APPENDIX A

COMPUTER PROGRAMMES

A.1 Introduction

The computations in this work were accomplished by means of FORTRAN programmes written for an IBM 1620 computer. For all the programmes the input data are in the form of punched cards and the results are either obtained as printed output or punched cards or both. The language used is FORTRAN - I.

The relatively small memory unit of the local computer, with a capacity of 20 K, has imposed severe restrictions on the development of the programmes necessitating breakup of some of the programmes into smaller units. The pure component properties required for the estimation of liquid phase activity coefficients are computed using separate programmes. Liquid phase activity coefficients and other related quantities are computed using $t - x - y$ data and pure component properties as input quantities in the activity coefficient programmes. The output from these programmes is used to evaluate the data fit in different correlation programmes. Separate programmes are written for thermodynamic consistency tests and azeotrope prediction.

The following paragraphs describe briefly the outlines of some of the important programmes which are supplemented by complete FORTRAN
listings. The major variables used in the programmes are defined in the nomenclature which forms part of the listing for each programme. Any number of data sets can be executed sequentially for all the programmes.

A.2 Pure Component Properties

The purpose of these programmes is to calculate vapour pressures, second virial coefficients, and liquid molar volumes for the pure components as a function of temperature by different methods. (i) 'VAPOUR PRESSURE'

This programme uses the Antoine [12], Miller semireduced [261], Miller-Erpenbeck nonreduced [261], and RPME and RPMH versions of Riedel-Plank-Miller [261,263] correlations to calculate the pure component vapour pressures.

The number of data points and the number of components, for which vapour pressures are to be calculated at the same temperature are read as the first input card followed by the set of cards each containing one temperature value. Then two cards for each component, one containing the Antoine Constants, enthalpy of vapourisation, and normal boiling point and the other containing critical temperature and critical pressure, are read. Finally an identification card containing the name of the component is read followed by two blank cards.

The printout consists of the name of the component followed by the name of each of the correlations and the calculated vapour pressures against the corresponding temperatures. When all the correlations are covered for the first component, the process is repeated for the next one if there is any. When all the components
(there is provision for a maximum of three in this programme, which can be increased by modifying the DIMENSION statement) are covered, the programme asks for the next set of data.

Complete listing of the programme is given in Table A.1.

(ii) 'VIRIAL'

This programme calculates second virial coefficients for pure components by the Pitzer-Curl [315], O'Connell-Prausnitz [286], Black [24], and Wohl [441] correlations. Further it also calculates the liquid molar volumes by an equation proposed by Wicks [431] which represents the Lydersen-Greenkorn-Hougen correlation for the range of critical compressibility factors between 0.25 and 0.29 and reduced temperatures up to 0.99.

The programme starts by reading an identification card containing the name of the compound followed by another card containing the critical properties, acentric factor, dipole moment, number of data sets, and two fixed point dummy variables L and K to select the route to be followed from among several alternatives depending upon the nature of the compound and nature of the available input data. For a polar compound, homomorph acentric factor is to be read in place of its actual acentric factor.

A table of instructions to assist selection of the values for L and K proceeds the beginning of the executable steps. The contents of the identification card and the table headings are printed. The critical compressibility factor required for the calculation of liquid molar volumes, and the reduced dipole moment, \( \mu_\text{r} \), are then calculated. If \( \mu_\text{r} \) is more than 4.0, the polar effects are taken into account in the O'Connell-Prausnitz correlation and the constant terms evaluated.
TABLE A.1 LISTING OF THE PROGRAMME 'VAPOUR PRESSURE'

VAPOUR PRESSURE

ESTIMATION OF VAPOUR PRESSURES BY EQUATIONS AA, M, E, R, PM AND RPHH
AA, M, E, R, PM AND RPHH-ANTOINE, MILLER-REDUCED, MILLER-ERKNEBECK
RIEDEL-FLANK-MILLER AND RIEDEL-FLANK-MILLER HIGH PRESSURES RESPECTIVELY.

REFERENCES
MILLER, D. G., IEC, VOL. 56(3), P. 46 (1964)
MILLER, D. G., J. PHYS. CHEM., VOL. 69(9), P. 3209 (1965)
REID, R. C., AND SHERWOOD, T. K., PROPERTIES OF GASES AND LIQUIDS, 2ND ED., P. 114, McGRAW-HILL, NEW YORK, 1966

NOMENCLATURE
A, B, C = ANTOINE CONSTANTS
HV = LATENT HEAT OF VAPOURISATION
K = NUMBER OF COMPOUNDS FOR WHICH VAPOUR PRESSURES ARE TO BE CALCULATED AT THE SAME TEMPERATURES
N = NUMBER OF DATA POINTS
P = VAPOUR PRESSURE, MM. HG
PC = CRITICAL PRESSURE, MM. HG
T = TEMPERATURE, DEG. C
TC = CRITICAL TEMPERATURE, DEG. K

DIMENSION T(150), A(3), B(3), C(3), HV(3), TB(2), TC(3), PC(3)

1 READ 2, N, K
2 FORMAT (214)
   DO 3 I = 1, N
3 READ 4, T(I)
4 FORMAT (F7.2)
   DO 100 J = 1, K
       READ 6, (A(J), B(J), C(J), HV(J), TB(J), TC(J), PC(J))
100 FORMAT (3F14.8, F14.5, F10.2)
7 FORMAT (2F10.2)
   DO 17 J = 1, K
17 FORMAT (2X50H)
   PRINT 5
   PRINT 8
5 FORMAT (/ , 'BY ANTOINE EQUATION', /)
   TBK(1) = TB(J)/TC(J)
   PRINT 8
6 FORMAT (/ , 'X49H')

...
TABLE A.1 (CONTINUED)

PRINT 5
9 FORMAT(9X1HT,14X1HP,/) 
DO 10 I=1,N 
P=EXP((A(J)-B(J))/(T(I)+C(J)))*2.3025851) 
PRINT20,T(I),P 
20 FORMAT(6XF 7.2,6XF 9.3 )
10 CONTINUE
PRINT 11 
11 FORMAT(//,2X33HP-BY MILLER SEMI REDUCED EQUATION,/) 
PRINT 9 
AK=HV(J)/(2.3025851*1.987*TC(J)*(.1-TBR)**0.58) 
E1B=1.44779*(TBR**2-1.0)/TBR+0.60706*(TBR**3-4.1)/TBR 
DO 13 I=1,N 
TR=T(I)+273.16/TC(J) 
D=(AK/TR)*((1.67467*TR**3-1.44779*TR**2-E1B*TR-.98045) 
P=(EXP(D*2.3025851))*760. 
PRINT20,T(I),P 
13 CONTINUE
PRINT 14
14 FORMAT(//,2X42HP-BY ERPENBECK MILLER NON REDUCED EQUATION,/) 
PRINT 9 
CB=0.512+0.00043*TB(J) 
BP=.225 1278*HV(J)/(1-J)+.4343*CB/(1.-CB) 
DO 15 I=1,N 
TT=T(I)+273.16 
D=BP*TT*(TT-TB(J))/TT+(LOGF((1.-CB*TT/TB(J))/(1.-CB))/2.3025851 
P=(EXP(D*2.3025851))*760. 
PRINT20,T(I),P 
15 CONTINUE
PRINT 16
16 FORMAT(//,2X33HP-BY RIEDEL PLANK MILLER EQUATION,/,9X1HT,14X1HP,/) 
AA=TBR*LOGF(PC(J)/760.)/(1.-TBR) 
G=.21+.2*AA 
AK=(AA/(2.3025851*G)-(1.+TBR))/((3.+TBR)*(1.-TBR)**2) 
DO30I=1,N 
TR=(T(I)+273.16)/TC(J) 
D=-G/TR*(1.-TR**2+AK*(1.-TR)**3) 
P=PC(J)*EXP(D*2.3025851) 
PRINT20,T(I),P 
30 CONTINUE
PRINT 18
18 FORMAT(1H0,2X18HP-BY RPMH EQUATION,/,9X1HT,14X1HP,1H ) 
END
Depending upon the value of \( L \), a conditional GO TO statement permits reading of the association constant in the O'Connell-Prausnitz correlation or its estimation by reading one experimental second virial coefficient - temperature set or the assumption that the association constant is zero. Polar effects are neglected if the reduced temperature is greater than 0.95. For most of the polar compounds the values of all the constants except \( E' \) in the Black correlation are taken to be the same as the generalised constants suggested by Black whereas \( E' \) is estimated from one set of either experimental vapour density or second virial coefficient data. For polar halogen, ether, and sulphur compounds \( D' \) is estimated from either of the above data taking \( E' \) as zero. Value of \( K \), by the use of the conditional GO TO and SENSE SWITCH 3 statements, accomplishes the above control decisions.

With all the constant terms calculated, the programme enters the DO loop and, for each temperature data card read, calculates the second virial coefficient by each of the correlations and liquid molar volume by the Wicks' equation. If polar contributions are negligible, second virial coefficients calculated by the Pitzer-Curl and O'Connell-Prausnitz correlations will be identical. The final printout contains the calculated second virial coefficients by each of the correlations and the liquid molar volumes by the Wicks' equation against the corresponding temperature value.

Complete listing of the programme is given in Table A.2.

(iii) 'MOLAL VOLUME'

This programme calculates pure component liquid molar volumes and densities by the modified Goldhammer [124], Lyckman-Eckert-Prausnitz [235], Bradford-Thodos [35], and Yen-Woods [445] correlations using
TABLE A.2 LISTING OF THE PROGRAMME 'VIRIAL'

VIRIAL

ESTIMATION OF SECOND VIRIAL COEFFICIENTS BY
PITZER, O'CONNELL, BLACK, AND WOHL CORRELATIONS,
AND LIQUID MOLE VOLUMES BY LIDERSEN-GREENKORN-HOUGEN CORRELATION
AS EXPRESSED BY WICKS EQUATION APPLICABLE
FOR ZC=0.25 TO 0.29, TR=UPTO 0.99

REFERENCES
(1) PITZER, K.S., CURL, R.F., J.A.C.S., VOL. 79, 2369 (1957)
(2) O'CONNELL, J.P., FRAUSNITZ, J.H., IEC
PROC. DES. AND DEV., VOL. 6(2), 245 (1967)
(3) BLACK, C., IEC, VOL. 50 (3), 391 (1958)
(4) KURT WOHL, Z. PHYS. CHEM., VOL. B2, 77 (1929)
(5) WICKS, MGYE, III, PETROL. REFINER, VOL. 40(3), 196 (1961)

