Thermodynamic Reference Database

Final Report of Phase II [01.10.2009 – 31.03.2013]

“Oceanic Salt Systems and Carbonates”

Prof. Dr. Wolfgang Voigt

Dipl. - Chem. Dmitry Sukhanov

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1 Zusammenfassung

Ziel der Projektphase II von THEREDA war die Einbindung von CO_2 und den Carbonaten, um entsprechende Lösegleichgewichte bei CO_2 – drucken bis 300 bar und Temperaturen bis 110 °C berechnen zu können. Die besondere Herausforderung bestand darin, die gekoppelten Abhängigkeiten von Druck und Temperatur kompatibel in die bereits bestehende thermodynamische Datenbasis zu implementieren und die Anwendbarkeit für die geochemischen Zielcodes PHREEQS, CHEMAPP und EQ3/6 zu sichern. Eine notwendige Bedingung für die Beschreibung von Lösegleichgewichten mit CO_2 unter Drucken bis 300 bar und Temperaturen zwischen 0 °C bis ca. 110 °C ist die Verwendung einer Zustandsgleichung, die die Fugazität (wirksame Drucke) des CO_2 in diesem Parameterbereich mit hinreichender Genauigkeit beschreibt. Die in der Literatur publizierten Modelle deckten entweder völlig andere T – p – Bereiche ab oder basierten auf Gleichungsformen, die für die obengenannten Zielcodes nicht verarbeitbar sind. Es wurden daher unter Zuhilfenahme experimenteller pVT–Daten von CO_2 die Modelle von TSONOPOULOS sowie SPYCHER – REED für den hier vorgesehenen T – p – Bereich angepasst und getestet. Details sind in den „Technischen Reports“

- TP “Calculation of fugacities for $H_2O(g)$”
- TP “Fugacity – CO_2“
- TP “H_2O - CO_2“

dargelegt.

Für die Löslichkeit des CO_2 in Wasser und Salzlösungen wurden die Henry – konstante als Funktion der Temperatur sowie die Säurekonstanten für das THEREDA - System umformuliert und die Beschreibungsgüte anhand verfügbarer experimenteller Daten überprüft.

Die Wirkung von NaCl (Aussalzeffekt) auf die Löslichkeit von CO_2 über den gesamten T – p – Bereich konnte erfolgreich beschrieben werden.

Hierbei wurden entsprechende Wechselwirkungskoeffizienten zwischen gelöstem CO_2 und den Ionen Na^+ und Cl^- als Funktion der Temperatur eingeführt.

Schließlich konnten auch die Löslichkeit von Calcit in Abhängigkeit von Temperatur, CO_2 -Druck und NaCl-Gehalt erfolgreich in die Datenbasis eingebaut werden.

Die Einbeziehung der leichtlöslichen Alkalimetallcarbonate gelang bisher nur für das System NaCl – Na_2CO_3 – H_2O über den angestrebten Temperaturbereich. Für alle anderen carbonathaltigen Systeme wurde die Datenbasis nur für T = 298 K von Harvie, Möller und Weare (1984) in Thereda überführt. Zur Erweiterung der Datenbasis für die Berechnung von Carbonatgleichgewichten innerhalb des Systems ozeanischer Salze bei höheren Temperaturen fehlt es an zuverlässigen experimentellen Daten.

2 Summary

The aim of the project phase II was to extend the thermodynamic database of the oceanic salt system by the components CO_2 and carbonates to enable solubility calculations in presence of these components at temperatures from 0 ºC to 110 ºC and CO_2 - pressures up to 300 bar. A particular challenge represented the demand for compatibility with the already existing system of standard data and Pitzer coefficients on the one side and the use of equations of state for compressed CO_2, which are available in the target geochemical codes PHREEQC, CHEMAPP and EQ3/6 on the other side.

An analysis of the literature in respect to thermodynamic models of CO_2 solubility in water and salt solution revealed that none of these models could be implemented into the THEREDA database, since the authors developed special purpose equations for specialized codes. The target codes of THEREDA allow to work for high gas pressure with the Tsonopoulos and the Spycher-Reed equation of state. It is shown in this project that with these equation of states and proper re-fitting of the model parameter the solubility equilibria between CO_2-H_2O-$CaCO_3$-NaCl can be described mostly within the accuracy of the available experimental data.

Detailed descriptions of these models are given in Technical Reports stored and available at the THEREDA – website (www.thereda.de)

- TP “Calculation of fugacities for H_2O(g)”

- TP “Fugacity – CO_2 “

- TP “H_2O - CO_2“

Since phase equilibria with pressurized CO_2 in aquiferic geological environments represent a highly actual topic, some of the models, experimental data and data evaluations were published from other groups during the projects time frame.

One of the main advantage of the approach realised in this project is, that the model can be combined in a consistent way with the model parameters of all components of the oceanic system. However, for most of the systems metal carbonate – metal chlo-

ride - water or metal carbonate – metal sulphate water the experimental data for enhanced temperatures and the presence of CO_2 are very scarce or absent. Thus, the derivation of model parameters at present is necessarily very limited. Consequently, a systematic thermodynamic description of these systems remains limited and for most systems the parameters are available only at 298 K.

3 Systems with CO_2 and carbonates at variable temperature and pressure.

In phase I of the Thereda project a database for the oceanic salt systems was established, which can be applied for the calculation of solubility equilibria including the ions H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-} and OH^- for a temperature range from 0 ºC to about 110 ºC. Carbonates and CO_2 were only implemented for 25 ºC and pressures up to 1 bar.

In phase II the temperature range and pressure range for CO_2 and carbonates should be extended also to 0 - 110 ºC and pressure up to about 300 bar CO_2. This required the adaption of equation of state for CO_2 and CO_2-H_2O mixtures for an implementation into the THEREDA database.

3.1 Fugacity of water in gaseous state

For the calculation of fugacity of either $H_2O(g)$ or $CO_2(g)$ in a H_2O-CO_2 mixture the EOS (Equation of State) for pure $H_2O(g)$ should be considered first. The thermodynamics of water evaporation between 273 K and 393 K was derived consistently in [VOI/Suk2011a] assuming ideal gas behaviour. Neglecting the fugacity coefficient of water causes a deviation in vapour pressure of 2.4 % at 393 K. In [VOI/SUK2011] the fugacity of water vapour with the necessary thermodynamic formalism was described with EOS of Dymond [DYM/SMI1980] and Spycher-Reed [SPY/REE1988]. The results are reproduced in figure 2.1.

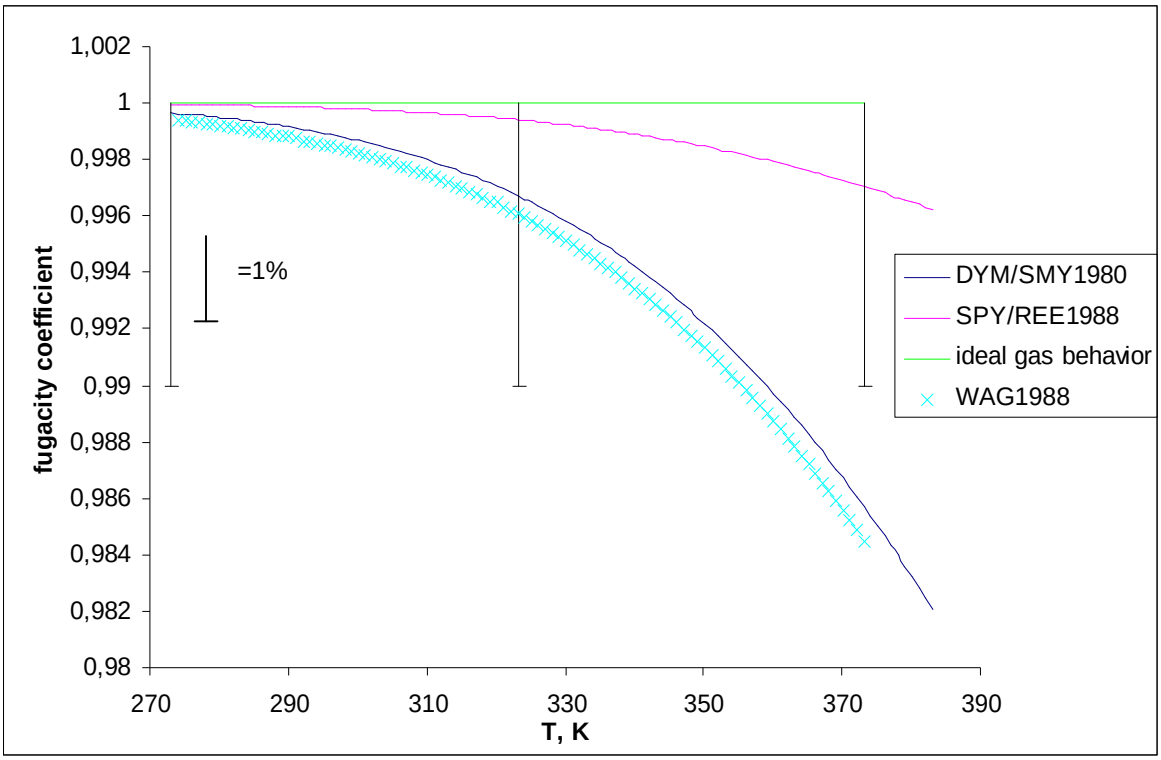

Figure 2.1 **Calculated water fugacity coefficient in the 0 - 110 ºC temperature interval by saturation pressure of water with Dymond and Spycher-Reed model**

