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ANALYZING ELECTROLYTIC CONDUCTIVITY DATA BY THE FUOSS–JUSTICE EQUATION WITH A PROGRAMMABLE CALCULATOR

W. LINERT and P. RECHBERGER
Institute of Inorganic Chemistry, Technical University of Vienna, Getreidemarkt 9, 1060 Vienna, Austria

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Abstract—The dissociation constant K_c and the equivalent conductivity at infinite dilution Λ_0 of 1–1 electrolytes are computed according to the Fuoss–Justice method as well as modifications of this program to analyze symmetric $z:z$ electrolytes. The algorithm is presented for a Texas Instruments TI 59. The analyzing of electrolytic conductivity with a programmable calculator by the simple Fuoss–Krauss method has been described earlier (Rechberger & Linert, 1980). In this work a much better and more complete model should be used, called the Fuoss–Justice model (Wachter & Barthel, 1979; Barthel *et al.*, 1973; Barthel, 1976; Fuoss & Hsia, 1967).

DESCRIPTION OF PROGRAM

Equivalent conductivity values ($\Lambda, \Omega^{-1}\,cm^2\,eq^{-1}$) of 1–1 electrolytes are obtained as a function of molar concentration c (mol.dm^{-3}) by experiment. If Λ_0, α, K_A and f are meaning the equivalent conductivity at infinite dilution, the degree of dissociation, the association constant and the mean activity coefficient respectively, the complete conductance equation (Wachter & Barthel, 1979; Barthel *et al.*, 1973; Barthel, 1976; Fuoss & Hsia, 1967). is given by

$$\Lambda[\Lambda_0 - S\sqrt{(\alpha c)} + E(\alpha c)\ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{3/2} - K_A\Lambda\alpha c f^2]$$

with S, E, J_1 and J_2 being functions of the dielectric constant ϵ, the absolute temperature T, the dynamic viscosity η and the equivalent conductivity at infinite dilution Λ_o.

That is in detail:

$$\log f = -(A\sqrt{(c\alpha)})/(1 + aB\sqrt{(\alpha c)})$$

and

$$A = 1.8246 \times 10^6 \times (\epsilon T)^{-3/2}$$

and

$$B = 5.029 \times 10^9 \times (\epsilon T)^{-1/2}$$

a being the ion size parameter in cm.

According to Fuoss and Justice (1973) the conductivity coefficients are given by

$$S = S_1\Lambda_0 + S_2$$

$$S_1 = 0.82043 \times 10^6 \times (\epsilon T)^{-3/2}$$

$$S_2 = 82.484 \times \eta^{-1} \times (\epsilon T)^{-1/2}$$

$$E = E_1\Lambda_0 = 2E_2$$

$$E_1 = 0.4343 \times 6.7749 \times 10^{12} \times (\epsilon T)^{-3}$$

$$E_2 = 0.4343 \times 0.9975 \times 10^8 \times \eta^{-1}(\epsilon T)^{-2}$$

$$J_1 = \sigma_1\Lambda_0 + \sigma_2$$

$$\sigma_1 = 2E_1\left[\frac{2b^2+2b-1}{b^3} + 0.9074 + \ln\frac{0.5029 \times 10^{10} \times a}{(\epsilon T)^{1/2}}\right]$$

$$\sigma_2 = E_2\left[\frac{35}{3b} + \frac{2}{b^2} - 2.0689 - 4\ln\frac{0.5029 \times 10^{10} \times a}{(\epsilon T)^{1/2}}\right]$$

$$J_2 = \sigma_3\Lambda_0 + \sigma_4$$

$$\sigma_3 = E_1 \times \frac{0.5029 \times 10^{10} \times a}{(\epsilon T)^{1/2}}\left[0.6094 + \frac{4.4748}{b} + \frac{3.8284}{b^2}\right]$$

$$\sigma_4 = E_2 \times \frac{0.5029 \times 10^{10} \times a}{(\epsilon T)^{1/2}}\left[\frac{34}{3b} - 1.3693 - \frac{2}{b^2}\right]$$

$$b = \frac{16.709 \times 10^{-4}}{\epsilon T a}.$$

Printing errors in Barthel (1976) have been corrected.

Data analysis is performed according to the Newton–Gauss method (Bevington, 1969). Starting from estimates of K_A and Λ_0 $\Lambda(\Lambda_0, K_A)$ is expanded into a Taylor series. Neglecting higher terms yields:

$$\Lambda^{calc} = \mathring{\Lambda} + \left(\frac{\delta\Lambda}{\delta\Lambda}\right)\Delta\Lambda_0 + \left(\frac{\delta\Lambda}{\delta K_A}\right)\Delta K_A$$

with $\mathring{\Lambda}$ being $\Lambda_{calc.}$ of estimates of K_A and Λ_0. Demanding $\sum_{i=1}^{N}(\Lambda_i^{calc} - \Lambda_i^{obs})^2$ being a minimum gives two linear equations in $\Delta\Lambda_0$ and ΔK_a (N: number of data pairs).