NOMENCLATURE

BC = VIRIAL COEFFT. BY BLACK METHOD
BPC = VIRIAL COEFFT. BY PITZER-CURL METHOD, ML/G.MOLE
BEXP, BI = INPUT EXPTL. VIRIAL COEFFT. FOR EVALUATION OF
O-CONNELL ASSOCIATION CONSTANT, BLACK CONSTANTS
BD = VIRIAL COEFFT. BY O-CONNELL METHOD, ML/G.MOLE
DP, EP = CONSTANTS IN BLACK CORRELATION
E = ASSOCIATION CONSTANT IN O-CONNELL CORRELATION
EM = DIPOLE MOMENT, DEBYE UNITS
EMR = REDUCED DIPOLE MOMENT DEFINED BY O-CONNELL
EO = FUNCTION DEPENDANT ON TR DEFINED BY BLACK
FA = ASSOCIATION FUNCTION DEFINED BY O-CONNELL
FBO, FBl = PITZER'S NONPOLAR FUNCTIONS DEPENDANT ON TR
FM = O-CONNELL'S POLAR FUNCTION DEPENDANT ON TR AND EMR
K, L = INPUT FIXED POINT COUNTERS FOR CONTROL DECISIONS
N = NUMBER OF DATA POINTS
PC = CRITICAL PRESSURE, ATMOSPHERES
PI = PRESSURE CORRESPONDING TO INPUT VAP. DENSITY, ATM
PO = VAPOR PRESSURE AT TI DEG. K, ATM
KQ = LIT. VAPOUR DENSITY FOR CALCULATING EP, G.MOLES/ML
T = INPUT TEMPERATURE, DEG. K
TC = CRITICAL TEMPERATURE, DEG. K
TEXP = INPUT TEMPERATURE CORRESPONDING TO BEXP, DEG. K
TI = TEMP. CORRESPONDING TO INPUT VAP. DENSITY OR ETA
VC = CRITICAL VOLUME, ML/G.MOLE
W = ACENTRIC FACTOR OF COMPOUND (IF NONPOLAR)
OR HOMOMORPH (IF POLAR)
ZC = CRITICAL COMPRESSIBILITY FACTOR

INSTRUCTIONS

. . .
TABLE A.2 (CONTINUED)

```
VALUE OF L OR K   REMARKS FOR L   REMARKS FOR K

1  READ E   NONPOLAR
2  READ BEXP, TEXP   POLAR(READ K0, PU, PI, TI)
3  TO CALCULATE E   NONASSOCIATING  POLAR(READ HI, TI)

POSITION OF SWITCH 3

ON  POLAR(HALOGEN, ETHER, ETC)
OFF  POLAR(ALCOHOL, ALDEHYDE,
        KETONE, NITRILE, WATER, ETC)

PRINT HEADINGS AND READ INPUT CONSTANTS

1 READ 100
   READ 300, TC, PC, VC, W, EM, N, L, K

PRINT 100
PRINT 200

CALCULATE TERMS INVOLVING CONSTANTS ONLY

1  IPC=TC/PC
   ZC=VC/(82.057*TPC)
   EMR=100000.*Eh**2/(1IPC*1C)
   IF(EMR-4.110,10,2

2  EMRL=LU GF (EMR)
   R=-5.23722+5.665807*EMRL-2.133816*EMRL**2+0.2525373*EMRL**3
   S=5.76979-6.51427*EMRL+2.28327*EMRL**2-0.2649074*EMRL**3
   GO TU (3,4,9), L

3 READ 300, E

GO TU 10

4 READ 300, BEXP, TEXP

TR=TEXP/TC
FBO=.1445-.33/TR-.1385/TR**2-.0121/TR**3
FB1=.073+.46/TR-.5/TR**2-.097/TR**3-.0073/TR**4
IF(.95-TR)9,9,5
FA=EXP(4.62-6.6*TR)
IF(EMK-4.16,6,1;
6 FM=0.0
GO TU b
7 FM=R+S/TR
8 E=(PC*BEXP/(82.057*1C)-FBL-W*FB1-FM)/FA
GO TO 10

• • •
```
TABLE A.2 (CONTINUED)

9 E=0.0
10 GO TO (14, 11, 23), K

C

11 READ 300, RO, PO, PI, 11

C

TIR = TI/TC
RR = PI/PC/TIR
EE = TIR*(2.3703703/R + 0.2962963) - 0.02888532*PC/(TC*RO)
EZ = EE - (RR/TIR**3)*0.148 + 0.103*RR + 0.091*RR**2 - 0.177*(PI/PO)**3
GO TO 24

C

23 READ 300, BI, TI

C

12 IF (SENSE SWITCH 3) 12, 13
13 DP = TIR**3*(EZ - 0.396) - 1.181*TIR**2 + 0.864*TIR
GO TO 14

C

14 DO 26 I = 1, N

C

READ 500, T

C

TR = (T + 273.16)/TC

C

CALCULATE NONPOLAR BETA BY PITZER-CURL CORRELATION

C

FB0 = 0.1445 - 0.33/TR - 0.1385/TR**2 - 0.0121/TR**3
FB1 = 0.073 + 0.46/TR - 0.5/TR**2 - 0.097/TR**3 - 0.0073/TR**8
BPC = 82.057*TPC*(FB0 + W*FB1)

C

ADD POLAR CONTRIBUTION AT TR BELOW 0.95 WHEN REDUCED DIPOLE MOMENT, EMR, GREATER THAN 4.8

C

IF (.95 - TR) 16, 16, 15
15 FA = EXPF(4.62 - 0.6*TR)
16 BO = BPC
GO TO 18

C

FM = R + S/TR
BO = 82.057*TPC*(FD0 + k*FB1 + FM + E*FA)

C

CALCULATE BETA BY BLACK CORRELATION

C

X = 0.396 + 1.181/TR - 0.864/TR**2
GO TO (19, 20, 20), K

C

19 EO = X + 0.284/TR**3
GO TO 22

...
TABLE A.2 (CONTINUED)

20 IF (SENSE SWITCH 3) 21, 25
21 E0=X+DP/TR**3
  GO TO 22
25 E0=X+0.384/TR**3+2.3703*EP/TR**4.75
  GO TO 22
22 BC=TPC*(10.257125-34.6177965*EO/TR)

C CALCULATE BETA BY WOHL CORRELATION
C BW=82.057*TPC*(0.197-0.012*TR-0.4/TR-0.146/TR**3.27)

C CALCULATE LIQUID MOLAL VOLUMES BY WICKS CORRELATION
C VW=VC/(1.2+15.563-11.03*ZC)*(1-TR)**(0.8*ZC+0.31))
  PRINT 400,T,TPC,EO,BC,BW,VW
26 CONTINUE
  GO TO 1

C 100 FORMAT(2X49H)
200 FORMAT(1X,12X3HBC,12X2HBW,12X2HVW,1)
300 FORMAT(F14.8,4F10.4,314)
400 FORMAT(6F14.2)
500 FORMAT(F7.2)
END
normal boiling point, critical properties, acentric factor, molecular weight, and one experimental density - temperature set as input data which are all read on one card which follows the card containing the number of temperature values at which liquid molar volumes are to be calculated. Then the identification card containing the name of the compound is read.

The programme headings, contents of the identification card, experimental temperature - density set, acentric factor, molecular weight, and the table headings are printed before any arithmetic statements are executed. Then the constant terms in the correlations are evaluated before entry into the DO loop to calculate the liquid molar volumes and densities for each value of the temperature read on a separate card.

For \(0.56 < T_r < 0.995\), calculations by the Lyckman-Eckert-Prausnitz correlation are bypassed as it is not applicable. Table A.3 gives a complete listing of the programme.

A.3 Activity Coefficients from Experimental Data

These programmes calculate activity coefficients as a function of composition from experimental temperature - composition data and the pure component vapour pressures, second virial coefficients, and liquid molar volumes. One of these programmes calculates activity coefficients at infinite dilution using the Ellis - Jonah correlation [84]. The pure component properties are obtained from the programmes described earlier.

(i) 'BINARY ACTCO'

This programme calculates the activity coefficients and related functions from the experimental temperature - composition and pure
## Table A.3 Listing of the Programme 'Molal Volume'

<table>
<thead>
<tr>
<th>MOLAL VOLUME</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SATURATED LIQUID DENSITIES AND MOLAL VOLUMES BY SURFACE TENSION,</td>
<td></td>
</tr>
<tr>
<td>LYKMAN-ECKERT-PRAUSNITZ, BRADFORD-THODUS AND YEN-HOOGS METHODS</td>
<td></td>
</tr>
<tr>
<td>REFERENCES:</td>
<td></td>
</tr>
<tr>
<td>Z. PHYSIK. CHEM., VOL. 5, 374 (1890)</td>
<td></td>
</tr>
<tr>
<td>J. APPL. CHEM., VOL. 11, 195 (1961)</td>
<td></td>
</tr>
<tr>
<td>CHEM. ENG. SCI., VOL. 20, 705 (1965)</td>
<td></td>
</tr>
<tr>
<td>A. CHEM., VOL. 12 (1), 55 (1965)</td>
<td></td>
</tr>
<tr>
<td>NOMENCLATURE</td>
<td></td>
</tr>
<tr>
<td>b, Rh = LIQUID DENSITY BY BRADFORD-THODUS METHOD, g/mol/L</td>
<td></td>
</tr>
<tr>
<td>m = MOLECULAR WEIGHT</td>
<td></td>
</tr>
<tr>
<td>L, RhD = LIQUID DENSITY BY LYKMAN-ECKERT-PRAUSNITZ METHOD, g/mol/L</td>
<td></td>
</tr>
<tr>
<td>N = NUMBER OF DATA POINTS</td>
<td></td>
</tr>
<tr>
<td>Omega = ACENTRIC FACTOR</td>
<td></td>
</tr>
<tr>
<td>P, C = CRITICAL PRESSURE, ATOMOSPHERES</td>
<td></td>
</tr>
<tr>
<td>RHUE = EXPERIMENTAL LIQUID DENSITY, g/mol/L</td>
<td></td>
</tr>
<tr>
<td>S, RhDS = LIQUID DENSITY BY SURFACE TENSION METHOD, g/mol/L</td>
<td></td>
</tr>
<tr>
<td>T = TEMPERATURE, DEGREES CELSIUS</td>
<td></td>
</tr>
<tr>
<td>Td = NORMAL BOILING POINT, DEGREES CELSIUS</td>
<td></td>
</tr>
<tr>
<td>IC = CRITICAL TEMPERATURE, DEGREES CELSIUS</td>
<td></td>
</tr>
<tr>
<td>TE = TEMPERATURE OF INPUT DENSITY, DEGREES CELSIUS</td>
<td></td>
</tr>
<tr>
<td>VD = LIQUID VOLUME BY BRADFORD-THODUS METHOD, mL/g-mole</td>
<td></td>
</tr>
<tr>
<td>VC = CRITICAL VOLUME, mL/g-mole</td>
<td></td>
</tr>
<tr>
<td>VL = LIQUID VOLUME BY LYKMAN-ECKERT-PRAUSNITZ METHOD, mL/g-mole</td>
<td></td>
</tr>
<tr>
<td>VS = LIQUID VOLUME BY SURFACE TENSION METHOD, mL/g-mole</td>
<td></td>
</tr>
<tr>
<td>W, RhDWS = LIQUID DENSITY BY YEN-HOOGS METHOD, g/mol/L</td>
<td></td>
</tr>
</tbody>
</table>

