



LEVEL

12

RESEARCH AND DEVELOPMENT TECHNICAL REPORT

DELET-TR-81-6

SIMPLIFIED ANALYSIS OF COMPLEX CONDUCTIVITY DATA

AD A 098277

DTIC
SELECTED
APR 28 1981
S D C

MARK SALOMON
ELECTRONICS TECHNOLOGY & DEVICES LABORATORY

MARCH 1981

DISTRIBUTION STATEMENT

Approved for public release;
distribution unlimited.

ERADCOM

US ARMY ELECTRONICS RESEARCH & DEVELOPMENT COMMAND
FORT MONMOUTH, NEW JERSEY 07703

DTIC FILE COPY

0 1 4 2 8 0 5 6

CONTENTS

	<u>Page</u>
INTRODUCTION	1
RESULTS	5

TABLES

1. RESULTS OF ANALYSES OF CONDUCTIVITY DATA BY VARIOUS METHODS .	6
2. RESULTS OF ANALYSES BASED ON EQUATION (18) FOR SALTS IN SOCl_2	7

APPENDIX

A. TI-59 PROGRAM FOR SOLUTION OF EQUATION (15)	8
--	---

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Avail and/or	
Dist	Special
A	

SIMPLIFIED ANALYSIS OF COMPLEX CONDUCTIVITY DATA

INTRODUCTION

Conductivity measurements constitute some of the most accurate data which can be obtained in the laboratory. There is a long history of the theory and experimental techniques of conductivity data, and one of the most important features of this data is that it allows one to analyze the complex behavior of electrolyte solutions in solvents possessing a large range of dielectric constants. The development of the mathematical treatments of these data, particularly in analyzing for ion pair formation, has reached the point where sophisticated computational facilities are required. The purpose of this report is to present a method which simplifies the computational analyses, and at the same time retain the essential features of modern theory. A brief introduction to the analytical expressions for conductivity data for 1:1 electrolytes developed over the years will be given first.

The first expression developed by Onsager¹ which applies to very dilute solutions is:

$$\Lambda = \Lambda^{\infty} - (\Lambda^{\infty}\beta_1 + \beta_2) c^{1/2} = \Lambda^{\infty} - S c^{1/2} \quad (1)$$

Here Λ is the experimental molar conductivity for a completely dissociated salt at concentration c mol dm⁻³, Λ^{∞} is the molar conductivity at infinite dilution, and β_1 and β_2 are constants which reflect upon ion-ion interactions. As early as 1883, Arrhenius proposed that the reason why Λ values for certain electrolytes were much smaller than expected was due to the association of ions. Arrhenius thus expressed the degree of ionization, α , of a salt in terms of conductivities as:

$$\alpha = \Lambda/\Lambda^{\infty} \quad (2a)$$

The equation holds at very high dilutions, and a more accurate expression for α is defined as the ratio of the experimental molar conductivity, Λ , to the molar conductivity Λ_f , which would be observed if the salt was completely ionized.

$$\alpha = \Lambda/\Lambda_f \quad (2b)$$

The chemical equation involving ion pairing of M^+ cations and X^- anions is given by



where MX is the undissociated ion pair. The thermodynamic dissociation

¹L. Onsager, Z. Physik 27, 388 (1926); 28, 277 (1927).

constant for reaction (3) is given by:

$$K_D^0 = [M^+][X^-]y_+^2/[MX]y_n \quad (4a)$$

where y_+ and y_n are, respectively, the mean molar activity coefficients for the ions and the neutral species MX. In terms of the degree of dissociation, Equation (4a) becomes:

$$K_D^0 = \alpha^2 c y_+^2 / (1 - \alpha) y_n \quad (4b)$$

and rearranging,

$$\alpha = 1 - \alpha^2 c y_+^2 / K_D^0 y_n \quad (4c)$$

Taking Λ_f equal to that value given by the Onsager Equation (1), the equation for the experimental conductivity connected for ion pairing is obtained by combining Equations (1), (2b), and (4c):

$$\Lambda = \Lambda^\infty - S(\alpha c)^{1/2} - \Lambda \alpha c y_+^2 / K_D^0 y_n \quad (5)$$

