Bowers-Helgeson Equation of State

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b)\sqrt{T}}$$

rewrite: $$z = \frac{v}{v-b} - \frac{a}{(v+b)RT\sqrt{T}}$$

$$v^3 - \frac{RT}{p}\cdot v^2 + \left(\frac{a}{p\sqrt{T}} - b^2 - \frac{bRT}{p}\right)\cdot v - \frac{ab}{p\sqrt{T}} = 0$$

$$p = \frac{n_T RT}{V - n_T b} - \frac{n_T{}^2 a}{V(V+n_T b)\sqrt{T}}$$

Mixing rules:

<u>b parameter</u>: $$b_{mix} = \left(x_{NaCl} + x_{H_2O}\right) b_{H_2O} + x_{CO_2} b_{CO_2} + x_{CH_4} b_{CH_4} + \ldots$$

$$n_T b = n_{NaCl} b_{NaCl} + n_{H_2O} b_{H_2O} + n_{CO_2} b_{CO_2} + n_{CH_4} b_{CH_4} = \sum_i n_i b_i$$

$$b_{NaCl} = b_{H_2O} = 14.6 - 0.04420283 \cdot w$$

where $$w = \left(\frac{n_{NaCl}\cdot MM_{NaCl}}{n_{H_2O}\cdot MM_{H_2O} + n_{NaCl}\cdot MM_{NaCl}}\right)\cdot 100$$

other gases: according to pseudo critical point definition

<u>a parameter</u>:

$$\begin{aligned} a_{mix} = {} & (x_{H_2O} + x_{NaCl})^2 a_{H_2O-H_2O} + (x_{CO_2})^2 a_{CO_2-CO_2} + (x_{CH_4})^2 a_{CH_4-CH_4} \\ & + 2(x_{H_2O} + x_{NaCl}) x_{CO_2} a_{H_2O-CO_2} + 2(x_{H_2O} + x_{NaCl}) x_{CH_4} a_{H_2O-CH_4} \\ & + 2 x_{CO_2} x_{CH_4} a_{CO_2-CH_4} + \ldots \end{aligned}$$

$$a_{mix} = \sum_i \sum_j x_i x_j a_{ij}$$ where: $$a_{ij} = \sqrt{a_i \cdot a_j}$$

$$\begin{aligned} n_T^2 a_{mix} = {} & (n_{NaCl})^2 a_{NaCl-NaCl} + (n_{H_2O})^2 a_{H_2O-H_2O} + (n_{CO_2})^2 a_{CO_2-CO_2} + (n_{CH_4})^2 a_{CH_4-CH_4} \\ & + 2 n_{NaCl} n_{H_2O} a_{NaCl-H_2O} + 2 n_{NaCl} n_{CO_2} a_{NaCl-CO_2} + 2 n_{NaCl} n_{CH_4} a_{NaCl-CH_4} \\ & + 2 n_{H_2O} n_{CO_2} a_{H_2O-CO_2} + 2 n_{H_2O} n_{CH_4} a_{H_2O-CH_4} + 2 n_{CO_2} n_{CH_4} a_{CO_2-CH_4} + \ldots \end{aligned}$$

where: $a_{NaCl} = a_{H_2O}$, $a_{NaCl-H_2O} = a_{H_2O}$, and $a_{NaCl-gas} = a_{H_2O-gas}$

general rule: $$n_T{}^2 a = \sum_i \sum_j n_i n_j a_{ij}$$

if i = j (pure gases)

temperature/salinity dependent parameters:

H_2O: $a_{H_2O-H_2O} = \sqrt{a_i \cdot a_j} = a_{H_2O}$

$$a_{H_2O} = 10^6 \cdot (c_0 + c_1 w) \cdot 0.101325$$

$$c_0 = 111.3057 + 50.70033 \cdot \exp\left(-9.82646 \cdot 10^{-3} T_C\right)$$

$$c_1 = -8.05658 \cdot \exp\left(-9.82646 \cdot 10^{-3} T_C\right)$$

where w is the salinity in mass%

$$w = \left(\frac{n_{NaCl} \cdot MM_{NaCl}}{n_{H_2O} \cdot MM_{H_2O} + n_{NaCl} \cdot MM_{NaCl}}\right) \cdot 100$$

CO_2: $a_{CO_2-CO_2} = \sqrt{a_i \cdot a_j} = a_{CO_2}$

$$a_{CO_2} = \left(73.03 \cdot 10^6 - 0.0714 \cdot 10^6 \cdot T_C + 21.57 \cdot T_C{}^2\right) \cdot 0.101325$$

CH_4: $a_{CH_4-CH_4} = \sqrt{a_i \cdot a_j} = a_{CH_4}$

$$a_{CH_4} = 3.12444 \cdot 10^6 - 2400.0 \cdot T_C$$

N_2: $a_{N_2-N_2} = \sqrt{a_i \cdot a_j} = a_{N_2}$

$$a_{N_2} = 1.63425 \cdot 10^6 - 5000.0 \cdot T_C$$

other gases according to pseudo critical point definition (constant value)

if i ≠ j then:

non polar - non polar $a_{ij} = \sqrt{a_i \cdot a_j}$

non polar - polar (H_2O or CO_2) $a_{ij} = \sqrt{a_i \cdot a_j^0}$

polar - polar (H_2O and CO_2) $a_{ij} = \sqrt{a_{H_2O}^0 \cdot a_{CO_2}^0} + \frac{1}{2} R^2 T^{5/2} \cdot K$

$$K = \frac{10}{1.01325} \cdot \exp\left(-11.071 + \frac{5953.0}{T} - \frac{2746 \cdot 10^3}{T^2} + \frac{464.6 \cdot 10^6}{T^3}\right)$$

H_2O: $a^0_{H_2O} = 10^6 \cdot \exp\left(c^0_0 + c^0_1 w + c^0_2 w^2 + c^0_3 w^3\right) \cdot 0.101325$

where

$$c^0_0 = 4.881243 + 1.823047 \cdot 10^{-3} T_C - 1.712269 \cdot 10^{-5} T_C{}^2 + 6.479419 \cdot 10^{-9} T_C{}^3$$

$$c^0_1 = 0.02636494 - 5.36994 \cdot 10^{-4} T_C + 2.687074 \cdot 10^{-6} T_C{}^2 - 4.321741 \cdot 10^{-9} T_C{}^3$$

$$c^0_2 = 6.802827 \cdot 10^{-3} - 9.48023 \cdot 10^{-5} T_C + 3.770339 \cdot 10^{-7} T_C{}^2 - 5.075318 \cdot 10^{-10} T_C{}^3$$

$$c^0_3 = 5.235827 \cdot 10^{-5} - 3.505272 \cdot 10^{-8} T_C$$

CO_2: $a^0_{CO_2} = 4.66095 \cdot 10^6$

other gases: according to pseudo critical point definition

Derivative Pseudo Critical Point

1. General rules

$$\frac{\partial p}{\partial v} = \frac{-RT}{(v-b)^2} + \frac{a\cdot(2v+b)}{v^2(v+b)^2\sqrt{T}} = 0$$

rewrite: $$RT\sqrt{T} = \frac{a\cdot(2v+b)\cdot(v-b)^2}{v^2(v+b)^2}$$

$$\frac{\partial^2 p}{\partial v^2} = \frac{2RT}{(v-b)^3} - \frac{2a\cdot(2v+b)^2}{v^3(v+b)^3\sqrt{T}} + \frac{2a}{v^2(v+b)^2\sqrt{T}} = 0$$

rewrite: $$RT\sqrt{T} = \frac{a\cdot(2v+b)^2\cdot(v-b)^3}{v^3(v+b)^3} - \frac{a\cdot(v-b)^3}{v^2(v+b)^2}$$

combination: $$(2v+b) = \frac{(2v+b)^2(v-b)}{v(v+b)} - (v-b)$$

$$v^3 - 3bv^2 - 3b^2v - b^3 = 0$$

Solution of cubic equation

replace: $$v = x + b$$

$$x^3 - 6b^2x - 6b^3 = 0$$

solution: $$A = \sqrt[3]{\frac{6b^3}{2} + \left(\frac{36b^6}{4} - \frac{216b^6}{27}\right)^{1/2}} = \sqrt[3]{4b^3} = 2^{2/3}b$$

$$B = \sqrt[3]{\frac{6b^3}{2} - \left(\frac{36b^6}{4} - \frac{216b^6}{27}\right)^{1/2}} = \sqrt[3]{2b^3} = 2^{1/3}b$$

$$v = A + B + b = \left(2^{2/3} + 2^{1/3} + 1\right)\cdot b = \frac{b}{\left(2^{1/3}-1\right)} \approx 3.8473\cdot b$$

2. Calculation T_{crit} (pseudo critical point)

$$RT\sqrt{T} = \frac{a\cdot(2v+b)\cdot(v-b)^2}{v^2(v+b)^2}$$

replace v: $$RT\sqrt{T} = \frac{a\cdot\left(2\frac{b}{(2^{1/3}-1)}+b\right)\cdot\left(\frac{b}{(2^{1/3}-1)}-b\right)^2}{\left(\frac{b}{(2^{1/3}-1)}\right)^2\cdot\left(\frac{b}{(2^{1/3}-1)}+b\right)^2}$$

$$RT\sqrt{T} = \frac{a\cdot\left(2^{1/3}-1\right)\cdot\left(2^{1/3}+1\right)\cdot\left(2-2^{1/3}\right)}{b\cdot\left(2^{1/3}\right)^2}$$

$$T_C = \left(2^{1/3}-1\right)^{4/3}\cdot\left(\frac{3a}{bR}\right)^{2/3}$$

3. Calculation P_{crit} (pseudo critical point)

$$p = \frac{RT}{v-b} - \frac{a_T}{v(v+b)\sqrt{T}}$$

substitution of previously obtained formulas

$$p_c = \frac{R\cdot\left(2^{1/3}-1\right)^{7/3}\cdot\left(\frac{3a}{bR}\right)^{2/3}}{b\cdot\left(2-2^{1/3}\right)} - \frac{a\cdot\left(2^{1/3}-1\right)^{4/3}}{b^2\cdot 2^{1/3}\cdot\left(\frac{3a}{bR}\right)^{1/3}}$$

$$p_c = \frac{3a\cdot\left(2^{1/3}-1\right)^{7/3}\cdot 2^{1/3} - a\cdot\left(2^{1/3}-1\right)^{4/3}\cdot\left(2-2^{1/3}\right)}{b^2\cdot\left(2-2^{1/3}\right)\cdot 2^{1/3}\cdot\left(\frac{3a}{bR}\right)^{1/3}}$$

$$p_C = \left(2^{1/3}-1\right)^{7/3}\cdot\left(\frac{a^2R}{3b^5}\right)^{1/3}$$

4. Calculation Z_{crit} (pseudo critical point)

$$Z_C = \frac{P_C V_C}{RT_C} = \frac{1}{3} \approx 0.3333$$

5. Calculation of b of pure gases

$$b = \left(2^{1/3}-1\right)\frac{RT_C}{3P_C} \approx 0.08664\frac{RT_C}{P_C}$$

6. Calculation of a of pure gases

$$a = \frac{R^2 T_C^{5/2}}{9\left(2^{1/3}-1\right)P_C} \approx 0.42748\frac{R^2 T_C^{5/2}}{P_C}$$

Thermodynamics

1. Equation of state

$$p = \frac{n_T RT}{V - n_T b} - \frac{n_T{}^2 a}{V(V + n_T b)\sqrt{T}}$$

where $$n_T{}^2 a = \left(\frac{n_T}{n_{gases}}\right)^2 \sum_i \sum_j n_i n_j a_{ij}$$

$$n_T b = \frac{n_T}{n_{gases}} \sum_i n_i b_i$$

Splitting of equation

$$p = p_{ideal} + \Delta p$$

$$p = \frac{n_T RT}{V} + \left[\frac{n_T RT}{V - n_T b} - \frac{n_T{}^2 a}{V(V + n_T b)\sqrt{T}} - \frac{n_T RT}{V}\right]$$

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2. Partial derivative to temperature

$$\frac{\partial p}{\partial T} = \frac{n_T R}{V - n_T b} + \frac{1}{V(V + n_T b)\sqrt{T}} \cdot \left[\frac{n_T{}^2 a}{2T} - \left(\frac{\partial n_T{}^2 a}{\partial T}\right)\right]$$

$$\left(\frac{\partial n_T{}^2 a}{\partial T}\right) = \sum_i \sum_j n_i n_j \frac{\partial a_{ij}}{\partial T}$$

if i=j $$\frac{\partial a_{ij}}{\partial T} = \frac{\partial a_i}{\partial T}$$

H_2O: $$\frac{\partial a_{H_2O}}{\partial T} = 10^6 \cdot \left(\frac{\partial c_0}{\partial T} + w\frac{\partial c_1}{\partial T}\right) \cdot 0.101325$$

$$\frac{\partial c_0}{\partial T} = -9.82646 \cdot 10^{-3} \cdot 50.70033 \cdot \exp\left(-9.82646 \cdot 10^{-3} T_C\right)$$

$$\frac{\partial c_1}{\partial T} = 9.82646 \cdot 10^{-3} \cdot 8.05658 \cdot \exp\left(-9.82646 \cdot 10^{-3} T_C\right)$$

CO_2: $$\frac{\partial a_{CO_2}}{\partial T} = \left(-0.0714 \cdot 10^6 + 2 \cdot 21.57 \cdot T_C\right) \cdot 0.101325$$