3.2 Fugacity of the CO_2 gas

To calculate the fugacity of CO_2 in the gas phase an appropriate EOS should be chosen. Four EOS have been considered and critical evalkuated: Tsonopoulos EOS [TSO1974], Dymond and Smith [DYM/SMY1980] Duan EOS [DUA1992], Spycher and Reed [SPY/REE1988]. Discussion and results are documented in [VOI/SUK2011c]. As a main conclusion it can be pointed out that for broad pressure and temperature ranges the complexity (number of adjustable parameters) of the equation of state increases dramatically. The most accurate Duan model [DUA2006] needs 6 sets of 7 – 10 parameters in 6 different p-T regions to cover a range from 313 to 1273 K and from 1 to 1000 bar. For the THEREDA project 3 of these p-T regions would be necessary as shown in figure 2.2. The Duan equation is not implemented in geochemical codes. Therefore, more simple models have been considered as a basis for geochemical calculations consistent with codes. This concerns the Tsonopoulos EOS [TSO1974] and the Spycher-Reed model [SPY/REE1988]. The first one can be chosen in the ChemApp family of codes and the second one in

EQ3/6. Both equations allow a fairly good description of the fugacity of CO_2. The Spycher-Reed parameters were re-fitted in this project to extend the validity down to 273 K (originally only above 313 K). Near critical conditions of CO_2 (T < 305 K, p > 60 bar) the approximations are very crude and therefore for this p -T range until now no accurate calculations will be possible with these codes.

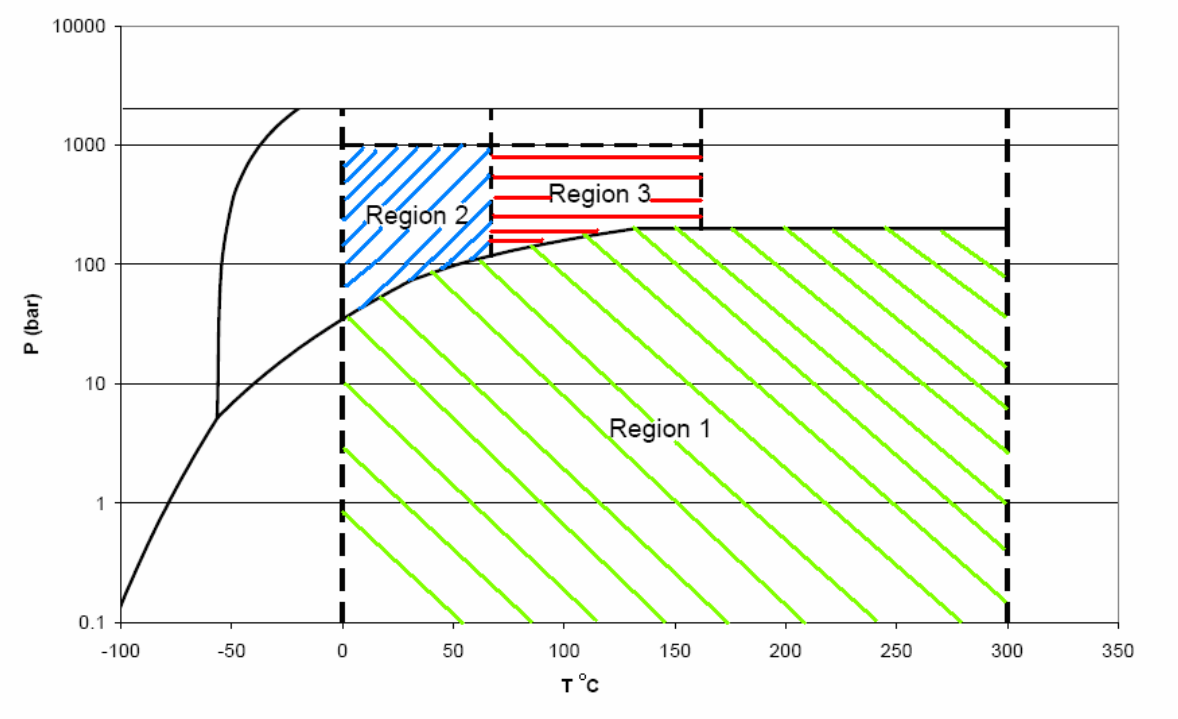

Figure 2.2 **The p - T- ranges for which the parameters of Duan EOS will apply to THEREDA project. Lines: sublimation saturation and melting line of CO_2; broken lines shows the borders of T-P regions**

3.3 The system CO_2 – H_2O

3.3.1 Dissociation constants of carbonic acid

The description of the system CO_2-H_2O is inherently connected with the formation of carbonic acid of the dissolved CO_2.

The dissociation constants of carbonic acid have been measured from 273 K to 523 K but most of the data were measured at 1 bar or at saturation pressure of water. The

only high-pressure data were reported by Ellis [ELI1959] and Read [REA1975], who determined the first dissociation constant up to 3000 bar.

The most widely used correlations for the dissociation constants of carbonic acid are the ones of Plummer and Busenberg [PLU/BUS1982]. The equation of Plummer and Busenberg for the first dissociation constant of carbonic acid corresponds well with the values of [HAR/DEV1943]. A more recent correlation was developed by Li and Duan [LI/DUA2007] and the major advantage of their equation is that it includes the effect of pressure:

$$\ln K = A + BT + CT^{-1} + DT^{-2} + E\ln T + (FT^{-1} + GT^{-2} + HT^{-1}\ln T)(P - P_r) + \\ + (IT^{-1} + JT^{-2} + KT^{-1}\ln T)(P - P_r)^2 \quad (3.1)$$

The temperature-dependent portion of the eq. (3.1) has the same form as the equation used by Plummer and Busenberg. In the recent paper of Alex De Visscher [DEV/VAN2012] the author fitted such form of equation of [LI/DUA2007] to the data of Read [REA1975] and the reanalyzed data of Harned and Davis [HAR/DAV1943] and combined with the pressure dependent portion of the equation (3.1). As a result the same form of equation but with new coefficients for the temperature dependence was obtained.

Few determinations of the second dissociation constant of carbonic acid are available in the literature [HAR/SCH1941]. Plummer and Busenberg relied on these data for the determination of their equation. Thermodynamic data derived from their equation are not consistent with CODATA [COX/WAG1989] within experimental error. New coefficients were calculated by De Visscher [DEV/VAN2012] using the data of [HAR/SCH1941] and the pressure dependence of the original equation (3.1).

The pressure dependence of De Visscher [DEV/VAN2012] equation for the first and second dissociation constants was used to derive thermodynamic functions for CO_2, HCO_3^- and CO_3^{2-} with the reference to carbonate as the primary species [Appendix 1].

Temperature and pressure coefficients for the NEA equation have been calculated with fixing the coefficients at T = 25 ºC. Equation (3.1) is divided into 2 parts. The temperature-dependant portion was re-fitted with coefficients of the NEA equation for Gibbs energy. Then an extra p-dependant coefficient was added. The final form of the equation for each component is written below:

$dfG_{T,P}(HCO_3) = -0{,}41700 \cdot T^2 + 99{,}10238 \cdot T - 579358{,}4856 + 2{,}75 \cdot P$ (3.2)

$dfG_{T,P}(CO_2\langle 0\rangle) = -0{,}8682 \cdot T^2 + 274{,}42 \cdot T - 390674 + 5{,}57 \cdot P$ (3.3)

$dfG°_{T,P}(CO_2\langle g\rangle) = -0{,}6838878 \cdot T^2 + 77{,}815737 \cdot T - 356914{,}2767 + 2{,}31 \cdot P$ (3.4)

3.3.2 Phase equilibrium in the system $CO_2 – H_2O$

The phase equilibrium is calculated using the equality rule of the fugacity:

$$f_i^L = f_i^g \quad (3.5)$$

The calculation of the fugacity in the aqueous phase of component *i* is not straight-forward. A possible way is to introduce an activity coefficient,

$$\gamma_i = \frac{f_i^i(P,T,x)}{f_i^0 x_i} \quad (3.6)$$

where f_i^0 is the reference fugacity of reference solution, x_i the mole fraction of component *i* in solution. We can further define the activity of water as $a_{H_2O} = x_{H_2O} \times \gamma_{H_2O}$ and write for $f_{H_2O}^l$ and $f_{H_2O}^g$

$$f_{H_2O}^l(P,T) = a_{H_2O} \times P_{H_2O}^{sat} \times \varphi_{H_2O}^{sat} \times \exp\frac{1}{RT}\left[\int_{Pvap(T)}^{P} V_{H_2O}^l dP\right] \quad (3.7)$$

$$f_{H_2O}^g(P,T) = y_{H_2O} \times P \times \varphi_{H_2O}^g \quad (3.8)$$

, where y_{H_2O} is the mole fraction of water in the gas phase, $\varphi_{H_2O}^g$ fugacity coefficient of water in the gas phase.