$\Delta\Lambda_0$ and ΔK_A are added to Λ_0 and K_A respectively. Calculation is repeated until K_A values of consecutive runs are within 0.01%.

The program for calculating Λ_0 and K_A on a Texas Instruments TI 59 calculator consists of two parts: Program I stores the Λ/c data pairs, ϵ, η, T, the estimate of Λ_0, the estimate of K_A and the ion size parameter a has been chosen, the sum of the crystallographic radii being the lowest limit. Program II has to be entered and the Calculation is repeated until K_A values of consecutive is performed.

First the degree of dissociation α is obtained by iteration:

$$\alpha_i = \Lambda_i/\Lambda_0 - s\sqrt{(\alpha_0 c_i)} + E(\alpha_0 c_i)\ln(\alpha_0 c_i) + J_1(\alpha_0 c_i) - J_2(\alpha_0 c_i)^{3/2}$$

α_0 being Λ_i/Λ_0. Then α_0 is substituted by α_i and iteration is repeated until α_i's of consecutive runs are within 10^{-6}.

$$\Delta\Lambda_i(\Lambda_i^{obs} - \Lambda_i^{calc}), \left(\frac{\delta\Lambda}{\delta\Lambda_0}\right), \left(\frac{\delta\Lambda}{\delta K_A}\right)$$

squares of the derivates and mixed products are computed and summed into registers:

$$\Delta\Lambda_0 \cdot \sum \left(\frac{\delta\Lambda}{\delta\Lambda_0}\right)^2 + \Delta K_A \cdot \sum \left(\frac{\delta\Lambda}{\delta\Lambda_0}\right)\left(\frac{\delta\Lambda}{\delta K_A}\right) = \sum \Delta\Lambda_i \cdot \left(\frac{\delta\Lambda}{\delta\Lambda_0}\right)$$

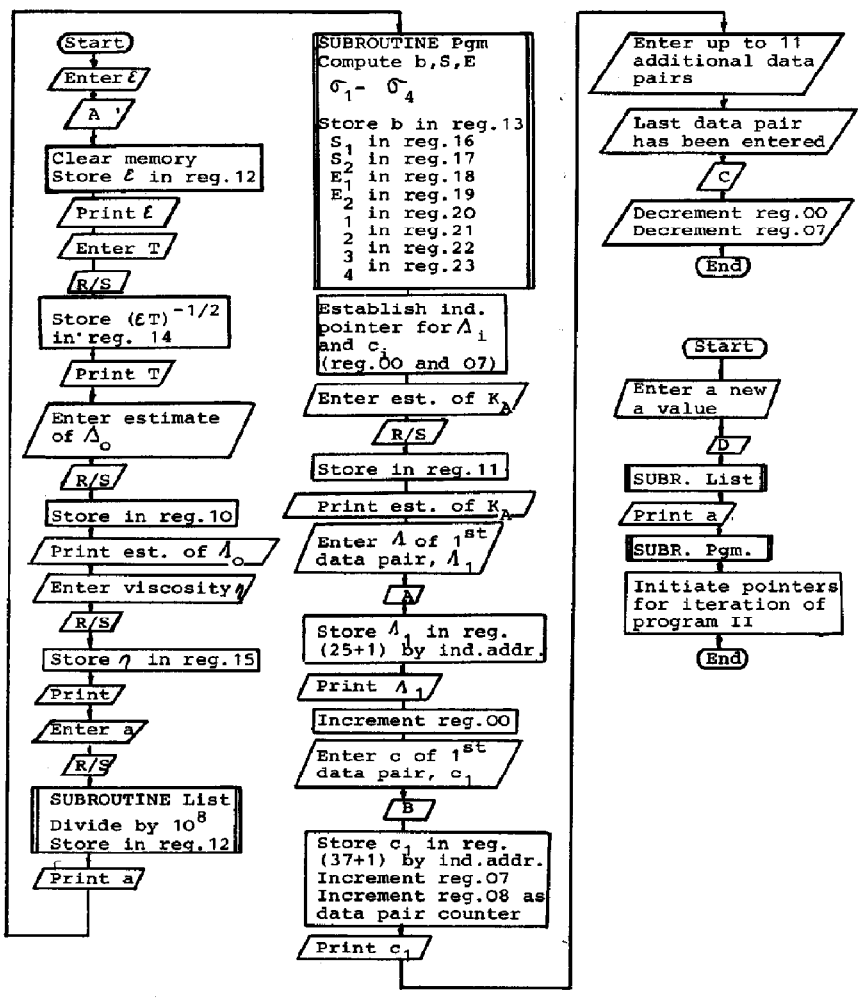
$$\Delta\Lambda_0 \cdot \sum \left(\frac{\delta\Lambda}{\delta\Lambda_0}\right)\left(\frac{\delta\Lambda}{\delta K_A}\right) + \Delta K_A \cdot \sum \left(\frac{\delta\Lambda}{\delta K_A}\right)^2 = \sum \Delta\Lambda_i \cdot \left(\frac{\delta\Lambda}{\delta K_A}\right).$$

This is done with all data pairs (up to 12 pairs can be handled). Solving the linear equations yields $\Delta\Lambda_0$ and ΔK_A which are summed to Λ_0 and K_A respectively. Procedure is repeated until K_A is within 0.01%.