A semiempirical form of Equation (5) has been developed by Fuoss and Kraus² and by Shedlovsky:³

$$\frac{1}{\Lambda F(z)} = \frac{1}{\Lambda^\infty} + \frac{\Lambda F(z) y_+^2 c}{K_D^0 (\Lambda^\infty)^{3/2}} \quad (6)$$

In Equation (6), the activity coefficient y_n is assumed to equal unity, and the function $F(z)$ is defined as follows:

$$F(z) = \left[(z/2) + \left[1 + (z/2)^2 \right]^{1/2} \right]^2 \quad (7)$$

and

$$z = S (\alpha c)^{1/2} / (\Lambda^\infty)^{3/2} \quad (8)$$

Equation (6), which suggests that Λ^∞ and $K_D^0 (\Lambda^\infty)^{3/2}$ can be obtained from a plot of $1/\Lambda F(z)$ against $F(z) y_+^2 c$, was used as the primary method of analysis for several decades. Its use is now being restricted since it still applies to very dilute solutions, and accurate Λ^∞ and K_D^0 values are obtained only when K_D^0 is in the range of 10^{-1} to 10^{-3} mol dm⁻³. A major problem associated with the use of the Onsager Equation (1) is that it fails to account for higher order terms involving relaxation fields and electrophoretic velocity.

²R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc. 55, 476 (1933).

³T. Shedlovsky, J. Franklin Inst. 225, 739 (1938).

One of the first attempts to produce a more accurate relation for expressing conductivity data was by Fuoss and Onsager:⁴

$$\Lambda = \Lambda^\infty - S c^{1/2} + E c \ln c + J c \quad (9)$$

where E is a constant dependent upon the nature of the solvent, and J is a constant dependent in part on the distance (R) of approach of the free ions. Combining Equations (2b), (4c), and (9) yields:

$$\Lambda = \Lambda^\infty - S (\alpha c)^{1/2} + E \alpha c \ln(\alpha c) + J \alpha c - \Lambda \alpha c y_{\pm}^2 / K_D^0 y_n \quad (10)$$

Later work⁵ produced a more accurate expression which takes the form^{6,7}

$$\Lambda = \Lambda^\infty - S c^{1/2} + E c \ln c + J_1 c - J_2 c^{3/2} \quad (11)$$

Combining this equation with Equations (2b) and (4c) yields

$$\Lambda = \Lambda^\infty - S (\alpha c)^{1/2} + E \alpha c \ln(\alpha c) + J_1 \alpha c - J_2 (\alpha c)^{3/2} - \Lambda \alpha c y_{\pm}^2 / K_D^0 y_n \quad (12)$$

Both J_1 and J_2 are complex functions of the distance R, and complete analysis of Equation (12) requires the use of high speed computers. There is little doubt that both J_1 and J_2 terms are significant and essential for high accuracy. In solving Equation (12) for Λ^∞ and K_D^0 , it is generally assumed that the extended Debye-Hückel relation (13) can be used for the mean molar activity coefficient,

$$\log y_{\pm} = -A (\alpha c)^{1/2} / \{ 1 + BR (\alpha c)^{1/2} \} \quad (13)$$

and that y_n is unity. In Equation (13), B is a constant and R is the distance of closest approach of the free ions. Since Justice⁸ has presented convincing evidence that the distance R should be associated with the Bjerrum⁹ critical distance q defined by

$$R = q = z^2 q^2 / (2 \epsilon kT), \quad (14)$$

much controversy^{10,11} has been centered on the correct value for R. It is to be noted that if R is associated with q which has values about 10 times

⁴R. M. Fuoss and L. Onsager, J. Phys. Chem. 61, 668 (1957).

⁵R. M. Fuoss and K. L. Hsia, Proc. Nat. Acad. Sci. 57, 1550 (1967).