CH_4: $$\frac{\partial a_{CH_4}}{\partial T} = -2400.0$$

N_2: $$\frac{\partial a_{N_2}}{\partial T} = -5000.0$$

other gases: $$\frac{\partial a_{gas}}{\partial T} = 0.0$$

if i≠j non polar - non polar
$$\frac{\partial a_{ij}}{\partial T} = \frac{1}{2\sqrt{a_i \cdot a_j}} \cdot \left(a_i \frac{\partial a_j}{\partial T} + a_j \frac{\partial a_i}{\partial T} \right)$$

non polar (i) - polar (j)
$$\frac{\partial a_{ij}}{\partial T} = \frac{1}{2\sqrt{a_i \cdot a_j^0}} \cdot \left(a_j^0 \frac{\partial a_i}{\partial T} + a_i \frac{\partial a_j^0}{\partial T} \right)$$

polar (H_2O) - polar (CO_2)
$$\frac{\partial a_{ij}}{\partial T} = \frac{1}{2\sqrt{a_i^0 \cdot a_j^0}} \cdot \left(a_j^0 \frac{\partial a_i^0}{\partial T} + a_i \frac{\partial a_j^0}{\partial T} \right) + \tfrac{1}{2} R^2 \frac{\partial (T^{5/2} \cdot K)}{\partial T}$$

$$\frac{\partial \left(T^{5/2} \cdot K \right)}{\partial T} = \tfrac{5}{2} \cdot T\sqrt{T} \cdot K + T^2 \sqrt{T} \cdot \frac{\partial K}{\partial T}$$

$$\frac{\partial K}{\partial T} = \frac{10}{1.01325} \cdot \left(-\frac{5953.0}{T^2} + 2\frac{2746 \cdot 10^3}{T^3} - 3\frac{464.6 \cdot 10^6}{T^4} \right) \times \exp\left(-11.071 + \frac{5953.0}{T} - \frac{2746 \cdot 10^3}{T^2} + \frac{464.6 \cdot 10^6}{T^3} \right)$$

$$\frac{\partial a_i^0 (H_2O)}{\partial T} = 10^6 \cdot \exp\left(c_0^0 + c_1^0 w + c_2^0 w^2 + c_3^0 w^3 \right) \cdot 0.101325 \times \left(\frac{\partial c_0^0}{\partial T} + \frac{\partial c_1^0}{\partial T} w + \frac{\partial c_2^0}{\partial T} w^2 + \frac{\partial c_3^0}{\partial T} w^3 \right)$$

$$\frac{\partial c_0^0}{\partial T} = 1.823047 \cdot 10^{-3} - 2 \cdot 1.712269 \cdot 10^{-5} T_C + 3 \cdot 6.479419 \cdot 10^{-9} {T_C}^2$$

$$\frac{\partial c_1^0}{\partial T} = -5.36994 \cdot 10^{-4} + 2 \cdot 2.687074 \cdot 10^{-6} T_C - 3 \cdot 4.321741 \cdot 10^{-9} {T_C}^2$$

$$\frac{\partial c_2^0}{\partial T} = -9.48023 \cdot 10^{-5} + 2 \cdot 3.770339 \cdot 10^{-7} T_C - 3 \cdot 5.075318 \cdot 10^{-10} {T_C}^2$$

$$\frac{\partial c_3^0}{\partial T} = -3.505272 \cdot 10^{-8}$$

other gases: $$\frac{\partial a_{gas}^0}{\partial T} = 0.0$$

3. Entropy

principle equation: $$dS = \left(\frac{\partial p}{\partial T}\right)_{V,n_T} dV$$

$$dS = \left(\frac{\partial (p_{ideal} + \Delta p)}{\partial T}\right)_{V,n_T} dV$$

$$\int_{S_0}^{S_1} dS = \int_{V_0}^{V_1} \left[\frac{n_T R}{V} + \frac{n_T R}{V - n_T b} - \frac{1}{V(V + n_T b)\sqrt{T}}\left(\frac{\partial (n_T{}^2 a)}{\partial T} - \frac{n_T{}^2 a}{2T}\right) - \frac{n_T R}{V}\right] dV$$

$$\int_{S_0}^{S_1} dS = \left.\begin{pmatrix} n_T R \cdot \ln V + n_T R \cdot \ln(V - n_T b) - n_T R \cdot \ln V \\ + \left(\frac{1}{n_T b\sqrt{T}}\right) \cdot \left(\frac{\partial (n_T{}^2 a)}{\partial T} - \frac{n_T{}^2 a}{2T}\right) \cdot \ln\left(\frac{(V + n_T b)}{V}\right) \end{pmatrix}\right|_{V_0}^{V_1}$$

$$S_1 = S_0 + n_T R \cdot \ln\left(\frac{V_1}{V_0}\right) + n_T R \cdot \ln\left(\frac{(V_1 - n_T b) \cdot V_0}{(V_0 - n_T b) \cdot V_1}\right)$$
$$+ \left(\frac{1}{n_T b\sqrt{T}}\right) \cdot \left(\frac{\partial (n_T{}^2 a)}{\partial T} - \frac{n_T{}^2 a}{2T}\right) \cdot \ln\left(\frac{V_0 (V_1 + n_T b)}{V_1 (V_0 + n_T b)}\right)$$

where $$S_0 = \sum_i n_i s_{i,0}$$

$$n_T R \cdot \ln\left(\frac{V_1}{V_0}\right) = \sum_i n_i R \cdot \ln\left(\frac{p_0 V_1}{n_i R T}\right)$$

$$\lim_{V_0 \to \infty}\left[\ln\left(\frac{V_0}{V_0 + n_T b}\right)\right] = 0$$

$$S = \sum_i n_i s_{i,0} + \sum_i n_i R \cdot \ln\left(\frac{p_0 V_1}{n_i R T}\right) + n_T R \cdot \ln\left(\frac{V - n_T b}{V}\right)$$
$$+ \left(\frac{1}{n_T b\sqrt{T}}\right) \cdot \left(\frac{\partial (n_T{}^2 a)}{\partial T} - \frac{n_T{}^2 a}{2T}\right) \cdot \ln\left(\frac{V + n_T b}{V}\right)$$

4. Internal energy

principle equation: $dU = \left[T\left(\frac{\partial p}{\partial T}\right)_{V,n_T} - p\right]dV$

$$\int_{U_0}^{U_1} dU = \int_{V_0}^{V_1}\left[\frac{3n_T{}^2a}{2\sqrt{T}} - \sqrt{T}\cdot\frac{\partial(n_T{}^2a)}{\partial T}\right]\cdot\frac{1}{V(V+n_Tb)}dV$$

$$U = U_0 + \left(\frac{-1}{n_Tb}\right)\cdot\left[\frac{3n_T{}^2a}{2\sqrt{T}} - \sqrt{T}\cdot\frac{\partial(n_T{}^2a)}{\partial T}\right]\cdot\ln\left(\frac{V+n_Tb}{V}\right)$$

where $U_0 = \sum_i n_i u_{i,0}$

5. Enthalpy

principle equation: $H = U + p\cdot V$

$$H = \sum_i n_i u_{i,0} + \left(\frac{-1}{n_Tb}\right)\cdot\left[\frac{3n_T{}^2a}{2\sqrt{T}} - \sqrt{T}\cdot\frac{\partial(n_T{}^2a)}{\partial T}\right]\cdot\ln\left(\frac{V+n_Tb}{V}\right) + \frac{n_TRTV}{V-n_Tb} - \frac{n_T{}^2a}{(V+n_Tb)\sqrt{T}}$$

6. Helmholtz energy

principle equation: $A = U - TS$

$$A = \sum_i n_i\left(u_{i,0} - Ts_{i,0}\right) + \left(\frac{-1}{n_Tb}\right)\cdot\left[\frac{3n_T{}^2a}{2\sqrt{T}} - \sqrt{T}\cdot\frac{\partial(n_T{}^2a)}{\partial T}\right]\cdot\ln\left(\frac{V+n_Tb}{V}\right) - n_TRT\ln\left(\frac{V-n_Tb}{V}\right) + \left(\frac{-1}{n_Tb}\right)\cdot\left(\sqrt{T}\cdot\frac{\partial(n_T{}^2a)}{\partial T} - \frac{n_T{}^2a}{2\sqrt{T}}\right)\cdot\ln\left(\frac{V+n_Tb}{V}\right) - \sum_i\left[n_iRT\ln\left(\frac{0.1\cdot V}{n_iRT}\right)\right]$$

$$A = \sum_i n_i\left(u_{i,0} - Ts_{i,0}\right) - \frac{n_T{}^2a}{n_Tb\sqrt{T}}\ln\left(\frac{V+n_Tb}{V}\right) - n_TRT\ln\left(\frac{V-n_Tb}{V}\right) - \sum_i\left[n_iRT\ln\left(\frac{0.1\cdot V}{n_iRT}\right)\right]$$

7. Gibbs energy

principle equation: $G = A + pV$

$$G = \sum_i n_i\left(u_{i,0} - Ts_{i,0}\right) - \frac{{n_T}^2 a}{n_T b\sqrt{T}}\ln\left(\frac{V + n_T b}{V}\right) - n_T RT\ln\left(\frac{V - n_T b}{V}\right)$$
$$- \sum_i\left[n_i RT\ln\left(\frac{0.1\cdot V}{n_i RT}\right)\right] + \frac{n_T RTV}{V - n_T b} - \frac{{n_T}^2 a}{(V + n_T b)\sqrt{T}}$$

8. Chemical potential

principle equation: $\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j}$

$$\mu_i = u_{i,0} - Ts_{i,0} - \left[\frac{1}{n_T b\sqrt{T}}\cdot\left(\frac{\partial {n_T}^2 a}{\partial n_i}\right) - \frac{{n_T}^2 a}{(n_T b)^2\sqrt{T}}\cdot\left(\frac{\partial n_T b}{\partial n_i}\right)\right]\ln\left(\frac{V + n_T b}{V}\right)$$
$$- \frac{{n_T}^2 a}{n_T b\sqrt{T}}\cdot\frac{1}{\left(V + n_T b\right)}\cdot\left(\frac{\partial n_T b}{\partial n_i}\right) - RT\ln\left(\frac{V - n_T b}{V}\right) + \frac{n_T RT}{\left(V - n_T b\right)}\cdot\left(\frac{\partial n_T b}{\partial n_i}\right)$$
$$- RT\ln\left(\frac{0.1\cdot V}{n_i RT}\right) + RT$$

<u>b derivative:</u>

$$\frac{\partial(n_T b)}{\partial n_i} = \sum_p\left(\frac{\partial n_p}{\partial n_i}b_p + n_p\frac{\partial b_p}{\partial n_i}\right) \qquad \frac{\partial(n_T b)}{\partial n_i} = b_i + \sum_p\left(n_p\frac{\partial b_p}{\partial n_i}\right)$$

H_2O: $$\frac{\partial(n_T b)}{\partial n_{H_2O}} = b_{H_2O} + n_{H_2O}\cdot\frac{\partial b_{H_2O}}{\partial n_{H_2O}} + n_{NaCl}\cdot\frac{\partial b_{NaCl}}{\partial n_{H_2O}}$$

where: $$\frac{\partial b_{H_2O}}{\partial n_{H_2O}} = \frac{\partial b_{NaCl}}{\partial n_{H_2O}} = -0.04420283\cdot\frac{\partial w}{\partial n_{H_2O}}$$

where: $$\frac{\partial w}{\partial n_{H_2O}} = \frac{-MM_{H_2O}\cdot n_{NaCl}\cdot MM_{NaCl}}{\left(n_{H_2O}\cdot MM_{H_2O} + n_{NaCl}\cdot MM_{NaCl}\right)^2}\cdot 100$$

NaCl: $$\frac{\partial(n_T b)}{\partial n_{NaCl}} = b_{NaCl} + n_{NaCl}\cdot\frac{\partial b_{NaCl}}{\partial n_{NaCl}} + n_{H_2O}\cdot\frac{\partial b_{H_2O}}{\partial n_{NaCl}}$$

where: $$\frac{\partial b_{NaCl}}{\partial n_{NaCl}} = \frac{\partial b_{H_2O}}{\partial n_{NaCl}} = -0.04420283\cdot\frac{\partial w}{\partial n_{NaCl}}$$

where $$\frac{\partial w}{\partial n_{NaCl}} = \frac{MM_{NaCl}\cdot n_{H_2O}\cdot MM_{H_2O}}{\left(n_{H_2O}\cdot MM_{H_2O} + n_{NaCl}\cdot MM_{NaCl}\right)^2}\cdot 100$$

