CHAPTER IV

ANALYSIS OF CONDUCTANCE DATA

4.1 Graphical Analysis

4.1.1 Method of Analysis

An apparently limiting equivatent conductivity is obtained from the Onsager and Shedlovsky extrapolation functions. The Onsager extrapolation method is the plot of the equivalent conductivity against the square root of the concentration of the electrolyte solution. A linear extrapolation to infinite dilution would yield the limiting equivalent conductivity Λ^{o}.

Considered as a better extrapolation method is the plot of the Shedlovsky extrapolation function $\Lambda^{o\prime}$ against the concentration of the electrolyts solution. According to the equation 4 , Chapter 2, a linear extrapolation to infinite dilution would yield the limiting equivalent conductivity Λ^{o}. Detail of this calculation is given in Appendix C.

From the values of Λ^{o}, the Onsager slopes were obtained using equation 2 , Chapter 2.

4.1.2 Results

Plots of Λ as a function of $C^{1/2}$ under concentration range studied of Zn $(ClO_4)_2$, $ZnSO_4$, $ZnCl_2$ and $CdSO_4$ solutions are shown in Figs 4.1, 4.2, 4.3, and 4.4, respectively. The same plots for the concentration below 4.75×10^{-3} mol kg^{-1} of these electrolyte solutions are given in Figs4.5, 4.6, 4.7, and 4.8. Included in these plots are experimental points of the literature conductance data of these electrolytes, details of which have been given in Section 1.3, Chapter 1. The observed conductances of dilute solutions shown in Figs 4.5, 4.6, 4.7, and 4.8 are an apparently linear function of $C^{1/2}$. Linear extrapolations of these plots (curve B) to infinite dilution by the least squares method gave the limiting equivalent conductivity of 120.72, 133.47, 130.92, and 134.82 $cm^{2}\ \Omega^{-1}$ $equiv^{-1}$ for $Zn(ClO_4)_2$, $ZnSO_4$, $ZnCl_2$, and $CdSO_4$, respectively. These

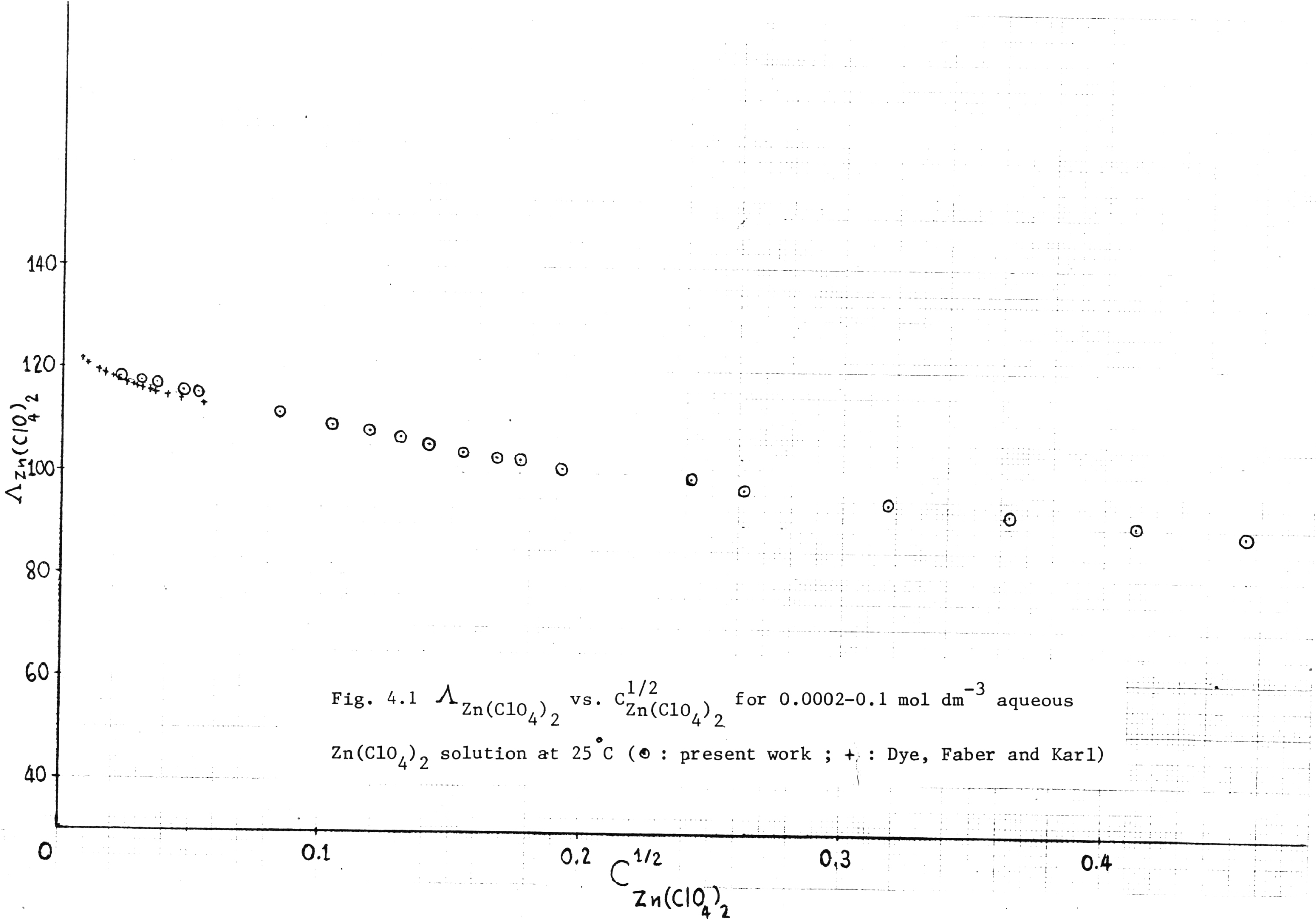


Fig. 4.1 $\Lambda_{Zn(ClO_4)_2}$ vs. $C^{1/2}_{Zn(ClO_4)_2}$ for 0.0002-0.1 mol dm^{-3} aqueous $Zn(ClO_4)_2$ solution at 25 °C (⊙ : present work ; + : Dye, Faber and Karl)

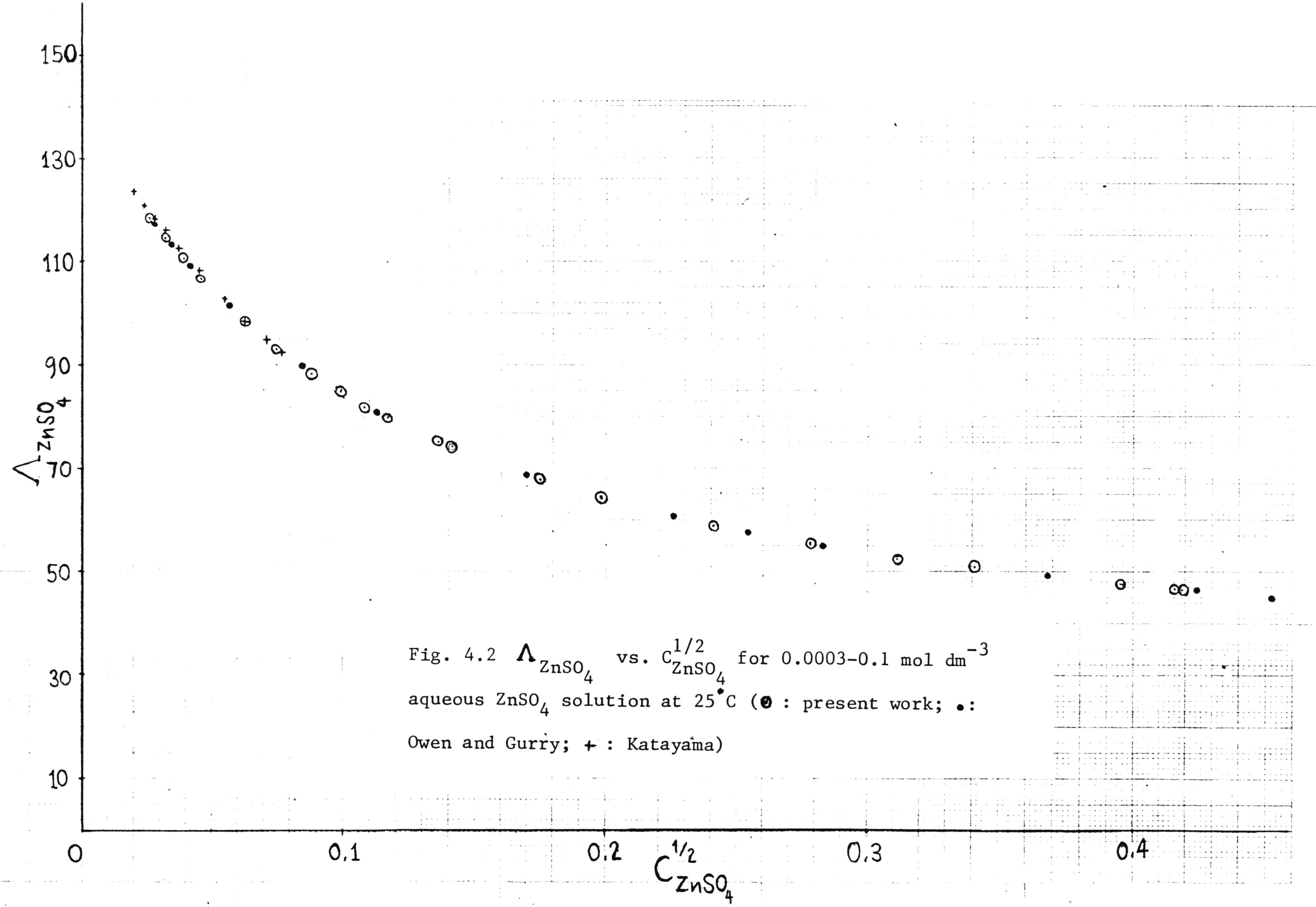


Fig. 4.2 Λ_{ZnSO_4} vs. $C^{1/2}_{ZnSO_4}$ for 0.0003-0.1 mol dm^{-3} aqueous $ZnSO_4$ solution at 25°C (⊙ : present work; •: Owen and Gurry; + : Katayama)

