The Extended UNIQUAC model

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1. Introduction

This document contains the equations necessary to implement the Extended UNIQUAC thermodynamic model for electrolyte solutions[1] as an activity coefficient model. Once these equations are implemented in a computer program, they have to be combined with a gibbs energy minimization routine in order to perform speciation equilibrium calculations and phase equilibrium calculations.

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[1] Thomsen K., Rasmussen P.: "Modeling of Vapor-Liquid-Solid Equilibria in Gas - Aqueous Electrolyte Systems. Chemical Engineering Science, 54(1999) 1787-1802.

2. Residual part of the UNIQUAC gibbs excess energy function

$$\frac{ng^E_{Residual}}{RT} = -\sum_i n_i q_i \ln\left(\sum_j \theta_j \psi_{ji}\right) = -\sum_i MOL(I) \bullet QPAR(I) \bullet \ln TP(I)$$

$$TP(I) = \sum_j \theta_j \psi_{ji}$$

$$TPI(I) = \frac{1}{TP(I)}$$

$$\theta_j = \frac{n_j q_j}{\sum_l n_l q_l} = MOL(J) \bullet QPAR(J) \bullet DENQ = THETA(J)$$

$$\psi_{ji} = \exp\left(-\frac{a_{ji}}{T}\right) = \exp(-AKI \bullet TKI) = PSI(J, I)$$

$$-\frac{a_{ji}}{T} = -AKI \bullet TKI = LPSI(J, I)$$

$$a_{ji} = u_{ji} - u_{ii} = u^0_{ji} + u^t_{ji}(T - 298.15) - \left[u^0_{ii} + u^t_{ii}(T - 298.15)\right] = AKI$$

$$\left[\frac{\partial\left(\frac{ng^E_{Residual}}{RT}\right)}{\partial n_i}\right]_{T,P,n_j} = -q_i \ln TP(I) - \sum_j \frac{n_j q_j}{TP(J)}\left[\frac{\partial TP(J)}{\partial n_i}\right]_{T,P,n_j}$$

$$\left[\frac{\partial TP(J)}{\partial n_i}\right]_{T,P,n_j} = \sum_k \left(\frac{\partial \theta_k}{\partial n_i}\psi_{kj} + \theta_k \frac{\partial \psi_{kj}}{\partial n_i}\right)$$

$$\frac{\partial \psi_{kj}}{\partial n_i} = 0$$

$$\frac{\partial \theta_k}{\partial n_i} = q_i \frac{\sum_l n_l q_l - n_i q_i}{\left(\sum_l n_l q_l\right)^2} = QPAR(I) \bullet DENQ\left(1 - THETA(I)\right) \quad for\ i = k$$

$$\frac{\partial \theta_k}{\partial n_i} = q_i \frac{-n_k q_k}{\left(\sum_l n_l q_l\right)^2} = -QPAR(I) \bullet DENQ \bullet THETA(K) \quad for\ i \neq k$$

$$\left[\frac{\partial TP(J)}{\partial n_i}\right]_{T,P,n_j} = -QPAR(I)\bullet DENQ$$

$$\left(\sum_k THETA(K)\bullet PSI(K,J) - THETA(I)\bullet PSI(I,J) - (1-THETA(J))\bullet PSI(I,J)\right)$$

$$= -QPAR(I)\bullet DENQ\bullet (TP(J)-PSI(I,J))$$

$$\left[\frac{\partial\left(\frac{ng^E_{Residual}}{RT}\right)}{\partial n_i}\right]_{T,P,n_j} = -QPAR(I)\left(\ln TP(I) - \sum_j \frac{MOL(J)\bullet QPAR(J)}{TP(J)} DENQ\bullet\left(TP(J)-PSI(I,J)\right)\right)$$

$$= -QPAR(I)\left(\ln TP(I) - \sum_j \frac{THETA(J)}{TP(J)}(TP(J)-PSI(I,J))\right)$$

$$= -QPAR(I)\left(\ln TP(I) - \sum_j THETA(J) + \sum_j \frac{THETA(J)\bullet PSI(I,J)}{TP(J)}\right)$$

$$= -QPAR(I)\left(\ln TP(I) - 1 + \sum_j \frac{THETA(J)\bullet PSI(I,J)}{TP(J)}\right)$$

$$= QPAR(I)\bullet\left(1 - LNTP(I) - TPT(I)\right) = \ln\gamma_i^{\text{Residual}}$$

$$TPT(I) = \sum_j THETA(J)\bullet PSI(I,J)\bullet TPI(J)$$

3. Combinatorial part of the UNIQUAC gibbs excess energy function

$$\frac{ng^E_{Combinatorial}}{RT} = \sum_i n_i \ln\frac{\phi_i}{x_i} - \frac{z}{2}\sum_i q_i n_i \ln\frac{\phi_i}{\theta_i} = \sum_i n_i \ln\frac{n\phi_i}{n_i} - \frac{z}{2}\sum_i q_i n_i \ln\frac{\phi_i}{\theta_i} = BCO - ZCO2\bullet CCO$$

$$\phi_i = \frac{n_i r_i}{\sum_l n_l r_l} = MOL(I)\bullet RPAR(I)\bullet DENR = PHI(I)$$

$$\frac{\phi_i}{x_i} = \frac{n\phi_i}{n_i} = \frac{nr_i}{\sum_l n_l r_l} = TMOL\bullet RPAR(I)\bullet DENR = PHIT(I)$$

