	E volts	$-\log \gamma_c$	$-\log \gamma_c^\circ$	$-\log \frac{\gamma_c}{\gamma_c^\circ}$
9 + A	0.050000	0	-0.03360	0.0849 ^a	0.0849	0
	"	0.48602	-0.03716	0.1150	"	0.0301
	"	1.0288	-0.04024	0.1410	"	0.0561
	"	1.5677	-0.04269	0.1617	"	0.0768
	"	2.6298	-0.04631	0.1923	"	0.1074
6 + A	0.050000	0	0.07246	0.0849 ^a	0.0849	0
	"	0.44552	0.06904	0.1138	"	0.0289
	"	0.97619	0.06589	0.1404	"	0.0555
	"	1.4964	0.06344	0.1611	"	0.0762
	"	2.1545	0.06093	0.1823	"	0.0974
	"	2.7275	0.05919	0.1971	"	0.1122
	"	Satd.	0.05737	0.2124	"	0.1275
9 + G	0.070000	0	-0.01748	0.0959 ^a	0.0959	0
	"	0.36538	-0.02007	0.1177	"	0.0218
	"	1.0794	-0.02400	0.1510	"	0.0551
	"	1.6009	-0.02622	0.1697	"	0.0738
	"	2.1698	-0.02819	0.1864	"	0.0905
	"	2.7810	-0.02992	0.2010	"	0.1051
	"	Satd.	-0.03135	0.2131	"	0.1172
6 + A	0.070000	0	0.08704	0.0959 ^a	0.0959	0
	"	0.65599	0.08265	0.1330	"	0.0371
	"	1.4707	0.07874	0.1660	"	0.0701
	"	2.1699	0.07624	0.1871	"	0.0912
	"	2.6365	0.07489	0.1985	"	0.1026
	"	Satd.	0.07301	0.2144	"	0.1185
1 + E	0.10000	0	0.00087	0.1088 ^b	0.1088	0
	"	0.10939	0.00010	0.1153	"	0.0065
	"	0.24420	-0.00086	0.1234	"	0.0146
	"	0.49957	-0.00249	0.1372	"	0.0284
	"	0.81703	-0.00421	0.1517	"	0.0429
	"	1.1457	-0.00583	0.1654	"	0.0566
	"	1.5422	-0.00746	0.1792	"	0.0709
	"	2.0699	-0.00929	0.1947	"	0.0859

(contd.)

TABLE B-3 (contd.)

Electrode	m_c	m_B	E volts	$-\log \gamma_c$	$-\log \gamma_c^\circ$	$-\log \frac{\gamma_c}{\gamma_c^\circ}$
1 + E	0.10000	0	-0.00017	0.1088 ^b	0.1088	0
	"	0.13744	-0.00120	0.1175	"	0.0087
	"	0.61137	-0.00418	0.1427	"	0.0339
	"	1.2597	-0.00727	0.1688	"	0.0600
	"	1.4180	-0.00791	0.1742	"	0.0654
5 + B	0.10000	0	0.10322	0.1088 ^b	0.1088	0
	"	0.17469	0.10189	0.1200	"	0.0112
	"	0.36719	0.10059	0.1310	"	0.0222
	"	0.60352	0.09920	0.1428	"	0.0340
	"	1.0169	0.09702	0.1612	"	0.0524
	"	1.4612	0.09504	0.1779	"	0.0691
5 + B	0.10000	0	0.10138	0.1088 ^b	0.1088	0
	"	0.13911	0.10039	0.1172	"	0.0084
	"	0.84742	0.09621	0.1525	"	0.0437
	"	1.1179	0.09506	0.1622	"	0.0534
	"	1.3619	0.09391	0.1719	"	0.0631
	"	1.6048	0.09289	0.1806	"	0.0718
5 + D	0.30000	0	0.15155	0.1487 ^b	0.1487	0
	"	0.16778	0.15068	0.1560	"	0.0073
	"	0.38519	0.14966	0.1646	"	0.0159
	"	0.74808	0.14813	0.1776	"	0.0289
	"	1.1538	0.14667	0.1899	"	0.0412
	"	1.5785	0.14535	0.2011	"	0.0524
	"	2.0039	0.14418	0.2110	"	0.0623
5 + D	0.30000	0	0.15042	0.1487 ^b	0.1487	0
	"	0.13011	0.14979	0.1540	"	0.0053
	"	0.41200	0.14848	0.1651	"	0.0164
	"	0.86112	0.14668	0.1803	"	0.0316
	"	1.5898	0.14431	0.2003	"	0.0516
	"	2.3914	0.14330	0.2184	"	0.0697

(contd.)

TABLE B-3 (contd.)