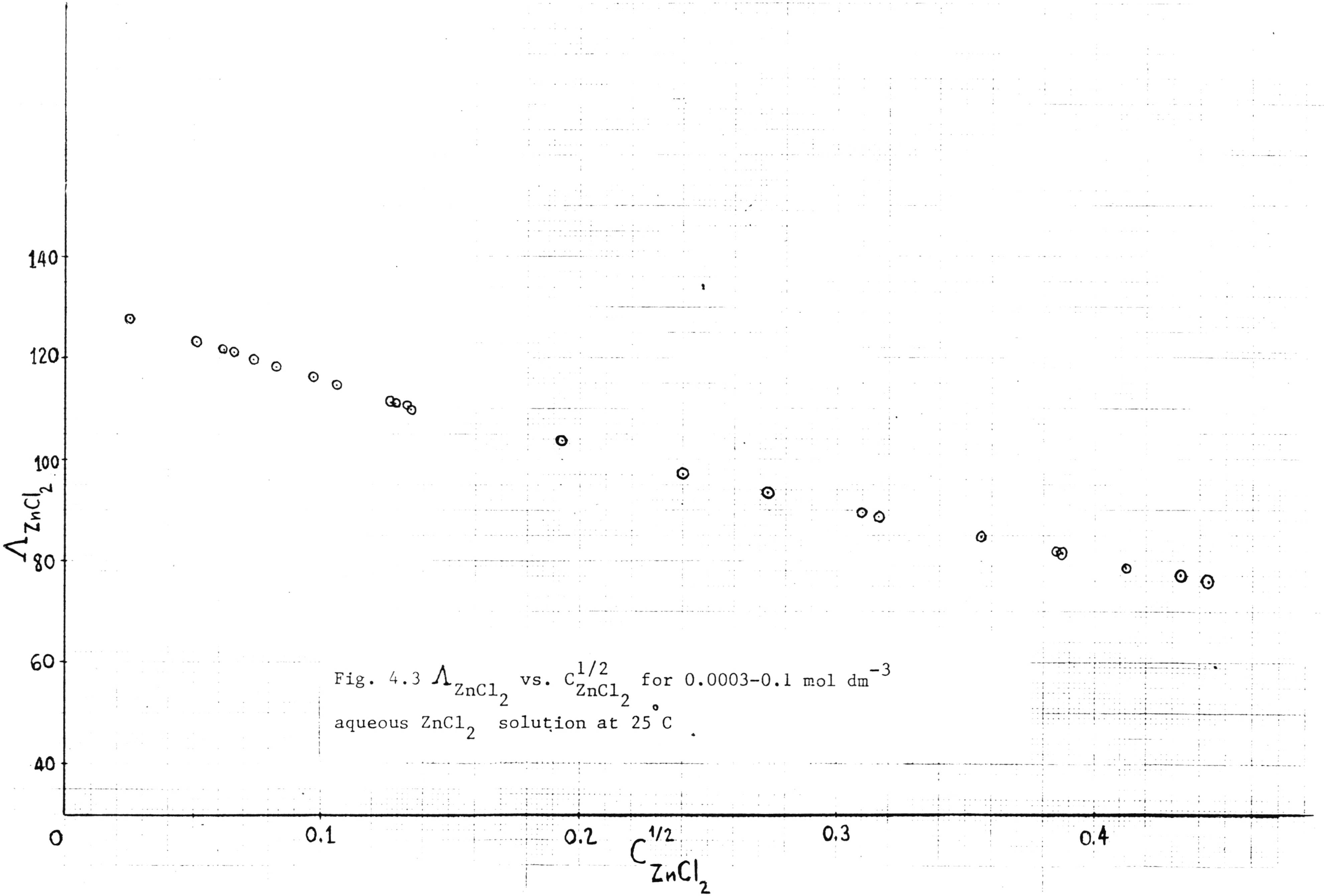


Fig. 4.3 Λ_{ZnCl_2} vs. $C^{1/2}_{ZnCl_2}$ for 0.0003-0.1 mol dm^{-3} aqueous $ZnCl_2$ solution at 25 °C

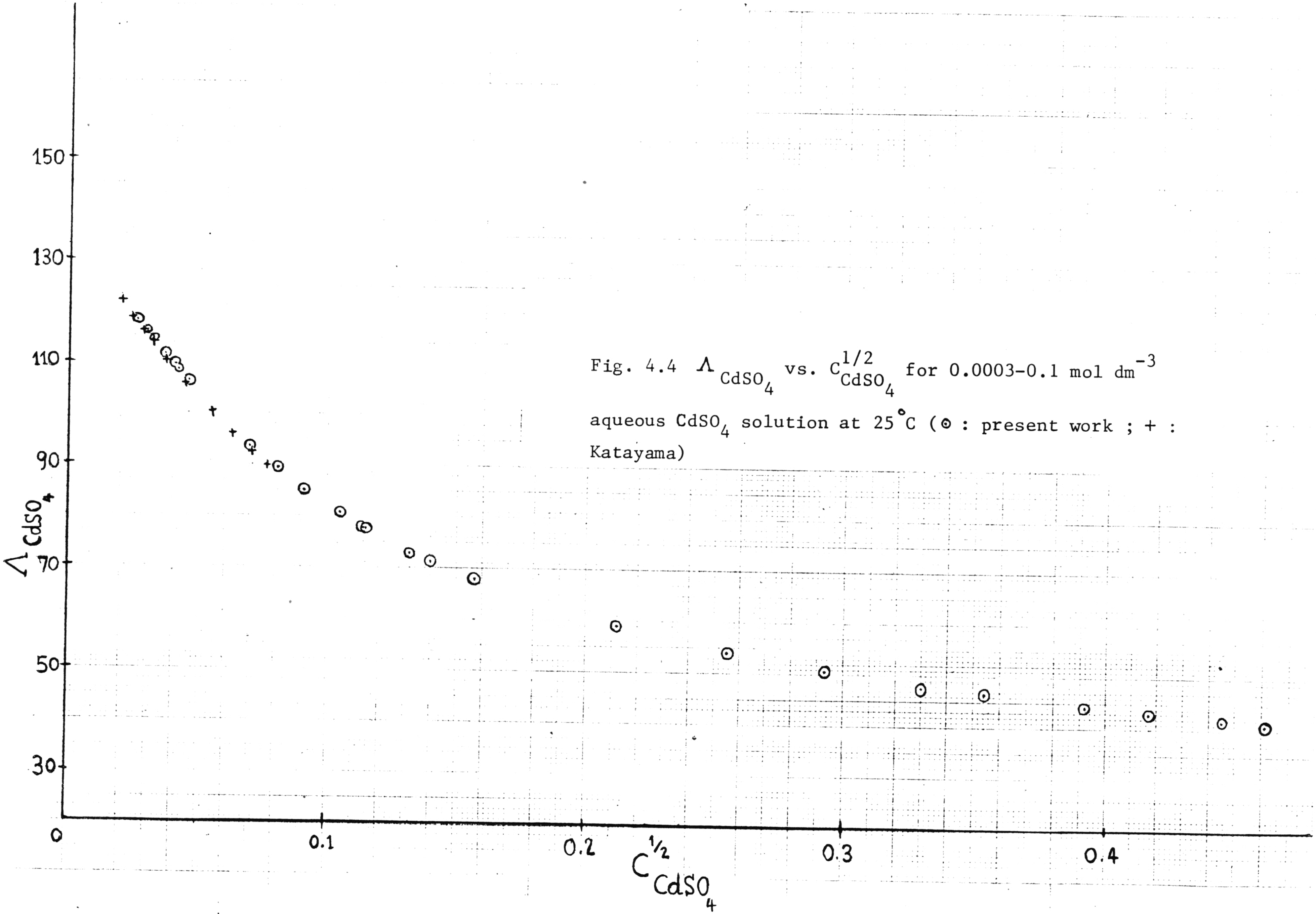
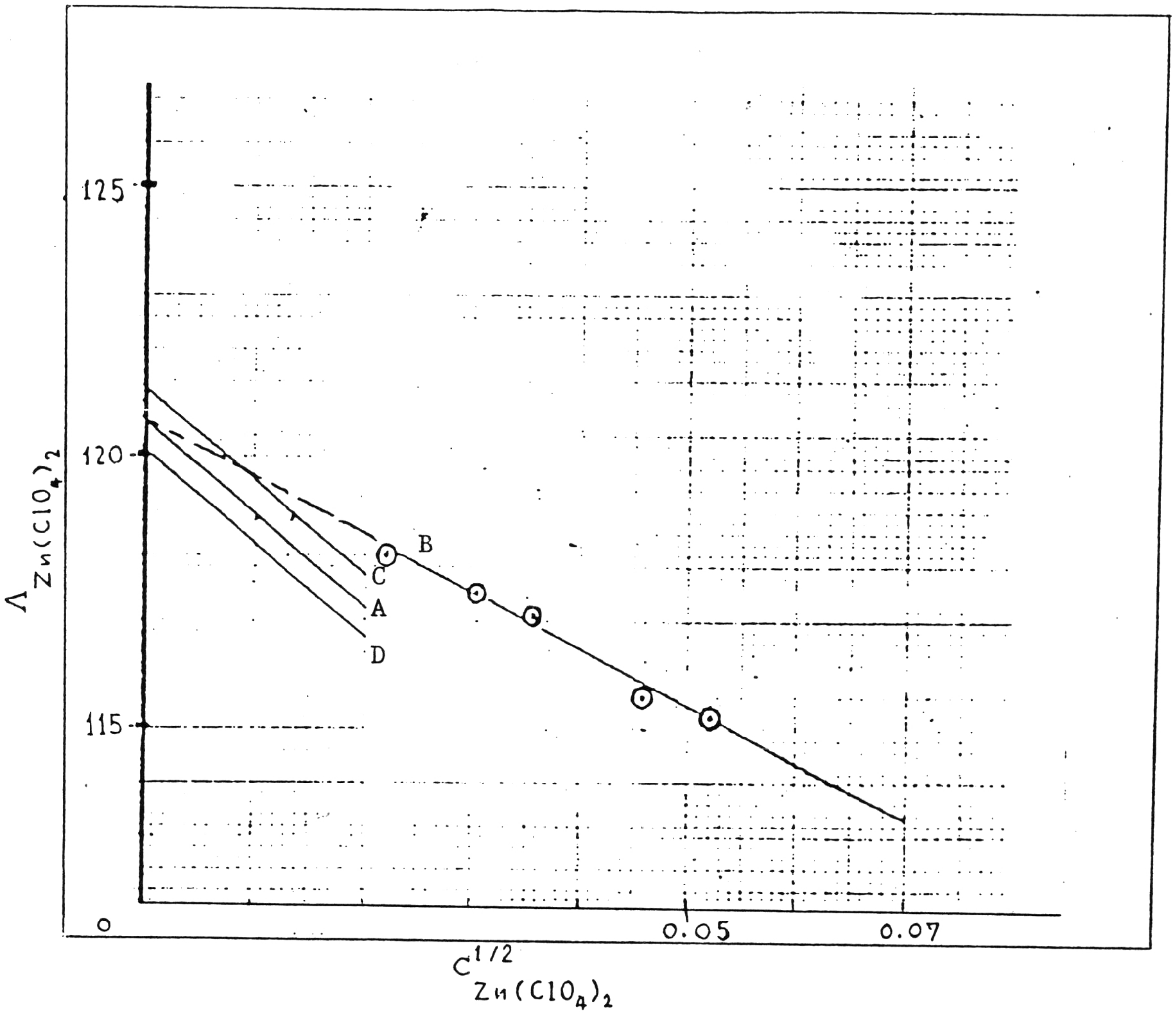