$$\ln(PHIT(I)) = LPHIT(I)$$

$$\left[\frac{\partial BCO}{\partial n_i}\right]_{T,P,n_j} = \ln\frac{n\phi_i}{n_i} + \sum_j n_j \frac{n_j}{n\phi_j}\frac{\partial\left(n\phi_j/n_j\right)}{\partial n_i}$$

$$\frac{\partial\left(n\phi_j/n_j\right)}{\partial n_i} = \frac{r_j}{\sum_l n_l r_l} - nr_j\frac{r_i}{\left(\sum_l n_l r_l\right)^2} = \frac{r_j}{\sum_l n_l r_l}\left(1 - \frac{nr_i}{\sum_l n_l r_l}\right) = \frac{\phi_j}{n_j}\left(1 - \frac{n\phi_i}{n_i}\right)$$

$$\left[\frac{\partial BCO}{\partial n_i}\right]_{T,P,n_j} = \ln\frac{n\phi_i}{n_i} + \sum_j n_j \frac{n_j}{n\phi_j}\frac{\phi_j}{n_j}\left(1-\frac{n\phi_i}{n_i}\right) = \ln\frac{n\phi_i}{n_i} + \sum_j \frac{n_j}{n}\left(1-\frac{n\phi_i}{n_i}\right) = \ln\frac{n\phi_i}{n_i} + 1 - \frac{n\phi_i}{n_i}$$

$$= LPHIT(I) + 1 - PHIT(I)$$

$$\frac{\partial CCO}{\partial n_i} = q_i \ln\frac{\phi_i}{\theta_i} + \sum_j q_j n_j \frac{\partial \ln(\phi_j/\theta_i)}{\partial n_i}$$

$$\frac{\phi_i}{\theta_i} = \frac{n_i r_i}{\sum_l n_l r_l}\frac{\sum_l n_l q_l}{n_i q_i} = \frac{r_i}{q_i}\frac{\sum_l n_l q_l}{\sum_l n_l r_l} = \frac{RPAR(I)\bullet DENR}{QPAR(I)\bullet DENQ} = PHTH(I)$$

$$\ln(PHTH(I)) = LPHTH(I)$$

$$\frac{\partial \ln\frac{\phi_j}{\theta_j}}{\partial n_i} = \frac{\theta_j}{\phi_j}\frac{r_j}{q_j}\left(\frac{q_i}{\sum_l n_l r_l} - \frac{r_i \sum_l n_l q_l}{\left(\sum_l n_l r_l\right)^2}\right) = \frac{\theta_j}{\phi_j}\frac{r_j}{q_j}\frac{1}{\sum_l n_l r_l}\left(q_i - r_i\frac{\sum_l n_l q_l}{\sum_l n_l r_l}\right) = \frac{\theta_j}{\phi_j}\frac{r_j}{q_j}\frac{1}{\sum_l n_l r_l}\left(q_i - q_i\frac{\phi_i}{\theta_i}\right)$$

$$= \frac{\theta_j}{\phi_j}\frac{r_j}{q_j}\frac{q_i}{\sum_l n_l r_l}\left(1-\frac{\phi_i}{\theta_i}\right) = \frac{q_i}{\sum_l n_l q_l}\left(1-\frac{\phi_i}{\theta_i}\right) = QPAR(I)\bullet DENQ(1-PHTH(I))$$

$$\frac{\partial CCO}{\partial n_i} = q_i \ln\frac{\phi_i}{\theta_i} + \sum_j q_j n_j \frac{q_i}{\sum_l n_l q_l}\left(1-\frac{\phi_i}{\theta_i}\right) = q_i \ln\frac{\phi_i}{\theta_i} + q_i\left(1-\frac{\phi_i}{\theta_i}\right)\frac{1}{\sum_l n_l q_l}\sum_j n_j q_j = q_i\left[\ln\frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i}\right]$$

$$= QPAR(I)\bullet\left(1 + LPHTH(I) - PHTH(I)\right)$$

$$\frac{\partial \frac{ng^E_{\text{Combinatorial}}}{RT}}{\partial n_i} = \ln\frac{n\phi_i}{n_i} + 1 - \frac{n\phi_i}{n_i} - \frac{z}{2}q_i\left[\ln\frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i}\right] =$$

$$= 1 + LPHIT(I) - PHIT(I) - ZCO2\bullet QPAR(I)\bullet\left[1 + LPHTH(I) - PHTH(I)\right] = \ln\gamma_i^{\text{Combinatorial}}$$

4. Excess enthalpy

$$\frac{nh^E}{R} = -T^2\left[\frac{\partial\left(ng^E/RT\right)}{\partial \mathrm{T}}\right]_{P,x} = TK^2\sum_i MOL(I)\bullet QPAR(I)\bullet TPX(I)$$

$$-\frac{h_i^E}{RT^2} = \left[\frac{\partial \ln\gamma_i^{\text{Residual}}}{\partial T}\right]_{P,n_j} = -q_i\left(\frac{\partial \ln TP(I)}{\partial T} + \frac{\partial\left(\sum_j \frac{\theta_j \psi_{ij}}{TP(J)}\right)}{\partial T}\right)$$

$$\frac{\partial TP(I)}{\partial T} = \sum_j \theta_j \cdot \frac{d\psi_{ji}}{dT} = \sum_j \theta_j \psi_{ji} \cdot \xi_{ji}$$

