CALCULATION OF ACTIVITY COEFFICIENTS FROM TOTAL PRESSURES

A, B, C, are constants to be determined in the empirical equation for excess free energy. \( V_1, V_2, B_1, B_2, X_1, X_2, Y_1, Y_2, P_1R \) and \( P_2R \) denote molar volumes, virial coefficients, mole fractions, activity coefficients and partial pressures of the two components respectively. \( P, P_T \) and \( R_P \) denote total vapour pressure, (experimental), calculated total pressure and residual vapour pressure. \( P_0 \) denotes the vapour pressure of the pure component 2. \( R, T \) and \( N \) denote gas constant, temperature and number of concentrations studied respectively.

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APPENDIX D

Computer Programmes

I. B. M. 1620 Computer has been used for all the calculations presented in this thesis. As the core capacity of this computer is very small, programming had to be done in parts. Various programmes used in the present calculations are given in the following pages.

Programme 1: Calculation of activity coefficients from total pressures.

C CALCULATION OF ACTIVITY COEFFICIENTS FROM TOTAL PRESSURES
C A, B, C, are constants to be determined in the empirical equation
C for excess free energy. \( V_1, V_2, B_1, B_2, X_1, X_2, Y_1, Y_2, P_1R \) and
C \( P_2R \) denote molar volumes, virial coefficients, mole fractions,
C activity coefficients and partial pressures of the two components
C respectively. \( P, P_T \) and \( R_P \) denote total vapour pressure
C (experimental), calculated total pressure and residual vapour
C pressure. \( P_0 \) denotes the vapour pressure of the pure component 2.
C \( R, T \) and \( N \) denote gas constant, temperature and number of
C concentrations studied respectively.
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DIMENSION M1(14), AN2(14), DA(14), DB(14), DC(14), P1R(14), P2R(14)

DIMENSION X1(14), X2(14), V1(14), V2(14), P1(14), P2(14), P(14)

DIMENSION P1F(14), AL1(14), AL2(14), AM1(14), AM2(14)

1 READ2
PRINT2

2 FORMAT(49H)

3 READ4, A, B, C

READ4, R, T, V1, V2, B1, B2, P0, N

4 FORMAT(7F7.0,15)

READ 5, X1(1), X1(2), X1(3), X1(4), X1(5), X1(6), X1(7), X1(8), X1(9)

READ 5, X1(10), X1(11), X1(12), X1(13), X1(14)

READ 5, P1(1), P(2), P(3), P(4), P(5), P(6), P(7), P(8), P(9), P(10), P(11), P(12), P(13), P(14)

5 FORMAT(11F6.0)

DO 6 J=1, N

X2(J)=1.-X1(J)

P1(J)=X1(J)*P(1)*EXP(((V1-B1)*(P(J)-P(1)))/(R*T))

P2(J)=X2(J)*P0*EXP(((V2-B2)*(P(J)-P0)))/(R*T))
\[ A_{11}(J) = X_2(J)^2 \]
\[ A_{12}(J) = X_1(J)^2 \]
\[ A_{M1}(J) = -A_{11}(J) \cdot (1. - 4\cdot X_1(J)) \]
\[ M_2(J) = A_{12}(J) \cdot (1. - 4\cdot X_2(J)) \]
\[ M_1(J) = A_{11}(J) \cdot (1. - 8\cdot X_1(J) + 12\cdot A_{12}(J)) \]
\[ A_{N2}(J) = A_{12}(J) \cdot (1. - 8\cdot X_2(J) + 12\cdot A_{11}(J)) \]
\[ Y_1(J) = \exp(A_{11}(J) + B\cdot A_{M1}(J) + G\cdot A_{N2}(J)) \]
\[ Y_2(J) = \exp(A_{12}(J) + B\cdot M_2(J) + C\cdot A_{N2}(J)) \]
\[ P_{1R}(J) = Y_1(J) \cdot P_1(J) \]
\[ P_{2R}(J) = Y_2(J) \cdot P_2(J) \]
\[ P(T) = P_{1R}(J) + P_{2R}(J) \]
\[ R(T) = P(J) - P(T) \]