Fig. 4.4 Λ_{CdSO_4} vs. $C^{1/2}_{CdSO_4}$ for 0.0003-0.1 mol dm^{-3} aqueous $CdSO_4$ solution at 25 °C (⊙ : present work ; + : Katayama)



A : Onsager limiting slope using $\Lambda_{Zn(ClO_4)_2} = 120.72\ cm^2 \Omega^{-1}\ equiv.^{-1}$

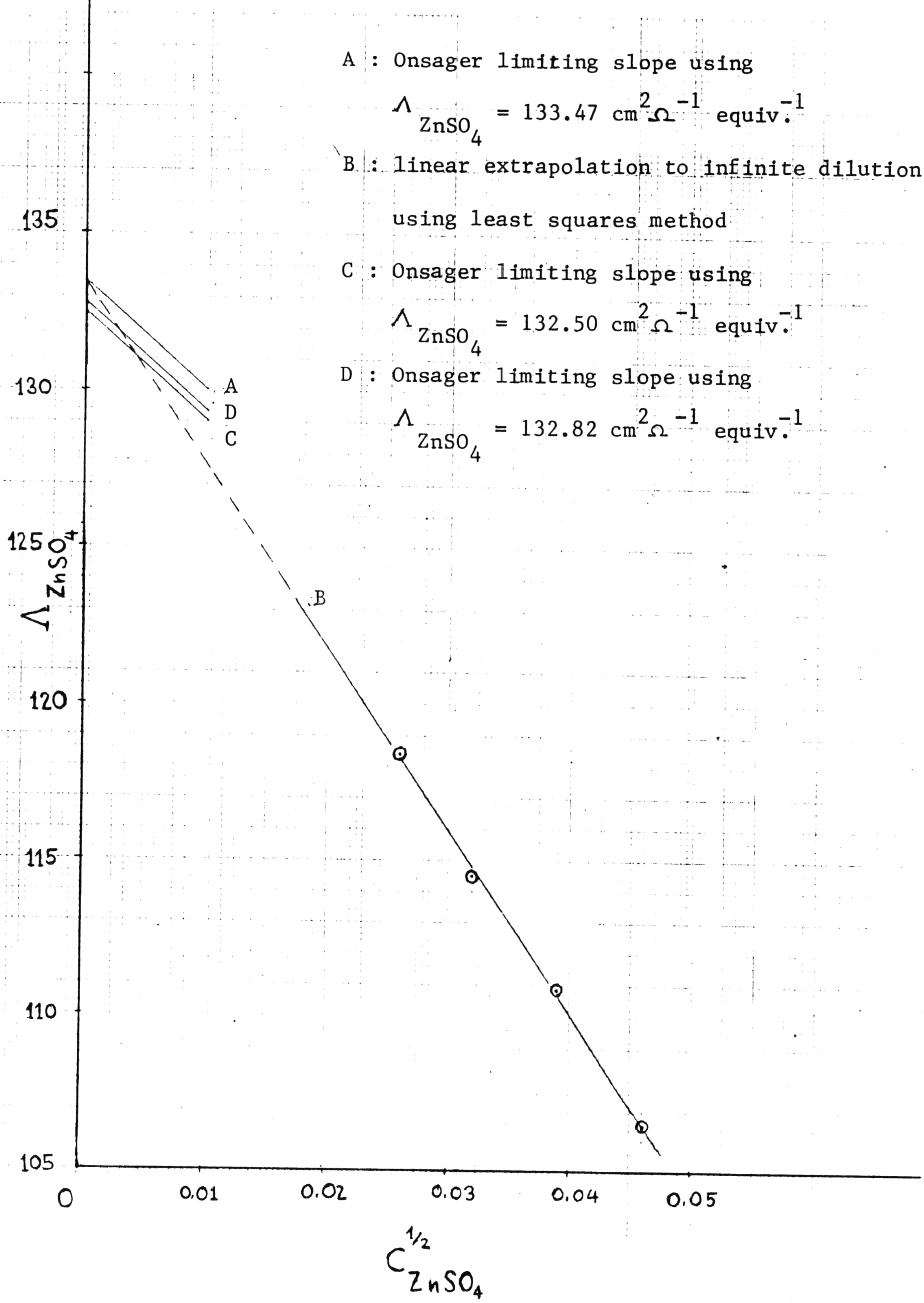
B : linear extrapolation to infinite dilution using least squares method

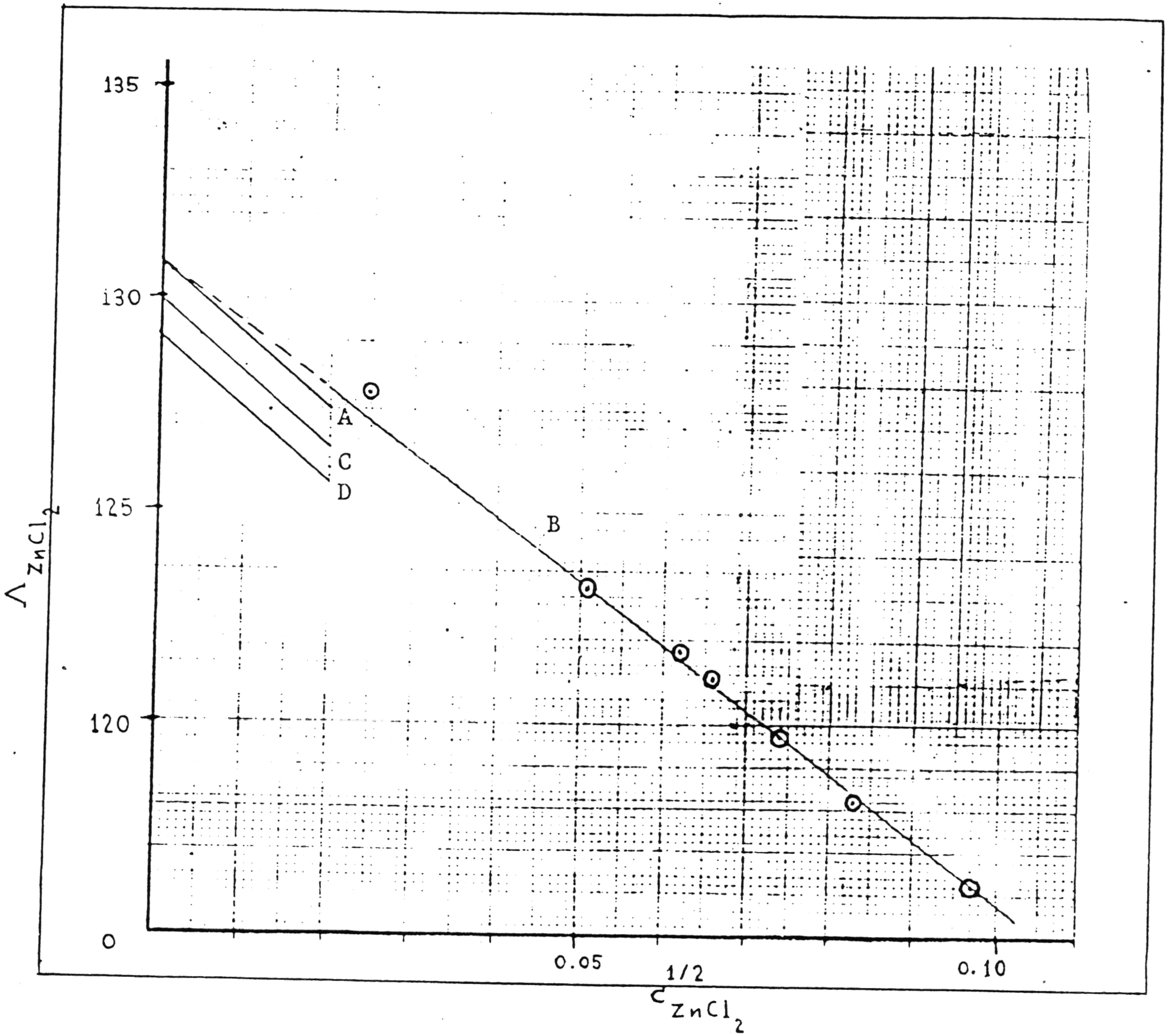
C : Onsager limiting slope using $\Lambda_{Zn(ClO_4)_2} = 121.29\ cm^2 \Omega^{-1}\ equiv.^{-1}$