Calculation can be repeated with a different ion-size parameter a and program II includes the facility of choosing the best-fitting ion-size parameter. For this reason $(\Sigma(\Delta\Lambda_i)^2/N)^{1/2}$ symbolized by INV $\bar{x}$ is computed and printed as a measure for accuracy of experiment and of goodness of fit for the ion size parameter chosen.

Calculation can be repeated with different ion size parameters: Using program I the appropriate conductivity coefficients are calculated. Program II computes the K_A- and Λ_0 values for the new ion size parameter. Program I and program II contain 476 and 474 steps respectively. A Texas Instruments TI5P, the Standard Software Module, and Printer PC100A is needed. If PC100A is not available, output of results can be obtained manually after changing all "PRT"-statements which are not following directly after a "RS"-statement by "RS"-statements. The necessary modifications to use this program for symmetric $z:z$ electrolytes are given in the appendix.

Flow Chart of Program I



Flow Chart of Program II

Main features of program II are subroutines used for computing

$\left(\frac{\partial \Lambda}{\partial \Lambda_o}\right)$ and $\left(\frac{\partial \Lambda}{\partial K_A}\right)$

$$\left(\frac{\partial \Lambda}{\partial \Lambda_o}\right) = \frac{1}{1 + K_A c_i \alpha_i f^2} \cdot \quad 1 - S_1 \sqrt{\alpha_i c_i} + E_1(\alpha_i c_i)\ln(\alpha_i c_i)\ln(\alpha_i c_i) + \\ + \sigma_1(\alpha_i c_i) - \sigma_3(\alpha_i c_i)^{3/2}$$

$$\left(\frac{\partial \Lambda}{\partial K_A}\right) = \frac{-c_i \alpha_i f^2}{1 + K_A c_i \alpha_i f^2} \cdot \quad \Lambda_o - S\sqrt{\alpha_i c_i} + E(\alpha_i c_i)\ln(\alpha_i c_i) + \\ J_1(\alpha_i c_i) - J_2(\alpha_i c_i)^{3/2}$$

Subroutine INV computes f^2

Subroutine $\sqrt{x}$ computes $\Lambda_o - S \sqrt{\alpha_i c_i} + E(\alpha_i c_i)\ln(\alpha_i c_i) + J_1(\alpha_i c_i) - J_2(\alpha_i c_i)^{3/2}$

Subroutine tan calculates $(1 + K_A c_i \alpha_i f^2)^{-1}$

Subroutine sin yields $1 - S_1 \sqrt{\alpha_i c_i} + E_1(\alpha_i c_i)\ln(\alpha_i c_i) + \sigma_1(\alpha_i c_i) - \sigma_3(\alpha_i c_i)$

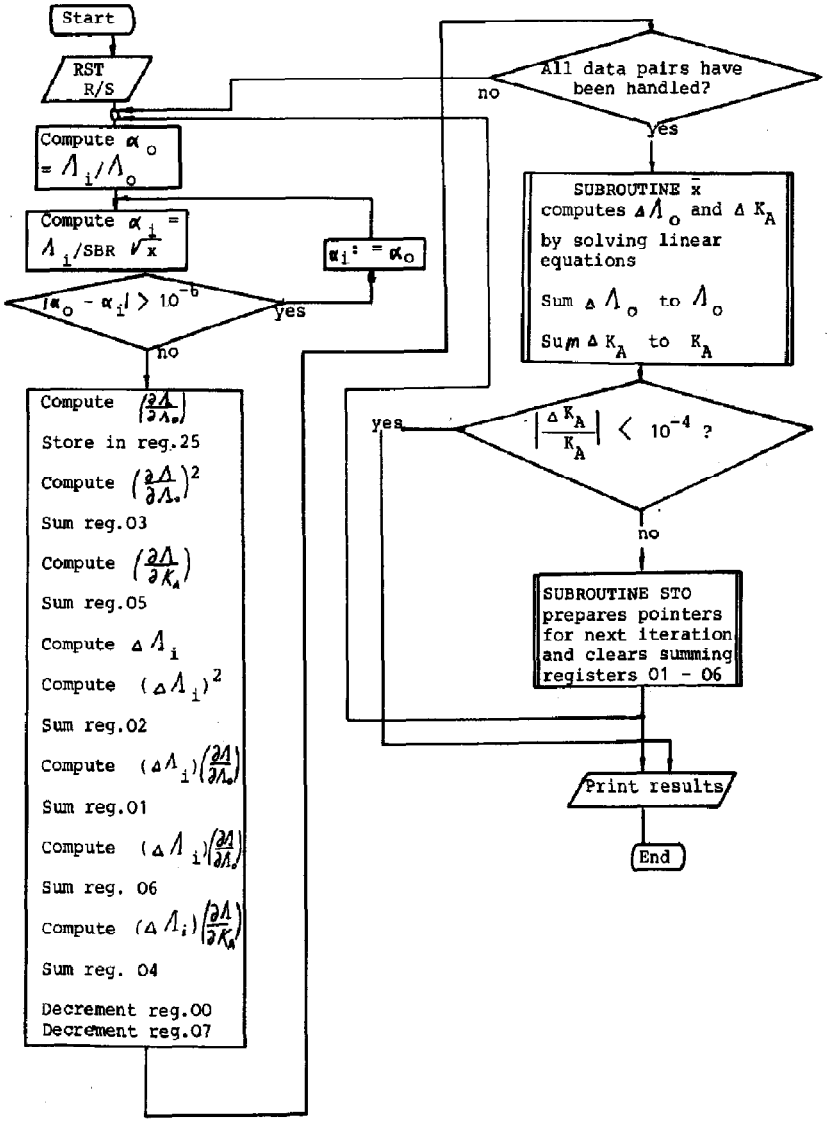
$\left(\frac{\partial \Lambda}{\partial \Lambda_o}\right)$ = SUBR tan · SUBR sin