CO_2: $$\frac{\partial(n_T b)}{\partial n_{CO_2}} = b_{CO_2}$$

CH_4: $$\frac{\partial(n_T b)}{\partial n_{CH_4}} = b_{CH_4}$$

a derivative:

$$\frac{\partial(n_T{}^2 a)}{\partial n_i} = \sum_p \sum_q \left(\frac{\partial n_p}{\partial n_i} n_q + \frac{\partial n_q}{\partial n_i} n_p \right) \cdot a_{pq} + \sum_p \sum_q n_p n_q \frac{\partial a_{pq}}{\partial n_i}$$

where: $$\sum_p \sum_q \left(\frac{\partial n_p}{\partial n_i} n_q + \frac{\partial n_q}{\partial n_i} n_p \right) \cdot a_{pq} = 2 \sum_p n_p a_{ip}$$

where: $$a_{pq} = \sqrt{a_p \cdot a_q}$$

where $$\frac{\partial a_{pq}}{\partial n_i} = \frac{1}{2\sqrt{a_p a_q}} \left(\frac{\partial a_p}{\partial n_i} a_q + \frac{\partial a_q}{\partial n_i} a_p \right)$$

for example:

$$\frac{\partial(n_T{}^2 a)}{\partial n_{H_2O}} = 2n_{H_2O} \cdot a_{H_2O-H_2O} + 2n_{NaCl} \cdot a_{H_2O-NaCl} + 2n_{CO_2} \cdot a_{H_2O-CO_2} + 2n_{CH_4} \cdot a_{H_2O-CH_4} + \ldots$$

$$+ (n_{NaCl})^2 \frac{\partial a_{NaCl-NaCl}}{\partial n_{H_2O}} + (n_{H_2O})^2 \frac{\partial a_{H_2O-H_2O}}{\partial n_{H_2O}}$$

$$+ 2n_{NaCl} n_{H_2O} \frac{\partial a_{H_2O-NaCl}}{\partial n_{H_2O}} + 2n_{NaCl} n_{CO_2} \frac{\partial a_{NaCl-CO_2}}{\partial n_{H_2O}} + 2n_{H_2O} n_{CO_2} \frac{\partial a_{H_2O-CO_2}}{\partial n_{H_2O}}$$

$$+ 2n_{NaCl} n_{CH_4} \frac{\partial a_{NaCl-CH_4}}{\partial n_{H_2O}} + 2n_{H_2O} n_{CH_4} \frac{\partial a_{H_2O-CH_4}}{\partial n_{H_2O}} + \ldots$$

where: $$\frac{\partial a_{H_2O-H_2O}}{\partial n_{H_2O}} = 10^6 \cdot 0.101325 \cdot c_1 \cdot \frac{\partial w}{\partial n_{H_2O}}$$

$$\frac{\partial a_{NaCl-NaCl}}{\partial n_{H_2O}} = \frac{\partial a_{NaCl-H_2O}}{\partial n_{H_2O}} = \frac{\partial a_{H_2O-H_2O}}{\partial n_{H_2O}}$$

$$\frac{\partial a_{H_2O-CO_2}}{\partial n_{H_2O}} = \frac{a^0_{CO_2}}{2\sqrt{a^0_{H_2O} \cdot a^0_{CO_2}}} \cdot \frac{\partial a^0_{H_2O}}{\partial n_{H_2O}}$$

$$\frac{\partial a_{NaCl-CO_2}}{\partial n_{H_2O}} = \frac{\partial a_{H_2O-CO_2}}{\partial n_{H_2O}}$$

$$\frac{\partial a_{H_2O-CH_4}}{\partial n_{H_2O}} = \frac{a^0_{CH_4}}{2\sqrt{a^0_{H_2O}\cdot a^0_{CH_4}}}\cdot\frac{\partial a^0_{H_2O}}{\partial n_{H_2O}}$$

$$\frac{\partial a_{NaCl-CH_4}}{\partial n_{H_2O}} = \frac{\partial a_{H_2O-CH_4}}{\partial n_{H_2O}}$$

where:

$$\frac{\partial a^0_{H_2O}}{\partial n_{H_2O}} = 10^6\cdot\exp\left(c^0_0 + c^0_1 w + c^0_2 w^2 + c^0_3 w^3\right)\cdot 0.101325$$

$$\times\left[c^0_1 + 2\cdot c^0_2\cdot w + 3\cdot c^0_3\cdot w^2\right]\cdot\frac{\partial w}{\partial n_{H_2O}}$$

for example:

$$\frac{\partial (n_T{}^2 a)}{\partial n_{NaCl}} = 2n_{NaCl}\cdot a_{NaCl-NaCl} + 2n_{H_2O}\cdot a_{NaCl-H_2O} + 2n_{CO_2}\cdot a_{NaCl-CO_2} + 2n_{CH_4}\cdot a_{NaCl-CH_4} + \ldots$$

$$+ (n_{NaCl})^2\frac{\partial a_{NaCl-NaCl}}{\partial n_{NaCl}} + (n_{H_2O})^2\frac{\partial a_{H_2O-H_2O}}{\partial n_{NaCl}}$$

$$+ 2n_{NaCl}n_{H_2O}\frac{\partial a_{NaCl-H_2O}}{\partial n_{NaCl}} + 2n_{NaCl}n_{CO_2}\frac{\partial a_{NaCl-CO_2}}{\partial n_{NaCl}} + 2n_{H_2O}n_{CO_2}\frac{\partial a_{H_2O-CO_2}}{\partial n_{NaCl}}$$

$$+ 2n_{NaCl}n_{CH_4}\frac{\partial a_{NaCl-CH_4}}{\partial n_{NaCl}} + 2n_{H_2O}n_{CH_4}\frac{\partial a_{H_2O-CH_4}}{\partial n_{NaCl}} + \ldots$$

where: $$\frac{\partial a_{H_2O-H_2O}}{\partial n_{NaCl}} = 10^6\cdot 0.101325\cdot c_1\cdot\frac{\partial w}{\partial n_{NaCl}}$$

$$\frac{\partial a_{NaCl-NaCl}}{\partial n_{NaCl}} = \frac{\partial a_{NaCl-H_2O}}{\partial n_{NaCl}} = \frac{\partial a_{H_2O-H_2O}}{\partial n_{NaCl}}$$

$$\frac{\partial a_{H_2O-CO_2}}{\partial n_{NaCl}} = \frac{a^0_{CO_2}}{2\sqrt{a^0_{H_2O}\cdot a^0_{CO_2}}}\cdot\frac{\partial a^0_{H_2O}}{\partial n_{NaCl}}$$

$$\frac{\partial a_{NaCl-CO_2}}{\partial n_{NaCl}} = \frac{\partial a_{H_2O-CO_2}}{\partial n_{NaCl}}$$

$$\frac{\partial a_{H_2O-CH_4}}{\partial n_{NaCl}} = \frac{a^0_{CH_4}}{2\sqrt{a^0_{H_2O}\cdot a^0_{CH_4}}}\cdot\frac{\partial a^0_{H_2O}}{\partial n_{NaCl}}$$

$$\frac{\partial a_{NaCl-CH_4}}{\partial n_{NaCl}} = \frac{\partial a_{H_2O-CH_4}}{\partial n_{NaCl}}$$

where:

$$\frac{\partial a^0_{H_2O}}{\partial n_{NaCl}} = 10^6 \cdot \exp\left(c^0_0 + c^0_1 w + c^0_2 w^2 + c^0_3 w^3\right) \cdot 0.101325$$
$$\times \left[c^0_1 + 2 \cdot c^0_2 \cdot w + 3 \cdot c^0_3 \cdot w^2\right] \cdot \frac{\partial w}{\partial n_{NaCl}}$$

for example:

$$\frac{\partial (n_T{}^2 a)}{\partial n_{CO_2}} = 2n_{CO_2} \cdot a_{CO_2-CO_2} + 2n_{NaCl} \cdot a_{NaCl-CO_2} + 2n_{H_2O} \cdot a_{H_2O-CO_2} + 2n_{CH_4} \cdot a_{CO_2-CH_4} + \ldots$$

for example:

$$\frac{\partial (n_T{}^2 a)}{\partial n_{CH_4}} = 2n_{CH_4} \cdot a_{CH_4-CH_4} + 2n_{NaCl} \cdot a_{NaCl-CH_4} + 2n_{H_2O} \cdot a_{H_2O-CH_4} + 2n_{CO_2} \cdot a_{CO_2-CH_4} + \ldots$$

9. Fugacity

principle equation: $RT \ln\left(\frac{f_i}{f_i^0}\right) = \mu_i - \mu_i^0$

$$f_i^0 = x_i p \qquad \text{fugacity coefficient} \quad \varphi_i = \frac{f_i}{x_i p}$$

$$RT\, ln\left(\varphi_i\right) = -\left[\frac{1}{n_T b \sqrt{T}} \cdot \left(\frac{\partial n_T{}^2 a}{\partial n_i}\right) - \frac{n_T{}^2 a}{(n_T b)^2 \sqrt{T}} \cdot \left(\frac{\partial n_T b}{\partial n_i}\right)\right] ln\left(\frac{V + n_T b}{V}\right)$$
$$- \frac{n_T{}^2 a}{n_T b \sqrt{T}} \cdot \frac{1}{\left(V + n_T b\right)} \cdot \left(\frac{\partial n_T b}{\partial n_i}\right) - RT\, ln\left(\frac{V - n_T b}{V}\right) + \frac{n_T RT}{\left(V - n_T b\right)} \cdot \left(\frac{\partial n_T b}{\partial n_i}\right) - RT\, ln\left(\frac{V}{n_i RT}\right)$$

Derivatives of the Helmholtz energy function

Bowers-Helgeson - Helmholtz Energy

$$A(T,V,n) = A_0 - \frac{{n_T}^2 a}{n_T b\sqrt{T}} ln\left(\frac{V + n_T b}{V}\right) - n_T RT\, ln\left(\frac{V - n_T b}{V}\right) - \sum_i \left[n_i RT\, ln\left(\frac{0.1 \cdot V}{n_i RT}\right)\right]$$

where: $A_0 = \sum_i n_i\left(u_i^0 - Ts_i^0\right)$

Molar Helmholtz energy:

$$\frac{A(T,V,n_i)}{n_T} = A_m(T,V_m,x_i)$$

$$A_m = A_m(0) - \frac{a}{b\sqrt{T}} \ln\left(\frac{V_m + b}{V_m}\right) - RT\ln\left(\frac{V_m - b}{V_m}\right) - RT\sum_i \left[x_i \ln\left(\frac{0.1 \cdot V_m}{x_i RT}\right)\right]$$

$$A_m(0) = \sum_i x_i\left(u_i^0 - Ts_i^0\right)$$

1. volume

$$A_V = \left(\frac{\partial A}{\partial V}\right)_{n_i,n_j,\ldots} = \frac{{n_T}^2 a}{V\left(V + n_T b\right)\sqrt{T}} - \frac{n_T RT}{V - n_T b} \qquad (= -p)$$

Molar expression:

$$\left(\frac{\partial A}{\partial V}\right)_{n_i,n_j,\ldots} = \frac{a}{V_m\left(V_m + b\right)\sqrt{T}} - \frac{RT}{V_m - b}$$

2. volume - volume

$$A_{VV} = \left(\frac{\partial^2 A}{\partial V^2}\right)_{n_i,n_j,\ldots} = -\frac{{n_T}^2 a}{\sqrt{T}}\left[\frac{2V + n_T b}{V^2\left(V + n_T b\right)^2}\right] + \frac{n_T RT}{\left(V - n_T b\right)^2}$$

Molar expression:

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{n_i,n_j,\ldots} = \frac{1}{n_T} \cdot \left[-\frac{a}{\sqrt{T}}\left(\frac{2V_m + b}{{V_m}^2\left(V_m + b\right)^2}\right) + \frac{RT}{\left(V_m - b\right)^2}\right]$$

<u>Molar partial derivative:</u>

$$\left(\frac{\partial^2 A_m}{\partial {V_m}^2}\right)_x = -\frac{a}{\sqrt{T}}\left[\frac{2V_m + b}{{V_m}^2\left(V_m + b\right)^2}\right] + \frac{RT}{\left(V_m - b\right)^2}$$

3. amount i - amount j

$$A_{n_i n_j} = \left(\frac{\partial^2 A}{\partial n_i \partial n_j}\right)_V$$

$$\left(\frac{\partial^2 A}{\partial n_i \partial n_j}\right)_V =$$

$$\left[-\frac{\partial^2 n_T{}^2 a}{\partial n_i \partial n_j} + \frac{1}{n_T b}\left(\frac{\partial n_T b}{\partial n_j}\cdot\frac{\partial n_T{}^2 a}{\partial n_i} + \frac{\partial n_T b}{\partial n_i}\cdot\frac{\partial n_T{}^2 a}{\partial n_j}\right) + \frac{n_T{}^2 a}{n_T b}\left(\frac{\partial^2 n_T b}{\partial n_i \partial n_j} - \frac{2}{n_T b}\cdot\frac{\partial n_T b}{\partial n_i}\cdot\frac{\partial n_T b}{\partial n_j}\right)\right]$$

$$\times \frac{1}{n_T b\sqrt{T}}\cdot\ln\left(\frac{V + n_T b}{V}\right)$$

$$- \frac{1}{n_T b\sqrt{T}\left(V + n_T b\right)}\cdot\frac{\partial n_T{}^2 a}{\partial n_i}\cdot\frac{\partial n_T b}{\partial n_j} - \frac{1}{n_T b\sqrt{T}\left(V + n_T b\right)}\cdot\frac{\partial n_T{}^2 a}{\partial n_j}\cdot\frac{\partial n_T b}{\partial n_i}$$

$$+ \frac{n_T{}^2 a}{n_T b\sqrt{T}\left(V + n_T b\right)}\cdot\left[\frac{2}{n_T b}\cdot\frac{\partial n_T b}{\partial n_i}\cdot\frac{\partial n_T b}{\partial n_j} - \frac{\partial^2 n_T b}{\partial n_i \partial n_j}\right]$$

$$+ \frac{n_T{}^2 a}{n_T b\sqrt{T}\left(V + n_T b\right)^2}\cdot\frac{\partial n_T b}{\partial n_i}\cdot\frac{\partial n_T b}{\partial n_j}$$

$$+ \frac{RT}{\left(V - n_T b\right)}\cdot\left[\frac{\partial n_T b}{\partial n_i} + \frac{\partial n_T b}{\partial n_j}\right]$$

$$+ \frac{n_T RT}{\left(V - n_T b\right)}\cdot\left[\frac{\partial^2 n_T b}{\partial n_i \partial n_j} + \frac{1}{\left(V - n_T b\right)}\cdot\frac{\partial n_T b}{\partial n_i}\cdot\frac{\partial n_T b}{\partial n_j}\right]$$

$$+ \frac{RT}{n_i}\cdot\frac{\partial n_i}{\partial n_j}$$

<u>b derivatives:</u>

$$\frac{\partial^2 (n_T b)}{\partial n_i \partial n_j} = \frac{\partial b_i}{\partial n_j} + \sum_p\left(\frac{\partial n_p}{\partial n_j}\cdot\frac{\partial b_p}{\partial n_i} + n_p\cdot\frac{\partial^2 b_p}{\partial n_i \partial n_j}\right) = \frac{\partial b_i}{\partial n_j} + \frac{\partial b_j}{\partial n_i} + \sum_p\left(n_p\cdot\frac{\partial^2 b_p}{\partial n_i \partial n_j}\right)$$