**READ INPUT CONSTANTS**

1 READ 100, N
READ 200, Tb, Te, IC, PC, VC, RHUE, Omega, Eh

**PRINT HEADINGS**

PRINT 600
PRINT 700
PRINT 800
PRINT 900
PRINT 1000
PRINT 1100

...
**TABLE A.3 (CONTINUED)**

<table>
<thead>
<tr>
<th>ZC = PC<em>VC/(82.06</em>TC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>En = 16 + 5.66*ZC</td>
</tr>
<tr>
<td>DELTA = 2.16 - 3.54*ZC</td>
</tr>
<tr>
<td>Beta = 2.924 - 1.34*ZC</td>
</tr>
<tr>
<td>Gamma = DELTA - 0.616</td>
</tr>
<tr>
<td>AA = 17.4425 - 2.14 - 0.78<em>ZC + 565.625</em>ZC - 1522.06*ZC - ZC - ZC</td>
</tr>
<tr>
<td>IF(ZC &gt; 2616)</td>
</tr>
<tr>
<td>BB = 64.2076 - 402.063*ZC + 501.2ZC - 641.2ZC - ZC</td>
</tr>
<tr>
<td>GO TO &gt;</td>
</tr>
<tr>
<td>BB = -5.26257 + 0.37777<em>ZC + 107.4544</em>ZC - 34.21*ZC - ZC</td>
</tr>
</tbody>
</table>

**C**

**SATURATED LIQUID DENSITIES AND TOTAl VOLUMES**

**C**

ZC = PC*VC/(82.06*TC)

En = 16 + 5.66*ZC

DELTA = 2.16 - 3.54*ZC

Beta = 2.924 - 1.34*ZC

Gamma = DELTA - 0.616

AA = 17.4425 - 2.14 - 0.78*ZC + 565.625*ZC - 1522.06*ZC - ZC - ZC

IF(ZC > 2616)

BB = 64.2076 - 402.063*ZC + 501.2ZC - 641.2ZC - ZC

GO TO >

BB = -5.26257 + 0.37777*ZC + 107.4544*ZC - 34.21*ZC - ZC

**D**

RHOV = En/(82.06*TB)

RH01 = (RHOE - RHOV)*EXP((5.1*T/11.1)*ZC/(ZC + 1)) / (1.1E/TC)*1

DO 11 I = 1, H

**C**

READ INPUT TEMPERATURE VALUES

**C**

GO TO 10

**C**

SURFACE TENSION (MODIFIED GOLDSHANER) METHOD

**C**

RHOV = RHOV*EXP((5.1*T/11.1)*ZC/(ZC + 1)) / (1.1E/TC)*1

VS = 1.1/VS1

**C**

LYKMAN, ECKEKT AND KRAUSZ ITZ Method

**C**

IF (TR < 0.56) 6, 7, 7

6 PRINT 1200

GO TO 10

7 IF (TR < 0.95) 19, 9, 8

8 GO TO 11

9 X = -11.917 + 0.05513*TR + 2.0151*TR*TR - 0.06492*TR*TR - 0.0746/TK

VH0 = X - 4.64416*LOGF(0.1 - TR)

Y = 0.0965 - 1.60375*TR + 1.624*TR*TR - 0.61432*TR*TR - 0.345676/TK

VK = Y + 0.87057*LOGF(0.1 - TR)

Z = -0.5514 + 1.57953*TR - 1.01601*TR - 1.54058*TR*TR - 0.46793/TK

VK2 = -0.23956*LOGF(0.1 - TR)

VR = VK0 + OMEGA VK1 + OMEGA VK2 + OMEGA VK3

VL = VK0*VC

RHUL = 1./VL

...
TABLE A.3 (CONTINUED)

C BRADFORD AND THOMAS METHOD
C
10  RHOK\(=1.0+BETA*(1.-TK)+GAMMA*(1.-TK)*DELTA*(1.-TK))**2+DELTA*(1.-TK)**2+DELTA*(1.-TK)**2+DELTA*(1.-TK)**2
RHOB=RHOK/VC
VBD=1./RHOB
C YEN AND WOODS METHOD
C
13  RHOKS=1.0+AA*(1.-TK)**.3333+DELTA*(1.-TK)**.6667+DELTA*(1.-TK)**1.3333
RHOYW=RHOKS/VC
VYW=1./RHOYW
IF (TK< .56)   12,13,13
11 CONTINUE
GO TO 78
12  PRINT 1400,1,VS,VL,VS,L,VY,W,RHOS,RHOL,RHOB,RHOYW
1400 RETURN
C
100  FORMAT (15)
200  FORMAT (3F10.3,2F10.3,F9.5,F6.4,F7.2)  
300  FORMAT (F12.2,F13.2,F13.5)
400  FORMAT (F12.2,F13.2,F13.5)
500  FORMAT (//,45H SATURATED LIQUID DENSITIES AND MOLAL VOLUMES)
600  FORMAT (1H,41H SURFACE TENSION,LYKAN- ECKERT-PRAUSNITZ)
700  FORMAT (1H,25H BRADFORD-THOMAS AND YEN- WOODS METHODS)
800  FORMAT (1H,45H)
900  FORMAT (//,13X4H TK=RE.2,15X5H ELA=F6.4,17X2H=0.5,7F10.3)
1000 FORMAT (9X1HT11X2HVS11X2HVL11X2HVD11X2HY11X1HS12X1HL12X1HY)
1100 FORMAT (7X5HLEG,2X15HR L / S I G M O L E S / L,/
1200 FORMAT (4X39HTR LESS THAN 0.56)
1300 FORMAT (4X40HTR GREATER THAN 0.955)
1400 FORMAT (F12.2,F13.2,F13.5)
1500 FORMAT (F12.2,F13.2,F13.5)
END
component data for isobaric binary systems.

The programme begins with the DIMENSION statement. Two cards one containing the name of the system and the other containing the number of data sets to be handled and the system pressure, are read and then the programme title, alphameric information from the identification card and table headings are printed. The programme enters the first DO loop, reads one card containing \( t - x - y - P^o - B - V \) data for the more volatile component and calculates the liquid and vapour compositions by the Raoults law, vapour phase imperfection coefficient, \( \gamma_1 \) for real vapour phase, \( \ln \gamma_1 \), relative volatility, excess free energy function, and other functions required for the graphical evaluation of the van Laar constants and prints these functions. This process is repeated till all the data cards for the more volatile component are read. The vapour pressure values for the more volatile component and the logarithmic values of its activity coefficients are stored.

The programme enters the second DO loop after printing the table headings, reads one \( t - x - y - P^o - B - V \) data card for the less volatile component, calculates its vapour phase imperfection coefficient, \( \gamma_2 \) for real vapour phase, \( \ln \gamma_2 \), \( \ln \gamma_1 / \gamma_2 \), relative volatility, excess free energy function, and other functions required for the graphical evaluation of the van Laar constants. These results are printed and if SENSE SWITCH 3 is ON, \( x_1 \), \( \ln \gamma_1 \), \( \ln \gamma_2 \), \( \gamma_1 \) and \( P^o \) values are punched for use in the binary correlation programmes. Table A.4 gives listing of the programme. The vapour phase imperfection coefficients for each component are calculated using the equation,

\[
Z_1 = \exp \left[ \frac{(P^o_i - x)(V_1 - B)}{RT} \right]
\]
A similar programme is written for the calculation of activity coefficients for each component for a multicomponent isobaric system using $t - x - y - P^0 - B - V$ data sets for each component.

(ii) 'GAMMA INFINITY'

This programme calculates activity coefficients at infinite dilution by the method of Ellis and Jonah [84] for isobaric binary systems.

After printing the programme title and table headings, the input data, consisting of the alphabetic information about the system, total pressure, normal boiling points, critical temperatures, latent heats of vapourisation with the corresponding temperatures, molecular weights, the Antoine vapour pressure constants for the pure components, and the terminal values of $\Delta t / x_1 x_2$ are read on five cards.

The input latent heats of vapourisation are corrected to values at the normal boiling points by the Watson correlation [422]. Pure component vapour pressures are calculated by the Antoine equation [12] using the input constants. The terminal values of $\Delta t / x_1 x_2$ are obtained graphically by plotting $x_1$ vs. $\Delta t / x_1 x_2$. The printed results include the alphabetic information on the system, activity coefficients at infinite dilution, and their logarithmic values (to the base 10).

The listing of the programme is given in Table A.5.

A.4 Thermodynamic Consistency Tests

These programmes are made to evaluate the appropriate functions from which conclusions can be drawn regarding the thermodynamic consistency of the vapour-liquid equilibrium data.
TABLE A.4 LISTING OF THE PROGRAMME 'BINARY ACTCO'

BINARY ACTCO

BINARY EXPERT ACTIVITY COEFFICIENTS AND RELATED QUANTITIES

This programme besides calculating expert activity coefficients, finds Raoult's law X and Y from expert X and Y, excess free energy function, LN(Gamma 1/Gamma 2), X1/X2, X2/X1, SQRT OF LN(Gamma 1), 1/LN(Gamma 1), LN(Gamma 2), 1/LN(Gamma 2),-.

VAPOR PHASE IMPERFECTION COEFFICIENTS, Z1, Z2, AND RELATIVE VOLATILITY

KEEP SWITCH 3 ON IF X1, LN(Gamma 1), LN(Gamma 2), Y1, P1 ARE TO BE PUNCHED IN 5F10.4

NOMENCLATURE

B = SECOND VIRIAL COEFFICIENT, ML/G.MOLE
DX = EXPERT - RAOULT'S LAW LIQUID COMPOSITION
DY = EXPERT - RAOULT'S LAW VAPOUR COMPOSITION
ELNG = LN(GAMMA)
G = ACTIVITY COEFFICIENT, GAMMA FOR REAL VAP.PHASE
N = NUMBER OF DATA POINTS
P = PURE COMPONENT VAPOUR PRESSURE, MM.HG
Q = EXCESS FREE ENERGY FUNCTION
R = LN(GAMMA 1/GAMMA 2)
RSL = RECIPROCAL OF SQRT(LN(GAMMA))
RT LNG, SL = SQRT(LN(GAMMA))
RX = RATIO X1/X2 OR X2/X1
T = SYSTEM TEMPERATURE, DEG. C
V = PURE COMPONENT LIQUID MOLAL VOLUME, ML/G.MOLE
X = MOLE FRACTION IN LIQUID PHASE
Y = MOLE FRACTION IN VAPOUR PHASE
Z = VAPOUR PHASE IMPERFECTION COEFFICIENT

SUBSCRIPTS 1, 2 = COMPONENTS 1, 2
*, I = IDEAL

DIMENSION P(30), ELNG(30)

PRINT HEADINGS AND READ INPUT DATA

-------------
1 READ 100
READ 200,N,P1
-------------
PRINT 100
PRINT 300
PRINT 400
DO 5 I=1,N
C
READ T,X,Y,P,B,V DATA FOR MORE VOLATILE COMPONENT
-------------
READ 500,T,X,Y,P1(I),B,V
--------------
TABLE A.4 (CONTINUED)