Combining these equations yields

$$a_{H_2O} \times P_{H_2O}^{sat} \times \varphi_{H_2O}^{sat} \times \exp\frac{1}{RT}\left[\int_{Pvap(T)}^{P} V_{H_2O}^l dP\right] = y_{H_2O} \times P \times \varphi_{H_2O}^g \quad (3.9)$$

Similarly for the equilibrium with CO_2 can be written

$$a_{CO_2} \times P_{CO_2}^{sat} \times \varphi_{CO_2}^{sat} \times \exp\frac{1}{RT}\left[\int_{Pvap(T)}^{P} V_{CO_2}^{\infty} dP\right] = y_{CO_2} \times P \times \varphi_{CO_2}^{g} \qquad (3.10)$$

Above the critical temperature of CO_2 (T=304.1 K) $P_{CO_2}^{sat}$ is not defined. The product $P_{CO_2}^{sat}\ \varphi_{CO_2}^{sat}$ is determined indirectly using solubility measurements and the corresponding equilibrium constants K_H denoted as Henry constant.

An equilibrium constant is introduced for the equilibrium

$$CO_2{}^{(l)} = CO_2{}^{(g)} \qquad (3.11)$$

$$K_{CO_2,T,P} = \frac{f_{CO_2}^{(g)} / f_{CO_2}^{0(g)}}{a_{CO_2(aq)}} \qquad (3.12)$$

Since the standard state adopted for gases is unit fugacity of the hypothetical gas at 1 bar and any temperature $f_{CO_2}^{0(g)}$ is equal to 1.

$$f_{CO_2}^{(g)} = K_{CO_2,T,P} \times a_{CO_2(aq)} \qquad (3.13)$$

The dependence of the thermodynamic constant on pressure is taken into account through the following expression,

$$K_{CO_2,T,P} = K_{CO_2,T,\mathrm{Pr}}^{0} \times \exp\left(\frac{(P - P_r)V_i}{RT}\right) \qquad (3.14)$$

where P_r is the reference pressure, which could be chosen as 1 bar or saturation pressure.

Substitution of this equation into equation (3.13) leads to

$$y_{CO_2} \times P \times \varphi_{CO_2}^{g} = K_{CO_2,T,\mathrm{Pr}}^{0} \times \gamma_{CO_2(aq)} \times x_{CO_2} \times \exp\left(\frac{(P - P_r)V_{CO_2}^{\infty}}{RT}\right) \qquad (3.15)$$

, where $\gamma_{CO_2(aq)}$ is the activity coefficient in the liquid phase on the scale defining ideality by means of Henry's law. $V^{\infty}_{CO_2}$ - is the partial molar volume of carbon dioxide at infinite dilution in water.

This equation is the key equation for the calculation of CO_2 solubility in water or salt solutions.

CO_2 solubility in pure water has been measured for a wide range of temperatures and pressures. The most reliable studies of CO_2 solubility in water are those of Wiebe and Gaddy [WIE/GAD1940], Bamberger [BAM2000], Koshel [KOS2006], Todheide and Franck [TOD/FRA193]. The solubility models of Duan [DUA/SUN2003], [LEM2003] Lemmon, E.W., McLinden, M.O., Friend, D.G., Thermophysical Properties of Fluid Systems, , *NIST Chemistry Webbook, NIST Standard Reference Database Number 69.,* Linstrom, P.J. Mallard, W.G., Eds.,(2003)

[LI/DUA2007]; Spycher and Reed [SPY/PRU2003], [SPY/PRU2005], Rumpf and Maurer [MAU/RUM1994] [MAU/RUM2007] represent the major contribution in respect to modeling of CO_2 solubility in water and salt solutions. All of them use equation (3.15) as a main equation for further calculation. However this equation cannot be treated without some simplifications, which can vary depending on the model and the final goals.

Most important simplifications should be mentioned:

The standard state for liquid water calls for unit activity of pure water at all pressures and temperatures. Since the solubility of CO_2 in the aqueous phase is relatively small for temperatures up to 383 K and pressures up to 600 bar, the activity of water was set equal to its mole fraction, x_{H_2O}.

The standard state for dissolved CO_2 calls for unit activity in a hypothetical one molal solution referenced to infinite dilution at any pressure and temperature. The mole fraction of dissolved CO_2 is related to its molal concentration through the relation:

$$x_{CO_2} = \frac{m_{CO_2}}{m_{CO_2} + m_{H_2O}} = \frac{m_{CO_2}}{m_{CO_2} + 55.508} \qquad (3.16)$$

$$m_{CO_2} = \frac{x_{CO_2} 55.508}{(1 - x_{CO_2})} \cong x_{CO_2} 55.508 \qquad (3.17)$$

The activity coefficient of dissolved CO_2 is mostly taken equal to 1, which means that in the Pitzer formalism all interactions of CO_2 molecules with itself are neglected. This is a reasonable approximation since CO_2 solubility is quite low in water and its only decreasing with adding electrolytes. However, additional calculations were made to proof this preposition, since some authors also report parameters for CO_2-CO_2 interactions. On Figure 2.3 one can see the comparison of different calculations at 373 K – one included neutral carbon dioxide interactions, another is done without this increment. The results are plotted together with experimental data and model calculations from [LI/DUA2007] model.

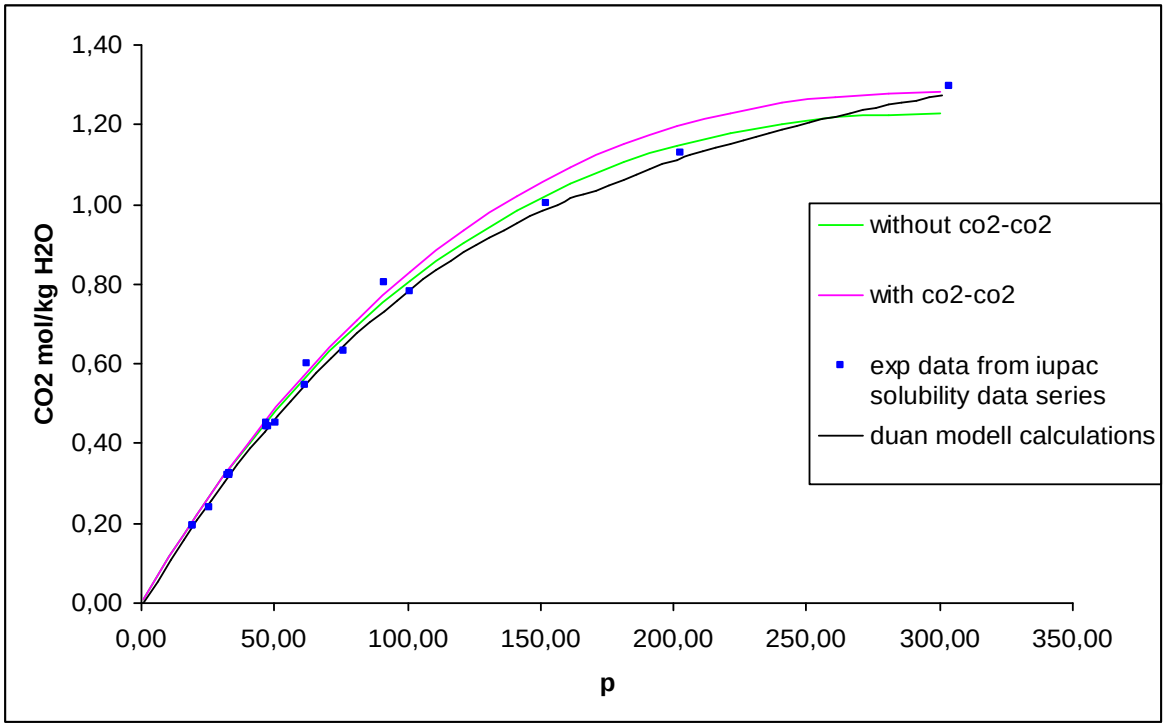

Figure 2.3 **Comparison for the calculations with and without λ(CO_2-CO_2)**

As clearly can be seen from this figure on the one hand the calculation proceeded without taking into account CO_2-CO_2 interaction agrees well with experimental data till 200 bar, but deviates at 300 bar from the experiment and the results obtained with the Duan-2007 model. On the other hand the calculations with a CO_2-CO_2 interaction term agree very well at high pressures with Duan model and some experimental data,

but at average pressure 100-200 the curve shows worse agreement then those without this term.

Henry's constant for the solubility of carbon dioxide was taken from [SPY/PRU2003]. It was compared with selected literature data and an empirical correlation of [MAU/RUM1994]. The influence of pressure on Henry's constant of carbon dioxide was calculated according to (3.14) using the partial molar volume. Since the temperature dependence of partial molar volume does not improve accuracy in CO_2 solubility calculation it is recommended to take the constant value of $V^{\infty}_{CO_2}$ = 32.6 cm^3mol^{-1} [SPY/PRU2003].