for example:

$$\frac{\partial^2 (n_T b)}{(\partial n_{H_2O})^2} = 2\frac{\partial b_{H_2O}}{\partial n_{H_2O}} + n_{H_2O}\cdot\frac{\partial^2 b_{H_2O}}{(\partial n_{H_2O})^2} + n_{NaCl}\cdot\frac{\partial^2 b_{NaCl}}{(\partial n_{H_2O})^2}$$

where $\frac{\partial^2 b_{H_2O}}{(\partial n_{H_2O})^2} = \frac{\partial^2 b_{NaCl}}{(\partial n_{H_2O})^2} = -0.04420283\cdot\frac{\partial^2 w}{(\partial n_{H_2O})^2}$

where $\frac{\partial^2 w}{(\partial n_{H_2O})^2} = \frac{2\cdot(MM_{H_2O})^2\cdot n_{NaCl}\cdot MM_{NaCl}}{\left(n_{H_2O}\cdot MM_{H_2O} + n_{NaCl}\cdot MM_{NaCl}\right)^3}\cdot 100$

for example:

$$\frac{\partial^2 (n_T b)}{\partial n_{H_2O} \partial n_{NaCl}} = \frac{\partial b_{H_2O}}{\partial n_{NaCl}} + \frac{\partial b_{NaCl}}{\partial n_{H_2O}} + n_{H_2O} \cdot \frac{\partial^2 b_{H_2O}}{\partial n_{H_2O} \partial n_{NaCl}} + n_{NaCl} \cdot \frac{\partial^2 b_{NaCl}}{\partial n_{H_2O} \partial n_{NaCl}}$$

$$\text{where} \quad \frac{\partial^2 b_{H_2O}}{\partial n_{H_2O} \partial n_{NaCl}} = \frac{\partial^2 b_{NaCl}}{\partial n_{H_2O} \partial n_{NaCl}} = -0.04420283 \cdot \frac{\partial^2 w}{\partial n_{H_2O} \partial n_{NaCl}}$$

$$\text{where} \quad \frac{\partial^2 w}{\partial n_{H_2O} \partial n_{NaCl}} = \frac{MM_{H_2O} \cdot MM_{NaCl} \cdot \left(n_{NaCl} \cdot MM_{NaCl} - n_{H_2O} \cdot MM_{H_2O}\right)}{\left(n_{H_2O} \cdot MM_{H_2O} + n_{NaCl} \cdot MM_{NaCl}\right)^3} \cdot 100$$

for example:

$$\frac{\partial^2 (n_T b)}{\partial n_{NaCl} \partial n_{H_2O}} = \frac{\partial^2 (n_T b)}{\partial n_{H_2O} \partial n_{NaCl}}$$

for example:

$$\frac{\partial^2 (n_T b)}{(\partial n_{NaCl})^2} = 2 \frac{\partial b_{NaCl}}{\partial n_{NaCl}} + n_{H_2O} \cdot \frac{\partial^2 b_{H_2O}}{(\partial n_{NaCl})^2} + n_{NaCl} \cdot \frac{\partial^2 b_{NaCl}}{(\partial n_{NaCl})^2}$$

$$\text{where} \quad \frac{\partial^2 b_{H_2O}}{(\partial n_{NaCl})^2} = \frac{\partial^2 b_{NaCl}}{(\partial n_{NaCl})^2} = -0.04420283 \cdot \frac{\partial^2 w}{(\partial n_{NaCl})^2}$$

$$\text{where} \quad \frac{\partial^2 w}{(\partial n_{NaCl})^2} = \frac{-2 \cdot (MM_{NaCl})^2 \cdot n_{H_2O} \cdot MM_{H_2O}}{\left(n_{H_2O} \cdot MM_{H_2O} + n_{NaCl} \cdot MM_{NaCl}\right)^3} \cdot 100$$

for example

$$\frac{\partial^2 (n_T b)}{\partial n_{NaCl} \partial n_{CO_2}} = \frac{\partial^2 (n_T b)}{\partial n_{H_2O} \partial n_{CO_2}} = 0$$

$$\frac{\partial^2 (n_T b)}{(\partial n_{CO_2})^2} = 0$$

a derivatives:

$$\frac{\partial^2 (n_T{}^2 a)}{\partial n_i \partial n_j} = 2\sum_p \frac{\partial n_p}{\partial n_j} a_{ip} + 2\sum_p n_p \frac{\partial a_{ip}}{\partial n_j} + \sum_p \sum_q \left(\frac{\partial n_p}{\partial n_j} n_q + \frac{\partial n_q}{\partial n_j} n_p \right) \cdot \frac{\partial a_{pq}}{\partial n_i} + \sum_p \sum_q n_k n_l \cdot \frac{\partial^2 a_{pq}}{\partial n_i \partial n_j}$$

$$\frac{\partial^2 (n_T{}^2 a)}{\partial n_i \partial n_j} = 2a_{ij} + 2\sum_p n_p \frac{\partial a_{ip}}{\partial n_j} + 2\sum_p n_p \frac{\partial a_{jp}}{\partial n_i} + \sum_p \sum_q n_p n_q \cdot \frac{\partial^2 a_{pq}}{\partial n_i \partial n_j}$$

where:

$$\frac{\partial^2 a_{pq}}{\partial n_i \partial n_j} = \frac{-1}{4 a_p a_q \sqrt{a_p a_q}} \cdot \left(\frac{\partial a_p}{\partial n_i} a_q + \frac{\partial a_q}{\partial n_i} a_p \right) \cdot \left(\frac{\partial a_p}{\partial n_j} a_q + \frac{\partial a_q}{\partial n_j} a_p \right) + \frac{1}{2\sqrt{a_p a_q}} \cdot \left(\frac{\partial^2 a_p}{\partial n_i \partial n_j} a_q + \frac{\partial a_p}{\partial n_i} \cdot \frac{\partial a_q}{\partial n_j} + \frac{\partial a_q}{\partial n_i} \cdot \frac{\partial a_p}{\partial n_j} + \frac{\partial^2 a_q}{\partial n_i \partial n_j} a_p \right)$$

for example:

$$\begin{aligned}
\frac{\partial^2 (n_T{}^2 a)}{(\partial n_{H_2O})^2} = {} & 2a_{H_2O-H_2O} + \\
& 2n_{H_2O} \frac{\partial a_{H_2O-H_2O}}{\partial n_{H_2O}} + 2n_{NaCl} \frac{\partial a_{H_2O-NaCl}}{\partial n_{H_2O}} + 2n_{CO_2} \frac{\partial a_{H_2O-CO_2}}{\partial n_{H_2O}} + 2n_{CH_4} \frac{\partial a_{H_2O-CH_4}}{\partial n_{H_2O}} + \ldots \\
& 2n_{H_2O} \frac{\partial a_{H_2O-H_2O}}{\partial n_{H_2O}} + 2n_{NaCl} \frac{\partial a_{H_2O-NaCl}}{\partial n_{H_2O}} + 2n_{CO_2} \frac{\partial a_{H_2O-CO_2}}{\partial n_{H_2O}} + 2n_{CH_4} \frac{\partial a_{H_2O-CH_4}}{\partial n_{H_2O}} + \ldots \\
& (n_{NaCl})^2 \frac{\partial^2 a_{NaCl-NaCl}}{(\partial n_{H_2O})^2} + (n_{H_2O})^2 \frac{\partial^2 a_{H_2O-H_2O}}{(\partial n_{H_2O})^2} + \\
& 2n_{NaCl} n_{H_2O} \frac{\partial^2 a_{NaCl-H_2O}}{(\partial n_{H_2O})^2} + 2n_{NaCl} n_{CO_2} \frac{\partial^2 a_{NaCl-CO_2}}{(\partial n_{H_2O})^2} + 2n_{H_2O} n_{CO_2} \frac{\partial^2 a_{H_2O-CO_2}}{(\partial n_{H_2O})^2} + \\
& 2n_{NaCl} n_{CH_4} \frac{\partial^2 a_{NaCl-CH_4}}{(\partial n_{H_2O})^2} + 2n_{H_2O} n_{CH_4} \frac{\partial^2 a_{H_2O-CH_4}}{(\partial n_{H_2O})^2} + \ldots
\end{aligned}$$

where: 1. $\frac{\partial^2 a_{H_2O-H_2O}}{(\partial n_{H_2O})^2} = 10^6 \cdot 0.101325 \cdot c_1 \cdot \frac{\partial^2 w}{(\partial n_{H_2O})^2}$

$$\frac{\partial^2 a_{NaCl-NaCl}}{(\partial n_{H_2O})^2} = \frac{\partial^2 a_{H_2O-NaCl}}{(\partial n_{H_2O})^2} = \frac{\partial^2 a_{H_2O-H_2O}}{(\partial n_{H_2O})^2}$$

2.

$$\frac{\partial^2 a_{H_2O-CO_2}}{(\partial n_{H_2O})^2} = \frac{1}{2\sqrt{a^0_{H_2O}\cdot a^0_{CO_2}}}\cdot a^0_{CO_2}\frac{\partial^2 a^0_{H_2O}}{(\partial n_{H_2O})^2} - \frac{1}{4a^0_{H_2O}\cdot a^0_{CO_2}\sqrt{a^0_{H_2O}\cdot a^0_{CO_2}}}\cdot\left(a^0_{CO_2}\frac{\partial a^0_{H_2O}}{\partial n_{H_2O}}\right)^2$$

$$\frac{\partial^2 a_{NaCl-CO_2}}{(\partial n_{H_2O})^2} = \frac{\partial^2 a_{H_2O-CO_2}}{(\partial n_{H_2O})^2}$$

where:

$$\frac{\partial^2 a^0_{H_2O}}{(\partial n_{H_2O})^2} = 10^6\cdot 0.101325\cdot\exp\left(c^0_0 + c^0_1 w + c^0_2 w^2 + c^0_3 w^3\right) \times\left[\frac{\partial w}{\partial n_{H_2O}}\cdot\frac{\partial w}{\partial n_{H_2O}}\cdot\left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right)^2 + \frac{\partial^2 w}{(\partial n_{H_2O})^2}\cdot\left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right) + \frac{\partial w}{\partial n_{H_2O}}\cdot\frac{\partial w}{\partial n_{H_2O}}\cdot\left(2c^0_2 + 6c^0_3 w\right)\right]$$

3.

$$\frac{\partial^2 a_{H_2O-CH_4}}{(\partial n_{H_2O})^2} = \frac{1}{2\sqrt{a^0_{H_2O}\cdot a^0_{CH_4}}}\cdot a^0_{CH_4}\frac{\partial^2 a^0_{H_2O}}{(\partial n_{H_2O})^2} - \frac{1}{4a^0_{H_2O}\cdot a^0_{CH_4}\sqrt{a^0_{H_2O}\cdot a^0_{CH_4}}}\cdot\left(a^0_{CH_4}\frac{\partial a^0_{H_2O}}{\partial n_{H_2O}}\right)^2$$

$$\frac{\partial^2 a_{NaCl-CH_4}}{(\partial n_{H_2O})^2} = \frac{\partial^2 a_{H_2O-CH_4}}{(\partial n_{H_2O})^2}$$

for example:

$$\frac{\partial^2(n_T{}^2 a)}{\partial n_{H_2O}\partial n_{NaCl}} = 2a_{H_2O-NaCl} +$$

$$2n_{H_2O}\frac{\partial a_{H_2O-NaCl}}{\partial n_{H_2O}} + 2n_{NaCl}\frac{\partial a_{NaCl-NaCl}}{\partial n_{H_2O}} + 2n_{CO_2}\frac{\partial a_{NaCl-CO_2}}{\partial n_{H_2O}} + 2n_{CH_4}\frac{\partial a_{NaCl-CH_4}}{\partial n_{H_2O}} + \ldots$$

$$2n_{H_2O}\frac{\partial a_{H_2O-H_2O}}{\partial n_{NaCl}} + 2n_{NaCl}\frac{\partial a_{H_2O-NaCl}}{\partial n_{NaCl}} + 2n_{CO_2}\frac{\partial a_{H_2O-CO_2}}{\partial n_{NaCl}} + 2n_{CH_4}\frac{\partial a_{H_2O-CH_4}}{\partial n_{NaCl}} + \ldots$$

$$(n_{NaCl})^2\frac{\partial^2 a_{NaCl-NaCl}}{\partial n_{H_2O}\partial n_{NaCl}} + (n_{H_2O})^2\frac{\partial^2 a_{H_2O-H_2O}}{\partial n_{H_2O}\partial n_{NaCl}} +$$

$$2n_{NaCl}n_{H_2O}\frac{\partial^2 a_{NaCl-H_2O}}{\partial n_{H_2O}\partial n_{NaCl}} + 2n_{NaCl}n_{CO_2}\frac{\partial^2 a_{NaCl-CO_2}}{\partial n_{H_2O}\partial n_{NaCl}} + 2n_{H_2O}n_{CO_2}\frac{\partial^2 a_{H_2O-CO_2}}{\partial n_{H_2O}\partial n_{NaCl}} +$$

$$2n_{NaCl}n_{CH_4}\frac{\partial^2 a_{NaCl-CH_4}}{\partial n_{H_2O}\partial n_{NaCl}} + 2n_{H_2O}n_{CH_4}\frac{\partial^2 a_{H_2O-CH_4}}{\partial n_{H_2O}\partial n_{NaCl}} + \ldots$$

where: 1. $$\frac{\partial^2 a_{H_2O-H_2O}}{\partial n_{H_2O}\partial n_{NaCl}} = 10^6\cdot 0.101325\cdot c_1\cdot\frac{\partial^2 w}{\partial n_{H_2O}\partial n_{NaCl}}$$

$$\frac{\partial^2 a_{NaCl-NaCl}}{\partial n_{H_2O}\partial n_{NaCl}} = \frac{\partial^2 a_{H_2O-NaCl}}{\partial n_{H_2O}\partial n_{NaCl}} = \frac{\partial^2 a_{H_2O-H_2O}}{\partial n_{H_2O}\partial n_{NaCl}}$$