Electrode	m_c	m_B	E volts	$-\log \gamma_c$	$-\log \gamma_c^\circ$	$-\log \frac{\gamma_c}{\gamma_c^\circ}$
4 + H	0.30000	0	0.14974	0.1487 ^b	0.1487	0
"	"	0.16088	0.14895	0.1554	"	0.0067
"	"	0.48285	0.14745	0.1680	"	0.0193
"	"	0.77990	0.14633	0.1775	"	0.0288
"	"	1.4283	0.14418	0.1957	"	0.0470
3 + D	0.50000	0	0.19820	0.1668 ^b	0.1668	0
"	"	0.26629	0.19722	0.1751	"	0.0083
"	"	0.75976	0.19552	0.1895	"	0.0227
"	"	1.3301	0.19371	0.2048	"	0.0380
"	"	1.9042	0.19235	0.2162	"	0.0494
"	"	2.7127	0.19065	0.2306	"	0.0638
"	"	Satd.	0.18976	0.2381	"	0.0713
3 + E	0.50000	0	0.19633	0.1668 ^b	0.1668	0
"	"	0.22643	0.19547	0.1741	"	0.0073
"	"	0.49546	0.19451	0.1822	"	0.0154
"	"	0.84277	0.19337	0.1918	"	0.0250
"	"	1.1683	0.19241	0.2002	"	0.0334
"	"	1.5655	0.19139	0.2086	"	0.0418
"	"	2.1502	0.19007	0.2197	"	0.0529
"	"	2.7890	0.18887	0.2299	"	0.0631
"	"	Satd.	0.18815	0.2359	"	0.0691
1 + C	0.50000	0	0.07241	0.1668 ^b	0.1668	0
"	"	0.12756	0.07182	0.1718	"	0.0050
"	"	0.33971	0.07110	0.1779	"	0.0111
"	"	0.61801	0.06996	0.1875	"	0.0207
"	"	0.93947	0.06895	0.1960	"	0.0292
"	"	1.2829	0.06786	0.2053	"	0.0385
"	"	1.7780	0.06660	0.2159	"	0.0491
"	"	2.3615	0.06555	0.2249	"	0.0581
4 + H	0.70000	0	0.18565	0.1759 ^b	0.1759	0
"	"	0.24001	0.18490	0.1822	"	0.0063
"	"	0.74839	0.18327	0.1960	"	0.0201
"	"	1.6822	0.18106	0.2147	"	0.0388
"	"	2.6341	0.17930	0.2296	"	0.0537

(contd.)

TABLE B-3 (contd.)

Electrode	m_c	m_B	E volts	$-\log \gamma_c$	$-\log \gamma_c^\circ$	$-\log \frac{\gamma_c}{\gamma_c^\circ}$
3 + H	0.70000	0	0.21111	0.1759 ^b	0.1759	0
"	"	0.20631	0.21037	0.1821	"	0.0062
"	"	0.48566	0.20945	0.1899	"	0.0140
"	"	0.76235	0.20862	0.1969	"	0.0210
"	"	1.0358	0.20789	0.2031	"	0.0272
"	"	1.4236	0.20696	0.2110	"	0.0351
"	"	1.8808	0.20598	0.2192	"	0.0433
"	"	2.4187	0.20501	0.2274	"	0.0515
"	"	3.0346	0.20405	0.2356	"	0.0597
"	"	Satd.	0.20339	0.2411	"	0.0652
5 + G	0.099998	0.095656	0.09583	0.1147 ^c	0.1088	0.0057
"	0.21928	"	0.13227	0.1477	0.1372	0.0105
"	0.70487	"	0.18841	0.1805	0.1758	0.0047
"	0.95942	"	0.20363	0.1856	0.1817	0.0039
"	1.2910	"	0.21874	0.1868	0.1835	0.0033
5 + G	0.099998	0.095656	0.09575	0.1147 ^c	0.1088	0.0057
"	0.22887	"	0.13473	0.1449	0.1388	0.0061
"	0.33256	"	0.15229	0.1587	0.1525	0.0062
"	0.43509	"	0.16509	0.1672	0.1618	0.0054
"	0.57253	"	0.17822	0.1756	0.1703	0.0053
"	0.71259	"	0.18881	0.1809	0.1761	0.0048
"	1.1143	"	0.21106	0.1871	0.1832	0.0039
5 + G	0.099998	0.095656	0.09461	0.1147 ^c	0.1088	0.0057
"	0.22066	"	0.13191	0.1431	0.1375	0.0056
"	0.33981	"	0.15225	0.1587	0.1533	0.0054
"	0.50094	"	0.17069	0.1714	0.1663	0.0051
"	0.72015	"	0.18820	0.1813	0.1763	0.0050
"	0.93938	"	0.20130	0.1858	0.1814	0.0044
"	1.2818	"	0.21707	0.1875	0.1835	0.0040

(contd.)

TABLE B-3 (contd.)

Electrode	m_c	m_B	E volts	$-\log \gamma_c$	$-\log \gamma_c^\circ$	$-\log \frac{\gamma_c}{\gamma_c^\circ}$
5 + G	0.29999	0.31500	0.14576	0.1618 ^d	0.1487	0.0131
	0.43587	"	0.16362	0.1730	0.1618	0.0112
	0.59514	"	0.17868	0.1811	0.1714	0.0097
	0.77850	"	0.19180	0.1869	0.1781	0.0088
	1.0517	"	0.20689	0.1899	0.1827	0.0072
	1.3606	"	0.22024	0.1889	0.1833	0.0056
1 + G	0.29999	0.31500	0.0483	0.1618 ^d	0.1487	0.0131
	0.44673	"	0.06745	0.1739	0.1626	0.0113
	0.68835	"	0.08842	0.1845	0.1752	0.0093
	1.0413	"	0.10911	0.1893	0.1826	0.0067
1 + G	0.30001	0.75327	0.04605	0.1770 ^d	0.1487	0.0283
	0.42046	"	0.06239	0.1855	0.1606	0.0249
	0.57503	"	0.07768	0.1923	0.1704	0.0219
	0.76818	"	0.09196	0.1973	0.1778	0.0195
	1.0709	"	0.10890	0.1984	0.1829	0.0155
	1.3994	"	0.12293	0.1958	0.1831	0.0127
5 + G	0.30001	0.75327	0.14350	0.1770 ^d	0.1487	0.0283
	0.44306	"	0.16238	0.1867	0.1624	0.0243
	0.74207	"	0.18777	0.1960	0.1770	0.0190
	1.0746	"	0.20654	0.1984	0.1829	0.0155
4 + G	0.30002	1.2738	0.13937	0.1923 ^d	0.1487	0.0436
	0.44781	"	0.15889	0.2013	0.1627	0.0386
	0.61608	"	0.17466	0.2065	0.1724	0.0341
	0.81698	"	0.18886	0.2091	0.1790	0.0301
	1.0849	"	0.20343	0.2091	0.1830	0.0261
	1.3772	"	0.21603	0.2062	0.1833	0.0229
5 + G	0.30002	1.2738	0.14370	0.1923 ^d	0.1487	0.0436
	0.42452	"	0.16055	0.2007	0.1610	0.0397
	1.2204	"	0.21400	0.2074	0.1843	0.0231

(contd.)