$$a_{ji}^t = u_{ji}^t - u_{ii}^t$$

$$\frac{d\psi_{ji}}{dT} = \psi_{ji} \cdot \left(\frac{a_{ji}}{T^2} - \frac{a_{ji}^t}{T} \right) = \psi_{ji} \cdot \left(\frac{a_{ji} - Ta_{ji}^t}{T^2} \right) = \psi_{ji} \cdot \xi_{ji}$$

$$\xi_{ji} = \frac{a_{ji} - Ta_{ji}^t}{T^2} = XI(J,I)$$

$$\frac{\partial \ln TP(I)}{\partial T} = \frac{1}{TP(I)} \frac{\partial TP(I)}{\partial T} = \frac{1}{TP(I)} \sum_j \theta_j \psi_{ji} \xi_{ji} = TPI(I) \sum_j \theta_j \psi_{ji} \xi_{ji} = TPX(I)$$

$$\frac{\partial \left(\sum_j \frac{\theta_j \psi_{ij}}{TP(J)} \right)}{\partial T} = \sum_j \left(-\frac{1}{TP(J)^2} \frac{\partial TP(J)}{\partial T} \theta_j \psi_{ij} + \frac{\theta_j \psi_{ij} \xi_{ij}}{TP(J)} \right) = \sum_j \left(-\frac{\theta_j \psi_{ij}}{TP(J)^2} \sum_k \theta_k \psi_{ki} \cdot \xi_{ki} + \frac{\theta_j \psi_{ij} \xi_{ij}}{TP(J)} \right)$$

$$= \sum_j \frac{\theta_j \psi_{ij}}{TP(J)} \left(-\frac{\sum_k \theta_k \psi_{kj} \cdot \xi_{kj}}{TP(J)} + \xi_{ij} \right)$$

$$\frac{h_i}{R} = q_i T^2 \left(\frac{\sum_k \theta_k \psi_{ki} \xi_{ki}}{TP(I)} + \sum_j \frac{\theta_j \psi_{ij}}{TP(J)} \left(\xi_{ij} - \frac{\sum_k \theta_k \psi_{kj} \cdot \xi_{kj}}{TP(J)} \right) \right)$$

$$= QPAR(I) \bullet T^2 \left(TPX(I) + \sum_j \frac{\theta_j \psi_{ij}}{TP(J)} \left(XI(I,J) - TPX(J) \right) \right)$$

$$= QPAR(I) \bullet T^2 \left(TPX(I) + TPTH(I) \right)$$

$$TPTH(I) = \sum_j \frac{\theta_j \psi_{ij}}{TP(J)} \left(XI(I,J) - TPX(J) \right) = \sum_j THETA(J) \bullet PSI(I,J) \bullet TPI(J) \bullet \left(XI(I,J) - TPX(J) \right)$$

5. Excess Heat Capacity

$$\frac{nC_p^E}{R} = \frac{d\left(nh^E / R\right)}{dT} = \frac{d}{dT} \left(T^2 \left(\sum_i MOL(I) \bullet QPAR(I) \bullet TPX(I) \right) \right)$$

$$= 2T \bullet \sum_i MOL(I) \bullet QPAR(I) \bullet TPX(I) + T^2 \sum_i MOL(I) \bullet QPAR(I) \bullet \frac{dTPX(I)}{dT}$$

$$= 2T \bullet \sum_i MOL(I) \bullet QPAR(I) \bullet TPX(I) + T^2 \sum_i MOL(I) \bullet QPAR(I) \bullet DTPX(I)$$

$$= 2 \bullet TK \frac{nh^E}{R} + TK^2 \sum_i MOL(I) \bullet QPAR(I) \bullet DTPX(I)$$

$$\frac{h_i^E}{R} = -T^2 \left[\frac{\partial \ln \gamma_i^{\text{Residual}}}{\partial T} \right]_{P,n_j}$$

$$\frac{C_{p,i}^E}{R}=\left[\frac{\partial h_i^E/R}{\partial T}\right]_{P,n_j}=-2T\left[\frac{\partial\ln\gamma_i^{\text{Residual}}}{\partial T}\right]_{P,n_j}-T^2\left[\frac{\partial^2\ln\gamma_i^{\text{Residual}}}{\partial T^2}\right]_{P,n_j}$$

$$=2T\frac{h_i^E}{RT^2}-T^2\left[\frac{\partial^2\ln\gamma_i^{\text{Residual}}}{\partial T^2}\right]_{P,n_j}=2\frac{h_i^E}{RT}-T^2\left[\frac{\partial^2\ln\gamma_i^{\text{Residual}}}{\partial T^2}\right]_{P,n_j}$$

$$-\left[\frac{\partial^2\ln\gamma_i^{\text{Residual}}}{\partial T^2}\right]_{P,n_j}=QPAR(I)\frac{\partial}{\partial T}\left(TPX(I)+\sum_J\frac{\theta_j\psi_{ij}}{TP(J)}(XI(I,J)-TPX(J)\right)$$

$$\frac{d\xi_{ji}}{dT}=-2\frac{a_{ji}}{T^3}+\frac{a_{ji}^t}{T^2}+\frac{a_{ji}^t}{T^2}=-2\frac{a_{ji}-Ta_{ji}^t}{T^3}=-2\bullet TKI\bullet XI(J,I)$$

$$\frac{\partial TPX(I)}{\partial T}=\frac{\partial}{\partial T}\left(\frac{1}{TP(I)}\sum_J\theta_j\psi_{ji}\xi_{ji}\right)$$