2.
$$\frac{\partial^2 a_{H_2O-CO_2}}{\partial n_{H_2O}\partial n_{NaCl}} = \frac{a^0_{CO_2}}{2\sqrt{a^0_{H_2O}\cdot a^0_{CO_2}}}\cdot\frac{\partial^2 a^0_{H_2O}}{\partial n_{H_2O}\partial n_{NaCl}} - \frac{a^0_{CO_2}}{4a^0_{H_2O}\sqrt{a^0_{H_2O}\cdot a^0_{CO_2}}}\cdot\left(\frac{\partial a^0_{H_2O}}{\partial n_{H_2O}}\right)\cdot\left(\frac{\partial a^0_{H_2O}}{\partial n_{NaCl}}\right)$$

$$\frac{\partial^2 a_{NaCl-CO_2}}{\partial n_{H_2O}\partial n_{NaCl}} = \frac{\partial^2 a_{H_2O-CO_2}}{\partial n_{H_2O}\partial n_{NaCl}}$$

where

$$\frac{\partial^2 a^0_{H_2O}}{\partial n_{H_2O}\partial n_{NaCl}} = 10^6\cdot 0.101325\cdot\exp\left(c^0_0 + c^0_1 w + c^0_2 w^2 + c^0_3 w^3\right) \times\left[\begin{array}{l}\frac{\partial w}{\partial n_{H_2O}}\cdot\left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right)^2\cdot\frac{\partial w}{\partial n_{NaCl}} \\ + \frac{\partial^2 w}{\partial n_{H_2O}\partial n_{NaCl}}\cdot\left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right) \\ + \frac{\partial w}{\partial n_{H_2O}}\cdot\frac{\partial w}{\partial n_{NaCl}}\cdot\left(2c^0_2 + 6c^0_3 w\right)\end{array}\right]$$

for example:

$$\frac{\partial^2 (n_T{}^2 a)}{(\partial n_{NaCl})^2} = 2a_{NaCl-NaCl} +$$

$$2n_{H_2O}\frac{\partial a_{H_2O-NaCl}}{\partial n_{NaCl}} + 2n_{NaCl}\frac{\partial a_{NaCl-NaCl}}{\partial n_{NaCl}} + 2n_{CO_2}\frac{\partial a_{NaCl-CO_2}}{\partial n_{NaCl}} + 2n_{CH_4}\frac{\partial a_{NaCl-CH_4}}{\partial n_{NaCl}} + \ldots$$

$$2n_{H_2O}\frac{\partial a_{H_2O-NaCl}}{\partial n_{NaCl}} + 2n_{NaCl}\frac{\partial a_{NaCl-NaCl}}{\partial n_{NaCl}} + 2n_{CO_2}\frac{\partial a_{NaCl-CO_2}}{\partial n_{NaCl}} + 2n_{CH_4}\frac{\partial a_{NaCl-CH_4}}{\partial n_{NaCl}} + \ldots$$

$$(n_{NaCl})^2\frac{\partial^2 a_{NaCl-NaCl}}{(\partial n_{NaCl})^2} + (n_{H_2O})^2\frac{\partial^2 a_{H_2O-H_2O}}{(\partial n_{NaCl})^2} +$$

$$2n_{NaCl}n_{H_2O}\frac{\partial^2 a_{NaCl-H_2O}}{(\partial n_{NaCl})^2} + 2n_{NaCl}n_{CO_2}\frac{\partial^2 a_{NaCl-CO_2}}{(\partial n_{NaCl})^2} + 2n_{H_2O}n_{CO_2}\frac{\partial^2 a_{H_2O-CO_2}}{(\partial n_{NaCl})^2} +$$

$$2n_{NaCl}n_{CH_4}\frac{\partial^2 a_{NaCl-CH_4}}{(\partial n_{NaCl})^2} + 2n_{H_2O}n_{CH_4}\frac{\partial^2 a_{H_2O-CH_4}}{(\partial n_{NaCl})^2} + \ldots$$

where: 1. $$\frac{\partial^2 a_{H_2O-H_2O}}{(\partial n_{NaCl})^2} = 10^6 \cdot 0.101325 \cdot c_1 \cdot \frac{\partial^2 w}{(\partial n_{NaCl})^2}$$

$$\frac{\partial^2 a_{NaCl-NaCl}}{(\partial n_{NaCl})^2} = \frac{\partial^2 a_{NaCl-H_2O}}{(\partial n_{NaCl})^2} = \frac{\partial^2 a_{H_2O-H_2O}}{(\partial n_{NaCl})^2}$$

2.

$$\frac{\partial^2 a_{H_2O-CO_2}}{(\partial n_{NaCl})^2} = \frac{a^0_{CO_2}}{2\sqrt{a^0_{H_2O}\cdot a^0_{CO_2}}}\cdot\frac{\partial^2 a^0_{H_2O}}{(\partial n_{NaCl})^2} - \frac{a^0_{CO_2}}{4a^0_{H_2O}\cdot\sqrt{a^0_{H_2O}\cdot a^0_{CO_2}}}\cdot\left(\frac{\partial a^0_{H_2O}}{\partial n_{NaCl}}\right)^2$$

$$\frac{\partial^2 a_{NaCl-CO_2}}{(\partial n_{NaCl})^2} = \frac{\partial^2 a_{H_2O-CO_2}}{(\partial n_{NaCl})^2}$$

where:

$$\frac{\partial^2 a^0_{H_2O}}{(\partial n_{NaCl})^2} = 10^6 \cdot 0.101325 \cdot \exp\left(c^0_0 + c^0_1 w + c^0_2 w^2 + c^0_3 w^3\right) \times \left[\frac{\partial w}{\partial n_{NaCl}}\cdot\frac{\partial w}{\partial n_{NaCl}}\cdot\left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right)^2 + \frac{\partial^2 w}{(\partial n_{NaCl})^2}\cdot\left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right) + \frac{\partial w}{\partial n_{NaCl}}\cdot\frac{\partial w}{\partial n_{NaCl}}\cdot\left(2c^0_2 + 6c^0_3 w\right)\right]$$

for example:

$$\frac{\partial^2 (n_T{}^2 a)}{\partial n_{NaCl} \partial n_{CO2}} = 2a_{NaCl-CO_2} + 2n_{NaCl} \frac{\partial a_{NaCl-CO_2}}{\partial n_{NaCl}} + 2n_{H_2O} \frac{\partial a_{H_2O-CO_2}}{\partial n_{NaCl}}$$

for example:

$$\frac{\partial^2 (n_T{}^2 a)}{(\partial n_{CO2})^2} = 2a_{CO_2-CO_2}$$

4. volume - amount i

$$A_{Vn_i} = \left(\frac{\partial^2 A}{\partial V \partial n_i} \right) \quad \text{and} \quad \left(\frac{\partial^2 A}{\partial V \partial n_i} \right)_{n_j} = \left(\frac{\partial^2 A}{\partial n_i \partial V} \right)_{n_j}$$

$$\left(\frac{\partial^2 A}{\partial V \partial n_i} \right)_{n_j} = \frac{1}{V(V + n_T b)\sqrt{T}} \cdot \frac{\partial n_T{}^2 a}{\partial n_i} - \frac{n_T{}^2 a}{V(V + n_T b)^2 \sqrt{T}} \cdot \frac{\partial n_T b}{\partial n_1}$$
$$- \frac{RT}{V - n_T b} - n_T RT \frac{1}{(V - n_T b)^2} \cdot \frac{\partial n_T b}{\partial n_i}$$

5. volume - volume - volume

$$A_{VVV} = \left(\frac{\partial^3 A}{\partial V^3} \right)_n = -\frac{2n_T RT}{(V - n_T b)^3} + \frac{2n_T{}^2 a}{V^2 (V + n_T b)^2 \sqrt{T}} \cdot \left[\frac{(2V + n_T b)^2}{V(V + n_T b)} - 1 \right]$$

6. amount i - amount j - amount k

$$A_{n_i n_j n_k} = \left(\frac{\partial^3 A}{\partial n_i \partial n_j \partial n_k} \right) = \sum_{p=1\cdots 10} dA_p$$

dA₁ =

$$\ln\left(\frac{V + n_T b}{V}\right) \cdot \left[\begin{aligned} & \frac{1}{n_T b \sqrt{T}} \cdot \left(-\frac{\partial^3 (n_T{}^2 a)}{\partial n_i \partial n_j \partial n_k} \right) \\ & + \frac{1}{(n_T b)^2 \sqrt{T}} \cdot \left(\begin{aligned} & \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial^2 (n_T{}^2 a)}{\partial n_j \partial n_k} + \frac{\partial n_T b}{\partial n_j} \cdot \frac{\partial^2 (n_T{}^2 a)}{\partial n_i \partial n_k} + \frac{\partial n_T b}{\partial n_k} \cdot \frac{\partial^2 (n_T{}^2 a)}{\partial n_i \partial n_j} \\ & + \frac{\partial (n_T{}^2 a)}{\partial n_i} \cdot \frac{\partial^2 n_T b}{\partial n_j \partial n_k} + \frac{\partial (n_T{}^2 a)}{\partial n_j} \cdot \frac{\partial^2 n_T b}{\partial n_i \partial n_k} + \frac{\partial (n_T{}^2 a)}{\partial n_k} \cdot \frac{\partial^2 n_T b}{\partial n_i \partial n_j} \\ & + n_T{}^2 a \frac{\partial^3 n_T b}{\partial n_i \partial n_j \partial n_k} \end{aligned} \right) \\ & - \frac{2}{(n_T b)^3 \sqrt{T}} \cdot \left(\begin{aligned} & \frac{\partial (n_T{}^2 a)}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_j} \cdot \frac{\partial n_T b}{\partial n_k} + \frac{\partial (n_T{}^2 a)}{\partial n_j} \cdot \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_k} + \frac{\partial (n_T{}^2 a)}{\partial n_k} \cdot \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_j} \\ & + n_T{}^2 a \cdot \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial^2 n_T b}{\partial n_j \partial n_k} + n_T{}^2 a \cdot \frac{\partial n_T b}{\partial n_j} \cdot \frac{\partial^2 n_T b}{\partial n_i \partial n_k} + n_T{}^2 a \cdot \frac{\partial n_T b}{\partial n_k} \cdot \frac{\partial^2 n_T b}{\partial n_i \partial n_j} \end{aligned} \right) \\ & + \frac{6}{(n_T b)^4 \sqrt{T}} \cdot \left(n_T{}^2 a \cdot \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_j} \cdot \frac{\partial n_T b}{\partial n_k} \right) \end{aligned} \right]$$

$dA_2 =$

$$\frac{1}{V + n_T b} \cdot \left[\begin{aligned} & - \frac{1}{n_T b \sqrt{T}} \cdot \left(\begin{aligned} & \frac{\partial^2 (n_T{}^2 a)}{\partial n_i \partial n_j} \cdot \frac{\partial n_T b}{\partial n_k} + \frac{\partial^2 (n_T{}^2 a)}{\partial n_i \partial n_k} \cdot \frac{\partial n_T b}{\partial n_j} + \frac{\partial^2 (n_T{}^2 a)}{\partial n_j \partial n_k} \cdot \frac{\partial n_T b}{\partial n_i} \\ & + \frac{\partial (n_T{}^2 a)}{\partial n_i} \cdot \frac{\partial^2 n_T b}{\partial n_j \partial n_k} + \frac{\partial (n_T{}^2 a)}{\partial n_j} \cdot \frac{\partial^2 n_T b}{\partial n_i \partial n_k} + \frac{\partial (n_T{}^2 a)}{\partial n_k} \cdot \frac{\partial^2 n_T b}{\partial n_i \partial n_j} \\ & + n_T{}^2 a \cdot \frac{\partial^3 n_T b}{\partial n_i \partial n_j \partial n_k} \end{aligned} \right) \\ & + \frac{2}{(n_T b)^2 \sqrt{T}} \cdot \left(\begin{aligned} & \frac{\partial (n_T{}^2 a)}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_j} \cdot \frac{\partial n_T b}{\partial n_k} + \frac{\partial (n_T{}^2 a)}{\partial n_j} \cdot \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_k} + \frac{\partial (n_T{}^2 a)}{\partial n_k} \cdot \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_j} \\ & + n_T{}^2 a \cdot \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial^2 n_T b}{\partial n_j \partial n_k} + n_T{}^2 a \cdot \frac{\partial n_T b}{\partial n_j} \cdot \frac{\partial^2 n_T b}{\partial n_i \partial n_k} + n_T{}^2 a \cdot \frac{\partial n_T b}{\partial n_k} \cdot \frac{\partial^2 n_T b}{\partial n_i \partial n_j} \end{aligned} \right) \\ & - \frac{6}{(n_T b)^3 \sqrt{T}} \cdot \left(n_T{}^2 a \cdot \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_j} \cdot \frac{\partial n_T b}{\partial n_k} \right) \end{aligned} \right]$$