$\left(\frac{\partial \Lambda}{\partial K_A}\right)$ = - [(SUBR tan)^2 · SUBR INV · $\alpha_i c_i$ · SUBR $\sqrt{x}$]

$\Delta \Lambda_i = \Lambda_{i\ obs.} - \Lambda_{i\ calc.} = \Lambda_i$ - SUBR $\sqrt{x}$ + SUBR INV · $K_A \Lambda_i c_i \alpha_i$

Subroutine $\bar{x}$ solves the linear equations in ΔK_A and $\Delta \Lambda_o$ using TI 59 Op codes for linear regression analysis.

Subroutine STO prepares indirect addressing pointers (reg.00 for Λ_i, reg.07 for c_i) for next iteration and clears summing registers.



Instructions for Entering Programs and Data

TI Programmable 59, Printer PC 100 A and Library Module 1 is needed.

1) Clear program and memories
2) Partition to 479.59 (6 2^{nd} Op 17 or status after turining on calculator)
3) Enter program I (Storage of data and computing of coefficients)
4) Record bank 1 and 2 on magnetic card.

ENTER	PRESS	OUTPUT/MODE (see legend below)	COMMENT
Dielectric Constant ε	A'	ε* *DK*	
Temperature T	R/S	(T)* $[\frac{\eta}{\sqrt{\varepsilon T}}]$ *T*	
Estimate of Λ_o	R/"	Est. of Λ_o* *LOES*	
Viscosity (poise) η	R/S	η * *VISK*	
Ion size parameter a (A-units)	R/S	(a)* [38] *A*	
Estimate of K_A	R/S	K_A * *KAES*	
Λ of 1^{st} data point	A	Λ_1 * *L*	
c of 1^{st} data point	B	c_1* *C*	
⋮	⋮	⋮ ⋮	Store up to 12 data points
Λ of last data p.	A	$_n$ * *L*	
c of last data p.	B	c_n* *C*	
	C	$[c_n]$	End of data storage

5) Clear Program
6) Enter Program II (Iteration procedure)
7) Record bank 1' and 2' on magnetic card

ENTER	PRESS	OUTPUT/MODE	COMMENT
	RST		Start of iteration
	R/S		
		(ΔK_A)*	ΔK_A of 1^{st} it.
		⋮	⋮
		(ΔK_A)*	ΔK_A of last it.
		(Λ_o)* *LO*	Λ_o of last it.
		(K_A)* *KA*	K_A of last it.
		(K_{DIS})* *KDIS*	Dissociation constant $(K_A)^{-1}$
		INV$\bar{x}$* *INV$\bar{x}$*	measure for goodness of fit

8) Variation of a, using the same /c data set.
Read bank 1 and 2 on magnetic card.

ENTER	PRESS	OUTPUT/MODE	COMMENT
Ion size parameter a (A-units)	D (a)*	37+n *A*	

9) Read bank 1' and 2' on magnetic card.

ENTER	PRESS	OUTPUT/MODE	COMMENT
	RST		Start of iteration
	R/S		
		(ΔK_A)*	ΔK_A of 1^{st} it.
		⋮	⋮
		(ΔK_A)*	ΔK_A of last it.
		(Λ_o)* *LO*	Λ_o of last it.
		(K_A) * *KA*	K_A of last it.
		(K_{DIS})* *KDIS*	dissoc. const.
		INV$\bar{x}$ * *INV$\bar{x}$*	measure for goodness of fit

Modes: (n)* printed only
[n] displayed only
n* printed and displayed
n alphanumeric comments additionally printed

Test data set (For further examples see Gritzner *et al.* (1981)