$$=-\frac{1}{TP(I)^2}\frac{\partial TP(I)}{\partial T}\sum_J\theta_j\psi_{ji}\xi_{ji}+\frac{1}{TP(I)}\sum_j\theta_j\left(\frac{\partial\psi_{ji}}{\partial T}\xi_{ji}+\frac{\partial\xi_{ji}}{\partial T}\psi_{ji}\right)$$

$$=-TPX(I)^2+\frac{1}{TP(I)}\sum_j\theta_j\left(\psi_{ji}\xi_{ji}^2-\frac{2}{T}\xi_{ji}\psi_{ji}\right)=-TPX(I)^2+\frac{1}{TP(I)}\sum_j\theta_j\left(\psi_{ji}\xi_{ji}\left(\xi_{ji}-\frac{2}{T}\right)\right)$$

$$=-TPX(I)^2+\frac{1}{TP(I)}\sum_j THETA(J)\left(PSI(J,I)\bullet XI(J,I)\left(XI(J,I)-2TKI\right)\right)$$

$$=-TPX(I)^2+TPI(I)\sum_j THETA(J)\left(PSI(J,I)\bullet XI(J,I)\left(XI(J,I)-2TKI\right)\right)=DTPX(I)$$

$$\frac{\partial}{\partial T}\left(\sum_j\frac{\theta_j\psi_{ij}}{TP(J)}(XI(I,J)-TPX(J))\right)$$

$$=\sum_j\left[\frac{\partial}{\partial T}\left(\frac{\theta_j\psi_{ij}}{TP(J)}\right)(XI(I,J)-TPX(J))+\frac{\theta_j\psi_{ij}}{TP(J)}\frac{\partial}{\partial T}(XI(I,J)-TPX(J))\right]$$

$$\frac{\partial}{\partial T}\left(\frac{\theta_j\psi_{ij}}{TP(J)}\right)=\sum_j\frac{\theta_j\psi_{ij}}{TP(J)}\left(XI(I,J)-TPX(J)\right)$$

$$-\left[\frac{\partial^2\ln\gamma_i^{\text{Residual}}}{\partial T^2}\right]_{P,n_j}=QPAR(I)\frac{\partial}{\partial T}\left(TPX(I)+\sum_j\frac{\theta_j\psi_{ij}}{TP(J)}(XI(I,J)-TPX(J))\right)$$

$$=QPAR(I)\left(DTPX(I)+\sum_j\left[\frac{\theta_j\psi_{ij}}{TP(J)}(XI(I,J)-TPX(J))^2+\frac{\theta_j\psi_{ij}}{TP(J)}(-2TKI\bullet XI(I,J)-DTPX(J))\right]\right)$$

$$=QPAR(I)\left(DTPX(I)+\sum_j\left[\frac{\theta_j\psi_{ij}}{TP(J)}\left((XI(I,J)-TPX(J))^2-2TKI\bullet XI(I,J)-DTPX(J)\right)\right]\right)$$

$$=QPAR(I)\left(\begin{array}{l}DTPX(I)+\\ \sum_j\left[THEATA(J)PSI(I,J)\bullet TPI(J)\bullet\left((XI(I,J)-TPX(J))^2-2TKI\bullet XI(I,J)-DTPX(J)\right)\right]\end{array}\right)$$

$$\frac{C_{p,i}^E}{R} = 2\frac{h_i^E}{RT} - T^2\left[\frac{\partial^2 \ln\gamma_i^{\text{Residual}}}{\partial T^2}\right]_{P,n_j}$$

$$= 2\frac{h_i^E}{RT} + T^2 \bullet QPAR(I) \bullet$$

$$\left(\begin{array}{l} DTPX(I) + \\ \sum_j \left[THETA(J) \bullet PSI(I,J) \bullet TPI(J) \bullet \left(\left(XI(I,J) - TPX(J) \right)^2 - 2TKI \bullet XI(I,J) - DTPX(J) \right) \right] \end{array}\right)$$

6. Composition derivatives of residual part of activity coefficients

$$\frac{\partial \ln\gamma_i^{\text{residual}}}{\partial n_j} = \frac{\partial}{\partial n_j} QPAR(I) \bullet \left(1 - LNTP(I) - TPT(I)\right)$$

$$= -QPAR(I)\left(\frac{\partial LNTP(I)}{\partial n_j} + \frac{\partial TPT(I)}{\partial n_j}\right)$$

$$\frac{\partial LNTP(I)}{\partial n_j} = \frac{1}{TP(I)}\frac{\partial TP(I)}{\partial n_j} = -\frac{1}{TP(I)} QPAR(J) \bullet DENQ \bullet (TP(I) - PSI(J,I))$$

$$= QPAR(J) \bullet DENQ\left(\frac{PSI(J,I)}{TP(I)} - 1\right)$$

$$\frac{\partial TPT(I)}{\partial n_j} = \frac{\partial}{\partial n_j}\sum_k \frac{THETA(K) \bullet PSI(I,K)}{TP(K)}$$

$$= \sum_k \left(\frac{PSI(I,K)\frac{\partial THETA(K)}{\partial n_j} TP(K) - PSI(I,K) \bullet THETA(K)\frac{\partial TP(K)}{\partial n_j}}{TP(K)^2} \right)$$

$$= \sum_k \frac{PSI(I,K)}{TP(K)^2}\left(TP(K)\frac{\partial THETA(K)}{\partial n_j} - THETA(K)\frac{\partial TP(K)}{\partial n_j} \right)$$