^{6a}E. Pitts, Proc. Roy Soc. (London) A217, 43 (1953).

^{6b}E. Pitts, B.F. Tabor, and J. Daly, Trans. Faraday Soc. 65, 849 (1969).

⁷R. Fernandez-Prini, "Physical Chemistry of Organic Solvent Systems,"

A. K. Covington and T. Dickinson, eds., Plenum Press, London, 1973.

⁸J.-C. Justice, J. Chim. Phys. 65, 353 (1968); Electrochim Acta 16, 701 (1971).

⁹N. Bjerrum, K. Danske Videnskab Selskab; Mat.-Fys.-Medd. 7, 9 (1926).

¹⁰R. Fernandez-Prini and J. E. Prue, Trans. Faraday Soc. 62, 1257 (1966).

¹¹J.-C. Justice, R. Bury, and C. Treiner, J. Chim. Phys. 65, 1708 (1968).

greater than that required by Debye-Hückel theory, then by increasing y_{\pm} (see Equation (13)), compensating changes will occur in the numerical values of J_1 and J_2 . In order to simplify the analysis of Equation (12) and avoid the controversy involving the correct magnitude of R , a method has been developed which can be used with a hand-held calculator such as the TI-59 pocket calculator. The details of this method are discussed below and applications to numerous electrolytes and solvents are discussed which include analyses of conductivity data for systems of importance in lithium primary battery development.

METHOD

The Fuoss-Hsia Equation (12) is recast into an empirical form

$$\Lambda = \Lambda^{\infty} - S(\alpha c)^{\frac{1}{2}} + E \alpha c \ln(\alpha c) + J_1' \alpha c + J_2' (\alpha c)^{3/2} - \Lambda \alpha c y_{\pm}^2 / K_D^0 y_n \quad (15)$$

where J_1' and J_2' are now empirical constants. The mean molar activity coefficient for the ions is also calculated empirically using the Davies equation

$$\log y_{\pm} = -A(\alpha c)^{\frac{1}{2}} / \left[1 + (\alpha c)^{\frac{1}{2}} \right] + 0.3 A \alpha c \quad (16)$$

For the activity coefficient of the neutral ion pair, it is assumed that

$$\log y_n = 0.3 A \alpha c \quad (17)$$

Equation (17) appears to hold well for aqueous solutions. Equation (15) can be rearranged in the form

$$Y = J_1' + J_2' (\alpha c)^{\frac{1}{2}} \quad (18)$$

where

$$Y = \Lambda \{ 1 + y_{\pm}^2 \alpha c / (K_D^0 y_n) \} / \alpha c - \{ \Lambda^{\infty} - S(\alpha c)^{\frac{1}{2}} + E \alpha c \ln(\alpha c) \} / \alpha c \quad (19)$$

In evaluating Equation (18) by least squares, values of Λ^{∞} and K_D^0 are varied until the error, σ_{Λ} , in the observed conductivities is minimized. σ_{Λ} is defined by

$$\sigma_{\Lambda} = \{ \sum (\Lambda_{\text{obs}} - \Lambda_{\text{calc}})^2 / (N-3) \}^{\frac{1}{2}} \quad (20)$$

where N is the number of data points. To perform the calculations, initial guesses at Λ^{∞} and K_D^0 are made, and α calculated by an iteration method using Equations (4b) and (16). The calculations are then repeated until σ_{Λ} is minimized by the appropriate Λ^{∞} and K_D^0 values. All calculations are begun by evaluating S , E , and the Debye-Hückel constants A and B :

$$\Lambda / \text{mol}^{-\frac{1}{2}} \text{ dm}^{3/2} = 1.8246 \times 10^6 / (eT)^{3/2} \quad (21)$$

$$B/cm \text{ mol}^{-1/2} \text{ dm}^{3/2} = 5.029 \times 10^7 / (\epsilon T)^{1/2} \quad (22)$$