1) Read bank 1 and 2 on magnetic card

ENTER	PRESS	OUTPUT/MODE			COMMENT
ε = 50	A'	50 *		*DK*	3 sec
T = 300	R/S	(300)*	[.0081649658]	*T*	2,5 sec
Estimate of Λ_o					
= 22	R/S	22 *		*LOES*	2,6 sec
η = 0,04	R/S	0,04*		*VISK*	2,7 sec
a = 5	R/S	(5)*	[38]	*A*	19 sec
Estimate of K_A					
= 100	R/S	100 *		*KAES*	2,6 sec
Λ_1= 20	A	20 *		*L*	2,3 sec
c_1= 0,001	B	0,001*		*C*	2,4 sec
Λ_2= 19	A	19 *		*L*	
c_2= 0,002	B	0,002*		*C*	
Λ_3= 18	A	18 *		*L*	
c_3= 0,003	B	0,003*		*C*	
	C		[.003]		1,4 sec

2) Read bank 1' and 2' on magnetic card

ENTER	PRESS	OUTPUT/MODE		COMMENT
	RST			
	R/S			
		(-4.0317837 . 10^{1})*		ΔK_A of 1st it.
		(1.2334625 . 10^{1})*		
		(-7.0871984 . 10^{-1})*		
		(-5.4079926 . 10^{-2})*		
		(2.722316 . 10^{-2})*		
		(-4.5023213 . 10^{-3})*		ΔK_A of last it.
		(2.2001794 . 10^{1})*	*LO*	time of calculation
		(7.1276709 . 10^{1})*	*KA*	
		(1.4029828 . 10^{-2})*	*KDIS*	20 min
		7.561452 . 10^{-2})*	*INV$\bar{x}$*	30 sec

3) Read bank 1 and 2 on magnetic card

ENTER	PRESS	OUTPUT/MODE			COMMENT
a = 10	D	(10)*	[40]	*A*	variation of a 19 sec

4) Read bank 1' and 2' on magnetic card

ENTER	PRESS	OUTPUT/MODE		COMMENT
	RST			
	R/S			
		(2.5792605)*		ΔK_A of 1st it.
		(1.8197257)*		
		(-4.8771442 . 10^{-1})*		
		(6.606029 . 10^{-2})*		
		(-2.7550863 . 10^{-3})*		ΔK_A of last it.
		(2.1993234 . 10^{1})*	*LO*	
		(7.5251286 . 10^{1})*	*KA*	time of calculation
		(1.3288809 . 10^{-2})*	*KDIS*	
		7.507126 . 10^{-2} *	*INV$\bar{x}$*	17 min