D : Onsager limitingslope using $\Lambda_{Zn(ClO_4)_2} = 120.16\ cm^2 \Omega^{-1}\ equiv.^{-1}$

Fig. 4.5 $\Lambda_{Zn(ClO_4)_2}$ vs. $C^{1/2}_{Zn(ClO_4)_2}$ for $M_{Zn(ClO_4)_2}$ $< 1.3702 \times 10^{-3}$ mol dm^{-3}

Fig. 4.6 Λ_{ZnSO_4} vs. $C^{1/2}_{ZnSO_4}$ for $M_{ZnSO_4} < 1.0639 \times 10^{-3}$ mol dm^{-3}





A : Onsager limiting slope using $\Lambda_{ZnCl_2} = 130.92$ cm$^2\Omega^{-1}$equiv

B : linear extrapolation to infinite dilution using least squares method

C : Onsager limiting slope using $\Lambda_{ZnCl_2} = 130.00$ cm$^2\Omega^{-1}$equiv

D : Onsager limiting slope using $\Lambda_{ZnCl_2} = 129.15$ cm$^2\Omega^{-1}$equiv

Fig. 4.7 Λ_{ZnCl_2} vs. $C^{1/2}_{ZnCl_2}$ for $M_{ZnCl_2} < 4.72391 \times 10^{-3}$ mol dm^{-3}

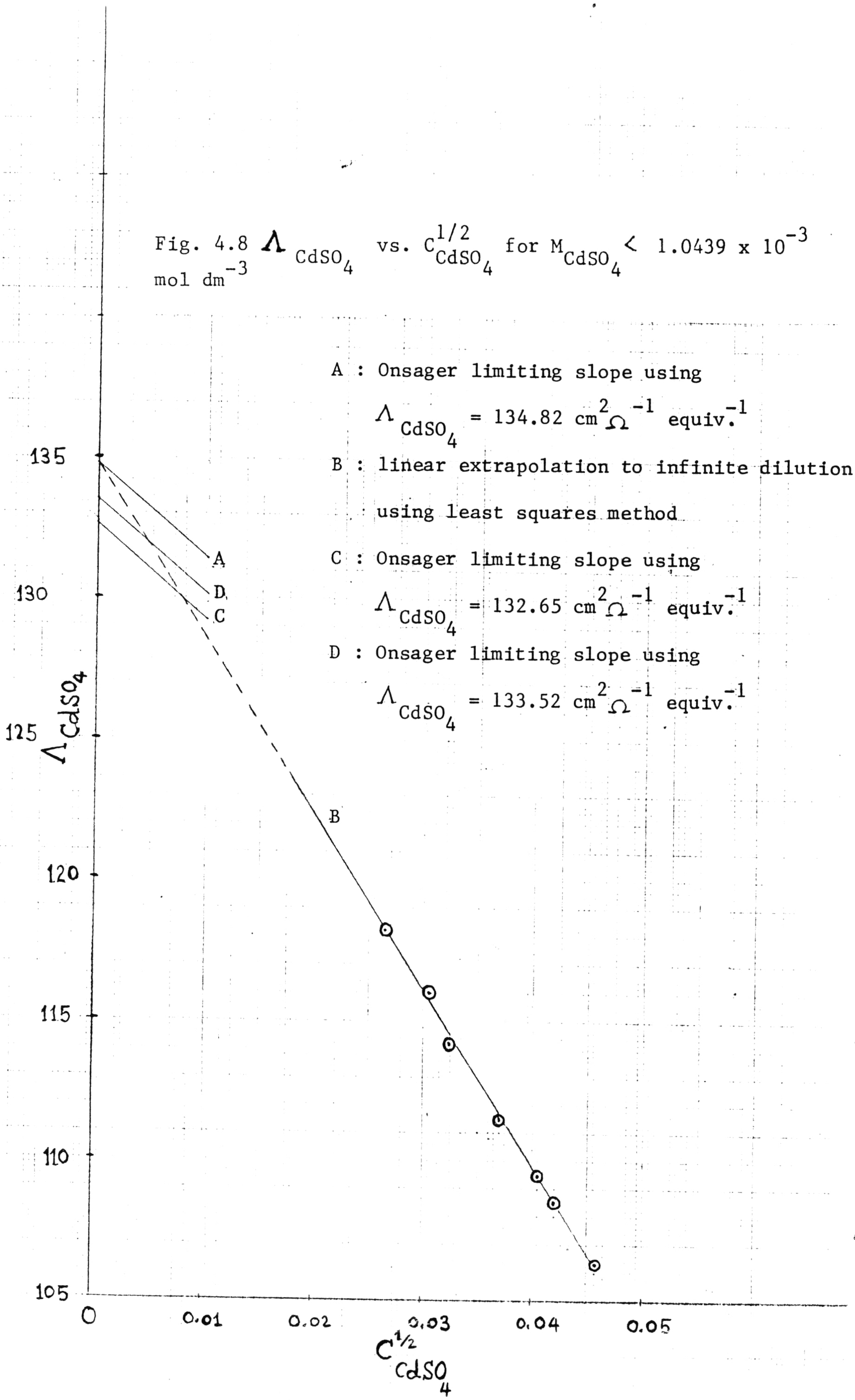


Fig. 4.8 Λ_{CdSO_4} vs. $C^{1/2}_{CdSO_4}$ for $M_{CdSO_4} < 1.0439 \times 10^{-3}$ mol dm^{-3}

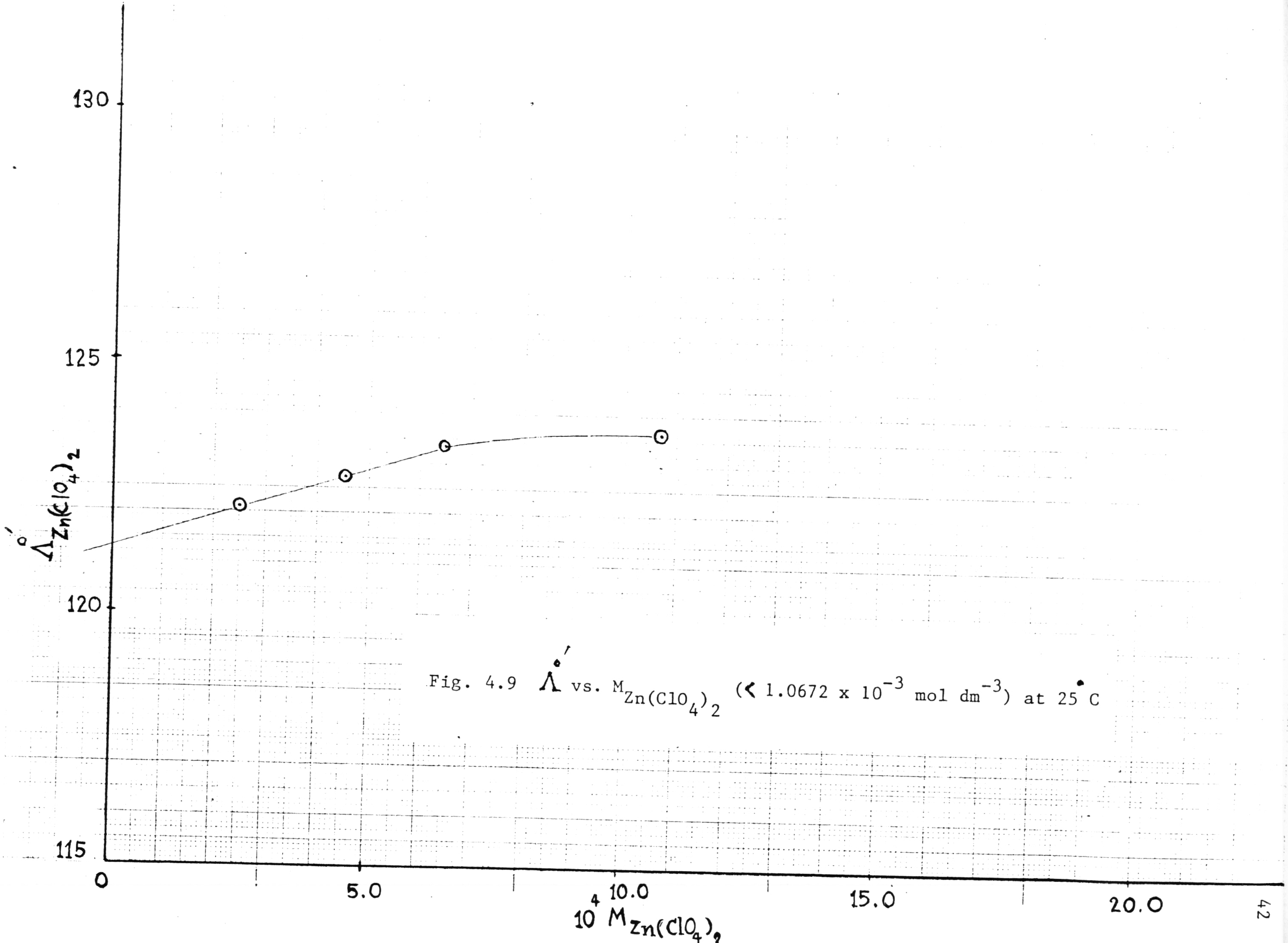


Fig. 4.9 $\Lambda^{\circ\prime}$ vs. $M_{Zn(ClO_4)_2}$ ($<$ 1.0672 x 10^{-3} mol dm^{-3}) at 25°C