$dA_3 =$

$$\frac{1}{(V + n_T b)^2} \cdot \left[\begin{aligned} & \frac{1}{n_T b \sqrt{T}} \cdot \left(\begin{aligned} & \frac{\partial (n_T{}^2 a)}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_j} \cdot \frac{\partial n_T b}{\partial n_k} + \frac{\partial (n_T{}^2 a)}{\partial n_j} \cdot \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_k} + \frac{\partial (n_T{}^2 a)}{\partial n_k} \cdot \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_j} \\ & + n_T{}^2 a \cdot \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial^2 n_T b}{\partial n_j \partial n_k} + n_T{}^2 a \cdot \frac{\partial n_T b}{\partial n_j} \cdot \frac{\partial^2 n_T b}{\partial n_i \partial n_k} + n_T{}^2 a \cdot \frac{\partial n_T b}{\partial n_k} \cdot \frac{\partial^2 n_T b}{\partial n_i \partial n_j} \end{aligned} \right) \\ & - \frac{3}{(n_T b)^2 \sqrt{T}} \cdot \left(n_T{}^2 a \cdot \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_j} \cdot \frac{\partial n_T b}{\partial n_k} \right) \end{aligned} \right]$$

$$dA_4 = \frac{1}{(V + n_T b)^3} \cdot \frac{-2}{n_T b \sqrt{T}} \cdot \left(n_T{}^2 a \cdot \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_j} \cdot \frac{\partial n_T b}{\partial n_k} \right)$$

$$dA_5 = \frac{RT}{V - n_T b} \cdot \left[\frac{\partial^2 n_T b}{\partial n_i \partial n_j} + \frac{\partial^2 n_T b}{\partial n_i \partial n_k} + \frac{\partial^2 n_T b}{\partial n_j \partial n_k} \right]$$

$$dA_6 = \frac{RT}{(V - n_T b)^2} \cdot \left[\frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_j} + \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_k} + \frac{\partial n_T b}{\partial n_j} \cdot \frac{\partial n_T b}{\partial n_k} \right]$$

$$dA_7 = \frac{n_T RT}{V - n_T b} \cdot \left[\frac{\partial^3 n_T b}{\partial n_i \partial n_j \partial n_k} \right]$$

$$dA_8 = \frac{n_T RT}{(V - n_T b)^2} \cdot \left[\frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial^2 n_T b}{\partial n_j \partial n_k} + \frac{\partial n_T b}{\partial n_j} \cdot \frac{\partial^2 n_T b}{\partial n_i \partial n_k} + \frac{\partial n_T b}{\partial n_k} \cdot \frac{\partial^2 n_T b}{\partial n_i \partial n_j} \right]$$

$$dA_9 = \frac{n_T RT}{(V - n_T b)^3} \cdot \left[2 \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_j} \cdot \frac{\partial n_T b}{\partial n_k} \right]$$

$$dA_{10} = \frac{RT}{n_i} \cdot \left[\frac{-1}{n_i} \cdot \frac{\partial n_i}{\partial n_j} \cdot \frac{\partial n_i}{\partial n_k} + \frac{\partial^2 n_i}{\partial n_j \partial n_k} \right]$$

if i = j = k: $dA_{10} = -\frac{RT}{n_i^2}$ else $dA_{10} = 0$

<u>b derivatives</u>

$$\frac{\partial^3 (n_T b)}{\partial n_i \partial n_j \partial n_k} = \frac{\partial^2 b_i}{\partial n_j \partial n_k} + \frac{\partial^2 b_j}{\partial n_i \partial n_k} + \sum_p \left(\frac{\partial n_p}{\partial n_k} \cdot \frac{\partial^2 b_p}{\partial n_i \partial n_j} + n_p \cdot \frac{\partial^3 b_p}{\partial n_i \partial n_j \partial n_k} \right)$$

$$\frac{\partial^3 (n_T b)}{\partial n_i \partial n_j \partial n_k} = \frac{\partial^2 b_i}{\partial n_j \partial n_k} + \frac{\partial^2 b_j}{\partial n_i \partial n_k} + \frac{\partial^2 b_k}{\partial n_i \partial n_j} + \sum_p \left(n_p \cdot \frac{\partial^3 b_p}{\partial n_i \partial n_j \partial n_k} \right)$$

for example:

$$\frac{\partial^3 (n_T b)}{(\partial n_{H_2O})^3} = 3 \frac{\partial^2 b_{H_2O}}{(\partial n_{H_2O})^2} + n_{H_2O} \cdot \frac{\partial^3 b_{H_2O}}{(\partial n_{H_2O})^3} + n_{NaCl} \cdot \frac{\partial^3 b_{NaCl}}{(\partial n_{H_2O})^3}$$

where: $\frac{\partial^3 b_{H_2O}}{(\partial n_{H_2O})^3} = \frac{\partial^3 b_{NaCl}}{(\partial n_{H_2O})^3} = -0.04420283 \cdot \frac{\partial^3 w}{(\partial n_{H_2O})^3}$

where: $\frac{\partial^3 w}{(\partial n_{H_2O})^3} = \frac{-6 \cdot (MM_{H_2O})^3 \cdot n_{NaCl} MM_{NaCl}}{\left(n_{H_2O} MM_{H_2O} + n_{NaCl} MM_{NaCl} \right)^4} \cdot 100$

for example:

$$\frac{\partial^3 (n_T b)}{(\partial n_{H_2O})^2 \partial n_{NaCl}} = 2 \frac{\partial^2 b_{H_2O}}{\partial n_{H_2O} \partial n_{NaCl}} + \frac{\partial^2 b_{H_2O}}{(\partial n_{H_2O})^2} + n_{H_2O} \cdot \frac{\partial^3 b_{H_2O}}{(\partial n_{H_2O})^2 \partial n_{NaCl}} + n_{NaCl} \cdot \frac{\partial^3 b_{NaCl}}{(\partial n_{H_2O})^2 \partial n_{NaCl}}$$

$$\text{where: } \frac{\partial^3 b_{H_2O}}{(\partial n_{H_2O})^2 \partial n_{NaCl}} = \frac{\partial^3 b_{NaCl}}{(\partial n_{H_2O})^2 \partial n_{NaCl}} = -0.04420283 \cdot \frac{\partial^3 w}{(\partial n_{H_2O})^2 \partial n_{NaCl}}$$

$$\text{where: } \frac{\partial^3 w}{(\partial n_{H_2O})^2 \partial n_{NaCl}} = \frac{(MM_{H_2O})^2 \cdot MM_{NaCl} \cdot \left(2n_{H_2O}MM_{H_2O} - 4n_{NaCl}MM_{NaCl}\right)}{\left(n_{H_2O}MM_{H_2O} + n_{NaCl}MM_{NaCl}\right)^4} \cdot 100$$

for example:

$$\frac{\partial^3 (n_T b)}{\partial n_{NaCl}(\partial n_{H_2O})^2} = \frac{\partial^3 (n_T b)}{\partial n_{H_2O} \partial n_{NaCl} \partial n_{H_2O}} = \frac{\partial^3 (n_T b)}{(\partial n_{H_2O})^2 \partial n_{NaCl}}$$

for example:

$$\frac{\partial^3 (n_T b)}{\partial n_{H_2O}(\partial n_{NaCl})^2} = 2\frac{\partial^2 b_{H_2O}}{\partial n_{H_2O} \partial n_{NaCl}} + \frac{\partial^2 b_{H_2O}}{(\partial n_{NaCl})^2} + n_{H_2O} \cdot \frac{\partial^3 b_{H_2O}}{\partial n_{H_2O}(\partial n_{NaCl})^2} + n_{NaCl} \cdot \frac{\partial^3 b_{NaCl}}{\partial n_{H_2O}(\partial n_{NaCl})^2}$$

$$\text{where: } \frac{\partial^3 b_{H_2O}}{\partial n_{H_2O}(\partial n_{NaCl})^2} = \frac{\partial^3 b_{NaCl}}{\partial n_{H_2O}(\partial n_{NaCl})^2} = -0.04420283 \cdot \frac{\partial^3 w}{\partial n_{H_2O}(\partial n_{NaCl})^2}$$

$$\text{where: } \frac{\partial^3 w}{\partial n_{H_2O}(\partial n_{NaCl})^2} = \frac{MM_{H_2O} \cdot (MM_{NaCl})^2 \cdot \left(4n_{H_2O}MM_{H_2O} - 2n_{NaCl}MM_{NaCl}\right)}{\left(n_{H_2O}MM_{H_2O} + n_{NaCl}MM_{NaCl}\right)^4} \cdot 100$$

for example:

$$\frac{\partial^3 n_T b}{(\partial n_{NaCl})^2 \partial n_{H_2O}} = \frac{\partial^3 n_T b}{\partial n_{NaCl} \partial n_{H_2O} \partial n_{NaCl}} = \frac{\partial^3 n_T b}{\partial n_{H_2O}(\partial n_{NaCl})^2}$$

for example:

$$\frac{\partial^3 (n_T b)}{(\partial n_{NaCl})^3} = 3\frac{\partial^2 b_{H_2O}}{(\partial n_{NaCl})^2} + n_{H_2O} \cdot \frac{\partial^3 b_{H_2O}}{(\partial n_{NaCl})^3} + n_{NaCl} \cdot \frac{\partial^3 b_{NaCl}}{(\partial n_{NaCl})^3}$$

$$\text{where: } \frac{\partial^3 b_{H_2O}}{(\partial n_{NaCl})^3} = \frac{\partial^3 b_{NaCl}}{(\partial n_{NaCl})^3} = -0.04420283 \cdot \frac{\partial^3 w}{(\partial n_{NaCl})^3}$$

$$\text{where: } \frac{\partial^3 w}{(\partial n_{NaCl})^3} = \frac{6 \cdot (MM_{NaCl})^3 \cdot n_{H_2O}MM_{H_2O}}{\left(n_{H_2O}MM_{H_2O} + n_{NaCl}MM_{NaCl}\right)^4} \cdot 100$$

<u>a derivatives</u>

$$\frac{\partial^3 (n_T{}^2 a)}{\partial n_i \partial n_j \partial n_k} = 2\cdot\left(\frac{\partial a_{ij}}{\partial n_k} + \frac{\partial a_{ik}}{\partial n_j} + \frac{\partial a_{jk}}{\partial n_i}\right) + 2\sum_p n_p \frac{\partial^2 a_{ip}}{\partial n_j \partial n_k} + 2\sum_p n_p \frac{\partial^2 a_{jp}}{\partial n_i \partial n_k} + 2\sum_p n_p \frac{\partial^2 a_{kp}}{\partial n_i \partial n_j} + \sum_p \sum_q n_p n_q \frac{\partial^3 a_{pq}}{\partial n_i \partial n_j \partial n_k}$$

where:

$$\begin{aligned}\frac{\partial^3 a_{pq}}{\partial n_i \partial n_j \partial n_k} = {} & \tfrac{3}{8}\left(a_p \cdot a_q\right)^{-5/2}\cdot \prod_{z=i,j,k}\left(\frac{\partial a_p}{\partial n_z}\cdot a_q + \frac{\partial a_q}{\partial n_z}\cdot a_p\right) \\
& - \tfrac{1}{4}\left(a_p \cdot a_q\right)^{-3/2}\cdot \left[\begin{aligned} & \left(\frac{\partial a_p}{\partial n_i}\cdot a_q + \frac{\partial a_q}{\partial n_i}\cdot a_p\right)\cdot\left[\frac{\partial^2 a_p}{\partial n_j \partial n_k} a_q + \frac{\partial a_p}{\partial n_j}\frac{\partial a_q}{\partial n_k} + \frac{\partial a_p}{\partial n_k}\frac{\partial a_q}{\partial n_j} + \frac{\partial^2 a_q}{\partial n_j \partial n_k} a_p\right] \\
+ & \left(\frac{\partial a_p}{\partial n_j}\cdot a_q + \frac{\partial a_q}{\partial n_j}\cdot a_p\right)\cdot\left[\frac{\partial^2 a_p}{\partial n_i \partial n_k} a_q + \frac{\partial a_p}{\partial n_i}\frac{\partial a_q}{\partial n_k} + \frac{\partial a_p}{\partial n_k}\frac{\partial a_q}{\partial n_i} + \frac{\partial^2 a_q}{\partial n_i \partial n_k} a_p\right] \\
+ & \left(\frac{\partial a_p}{\partial n_k}\cdot a_q + \frac{\partial a_q}{\partial n_k}\cdot a_p\right)\cdot\left[\frac{\partial^2 a_p}{\partial n_i \partial n_j} a_q + \frac{\partial a_p}{\partial n_i}\frac{\partial a_q}{\partial n_j} + \frac{\partial a_p}{\partial n_j}\frac{\partial a_q}{\partial n_i} + \frac{\partial^2 a_q}{\partial n_i \partial n_j} a_p\right]\end{aligned}\right] \\
& + \tfrac{1}{2}\left(a_p \cdot a_q\right)^{-1/2}\cdot \left[\begin{aligned} & \frac{\partial^3 a_p}{\partial n_i \partial n_j \partial n_k} a_q + \frac{\partial^3 a_q}{\partial n_i \partial n_j \partial n_k} a_p \\
+ & \frac{\partial^2 a_p}{\partial n_i \partial n_j}\cdot\frac{\partial a_q}{\partial n_k} + \frac{\partial^2 a_p}{\partial n_i \partial n_k}\cdot\frac{\partial a_q}{\partial n_j} + \frac{\partial^2 a_p}{\partial n_j \partial n_k}\cdot\frac{\partial a_q}{\partial n_i} \\
+ & \frac{\partial^2 a_q}{\partial n_i \partial n_j}\cdot\frac{\partial a_p}{\partial n_k} + \frac{\partial^2 a_q}{\partial n_i \partial n_k}\cdot\frac{\partial a_p}{\partial n_j} + \frac{\partial^2 a_q}{\partial n_j \partial n_k}\cdot\frac{\partial a_p}{\partial n_i}\end{aligned}\right]\end{aligned}$$

and $\dfrac{\partial^3 (n_T{}^2 a)}{\partial n_i \partial n_j \partial n_k} = \dfrac{\partial^3 (n_T{}^2 a)}{\partial n_j \partial n_i \partial n_k} = \dfrac{\partial^3 (n_T{}^2 a)}{\partial n_j \partial n_k \partial n_i}$

for example:

$$\frac{\partial^3(n_T{}^2 a)}{(\partial n_{H_2O})^3} = 6\frac{\partial a_{H_2O-H_2O}}{\partial n_{H_2O}}$$