C CALCULATE RAOUlTS LAW COMPOSITIONS
C XI=PI*Y/P1(I)
YI=P1(I)*X/PI
DX=X-XI
DY=Y-YI
C CALCULATE ACTIVITY COEFFTS. AND RELATED QUANTITIES FOR COMPONENT 1
C
Z=EXP((Pl(I)-PI)*(V-B)/(62363.32*(T+273.16)))
G=Z*PI*Y/(P(I)*X)
ELNG1(I)=LOG(G)
RX=X/(1.-X)
SL=(ELNG1(I)*ELNG1(I))**0.25
IF(SL)<3.2
2 RSL=1./SL
GO TO 4
3 RSL=999.9999
4 PRINT 700,X,Y,XI,YI,DX,DY,Z,G,ELNG1(I),RX,SL,RSL
5 CONTINUE
C
C PRINT HEADINGS
C PRINT 800
PRINT 900
DO 10 I = 1, N
C READ T,X,Y,P,B,V DATA FOR LESS VOLATILE COMPONENT
C ---------------------------------------------
READ 500,T,X,Y,P,B,V
C--------------------------------------------------------------------------------------
Z=EXP((P-PI)*(V-B)/(62363.32*(T+273.16)))
G=P*PI*Y/(P*X)
ELNG2=LOG(G)
R=ELNG1(I)-ELNG2
X1=1.-X
Y1=1.-Y
ALPHA=Y1*X/(1.-X)*Y)
G=X1*ELNG1(I)+X*ELNG2
RX=X/X1
SL=(ELNG2*ELNG2)**0.25
IF(SL)<3.6
6 RSL=1./SL
GO TO 8
7 RSL=999.9999
8 PRINT 700,Q,Z,G,ELNG2,R,RX,SL,RSL,ALPHA
IF(SENSE SWITCH 3)9,10
9 PUNCH 700,X1,ELNG1(I),ELNG2,Y1,P1(I)
10 CONTINUE
PRINT 600
GO TO 1
• • •
TABLE A.4 (CONTINUED)

100 FORMAT(2X49H)
200 FORMAT(14,F10.2)
300 FORMAT(/,7X1MX5X1MY5X2H*4X2HY*8X2HDX6X2HDY7X2H18X2HG17X4HLNG1)
400 FORMAT(1H1,49X45X26HX1/X2 RT LNG1 1/RT LNG1,/)  
500 FORMAT(F7.2,2F7.4,2F10.2)
600 FORMAT(/)
700 FORMAT(2F10.4)
800 FORMAT(/,7X1M0,8X2HZ2,8X2HZ2,7X4HLNG2,7X1HR,8X5HX2/X1)
900 FORMAT(1H1,45X15X17HR7 LNG2 1/X7 LNG2,45SALPHA,/)  
END
TABLE A.5 LISTING OF THE PROGRAMME 'GAMMA INFINITY'

```
C
C GAMMA INFINITY
C=================================================================================================
C ACTIVITY COEFFICIENTS AT INFINITE DILUTION-ELLIS AND JONAH METHOD
C=================================================================================================
C
C
C NOMENCLATURE
C ************
C A,B,C = ANTOINE VAPOUR PRESSURE CONSTANTS
C G = ACTIVITY COEFFICIENT AT INFINITE DILUTION
C FT = TERMINAL VALUES OF DELTA T/(X1*X2)
C GL, LNG = LGG(G) TO THE BASE 10
C H = HEAT OF VAPOURISATION AT T,G, CAL/GM.
C P1 = SYSTEM PRESSURE, MM . HG.
C T = TEMPERATURE AT WHICH H IS READ, DEG.C
C Tb = NORMAL BOILING POINT, DEG.C
C TC = CRITICAL TEMPERATURE, DEG.K
C SUBSCRIPTS 1,2
C
C NOTE - WATSON RELATION USED FOR LATENT HEAT ESTIMATION AND
C ANTOINE EQUATION FOR VAPOUR PRESSURES.
C
C READ INPUT DATA AND PRINT HEADINGS
C
PRINT 100
PRINT 200
C
1 READ 300
READ 400,PI,TB1,TB2,TC1,TC2
READ 50C,T1,T2,H1,H2,E1,E2
READ 600,A1,B1,C1,A2,B2,C2
READ 700,FT1,FT2
C
PRINT 300
HB1=E1*H1*((1.-(TB1+273.16)/TC1)/(1.-(T1+273.16)/TC1))**0.38
HB2=E2*H2*((1.-(TB2+273.16)/TC2)/(1.-(T2+273.16)/TC2))**0.38
ALPH1=HB1*PI/(1.9872*(TB1+273.16)**2)
ALPH2=HB2*PI/(1.9872*(TB2+273.16)**2)
BETA1=TB1-TB2-FT1
BETA2=TB2-TB1-FT2
P1=EXP((A1-B1/(C1+TB2))*2.3025851)
P2=EXP((A2-B2/(C2+TB1))*2.3025851)
GL1=(PI-ALPH2*BETA1)/P1
GL2=(PI-ALPH1*BETA2)/P2
GL1=(LGGF(GL1))/2.3025851
GL2=(LGGF(GL2))/2.3025851
PRINT 800,GI,GL2,GM1,GM2,GTU 1
C
100 FORMAT(25X45H INFINITE DILUTION GAMMAS - ELLIS-JONAH METHOD)
200 FORMAT(7X,6X6HSYSTEM/42X2H611X2H629X4HLNG18X4HLNG2,/
300 FORMAT(2X4SH)
400 FORMAT(5F10.2)
500 FORMAT(6F10.2)
600 FORMAT(6F10.5)
700 FORMAT(2F10.4)
800 FORMAT(1H1,4XF9.4,4XF9.4,4XF8.4,4XF8.4)
END
```
This programme calculates the functions needed to determine the thermodynamic consistency of binary t - x - y data based on Equation 2.41 using numerical differentiation technique.

The programme starts with a DIMENSION statement for storing two sets of t - x - y data at any time during the calculations. Alphameric data on the system, number of data sets, normal boiling points, latent heats of vapourisation, and critical temperatures are read and the programme title, contents of the identification card, and the table headings are printed before executing the arithmetic statements.

The counters L and I are set to zero first and then given an increment of unity. One set of t - x - y data is read, the latent heats at the system temperature are calculated by the Watson correlation [422] using the input latent heats, and the right-hand side of Equation 2.41 is evaluated. Since the value of I is unity, the programme transfers to statement 3 which, together with the next statement, sets the value of y as \( \Delta y \) and the difference between the normal boiling point and the system temperature as \( \Delta t \). The slope of the t vs. y curve, \( \Delta y / \Delta t \), is then calculated followed by the left-hand side of Equation 2.41. Small difference between the quantities on both the sides indicates the thermodynamic consistency of the data point processed.

The results, consisting of x - y - t data, slope, left and right-hand sides of Equation 2.41, and the deviation between the two, are printed. For this set of results printed, the counters L and I are unity. An IF statement using the counter I, tests whether all the t - x - y data cards are processed. If not, the control transfers to statement 2 which gives an increment of unity to both L and I, the right-hand side of
Equation 2.41 is evaluated for the next set of t - x - y data read and since now I is 2, an IF statement transfers control to the IF statement 4 which in turn transfers control to statement 5 since L = 2. The differences between the new values of y and t read and their preceding values stored are calculated and then the slope, the left-hand side of Equation 2.41, and the deviation are evaluated and the results printed. L is reset to unity and the calculations are repeated till all the t - x - y data sets are read. After this, the control transfers to statement 7 which makes the printer to skip 3 lines. Now the programme is ready to handle data for the next system, if any.

The programme listing is given in Table A.6.

(ii) TERNARY CONSISTENCY

This programme calculates the functions needed for testing the thermodynamic consistency of ternary isobaric vapour-liquid equilibrium data by the McDermott-Ellis method [253].

The programme has been written to operate on three experimental points at a time providing a test on three pairs of points. The programme calculates activity coefficients by Equation 2.4 using t - x - y and pure component data.

The programme starts with a DIMENSION statement which stores three sets of $x_i$ and $\ln \gamma_i$ values for the three components in the ternary. Two data cards, one containing alphanumerical identification data and the other containing the number of data sets and the system pressure, are read and the programme title, contents of the identification data card, and table headings are then printed.
**TABLE A.6** LISTING OF THE PROGRAMME 'BINARY CONSISTENCY'

### Binary Consistency

**Isobaric Binary Consistency of T-X-Y Data**

**Equation**

\[ \frac{(X-Y)}{(Y(1-Y))} \frac{dY}{dT} = \frac{\Delta H}{RT^2} \]

**References**


**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔHV</td>
<td>Temperature difference, deg. C</td>
</tr>
<tr>
<td>ΔY</td>
<td>Composition difference in vapour phase</td>
</tr>
<tr>
<td>LHS</td>
<td>Left hand side of the equation</td>
</tr>
<tr>
<td>ΔΔH</td>
<td>Enthalpy of vapourisation at T, cal/g mole</td>
</tr>
<tr>
<td>ΔΔHb</td>
<td>Enthalpy of vapourisation at T, cal/g mole</td>
</tr>
<tr>
<td>N</td>
<td>Number of data points</td>
</tr>
<tr>
<td>RHS</td>
<td>Right hand side of the equation</td>
</tr>
<tr>
<td>T,</td>
<td>System temperature, deg. C</td>
</tr>
<tr>
<td>T</td>
<td>Normal boiling point, deg. C</td>
</tr>
<tr>
<td>Tc</td>
<td>Critical temperature, deg. C</td>
</tr>
<tr>
<td>X,XX</td>
<td>Mole fraction in liquid phase</td>
</tr>
<tr>
<td>Y,YY</td>
<td>Mole fraction in vapour phase</td>
</tr>
</tbody>
</table>

**Subscripts**

1,2 = components 1,2

---

**Note**

Watson relation is used to calculate hv at T from hvb

**Dimension**

TT(2), XX(2), YY(2)

**Read input data and print headings**

```
1 READ 200
READ 300,N
READ 400, T1, T2, H1, H2, T1, T2
```

**Print**

```
PRINT 100
PRINT 200
PRINT 500
L=0
I=0
2 L=L+1
I=I+1
```

**Read**

```
600, TT(L), XX(L), YY(L)
```
TABLE A.6 (CONTINUED)

\[ 1R = T T(L) + 273.16 \]
\[ T R B 1 = (T B 1 + 273.16) / T C 1 \]
\[ T R B 2 = (T B 2 + 273.16) / T C 2 \]
\[ H V 1 = H B 1 * \left( \frac{1 - 1R / T C 1 }{1 - 1RB 1 } \right) ^ {0.38} \]
\[ H V 2 = H B 2 * \left( \frac{1 - 1R / T C 2 }{1 - 1R B 2 } \right) ^ {0.38} \]
\[ D E L H V = X X (L) * H V 1 + \left( 1 - X X (L) \right) * H V 2 \]
\[ R H S = D E L H V / ( 1 - X X (L) / T R ) ^ {0.38} \]

1) IF(1 - 1)2, 3, 4
2) DY = YY(L)
3) DT = T B 1 - T T(L)
4) IF(L - 1)2, 3, 4
5) DY = YY(L) - YY(1)
6) SLOPE = DY/DT
7) ELHS = (X X(L) - YY(L))/YY(L)*\left( 1 - YY(L) \right) * SLOPE
8) DVATN = ELHS - RHS
9) L = 1
10) IF(N - 1)7, 7, 2
11) PRINT 700, XX(L), YY(L), IT(L), SLOPE, ELHS, RHS, DVATN

END
The counters $L$ and $I$ are set to zero, $KOUNT$ is set to unity and $L$ is increased by one. Three data cards for the three components, containing $t - x - y$ and pure component data are read, $\ln \gamma$ is calculated for each component, and $x_i$ and $\ln \gamma_i$ sets for the three components are stored. An IF statement transfers control back to statement 2 which sets the value of $L$ as 2. Another three cards are read and the calculations repeated. When three sets of data are handled, the IF statement transfers control to statement 3 which sets the counter $M$ at unity followed by $I$ which is increased from zero to unity. The counters $M$ and $KOUNT$ are increased by one, setting their new values at two. The deviation $D$, from thermodynamic consistency for the data pair 1 - 2 is calculated using the data stored and the values of $I$, $KOUNT$, and $D$ are printed.