PRINT7

7 FORMAT(53HO X1 Y1 Y2 P1R P2R PT P RP)
D08J=1,N

8 PRINT9,X1(J),Y1(J),Y2(J),P1R(J),P2R(J),PT(J),P(J),R(J)

9 FORMAT(1HO3F7.4,5F7.2)
D010I=1,9

10 S(I)=0
D011J=1,N
12 PRINT 13, S(I), S(I+1), S(I+2)
13 FORMAT(3F9.2)
GOT 01
A 1=1,9,3
DA(J) = AL1(J) * Y1(J) * P1(J) + ...
DB(J) = AM1(J) * Y1(J) * P1(J) + ...
DC(J) = AN1(J) * Y1(J) * P1(J) + ...
S(I) = S(I) + DA(J)
S(2) = S(2) + DA(J) * DB(J)
S(3) = S(3) + DA(J) * DC(J)
S(4) = S(4) + B(J) * RP(J)
S(5) = S(5) + DB(J) * DB(J)
S(6) = S(6) + DB(J) * DC(J)
S(7) = S(7) + DB(J) * KP(J)
S(8) = S(8) + BC(J) * DC(J)
S(9) = S(9) + DC(J) * RP(J)
Programme 2:

Calculation of new values of A, B and C from those used in programme 1 and using the sums (S(1)-S(9)) obtained from the results of programme 1.

A, B and C are constants to be determined in the empirical equation for excess free energy. S(1)-S(9) are the sums as calculated in Programme Number 1. DELA, DELB, DELC are the corrections to be made in the original values of A, B and C.

DIMENSION S(9)

1 READ 2
2 FORMAT (2X49H )
PRINT 2
READ 4, S(1), S(2), S(3), S(4), S(5), S(6), S(7), S(8), S(9)
4 FORMAT (9F8.0)
READ 5, A, B, C
5 FORMAT (3F7.0)

Pl = S(5) * S(8) - S(6) * S(9)
P2 = S(6) * S(3) - S(2) * S(8)
P3 = S(6) * S(9) - S(7) * S(8)
P4 = S(2) * S(6) - S(3) * S(5)
P5 = S(5) * S(9) - S(7) * S(6)
P6 = S(7) * S(3) - S(2) * S(9)
V = S(1) * P1 + S(2) * P2 + S(3) * P4
VA = S(4) * P1 + S(2) * P2 - S(3) * P5
VB = - S(1) * P3 + S(4) * P2 - S(3) * P6
VC = S(1) * P5 + S(2) * P6 + S(4) * P4
DELa = VA / V
DELB = VB / V
DELC = VC / V
PRINT 6, DELA, DELB, DELC
6 FORMAT (2X5, HDELa =, F7.4, 2X5, HDELB =, F7.4, 2X5, HDELC =, F7.4)
PRINT 7, A, B, C
7 FORMAT (2X2, ha =, F7.4, 2X2, hb =, F7.4, 2X2, hc =, F7.4)
PUNCH 8, A, B, C
8 FORMAT (3F7.4)
GOTO 1
END
Programme 3: Calculation of activity coefficients in case of systems having one component non-volatile.

Calculation of activity coefficients, in case of systems having one component non-volatile.

A, B, C, and D are the four constants to be determined in the free energy equation. P, Po and V denote virial coefficient, vapour pressure and molar volume of the component 1. X, and X2 denote the mole fractions of the two components in the mixture. P and N are total vapour pressure and number of concentrations respectively. Y1, Y2 denote the activity coefficients while Y11 and Y12 are their corresponding logarithms. G is excess free energy.

DIMENSIONX(20), P(20), S(4,5)

READ2
PRINT2

FORMAT (49H)

READ2, X(1), X(2), X(3), X(4), X(5), X(6), X(7), X(8), X(9), X(10)
READ3, X(11), X(12), X(13), X(14), X(15), X(16), X(17), X(18), X(19), X(20), ...
READ3, P(1), P(2), P(3), P(4), P(5), P(6), P(7), P(8), P(9), P(10)
READ3, P(ll), P(12), P(13), P(14), P(15), P(16), P(17), P(18), P(19), P(20)