For the Onsager constant $S = \Lambda^\infty \beta_1 + \beta_2$

$$\beta_1 / \text{mol}^{-1/2} \text{ dm}^{3/2} = 8.2046 \times 10^5 / (\epsilon T)^{3/2} \quad (23)$$

$$\beta_2 / S \text{ cm}^2 \text{ mol}^{-3/2} \text{ dm}^{3/2} = 82.487 / \{\eta (\epsilon T)^{1/2}\} \quad (24)$$

For the Fuoss-Onsager constant $E = \Lambda^\infty E_1 - E_2$,

$$E_1 / \text{mol}^{-1} \text{ dm}^3 = 2.94257 \times 10^{12} / (\epsilon T)^3 \quad (25)$$

$$E_2 / S \text{ cm}^2 \text{ mol}^{-1} \text{ dm}^3 = 4.33244 \times 10^7 / \{\eta (\epsilon T)^2\} \quad (26)$$

Finally, the present method of treatment of conductivity data also permits a simple solution of Equation (10) by the least squares method; i.e.,

$$Y = J' - \Lambda y_{\pm}^2 / K_D^0 y_n \quad (27)$$

where

$$Y = \{\Lambda - \Lambda^\infty + S (\alpha c)^{1/2} - E \alpha c \ln(\alpha c)\} / \alpha c \quad (28)$$

RESULTS

To test the accuracy of the present method for evaluating Λ^∞ and K_D^0 , the conductance data for various electrolytes in solvents having dielectric constants varying from $\epsilon = 78.3$ D to $\epsilon = 9.53$ D were analyzed and compared to previous results. The results of these analyses are given in Table 1 where all data refer to 25°C. The use of Equation (18) is seen to lead to equivalent values for Λ^∞ and K_D^0 when comparisons are made with the results obtained from the direct analyses of Equations (10) and (12). In several cases, the present method appears superior as indicated by much smaller σ_A values. In Table 2 results are given for the analyses of conductivity data for salts in thionyl chloride. These salts are all of interest for improvement of lithium primary batteries (Note: Pr_4N refers to the tetrapropylammonium ion $(\text{C}_3\text{H}_7)_4\text{N}^+$). The program written for the TI-59 calculator to solve Equation (15) is given in Appendix A.

TABLE 1. * RESULTS OF ANALYSES OF CONDUCTIVITY DATA BY VARIOUS METHODS

Solvent (ϵ/D) (η/cP)	Salt	Reference	N	$10^4 c_{max}$	Equation Number	J_1	J_2	A^∞ (σ)	K_D^∞ (σ)	σ_A	
water (78.30) (0.8903)	AgNO ₃	12 ^a	26	915				133.39	0.56	0.016	
		13	?	?	18	237.60	-279.77	133.43	1.157	0.028	
			9	915	18 ^b	235.09	-268.95	133.43(0.04)	1.04(0.02)	0.030	
water	CH ₃ COOH	14 ^a	10	100	c			390.59	$1.753 \cdot 10^{-5}$	
			8	130	18	540.7	-52.872	390.70(0.16)	$1.751 \cdot 10^{-5}$	$(1 \cdot 10^{-8})$	0.034
			8	130	27	-303.4	390.71(0.16)	$1.751 \cdot 10^{-5}$	$(2 \cdot 10^{-8})$	0.029
acetone (35.95) (0.3409)	Am ₄ NbAm ₄	15 ^c	7	29	10	1643.2	114.48	0.04	
		8 ^b	7	29	12	2403	-7905	114.33(0.23)	0.42(0.16)	0.22	
			7	29	18	2247.5	-8143.3	114.35(0.02)	0.70(0.11)	0.02	
methanol (32.62) (0.5445)	Me ₄ NCl	16 ^a	8	86	10	120.82	0.137	0.04	
			8	85	18	2662.2	-6610.2	121.098(0.004)	$0.046(2 \cdot 10^{-5})$	0.003	
n-propanol (20.33) (2.004)	Me ₄ NCl	17 ^a	9	56	10	25.02	$2.19 \cdot 10^{-3}$	0.01	
		8 ^b	7	43	12	3126	-14846	25.29(0.07)	$1.70 \cdot 10^{-3}$	$(5 \cdot 10^{-6})$	0.01
		18	7	43	10	25.05	$2.19 \cdot 10^{-3}$	0.01	
		18	7	43	12	25.06	$2.13 \cdot 10^{-3}$	0.005	
82 wt% p-dioxane in water (9.53) (1.671)	HCl	19 ^c	21	41	6	57.5	$2.02 \cdot 10^{-3}$	
		8 ^b	4	15	12	83300	-675000	57.93(0.08)	$2.03 \cdot 10^{-3}$	$(2 \cdot 10^{-7})$	0.01
			4	15	18	52424	-279423	57.30(0.004)	$2.55 \cdot 10^{-3}$	$(5 \cdot 10^{-8})$	0.002