An IF statement transfers control to statement 4 which increases $M$ by one setting its new value at three $KOUNT$ also is increased from two to three, $D$ for the pair 1 - 3 is calculated, and the results printed. The IF statement transfers control to statement 5, the programme entering a DO loop to make the second data set as first and the third set as second. An IF statement tests whether the total number of data sets are equal to $1 + 2$ and if not control is transferred to statement 7 which decreases $KOUNT$ by 1. A GO TO statement transfers control to statement 2 which increases $L$ by 1 setting its new value at 3. Statements from 2 to 6 are executed as described earlier, the value of $L$ is reset to 2 and the process repeated till the total number of data sets are equal to $1 + 2$ when the control is transferred to statement 8 which makes the printer skip three lines. Now the programme is ready to
process the data for the next system, if any. Table A.7 gives listing of the programme.

A.5 Correlations

These programmes, using either input parameters or the parameters calculated within the programme by the least squares method, calculate activity coefficients and vapour compositions for isobaric systems and compare them with the input activity coefficient - composition or temperature - composition data to assess the data fit in different correlations. The activity coefficient - composition data needed for the binary programmes are obtained as punched card output from the 'BINARY ACTCO' programme. All the programmes start with a DIMENSION statement which provides for storing some of the input data and results.

(i) 'WILSON PARAMETERS'

This programme evaluates the constants in the Wilson equation [290] for isobaric binary systems using a nonlinear least squares method.

The input consists of an identification data card containing alphabetic information, a card containing approximate constants and permissible deviation in the desired constants, another containing the number of data sets, and finally $x_1 - \ln \gamma_1 - \ln \gamma_2$ data cards which are read and stored.

The printout includes the programme title, constants of the identification and input parameter cards and table headings besides the results.

All the functions which come as summations in the programme are initially set to zero before the programme enters the DO loop in which $\ln \gamma_1$ and $\ln \gamma_2$ are calculated for each data set using the input constants. The differences between the input and calculated $\ln \gamma$ values
TABLE A.7 LISTING OF THE PROGRAMME 'TERNARY CONSISTENCY'

TERARY CONSISTENCY

MCDOHERT-ELLIS TERNARY THERMODYNAMIC CONSISTENCY TEST

REFERENCE  MCDOHERT,C.,AND ELLIS,S.K.,
CHEM.ENG.SCI., VOL.20,P.293(1965)

NOMENCLATURE

B = PURE COMPONENT SECOND VIRIAL COEFF., ML/lg,MOLE
D = DEVIATION FROM CONSISTENCY
ELNG = LN(GAMMA)
N = NUMBER OF DATA POINTS
P = PURE COMPONENT VAPOUR PRESSURE,MMHG
PI = SYSTEM PRESSURE,MMHG
T = SYSTEM TEMPERATURE,DEG. C
V = PURE COMPONENT LIQUID MOLAL VOLUME,ML/lG,MOLE
X = MOLE FRACTION IN LIQUID PHASE
Y = MOLE FRACTION IN VAPOUR PHASE

SUBSCRIPTS

1,2,3 = COMPONENTS 1,2,3

DIMENSION XI(L),X2(L),X3(L),ELNG1(L),ELNG2(L),ELNG3(L)

PRINT HEADINGS AND READ INPUT DATA

1 READ 200
READ 300,N,PI
---
PRINT 100
PRINT 200.
PRINT 400
L=0
I=0
KOUNT=1
2 L=L+1
---
READ 500,T,X1(L),Y1,PI,UI,V1
READ 500,T,X2(L),Y2,P2,H2,V2
READ 500,T,X3(L),Y3,P3,H3,V3
---
RT=62.36332*(T+273.16)
Z1=EXP((PI-PI)*((V1-B1)/RT))
Z2=EXP((P2-PI)*((V2-B2)/RT))
Z3=EXP((P3-PI)*((V3-B3)/RT))
ELNG1(L)=LOGF(Z1*PI*Y1/(PI*X1(L)))
ELNG2(L)=LOGF(Z2*PI*Y2/(P2*X2(L)))
ELNG3(L)=LOGF(Z3*PI*Y3/(P3*X3(L)))

...
TABLE A.7 (CONTINUED)

IF(L-2)2,3,5
3 M=1
1=1+1
4 M=M+1
KOUNT=KOUNT+1
F1=(X1(1)+X1(M))*(ELNG1(M)-ELNG1(1))
F2=(X2(1)+X2(M))*(ELNG2(M)-ELNG2(1))
F3=(X3(1)+X3(M))*(ELNG3(M)-ELNG3(1))
D=F1+F2+F3
PRINT 600,1,KOUNT,D
IF(M-2)4,5,5
5 DO 6 K=1,2
X1(K)=X1(K+1)
X2(K)=X2(K+1)
X3(K)=X3(K+1)
ELNG1(K)=ELNG1(K+1)
ELNG2(K)=ELNG2(K+1)
ELNG3(K)=ELNG3(K+1)
6 CONTINUE
L=2
IF(N-1-2)8,8,7
7 KOUNT=KOUNT-1
GO TO 2
8 PRINT 700
GO TO 1
C
100 FORMAT(2X44H;CDERMO17-ELLIS TERNARY VLE CONSISTENCY TEST,/)  
200 FORMAT(2X49H)  
300 FORMAT(14,F14.2)  
400 FORMAT(/,26X9HDATA PAIR,BX9HDEVIATION,/)  
500 FORMAT(F7.2,F7.4,F10.3)  
600 FORMAT(25X,14,3H-,14,F14.4)  
700 FORMAT(//)  
END
and the functions involving the summations are calculated and the composition, input and calculated values of $\ln \gamma_1$ and $\ln \gamma_2$, and the differences are printed. After the DO loop is satisfied, the corrections to be applied to the constants are calculated and added to the constants. The new set of constants are then printed. If these constants differ from the input ones, by more than the input deviations, the control transfers to statement 3 and the fit is re-evaluated. Otherwise the programme terminates and asks for data for the next system. Table A.8 gives the programme listing.

(ii) 'LEAST SQUARE COEFFICIENTS'

This programme evaluates the coefficients in the least square normal equations derived from the Margules third order [132] and the Redlich-Kister and Chao fourth order [50, 344] expressions for the free energy function.

The input includes alphameric information on the system and the activity coefficient - composition data. The coefficients are evaluated for all the three correlations and stored. With the use of SENSE SWITCH and conditional GO TO statements, the results might be obtained either for all the three equations or for some of them. A table of instructions, giving details of the equations for which output is obtained corresponding to the value of $L$ used with the conditional GO TO statement and the position of SENSE SWITCH 3, is included in the comments. The output is both printed and punched. The punched output is used in a standard programme for the solution of simultaneous equations to obtain the constants in the correlations. Table A.9 gives the programme listing.

(iii) 'BINARY FIT'

This programme is written for the evaluation of isobaric vapour-liquid equilibrium data fit in the van Laar [46], Wilson [290], Redlich-Kister [344], and Chao [50] correlations.
TABLE A:B LISTING OF THE PROGRAMME 'WILSON PARAMETERS'

WILSON PARAMETERS

EVALUATION OF PARAMETERS IN WILSON EQUATION FOR BINARY VLE DATA


NOMENCLATURE

\( A_{12}, A_{21} = \) WILSON PARAMETERS

\( D_{G} = \) DIFFERENCE BETWEEN CALCD. AND EXPTL. LN(GAMMA)

\( G, G_{1}, G_{2} = \) EXPTL. AND CALCD. LN(GAMMA)

\( N = \) NUMBER OF DATA POINTS

\( X_{1}, X_{2} = \) FRACTION IN LIQUID PHASE

SUBSCRIPTS 1,2 = COMPONENTS 1,2

NOTE - INPUT VALUES OF A12 AND A21 ARE APPROXIMATE VALUES

DIMENSION XX1(30), GG1(30), GG2(30)

PRINT HEADINGS AND READ INPUT DATA

PRINT 100
PRINT 200

1 READ 300
READ 400, A12, A21, ERROR
READ 800, N

PRINT 300
PRINT 500, A12, A21, ERROR
PRINT 600
PRINT 700
DO 2 J=1,N

2 READ 500, XX1(J), GG1(J), GG2(J)

3 SG1F1=0.0
SG2H1=0.0
SF1SU=0.0
SH1SU=0.0
SF1F2=0.0
SH1H2=0.0
SG1F2=0.0
SG2H2=0.0
SF2SU=0.0
SH2SU=0.0
DO 4 J=1,N
X1=XX1(J)
G1=GG1(J)
G2=GG2(J)
X2=1.-X1
P=X1*A12*X2
Q=X2*A21*X1
\[
R = \frac{A_{12}}{P} - \frac{A_{21}}{Q} \\
G_{1C} = -\frac{L}{G} F(P) + X_2 R \\
G_{2C} = -\frac{L}{G} F(Q) - X_1 R \\
D_{G1} = G_1 - G_{1C} \\
D_{G2} = G_2 - G_{2C} \\
F_1 = -\frac{X_2}{P} + \frac{A_{12}}{P} X_1 - \frac{X_2}{Q} \\
F_2 = -\frac{X_1}{P} + \frac{A_{12}}{P} X_2 + \frac{X_1}{Q} - \frac{X_2}{Q} \\
H_1 = -\frac{X_1}{P} + \frac{A_{12}}{P} X_2 (P - P) \\
H_2 = -\frac{X_2}{Q} + \frac{A_{21}}{Q} X_1 (Q - Q) \\
S_{G1F1} = S_{G1F1} + D_{G1} F_1 \\
S_{G2H1} = S_{G2H1} + D_{G2} H_1 \\
S_{F1SQ} = S_{F1SQ} + F_1 F_1 \\
S_{H1F2} = S_{H1F2} + H_1 F_2 \\
S_{F2SQ} = S_{F2SQ} + F_2 F_2 \\
S_{Pi1SQ} = S_{Pi1SQ} + P_i1 P_i1 \\
S_{H2SQ} = S_{H2SQ} + H_2 F_2 \\
T_1 = S_{G3F1} + S_{G2P1} \\
T_2 = S_{G1F2} + S_{G2H2} \\
C_1 = S_{F1C1} + S_{H1C1} \\
D_1 = S_{F1F2} + S_{H2H2} \\
C_2 = S_{F2C2} + S_{H2C2} \\
D_2 = S_{F2F2} + S_{H2H2} \\
A_{12} = A_{12} + D_1 \\
A_{21} = A_{21} + D_2 \\
IF (D_1 \leq 0) 5 \{ D_1 = -U_1 \} \\
IF (D_2 \leq 0) 7 \{ D_2 = -D_2 \} \\
IF (D_1 < 0) 9 \{ D_1 = -U_1 \} \\
IF (D_2 < 0) 10 \{ D_2 = -D_2 \} \\
GO TO 3 \\
END
\]
TABLE A.9 LISTING OF THE PROGRAMME 'LEAST SQUARE COEFFICIENTS'