3 FORMAT(10F6.0)
READ4, B, T, P0, V, N
4 FORMAT(4F8.0, I4)
D05I=1,4
D08J=1,5
5 S(I,J)=0
PRINT6
6 FORMAT(/)
PRINT7
7 FORMAT(2X8HXR 0LVENT7X2HX25X1NP0X5HGaMA1)
D08I=1,N
X2=1.-X(I)
R=62361.04
C=(1.-X(I))**2
D=((1.-X(I))**2)*(4.*X(I)-1.)
E=((1.-X(I))**2.)*(1.-8.*X(I)+13.*X(I)**2)
F=-X2*X2*(1.-12.*X(I)+36.*X(I)*X(I)-32.*X(I)**3)
Y1=P(I)/(P0*X(I))
G=((B-V)*(P(I)-P0))/(R*T)
\[ H = R \cdot B \cdot ((P(I) \cdot F(I)) - (P0 \cdot P0)) / (2 \cdot R \cdot R \cdot T \cdot T) \]
\[ Y1 = Y1 \cdot \exp (G-H) \]
\[ S(1,1) = S(1,1) + C \cdot \gamma \]
\[ S(1,2) = S(1,2) + C \cdot D \]
\[ S(1,3) = S(1,3) + C \cdot E \]
\[ S(1,4) = S(1,4) + C \cdot F \]
\[ S(1,5) = S(1,5) + \log F(Y1) \cdot C \]
\[ S(2,1) = S(1,2) \]
\[ S(2,2) = S(2,2) + D \cdot D \]
\[ S(2,3) = S(2,3) + D \cdot E \]
\[ S(2,4) = S(2,4) + D \cdot F \]
\[ S(2,5) = S(2,5) + \log F(Y1) \cdot D \]
\[ S(3,1) = S(1,3) \]
\[ S(3,2) = S(2,3) \]
\[ S(3,3) = S(3,3) + E \cdot E \]
\[ S(3,4) = S(3,4) + E \cdot F \]
\[ S(3,5) = S(3,5) + \log F(Y1) \cdot E \]
\[ S(4,1) = S(1,4) \]
\[ S(4,2) = S(2,4) \]
\[ S(4,3) = S(3,4) \]
S(4,4) = S(4,4) + 4*F*F
S(4,5) = S(4,5) + LOGF(Y1)*F
8 PRINT9, X(I), \$2, P(I), Y1
9 FORMAT(4F10.5)
PRINT6
D010 I=1,4
D010 J=1,5
10 PRINT11, S(I, J)
11 FORMAT(F12.8)
PRINT6
D0107 K=1,4
D0103 J=1,5
IF(J-K)102,103,102
102 S(K, J) = S(K, J) / S(K, K)
103 CONTINUE
D0107 I=1,4
IF(I-K)104,107,104
104 D0107 J=1,5
IF(J-K)106,107,106
106 S(I, J) = S(I, J) - S(I, K)*S(K, J)
107 CONTINUE
   \[ a = s(1,5) \]
   \[ b = s(2,5) \]
   \[ c = s(3,5) \]
   \[ d = s(4,5) \]
   PRINT12
12 FORMAT(5X1HA10X1HB10X1HC10X1HD)
   PRINT13, a, b, c, d
   PRINT6
13 FORMAT(4F10.6)
   DO14I=1,N
   u=x(i)**2
   x2=1.-x(i)
   q=x2**2
   y1=d*q*(1.-12.*x(i)+36.*u-32.*u*x(i))
   y1=expf(a*q+b*q*(4.*x(i)-1.)+c*q*(1.-8.*x(i)+12.*u)-y1)
   y2=u*(1.-12.*x2+36.*q-32.*q*x2)*d
   y2=expf(a*u+b*u*(1.-4.*x2)+c*u*(1.-8.*x2+12.*q)+y2)
   yll=.43429*logf(y1)
   y22=.43429*logf(y2)
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\[ Y = Y_{22} - Y_{11} \]

\[ G = 8.3147 \times X(I) \times T \times X^2 \times (A + B \times (X(I) - X^2) + C \times (X(I) - X^2)^2 + D \times (X(I) - X^2)^3) \]

14 PRINT16, X(I), X^2, Y1, Y2, Y11, Y22, Y, G
15 FORMAT(8F12.5)
PRINT6
END

Programme 4: - Calculation of excess thermodynamic functions by using the constants A, B, C and D as calculated in programmes 2 and 3.