Since the program code "Chemsage" gives the possibility to use one or two pressure dependent coefficients for chemical potentials of pure components we can rewrite equation (3.14) in the form of lnK as following.

$$RT \ln K_{CO_2,T,P} = RT \ln K^{0}_{CO_2,T,\mathrm{Pr}} + (P - P_r)V_i \qquad (3.18)$$

As we can see the pressure and temperature dependence is now divided into 2 parts – first summand of the right part of equation represents the temperature dependence and the second summand represents pressure dependence. In this form the equation can be exported into the THEREDA databank using the standard NEA-function with addition of one single p-dependent coefficient, taking into account that *Vi* is constant for all T. It should be noticed that in the THEREDA databank the primary species for dissolved carbon is CO_3^{2-}, which means that the Henry constant had to be recalculated according to the formation reaction of CO_2(g) from CO_3^{2}.

The only available non-ideal model for gases in "Chemsage" is the Tsonopoulos model. Combining the fugacity coefficients calculated with Tsonopoulos (3.18), mutual CO_2-H_2O solubilities in the range 0-120 ºC, 1-300 bar can be computed in a direct manner from equation (3.15), yielding CO_2 solubilities with an accuracy (typically< 7%) within the spread of experimental data. In Figure 2.4 and Figure one can observe the average agreement of the model within the spread of experimental data and with calculations with the Duan model [DUA/SUN2003].

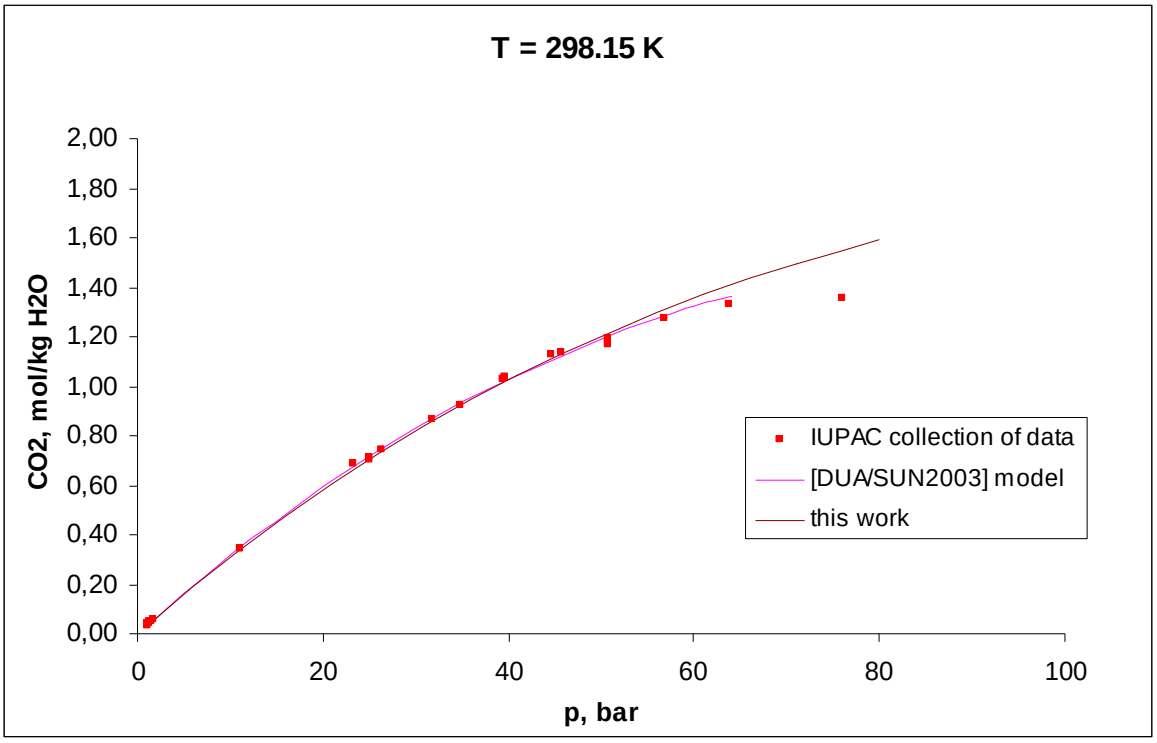

Figure 2.4 **CO_2 solubility in H_2O at 25 ºC as function of CO_2 pressure**

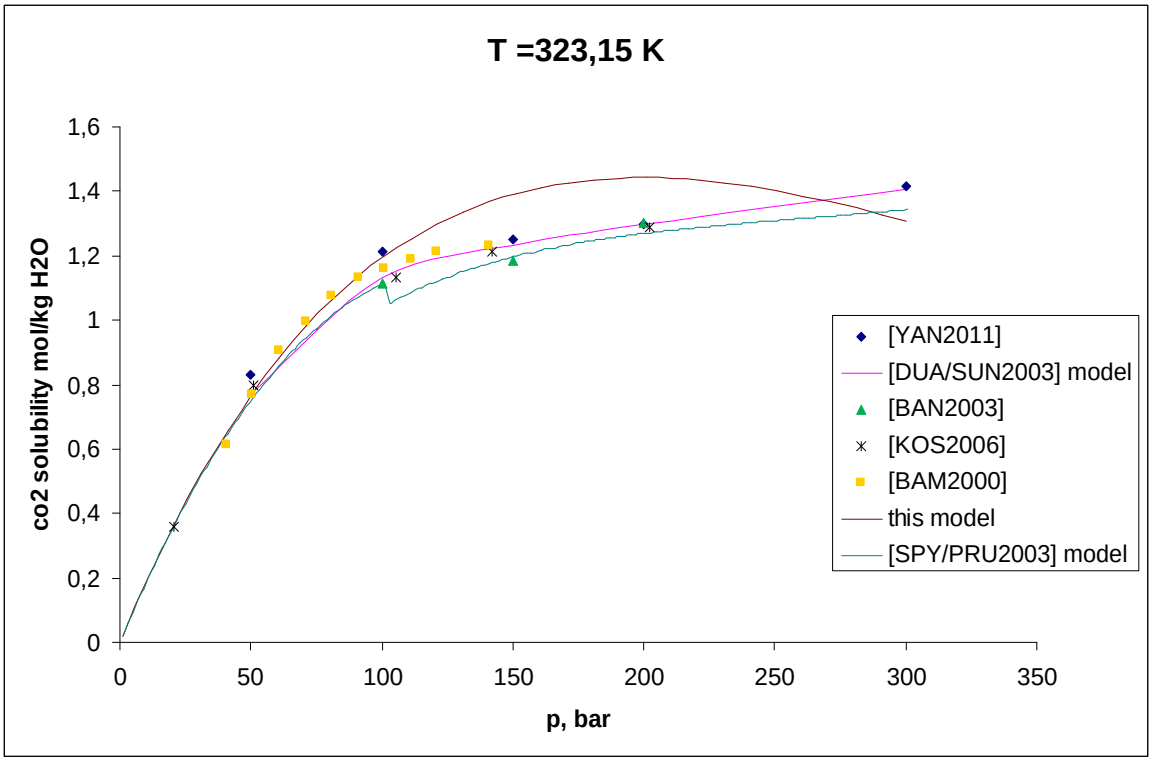

Figure 2.5 **Comparison of CO_2 solubility in H_2O at 50 ºC and pressures up to 300 bar with experimental data and different models**