Program I (Storing of data and computing of coefficients)

```
000 76 LBL  060 42 STO  120 06  6   180 43 RCL  240 42 STO  300 43 RCL
001 11  A   061 12  12  121 42 STO  181 15  15  241 19  19  301 14  14
002 72 STø  062 32 X⇄T  122 00  00  182 65  ×   242 43 RCL  302 65  ×
003 00  00  063 01  1   123 03  3   183 08  8   243 13  13  303 93  .
004 32 X⇄T  064 06  6   124 08  8   184 02  2   244 33 x²  304 05  5
005 02  2   065 02  2   125 42 STO  185 93  .   245 65  ×   305 00  0
006 07  7   066 06  6   126 07  07  186 04  4   246 02  2   306 02  2
007 71 SBR  067 71 SBR  127 91 R/S  187 08  8   247 85  +   307 09  9
008 68 NOP  068 68 NOP  128 42 STO  188 04  4   248 43 RCL  308 52 EE
009 69 OP   069 91 R/S  129 11  11  189 95  =   249 13  13  309 01  1
010 20  20  070 32 X⇄T  130 32 X⇄T  190 42 STO  250 65  ×   310 00  0
011 91 R/S  071 03  3   131 02  2   191 17  17  251 02  2   311 54  )
012 76 LBL  072 07  7   132 06  6   192 43 RCL  252 75  -   312 23 LNX
013 12  B   073 71 SBR  133 01  1   193 14  14  253 01  1   313 65  ×
014 72 STø  074 68 NOP  134 03  3   194 33 x²  254 95  =   314 04  4
015 07  07  075 65  ×   135 01  1   195 45 Y^x  255 55  ÷   315 94 +/-
016 32 X⇄T  076 43 RCL  136 07  7   196 03  3   256 43 RCL  316 75  -
017 01  1   077 12  12  137 03  3   197 65  ×   257 13  13  317 02  2
018 05  5   078 95  =   138 06  6   198 06  6   258 45 Y^x  318 93  .
019 71 SBR  079 34 √x  139 71 SBR  199 93  .   259 03  3   319 00  0
020 68 NOP  080 35 1/X  140 68 NOP  200 07  7   260 95  =   320 06  6
021 69 OP   081 42 STO  141 91 R/S  201 07  7   261 85  +   321 08  8
022 27  27  082 14  14  142 76 LBL  202 04  4   262 93  .   322 09  9
023 69 OP   083 91 R/S  143 36 PGM  203 09  9   263 09  9   323 85  +
024 28  28  084 42 STO  144 43 RCL  204 52 EE  264 00  0   324 53  (
025 91 R/S  085 10  10  145 14  14  205 01  1   265 07  7   325 43 RCL
026 76 LBL  086 32 X⇄T  146 33 x²  206 02  2   266 04  4   326 13  13
027 13  C   087 02  2   147 55  ÷   207 65  ×   267 85  +   327 33 x²
028 69 OP   088 07  7   148 43 RCL  208 53  (   268 53  (   328 35 1/X
029 30  30  089 00  0   149 12  12  209 01  1   269 53  (   329 65  ×
030 69 OP   090 01  1   150 65  ×   210 00  0   270 43 RCL  330 02  2
031 37  37  091 01  1   151 01  1   211 23 LNX  271 12  12  331 54  )
032 91 R/S  092 07  7   152 06  6   212 35 1/X  272 65  ×   332 85  +
033 76 LBL  093 03  3   153 93  .   213 54  )   273 43 RCL  333 53  (
034 14  D   094 06  6   154 07  7   214 95  =   274 14  14  334 43 RCL
035 32 X⇄T  095 71 SBR  155 00  0   215 42 STO  275 65  ×   335 13  13
036 71 SBR  096 68 NOP  156 09  9   216 18  18  276 93  .   336 35 1/X
037 99 PRT  097 91 R/S  157 52 EE  217 43 RCL  277 05  5   337 65  ×
038 71 SBR  098 42 STO  158 94 +/-  218 14  14  278 00  0   338 03  3
039 90 LST  099 15  15  159 04  4   219 33 x²  279 02  2   339 05  5
040 71 SBR  100 32 X⇄T  160 95  =   220 33 x²  280 09  9   340 55  ÷
041 36 PGM  101 04  4   161 42 STO  221 55  ÷   281 52 EE  341 03  3
042 43 RCL  102 02  2   162 13  13  222 43 RCL  282 01  1   342 54  )
043 08  08  103 02  2   163 43 RCL  223 15  15  283 00  0   343 95  =
044 85  +   104 04  4   164 14  14  224 65  ×   284 54  )   344 65  ×
045 02  2   105 03  3   165 45 Y^x  225 93  .   285 23 LNX  345 43 RCL
046 05  5   106 06  6   166 03  3   226 09  9   286 54  )   346 19  19
047 95  =   107 02  2   167 65  ×   227 09  9   287 95  =   347 95  =
048 42 STO  108 06  6   168 08  8   228 07  7   288 65  ×   348 42 STO
049 00  00  109 71 SBR  169 02  2   229 05  5   289 02  2   349 21  21
050 85  +   110 68 NOP  170 00  0   230 52 EE  290 65  ×   350 53  (
051 01  1   111 91 R/S  171 04  4   231 08  8   291 43 RCL  351 43 RCL
052 02  2   112 32 X⇄T  172 03  3   232 65  ×   292 18  18  352 13  13
053 95  =   113 71 SBR  173 00  0   233 53  (   293 95  =   353 33 x²
054 42 STO  114 99 PRT  174 95  =   234 01  1   294 42 STO  354 35 1/X
055 07  07  115 71 SBR  175 42 STO  235 00  0   295 20  20  355 65  ×
056 91 R/S  116 90 LST  176 16  16  236 23 LNX  296 53  (   356 03  3
057 76 LBL  117 71 SBR  177 43 RCL  237 35 1/X  297 43 RCL  357 93  .
058 16  A'  118 36 PGM  178 14  14  238 54  )   298 12  12  358 08  8
059 47 CMS  119 02  2   179 55  ÷   239 95  =   299 65  ×   359 02  2
```

Program I (continued)

```
360 08  8      385 65  x      410 43 RCL      435 12  12     453 90 LST     465 04  04
361 04  4      386 43 RCL     411 13  13     436 65  x      454 55  :      466 32 X≠T
362 85  +      387 12  12     412 54  )      437 43 RCL     455 01  1      467 69 OP
363 53  (      388 65  x      413 75  -      438 19  19     456 52 EE      468 06  06
364 43 RCL     389 93  .      414 01  1      439 65  x      457 08  8      469 92 RTN
365 13  13     390 05  5      415 93  .      440 93  .      458 95  =      470 76 LBL
366 35 1/X     391 00  0      416 03  3      441 05  5      459 42 STO     471 99 PRT
367 65  x      392 02  2      417 06  6      442 00  0      460 12  12     472 01  1
368 04  4      393 09  9      418 09  9      443 02  2      461 92 RTN     473 03  3
369 93  .      394 52 EE      419 03  3      444 09  9      462 76 LBL     474 71 SBR
370 04  4      395 01  1      420 75  -      445 53 EE      463 68 NOP     475 68 NOP
371 07  7      396 00  0      421 53  (      446 01  1      464 69 OP      476 92 RTN
372 04  4      397 65  x      422 43 RCL     447 00  0
373 08  8      398 43 RCL     423 13  13     448 95  =
374 54  )      399 18  18     424 33 X²      449 42 STO
375 85  +      400 95  =      425 35 1/X     450 23  23
376 93  .      401 42 STO     426 65  x      451 92 RTN
377 06  6      402 22  22     427 02  2      452 76 LBL
378 00  0      403 53  (      428 54  )
379 09  9      404 53  (      429 54  )
380 04  4      405 03  3      430 65  x
381 95  =      406 04  4      431 43 RCL
382 65  x      407 55  :      432 14  14
383 43 RCL     408 03  3      433 65  x
384 14  14     409 55  :      434 43 RCL
```