TABLE B-3 (contd.)

Electrode	m_c	m_B	E volts	$-\log \gamma_c$	$-\log \gamma_c^\circ$	$-\log \frac{\gamma_c}{\gamma_c^\circ}$
9 + A	0.030000	0.55062	-0.06215	0.1068 ^e	0.0698	0.0370
	0.051016	"	-0.03641	0.1197	0.0855	0.0342
	0.070274	"	-0.02097	0.1285	0.0960	0.0325
	0.089401	"	-0.00941	0.1352	0.1043	0.0309
	0.10761	"	-0.00053	0.1407	0.1109	0.0298
9 + C	0.028669	0	-0.05995	0.0686 ^a	0.0686	0
	0.028669	1.4928	-0.06950	0.1493	0.0686	0.0807
	0.055137	"	-0.03737	0.1618	0.0880	0.0738
	0.081143	"	-0.01851	0.1701	0.1009	0.0692
	0.098111	"	-0.00929	0.1747	0.1076	0.0671
	0.11901	"	0.00016	0.1786	0.1145	0.0641
9 + G	0.028669	0	-0.05983	0.0686 ^a	0.0686	0
	0.028669	2.5482	-0.07354	0.1845	0.0686	0.1159
	0.055138	"	-0.04087	0.1924	0.0880	0.1044
	0.079749	"	-0.02263	0.1985	0.1003	0.0982
	0.10155	"	-0.01069	0.2025	0.1088	0.0937

Notes:

1. a, b, c and d indicate the reference activity coefficients. a values are calculated from Equation 6-4 (Reference 7, Chapter 6). b values are tabulated by Robinson and Stokes (Reference 9, Chapter 6). c, d and e values are obtained graphically from the experiments where the concentration of sodium chloride was held constant at 0.1 m, 0.3 m, and 0.03 m respectively (see Results, Chapter 7).
2. γ_c° is the activity coefficient of sodium chloride in water.
3. $-\log \gamma_c^\circ$ values are either calculated from Equation 6-4 (Reference 7, Chapter 6) or taken from values tabulated by Robinson and Stokes (Reference 9, Chapter 6).
4. Satd. indicate saturation.

TABLE B-4

The activity coefficients of sodium chloride in glycine-water mixtures.

NaCl-Glycine-Water at 50°.

Electrode	m_c	m_B	E volts	$-\log \gamma_c$	$-\log \gamma_c^\circ$	$-\log \frac{\gamma_c}{\gamma_c^\circ}$
8 + Q	0.03	0	-0.06299	0.0717 ^a	0.0717	0
	"	0.56407	-0.06757	0.1074	"	0.0357
	"	1.3141	-0.07195	0.1416	"	0.0699
	"	1.9750	-0.07492	0.1647	"	0.0930
	"	2.7180	-0.07744	0.1844	"	0.1127
	"	3.5142	-0.07954	0.2007	"	0.1290
8 + Q	0.05	0	-0.03666	0.0870 ^a	0.0870	0
	"	0.54248	-0.04071	0.1186	"	0.0316
	"	1.2311	-0.04460	0.1489	"	0.0619
	"	1.9758	-0.04769	0.1730	"	0.0860
	"	2.6240	-0.04978	0.1893	"	0.1023
	"	3.3531	-0.05169	0.2042	"	0.1172
9 + S	0.13183	0	0.00433	0.1214 ^a	0.1214	0
	"	0.64649	0.00066	0.1500	"	0.0286
	"	1.2930	-0.00220	0.1723	"	0.0509
	"	1.9527	-0.00451	0.1903	"	0.0689
	"	2.5579	-0.00621	0.2036	"	0.0822
	"	3.4943	-0.00826	0.2196	"	0.0982
"	4.4135	-0.00986	0.2321	"	0.1107	
9 + G	0.30002	0	0.05114	0.1536 ^a	0.1536	0
	"	0.56591	0.04842	0.1748	"	0.0212
	"	1.2684	0.04588	0.1948	"	0.0410
	"	1.9969	0.04389	0.2101	"	0.0565
	"	2.6379	0.04242	0.2216	"	0.0680
	"	3.6796	0.04065	0.2354	"	0.0818
9 + A	0.49995	0	0.07768	0.1712 ^a	0.1712	0
	"	0.47678	0.07585	0.1855	"	0.0143
	"	1.1050	0.07384	0.2011	"	0.0299
	"	1.7237	0.07229	0.2132	"	0.0420
	"	2.3223	0.07104	0.2230	"	0.0518
	"	3.0000	0.06986	0.2322	"	0.0610
	"	3.7583	0.06878	0.2406	"	0.0694
	"	4.6096	0.06777	0.2485	"	0.0773

(contd.)

TABLE B-4 (contd.)