LEAST SQUARE COEFFICIENTS

EVALUATION OF COEFFICIENTS IN LEAST SQUARE NORMAL EQUATIONS
FOR MARGULES-REDLICH-KISLER AND CHAO BINARY G-FUNCTIONS

INSTRUCTIONS FOR THE EXECUTION OF THE PROGRAMME

VALUES OF L POSITION OF SWITCH 3 EQUATIONS HANDLED

VALUES OF L

1 OFF R-K AND CHAO
2 ON M AND R-K
2 OFF R-K AND CHAO
3 OFF ONLY CHAO
3 ON NONE

NOMENCLATURE

CG = ACTIVITY COEFFICIENT FROM EXPTL. DATA
N = NUMBER OF DATA POINTS
X = MOLE FRACTION IN LIQUID PHASE
Y = MOLE FRACTION IN VAPOUR PHASE

SUBSCRIPTS 1, 2 = COMPONENTS 1, 2

DIMENSION X(20), QE(30), SFM(6), SFR(12), SFC(20)

READ INPUT DATA AND PRINT HEADINGS

PRINT 100
PRINT 200

1 READ 200
READ 400, N, L

PRINT 300
DO 2 J = 1, N

READ 500, X(J), GG1, GG2

2 QE(J) = X(J) * LCF(GG1) + (1. - M(J)) * LCF(GG2)

DO 3 1 = 1, 6
3 SFM(1) = 0.
DO 4 1 = 1, N
X1 = X(I)
X2 = 1. - X1

• • •
TABLE A.9 (CONTINUED)

\[ SFR(1) = SFH(1) + X1 \times X1 \times X2 \times X2 \]
\[ SFR(2) = SFH(2) + X1 \times X1 \times X2 \times X2 \times (X1 - X2) \]
\[ SFR(3) = SFH(3) + QE(1) \times X1 \times X2 \]
\[ SFR(4) = SFH(4) + QE(1) \times X1 \times X2 \times (X1 - X2) \]
\[ SFR(5) = SFH(5) + QE(1) \times X1 \times X2 \times (X1 - X2) \]
\[ SFR(6) = SFH(6) + QE(1) \times X1 \times X2 \times (X1 - X2) \]

C CONTINUE

C COEFFICIENTS IN NORMAL EQUATIONS FOR REDLICH-KISTER C-FUNCTION

DO 5 I = 1, 12
  SFR(I) = 0.
  DO 6 I = 1, N
    X1 = X(I)
    X2 = 1. - X1
    SFR(1) = SFR(1) + X1 \times X1 \times X2 \times X2
    SFR(2) = SFR(2) + X1 \times X1 \times X2 \times X2 \times (X1 - X2)
    SFR(3) = SFR(3) + X1 \times X1 \times X2 \times X2 \times (X1 - X2) \times (X1 - X2)
    SFR(4) = SFR(4) + QE(1) \times X1 \times X2
    SFR(5) = SFR(5) + QE(1) \times X1 \times X2 \times (X1 - X2)
    SFR(6) = SFR(6) + QE(1) \times X1 \times X2 \times (X1 - X2) \times (X1 - X2)
  6 CONTINUE

C COEFFICIENTS IN NORMAL EQUATIONS FOR CHAU Q-FUNCTION

DO 7 I = 1, 20
  SFC(I) = 0.
  DO 8 I = 1, N
    X1 = X(I)
    X2 = 1. - X1
    SFC(1) = SFC(1) + X1 \times X1
    SFC(2) = SFC(2) + X1 \times X1 \times X2
    SFC(3) = SFC(3) + X1 \times X1 \times X2 \times (X1 - X2)
    SFC(4) = SFC(4) + X1 \times X1 \times X2 \times (X1 - X2) \times (X1 - X2)
    SFC(5) = SFC(5) + QE(1) \times X1 \times X2
    SFC(6) = SFC(6) + QE(1) \times X1 \times X2 \times (X1 - X2)
    SFC(7) = SFC(7) + QE(1) \times X1 \times X2 \times (X1 - X2) \times (X1 - X2)
    SFC(8) = SFC(8) + X1 \times X1 \times X2 \times X2
    SFC(9) = SFC(9) + X1 \times X1 \times X2 \times X2 \times (X1 - X2)
    SFC(10) = SFC(10) + QE(1) \times X1 \times X2
    SFC(11) = SFC(11) + QE(1) \times X1 \times X2 \times (X1 - X2)
    .

...
TABLE A.9 (CONTINUED)

<table>
<thead>
<tr>
<th>Table Row</th>
<th>Mathematical Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFC(12)</td>
<td>SFC(8)</td>
</tr>
<tr>
<td>SFC(13)</td>
<td>SFC(9)</td>
</tr>
<tr>
<td>SFC(14)</td>
<td>SFC(14) + ((X1-X2)**3)<em>X1</em>X1<em>X2</em>X2</td>
</tr>
<tr>
<td>SFC(15)</td>
<td>SFC(15) + QE(I)<em>X1</em>X2*(X1-X2)</td>
</tr>
<tr>
<td>SFC(16)</td>
<td>SFC(4)</td>
</tr>
<tr>
<td>SFC(17)</td>
<td>SFC(9)</td>
</tr>
<tr>
<td>SFC(18)</td>
<td>SFC(14)</td>
</tr>
<tr>
<td>SFC(19)</td>
<td>SFC(19) + ((X1-X2)**4)<em>X1</em>X1<em>X2</em>X2</td>
</tr>
<tr>
<td>SFC(20)</td>
<td>SFC(20) + QE(I)<em>X1</em>X2*(X1-X2)**2</td>
</tr>
</tbody>
</table>

CONTINUE
GO TO (9,11,13), L

DO 10 I=1,6
  PRINT 700, SFN(I)
10 PUNCH 700, SFM(I)

DO 12 I=1,12
  PRINT 700, SFR(I)
12 PUNCH 700, SFR(I)

IF(SENSE SWITCH 3)16,14

DO 15 I=1,20
  PRINT 700, SFC(I)
15 PUNCH 700, SFC(I)

GO TO 1

C
100 FORMAT(2X45HC0EFFICIENTS IN LEAST SQUARE NORMAL EQUATIONS)
200 FORMAT(2X45H/------------------------------------------/)
300 FORMAT(1H0,45H                          ,1M )
400 FORMAT(14)
500 FORMAT(3F10.4)
600 FORMAT(2X41HC0EFFICIENTS IN MARGULES NORMAL EQUATIONS,/) 
700 FORMAT(F14.8)
800 FORMAT(2X47HC0EFFICIENTS IN REDLICH-KISTER NORMAL EQUATIONS,/) 
900 FORMAT(2X37HC0EFFICIENTS IN CHAO NORMAL EQUATIONS,/) 
END
A card containing the name of the system is read followed by three
blank cards and another card containing the number of data sets to be
processed and the system pressure. The data cards, containing \(x_1, \ln \gamma_1\)
\(\ln \gamma_2, \gamma_1, \) and \(P_0\) data sets, are then read and stored. For the van Laar,
Wilson, Redlich-Kister, and Chao correlations, the variable \(K\) assumes
the values 1, 2, 3, and 4 respectively.

For each correlation its title is first printed, the constants
read, and in a DO loop, \(\ln \gamma_1\) and \(\ln \gamma_2\) values are calculated for the
first data set. Then the control is transferred to statement 22. Between
statement 22 and the PRINT statement, the experimental and calculated
values of activity coefficients and vapour compositions, and the
deviations between them are evaluated and printed. Depending upon the
value of \(K\), the conditional GO TO statement re-transfers the control to
the appropriate DO loop. For finding data fit in the Wilson equation,
SENSE SWITCH 3 should be ON. Table A.10 gives the listing of the programme.

(iv) "MARGULE BINARY FIT"

This programme evaluates the fit of the isobaric activity
coefficient - composition data in the Margules fourth and third order
equations. The constants are either evaluated by the least squares method
or read as part of the input data making use of the SENSE SWITCH statement.

The title is first printed, the input identification, number of
data sets, system pressure, and the activity coefficient - composition
data sets are read and the identification data printed before the control
transfers to the SENSE SWITCH 3 statement which checks for the position
of the SENSE SWITCH 3. If it is ON, the constants are calculated by the
least squares method using the expression for the free energy function.
If the SWITCH is OFF, the constants are read and the statements
TABLE A.10 LISTING OF THE PROGRAMME 'BINARY FIT'

BINARY FIT

====================================================================================================
COMPARISON OF VAN LAAR, WILSON, REDLICH-KISTER AND CHAO CORRELATIONS

====================================================================================================

NOMENCLATURE

************

A, b = VAN LAAR (CARLSON-COLBURN CONSTANTS)
A12, A21 = WILSON PARAMETERS
AC, BC, CC, DC = CHAO CONSTANTS
BR, CR, DR = REDLICH-KISTER CONSTANTS
G, H = CALCL. LN(GAMMA-1), LN(GAMMA-2)
G, GB = EXPCL. LN(GAMMA-1), LN(GAMMA-2)
GAC, GBC = CALCL. GAMMA-1, GAMMA-2
GAE, GBE = EXPCL. GAMMA-1, GAMMA-2
N = NUMBER OF DATA POINTS
PA = VAPOUR PRESSURE OF LIGHTER COMPONENT, MM Hg
PY = TOTAL PRESSURE OF THE SYSTEM
X = MOLE FRACTION OF MORE VOLATILE COMPONENT IN LIQUID PHASE
Y = MOLE FRACTION OF MORE VOLATILE COMPONENT IN VAPOUR PHASE

INSTRUCTIONS

(1) KEEP SWITCH 2 ON FOR ALL EQUATIONS
(2) ** ** ** OFF TO EXCLUDE WILSON EQU.
(3) KEEP 3 BLANK CARDS FOLLOWING IDENTITY CARD

REFERENCES

(1) CARLSON, H., CARLSON-CONBURN, A., IEC, VOL. 34, 561 (1942)
(2) DRYER, V., PRAUSNITZ, J., IEC, VOL. 57 (5), 18 (1965)
(3) REDLICH, K., KISIER, A., IEC, VOL. 40, 385 (1948)
(4) CHAO, K. C., HUGEN, O., A., CHEM. ENG. SCI., VOL. 7, 266 (1958)

DIMENSION X(30), Y(30), PA(30), GA(30), GB(30)