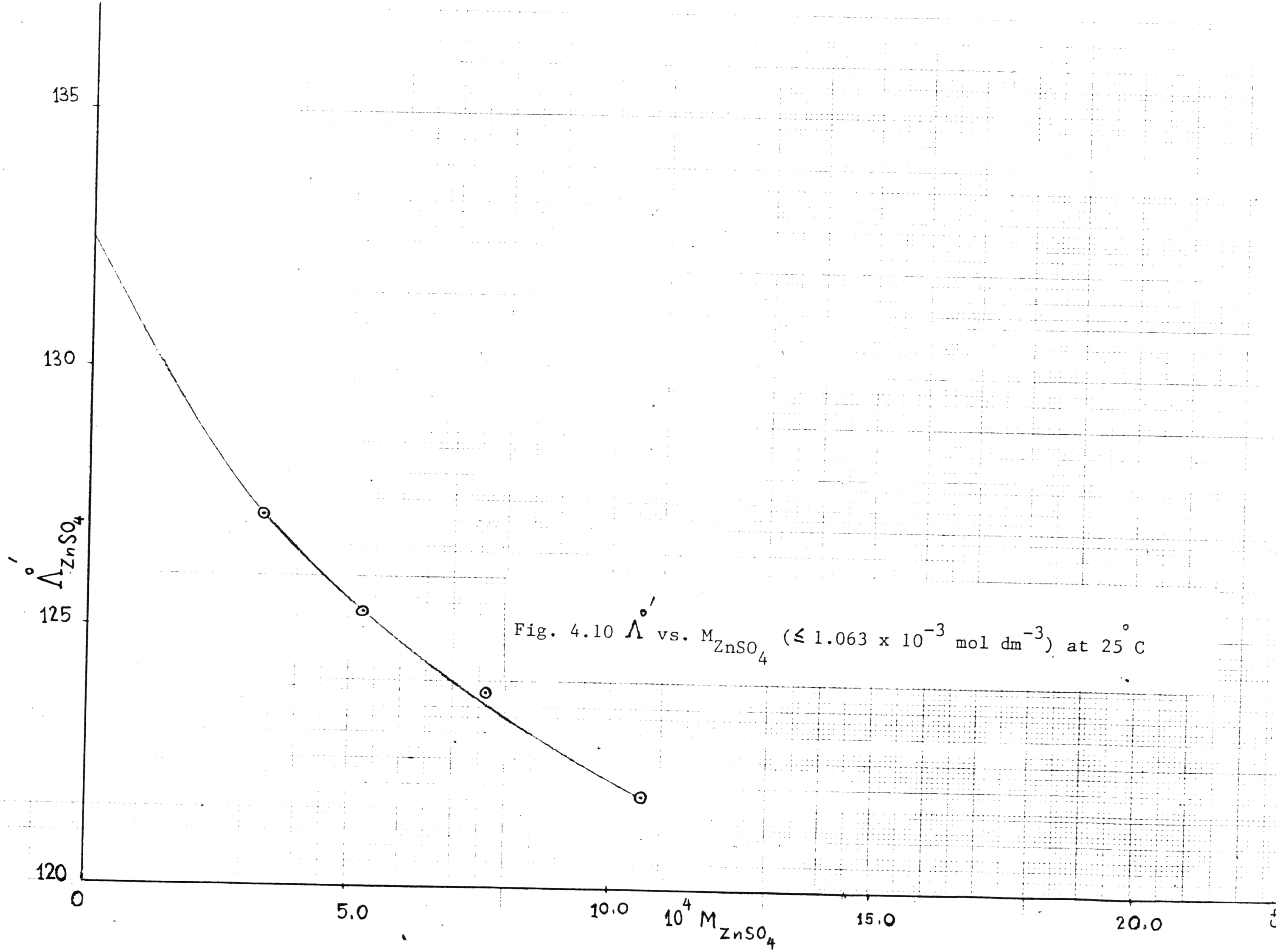


Fig. 4.10 $\Lambda^{o\prime}$ vs. M_{ZnSO_4} ($\leq 1.063 \times 10^{-3}$ mol dm^{-3}) at 25 °C

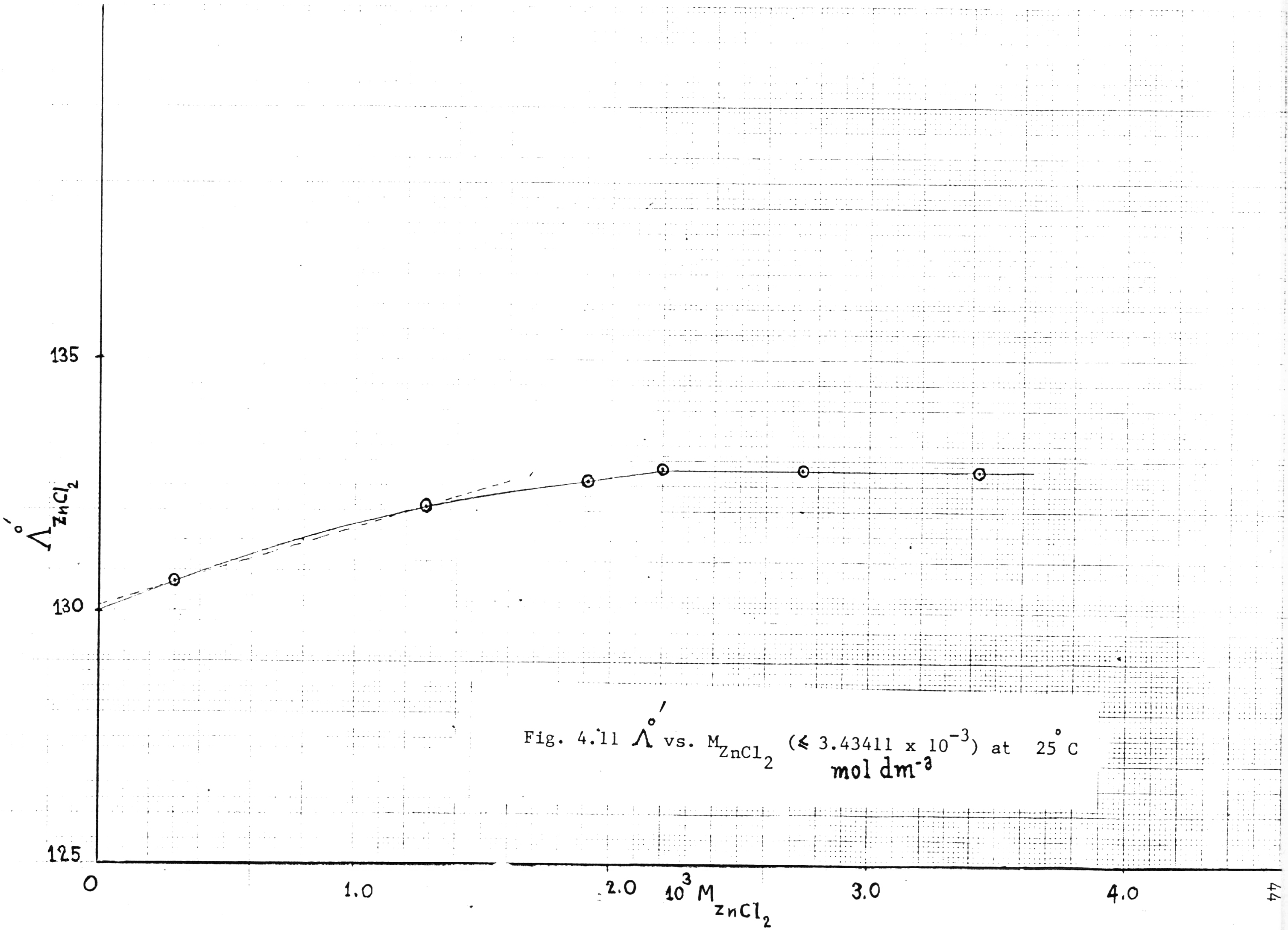


Fig. 4.11 $\Lambda^{o\prime}$ vs. M_{ZnCl_2} ($\leqslant 3.43411 \times 10^{-3}$ mol dm^{-3}) at 25°C