* See page 3.

11. D. McKenzie and R. M. Fuoss, *J. Phys. Chem.* **73**, 1501 (1969).
 12. E. Hanna, A. D. Pethybridge, and J. E. Prue, *Electrochim. Acta* **16**, 677 (1971).
 13. A. MacInnes and T. Shedlovsky, *J. Am. Chem. Soc.* **54**, 1429 (1932).
 14. J. F. Goetzee and G. P. Cunningham, *J. Am. Chem. Soc.* **87**, 2529 (1965).
 15. R. L. Kay, C. Zawoycki, and D. F. Evans, *J. Phys. Chem.* **69**, 4208 (1965).
 16. D. F. Evans and P. Gardham, *J. Phys. Chem.* **72**, 3281 (1968).
 17. P. Beronius, *Acta Chem. Scand.* **A29**, 289 (1975).
 18. B. Owen and G. W. Waters, *J. Am. Chem. Soc.* **60**, 2371 (1938).

*NOTES:

- N is the number of data points and c_{max} is the highest concentration used in the calculations.
 a - This is the reference to the original publications which contain the A and c data.
 b - See Reference 8 for method.
 c - See Reference 14 for method.

TABLE 2.* RESULTS OF ANALYSES BASED ON EQUATION (18) FOR SALTS IN SOCl_2

SALT	J_1	$-J_2$	$\Lambda^\infty(\sigma)$	$10^5 K_D^0(\sigma)$	σ_A
LiAlCl_4	7.649×10^4	3.531×10^5	75.5 (1.7)	3.0 (0.1)	0.28
Pr_4NClO_4	1.015×10^5	2.142×10^5	106.2 (1.2)	6.0 (0.2)	0.72
Pr_4NCl	1.302×10^5	9.768×10^5	106.6 (1.3)	15.0 (0.6)	0.82
$\text{Pr}_4\text{NAlCl}_4$	8.411×10^4	8.149×10^4	97.0 (2.0)	10.0 (0.5)	0.88

*All data are for 25°C. Λ^∞ units are $\text{S cm}^2 \text{mol}^{-1}$, and K_D^0 units are mol dm^{-3} .

APPENDIX A. -- TI-59 PROGRAM FOR SOLUTION OF EQUATION (15)