$$+ 6\cdot\left[n_{H_2O}\frac{\partial^2 a_{H_2O-H_2O}}{(\partial n_{H_2O})^2} + n_{NaCl}\frac{\partial^2 a_{NaCl-H_2O}}{(\partial n_{H_2O})^2} + n_{CO_2}\frac{\partial^2 a_{H_2O-CO_2}}{(\partial n_{H_2O})^2} + n_{CH_4}\frac{\partial^2 a_{H_2O-CH_4}}{(\partial n_{H_2O})^2} + \ldots\right]$$

$$+ (n_{NaCl})^2\frac{\partial^3 a_{NaCl-NaCl}}{(\partial n_{H_2O})^3} + (n_{H_2O})^2\frac{\partial^3 a_{H_2O-H_2O}}{(\partial n_{H_2O})^3}$$

$$+ 2n_{NaCl}n_{H_2O}\frac{\partial^3 a_{NaCl-H_2O}}{(\partial n_{H_2O})^3} + 2n_{NaCl}n_{CO_2}\frac{\partial^3 a_{NaCl-CO_2}}{(\partial n_{H_2O})^3} + 2n_{NaCl}n_{CH_4}\frac{\partial^3 a_{NaCl-CH_4}}{(\partial n_{H_2O})^3}$$

$$+ 2n_{H_2O}n_{CO_2}\frac{\partial^3 a_{H_2O-CO_2}}{(\partial n_{H_2O})^3} + 2n_{H_2O}n_{CH_4}\frac{\partial^3 a_{H_2O-CH_4}}{(\partial n_{H_2O})^3} + \ldots$$

where: 1. $\frac{\partial^3 a_{H_2O-H_2O}}{(\partial n_{H_2O})^3} = 10^6\cdot 0.101325\cdot c_1\cdot\frac{\partial^3 w}{(\partial n_{H_2O})^3}$

and $\frac{\partial^3 a_{NaCl-NaCl}}{(\partial n_{H_2O})^3} = \frac{\partial^3 a_{NaCl-H_2O}}{(\partial n_{H_2O})^3} = \frac{\partial^3 a_{H_2O-H_2O}}{(\partial n_{H_2O})^3}$

2.

$$\frac{\partial^3 a_{H_2O-CO_2}}{(\partial n_{H_2O})^3} = \frac{3}{8\cdot(a^0_{H_2O}\cdot a^0_{CO_2})^{5/2}}\cdot\left(\frac{\partial a^0_{H_2O}}{\partial n_{H_2O}}\cdot a^0_{CO_2}\right)^3$$

$$- \frac{3}{4\cdot(a^0_{H_2O}\cdot a^0_{CO_2})^{3/2}}\cdot\frac{\partial a^0_{H_2O}}{\partial n_{H_2O}}\cdot a^0_{CO_2}\cdot\frac{\partial^2 a^0_{H_2O}}{(\partial n_{H_2O})^2}\cdot a^0_{CO_2}$$

$$+ \frac{1}{2\cdot\sqrt{a^0_{H_2O}\cdot a^0_{CO_2}}}\cdot\frac{\partial^3 a^0_{H_2O}}{(\partial n_{H_2O})^3}\cdot a^0_{CO_2}$$

and $\frac{\partial^3 a_{NaCl-CO_2}}{(\partial n_{H_2O})^3} = \frac{\partial^3 a_{H_2O-CO_2}}{(\partial n_{H_2O})^3}$

where:

$$\frac{\partial^3 a^0_{H_2O}}{(\partial n_{H_2O})^3} = 10^6\cdot 0.101325\cdot\exp\left(c^0_0 + c^0_1 w + c^0_2 w^2 + c^0_3 w^3\right)$$

$$\times\left[\begin{array}{l}\left(\frac{\partial w}{\partial n_{H_2O}}\right)^3\cdot\left[\begin{array}{l}\left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right)^3 + 3\cdot\left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right)\cdot\left(2c^0_2 + 6c^0_3 w\right)\\ + 6c^0_3\end{array}\right]\\ + \frac{\partial w}{\partial n_{H_2O}}\cdot\frac{\partial^2 w}{(\partial n_{H_2O})^2}\cdot\left[3\cdot\left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right)^2 + 3\cdot\left(2c^0_2 + 6c^0_3 w\right)\right]\\ + \frac{\partial^3 w}{(\partial n_{H_2O})^3}\cdot\left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right)\end{array}\right]$$

for example:

$$\frac{\partial^3(n_T{}^2 a)}{(\partial n_{H_2O})^2 \partial n_{NaCl}} = 2\cdot\left[\frac{\partial a_{H_2O-H_2O}}{\partial n_{NaCl}} + 2\frac{\partial a_{NaCl-H_2O}}{\partial n_{H_2O}}\right]$$
$$+ 4\cdot\left[n_{NaCl}\frac{\partial^2 a_{NaCl-H_2O}}{\partial n_{H_2O}\partial n_{NaCl}} + n_{H_2O}\frac{\partial^2 a_{H_2O-H_2O}}{\partial n_{H_2O}\partial n_{NaCl}} + n_{CO_2}\frac{\partial^2 a_{H_2O-CO_2}}{\partial n_{H_2O}\partial n_{NaCl}} + n_{CH_4}\frac{\partial^2 a_{H_2O-CH_4}}{\partial n_{H_2O}\partial n_{NaCl}} + \ldots\right]$$
$$+ 2\cdot\left[n_{NaCl}\frac{\partial^2 a_{NaCl-NaCl}}{(\partial n_{H_2O})^2} + n_{H_2O}\frac{\partial^2 a_{NaCl-H_2O}}{(\partial n_{H_2O})^2} + n_{CO_2}\frac{\partial^2 a_{NaCl-CO_2}}{(\partial n_{H_2O})^2} + n_{CH_4}\frac{\partial^2 a_{NaCl-CH_4}}{(\partial n_{H_2O})^2} + \ldots\right]$$
$$+ (n_{NaCl})^2\frac{\partial^3 a_{NaCl-NaCl}}{(\partial n_{H_2O})^2\partial n_{NaCl}} + (n_{H_2O})^2\frac{\partial^3 a_{H_2O-H_2O}}{(\partial n_{H_2O})^2\partial n_{NaCl}}$$
$$+ 2n_{NaCl}n_{H_2O}\frac{\partial^3 a_{NaCl-H_2O}}{(\partial n_{H_2O})^2\partial n_{NaCl}} + 2n_{NaCl}n_{CO_2}\frac{\partial^3 a_{NaCl-CO_2}}{(\partial n_{H_2O})^2\partial n_{NaCl}} + 2n_{H_2O}n_{CO_2}\frac{\partial^3 a_{H_2O-CO_2}}{(\partial n_{H_2O})^2\partial n_{NaCl}}$$
$$+ 2n_{NaCl}n_{CH_4}\frac{\partial^3 a_{NaCl-CH_4}}{(\partial n_{H_2O})^2\partial n_{NaCl}} + 2n_{H_2O}n_{CH_4}\frac{\partial^3 a_{H_2O-CH_4}}{(\partial n_{H_2O})^2\partial n_{NaCl}} + \ldots$$

and: $$\frac{\partial^3(n_T{}^2 a)}{(\partial n_{H_2O})^2\partial n_{NaCl}} = \frac{\partial^3(n_T{}^2 a)}{\partial n_{H_2O}\partial n_{NaCl}\partial n_{H_2O}} = \frac{\partial^3(n_T{}^2 a)}{\partial n_{NaCl}(\partial n_{H_2O})^2}$$

where: 1. $$\frac{\partial^3 a_{H_2O-H_2O}}{(\partial n_{H_2O})^2\partial n_{NaCl}} = 10^6\cdot 0.101325\cdot c_1\cdot\frac{\partial^3 w}{(\partial n_{H_2O})^2\partial n_{NaCl}}$$

and $$\frac{\partial^3 a_{NaCl-NaCl}}{(\partial n_{H_2O})^2\partial n_{NaCl}} = \frac{\partial^3 a_{NaCl-H_2O}}{(\partial n_{H_2O})^2\partial n_{NaCl}} = \frac{\partial^3 a_{H_2O-H_2O}}{(\partial n_{H_2O})^2\partial n_{NaCl}}$$

2.
$$\frac{\partial^3 a_{H_2O-CO_2}}{(\partial n_{H_2O})^2\partial n_{NaCl}} = \frac{3}{8\cdot\left(a^0_{H_2O}\cdot a^0_{CO_2}\right)^{5/2}}\cdot\left(\frac{\partial a^0_{H_2O}}{\partial n_{H_2O}}a^0_{CO_2}\right)^2\cdot\left(\frac{\partial a^0_{H_2O}}{\partial n_{NaCl}}a^0_{CO_2}\right)$$
$$-\frac{1}{4\cdot\left(a^0_{H_2O}\cdot a^0_{CO_2}\right)^{3/2}}\cdot\left[2\frac{\partial a^0_{H_2O}}{\partial n_{H_2O}}a^0_{CO_2}\cdot\frac{\partial^2 a^0_{H_2O}}{\partial n_{H_2O}\partial n_{NaCl}}a^0_{CO_2} + \frac{\partial a^0_{H_2O}}{\partial n_{NaCl}}a^0_{CO_2}\cdot\frac{\partial^2 a^0_{H_2O}}{(\partial n_{H_2O})^2}a^0_{CO_2}\right]$$
$$+\frac{1}{2\cdot\sqrt{a^0_{H_2O}\cdot a^0_{CO_2}}}\cdot\frac{\partial^3 a^0_{H_2O}}{(\partial n_{H_2O})^2\partial n_{NaCl}}a^0_{CO_2}$$

and $$\frac{\partial^3 a_{NaCl-CO_2}}{(\partial n_{H_2O})^2\partial n_{NaCl}} = \frac{\partial^3 a_{H_2O-CO_2}}{(\partial n_{H_2O})^2\partial n_{NaCl}}$$

where

$$\frac{\partial^3 a^0_{H_2O}}{(\partial n_{H_2O})^2 \partial n_{NaCl}} = 10^6 \cdot 0.101325 \cdot \exp\left(c^0_0 + c^0_1 w + c^0_2 w^2 + c^0_3 w^3\right)$$

$$\times \left[\begin{array}{l} \dfrac{\partial^3 w}{(\partial n_{H_2O})^2 \partial n_{NaCl}} \left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right) \\ + \dfrac{\partial^2 w}{(\partial n_{H_2O})^2} \cdot \dfrac{\partial w}{\partial n_{NaCl}} \left[\left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right)^2 + \left(2c^0_2 + 6c^0_3 w\right)\right] \\ + 2 \dfrac{\partial^2 w}{\partial n_{H_2O} \partial n_{NaCl}} \cdot \dfrac{\partial w}{\partial n_{H_2O}} \left[\left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right)^2 + \left(2c^0_2 + 6c^0_3 w\right)\right] \\ + \left(\dfrac{\partial w}{\partial n_{H_2O}}\right)^2 \cdot \dfrac{\partial w}{\partial n_{NaCl}} \left[\begin{array}{l} \left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right)^3 \\ + 3 \cdot \left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right) \cdot \left(2c^0_2 + 6c^0_3 w\right) \\ + 6c^0_3 \end{array} \right] \end{array} \right]$$

for example:

$$\frac{\partial^3 (n_T{}^2 a)}{(\partial n_{H_2O})(\partial n_{NaCl})^2} = 2 \cdot \left[\frac{\partial a_{NaCl-NaCl}}{\partial n_{H_2O}} + 2 \frac{\partial a_{NaCl-H_2O}}{\partial n_{NaCl}} \right]$$

$$+ 4 \cdot \left[n_{NaCl} \frac{\partial^2 a_{NaCl-NaCl}}{\partial n_{H_2O} \partial n_{NaCl}} + n_{H_2O} \frac{\partial^2 a_{NaCl-H_2O}}{\partial n_{H_2O} \partial n_{NaCl}} + n_{CO_2} \frac{\partial^2 a_{NaCl-CO_2}}{\partial n_{H_2O} \partial n_{NaCl}} + n_{CH_4} \frac{\partial^2 a_{NaCl-CH_4}}{\partial n_{H_2O} \partial n_{NaCl}} + \ldots \right]$$

$$+ 2 \cdot \left[n_{NaCl} \frac{\partial^2 a_{NaCl-H_2O}}{(\partial n_{NaCl})^2} + n_{H_2O} \frac{\partial^2 a_{H_2O-H_2O}}{(\partial n_{NaCl})^2} + n_{CO_2} \frac{\partial^2 a_{H_2O-CO_2}}{(\partial n_{NaCl})^2} + n_{CH_4} \frac{\partial^2 a_{H_2O-CH_4}}{(\partial n_{NaCl})^2} + \ldots \right]$$

$$+ (n_{NaCl})^2 \frac{\partial^3 a_{NaCl-NaCl}}{\partial n_{H_2O} (\partial n_{NaCl})^2} + (n_{H_2O})^2 \frac{\partial^3 a_{H_2O-H2O}}{\partial n_{H_2O} (\partial n_{NaCl})^2}$$

$$+ 2 n_{NaCl} n_{H_2O} \frac{\partial^3 a_{NaCl-H_2O}}{\partial n_{H_2O} (\partial n_{NaCl})^2} + 2 n_{NaCl} n_{CO_2} \frac{\partial^3 a_{NaCl-CO_2}}{\partial n_{H_2O} (\partial n_{NaCl})^2} + 2 n_{H_2O} n_{CO_2} \frac{\partial^3 a_{H_2O-CO_2}}{\partial n_{H_2O} (\partial n_{NaCl})^2}$$

$$+ 2 n_{NaCl} n_{CH_4} \frac{\partial^3 a_{NaCl-CH_4}}{\partial n_{H_2O} (\partial n_{NaCl})^2} + 2 n_{H_2O} n_{CH_4} \frac{\partial^3 a_{H_2O-CH_4}}{\partial n_{H_2O} (\partial n_{NaCl})^2} + \ldots$$

and: $$\frac{\partial^3 (n_T{}^2 a)}{\partial n_{H_2O} (\partial n_{NaCl})^2} = \frac{\partial^3 (n_T{}^2 a)}{\partial n_{NaCl} \partial n_{H_2O} \partial n_{NaCl}} = \frac{\partial^3 (n_T{}^2 a)}{(\partial n_{NaCl})^2 \partial n_{H_2O}}$$

where: 1. $$\frac{\partial^3 a_{H_2O-H_2O}}{\partial n_{H_2O} (\partial n_{NaCl})^2} = 10^6 \cdot 0.101325 \cdot c_1 \cdot \frac{\partial^3 w}{\partial n_{H_2O} (\partial n_{NaCl})^2}$$

and $$\frac{\partial^3 a_{NaCl-NaCl}}{\partial n_{H_2O} (\partial n_{NaCl})^2} = \frac{\partial^3 a_{NaClH_2O}}{\partial n_{H_2O} (\partial n_{NaCl})^2} = \frac{\partial^3 a_{H_2O-H_2O}}{\partial n_{H_2O} (\partial n_{NaCl})^2}$$