Electrode	m_c	m_B	E volts	$-\log \gamma_c$	$-\log \gamma_c^\circ$	$-\log \frac{\gamma_c}{\gamma_c^\circ}$
9 + G	0.73108	0	0.09757	0.1803 ^a	0.1803	0
	"	0.60679	0.09563	0.1954	"	0.0151
	"	1.2008	0.09410	0.2074	"	0.0271
	"	1.8566	0.09258	0.2192	"	0.0389
	"	2.5618	0.09136	0.2287	"	0.0484
	"	3.5204	0.08998	0.2395	"	0.0592
	"	4.4324	0.08894	0.2476	"	0.0673
8 + D	0.91156	0	0.11362	0.1834 ^a	0.1834	0
	"	0.54236	0.11191	0.1967	"	0.0133
	"	1.1404	0.11048	0.2079	"	0.0245
	"	1.7444	0.10926	0.2174	"	0.0340
	"	2.3357	0.10819	0.2257	"	0.0423
	"	3.2608	0.10691	0.2357	"	0.0523
	"	4.0086	0.10595	0.2432	"	0.0598
8 + G	1.1730	0	0.12440	0.1862 ^a	0.1862	0
	"	0.56536	0.12292	0.1977	"	0.0115
	"	1.1893	0.12160	0.2080	"	0.0218
	"	1.8168	0.12040	0.2174	"	0.0312
	"	2.3885	0.11958	0.2238	"	0.0376
	"	3.3649	0.11844	0.2327	"	0.0465
	"	4.3151	0.11734	0.2413	"	0.0551
9 + G	0.30000	0	0.05114	0.1536 ^a	0.1536	0
	0.30000	0.303113	0.04967	0.1650	0.1536	0.0114
	0.56085	"	0.08234	0.1820	0.1745	0.0075
	0.82236	"	0.10290	0.1879	0.1821	0.0058
	1.0573	"	0.11674	0.1891	0.1849	0.0042
8 + D	0.29673	0	0.05164	0.1531 ^a	0.1531	0
	0.29673	0.53301	0.04900	0.1737	0.1531	0.0206
	0.54372	"	0.08080	0.1888	0.1736	0.0152
	0.76925	"	0.09935	0.1948	0.1811	0.0137
	1.0144	"	0.11455	0.1964	0.1845	0.0119
	1.2417	"	0.12594	0.1954	0.1871	0.0083

(contd.)

TABLE B-4 (contd.)

Electrode	m_c	m_B	E volts	$-\log \gamma_c$	$-\log \gamma_c^\circ$	$-\log \frac{\gamma_c}{\gamma_c^\circ}$
9 + B	0.30002	0	0.04844	0.1536 ^a	0.1536	0
	0.30002	1.0005	0.04415	0.1870	0.1536	0.0334
	0.51712	"	0.07288	0.1994	0.1722	0.0272
	0.73146	"	0.09148	0.2050	0.1803	0.0247
	0.93825	"	0.10536	0.2049	0.1837	0.0212
	1.1628	"	0.11755	0.2030	0.1860	0.0170
8 + D	0.29925	0	0.05159	0.1534 ^a	0.1534	0
	0.29925	2.1099	0.04403	0.2124	0.1534	0.0590
	0.51245	"	0.07296	0.2204	0.1720	0.0484
	0.76219	"	0.09476	0.2228	0.1810	0.0418
	0.99612	"	0.10970	0.2219	0.1843	0.0376
	1.2702	"	0.12384	0.2179	0.1876	0.0303
8 + G	0.30002	0	0.05458	0.1536 ^a	0.1536	0
	0.30002	3.0593	0.04514	0.2272	0.1536	0.0736
	0.53903	"	0.07712	0.2323	0.1734	0.0589
	0.78794	"	0.09826	0.2323	0.1815	0.0508
	1.0330	"	0.11372	0.2293	0.1847	0.0446
	1.2720	"	0.12581	0.2254	0.1876	0.0378

Note:

1. a, reference activity coefficient, calculated from Equation 6-4 using the parameters in the fifth column of Table 6-2.
2. γ_c° is the activity coefficient of sodium chloride in water.
3. $-\log \gamma_c^\circ$ values are calculated from Equation 6-4:

$$\log \gamma_c^\circ = - \frac{Am_c}{1 + Bm_c}^{1/2} + 2Cm_c + \frac{3}{2} Dm_c^2 + \frac{4}{3} Em_c^3 \quad (6-4)$$

where A = 0.5373; B = 1.86484; C = -24.6254×10^{-3} ;
D = 56.9774×10^{-3} ; E = -24.762×10^{-3} .

APPENDIX CCOMPUTER PROGRAMS

These programs were written in Chippewa Fortran code, for use on the University of Adelaide C.D.C., 6400 computer.

1. Program MESSY

Least Squares Program for fitting the activity coefficients of sodium chloride in water to the equation

$$\log \gamma = - \frac{A\sqrt{m}}{1 + B\sqrt{m}} + 2Cm + \frac{3}{2} Dm^2 + \frac{4}{3} Em^3 \quad (6-4)$$

2. (a) Program TERNY and (b) Program ROBKY

Least Squares Programs for fitting the relative activity coefficients of sodium chloride in glycine-water mixtures to the equations

$$\begin{aligned} \text{(a)} \quad \log \frac{\gamma_c}{\gamma_c^\circ} = m_B (B_{10} + B_{11} m_c^{1/2} + B_{12} m_c + B_{13} m_c^{3/2}) \\ + m_B^2 (B_{20} + B_{21} m_c^{1/2}) \end{aligned} \quad (7-3)$$

and

$$\text{(b)} \quad \log \frac{\gamma_c}{\gamma_c^\circ} = m_B (B_{10} + B_{11} m_c^{1/2} + B_{12} m_c) + B_{20} m_B^2 \quad (7-1)$$

3. Program SIGMA

Least Squares Program for fitting the activity coefficients of sodium chloride at various temperatures to the equation

$$\log \gamma_c = I - \frac{A}{T} - B \log T \quad (7-20)$$

1. Program MESSY: The comments refer to Equation 6-4 on page C-1.

DATA INPUT

Card 1. TITLE

" 2. N, M, G

according to FORMAT (2I3, F10.0)

N \equiv No. of points to be least squared

M \equiv No. of coefficients to be determined, i.e. 4 in this case

G \equiv Value of A

" 3. D(1), D(2), D(3), D(4)

according to FORMAT (4F10.0)

They are guessed constants, i.e. near values of B, C, D and E respectively.