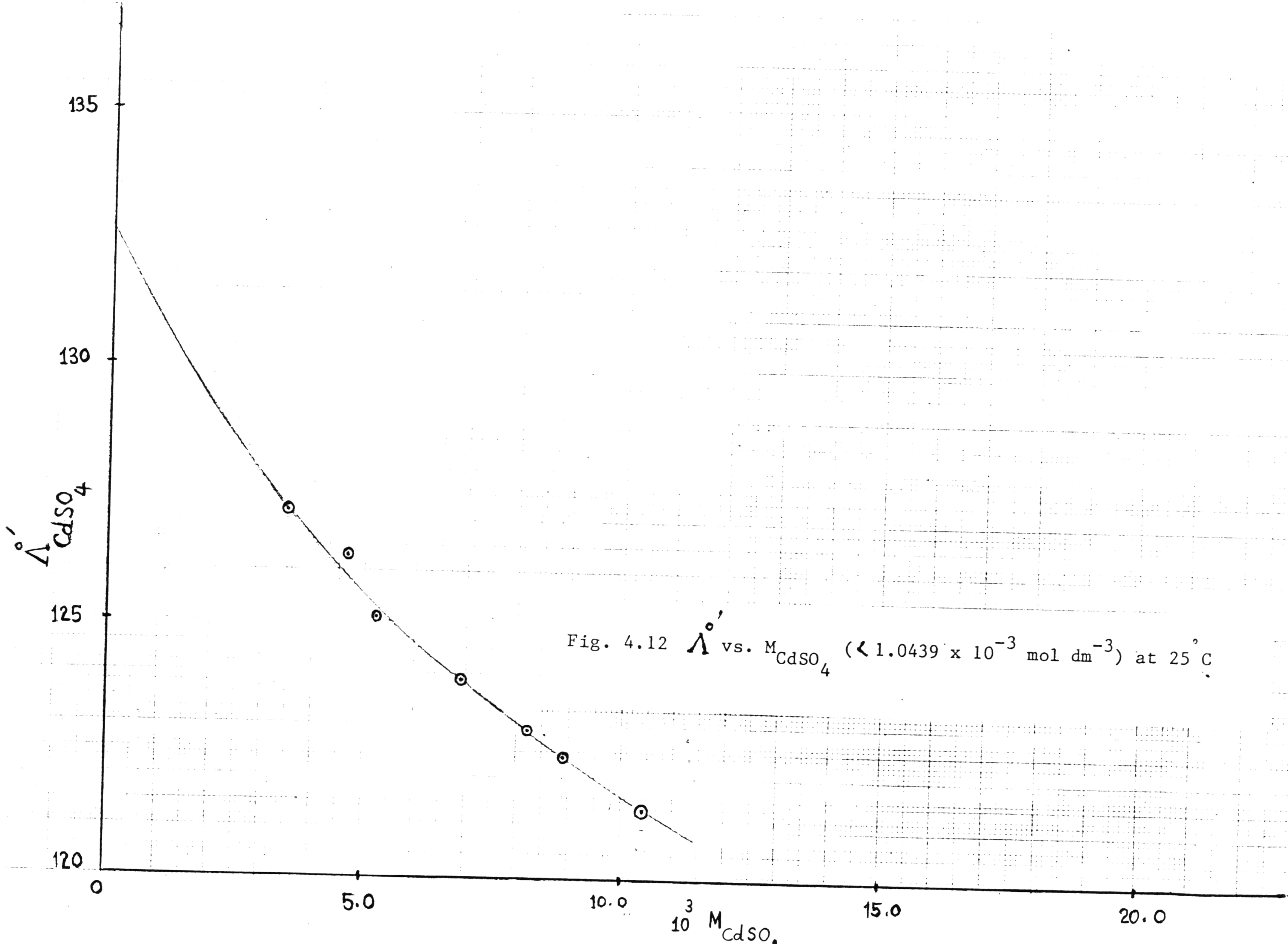


Fig. 4.12 $\Lambda^{o'}$ vs. M_{CdSO_4} ($< 1.0439 \times 10^{-3}$ mol dm^{-3}) at 25 °C

results are somewhat higher than the Λ^{o} values of 120.16, 132,82, 129.15, and 133.52 $cm^2\ \Omega^{-1}\ equiv^{-1}$ for $Zn(ClO_4)_2$, $ZnSO_4$, $ZnCl_2$, and $CdSO_4$ obtained by using the literature values of $\lambda^{o}_{Zn^{2+}}$ = 52.8 $cm^2\ \Omega^{-1}\ equiv^{-1}$ (10), $\lambda^{o}_{Cd^{2+}}$ = 53.5 $cm^2\ \Omega^{-1}\ equiv^{-1}$ (14), $\lambda^{o}_{Cl^-}$ = 76.35 $cm^2\ \Omega^{-1}\ equiv^{-1}$ (27,28), $\lambda^{o}_{(ClO_4)^-}$ = 67.36 $cm^2\ \Omega^{-1}\ equiv^{-1}$ (29,30) and $\lambda^{o}_{SO_4^{2-}}$ = 80.02 $cm^2\ \Omega^{-1}\ equiv^{-1}$ (31). The Onsager limiting slopes calculated from equation 2, Chapter 2, using Λ^{o} obtained from the present work and the literature values are shown as curve A and D in Figs4.5, 4.6, 4.7, and 4.8.

The Shedlovsky plots of dilute $Zn(ClO_4)_2$, $ZnSO_4$, $ZnCl_2$, and $CdSO_4$ solutions are given in Figs4.9, 4.10, 4.11, and 4.12,respectively. A linear extrapolation of the Shedlovsky function $\Lambda^{o\prime}$ to infinite dilution of $Zn(ClO_4)_2$ by least squares method gave $\Lambda^{o}_{Zn(ClO_4)_2}$ = 121.29 $cm^2\Omega^{-1}$ $equiv^{-1}$. This result is higher than the values obtained from the literature and the Onsager function. A non-linear extrapolation of Shedlovsky function for $ZnSO_4$, $ZnCl_2$, and $CdSO_4$ gave $\Lambda^{o}_{ZnSO_4}$ = 132.5 $cm^2\ \Omega^{-1}$ $equiv^{-1}$, $\Lambda^{o}_{ZnCl_2}$ = 130.0 $cm^2\ \Omega^{-1}\ equiv^{-1}$, and $\Lambda^{o}_{CdSO_4}$ = 132.65 $cm^2\Omega^{-1}$ $equiv^{-1}$. These results for $ZnSO_4$ and $CdSO_4$ are lower than the values obtained from the literature and the Onsager function. For $ZnCl_2$, this result is higher than the value obtained from the literature, but lower than the value obtained from the Onsager function. Using Λ^{o} of $Zn(ClO_4)$, $ZnSO_4$, $ZnCl_2$, and $CdSO_4$ obtained from the Shedlovsky extrapolation function, the Onsager limiting slopes are shown as curve C in Figs4.5, 4.6, 4.7, and 4.8,respectively.

4.2 Theoretical Analysis

4.2.1 Method of Analysis

In practice, the experimentally determined quantity is the conductivity, κ of the solution. By definition,

$$1000\ \kappa = \Lambda\ C = \sum_{i=1}^{s} |z_i|\ M_i\ \lambda_i$$

Comparison between the observed and theoretically predicted conductances by Lee and Wheaton equations can therefore be made. This allows the evaluation of the parameters such as λ^{o}_{i}, R, and K^{x}_{A} which are involved in the conductance expressions. The general procedure for the analysis of conductance data is described below.

It follows from conductance equations that

$$\Lambda = f(\overset{o}{\lambda}_1, \ldots, \overset{o}{\lambda}_s, R, C, M_1, \ldots, M_s) \quad (1)$$

For simple electrolyte mixtures, M_i $(i=1,\ldots,s)$ can be derectly obtained from the stoichiometric concentrations of an electrolyte. For associated electrolytes, however, M_i must be obtained from the knowledge of association constants and activity coefficients of all the species present in solution. For MX_n salt which undergoes x stages of association equilibria, each stage may be represented as

$$M^{n+} + xX^- \underset{}{\overset{K_A^x}{\rightleftharpoons}} MX_x^{(n-x)+} \quad (x = 1, 2, \ldots)$$

where

$$K_A^x = \frac{[MX^{(n-x)+}]}{[M^{n+}][X^-]^x} \cdot \gamma^x$$

where γ^x represents the ratio of activity coefficients of the species involved in the association equilibria, and

$$\gamma^x = f(M_1, \ldots, M_s, R)$$

Therefore,

$$M_i = f(K_A^1, \ldots, K_A^x, C)$$

In combination with the requirements of mass balance and electrical neutrality, these relationships provide a set of (x+2) simultaneous equations, from which M_i can be obtained. The activity coefficients of various species may be obtained from liturature data, otherwise they can be estimated from the Debye - Hückel or the extended Debye - Hückel expression. For associated electrolytes, therefore

$$\Lambda = f(\overset{o}{\lambda}_1, \ldots, \overset{o}{\lambda}_s, R, C, K_A^1, \ldots, K_A^x) \quad (2)$$

The normal method used for analysis of experimental conductance data is usually a multiparameter curve fitting ("optimisation") procedure. This procedure minimises the standard deviation, $\delta(\Lambda)$ between the calculated and measured conductances over a range of concentrations of electrolyte by adjusting the unknown parameters, where

$$\delta(\Lambda) = \left\{ \sum_{N=1}^{P} (\Lambda_{calc} - \Lambda_{expt})^2 / (P-1) \right\}^{1/2} \quad (3)$$

and P is the number of experimental points. The best fit values are thus obtained when $\delta(\Lambda)$ is at minimum. The principal difficulty in the analysis arises when a number of fitting parameters is involved. In most cases, considerable reduction of the number of independent parameters has been achieved by the assumption as to the degree of association and from reliable literature λ_i^o of certain ions.

The normal method of analysis described above was generally followed. The 'optimisation' procedure used in the present work is essentially an iterative least squares technique. In this method, initial parameter estimates were continually adjusted until the sums of the squares of the differences between Λ_{calc} and Λ_{expt}, viz

$$\sum_{N=1}^{P} (\Lambda_{calc} - \Lambda_{expt})^2 \quad (4)$$

were at minimum.

For the dilute aqueous $ZnCl_2$ system, the association equilibria involved are

$$Zn^{2+} + Cl^- \underset{}{\overset{K_A^1}{\rightleftharpoons}} ZnCl^+$$

$$Zn^{2+} + 2Cl^- \underset{}{\overset{K_A^2}{\rightleftharpoons}} ZnCl_2$$

where $K_A^1 = 4.5$ kg mol^{-1}. By assume $K_A^2 \ll K_A^1$, the only major associated species is $ZnCl^+$, it may be safe to assume that $M_{ZnCl_2} \simeq 0$. Since C and $\lambda^o_{Cl^-}$ are known, and $\lambda^o_{Zn^{2+}}$ has been determined, equation 2 becomes

$$\Lambda = f(\lambda^o_{ZnCl^+}, R, K_A^1)$$

Fortunately, association constant and activity coefficients of the aqueous $ZnCl_2$ system at 25°C by emf measurements (13) have been determined. These data were used to evaluate the free ion concentrations of the complex species at different zinc chloride concentrations. A summary of the calculation is given in Appendix D

Hence,

$$\Lambda = f(\lambda^{o}_{ZnCl^{+}}, R)$$

On the basis of the above considerations, two-parameter "optimisation" procedures were used by scanning these parameters in the range of appropriate values. Owing to the uncertainty in the literature value of $\lambda^{o}_{Zn^{2+}}$ (10) being apropriate for the $ZnCl_2$ system, analyses of the conductance data using the Lee and Wheaton equation were carried out to evaluate $\lambda^{o}_{Zn^{2+}}$ such that

$$\Lambda = f(\lambda^{o}_{Zn^{2+}}, R)$$

By scanning these two parameters in the range of appropriate values, the value of $\lambda^{o}_{Zn^{2+}}$ which gave the fit between Λ_{expt} and Λ_{calc} with the lowest $\delta(\Lambda)$ was then obtained.