Labels

```
001 11  A
013 12  B
027 13  C
034 14  D
058 16  A'
143 36 PGM
453 90 LST
463 68 NOP
471 99 PRT
```

Program II (Iteration)

```
000 73 RC*     030 71 SBR     060 33 X²      090 09  09     120 02  2      150 69 OP
001 00  00     031 30 TAN     061 44 SUM     091 65  x      121 04  4      151 04  04
002 55  :      032 65  x      062 05  05     092 43 RCL     122 95  =      152 43 RCL
003 43 RCL     033 71 SBR     063 71 SBR     093 25  25     123 42 STO     153 10  10
004 10  10     034 38 SIN     064 22 INV     094 95  =      124 09  09     154 69 OP
005 95  =      035 95  =      065 65  x      095 44 SUM     125 97 DSZ     155 06  06
006 42 STO     036 42 STO     066 43 RCL     096 01  01     126 09  09     156 02  2
007 09  09     037 25  25     067 11  11     097 43 RCL     127 00  00     157 06  6
008 01  1      038 33 X²      068 65  x      098 09  09     128 00  00     158 01  1
009 52 EE      039 44 SUM     069 73 RC*     099 65  x      129 71 SBR     159 03  3
010 94 +/-     040 03  03     070 00  00     100 43 RCL     130 79  x̄      160 69 OP
011 06  6      041 71 SBR     071 65  x      101 24  24     131 01  1      161 04  04
012 32 X≠T     042 30 TAN     072 73 RC*     102 95  =      132 52 EE      162 43 RCL
013 71 SBR     043 33 X²      073 07  07     103 44 SUM     133 94 +/-     163 11  11
014 34 √x      044 65  x      074 65  x      104 05  06     134 04  4      164 69 OP
015 35 1/X     045 71 SBR     075 43 RCL     105 43 RCL     135 32 X≠T     165 06  06
016 65  x      046 22 INV     076 09  09     106 24  24     136 43 RCL     166 32 X≠T
017 73 RC*     047 65  x      077 75  -      107 65  x      137 24  24     167 02  2
018 00  00     048 43 RCL     078 71 SBR     108 43 RCL     138 99 PRT     168 06  6
019 95  =      049 09  09     079 34 √x      109 25  25     139 55  :      169 01  1
020 48 EXC     050 65  x      080 85  +      110 95  =      140 43 RCL     170 06  6
021 09  09     051 73 RC*     081 73 RC*     111 44 SUM     141 11  11     171 02  2
022 75  -      052 07  07     082 00  00     112 04  04     142 95  =      172 04  4
023 43 RCL     053 65  x      083 95  =      113 69 OP      143 50 I×I     173 03  3
024 09  09     054 71 SBR     084 42 STO     114 30  30     144 77 GE      174 06  6
025 95  =      055 34 √x      085 09  09                    145 42 STO     175 69 OP
026 50 I×I     056 95  =      086 33 X²                     146 02  2      176 04  04
027 77 GE      057 94 +/-     087 44 SUM                    147 07  7      177 32 X≠T
028 00  00     058 42 STO     088 02  02                    148 00  0      178 35 1/X
029 08  08     059 24  24     089 43 RCL                    149 01  1      179 69 OP
```