C T1, T2, T3 AND T4 DENOTE THE FOUR EXPERIMENTAL TEMPERATURES. N
C DENOTES NUMBER OF CONCENTRATIONS. X1—X14 ARE THE MOLE
C FRACTIONS. A1, B1, C1, D1, A2,----D4 ARE THE CONSTANTS AT THE
C TEMPERATURES T1, T2, T3, AND T4 RESPECTIVELY. G1, G2, G3, AND G4
C DENOTE THE VALUES OF EXCESS FREE ENERGIES WHILE H13, H24, H14 AND
C H ARE THE EXCESS HEATS AS CALCULATED FROM THE CORRESPONDING G
C VALUES. TS1, TS2, TS3, AND TS4 ARE THE CORRESPONDING TS TERMS.
C  CALCULATION OF EXCESS THERMODYNAMIC FUNCTIONS
DIMENSION X1(14),X2(14),G1(14),G2(14),G3(14),G4(14),H13(14)
DIMENSION H24(14),H14(14),H(14),TS1(14),TS2(14),TS3(14),TS4(14)
1 READ14
14 FORMAT(2X49H)
READ2,R,T1,T2,T3,T4,N
2 FORMAT(6P7.0,I4)
READ3,X1(1),X1(2),X1(3),X1(4),X1(5),X1(6),X1(7),X1(8),X1(9),
READ3,X1(10),X1(11),X1(12),X1(13),X1(14)
3 FORMAT(9F6.0)
READ4,A1,B1,C1,D1,A2,B2,C2,D2,A3,B3,C3,D3
READ41,A4,B4,C4,D4
4 FORMAT(12F6.0)
41 FORMAT(4F6.0)
PRINT6
6 FORMAT(43H0   X1   G1   G2   G3   G4   )
D05J=1,N
X2(J)=1.-X1(J)
G1(J)=R*T1*X1(J)*X2(J)*(A1+B1*(X1(J)-X2(J)))+C1*(X1(J)-X2(J)**2)
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\[ G_1(J) = G_1(J) + D_1 \times ((X_1(J) - X_2(J))^3) \times R \times T_1 \times X_1(J) \times X_2(J) \]

\[ G_2(J) = R \times T_2 \times X_1(J) \times X_2(J) \times (A_2 + B_2 \times (X_1(J) - X_2(J))) + D_2 \times (X_1(J) - X_2(J))^3 \times R \times T_2 \times X_1(J) \times X_2(J) \]

\[ G_3(J) = R \times T_3 \times X_1(J) \times X_2(J) \times (A_3 + B_3 \times (X_1(J) - X_2(J))) + D_3 \times (X_1(J) - X_2(J))^3 \times R \times T_3 \times X_1(J) \times X_2(J) \]

\[ G_4(J) = R \times T_4 \times X_1(J) \times X_2(J) \times (A_4 + B_4 \times (X_1(J) - X_2(J))) + D_4 \times (X_1(J) - X_2(J))^3 \times R \times T_4 \times X_1(J) \times X_2(J) \]

\[ H_{13}(J) = \frac{((G_1(J)/T_1) - (G_3(J)/T_3)) \times T_1 \times T_3}{(T_3 - T_1)} \]

\[ H_{24}(J) = \frac{((G_2(J)/T_2) - (G_4(J)/T_4)) \times T_2 \times T_4}{(T_4 - T_2)} \]

\[ H_{14}(J) = \frac{((G_1(J)/T_1) - (G_4(J)/T_4)) \times T_1 \times T_4}{(T_4 - T_1)} \]

\[ H(J) = \frac{H_{13}(J) + H_{24}(J) + H_{14}(J)}{3} \]

\[ T_{S1}(J) = H(J) - G_1(J) \]

\[ T_{S2}(J) = H(J) - G_2(J) \]

\[ T_{S3}(J) = H(J) - G_3(J) \]

\[ T_{S4}(J) = H(J) - G_4(J) \]

5 PRINT 7, X_1(J), G_1(J), G_2(J), G_3(J), G_4(J)

7 FORMAT(1H0F7.4, 4F10.3)

PRINT8
Calculations by Flory's method.

Programme 5

Calculations by Flory's method.