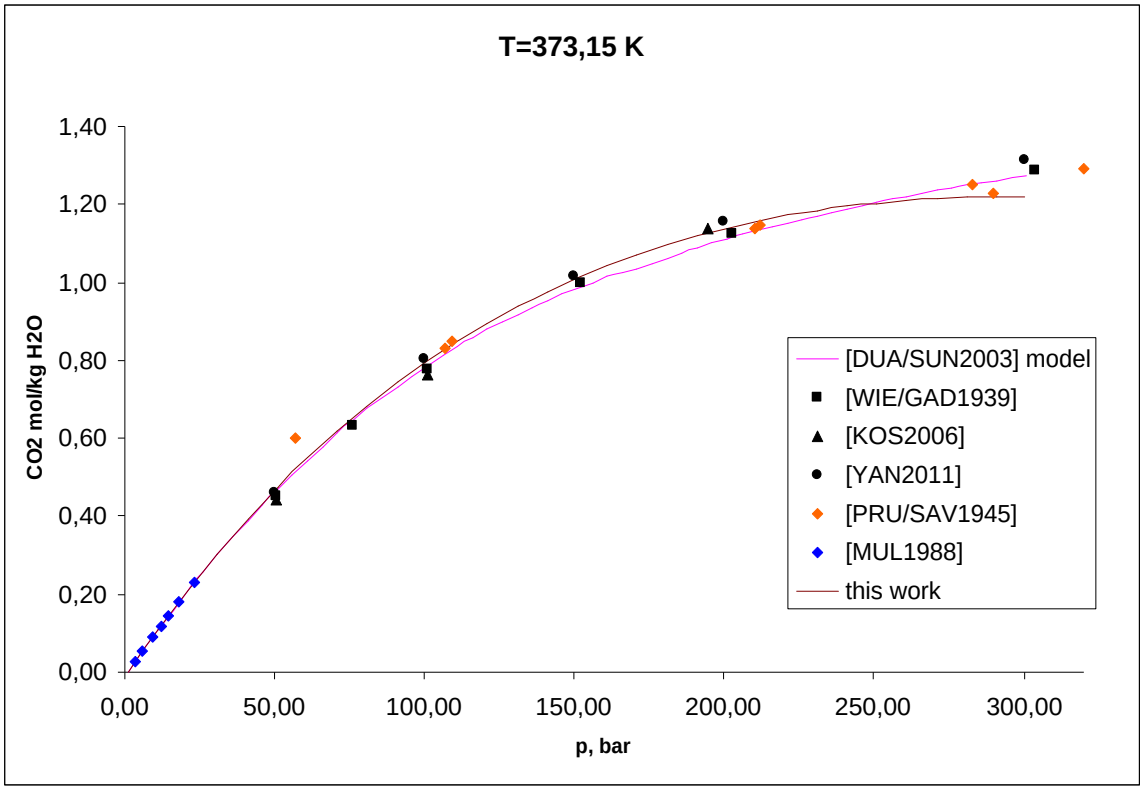

Figure 2.6 **Comparison of CO_2 solubility in H_2O at 100 ºC and pressures up to 300 bar with experimental data and different models**

3.4 Salting out of CO_2 by electrolytes – Pitzer approach

Salting out of CO_2 can have a significant effect on concentration of CO_2 in concentrated salt solutions. Estimating the solubility of aqueous species requires the calculation of their activity coefficients taking into account the effect of salinity and temperature. Neutral species may also behave in a non-ideal manner, exhibiting activity coefficients that deviate from unity.

There are different ways to express salting out effect. The simplest is to apply a correlation equation with empirical parameter such as in [HEL1969], [POR/ROC2005]

$$\ln y_{CO_2} = \sigma_{CO_2}(T) I \qquad (3.19)$$

, where σ is a fitting parameter called the salting out coefficient, which is determined from experimental data, I is the true ionic strength of the solution. This coefficient

should be determined for every salt composition, which seems to be a considerable disadvantage if one should model the solubility in complex systems.

Another approach is the use of the Sechenov equation, applied to CO_2

$$\lg c_{CO_2} = \lg c^{0}{}_{CO_2} - k_{scc} c_s \qquad (3.20)$$

With c(CO_2) the CO_2 solubility in the presence of salt, $c^0(CO_2)$ the solubility of CO_2 in water under the same conditions, C_s salt concentration and k_{scc} the Sechenov coefficient. Most reliable data using this approach are given by Markgam and Kobe (1941), Yasunishi and Yoshida (1979). Some other data were evaluated by De Visscher et. al [DEV/VAN2012].

The third approach is to use the Pitzer specific interaction model, which has been used to estimate the activity coefficients of chemical species in solutions up to high concentrations [PIT1973], [HAR/MOL1984], [HE/MOR1993]. The Pitzer equations have been discussed in many publications and here we only need to determine the Pitzer parameters.

In [RUM/MAU1994] it was assumed that the salt is fully ionized and at the concentrations of the dissolved gas considered in the paper, the formation of HCO_3^- in the liquid phase can be neglected. Therefore, for an aqueous system containing a non-reacting gas and a completely dissociating salt the activity coefficient of the dissolved gas is

$$\ln \gamma_{CO_2} = 2m_{CO_2}\beta^{(0)}_{CO_2CO_2} + 3m^2_{CO_2}\tau_{CO_2,CO_2,CO_2} + 2m_{NaCl}B^{(0)}_{CO_2NaCl} + 3m^2_{NaCl}\Gamma_{CO_2NaCl,NaCl} + 6m_{NaCl}m_{CO_2}\Gamma_{CO_2,CO_2,NaCl} \qquad (3.21)$$

$\beta^{(0)}_{CO_2CO_2}$ second virial coefficient for interaction of neutral species with itself

τ_{CO_2,CO_2,CO_2} third virial coefficient for interaction of neutral species with itself

$B^{(0)}_{CO_2NaCl}$ parameter for binary interaction between neutral species and ions

$\Gamma_{CO_2NaCl,NaCl}$ parameter for ternary interaction of neutral species with two ions

$\Gamma_{CO_2,CO_2,NaCl}$ parameter for ternary interaction of two neutral species with one ion

This equation can be simplified if not taking into account interaction of carbon dioxide molecules with itself. This can be a reasonable approximation as the molality of dissolved carbon dioxide remains relatively small even at high pressures, then:

$$\ln\gamma_{CO_2} = \ln\gamma_{CO_2}(m_{NaCl}=0) + 2m_{NaCl}B^{(0)}_{CO_2NaCl} + 3m^2_{NaCl}\Gamma_{CO_2NaCl,NaCl} + 6m_{NaCl}m_{CO_2}\Gamma_{CO_2,CO_2,NaCl} \quad (3.22)$$

$\ln\gamma_{CO_2}(m_{NaCl}=0)$ denotes the activity coefficient of the gas dissolved in pure water.

The parameters $B^{(0)}_{CO_2NaCl}; \Gamma_{CO_2NaCl,NaCl}; \Gamma_{CO_2,CO_2,NaCl}$ are combinations of the second and third virial coefficients β, τ for interaction between different species in Pitzer's original equation:

$$B^{(0)}_{CO_2NaCl} = \nu_+\beta^{(0)}_{CO_2,Na} + \nu_-\beta^{(0)}_{CO_2,Cl} \quad (3.23)$$

$$\Gamma_{CO_2NaCl,NaCl} = \nu^2_+\tau_{CO_2Na,Na} + 2\nu_-\nu_+\tau_{CO_2Na,Cl} + \nu^2_-\tau_{CO_2Cl,Cl} \quad (3.24)$$

$$\Gamma_{CO_2,CO_2,NaCl} = \nu_+\tau_{CO_2,CO_2,Na} + \nu_-\tau_{CO_2,CO_2,Cl} \quad (3.25)$$

Only parameters of ion combinations of interactions resulting in neutral molecules can be determined from experimental measurements. Therefore, if one want to express the interactions in ionic form as in the equations above, one ion has to be selected as reference and its value set to be zero. To correlate the experimental results for the

solubility of carbon dioxide in aqueous solutions of NaCl the ternary parameter $\Gamma_{CO_2,CO_2,NaCl}$ is usually neglected.

Thus, only one binary parameter as well as one ternary parameter is required. The influence of temperature on the binary parameter was taken into account. It is approximated by

$$B = a + b/T + c/T^2 + d/T^3 \qquad (3.26)$$

The influence of temperature on the ternary parameter was neglected in our case.

The correlation describes the measurements of [RUM/MAU1994] with an average relative deviation of 1.9%, the maximum relative deviation is 6.5% at 393.12 K and m(CO_2) = 0,305 mol/kg at P= 91,4 bar

3.5 Solubility in the system CO_2 - H_2O - NaCl

The Henry's constant parameters and CO_2 characteristic parameters identified for the CO_2-H_2O binary system remain valid for the CO_2-(Na/Ca)Cl-H_2O ternary systems. In order to include the effect of chloride salts in the aqueous phase the activity coefficients for aqueous CO_2 should be rewritten and Pitzer parameters for CO_2-Na, CO_2-Cl, CO_2-Na-Cl interactions should be given. Various formulations for the activity coefficient can be found in literature: Rumpf (1994), Duan and Sun (2003, 2006), Portier and Rochelle (2005), Drummond (1981), Millero (2007) and some others. These formulations were tested with the model accepted for pure CO_2 and CO_2-H_2O system discussed previously.

Duan and Sun (2003, 2007) presented a model for the CO_2 solubility in water and NaCl solutions applicable in a wide T-P-m range (0-1000 bar, 0-250 °C, 0-5 NaCl molality). Using the specific ion-interaction equations of Pitzer to calculate activity coefficients, this model allows to calculate the concentrations of HCO_3^-, CO_3^{2-} and $CO_{2(aq)}$ at given T-P-m conditions. The disadvantage of the model, however, is that it relies basically on a fifth-order virial EOS (Duan1992), which is discussed in (SUK/VOI2012), and cannot be directly implemented in any available program code, because of the complexity of this EOS, the dependence of Pitzer parameters and dissociation constants from P and T simultaneously. Nevertheless, Duan and Sun (2003)

presented useful Pitzer parameters to calculate activity coefficients for aqueous CO_2, which are needed to account for salting-out effects in CO_2-NaCl/$CaCl_2$-H_2O systems.

We noted the general lack of experimental measurements of CO_2 solubility in NaCl solutions at high pressures (100<P<300 bar) moderate temperatures (40<T<120 C) and in high ionic strength (up to 3 m solutions).

The solubility of carbon dioxide in aqueous solutions of sodium chloride was measured in the temperature range from 40 to 160 ° C, up to 6 mol/kg salt solutions and total pressures up to 100 bar by [RUM/MAU1993] [RUMMAU/1994]. They used a standard virial EOS truncated after the second term to compute fugacity coefficients. Pitzer's equations with their own coefficients as well as Chen and Evans model were used to correlate the new data. Results are reported and compared to literature data and correlations.