For the dilute aqueous $ZnSO_4$ and $CdSO_4$ system, the association equilibria involved are

$$M^{2+} + SO_4^{2-} \overset{K_A}{\rightleftharpoons} MSO_4 \quad (M = Zn, Cd)$$

MSO_4 is a neutral species and therefore does not contribute to the conductivity. Since C and $\lambda^{o}_{SO_4^{2-}}$ are known, equation 2 becomes

$$\Lambda = f(\lambda^{o}_{M^{2+}}, R, K_A)$$

By optimising $\lambda^{o}_{M^{2+}}$, R and K_A values, these values which gave the best fit were then obtained.

The following activity coefficients of MSO_4 system were assumed.

$$\log f_{\pm} = \frac{-A\,|Z_1 Z_2|\,\sqrt{I}}{1 + BR\sqrt{I}} \qquad (5)$$

Thus, the programme used to evaluate free ion concentrations of the complex species at different MSO_4 concentrations was combined with the programme which calculate Λ values ("function" programme).

For the dilute aqueous $Zn(ClO_4)_2$ and $Cd(ClO_4)_2$ systems, complete dissociation was assumed for both electrolytes. Thus, in equation 1 , the stoichiometric concentrations were used. Since $\lambda^{o}_{ClO_4^-}$ is known, equation 1 becomes

$$\Lambda = f(\lambda^{o}_{M^{2+}} , R)$$

By scanning these two parameters, the value of $\lambda^{o}_{M^{2+}}$ which gave the best fit between Λ_{expt} and Λ_{calc} was then obtained. The conductance data used for $Cd(ClO_4)_2$ in the present work is obtained from Matheson (14).

4.2.2 Calculations

Fortran programmes 1 and 2 were prepared for the calculations of the conductance of multicomponent $ZnCl_2$ system and the conductance of MSO_4 (M = Zn, Cd) system predicted by the Lee and Wheaton equations respectively. The original programme in Algol (3) was converted into Fortran and was modified for the use with the present study. Lists of the complete programmes 1 and 2 are given in Appendix E and Appendix F. The programme used to evaluate the free ion concentrations of the complex species of $ZnCl_2$ system at different concentrations are separately listed in Appendix G. For MSO_4 system this programme is combined with the function programme of programme 2 as in Appendix F.

For $M(ClO_4)$ (M = Zn, Cd) systems, complete dissociation was assumed, M_i and C in equation 1 were directly obtained from experiments. Thus, the function programme of programme 2 was used directly.

In the computation of Λ by the Lee and Wheaton equation, the expression of λ_i was written in terms of a ($\beta\kappa$) series, the form suggested by Wheaton (see Appendix H). The omission of some terms arising from the final term in the full exponential form of f_{ji} in the final conductance equation given by Lee and Wheaton (6) was suggested by Wheaton (3). These terms were therefore omitted in the computation in the present work (see Appendix E and Appendix H).

A test of programme 1 and programme used to evaluate free ion concentration of the complex species at different concentrations were made using the $CdCl_2$ conductance data at $25^{o}C$ (3).

4.2.3 Results

The method of analysis of the conductance data for all electrolytes studied, outlined in Section 4.2.1 was followed. The conductance data of electrolyte solutions with the concentration range of about 0.0002-0.025 mol dm^{-3} previously obtained from Chapter 3 and from the liturature (Chapter 1) were used. Results of the analysis of these electrolytes are listed in Table 4.1. The concentration of the complex species present in the solution of $ZnSO_4$, $ZnCl_2$ and $CdSO_4$ are given in Tables4.2, 4.3 and 4.4 respectively. Results of the predicted and the observed conductances of all electrolytes using a set of parameters which give the best fit are given in Tables4.5, 4.6, 4,7 4,8 and 4.9 for $Zn(ClO_4)_2$, $ZnSO_4$, $ZnCl_2$, $Cd(ClO_4)_2$ and $CdSO_4$ system respectively.

Table 4.1

Parameter Estimation

Lee and Wheaton Equation - Aqueous $Zn(ClO_4)_2$, $ZnSO_4$, $ZnCl_2$, $Cd(ClO_4)_2$, $CdSO_4$, $CdCl_2$

Electrolytes	$\lambda^\circ_{Zn^{2+}}$ or Cd^{2+} $cm^2\,\Omega^{-1}$ equiv.$^{-1}$	$\lambda^\circ_{ZnCl^+}$ or $CdCl^+$ $cm^2\,\Omega^{-1}$ equiv.$^{-1}$	R / A°	K_A Kg mol^{-1}	$\sigma(\Lambda)$	number of data points	Concentration range mol dm^{-3}	Comment
$Zn(ClO_4)_2$	55.14±0.03	-	9.60±0.05	-	0.34	12	$(2.5-139.0)10^{-4}$	P
	53.64±0.03	-	15.80±0.10	-	1.21	13	$(0.9-8.1)10^{-4}$	q
$ZnSO_4$	54.06±0.04	-	4.80±0.06	165*	0.09	10	$(2-30)10^{-4}$	r
	52.16±0.03	-	4.20±0.04	125±3	0.12	10	$(4-144)10^{-4}$	s
	52.11±0.02	-	4.50±0.04	140±2	0.18	12	$(3.3-99)10^{-4}$	P
$ZnCl_2$	56.20±0.01	35±10	4.00±0.10	4.5*	0.21	13	$(3-92)10^{-4}$	P
	55.67±0.01	-	2.7*	-	0.23	13	$(3-92)10^{-4}$	P, assume complete dissociate at minimum R value

Parameter Estimation

Lee and Wheaton Equation - Aqueous $Zn(ClO_4)_2$, $ZnSO_4$, $ZnCl_2$, $Cd(ClO_4)_2$, $CdSO_4$, $CdCl_2$

Electrolytes	$\lambda^\circ_{Zn^{2+}}$ or Cd^{2+} $cm^2\Omega^{-1}$ equiv.$^{-1}$	$\lambda^\circ_{ZnCl^+}$ or $CdCl^+$ $cm^2\Omega^{-1}$ equiv.$^{-1}$	R/A°	K_A kg mol^{-1}	$\sigma(\Lambda)$	number of data points	concentration range mol dm^{-3}	comment
$Cd(ClO_4)_2$	52.50±0.01	-	10.30±0.04	-	0.14	10	$(0.67-2.49)10^{-4}$	t
	53.5*	-	9.10±0.04	-	0.43	10	$(0.67-2.49)10^{-4}$	t, at fixed $\lambda^\circ_{Cd^{2+}}$ value
$CdSO_4$	53.00±0.02	-	5.70±0.04	212*	0.07	10	$(2-30)10^{-4}$	r
	53.20±0.02	-	4.00±0.04	165±3	0.14	15	$(3.5-98.0)10^{-4}$	p
$CdCl_2$	53.94	22	3.1	85*	0.22	20	$(1-200)10^{-4}$	u

*refers to fixed parameter

P : data from the present work

q : data from reference (8)

r : data from reference (11)

s : data from reference (10)

t : data from reference (14)

u : results obtained from reference (3)

Table 4.2

Conductance - Concentration Data of Aqueous $ZnSO_4$

Λ_{ZnSO_4} / $cm^2\ \Omega^{-1}\ equiv.^{-1}$	$10^3\ M_{Zn^{2+}}$ $mol\ dm^{-3}$	$10^3\ M_{SO_4^{2-}}$ / $mol\ dm^{-3}$	$10^3\ M_{ZnSO_4}$ / $mol\ dm^{-3}$	$10^3\ M^{*}_{ZnSO_4}$ $mol\ dm^{-3}$
74.45	8.23591	8.23591	1.71973	9.95565
75.21	7.64532	7.64532	1.57747	9.22279
79.21	5.72672	5.72672	1.10480	6.83152
81.93	4.96298	4.96298	0.91570	5.87868
84.85	4.18962	4.18962	0.72689	4.91651
88.33	3.37477	3.37477	0.53450	3.90927
93.14	2.50439	2.50439	0.34260	2.84699
98.43	1.78501	1.78501	0.20163	1.98664
106.57	0.98845	0.98845	0.07579	1.06425
110.77	0.71980	0.71980	0.04385	0.76365
114.49	0.50158	0.50158	0.02315	0.52473
118.44	0.32524	0.32524	0.01057	0.33581

$M^{*}_{ZnSO_4}$, the stoichiometric molar concentration of the Zinc sulfate solution $= M_{Zn^{2+}} + M_{ZnSO_4}$

M_{ZnSO_4}, the undissociated molar concentration of the Zinc sulfate solution.

Table 4.3

Conductance - Concentration Data of Aqueous $ZnCl_2$.