S. TR, M.EANS *, V10 AND V20 ARE THE MOLAR VOLUMES OF THE PURE COMPONENTS.

HE, VB, S AND T DENOTE EXCESS HEAT, EXCESS VOLUME, ENTROPY AT

TEMPERATURE T. RS DENOTES R1S1/R2S2 AND THETA IS EQUAL TO THETA 2

WHERE SUBSCRIPT ONE REFERS TO THE COMPONENT OTHER THAN N -ALKANE.
11 READ10
   PRINT10
10 FORMAT(49H
   PRINT100
   READ5,V1BAR,V1STR,T1STR,P1STR,V10
   READ5,V2BAR,V2STR,T2STR,P2STR,V20
   PRINT106
106 FORMAT(3X5HV1BAR,5X5HV1STR,5X5HT1STR,5X5HP1STR,5X3HV10)
   PRINT6,V1BAR,V1STR,T1STR,P1STR,V10
   PRINT100
   PRINT107
107 FORMAT(3X5HV2BAR,5X5HV2STR,5X5HT2STR,5X5HP2STR,5X3HV20)
   PRINT6,V2BAR,V2STR,T2STR,P2STR,V20
   PRINT100
   READ16,HE,RS,T
16 FORMAT(3F7.0)
   PRINT118
118 FORMAT(5X2HHE,4X9HR1S1/R2S2,1X4HTEMP)
   PRINT18,HE,RS,T
18 FORMAT(3F10.4)
PRINT100
FIE1=V1STR/(V1STR+V2STR)
FIE2=1.-FIE1
VOBAR=FIE1*V1BAR+FIE2*V2BAR
R=(FIE1*P1STR+FIE2*P2STR)
TOBAR= (FIE1*P1STR*T1STR/F1STR)+FIE2*P2STR*T/T2STR
TOBAR=TOBAR/R
THETA=1./((1.+RS)
E=((VOBAR)**(7./3.))*(TOBAR*FIE1*THETA)
S=(1.3333*VOBAR**(1./3.))*R
G=E/S
V0=(V10+V20)/2.
X=2.*HE-((P1STR*V1STR/V1BAR)+(P2STR*V2STR/V2BAR))
H=P1STR*V1STR+P2STR*V2STR
X12=(X*VOBAR+H)/(V1STR*THETA-X*G)
PRINT117
117 FORMAT(5X1HE, 10X1HS, 10X1HG, 10X1HH, 10X1HX, 10X3HX12)
PRINT17, E, S, G, H, X, X12
17 FORMAT(6F10.4)
PRINT100
PRINT15
15 FORMAT(1X$HX$SOLVENT,4X$X$HVE,6X$X$HHE,6X$X$HTS,3X$X$HTHETA2)
X1=0.1
D07I=1.9
X2=1.-X1
FIE1=X1*V1STR/(X1*V1STR+X2*V2STR)
FIE2=1.-FIE1
VOBAR=FIE1*V1BAR+FIE2*V2BAR
R=FIE1*P1STR+FIE2*P2STR
TOBAR=(FIE1*P1STR/T1STR+FIE2*P2STR/T2STR)*T/R
JHETA=1./(1.+RS*X1/X2)
V=X1*V1STR+X2*V2STR
TOBAR=TOBAR*FIE1*JHETA*X12/R
VEBAR=TOBAR*((VOBAR**7./3.))/((4./3.)-VOBAR**((1./3.)))
VE=VEBAR*V
VBAR=VOBAR+VEBAR
V3=V1BAR**((1./3.))
V4=V2BAR**((1./3.))
V5=VBAR**((1./3.)
S1 = -(3.*X1*P1STR*V1STR)/T1STR)*LOGF((V3-1.)/(V5-1.))
S2 = -(3.*X2*P2STR*V2STR)/T2STR)*LOGF((V4-1.)/(V5-1.))
S = (S1+S2)*T
H1 = X1*P1STR*V1STR*((1./V1BAR)-(1./VBAR))
H2 = X2*P2STR*V2STR*((1./V2BAR)-(1./VBAR))
HE = H1+H2+X12*X1*V1STR*THETA/VBAR
PRINT19,X1,VE,HE,S,THETA

7 X1=X1+0.1
19 FORMAT(5F8.2)

PRINT100
100 FORMAT(/)
GO TO 11
5 FORMAT(5F6.0)
6 FORMAT(5F10.4)
END

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