READ INPUT DATA

-------
1 READ2
2 END

PRINT2
3 FORMAT(14,F10.2)
4 END

4 READ5, X(I), GA(I), GB(I), Y(I), PA(I)
5 END

...
TABLE A.10 (CONTINUED)

```
PRINT6
6 FORMAT(2X41HDATA REPRESENTATION BY VAN LAAR EQUATIONS,/,)
C
    ---------------
    READ7, A, B
    ---------------
C
7 FORMAT(2F10.5)
PRINT8, //
8 FORMAT(2X2HA=, F9.5, 6X4HA21=, F9.5, /
D05I=1,N
G=(A*(1.-X(I))**2)/(1.-X(I)+(A/b)*X(I))**2
H=b*X(I)*X(I)/((X(I)+(E/A)*(1.-X(I))))**2
GOTO22
9 CONTINUE
L=2
IF(SENSE<SWITCH)10, 14
10 PRINT11
11 FORMAT(2X47HDATA REPRESENTATION BY WILSON EQUATIONS,/,)
C
    ---------------
    READ12, A12, A21
    ---------------
C
12 FORMAT(2X4F9.5, 6X4H21=, F9.5, /
D013I=1,N
P=X(I)+A12*(1.-X(I))
0=1.-X(I)+A21*X(I)
G=-LOGF(P)+(1.-X(I))*(A12/P-A21/0)
FG=-LOGF(G)-X(I)*(A12/P-A21/0)
GOTO22
13 CONTINUE
14 PRINT15
15 FORMAT(2X47HDATA REPRESENTATION BY REDLICH-KISTER EQUATIONS,/,)
K=3
C
    ---------------
    READ16, BK, CR, DR
    ---------------
C
16 FORMAT(3F10.5)
PRINT17, BK, CR, DR
17 FORMAT(2X2HA21=, F9.5, 6X2HC=, F9.5, 6X2HD=, F9.5, /
D018I=1,N
G=(1.-X(I))**2*(BK+CR*(4.*X(I)-1.))+DK*(2.*X(I)-1.)*(6.*X(I)-1.)
H=X(I)*X(I)*(BK+CR*(4.*X(I)-1.))+DK*(2.*X(I)-1.)*(6.*X(I)-1.)
GOTO22
18 CONTINUE
K=4

* *

* *
```
PRINT19
19 FORMAT(/,2X37HDATA REPRESENTATION BY CHAU EQUATIONS,/)
C
READ20,AC,BC,CC,DC
C
20 FORMAT(4F10.5)
PRINT26,AC,bC,CC,DC
DO 211=1,M
P=BC+CC*(2.*X(I)-1. )
G=AC+BC*(2.*X(I)-1.)+(CC+AC)*(6.*X(I)*(1.-X(I))-1.)
H=X(I)*(1.-X(I))*P+(1.-X(I))*G
GOTO22
21 CONTINUE
GOTO22
22 GAE=EXP(F(GA(I)))
GbE=EXP(F(Gb(I)))
GAC=EXP(F(G))
GBC=EXP(F(H))
EGA=(GAE-GAC)/GAE
EBE=(GbE-GBC)/GbE
YC=GAC*PA(I)*X(I)/PY
Ey=(Y(I)-YC)/Y(I)
PRT23*X(I),GAE,GAC,EGA,EBE,bbC,Egb,Y(I),YC,Ey
23 FORMAT(2X2H A = , F9.5,6X2H b = , F9.3,6X2 HC= , F9.3,6X2 H0 = , F9.3,/)
GO TO(9,13,18,21),K
26 FORMAT(2X2HA=,FS.5,6X2HE=,FS.5,6X2HC=,FS.5,6X2HD=,FS.5,/)
END
involving the least squares evaluation of the constants are skipped. In both the cases the data fit is evaluated by calculating the errors in $Y_1$, $Y_2$, and $y$ for each data set as well as the average errors for the whole of the data.

The printout includes the constants, the experimental and calculated values of the activity coefficients and vapour compositions besides the deviations for individual data points and their average. Table A.11 gives the listing of the programme. A similar programme is written for the correlation of the data by the Symmetrical equations.

(v) 'MARGULES TERNARY FIT'

This programme calculates the activity coefficients using the Margules correlation as developed by Wohl [440]. It also calculates the vapour compositions and the deviation of the calculated quantities from the input experimental ones.

The input data consist of the system pressure, number of data sets to be handled, binary and ternary constants, and liquid and vapour compositions, activity coefficients, and vapour pressures for each data set. The activity coefficients for each component are calculated using the Wohl's expressions. Either three different ternary constants or a single one can be used.

The printout includes the programme title, input values of the liquid and vapour compositions and the activity coefficients, and the calculated values of the activity coefficients, vapour compositions, and deviations of the calculated values from the experimental ones. The average deviations for the entire data are also printed.

Table A.12 gives the listing of the programme. Similar programmes are written for the Wilson and the Redlich and Kister ternary correlations.
TABLE A.11 LISTING OF THE PROGRAMME 'MARGULE BINARY FIT'

MARGULE BINARY FIT

-------------------------------
BINARY VLE REPRESENTATION BY MARGULES 4TH AND 3RD ORDER EQUATIONS
-------------------------------

IF SENSE SWITCH 2 IS ON, 4TH AND 3RD ORDER CONSTANTS ARE
EVALUATED BY LEAST SQUARE METHOD USING EXCESS FREE ENERGY FUNCTION
IF IT IS OFF, THE CONSTANTS ARE TO BE READ

REFERENCE HAAL A, ET AL., VAPOUR-LIQUID EQUILIBRIUM, 2ND ED., P.50,
PERGAMON PRESS, 1967

NOMENCLATURE

AEG = AVERAGE ABSOLUTE ERROR IN G
AAEY = AVERAGE ABSOLUTE ERROR IN Y
A12, A21, D12 = CONSTANTS IN MARGULES EQUATIONS
DLG = DIFFERENCE BETWEEN EXPTL. AND CALCD. GAMMAS
ELY = ERROR IN Y, (Y(EXPTL.) - Y(CALCD.)) / Y(EXPTL.)
G = ACTIVITY COEFFICIENT, CALCD.
GL = LN(G), EXPTL.
GLC = LN(G), CALCD.
N, POINTS = NUMBER OF DATA POINTS
P = PURE COMPONENT VAPOUR PRESSURE, mmHg
PI = TOTAL PRESSURE OF THE SYSTEM, mmHg
RASY = ROOT MEAN SQUARE DEVIATION IN Y
X, XX = MOLE FRACTION IN LIQUID PHASE
Y = MOLE FRACTION IN EQUILIBRIUM VAPOUR PHASE
SUBSCRIPTS 1, 2 = COMPONENTS 1, 2

DIMENSION XX(10), GL1(30), GL2(30), Y1(30), PI(30)

PRINT 100
---------------------
1 READ 200
READ 300, N, PI
---------------------
PRINT 200
PRINT 100
---------------------
PONTS = N

READ X AND ACTIVITY COEFFICIENT SETS

DO 2 I = 1, N
---------------------
2 READ 400, XX(I), GL1(I), GL2(I), Y1(I), PI(I)
---------------------
TABLE A.11 (CONTINUED)

IF(SENSE SWITCH 3)20,10

---------------------------------------------
10 READ 400,A12,A21,D12

GO TO 30

C

C

C

C

C

C

C

C

C

CALCULATION OF MATRIX COMPONENTS FOR LEAST SQUARES DATA FITTING

20 SF1=0.
SF2=0.
SF3=0.
SF4=0.
SF5=0.
SF6=0.
SF7=0.
SF8=0.
SF9=0.

DO 3 I=1,N
X1=XX(I)
X2=1.-X1
QI=X1*X2
R1=X1*X1
R2=R1*X1
R3=R1*X1
SF1=SF1+R3
SF2=SF2+R2*X1*X1
SF3=SF3+R3*X1
SF4=SF4+R1*X1*X1
SF5=SF5+R2*X2*X2
SF6=SF6-R2*X2
SF7=SF7+R1*X1*X1
SF8=SF8+R3*X1
SF9=SF9-R2*X2

GO TO 5
TABLE A. 11 (CONTINUED)

4 D12 = 0.
G0 TO 6
5 D12 = (Z4 * (SF1 * SF9 - SF4 * SF6) - Z3 * Z7 / (Z4 * Z5 - Z6 * Z6)
6 A12 = (SF4 - SF2 * A21 - SF2 * A12) / SF1
L = L + 1
C
C DATA FIT BY NARGULES EQUATIONS
C
30 PRINT 500, A12, A21, D12
AEG1 = 0.
AEG2 = 0.
AY Y1 = 0.
SSFY1 = 0.
DU 7 = 1, N
X1 = XX(I)
XZ = 1 + X1
GLC1 = X2 * X2 * (A12 + 2 * (A21 - A12 - D12) * X1 + 3 * D12 * X1 * X1)
GLC2 = X1 * X1 * (A21 + 2 * (A12 - A21 - D12) * X2 + 2 * D12 * X2 * X2)
G1 = EXPF(GLC1(I))
G2 = EXPF(GLC2(I))
GC1 = EXPF(GLC1)
GC2 = EXPF(GLC2)
YC1 = 6C1 * PI(I) * X1 / PI
DLG1 = G1 - GC1
DLG2 = G2 - GC2
DLY1 = Y1(I) - YC1
EG1 = DLY1 / G1
EG2 = DULG2 / G2
EY1 = DLY1 / Y1(I)
AEG1 = AEG1 + SQRTF(EG1 * EG1)
AEG2 = AEG2 + SQRTF(EG2 * EG2)
AY Y1 = AY Y1 + SQRTF(AY Y1 * AY Y1)
SSEY1 = SSEY1 + AY Y1
7 PRINT 7G, X1, G1, G2, GC2, EG2, Y1(I), YC1, EY1
AEG1 = AEG1 / POINTS
AEG2 = AEG2 / POINTS
AY Y1 = AY Y1 / POINTS
SSEY1 = SSEY1 / POINTS
PRINT 600, AAEG2, AAY Y1, KM SY1
IF (SENSE SWITCH 3) = 1,
8 IF (L-1) = 5, 4, 9
9 GO TO 1
C
200 FORMAT(2X49H)
300 FORMAT(14*F15.2)
400 FORMAT(15F10.4)
500 FORMAT(2X49H)
600 FORMAT(2X10F11.4,22XF11.4,22XF11.4,22XF11.4)
700 FORMAT(2X10F11.4)
END
TABLE A.12 LISTING OF THE PROGRAMME 'MARGULES TERNARY FIT'

C MARGULES TERNARY FIT
C==============================================================================
C TERNARY VAPOUR-LIQUID EQUILIBRIUM DATA REPRESENTATION BY
C MARGULES 4TH ORDER EQUATIONS
C==============================================================================
C NOMENCLATURE
C+++++++++++++++++++++
C
A12, A21, A23, A32, A31, A13 = MARGULES TERNARY CONSTANTS
D12, D13, D23, C1S, C2S, C3S =
K = k, DEVIATION OF CALCULATED QUANTITY FROM
EXPTL. QUANTITY, EXPTL.(F) - CALC'D.(F)
ELKG = CALCD. LR (GAMMA)
G = GAMMA-ACTIVITY COEFFICIENT (EXPTL.)
R, K = NUMBER OF DATA POINTS
P = PURE COMPONENT VAPOUR PRESSURE, MM HG
PADG = PERCENTAGE ABSOLUTE DEVIATION IN GAMMA
PADY = PERCENTAGE ABSOLUTE DEVIATION Y
PY = TOTAL PRESSURE OF THE SYSTEM, MM HG
W = DEFINED DEVIATION, OMEGA, IN GAMMA
Y = DEFINED DEVIATION, OMEGA, IN Y
X = MOLE FRACTION IN LIQUID PHASE
Y = MOLE FRACTION IN VAPOUR PHASE