" (4+n). X1,Y1; X2,Y2; X3,Y3; ...etc.

according to FORMAT (3(F10.0, F10.0))

i.e. 3 points to each card where X \equiv m, Y \equiv log γ .

OUTPUT

The output includes the following information:

- a. Values of the coefficients B, C, D and E.
- b. The sum of the squares of the deviation and the standard deviation.
- c. A comparison, at each input concentration, of the value of log γ calculated from the equation and that of the input. This is shown under the heading 'R' in the print-out.

```

PROGRAM MESSY ( INPUT,OUTPUT,TAPE 60 = INPUT)
DIMENSION D(5),X(50),Y(50),GAS(50),YC(50),R(50),F(50)
*,S(5,50),A(5,5),B(5,5),CY1(50),CY2(50),CY3(50),CY4(5
*0),TITLE(12),P1(5,100),P2(5,100),SF(20),SFA(20),V3(50
*),ACLOG(50),XX(50),GAY(50),CY5(50),CY6(50),CY7(50),V4
*(50)
66 READ 1, TITLE
1 FORMAT (12A6)
IF (EOF,60) 33,44
44 PRINT11, TITLE
11 FORMAT ( * * / 12A6)
READ 3, N,M,G
3 FORMAT (2I3,F10.0)
PRINT102
102 FORMAT(10X,*N*,10X,*M*,10X,*G*,5X)
PRINT63,N,M,G
63 FORMAT(7X,I3,7X,I3,7X,F10.0)
READ 4,(D(J),J=1,M)
4 FORMAT(5F10.0)
PRINT103
103 FORMAT(10X,*D1*,15X,*D2*,12X,*D3*,12X,*D4*,5X)
PRINT64,(D(J),J=1,M)
64 FORMAT (5F15.6)
READ 5,(X(I),Y(I),I=1,N)
5 FORMAT (3(F10.0,F10.0))
PRINT104
104 FORMAT(12X,*X*,14X,*Y*,14X,*X*,14X,*Y*,14X,*X*,14X,*Y
***,2X)
PRINT65,(X(I),Y(I),I=1,N)
65 FORMAT (3(F15.5,F15.5))
KK=1
17 I=1
PRINT105
105 FORMAT(13X,*POINTS*,8X,*GAS*,8X,*CY1*,10X,*CY2*,10X,*
*CY3*,10X,*YC*,10X,*R*,10X,*F*,10X)
SF(KK) = 0.0
7 GAS(I) = (1.0 + D(1)*SQRT(X(I)))
CY1(I)=- (G*SQRT(X(I)))/GAS(I)
CY2(I)=2.0*D(2)*X(I)
CY3(I)=1.5*D(3)*X(I)**2
V3(I)=(4.0/3.0)*D(4)*X(I)**3
YC(I)=(CY1(I)+CY2(I)+CY3(I)+V3(I))
R(I) = Y(I) - YC(I)
F(I) = (ABS(R(I)))**2
SF(KK) = SF(KK) + F(I)
PRINT 99 ,I,GAS(I),CY1(I),CY2(I),CY3(I),YC(I),R(I),F(
*I)
99 FORMAT ( * POINT NO. *,I4,4X,7F12.6)

```

```

      IF ( I.EQ.N) GO TO 8
      I= I+1
      GO TO 7
      8 SFA(KK) = SQRT ( SF(KK) / FLOAT (N-4))
C..... SEE J. TOPPING - BOOK ON ERRORS, P. 106
      PRINT 19, SF(KK),SFA(KK)
      19 FORMAT ( * SUM SQ. DEV.      = *,F15.8/ * STANDARD DE
      *V.      = *,F15.8)
      IF (KK.EQ.1) GO TO 13
      IF (ABS (SFA(KK)-SFA(KK-1)).GT.1.0E-08) GO TO 13
      14 PRINT 15,(D(I),I=1,4)
      15 FORMAT ( * FINAL COEFFICIENTS *, 4F15.7)
      GO TO 33
      13 DO 88 I=1,N
      S(1,I)=G*X(I)/GAS(I)**2
      S(2,I)=2.0*X(I)
      S(3,I)=(3.0/2.0)*X(I)**2
      S(4,I)=(4.0/3.0)*X(I)**3
      PRINT 101,I,S(1,I),S(2,I),S(3,I),S(4,I)
      101 FORMAT ( * DE. NO.*,I3,4F13.6)
      88 CONTINUE
      DO 10 I = 1,4
      DO 10 J = 1,4
      A(I,J) = 0.0
      DO 10 K=1,N
      A(I,J) = A(I,J) + S(I,K) * S(J,K)
      10 CONTINUE
      DO 60 I=1,4
      A(I,5) = 0.0
      DO 60 K=1,N
      A(I,5) = A(I,5) + S(I,K)*R(K)
      60 CONTINUE
      PRINT 77,((A(I,J),J=1,5),I=1,4)
      77 FORMAT ( //* COEFFICIENT MAT. *, 5F15.5)
      CALL MATRIX (10,4,5,1,A,5,B)
      PRINT 6, ((A(I,J),J=1,5),I=1,4)
      6 FORMAT ( // * CORRE. ON SOLS.*, 5F15.6)
      DO 30 I=1,4
      D(I) = D(I) + A(I,5)
      30 CONTINUE
      PRINT 9,(D(I),I=1,4)
      9 FORMAT ( * COEFFICIENTS * , 4F15.6)
      32 KK = KK+1
      GO TO 17
      GO TO 66
      33 STOP
      END

```

2. (a) Program TERNY and (b) Program ROBKY: The comments refer to Equations 7-1 and 7-3 on page C-1.

DATA INPUT

Card 1. N

N \equiv No. of points to be least squared and is fed in under FORMAT (I3)

" (2+n). Z1,YY1,X1; Z2,YY2,X2, ...etc.

according to FORMAT (6F10.0), i.e. 2 points to each card.