Λ_{ZnCl_2} $cm^2\Omega^{-1}$ $equiv.^{-1}$	10^3 $M_{Zn^{2+}}$ / mol dm^{-3}	10^2 M_{Cl^-} / mol dm^{-3}	10^5 M_{ZnCl^+} / mol dm^{-3}	10^2 $M^{\bullet}_{ZnCl_2}$ / mol dm^{-3}
127.81	0.30373	0.060812	0.068078	0.030441
123.18	1.2736	0.25568	0.99224	0.12836
121.70	1.8947	0.38089	2.0393	0.19151
121.14	2.1738	0.43724	2.6095	0.21999
119.74	2.7061	0.54487	3.8550	0.27446
118.18	3.3769	0.68075	5.6987	0.34339
116.20	4.6254	0.93434	9.8670	0.47241
114.60	5.5220	1.1169	13.398	0.56559
111.26	7.8109	1.5846	24.232	0.80532
111.11	8.0181	1.6271	25.333	0.82714
110.55	8.3585	1.6969	27.183	0.86304
110.22	8.6558	1.7578	28.840	0.89442
109.89	8.8837	1.8046	30.136	0.91850

$M^{\bullet}_{ZnCl_2}$, the stoichiometric molar concentration of the Zinc Chloride solution = $M_{Zn^{2+}} + M_{ZnCl^+}$

Table 4.4

Conductance - Concentration Data of Aqueous $CdSO_4$

Λ_{CdSO_4} / $cm^2 \Omega^{-1}$ equiv.$^{-1}$	10^3 $M^{Cd^{2+}}$ / mol dm^{-3}	10^3 $M^{SO_4^{2-}}$ / mol dm^{-3}	10^3 M_{CdSO_4} / mol dm^{-3}	10^3 $M^{*}_{CdSO_4}$ / mol dm^{-3}
71.26	7.87279	7.87279	1.92447	9.79727
72.95	7.06433	7.06433	1.69236	8.75668
77.63	5.39115	5.39115	1.20417	6.59533
77.87	5.32074	5.32074	1.18361	6.50436
80.68	4.57910	4.57910	0.968296	5.54739
85.11	3.50548	3.50548	0.665630	4.17111
89.29	2.77417	2.77417	0.471558	3.24572
93.60	2.15781	2.15781	0.320791	2.47860
106.33	0.959157	0.959157	0.0848769	1.04403
108.49	0.818125	0.818125	0.0645717	0.882696
109.48	0.765618	0.765618	0.0575533	0.823171
111.50	0.648957	0.648957	0.0430985	0.692056
114.25	0.498734	0.498734	0.0270092	0.525743
116.05	0.443450	0.443450	0.0218727	0.465323
118.22	0.339019	0.339019	0.0134381	0.352457

M^{*}, the stoichiometric molar concentration of the cadmium sulfate solution $= M_{Cd^{2+}} + M_{CdSO_4}$

M_{CdSO_4}, the undissociated molar concentration of the cadmium sulfate solution.

Table 4.5

Observed and Predicted Conductances

Lee and Wheaton equation - Aqueous $Zn(ClO_4)_2$

12 data points (M = (0.2 - 14.0) 10^{-3} mol dm^{-3})

10^4 M / mol dm^{-3}	Λ_{expt} / $cm^2\Omega^{-1}$ $equiv.^{-1}$	Λ_{calc} / $cm^2\Omega^{-1}$ $equiv.^{-1}$	Δ / %	$\Lambda^{o\prime}$
138.939	102.96	103.20	-0.23	132.51
119.382	103.83	104.26	-0.41	131.12
99.534	105.42	105.47	-0.05	130.27
85.208	106.85	106.45	0.38	129.82
69.362	108.16	107.67	0.46	128.83
53.843	109.04	109.06	-0.01	127.16
35.087	111.29	111.15	0.13	125.87
13.702	115.24	114.80	0.38	124.71
10.672	115.63	115.59	0.04	123.62
6.493	117.13	116.94	0.16	123.35
4.648	117.47	117.72	-0.21	122.73
2.529	118.23	118.88	-0.55	122.10

$\lambda^o_{Zn^{2+}}$ = 55.14 $cm^2\Omega^{-1}$ $equiv.^{-1}$

$\lambda^o_{ClO_4^-}$ = 67.36 $cm^2\Omega^{-1}$ $equiv.^{-1}$

Δ = $(\Lambda_{expt} - \Lambda_{calc}) \times 100 / \Lambda_{expt}$

Table 4.6

Observed and Predicted Conductances

Lee and Wheaton equation - Aqueous $ZnSO_4$

12 data points ($M = (0.3 - 10.0)\ 10^{-3}$ mol dm^{-3})

10^4 M/ mol dm^{-3}	Λ_{expt} / $cm^2 \Omega^{-1}$ $equiv.^{-1}$	Λ_{calc}/ $cm^2 \Omega^{-1}$ $equiv.^{-1}$	Δ/ %	$\Lambda^{o\prime}$
99.408	74.45	74.16	0.38	120.79
92.100	75.21	75.24	-0.05	119.60
68.240	79.21	79.64	-0.54	117.03
58.737	81.93	81.91	0.02	117.02
49.129	84.85	84.65	0.24	116.93
39.070	88.33	88.19	0.16	116.94
28.460	93.14	93.05	0.09	117.63
19.865	98.43	98.39	0.03	119.00
10.639	106.57	106.82	-0.23	121.79
7.635	110.77	110.72	0.05	123.77
5.246	114.49	114.58	-0.08	125.33
3.357	118.44	118.43	0.01	127.17

$\lambda^{o}_{Zn^{2+}}$ = 52.11 $cm^2\ \Omega^{-1}\ equiv.^{-1}$

$\lambda^{o}_{SO_4^{2-}}$ = 80.02 $cm^2\ \Omega^{-1}\ equiv.^{-1}$

Table 4.7

Observed and Predicted Conductances

Lee and Wheaton equation - Aqueous $ZnCl_2$

M = (0.3 - 10.0) 10^{-3} mol dm^{-3} (13 data points)

$M \times 10^3$ / mol dm^{-3}	Λ_{expt} / $cm^2 \Omega^{-1}$ $equiv.^{-1}$	Λ_{calc} / $cm^2 \Omega^{-1}$ $equiv.^{-1}$	Δ / %	$\Lambda^{o\prime}$
0.3044	127.81	128.11	-0.23	130.59
1.2836	123.18	123.50	-0.25	132.10
1.9151	121.70	121.57	0.10	132.61
2.1999	121.14	120.82	0.26	132.84
2.7445	119.74	119.53	0.18	132.81
3.4339	118.18	118.08	0.08	132.80
4.7241	116.20	115.79	0.30	133.37
5.6559	114.60	114.37	0.21	133.40
8.0532	111.26	111.26	0.00	133.70
8.2714	111.11	111.01	0.08	133.86
8.6304	110.55	110.61	-0.05	133.78
8.9442	110.22	110.26	-0.03	133.89
9.1850	109.89	110.00	-0.10	133.87

$\lambda^{o}_{Zn^{2+}}$ = 56.2 $cm^2 \Omega^{-1}$ $equiv.^{-1}$

$\lambda^{o}_{ZnCl^{+}}$ = 35.0 $cm^2 \Omega^{-1}$ $equiv.^{-1}$

$\lambda^{o}_{Cl^{-}}$ = 76.35 $cm^2 \Omega^{-1}$ $equiv.^{-1}$

Table 4.8

Observed and Predicted Conductances

Lee and Wheaton equation - Aqueous $Cd(ClO_4)_2$

10 data points ($M = (2.5 - 0.7)\ 10^{-2}$ mol dm^{-3})

10^2 M / mol dm^{-3}	Λ^*_{expt} / $cm^2\Omega^{-1}$ $equiv^{-1}$	Λ_{calc} / $cm^2\Omega^{-1}$ $equiv^{-1}$	Δ / %
2.4904	97.52	97.78	-0.27
2.0080	98.93	98.79	0.14
1.9219	99.12	99.06	0.06
1.6990	100.04	99.85	0.19
1.5832	100.47	100.31	0.16
1.5199	100.68	100.59	0.09
1.2312	101.98	101.99	-0.01
0.9622	103.45	103.55	-0.10
0.6903	105.31	105.48	-0.16
0.6752	105.48	105.60	-0.11

$\lambda^\circ_{Cd^{2+}}$ = 52.50 $cm^2\Omega^{-1}$ $equiv^{-1}$

$\lambda^\circ_{ClO_4^-}$ = 67.36 $cm^2\Omega^{-1}$ $equiv^{-1}$

*data from reference (14)

Table 4.9

Observed and Predicted Conductances

Lee and Wheaton equation - Aqueous $CdSO_4$

15 data points (M = (0.3 - 10.0) 10^{-3} mol dm^{-3}

$10^4 M$ / mol dm^{-3}	Λ_{expt} / $cm^2 \Omega^{-1}$ $equiv.^{-1}$	Λ_{calc} / $cm^2 \Omega^{-1}$ $equiv.^{-1}$	Δ/ %	$\Lambda^{o\prime}$
97.909	71.26	71.43	-0.23	116.47
87.516	72.95	73.15	-0.28	115.52
66.031	77.63	77.65	-0.02	114.45
65.015	77.87	77.87	-0.01	114.40
55.454	80.68	80.47	0.26	114.42
41.700	85.11	85.16	-0.06	114.36
32.451	89.29	89.29	-0.00	115.18
24.782	93.60	93.66	-0.06	116.32
10.439	106.33	106.42	-0.08	121.38
8.826	108.49	108.58	-0.09	122.38
8.230	109.48	109.45	0.03	122.92
6.919	111.50	111.51	-0.00	123.89
5.256	114.25	114.50	-0.22	125.09
4.652	116.05	115.72	0.28	126.29
3.523	118.22	118.26	-0.03	127.17

$\lambda^{o}_{Cd^{2+}}$ = 53.20 $cm^2 \Omega^{-1}$ $equiv.^{-1}$

$\lambda^{o}_{SO_4^{2-}}$ = 80.02 $cm^2 \Omega^{-1} equiv.^{-1}$.