Experimental gas solubility data for the CO_2-1mass% NaCl solution binary system are reported in [NIG1989]. Measurements were made at pressures up to 100 bar and temperatures 80, 120, 200 ° C. A thermodynamic model of this system is also presented. The model employs the Peng-Robinson EOS to represent the vapor phase and an empirical Henry's law constant correlation for the liquid phase. It is shown that the salting out effect of the 1 mass% NaCl solutions on CO_2 solubility is quite small [NIG1989].

The solubility of CO_2 in water and aqueous solutions of NaCl, KCl, $CaCl_2$, NaCl+KCl, NaCl+$CaCl_2$, KCl+$CaCl_2$, and NaCl+KCl+$CaCl_2$ was determined in [HAN/LIU2011] at 35, 45 and 55 ° C up to 16 MPa and salt concentrations up to 14,3 mass%. At the same salt concentration, the salting-out effect of KCl was considerably smaller than those of NaCl and $CaCl_2$.

[KIE2002] measured the CO_2 solubility in aqueous NaCl and KCl solutions by means of a static synthetic method in a temperature range from 40 to 120 °C and pressures up to 100 bar. The Henry coefficient for CO_2 in H_2O experimentally acquired and calculated with corrected PSRK by Kiepe et al. (2002) [KIE2002] shows a comparatively large deviation (10%) at enhanced temperatures (353 K<T<393 K) compared to [CRO1990]. But below this temperatures these data are in excellent agreement with the data of Rumpf et al (1994) [RUM/MAU1994] at m = 4 mol/kg.

By refitting the Pitzer parameters of [RUM/MAU1993] the solubility of CO_2 in NaCl and $CaCl_2$ solutions can be calculated.

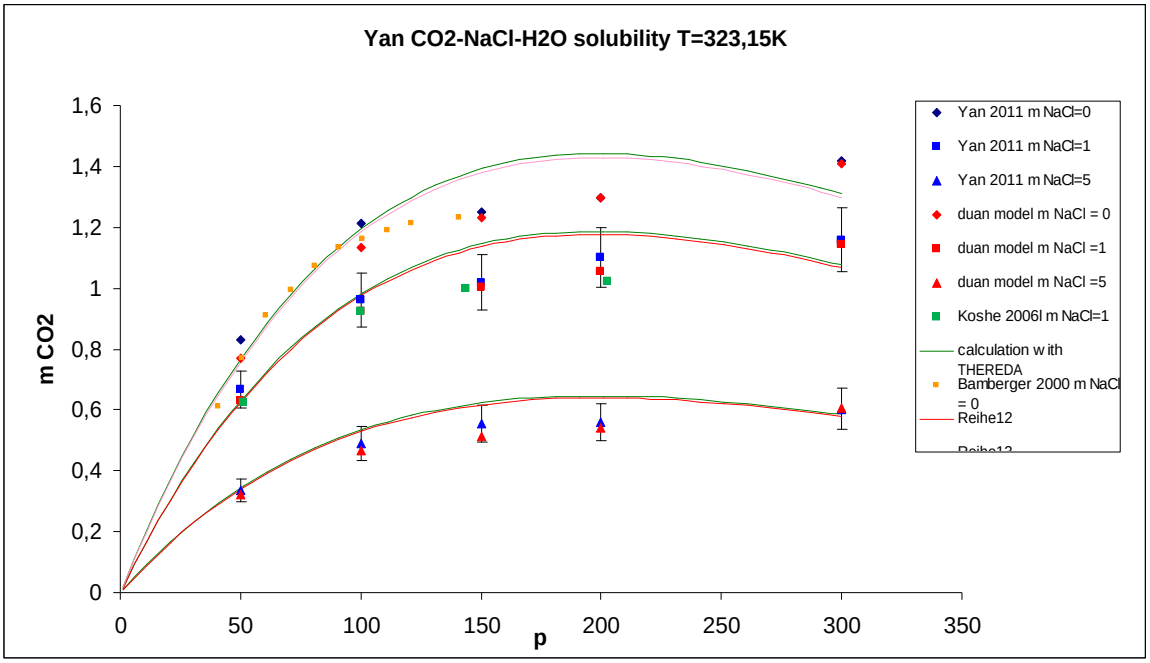

Figure 3.7 **CO_2 solubility in NaCl solutions at 323.15 K and pressures up to 300 bar**

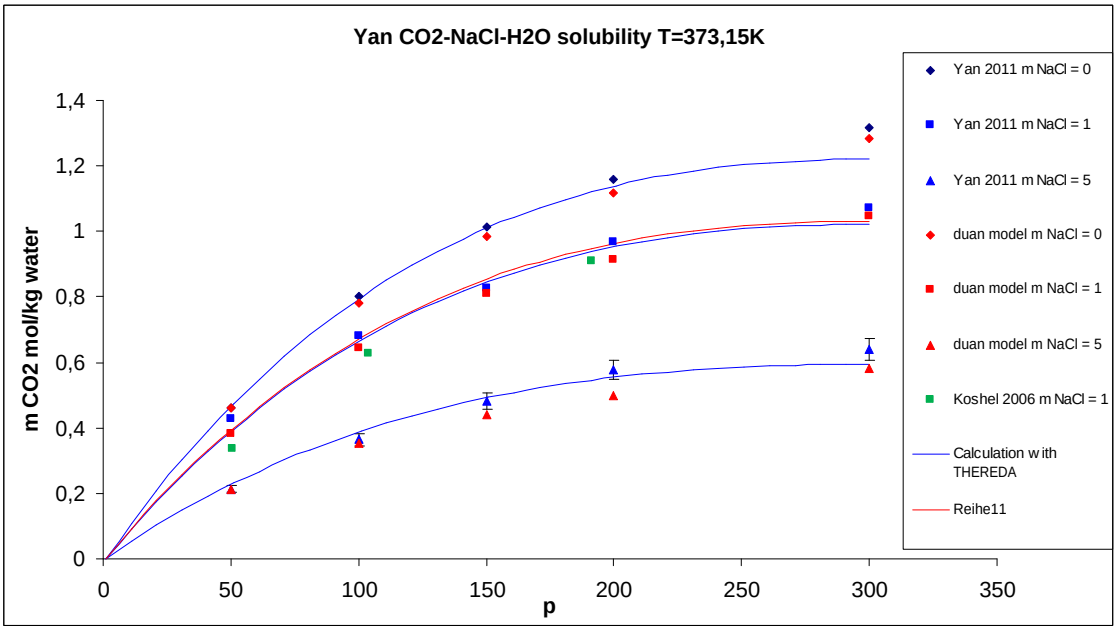

Figure 3.8 **CO_2 solubility in NaCl solutions at 373.15 K and pressures up to 300 bar**

3.6 Solubility of alkaline carbonates and bicarbonates

The parameters for alkali metal carbonates and bicarbonates were taken from [HARV/MOEL1984] and implemented in the THEREDA databasis. In figures 2.5 – 2.9 the solubilities calculated from the original HMW84 – model and from the Thereda database are compared. The figures give evidence that the implementation procedures did not change the quality of the original HMW84 model.

A detailed model could be developed for the system NaCl – Na_2CO_3 – H_2O for temperatures up to 373 K. The comparison of calculated solubilities and experimental data is presented in Figure 2.10 - 2.11. Sufficient agreement with the experimental data was achieved. However, the Pitzer coefficients are still not completely consistent with the THEREDA system. There are particular difficulties to overcome, because of the extreme solubility changes of $NaCO_3$ as a function of temperature. The CHEMAPP datafile used for the calculation can be found in Appendix 2.