Z \equiv $\log \frac{\gamma_c}{\gamma_c^\circ}$, YY \equiv m_c , X \equiv m_B

OUTPUT

The output includes the following information:

- a. Values of the coefficients B10, B11, B12, B13, B20, B21.
- b. The average deviation (under 'AUDEV') and the square root of the mean square deviation (under 'SRMS').
- c. A comparison, at each input concentration, of the value of $\log \frac{\gamma_c}{\gamma_c^\circ}$ calculated from the equation and that of the input. This is shown under 'DIF' in the print-out.


```

PROGRAM TERNY(INPUT,OUTPUT)
DIMENSION A(10,10),C(10,10),B(10),CO(10),S(6),SO(6),
*SN(6),SM(6),SB(6),
*SC(6),X(200),Y(200),Z(200),YY(200),VK(20),VKP1(20)
C..... N IS NO. OF OBSERVATIONS
21 READ10,N
10 FORMAT(I3)
   IF(N.EQ.0)GO TO 20
   READ30,(Z(I),YY(I),X(I),I=1,N)
30 FORMAT(6F10.6)
   DO777I=1,N
   Y(I)=SQRT(YY(I))
777 CONTINUE
C..... CLEAR ARRAYS A$C
   DO1K=1,10
   DO1L=1,10
   A(L,K)=0.0
1 C(L,K)=0.0
C..... CLEAR ARRAYS B$CO
   DO2K=1,10
   B(K)=0.0
2 CO(K)=0.0
C..... ARRAY CO CONTAINS COEFFICIENTS ON RETURN FROM INVERSE
C..... CLEAR ARRAYS S $ SO $ SN $ SM $ SB $ SC
   DO3K=1,6
   S(K)=0.0
   SO(K)=0.0
   SN(K)=0.0
   SM(K)=0.0
   SB(K)=0.0
3 SC(K)=0.0
C..... JS IS NO OF COEFFICIENTS
   JS=6
C..... CALCULATE ELEMENTS OF ARRAY A
C..... CALC. POWERS OF X
   DO4J=2,4
   DO4I=1,N
4 SO(J)=SO(J)+X(I)**J
C..... CALC (X(I)**2)*Y(I)**J
   DO5J=1,6
   DO5I=1,N
5 SN(J)=SN(J)+(X(I)**2)*(Y(I)**J)
C..... CALC (X(I)**3)*Y(I)**J
   DO6J=1,4
   DO6I=1,N
6 SM(J)=SM(J)+(X(I)**3)*(Y(I)**J)
C..... CALC (X(I)**4)*Y(I)**J
   DO7J=1,2

```

```

DO7I=1,N
  7 S(J)=S(J)+(X(I)**4)*(Y(I)**J)
C..... CALC. ELEMENTS OF ARRAY B
C..... CALC X(I)*(Y(I)**J)*Z(I)
      DO8J=1,4
      DO8I=1,N
  8 SB(J)=SB(J)+X(I)*(Y(I)**(J-1))*Z(I)
C..... CALC (X(I)**2*(Y(I)**J)*Z(I)
      DO9J=1,2
      DO9I=1,N
  9 SC(J)=SC(J)+(X(I)**2)*(Y(I)**(J-1))*Z(I)
C..... FILL ARRAY A
      A(1,1)=S0(2)
      A(1,5)=A(5,1)=S0(3)
      A(5,5)=S0(4)
      A(1,2)=A(2,1)=SN(1)
      A(1,3)=A(3,1)=A(2,2)=SN(2)
      A(1,4)=A(4,1)=A(2,3)=A(3,2)=SN(3)
      A(2,4)=A(3,3)=A(4,2)=SN(4)
      A(3,4)=A(4,3)=SN(5)
      A(4,4)=SN(6)
      A(1,6)=A(6,1)=A(2,5)=A(5,2)=SM(1)
      A(2,6)=A(6,2)=A(3,5)=A(5,3)=SM(2)
      A(3,6)=A(6,3)=A(4,5)=A(5,4)=SM(3)
      A(4,6)=A(6,4)=SM(4)
      A(5,6)=A(6,5)=S(1)
      A(6,6)=S(2)
C..... PRINT OUT ARRAY A
      PRINT110
  110 FORMAT(1H1,28X,*ARRAY A*)
      PRINT111,((A(L,K),K=1,6),L=1,6)
  111 FORMAT(1X,6(E14.7,4X,E14.7,4X,E14.7,4X,E14.7,4X,
3E14.7,4X,E14.7,//))
C..... FILL ARRAY B
      B(1)=SB(1)
      B(2)=SB(2)
      B(3)=SB(3)
      B(4)=SB(4)
      B(5)=SC(1)
      B(6)=SC(2)
C..... PRINT OUT ARRAY B
      PRINT102
  102 FORMAT(1H0,*ARRAY B*)
      DO13K=1,6
  13 PRINT103,B(K)
  103 FORMAT(1H0,1X,E14.7)
      CALL INVERSE(A,B,C,C0,JS)
      PRINT104