TITLE Solution of equation 15 PAGE OF

PROGRAMMER M. Salomon DATE 1980

TI Programmable
Program Record 

Partitioning (Op 17) [6,3,9, 39] Library Module N/A Printer Cards

USER INSTRUCTIONS

STEP	PROCEDURE	ENTER	PRESS	DISPLAY
1	Enter Debye-Hückel and Onsager constants	A		A
		B ₁		R/S B ₁
		B ₂		R/S B ₂
		E ₁		R/S E ₁
		E ₂		R/S E ₂
2	Enter Λ^{∞}	Λ^{∞}	2nd A'	0
3	Enter K_D°	K_D°	B	0
4	Enter data for $i = 1, \dots, n$	Λ_1	C	Λ_1
		c_1	R/S	c_1
		trial α	R/S	refined α_1
		If desired, read activity coefficients:	R/S	y_1
		R/S	y_n	
5	Compute constants J_1° and J_2° and the correlation coefficient, r .		D	J_1°
			R/S	J_2°
			R/S	r
6	Calculate standard deviations.		E	0
		(a) Λ_1	R/S	Λ_1
		(b) c_1	R/S	c_1
		(c) refined α_1	R/S	$-\frac{1}{\alpha_1}$
		.		.
		.		.
		α_n	R/S	$\sigma(\Lambda)$
	R/S	$\sigma(K_D^{\circ})$		
	R/S	$\sigma(\Lambda^{\infty})$		
7	Reset pointer to step 6(a)		2nd E'	
8	Remove last set of Λ_1, c_1, α_1 from step 6.		2nd B'	
9	After step 6 completed, to recalculate the std devs, press 2nd D'		2nd D'	$\sigma(\Lambda)$
			R/S	$\sigma(K_D^{\circ})$
			R/S	$\sigma(\Lambda^{\infty})$

000	76	LBL	059	42	STD	118	11	11	177	43	RCL
001	11	A	060	25	25	119	91	R/S	178	12	12
002	42	STD	061	71	SBR	120	43	RCL	179	34	FX
003	00	00	062	23	LNX	121	13	13	180	54	=
004	91	R/S	063	71	SBR	122	91	R/S	181	95	=
005	42	STD	064	33	X2	123	43	RCL	182	22	INH
006	01	01	065	75	-	124	14	14	183	28	LDG
007	91	R/S	066	43	RCL	125	91	R/S	184	42	STD
008	42	STD	067	25	25	126	76	LBL	185	13	13
009	02	02	068	95	=	127	32	X17	186	33	X2
010	91	R/S	069	50	121	128	01	1	187	65	X
011	42	STD	070	22	INH	129	52	EE	188	43	RCL
012	03	03	071	77	GE	130	06	6	189	12	12
013	91	R/S	072	00	00	131	94	+/-	190	55	-
014	42	STD	073	86	86	132	32	X17	191	43	RCL
015	04	04	074	43	RCL	133	92	RTH	192	14	14
016	91	R/S	075	11	11	134	76	LBL	193	95	=
017	76	LBL	076	66	PAU	135	25	CLP	194	42	STD
018	16	A	077	65	X	136	00	0	195	15	15
019	42	STD	078	43	RCL	137	42	STD	196	92	RTH
020	05	05	079	10	10	138	34	34	197	76	LBL
021	65	X	080	95	=	139	42	STD	198	59	INT
022	43	RCL	081	42	STD	140	35	35	199	42	STD
023	01	01	082	12	12	141	42	STD	200	09	09
024	85	+	083	61	GTD	142	36	36	201	91	R/S
025	43	RCL	084	00	00	143	42	STD	202	42	STD
026	02	02	085	57	57	144	37	37	203	10	10
027	95	=	086	71	SBR	145	42	STD	204	91	R/S
028	42	STD	087	45	YM	146	38	38	205	42	STD
029	06	06	088	43	RCL	147	42	STD	206	11	11
030	43	RCL	089	09	09	148	39	39	207	65	X
031	05	05	090	65	X	149	92	RTH	208	43	RCL
032	65	X	091	53	0	150	76	LBL	209	10	10
033	43	RCL	092	01	1	151	23	LNX	210	95	=
034	03	03	093	85	+	152	43	RCL	211	42	STD
035	75	-	094	43	RCL	153	00	00	212	12	12
036	43	RCL	095	15	15	154	65	X	213	92	RTH
037	04	04	096	55	+	155	43	RCL	214	76	LBL
038	95	=	097	43	RCL	156	12	12	215	45	YM
039	42	STD	098	08	08	157	65	X	216	53	0
040	07	07	099	54	0	158	93	.	217	43	RCL
041	71	SBR	100	75	-	159	03	3	218	05	05
042	25	CLP	101	43	RCL	160	95	=	219	75	-
043	91	R/S	102	16	16	161	22	INH	220	43	RCL
044	76	LBL	103	95	=	162	28	LDG	221	06	06
045	12	B	104	55	+	163	42	STD	222	65	X
046	42	STD	105	43	RCL	164	14	14	223	43	RCL
047	08	08	106	12	12	165	28	LDG	224	12	12
048	71	SBR	107	95	=	166	75	-	225	34	FX
049	25	CLP	108	42	STD	167	43	RCL	226	85	+
050	91	R/S	109	19	19	168	00	00	227	43	RCL
051	76	LBL	110	43	RCL	169	65	X	228	12	12
052	13	C	111	12	12	170	43	RCL	229	65	X
053	71	SBR	112	34	FX	171	12	12	230	23	LNX
054	59	INT	113	42	STD	172	34	FX	231	65	X
055	71	SBR	114	20	20	173	55	-	232	43	RCL
056	32	X17	115	71	SBR	174	53	0	233	07	07
057	43	RCL	116	44	SUB	175	01	1	234	95	=
058	11	11	117	43	RCL	176	85	+	235	42	STD