2.

$$\frac{\partial^3 a_{H_2O-CO_2}}{\partial n_{H_2O}(\partial n_{NaCl})^2} = \frac{3}{8\cdot\left(a^0_{H_2O}\cdot a^0_{CO_2}\right)^{5/2}}\cdot\left(\frac{\partial a^0_{H_2O}}{\partial n_{H_2O}}a^0_{CO_2}\right)\cdot\left(\frac{\partial a^0_{H_2O}}{\partial n_{NaCl}}a^0_{CO_2}\right)^2$$

$$-\frac{1}{4\cdot\left(a^0_{H_2O}\cdot a^0_{CO_2}\right)^{3/2}}\cdot\left[2\frac{\partial a^0_{H_2O}}{\partial n_{NaCl}}a^0_{CO_2}\cdot\frac{\partial^2 a^0_{H_2O}}{\partial n_{H_2O}\partial n_{NaCl}}a^0_{CO_2}+\frac{\partial a^0_{H_2O}}{\partial n_{H_2O}}a^0_{CO_2}\cdot\frac{\partial^2 a^0_{H_2O}}{(\partial n_{NaCl})^2}a^0_{CO_2}\right]$$

$$+\frac{1}{2\cdot\sqrt{a^0_{H_2O}\cdot a^0_{CO_2}}}\cdot\frac{\partial^3 a^0_{H_2O}}{\partial n_{H_2O}(\partial n_{NaCl})^2}a^0_{CO_2}$$

and $\frac{\partial^3 a_{NaCl-CO_2}}{\partial n_{H_2O}(\partial n_{NaCl})^2} = \frac{\partial^3 a_{H_2O-CO_2}}{\partial n_{H_2O}(\partial n_{NaCl})^2}$

where

$$\frac{\partial^3 a^0_{H_2O}}{\partial n_{H_2O}(\partial n_{NaCl})^2} = 10^6\cdot 0.101325\cdot\exp\left(c^0_0+c^0_1 w+c^0_2 w^2+c^0_3 w^3\right)$$

$$\times\left[\begin{array}{l}\frac{\partial^3 w}{\partial n_{H_2O}(\partial n_{NaCl})^2}\left(c^0_1+2c^0_2 w+3c^0_3 w^2\right)\\ +\frac{\partial^2 w}{(\partial n_{NaCl})^2}\cdot\frac{\partial w}{\partial n_{H_2O}}\left[\left(c^0_1+2c^0_2 w+3c^0_3 w^2\right)^2+\left(2c^0_2+6c^0_3 w\right)\right]\\ +2\frac{\partial^2 w}{\partial n_{H_2O}\partial n_{NaCl}}\cdot\frac{\partial w}{\partial n_{NaCl}}\left[\left(c^0_1+2c^0_2 w+3c^0_3 w^2\right)^2+\left(2c^0_2+6c^0_3 w\right)\right]\\ +\left(\frac{\partial w}{\partial n_{NaCl}}\right)^2\cdot\frac{\partial w}{\partial n_{H_2O}}\left[\begin{array}{l}\left(c^0_1+2c^0_2 w+3c^0_3 w^2\right)^3\\ +3\cdot\left(c^0_1+2c^0_2 w+3c^0_3 w^2\right)\cdot\left(2c^0_2+6c^0_3 w\right)\\ +6c^0_3\end{array}\right]\end{array}\right]$$

for example:

$$\frac{\partial^3(n_T{}^2 a)}{(\partial n_{NaCl})^3} = 6\frac{\partial a_{NaCl-NaCl}}{\partial n_{NaCl}}$$

$$+\ 6\cdot\left[n_{NaCl}\frac{\partial^2 a_{NaCl-NaCl}}{(\partial n_{NaCl})^2}+n_{H_2O}\frac{\partial^2 a_{H_2O-NaCl}}{(\partial n_{NaCl})^2}+n_{CO_2}\frac{\partial^2 a_{NaCl-CO_2}}{(\partial n_{NaCl})^2}+n_{CH_4}\frac{\partial^2 a_{NaCl-CH_4}}{(\partial n_{NaCl})^2}+\ldots\right]$$

$$+\ (n_{NaCl})^2\frac{\partial^3 a_{NaCl-NaCl}}{(\partial n_{NaCl})^3}+(n_{H_2O})^2\frac{\partial^3 a_{H_2O-H_2O}}{(\partial n_{NaCl})^3}$$

$$+\ 2n_{NaCl}n_{H_2O}\frac{\partial^3 a_{NaCl-H_2O}}{(\partial n_{NaCl})^3}+2n_{NaCl}n_{CO_2}\frac{\partial^3 a_{NaCl-CO_2}}{(\partial n_{NaCl})^3}+2n_{NaCl}n_{CH_4}\frac{\partial^3 a_{NaCl-CH_4}}{(\partial n_{NaCl})^3}$$

$$+\ 2n_{H_2O}n_{CO_2}\frac{\partial^3 a_{H_2O-CO_2}}{(\partial n_{NaCl})^3}+2n_{H_2O}n_{CH_4}\frac{\partial^3 a_{H_2O-CH_4}}{(\partial n_{NaCl})^3}+\ \ldots$$

where: 1. $$\frac{\partial^3 a_{H_2O-H_2O}}{(\partial n_{NaCl})^3} = 10^6 \cdot 0.101325 \cdot c_1 \cdot \frac{\partial^3 w}{(\partial n_{NaCl})^3}$$

and $$\frac{\partial^3 a_{NaCl-NaCl}}{(\partial n_{NaCl})^3} = \frac{\partial^3 a_{NaCl-H_2O}}{(\partial n_{NaCl})^3} = \frac{\partial^3 a_{H_2O-H_2O}}{(\partial n_{NaCl})^3}$$

2.
$$\frac{\partial^3 a_{H_2O-CO_2}}{(\partial n_{NaCl})^3} = \frac{3}{8 \cdot (a^0_{H_2O} \cdot a^0_{CO_2})^{5/2}} \cdot \left(\frac{\partial a^0_{H_2O}}{\partial n_{NaCl}} \cdot a^0_{CO_2} \right)^3 - \frac{3}{4 \cdot (a^0_{H_2O} \cdot a^0_{CO_2})^{3/2}} \cdot \frac{\partial a^0_{H_2O}}{\partial n_{NaCl}} \cdot a^0_{CO_2} \cdot \frac{\partial^2 a^0_{H_2O}}{(\partial n_{NaCl})^2} \cdot a^0_{CO_2} + \frac{1}{2 \cdot \sqrt{a^0_{H_2O} \cdot a^0_{CO_2}}} \cdot \frac{\partial^3 a^0_{H_2O}}{(\partial n_{NaCl})^3} \cdot a^0_{CO_2}$$

and $$\frac{\partial^3 a_{NaCl-CO_2}}{(\partial n_{NaCl})^3} = \frac{\partial^3 a_{H_2O-CO_2}}{(\partial n_{NaCl})^3}$$

where:
$$\frac{\partial^3 a^0_{H_2O}}{(\partial n_{NaCl})^3} = 10^6 \cdot 0.101325 \cdot \exp\left(c^0_0 + c^0_1 w + c^0_2 w^2 + c^0_3 w^3\right) \times \left[\begin{array}{l} \left(\frac{\partial w}{\partial n_{NaCl}} \right)^3 \cdot \left[\begin{array}{l} \left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right)^3 + 3 \cdot \left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right) \cdot \left(2c^0_2 + 6c^0_3 w\right) \\ + 6c^0_3 \end{array} \right] \\ + \frac{\partial w}{\partial n_{NaCl}} \cdot \frac{\partial^2 w}{(\partial n_{NaCl})^2} \cdot \left[3 \cdot \left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right)^2 + 3 \cdot \left(2c^0_2 + 6c^0_3 w\right) \right] \\ + \frac{\partial^3 w}{(\partial n_{NaCl})^3} \cdot \left(c^0_1 + 2c^0_2 w + 3c^0_3 w^2\right) \end{array} \right]$$

for example:
$$\frac{\partial^3 (n_T{}^2 a)}{(\partial n_{NaCl})^2 \partial n_{CO_2}} = 4 \frac{\partial a_{NaCl-CO_2}}{\partial n_{NaCl}} + 2n_{NaCl} \frac{\partial^2 a_{NaCl-CO_2}}{(\partial n_{NaCl})^2} + 2n_{H_2O} \frac{\partial^2 a_{H_2O-CO_2}}{(\partial n_{NaCl})^2}$$

for example:
$$\frac{\partial^3 (n_T{}^2 a)}{(\partial n_{H_2O})^2 \partial n_{CO_2}} = 4 \frac{\partial a_{H_2O-CO_2}}{\partial n_{H_2O}} + 2n_{NaCl} \frac{\partial^2 a_{NaCl-CO_2}}{(\partial n_{H_2O})^2} + 2n_{H_2O} \frac{\partial^2 a_{H_2O-CO_2}}{(\partial n_{H_2O})^2}$$

for example:
$$\frac{\partial^3 (n_T{}^2 a)}{\partial n_{NaCl} \partial_{H_2O} \partial n_{CO_2}} = 2 \frac{\partial a_{NaCl-CO_2}}{\partial n_{H_2O}} + 2 \frac{\partial a_{H_2O-CO_2}}{\partial n_{NaCl}} + 2n_{NaCl} \frac{\partial^2 a_{NaCl-CO_2}}{\partial n_{NaCl} \partial n_{H_2O}} + 2n_{H_2O} \frac{\partial^2 a_{H_2O-CO_2}}{\partial n_{NaCl} \partial n_{H_2O}}$$

7. amount i - volume - volume

$$A_{n_i VV} = \left(\frac{\partial^3 A}{\partial n_i \partial V^2}\right)$$

$$\left(\frac{\partial^3 A}{\partial n_i \partial V^2}\right) = -\frac{1}{\sqrt{T}} \cdot \left(\frac{2V + n_T b}{V^2 (V + n_T b)^2}\right) \cdot \frac{\partial (n_T{}^2 a)}{\partial n_i} + \frac{1}{\sqrt{T}} \cdot \frac{(3V + n_t b) \cdot n_T{}^2 a}{V^2 (V + n_T b)^3} \cdot \frac{\partial n_T b}{\partial n_i}$$

$$+ \left[\frac{1}{(V - n_T b)^2} + \frac{2 n_T}{(V - n_T b)^3} \cdot \frac{\partial n_T b}{\partial n_i}\right] \cdot RT$$

8. amount i - amount j - volume

$$A_{n_i n_j V} = \left(\frac{\partial^3 A}{\partial n_i \partial n_j \partial V}\right)$$

$$\left(\frac{\partial^3 A}{\partial n_i \partial n_j \partial V}\right) =$$

$$\left[-\frac{\partial^2 (n_T{}^2 a)}{\partial n_i \partial n_j} + \frac{1}{n_T b}\left(\frac{\partial n_T b}{\partial n_j} \cdot \frac{\partial n_T{}^2 a}{\partial n_i} + \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T{}^2 a}{\partial n_j}\right) + \frac{n_T{}^2 a}{n_T b}\left(\frac{\partial^2 (n_T b)}{\partial n_i \partial n_j} - \frac{2}{n_T b} \cdot \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_j}\right)\right]$$

$$\times \frac{-1}{V (V + n_T b) \sqrt{T}}$$

$$+ \frac{1}{n_T b \sqrt{T} (V + n_T b)^2} \cdot \frac{\partial n_T{}^2 a}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_j} + \frac{1}{n_T b \sqrt{T} (V + n_T b)^2} \cdot \frac{\partial n_T{}^2 a}{\partial n_j} \cdot \frac{\partial n_T b}{\partial n_i}$$

$$- \frac{n_T{}^2 a}{n_T b \sqrt{T} (V + n_T b)^2} \cdot \left(\frac{2}{n_T b} \cdot \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_j} - \frac{\partial^2 (n_T b)}{\partial n_i \partial n_j}\right)$$

$$- \frac{2 n_T{}^2 a}{n_T b \sqrt{T} (V + n_T b)^3} \cdot \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_j}$$

$$- \frac{RT}{(V - n_T b)^2} \cdot \left(\frac{\partial n_T b}{\partial n_i} + \frac{\partial n_T b}{\partial n_j}\right)$$

$$- \frac{n_T RT}{(V - n_T b)^2} \cdot \frac{\partial^2 (n_T b)}{\partial n_i \partial n_j} - \frac{2 n_T RT}{(V - n_T b)^3} \cdot \frac{\partial n_T b}{\partial n_i} \cdot \frac{\partial n_T b}{\partial n_j}$$