```

```

104 FORMAT(1H0,*INVERSE OF ARRAY A*)
    PRINT105,((C(L,K),K=1,6),L=1,6)
105 FORMAT(1X,6(E14.7,4X,E14.7,4X,E14.7,4X,E14.7,4X,
3E14.7,4X,E14.7,//))
    PRINT106
106 FORMAT(1H1,*COEFFICIENTS*)
101 PRINT100,C0(1),C0(2),C0(3),C0(4),C0(5),C0(6)
100 FORMAT(5X,*B10*,E14.7,///,5X,*B11*,E14.7,///,5X,*B12*,
1E14.7,///,5X,*B13*,E14.7,///,5X,*B20*,E14.7,///,5X,*B21*
*,E14.7)
    PRINT38
38  FORMAT(5X 1HZ 13X 2HYY 13X 1HX 13X 1HY 13X 5HZCALC 13
*X 3HDIF)
    DELL=0
    DO14I=1,N
    ZCALC=C0(1)*X(I)+C0(2)*X(I)*Y(I)+C0(3)*X(I)*(Y(I)**2)
    *+C0(4)*X(I)
    2*(Y(I)**3)+C0(5)*X(I)**2+C0(6)*(X(I)**2)*Y(I)
    DEL=(ZCALC-Z(I))
    DELL=DELL+ABS(DEL)
14  PRINT707,Z(I),YY(I),X(I),Y(I),ZCALC,DEL
707 FORMAT(6(1XE13.6))
    PRINT39
39  FORMAT(1H /1H ,4X,5HAVDEV)
    AVDEV=DELL/FLOAT(N)
    PRINT15,AVDEV
15  FORMAT(1XE15.8/1H )
    DELOP=0.0
    DO107I=1,N
    ZCALC=C0(1)*X(I)+C0(2)*X(I)*Y(I)+C0(3)*X(I)*(Y(I)**2)
    *+C0(4)*X(I)
    2*(Y(I)**3)+C0(5)*X(I)**2+C0(6)*(X(I)**2)*Y(I)
    DELO=(ZCALC-Z(I))**2
    DELOP=DELOP+DELO
107 CONTINUE
    PRINT108
108 FORMAT(1H0,*SRMS*)
    SRMS=DELOP/(N-1)
    PRINT109,SRMS
109 FORMAT(1XE15.8)
    PRINT23
23  FORMAT(21H COMPUTATION FINISHED/1H2)
    GO TO 21
20  STOP
    END
    SUBROUTINE INVERSE(A,H,C,B,N)
    DIMENSION A(10,10),C(10,10),B(10),H(10)
    CALLMATRIX(10,N,N+1,2,C,10,Z)

```

```
CALLMATRIX(1,N,1,0,C(1,N+1),10,B,10)  
CALLMATRIX(1,N,N,0,A,10,C,10)  
CALLMATRIX(1,N,1,0,H,10,C(1,N+1),10)  
RETURN$END
```

```

PROGRAM ROBKY(INPUT,OUTPUT)
  DIMENSION A(10,10),C(10,10),B(10),CO(10),S(5),SO(5),S
  IN(5),SM(5),SB(5),SC(5),X(200),Y(200),Z(200),YY(200)
C..... N IS NO. OF OBSERVATIONS
  21 READ10,N
  10 FORMAT(I3)
    IF(N.EQ.0)GO TO 20
    READ30,(Z(I),YY(I),X(I),I=1,N)
  30 FORMAT(6F10.6)
    D0777I=1,N
    Y(I)=SQRT(YY(I))
  777 CONTINUE
C..... CLEAR ARRAYS A$C
  D01K=1,10
  D01L=1,10
  A(L,K)=0.0
  1 C(L,K)=0.0
C..... CLEAR ARRAYS B$CO
  D02K=1,10
  B(K)=0.0
  2 CO(K)=0.0
C..... ARRAY CO CONTAINS COEFFICIENTS ON RETURN FROM INVERSE
C..... CLEAR ARRAYS S $ SO $ SN $ SM $ SB $ SC
  D03K=1,5
  S(K)=0.0
  SO(K)=0.0
  SN(K)=0.0
  SM(K)=0.0
  SB(K)=0.0
  3 SC(K)=0.0
C..... JS IS NO OF COEFFICIENTS
  JS=4
C..... CALCULATE ELEMENTS OF ARRAY A
C..... CALC. POWERS OF X
  D04J=2,4
  D04I=1,N
  4 S(J)=S(J)+X(I)**J
C..... CALC SUM (X(I)**2)*(Y(I)**J)
  D05J=1,4
  D05I=1,N
  5 SO(J)=SO(J)+(X(I)**2.)*(Y(I)**J)
C..... CALC SUM (X(I)**3)*(Y(I)**J)
  D06J=1,2
  D06I=1,N
  6 SN(J)=SN(J)+(X(I)**3.)*(Y(I)**J)
C..... FILL ARRAY A
  A(1,1)=S(2)
  A(1,2)=A(2,1)=S(3)

```

```

A(2,2)=S(4)
A(1,3)=A(3,1)=S0(1)
A(1,4)=A(4,1)=A(3,3)=S0(2)
A(3,4)=A(4,3)=S0(3)
A(4,4)=S0(4)
A(2,3)=A(3,2)=SN(1)
A(2,4)=A(4,2)=SN(2)
C..... CALC ELEMENTS OF ARRAY B
D011J=1,2
D011I=1,N
11 SB(J)=SB(J)+(X(I)**J)*Z(I)
D012J=1,2
D012I=1,N
12 SC(J)=SC(J)+X(I)*(Y(I)**J)*Z(I)
C..... FILL ARRAY B
B(1)=SB(1)
B(2)=SB(2)
B(3)=SC(1)
B(4)=SC(2)
CALL INVERSE(A,B,C,CO,JS)
PRINT106
106 FORMAT(1H1,*COEFFICIENTS*)
101 PRINT100,CO(1),CO(2),CO(3),CO(4)
100 FORMAT(5X,*B10*,E14.7,/,5X,*B20*,E14.7,/,5X,*B11*,E
*14.7,/,5X,*B12*,E14.7)
PRINT38
38 FORMAT(5X 1HZ 13X 2HYY 13X 1HX 13X 1HY 13X 5HZCALC 13
*X 3HDIF)
DELL=0
D014I=1,N
ZCALC=CO(1)*X(I)+CO(2)*X(I)**2+CO(3)*X(I)*Y(I)+CO(4)*
1X(I)*Y(I)**2
DEL=(ZCALC-Z(I))
DELL=DELL+ABS(DEL)
14 PRINT707,Z(I),YY(I),X(I),Y(I),ZCALC,DEL
707 FORMAT(6(1XE13.6))
PRINT39
39 FORMAT(1H /1H ,4X,5HAVDEV)
AVDEV=DELL/FLOAT(N)
PRINT15,AVDEV
15 FORMAT(1XE15.8/1H )
DELOP=0.0
D0102I=1,N
ZCALC=CO(1)*X(I)+CO(2)*X(I)**2+CO(3)*X(I)*Y(I)+CO(4)*
1X(I)*Y(I)**2
DELO=(ZCALC-Z(I))**2
DELOP=DELOP+DELO
102 CONTINUE