236	16	16	295	95	=	354	42	STD	418	32	32
237	54)	296	44	SUN	355	18	18	414	91	R/S
238	92	RTH	297	37	37	356	91	R/S	415	71	SBP
239	76	LBL	298	43	RCL	357	43	RCL	416	59	INT
240	33	X²	299	19	19	358	17	17	417	71	SBP
241	53	(300	44	SUN	359	91	R/S	418	45	Y
242	43	RCL	301	38	38	360	43	RCL	419	71	SBP
243	08	08	302	33	X²	361	36	36	420	23	LN
244	65	X	303	44	SUN	362	55	-	421	43	RCL
245	43	RCL	304	39	39	363	43	RCL	422	16	16
246	14	14	305	92	RTH	364	34	34	423	85	-
247	55	-	306	76	LBL	365	75	-	424	43	RCL
248	43	RCL	307	14	I	366	53	(425	18	18
249	13	13	308	43	RCL	367	43	RCL	426	65	X
250	33	X²	309	34	34	368	35	35	427	43	RCL
251	95	=	310	65	X	369	55	-	428	12	12
252	42	STD	311	43	RCL	370	43	RCL	429	85	+
253	21	21	312	36	36	371	34	34	430	43	RCL
254	33	X²	313	75	-	372	54)	431	17	17
255	85	+	314	43	RCL	373	33	X²	432	65	X
256	04	4	315	35	35	374	95	=	433	53	(
257	65	X	316	33	X²	375	34	RN	434	43	RCL
258	43	RCL	317	95	=	376	42	STD	435	12	12
259	21	21	318	42	STD	377	23	23	436	45	Y
260	65	X	319	22	22	378	43	RCL	437	03	3
261	43	RCL	320	35	LN	379	39	39	438	54)
262	10	10	321	65	X	380	55	-	439	34	RN
263	95	=	322	53	(381	43	RCL	440	95	=
264	34	RN	323	43	RCL	382	34	34	441	55	-
265	75	-	324	34	34	383	75	-	442	53	(
266	43	RCL	325	65	X	384	53	(443	01	1
267	21	21	326	43	RCL	385	43	RCL	444	85	+
268	95	=	327	37	37	386	38	38	445	43	RCL
269	55	-	328	75	-	387	55	-	446	15	15
270	02	2	329	43	RCL	388	43	RCL	447	55	+
271	55	-	330	38	38	389	34	34	448	43	RCL
272	43	RCL	331	65	X	390	54)	449	08	08
273	10	10	332	43	RCL	391	33	X²	450	54)
274	95	=	333	35	35	392	95	=	451	95	=
275	42	STD	334	54)	393	34	RN	452	75	-
276	11	11	335	95	=	394	35	LN	453	43	RCL
277	54)	336	42	STD	395	65	X	454	09	09
278	92	RTH	337	17	17	396	43	RCL	455	95	=
279	76	LBL	338	43	RCL	397	17	17	456	33	X²
280	44	SUN	339	36	36	398	65	X	457	42	STD
281	01	I	340	65	X	399	43	RCL	458	27	27
282	44	SUN	341	43	RCL	400	23	23	459	44	SUN
283	34	34	342	38	38	401	95	=	460	30	30
284	43	RCL	343	75	-	402	91	R/S	461	43	RCL
285	20	20	344	43	RCL	403	76	LBL	462	09	09
286	44	SUN	345	35	35	404	15	E	463	65	X
287	35	35	346	65	X	405	00	0	464	43	RCL
288	33	X²	347	43	RCL	406	42	STD	465	15	15
289	44	SUN	348	37	37	407	29	29	466	55	-
290	36	36	349	95	=	408	42	STD	467	53)
291	34	RN	350	55	-	409	30	30	468	43	RCL
292	65	X	351	43	RCL	410	42	STD	469	16	16
293	43	RCL	352	22	22	411	31	31	470	85	+
294	19	19	353	95	=	412	42	STD	471	43	RCL