$$= \sum_k \frac{PSI(I,K)}{TP(K)^2} QPAR(J) \bullet THETA(K) \bullet DENQ\left(-TP(K) + TP(K) - PSI(J,K)\right)$$

$$+ \frac{PSI(I,J)}{TP(J)} QPAR(J) \bullet THETA(J) \bullet DENQ + \frac{PSI(I,J)}{TP(J)} QPAR(J) \bullet (1 - THETA(J)) \bullet DENQ$$

$$= QPAR(J) \bullet DENQ\left(\frac{PSI(I,J)}{TP(J)} - \sum_k\left(\frac{THETA(K) \bullet PSI(I,K) \bullet PSI(J,K)}{TP(K)^2}\right)\right)$$

$$\frac{\partial \ln \gamma_i^{\text{residual}}}{\partial n_j} = -QPAR(I) \bullet QPAR(J) \bullet DENQ \bullet$$

$$\left(PSI(J,I) \bullet TPI(I) - 1 + PSI(I,J) \bullet TPI(J) - \sum_k THETA(K) \bullet PSI(I,K) \bullet PSI(J,K) \bullet TPI(K)^2 \right)$$

$$\frac{\partial \ln \gamma_i^{\text{Combinatorial}}}{\partial n_j} = \frac{\partial}{\partial n_j}\left(1 + LPHIT(I) - PHIT(I) - ZCO2 \bullet QPAR(I) \bullet [1 + LPHTH(I) - PHTH(I)]\right)$$

$$\frac{\partial PHIT(I)}{n_j} = \frac{PHIT(I)}{TMOL}\left(1 - PHIT(J)\right)$$

$$\frac{\partial PHTH(I)}{n_j} = PHTH(I) \bullet QPAR(J) \bullet DENQ \bullet (1 - PHTH(J))$$

$$\frac{\partial \ln \gamma_i^{\text{Combinatorial}}}{\partial n_j} = \frac{\left(1 - PHIT(J)\right)}{TMOL} - \frac{PHIT(I)}{TMOL}\left(1 - PHIT(J)\right)$$

$$-ZCO2 \bullet QPAR(I) \bullet [QPAR(J) \bullet DENQ \bullet (1 - PHTH(J)) - PHTH(I) \bullet QPAR(J) \bullet DENQ \bullet (1 - PHTH(J))]$$

$$= \frac{\left(1 - PHIT(J)\right)}{TMOL}\left(1 - PHIT(I)\right) - ZCO2 \bullet QPAR(I) \bullet QPAR(J) \bullet DENQ \bullet (1 - PHTH(J))[1 - PHTH(I)]$$

7. Infinite dilution terms

At infinite dilution all MOL(I) different from MOL(W) are equal to zero
All THETA(I) different from THETA(W) are equal to zero THETA(W)=1

$$TP(I) = PSI(W,I)$$

$$TP(W) = PSI(W,W) = 1$$

$$\ln \gamma_i^{\mathrm{Re}\,sidual,\infty} = QPAR(I) \bullet (1 - LPSI(W,I) - PSI(I,W))$$

At infinite dilution:

$$PHIT(I) = \frac{RPAR(I)}{RPAR(W)}$$

$$PHTH(I) = \frac{RPAR(I) \bullet QPAR(W)}{QPAR(I) \bullet RPAR(W)}$$

$$\ln \gamma_i^{\text{Combinatorial},\infty} = 1 + \ln \frac{RPAR(I)}{RPAR(W)} - \frac{RPAR(I)}{RPAR(W)}$$

$$-ZCO2 \bullet QPAR(I) \bullet \left[1 + \ln \frac{RPAR(I) \bullet QPAR(W)}{QPAR(I) \bullet RPAR(W)} - \frac{RPAR(I) \bullet QPAR(W)}{QPAR(I) \bullet RPAR(W)}\right]$$

$$\frac{\partial \ln \gamma_i^{\mathrm{Re}\,sidual,\infty}}{\partial T} = -QPAR(I) \bullet (XI(W,I) + XI(I,W) \bullet PSI(I,W))$$

$$\frac{nh^{E,\infty}}{R} = TK^2 \sum_{SOLUTES} MOL(I) \cdot QPAR(I) \cdot \left(XI(W,I) + PSI(I,W) \cdot XI(I,W)\right)$$

$$-\frac{h_i^{E,\infty}}{RT^2} = \left[\frac{\partial \ln \gamma_i^{\text{Residual},\infty}}{\partial T}\right]_{P,n_j} = -QPAR(I) \cdot \left(XI(W,I) + PSI(I,W) \cdot XI(I,W)\right)$$

$$\frac{h_i^{E,\infty}}{R} = TK^2 \cdot QPAR(I) \cdot \left(XI(W,I) + PSI(I,W) \cdot XI(I,W)\right)$$

$$\frac{\partial^2 \left(\ln \gamma_i^{\text{Residual},\infty}\right)}{\partial T^2} = \frac{\partial \left(\frac{\partial \ln \gamma_i^{\text{Residual},\infty}}{\partial T}\right)}{\partial T}$$

$$= -QPAR(I) \cdot \left(\frac{\partial XI(W,I)}{\partial T} + \frac{\partial XI(I,W)}{\partial T} \cdot PSI(I,W) + XI(I,W) \cdot \frac{\partial PSI(I,W)}{\partial T}\right)$$

$$= -QPAR(I) \cdot \left(-2 \cdot TKI \cdot XI(W,I) - 2 \cdot TKI \cdot XI(I,W) \cdot PSI(I,W) + XI(I,W)^2 \cdot PSI(I,W)\right)$$