```

```
PRINT103
103 FORMAT(1H0,*SRMS*)
    SRMS=DELOP/(N-1)
    PRINT104,SRMS
104 FORMAT(1XE15.8)
    PRINT23
    23 FORMAT(21H COMPUTATION FINISHED/1H2)
    GO TO 21
    20 STOP
    END
    SUBROUTINE INVERSE(A,B,C,CO,JS)
    DIMENSION A(10,10),C(10,10),B(10),CO(10)
    CALLMATRIX(1,JS,JS,0,A,10,C,10)
    CALLMATRIX(1,JS,1,0,B,10,C(1,JS+1),10)
    CALLMATRIX(10,JS,JS+1,2,C,10,Z)
    CALLMATRIX(1,JS,1,0,C(1,JS+1),10,CO,10)
    RETURN$END
```

3. Program SIGMA: The comments refer to Equation 7-20 on page C-1.

DATA INPUT

Card 1. N

N \equiv No. of points to be least squared and is fed in
under FORMAT (I3)

" (2+n). Z1, T1; Z2, T2; ...etc.

according to FORMAT (6F10.0), i.e. 3 points to each card.

Z \equiv $\log \gamma$, T = Temperature °K.

(In this research N = 4 since only values at 4 temperatures
were used in the least square.)

OUTPUT

The output includes the following information:

- a. Values of the coefficients.
- b. The average deviation (under 'AUDEV'), the relative partial molal heat capacity (under 'ZJ'), and the relative partial molal heat content (under 'ZL').
- c. A comparison, at each input temperature, of the value of $\log \gamma$ calculated from the equation and that of the input. This is shown under 'DIF' in the print-out.


```

PROGRAM SIGMA(INPUT,OUTPUT)
DIMENSION A(10,10),B(10),C(10,10),T(20),Z(20)
C..... N IS NO. OF OBSERVATIONS
  21 READ10,N
  10 FORMAT(I3)
  IF(N.EQ.0)GO TO 20
C..... CLEAR ARRAYS A&C
  DO1K=1,10
  DO1L=1,10
  A(L,K)=0.0
  1 C(L,K)=0.0
C..... CLEAR ARRAYS B&T&Z
  DO2K=1,20
  T(K)=0.0
  Z(K)=0.0
  2 B(K)=0.0
  READ30,(Z(I),T(I),I=1,N)
  30 FORMAT(6F10.6)
C..... CALCULATE ELEMENTS OF ARRAY A
  S=0.0
  DO4I=1,N
  4 S=S+1.0/T(I)
  SO=0.0
  DO5I=1,N
  5 SO=SO+ALOG10(T(I))
  SN=0.0
  DO6I=1,N
  6 SN=SN+1.0/(T(I)**2)
  SM=0.0
  DO7I=1,N
  7 SM=SM+ALOG10(T(I))/T(I)
  SE=0.0
  DO8I=1,N
  8 SE=SE+(ALOG10(T(I)))**2
C..... FILL ARRAY A
  A(1,1)=N
  A(1,2)=A(2,1)=S
  A(1,3)=A(3,1)=SO
  A(2,2)=SN
  A(2,3)=A(3,2)=SM
  A(3,3)=SE
C..... CALC. ELEMENTS OF ARRAY B
  SZ=0.0
  DO9I=1,N
  9 SZ=SZ+Z(I)
  SB=0.0
  DO11I=1,N
  11 SB=SB+Z(I)/T(I)

```

```

SC=0.0
DO12I=1,N
12 SC=SC+Z(I)*ALOG10(T(I))
C..... FILL ARRAY B
A(1,4)=SZ
A(2,4)=SB
A(3,4)=SC
CALL MATRIX (10,3,4,2,A,10,Y)
101 PRINT100
100 FORMAT(5X,*A*,17X,*B*,16X,*C*,17X,*ZJ*,17X,*ZL*,13X)
ZL=(-4.606)*1.98719*(A(2,4)-A(3,4)*298.0/2.303)
ZJ=2.0*1.9885*A(3,4)
X1=A(1,4)$X2=-A(2,4)$X3=-A(3,4)$X4=-ZJ$X5=-ZL
PRINT106,X1,X2,X3,X4,X5
106 FORMAT(2X,E14.7,3X,E14.7,3X,E14.7,3X,E14.7,3X,E14.7)
PRINT38
38 FORMAT(8X,*Z*,12X,*TEMP*,9X,*ZCALC*,8X,*DIF*,8X)
DELL=0
DO14I=1,N
ZCALC=A(1,4)+A(2,4)/T(I)+A(3,4)*ALOG10(T(I))
DEL=(ZCALC-Z(I))
DELL=DELL+ABS(DEL)
14 PRINT707,Z(I),T(I),ZCALC,DEL
707 FORMAT(4(1XE13.6))
PRINT39
39 FORMAT(8X,*AVDEV*,8X)
AVDEV=DELL/FLOAT(N)
PRINT15,AVDEV
15 FORMAT(8X,E15.8,8X)
GO TO 21
20 STOP

```