SUBSCRIPTS
1, 2, 3 = COMPONENTS 1, 2, 3
C = CALCULATED VALUE

INSTRUCTIONS
+++++++++++++++++++++
(1) FIT THE DATA IN 3RD ORDER EQUATIONS BY READING
D12, D23, D13 AS ZERO AND C1S=C2S=C3S
(2) FIT THE DATA IN 3RD ORDER EQUATIONS
USING THREE DIFFERENT TERNARY CONSTANTS
(3) FIT THE DATA IN 4TH ORDER EQUATIONS USING ALL CONSTANTS

REFERENCES - (1) KURT WOHL, TRANS. AIChE, VOL 42, p. 215 (1946)
(2) KURT WOHL, CHEM. ENG. PROC., VOL 44(4), p. 218 (195)3

DIMENSION AKG(3), ELKG(3), C(3), GC(3), PADG(2), SKG(3), SSKG(3), WG(2)

PRINT HEADINGS AND READ INPUT DATA

PRINT 100
-------------------------------
1 READ 200, N, PY
READ 300, A12, A21, A23, A32, A31, A13
READ 300, D12, D13, D23, C1S, C2S, C3S
-------------------------------
PRINT 400, A12, A21, A23, A32, A31, A13
PRINT 400, D12, D13, D23, C1S, C2S, C3S

...
TABLE A.12 (CONTINUED)

R=0.
SKY1=0.
SKY2=0.
SSKY1=0.
SSKY2=0.
DU 2 J=1,3
SSKG(J)=0.

DU 4 J=1,N

---

READ 300,X1,X2,G(1),G(2),{3}
READ 300,Y1,Y2,P1,P2
---

C

CALCULATE ACTIVITY COEFFICIENTS

---

C

R=R+1.
X3=X1-X2
S1X1=X1*X1
S1X2=X2*X2
S1X3=X3*X3
SXC=X1*X3+S2*G2+S3*G3

F1=SUX*{(A12+2.*X1*(A21-A12-D12))+2.*SUX*G1}
F2=SUX*{(A13+2.*X1*(A31-A13-D13))+2.*SUX*G2}
F3=SUXX*{(A23+2.*X2*(A32-A23-D23))+2.*SUX*G3}
F4=(X2-X3)*(A23-A32)+3.*SUX*G1-SUXX*G2
EL[NG]=F1+F2+F3+F4

---

C

DU 3 J=1:

GC[J]=EXP[EL+G(J)]
AKG(J)=G(J)-GC(J)
PA06(J)=100.*AKG(J)/G(J)
SSKG(J)=SSKG(J)+AKG(J)*G(J)

---

C

SKG(J)=SKG(J)+AKG(J)

---

Y1=GC(1)*P1*X1/PY
Y2=GC(2)*P2*X2/PY
AKY1=Y1-YC1
AKY2=Y2-YC2

...
TABLE A.12 (CONTINUED)

\[ \text{PADY}_1 = 100 \times \text{AKY}_1 / Y_1 \]
\[ \text{PADY}_2 = 100 \times \text{AKY}_2 / Y_2 \]
\[ \text{SSKY}_1 = \text{SSKY}_1 + \text{AKY}_1 \times \text{AKY}_1 \]
\[ \text{SSKY}_2 = \text{SSKY}_2 + \text{AKY}_2 \times \text{AKY}_2 \]
\[ \text{SKY}_1 = \text{SKY}_1 + \text{AKY}_1 \]
\[ \text{SKY}_2 = \text{SKY}_2 + \text{AKY}_2 \]

PRINT RESULTS

\[ \text{PRINT} 500, 1, X_1, Y_1, YC_1, \text{PADY}_1 \]
\[ \text{PRINT} 600, X_2, Y_2, YC_2, \text{PADY}_2 \]
\[ \text{DO } 4 \text{ J}=1, 3 \]
\[ \text{PRINT} 700, J, G(J), \text{PADG}(J) \]
\[ \text{SK} = K-1 \]
\[ \text{PRINT} 800 \]
\[ \text{DO } 5 \text{ J}=1, 3 \]
\[ \text{WG}(J) = (\text{SSKG}(J) - \text{SKG}(J)^2) * \sqrt{F(R)} / \text{Sk} \]
\[ \text{PRINT} 900, J, \text{WG}(J) \]
\[ \text{WY}_1 = (\text{SSKY}_1 - \text{SKY}_1^2) * \sqrt{F(R)} / \text{SR} \]
\[ \text{WY}_2 = (\text{SSKY}_2 - \text{SKY}_2^2) * \sqrt{F(R)} / \text{SR} \]
\[ \text{PRINT} 1000, \text{WY}_1, \text{WY}_2 \]

GO TO 1

100 FORMAT(2X, 42HAKY VLE DATA FIT IN FARGULES EQUATIONS, /)
200 FORMAT(15, F10.4)
300 FORMAT(6F10.4)
400 FORMAT(4X, 6F14.4, /)
500 FORMAT(15, 2X3H1=F8.4, 3) \[ 3 \text{ Y}=F8.4, 2X4H1=F8.4, 1X6H1=F8.4 \]
600 FORMAT(7X3HX2=F8.4, 3X3H2=F8.4, 2X4H2=F8.4, 1X6H2=F8.4, \text{PADG}(12), 1H=F8.4 \])
700 FORMAT(//)
800 FORMAT(23X2HWG, 1H=F8.4)
900 FORMAT(33X2HG, 1H=F8.4, 4)
1000 FORMAT(33X5H1=F8.4, 1H=F8.4, 33X5H2=F8.4)
END
A.6 Prediction of Azeotropes

The programme, 'AZEOTROPES', predicts the composition and temperature of binary azeotropes from a knowledge of the constants in either the Redlich-Kister [344] or the Chao [50] binary correlations evaluated from limited experimental data.

Four data cards are required to give all the input information for the programme, the first one with identification record, second with the system pressure, approximate azeotropic composition and tolerable error in it, the third with the constants in the Antoine vapour pressure equation, and the fourth with the Redlich-Kister or the Chao binary constants derived from infinite dilution activity coefficient data and one or two experimental data sets.

After evaluating the constant terms from either the Redlich-Kister or the Chao constants depending whether the SENSE SWITCH 3 is OFF or ON, the equation for the azeotropic composition is solved by Newton's method starting with the input composition, x, as the first trial value. If the calculated value of x differs by more than the input error, the calculations are repeated with the new value of x, otherwise the programme proceeds to calculate the azeotropic temperature and prints the results.

Table A.13 gives listing of the programme.
TABLE A.13 LISTING OF THE PROGRAMME 'AZEOTROPES'

AZEOTROPES
====================================================================
PREDICTION OF BINARY AZEOTROPIC CONDITIONS
====================================================================

NOMENCLATURE
++++++++++++
A, L, C = ARCTAN VAPOUR PRESSURE CONSTANTS
B, C, D, R = CONSTANTS IN R-K BINARY CORRELATION
A, B, C, D, E, F = CONSTANTS IN CHAU BINARY CORRELATION
P, T = SYSTEM PRESSURE MPa, HC.
X = AZEOTROPIC COMPOSITION, MOLE FRACTION OF 1
SUBSCRIPTS 1, 2 = COMPONENTS 1, 2 IN THE BINARY

NOTE-INPUT VALUE OF A IS APPROXIMATE AZEOTROPIC COMPOSITION
KEEP SWITCH 3 ON FOR CHAU EQUATION

READ INPUT DATA AND PRINT HEADINGS

PRINT 100
PRINT 200
------------------------
1 READ 300
READ 400,PI,X,ERKOK
READ 600,A1,B1,C1,C2
------------------------
PRINT 300
PRINT 900

CALCULATE CONSTANT TERMS IN THE EQUATION

IF(SENS E SWITCH 3) 20,10
------------------------
10 READ 800,BR,CR,DK
------------------------
AK1=12.*DK
AK2=16.*DK-4.*CR
AK3=-5.*DK+3.*CR-BK
AK4=-22.*DK+4.*CR
AK5=29.*DK-9.*CR+BR
AK6=-10.*DK+6.*CR-2.*ERK
AK7=DK-2.*CR+BR
GU TO 2
------------------------
20 READ 500,AC,BC,CC,LC
------------------------
AK1=12.*DC
AK2=16.*DC-4.*CC-2.*AC
AK3=-5.*DC+2.*CC-BC+2.*AC

...
TABLE A.13 (CONTINUED)

\[\begin{align*}
AK4 &= -32.4DC + 4.2CC + 2.4AC \\
AK5 &= 29.4DC - 9.4CC + 3.4BC - 3.4AC \\
AK6 &= -10.4DC + 6.4CC - 2.4BC + 4.4AC \\
AK7 &= DC - CC + BC + AC \\
\end{align*}\]

SOLVE THE EQUATION IN X BY METHOD OF NEWTON

\[\begin{align*}
2 \quad & \text{ALPHA} = AK1X^4 + AK4X^3 + AK5X^2 + AK6X + AK7 + A1 - \logf{\pi}/2.302585 \\
& \text{BETA} = -AK1X^4 + AK2X^3 + AK3X^2 - A2 + \logf{\pi}/2.302585 \\
& \text{GAMMA} = ALPHAB1/((C1-C2-b2/beta) \\
& \text{IF (GAMMA) 3, 7, 3} \\
3 \quad & \text{THETA} = 4.4AK1X^3 + 3.4AK4X^2 + 2.4AK5X + AK6 \\
& \text{DELTA} = -4.4AK1X^3 + 3.4AK2X^2 + 2.4AK3X \\
& \text{FXR} = GAMMA/(THETA+b1+b2*(DELTA/((C1-C2+beta-b2)^2))) \\
& X = X - FXR \\
& \text{IF (FXR)} 4, 5, 5 \\
& \text{IF (FXR-ERROR)} 7, 7, 6 \\
& \text{GO TO 2} \\
4 \quad & \text{FIND AZEOTROPIC TEMPERATURE} \\
& \text{PSI} = -AK1X^4 + AK2X^3 + AK3X^2 + Z + \logf{\pi}/2.302585 \\
& T = C2-b2/PSI \\
& \text{PRINT } 100, P1, 1, X \\
& \text{GO TO 1} \\
5 \quad & \text{GO TO 2} \\
6 \quad & \text{GO TO 2} \\
7 \quad & \text{GO TO 2} \\
8 \quad & \text{GO TO 2} \\
9 \quad & \text{END} \\
\end{align*}\]

100 FORMAT (2X42H PREDICTION OF BINARY AZEOTROPIC CONDITIONS) 
200 FORMAT (X2H ************ * ******** ********** ********** */ 
300 FORMAT (X24H ) 
400 FORMAT (F10.2, F10.4, F15.8) 
500 FORMAT (F10.5) 
600 FORMAT (F10.5) 
700 FORMAT (6X4HP1 =, F6.2, 6X3HT =, F6.3, 6X3HX =, F7.4, /) 
800 FORMAT (6F10.5) 
900 FORMAT (///) 

END