$$= QPAR(I) \cdot \left(2 \cdot TKI \cdot \left(XI(W,I) + XI(I,W) \cdot PSI(I,W)\right) - XI(I,W)^2 \cdot PSI(I,W)\right)$$

$$\frac{C_{pi}^{E\infty}}{R} = \left[\frac{\partial h_i^{E,\infty}/R}{\partial T}\right]_{P,n_j} = -2T\left[\frac{\partial \ln \gamma_i^{\text{Residual},\infty}}{\partial T}\right]_{P,n_j} - T^2\left[\frac{\partial^2 \ln \gamma_i^{\text{Residual},\infty}}{\partial T^2}\right]_{P,n_j}$$

$$= 2T\frac{h_i^{E,\infty}}{RT^2} - T^2\left[\frac{\partial^2 \ln \gamma_i^{\text{Residual},\infty}}{\partial T^2}\right]_{P,n_j} = 2\frac{h_i^{E,\infty}}{RT} - T^2\left[\frac{\partial^2 \ln \gamma_i^{\text{Residual},\infty}}{\partial T^2}\right]_{P,n_j}$$

$$= 2\frac{h_i^{E,\infty}}{RT} - TK^2 \cdot QPAR(I) \cdot \left(2 \cdot TKI \cdot \left(XI(W,I) + XI(I,W) \cdot PSI(I,W)\right) - XI(I,W)^2 \cdot PSI(I,W)\right)$$

8. The Debye-Hückel contribution

$$\frac{ng^E_{\text{Debye-Hückel}}}{RT} = -n_w M_w \frac{4A}{b^3}\left[\ln\left(1 + bI^{½}\right) - bI^{½} + \frac{b^2 I}{2}\right]$$

$$I = 0.5 \cdot \sum_{ions} m_i z_i^2$$

$$m_i = \frac{n_i}{n_w M_w}$$

$$\frac{dm_i}{dn_w} = -\frac{n_i}{\left(n_w M_w\right)^2} M_w = -\frac{n_i}{n_w^2 M_w} = -\frac{m_i}{n_w}$$

$$\frac{dI}{dn_w} = 0.5 \cdot \sum \frac{dm_i}{dn_w} z_i^2 = -0.5 \cdot \sum \frac{m_i}{n_w} z_i^2 = -\frac{0.5}{n_w}\sum_i m_i z_i^2 = -\frac{I}{n_w}$$

$$\frac{dI}{dn_i} = \frac{0.5}{n_w M_w} \cdot z_i^2$$

$$\frac{\partial\left(\frac{ng^E_{\text{Debye-Hückel}}}{RT}\right)}{\partial n_w} = -M_w \frac{4A}{b^3}\left[\ln\left(1+bI^{½}\right) - bI^{½} + \frac{b^2 I}{2}\right] - n_w M_w \frac{4A}{b^3}\left[\frac{\partial \ln\left(1+bI^{½}\right)}{\partial n_w} - b\frac{\partial I^{½}}{\partial n_w} + \frac{b^2}{2}\frac{\partial I}{\partial n_w}\right]$$

$$\frac{\partial I^{½}}{\partial n_w} = \frac{0.5}{I^{½}}\frac{\partial I}{\partial n_w} = -\frac{0.5}{I^{½}}\frac{I}{n_w} = -\frac{0.5}{n_w}I^{½}$$

$$\frac{\partial \ln\left(1+bI^{½}\right)}{\partial n_w} = \frac{b}{1+bI^{½}}\frac{\partial I^{½}}{\partial n_w} = -\frac{0.5b}{1+bI^{½}}\frac{I^{½}}{n_w}$$

$$\frac{\partial\left(\frac{ng^E_{\text{Debye-Hückel}}}{RT}\right)}{\partial n_w} = -M_w \frac{4A}{b^3}\left[\ln\left(1+bI^{½}\right) - bI^{½} + \frac{b^2 I}{2} - \frac{0.5bI^{½}}{1+bI^{½}} + 0.5bI^{½} - \frac{b^2 I}{2}\right]$$

$$= -M_w \frac{2A}{b^3}\left[2\ln\left(1+bI^{½}\right) - bI^{½} - \frac{bI^{½}}{1+bI^{½}}\right]$$

$$= -M_w \frac{2A}{b^3}\left[2\ln\left(1+bI^{½}\right) - 1 - bI^{½} + 1 - \frac{bI^{½}}{1+bI^{½}}\right]$$

$$= -M_w \frac{2A}{b^3}\left[2\ln\left(1+bI^{½}\right) - 1 - bI^{½} + \frac{1+bI^{½} - bI^{½}}{1+bI^{½}}\right]$$

$$= M_w \frac{2A}{b^3}\left[1 + bI^{½} - \frac{1}{1+bI^{½}} - 2\ln\left(1+bI^{½}\right)\right] = \ln\gamma_w^{DH}$$

$$\frac{\partial\left(\frac{ng^E_{\text{Debye-Hückel}}}{RT}\right)}{\partial n_i} = -n_w M_w \frac{4A}{b^3}\left[\frac{\partial \ln\left(1+bI^{½}\right)}{\partial n_i} - b\frac{\partial I^{½}}{\partial n_i} + \frac{b^2}{2}\frac{\partial I}{\partial n_i}\right]$$