472 18 18
 473 65)
 474 43 RCL
 475 12 12
 476 85 +
 477 43 RCL
 478 17 17
 479 65)
 480 53)
 481 43 RCL
 482 12 12
 483 45)
 484 03)
 485 54)
 486 34)
 487 75 -
 488 43 RCL
 489 09 09
 490 54)
 491 95 =
 492 75 -
 493 43 RCL
 494 08 08
 495 95 =
 496 33)
 497 42 STD
 498 28 28
 499 44 SUM
 500 31 31
 501 43 RCL
 502 09 09
 503 65 x
 504 53)
 505 01 1
 506 85 +
 507 43 RCL
 508 15 15
 509 55 +
 510 43 RCL
 511 08 08
 512 54)
 513 75 -
 514 43 RCL
 515 12 12
 516 65 x
 517 23 LHX
 518 65 x
 519 43 RCL
 520 07 07
 521 75 -
 522 43 RCL
 523 12 12
 524 65 x
 525 53)
 526 43 RCL
 527 18 18
 528 85 +
 529 43 RCL
 530 17 17

531 65)
 532 43 RCL
 533 12 12
 534 34)
 535 54)
 536 85 +
 537 43 RCL
 538 02 02
 539 65)
 540 43 RCL
 541 12 12
 542 34)
 543 95 =
 544 55 -
 545 53)
 546 01 1
 547 75 -
 548 43 RCL
 549 01 01
 550 65 x
 551 43 RCL
 552 12 12
 553 34)
 554 54)
 555 75 -
 556 43 RCL
 557 05 05
 558 95 =
 559 33)
 560 44 SUM
 561 32 32
 562 43 RCL
 563 34 34
 564 32)
 565 01 1
 566 44 SUM
 567 29 29
 568 43 RCL
 569 29 29
 570 67 E0
 571 05 05
 572 77 77
 573 94 +/-
 574 61 GTD
 575 04 04
 576 14 14
 577 75 -
 578 03 3
 579 95 =
 580 42 STD
 581 33 33
 582 35 LHX
 583 65 x
 584 43 RCL
 585 30 30
 586 95 =
 587 34)
 588 91 R/S
 589 43 RCL

590 31 31
 591 55 -
 592 43 RCL
 593 33 33
 594 95 =
 595 34)
 596 91 R/S
 597 43 RCL
 598 32 32
 599 55 -
 600 43 RCL
 601 33 33
 602 95 =
 603 34)
 604 91 R/S
 605 76 LBL
 606 17 B'
 607 43 RCL
 608 27 27
 609 94 +/-
 610 44 SUM
 611 30 30
 612 43 RCL
 613 28 28
 614 94 +/-
 615 44 SUM
 616 31 31
 617 01 1
 618 94 +/-
 619 44 SUM
 620 29 29
 621 61 GTD
 622 04 04
 623 14 14
 624 76 LBL
 625 10 E'
 626 61 GTD
 627 04 04
 628 14 14
 629 76 LBL
 630 19 B'
 631 61 GTD
 632 05 05
 633 01 01