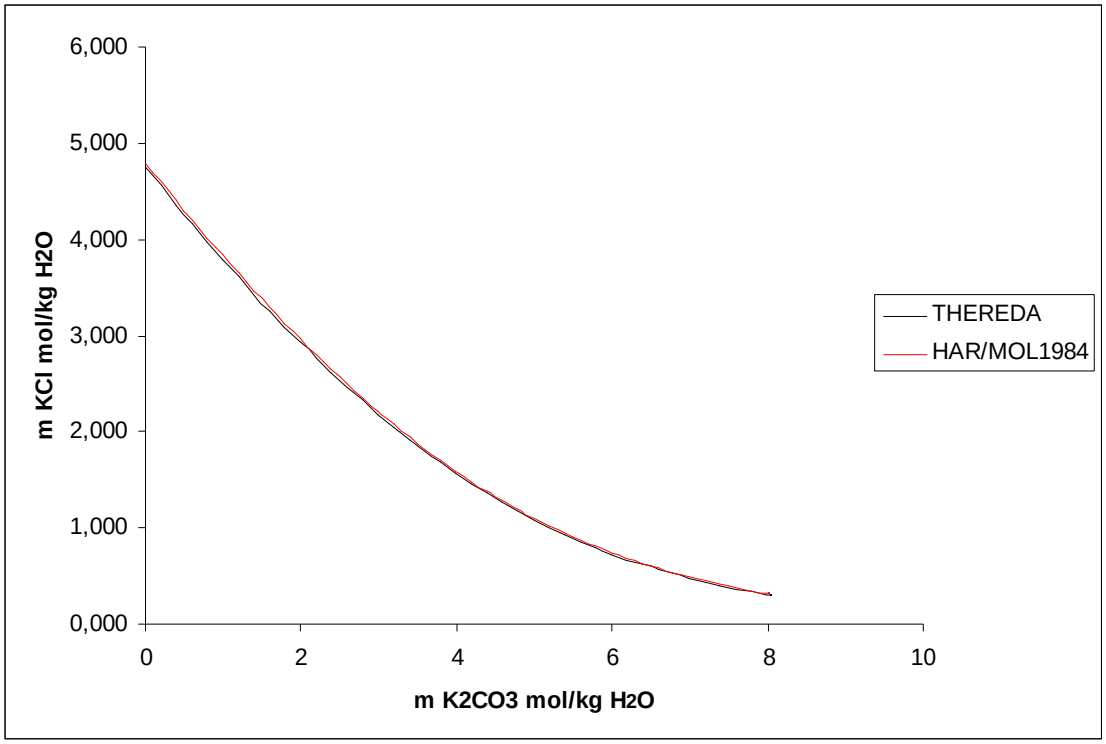

Figure 2.9 **Comparison between calculated solubilities between THEREDA and [HARV/MOEL1984] for the system KCl-K_2CO_3 H_2O at 298 K**

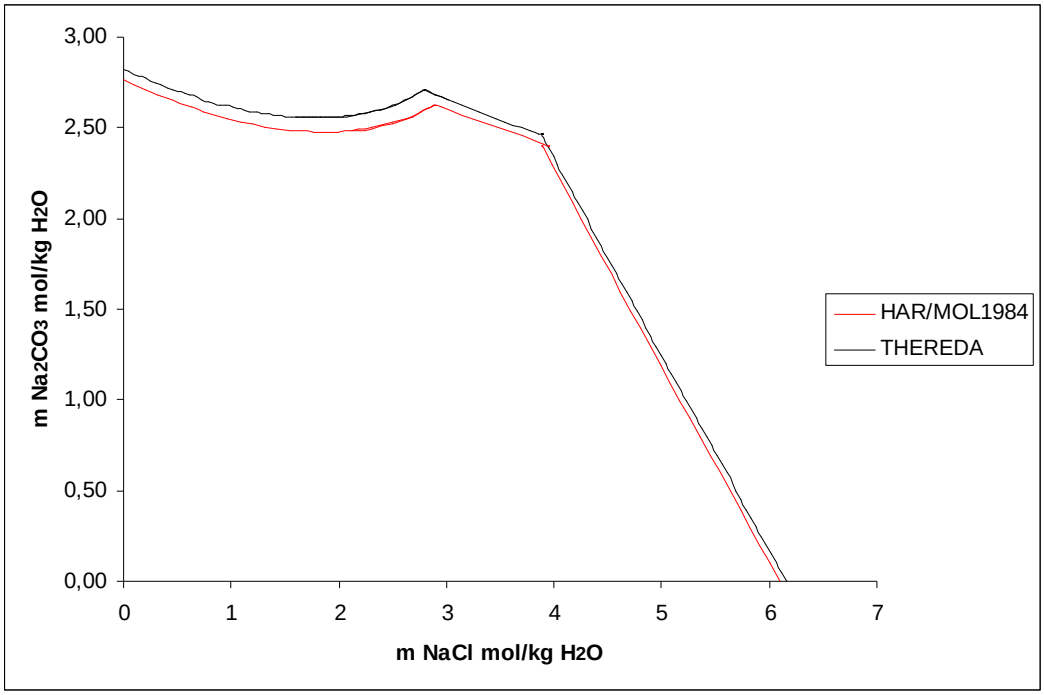

Figure 2.10 **Comparison between calculated solubilities between THEREDA and [HARV/MOEL1984] for the system NaCl-Na_2CO_3 H_2O at 298 K**

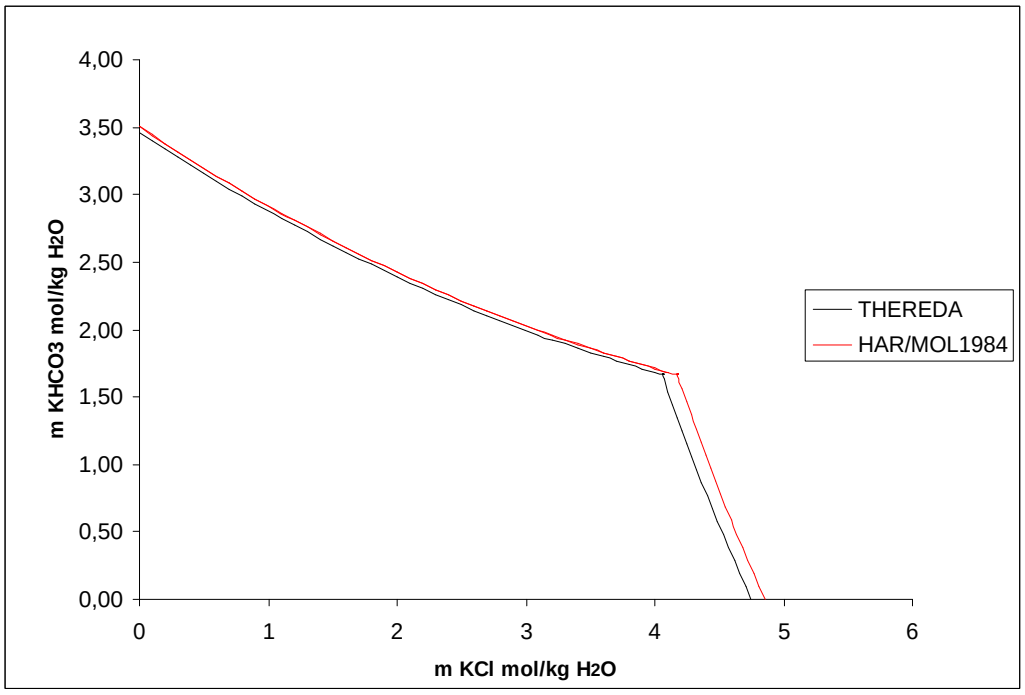

Figure 2.11 **Comparison between calculated solubilities between THEREDA and [HARV/MOEL1984] for the system KCl-KHCO3 H_2O at 298 K**

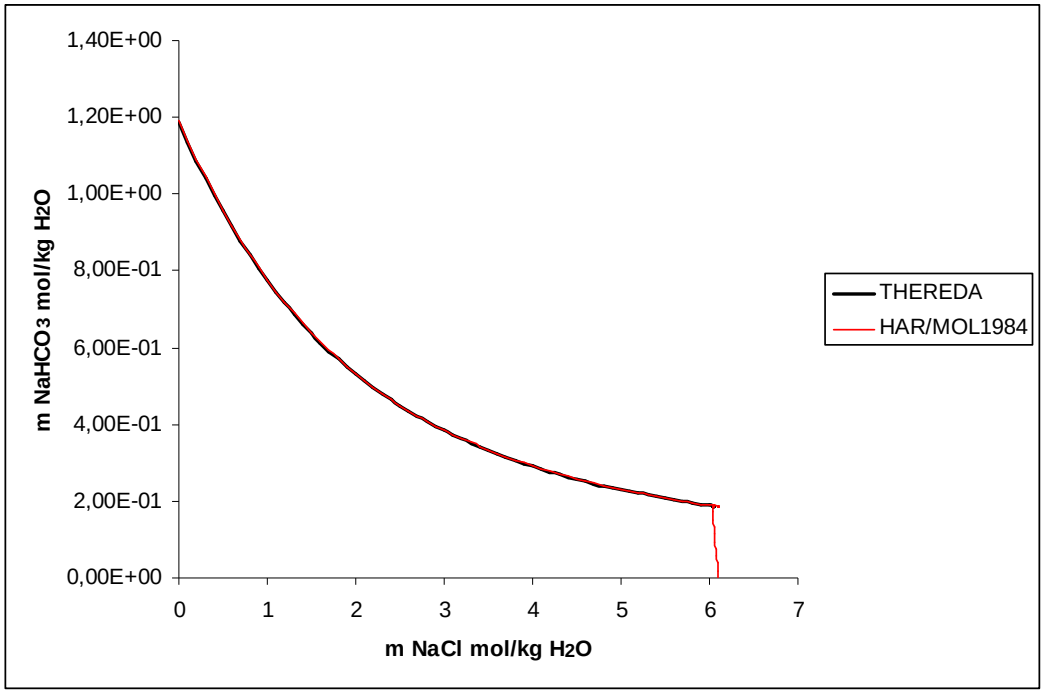

Figure 2.12 **Comparison between calculated solubilities between THEREDA and [HARV/MOEL1984] for the system NaCl-$NaHCO_3$ H_2O at 298 K**