$$\frac{\partial I^{½}}{\partial n_i} = \frac{0.5}{I^{½}}\frac{\partial I}{\partial n_i} = \frac{0.5}{I^{½}} \bullet \frac{0.5}{n_w M_w} z_i^2$$

$$\frac{\partial \ln\left(1+bI^{½}\right)}{\partial n_i} = \frac{b}{1+bI^{½}}\frac{\partial I^{½}}{\partial n_i} = \frac{b}{1+bI^{½}} \bullet \frac{0.5}{I^{½}} \bullet \frac{0.5}{n_w M_w} z_i^2$$

$$\frac{\partial\left(\frac{ng^E_{\text{Debye-Hückel}}}{RT}\right)}{\partial n_i} = -z_i^2 \frac{A}{b^3}\left[\frac{b}{1+bI^{½}} \bullet \frac{1}{I^{½}} - \frac{b}{I^{½}} + b^2\right] = -z_i^2 \frac{A}{b^2 I^{½}}\left[\frac{1}{1+bI^{½}} - 1 + bI^{½}\right]$$

$$= -z_i^2 \frac{A}{b^2 I^{½}}\left[\frac{1 - 1 - bI^{½} + bI^{½} + b^2 I}{1+bI^{½}}\right] = -z_i^2 \frac{A}{b^2 I^{½}}\left[\frac{b^2 I}{1+bI^{½}}\right] = -z_i^2 \frac{AI^{½}}{1+bI^{½}} = \ln\gamma_i^{*,DH}$$

The asterisk on γ signifies the unsymmetric mole fraction activity coefficient. The asterisk is omitted in the following due to the identity of the temperature derivatives.

Debye-Hückel contribution to excess enthalpy

$$\frac{nh^{E,DH}}{R} = -T^2\left[\frac{\partial\left(ng^E/RT\right)}{\partial \mathrm{T}}\right]_{P,x} = T^2\frac{dA}{dT}n_w M_w\frac{4}{b^3}\left[\ln\left(1+bI^{½}\right) - bI^{½} + \frac{b^2 I}{2}\right]$$

$$-\frac{h_i^{E,DH}}{RT^2} = \left[\frac{\partial \ln\gamma_i^{\mathrm{DH}}}{\partial T}\right]_{P,n_j} = -z_i^2\frac{I^{½}}{1+bI^{½}}\frac{dA}{dT}$$

$$-\frac{h_w^{E,DH}}{RT^2} = \left[\frac{\partial \ln\gamma_w^{\mathrm{DH}}}{\partial T}\right]_{P,n_j} = M_w\frac{2}{b^3}\left[1+bI^{½} - \frac{1}{1+bI^{½}} - 2\ln\left(1+bI^{½}\right)\right]\frac{dA}{dT}$$

$$A = \left[1.131 + 1.335\cdot 10^{-3}\cdot(T - 273.15) + 1.164\cdot 10^{-5}\cdot(T-273.15)^2\right]\left(kg\, mol^{-1}\right)^{½}$$

$$\frac{dA}{dT} = 1.335\bullet 10^{-3} + 2\bullet 1.164\bullet 10^{-5}T\left(kg\, mol^{-1}\right)^{½}K^{-1}$$

$$\frac{h_i^{E,DH}}{R} = T^2 z_i^2\frac{I^{½}}{1+bI^{½}}\frac{dA}{dT} = -\frac{\ln\gamma_i^{*,DH}}{A}T^2\frac{dA}{dT}$$

$$\frac{h_w^{E,DH}}{R} = -T^2 M_w\frac{2}{b^3}\left[1+bI^{½} - \frac{1}{1+bI^{½}} - 2\ln\left(1+bI^{½}\right)\right]\frac{dA}{dT} = -\frac{\ln\gamma_w^{*,DH}}{A}T^2\frac{dA}{dT}$$

Debye-Hückel contribution to excess heat capacity

$$\frac{nC_p^{E,DH}}{R} = \frac{d\left(nh^{E,DH}/R\right)}{dT} = \frac{d}{dT}\left(T^2\frac{dA}{dT}n_w M_w\frac{4}{b^3}\left[\ln\left(1+bI^{½}\right) - bI^{½} + \frac{b^2 I}{2}\right]\right)$$

$$= \left(\frac{2}{T}\frac{dA}{dT} + \frac{d^2A}{dT^2}\right)T^2 n_w M_w\frac{4}{b^3}\left[\ln\left(1+bI^{½}\right) - bI^{½} + \frac{b^2 I}{2}\right] = \left(\frac{2}{T}\frac{dA}{dT} + \frac{d^2A}{dT^2}\right)\frac{nh^{E,DH}}{R}/\frac{dA}{dT}$$

$$\frac{d^2A}{dT^2} = 2\bullet 1.164\bullet 10^{-5}\left(kg\ mol^{-1}\right)^{½}K^{-2}$$

$$\frac{C_{p,i}^{E,DH}}{R} = \left[\frac{\partial h_i^{E,DH}/R}{\partial T}\right]_{P,n_j} = -2T\left[\frac{\partial \ln\gamma_i^{\mathrm{DH}}}{\partial T}\right]_{P,n_j} - T^2\left[\frac{\partial^2 \ln\gamma_i^{\mathrm{DH}}}{\partial T^2}\right]_{P,n_j}$$

$$= 2T\frac{h_i^{E,DH}}{RT^2} - T^2\left[\frac{\partial^2 \ln\gamma_i^{\mathrm{DH}}}{\partial T^2}\right]_{P,n_j} = 2\frac{h_i^{E,DH}}{RT} - T^2\left[\frac{\partial^2 \ln\gamma_i^{\mathrm{DH}}}{\partial T^2}\right]_{P,n_j}$$