Program II (continued)

```
180 06  06      239 02  2       298 85  +       357 73 RC*  416 54  )       452 45 Y^x
181 02  2       240 09  9       299 01  1       358 07  07  417 54  )       453 01  1
182 04  4       241 52 EE       300 54  )       359 54  )   418 65  x       454 93  .
183 03  3       242 09  9       301 35 1/X      360 45 Y^x  419 43 RCL       455 05  5
184 01  1       243 65  x       302 54  )       361 01  1   420 18  18      456 65  x
185 04  4       244 43 RCL      303 92 RTN      362 93  .   421 75  -       457 43 RCL
186 02  2       245 14  14      304 76 LBL      363 05  5   422 53  (       458 22  22
187 06  6       246 65  x       305 35 √x       364 54  )   423 43 RCL      459 85  +
188 07  7       247 43 RCL      306 53  (       365 65  x   424 09  09      460 01  1
189 69 OP       248 12  12      307 43 RCL      366 53  (   425 65  x       461 54  )
190 04  04      249 85  +       308 09  09      367 43 RCL  426 73 RC*  462 92 RTN
191 43 RCL      250 01  1       309 65  x       368 10  10  427 07  07  463 76 LBL
192 02  02      251 54  )       310 73 RC*      369 65  x   428 54  )   464 79  x̄
193 55  :       252 35 1/X      311 07  07      370 43 RCL  429 34 √x   465 69 OP
194 43 RCL      253 65  x       312 65  x       371 22  22  430 65  x   466 12  12
195 08  08      254 53  (       313 53  (       372 85  +   431 43 RCL  467 44 SUM
196 95  =       255 53  (       314 24 CE       373 43 RCL  432 16  16  468 10  10
197 34 √x       256 43 RCL      315 23 LNX      374 23  23  433 85  +   469 32 X↔T
198 69 OP       257 09  09      316 54  )       375 54  )   434 53  (   470 42 STO
199 06  06      258 65  x       317 65  x       376 75  -   435 43 RCL  471 24  24
200 98 ADV      259 73 RC*      318 53  (       377 53  (   436 09  09  472 44 SUM
201 91 R/S      260 07  07      319 43 RCL      378 53  (   437 65  x   473 11  11
202 76 LBL      261 54  )       320 18  18      379 43 RCL  438 73 RC*  474 92 RTN
203 42 STO      262 34 √x       321 65  x       380 09  09  439 07  07
204 43 RCL      263 54  )       322 43 RCL      381 65  x   440 54  )
205 08  08      264 65  x       323 10  10      382 73 RC*  441 65  x
206 85  +       265 43 RCL      324 75  -       383 07  07  442 43 RCL
207 02  2       266 14  14      325 53  (       384 54  )   443 20  20
208 05  5       267 45 Y^x      326 02  2       385 34 √x   444 75  -
209 95  =       268 03  3       327 65  x       386 54  )   445 53  (
210 42 STO      269 65  x       328 43 RCL      387 65  x   446 43 RCL
211 00  00      270 01  1       329 19  19      388 53  (   447 09  09
212 85  +       271 08  8       330 54  )       389 43 RCL  448 65  x
213 01  1       272 02  2       331 54  )       390 10  10  449 73 RC*
214 02  2       273 04  4       332 85  +       391 65  x   450 07  07
215 95  =       274 06  6       333 53  (       392 43 RCL  451 54  )
216 42 STO      275 00  0       334 43 RCL      393 16  16
217 07  07      276 00  0       335 09  09      394 85  +
218 36 PGM      277 54  )       336 65  x       395 43 RCL
219 01  01      278 94 +/-      337 73 RC*      396 17  17
220 71 SBR      279 22 INV      338 07  07      397 54  )
221 25 CLR      280 28 LOG      339 65  x       398 85  +
222 81 RST      281 33 x^2      340 53  (       399 43 RCL
223 76 LBL      282 92 RTN      341 43 RCL      400 10  10
224 22 INV      283 76 LBL      342 20  20      401 54  )
225 53  (       284 30 TAN      343 65  x       402 92 RTN
226 53  (       285 53  (       344 43 RCL      403 76 LBL
227 53  (       286 53  (       345 10  10      404 38 SIN
228 43 RCL      287 71 SBR      346 85  +       405 53  (
229 09  09      288 22 INV      347 43 RCL      406 53  (
230 65  x       289 65  x       348 21  21      407 43 RCL
231 73 RC*      290 43 RCL      349 54  )       408 09  09
232 07  07      291 09  09      350 54  )       409 65  x
233 54  )       292 65  x       351 75  -       410 73 RC*
234 34 √x       293 73 RC*      352 53  (       411 07  07
235 65  x       294 07  07      353 53  (       412 65  x
236 05  5       295 65  x       354 43 RCL      413 53  (
237 93  .       296 43 RCL      355 09  09      414 24 CE
238 00  0       297 11  11      356 65  x       415 23 LNX
```

Labels

```
203 42 STO
224 22 INV
284 30 TAN
305 34 √x
404 38 SIN
464 79 x̄
```

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APPENDIX

Modifications for z:z *electrolytes*

The formulas and the program whould be changed by transforming $c_0 \rightarrow zc_0$ (possible only for symmetric electrolytes).

The terms S_1, S_2, E_1', E_2', a, b, K used in the formulas for 1:1 electrolytes have simply to be replaced by the following terms:

$$\bar{S}_1 = S_1 \cdot z^3 \qquad \bar{a} = z^2 a$$
$$\bar{S}_2 = S_2 \cdot z^2 \qquad \bar{b} = b$$
$$\bar{E}_1' = E_1' \cdot z^6 \qquad \bar{K} = z$$
$$\bar{E}_2' = E_2' \cdot z^5$$

Also c must be changed to $I = \sum_i c_i$.

This means for the calculation that in program I the following constants have to be changed:

constant in step	by value multiplied with
166–173	z^3
183–183	z^2
198–206	z^6
225–231	z^5
277–283	z^2
304–310	z^2
389–393	z^2
441–447	z^2