$$\left[\frac{\partial^2 \ln\gamma_i^{\mathrm{DH}}}{\partial T^2}\right]_{P,n_j} = -z_i^2\frac{I^{½}}{1+bI^{½}}\frac{d^2A}{dT^2}$$

$$\left[\frac{\partial \ln\gamma_w^{\mathrm{DH}}}{\partial T}\right]_{P,n_j} = M_w\frac{2}{b^3}\left[1+bI^{½} - \frac{1}{1+bI^{½}} - 2\ln\left(1+bI^{½}\right)\right]\frac{d^2A}{dT^2}$$

$$\frac{C_{p,i}^{E,DH}}{R} = 2\frac{h_i^{E,DH}}{RT} + T^2 z_i^2\frac{I^{½}}{1+bI^{½}}\frac{d^2A}{dT^2} = \left(\frac{2}{T} + \frac{d^2A}{dT^2}/\frac{dA}{dT}\right)\frac{h_i^{E,DH}}{RT}$$

$$\frac{C_{p,w}^{E,DH}}{R} = 2\frac{h_w^{E,DH}}{RT} - T^2 M_w\frac{2}{b^3}\left[1+bI^{½} - \frac{1}{1+bI^{½}} - 2\ln\left(1+bI^{½}\right)\right]\frac{d^2A}{dT^2} = \left(\frac{2}{T} + \frac{d^2A}{dT^2}/\frac{dA}{dT}\right)\frac{h_i^{E,DH}}{RT}$$

Composition derivatives of Debye-Hückel contribution to activity coefficients

$$\frac{\partial \ln \gamma_i^{*,DH}}{\partial n_w} = -z_i^2 A \frac{\partial}{\partial n_w} \frac{I^{½}}{1+bI^{½}} = -z_i^2 A \frac{\left(1+bI^{½}\right)\frac{\partial}{\partial n_w} I^{½} - bI^{½} \frac{\partial}{\partial n_w} I^{½}}{\left(1+bI^{½}\right)^2} = -z_i^2 A \frac{\frac{\partial}{\partial n_w} I^{½}}{\left(1+bI^{½}\right)^2}$$

$$= -z_i^2 A \frac{-\frac{0.5}{n_w} I^{½}}{\left(1+bI^{½}\right)^2} = -\frac{0.5}{\left(1+bI^{½}\right) n_w} \ln \gamma_i^{*,DH}$$

$$\frac{\partial \ln \gamma_i^{*,DH}}{\partial n_j} = -z_i^2 A \frac{\partial}{\partial n_j} \frac{I^{½}}{1+bI^{½}} = -z_i^2 A \frac{\left(1+bI^{½}\right)\frac{\partial}{\partial n_j} I^{½} - bI^{½} \frac{\partial}{\partial n_j} I^{½}}{\left(1+bI^{½}\right)^2} = -z_i^2 A \frac{\frac{\partial}{\partial n_j} I^{½}}{\left(1+bI^{½}\right)^2}$$

$$= -z_i^2 A \frac{\frac{0.5}{I^{½}} \bullet \frac{0.5}{n_w M_w} z_j^2}{\left(1+bI^{½}\right)^2} = -\frac{A z_i^2 z_j^2}{4 n_w M_w I^{½} \left(1+bI^{½}\right)^2}$$

$$\frac{\partial \ln \gamma_w^{DH}}{\partial n_w} = M_w \frac{2A}{b^3}\left[\frac{\partial}{\partial n_w}\left(1+bI^{½}\right) + \frac{1}{\left(1+bI^{½}\right)^2}\frac{\partial}{\partial n_w}\left(1+bI^{½}\right) - \frac{2}{1+bI^{½}}\frac{\partial}{\partial n_w}\left(1+bI^{½}\right)\right]$$

$$= M_w \frac{2A}{b^3}\left[1 + \frac{1}{\left(1+bI^{½}\right)^2} - \frac{2}{1+bI^{½}}\right]\frac{\partial}{\partial n_w}\left(1+bI^{½}\right) = M_w \frac{2A}{b^3}\frac{b^2 I}{\left(1+bI^{½}\right)^2} bI^{½} \frac{-1}{2n_w} = -\frac{M_w A I^{3/2}}{n_w \left(1+bI^{½}\right)^2}$$

$$\frac{\partial \ln \gamma_w^{DH}}{\partial n_j} = M_w \frac{2A}{b^3}\left[\frac{\partial}{\partial n_j}\left(1+bI^{½}\right) + \frac{1}{\left(1+bI^{½}\right)^2}\frac{\partial}{\partial n_j}\left(1+bI^{½}\right) - \frac{2}{1+bI^{½}}\frac{\partial}{\partial n_j}\left(1+bI^{½}\right)\right]$$

$$= M_w \frac{2A}{b^3}\left[1 + \frac{1}{\left(1+bI^{½}\right)^2} - \frac{2}{1+bI^{½}}\right]\frac{\partial}{\partial n_j}\left(1+bI^{½}\right) = M_w \frac{2A}{b^3}\frac{b^2 I}{\left(1+bI^{½}\right)^2} b \frac{0.5}{I^{½}} \bullet \frac{0.5}{n_w M_w} z_j^2$$

$$= \frac{A I^{½} z_j^2}{2 n_w \left(1+bI^{½}\right)^2}$$