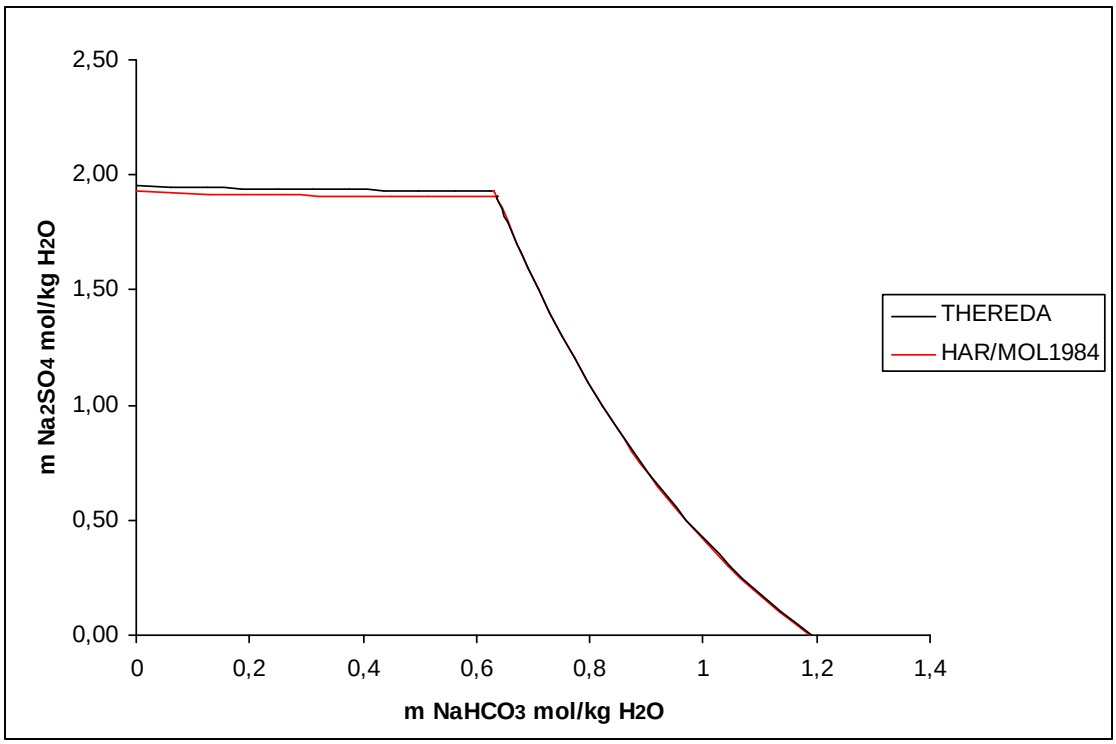

Figure 2.13 **Comparison between calculated solubilities between THEREDA and [HARV/MOEL1984] for the system $NaHCO_3$-Na_2SO_4 H_2O at 298 K**

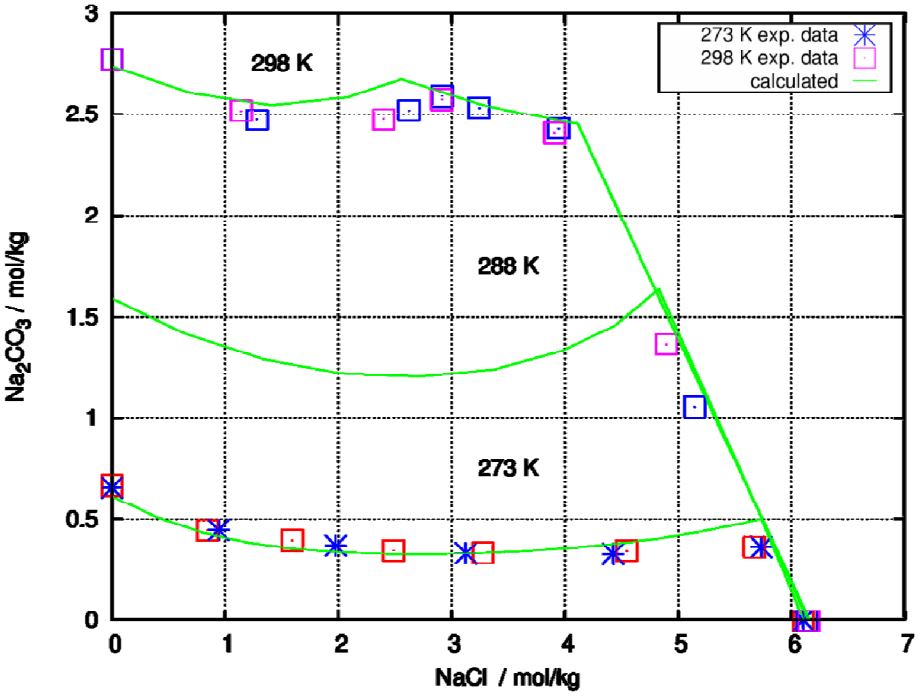

Figure 2.14 **Comparison of calculated data with experimental data between 273-298 K**

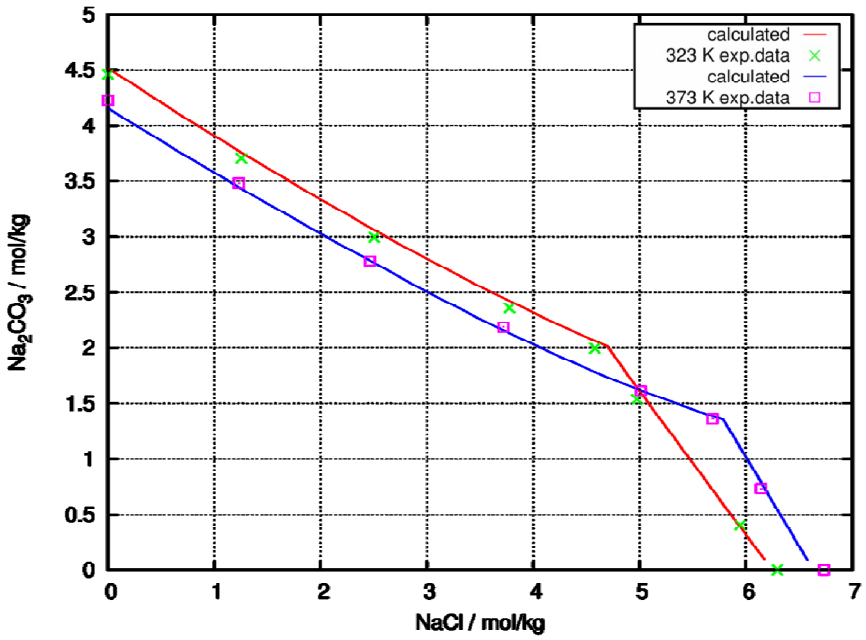

Figure 2.15 **Comparison of calculated data with experimental data between 323-377K**

3.7 Metal carbonate ion pairing

Both bicarbonate and carbonate can form ion pairs with alkaline earth metal ions in aqueous solution:

$$MHCO_3^+ \leftrightarrow M^{2+} + HCO_3^- \quad (3.27)$$

$$MCO_3^0 \leftrightarrow M^{2+} + CO_3^{2-} \quad (3.28)$$

Corresponding to these reactions, the dissociation constants are defined. The formation of $CaHCO_3^+$ ion pairs and $CaCO_3^0$ was first suggested by Greenwald [GRE1941]. There is little evidence supporting the formation of higher order complexes in Ca-HCO_3 solutions. After the suggestion these dissociation constants were determined from various types of experiments at temperatures up to 363 K [PLU/BUS1982], [REA/LAN1974]. The agreement in experimental values of K($CaHCO_3^+$) is generally not better than 0,2 $\log_{10}$K units between 0 and 363 K. De Visscher and Vandeerdeelen showed that some calcium carbonate solubility data are consistent with the existence of the calcium bicarbonate ion pair, whereas other solubility data are inconsistent with such an ion pair [DEV/VAN2012]. Most studies conducted at low ionic strength point at the existence of these ion pairs, whereas studies at higher ionic strength do not support any ion pairing. Because the main interest of the THEREDA project is to describe complex equilibrium up to high ionic strength of the system, the $CaHCO_3^+$ should not be considered and Pitzer parameters should be introduced instead.

Pitzer [PIT1985] first proposed values for β^0 and β^1 at 298 K based on electrochemical measurements in aqueous Ca(HCO_3)-$CaCl_2$ mixtures. Their values were confirmed by He and Morse [HE/MOR1993] who used potentiometric titrations of the carbonic acid in $CaCl_2$ solutions at 273-363 K. The values of Harvie [HAR/MOL1984] were obtained from solubility data of calcite. Since [LI/DUA2008] used the stability constant for Ca-HCO_3^+ ion pair they did not define Pitzer coefficients β^0, β^1,$C\varphi$(Ca-HCO_3) and the only available work considering temperature dependence is those of [HE/MOR1993]. Following [DEV/VAN2012] we approximated the temperature dependence with available data according to eq. (3.29):

$$P(T) = A + B/T + GT^{-2} \qquad (3.29)$$

Coefficients for β^0, β^1 (Ca-HCO_3) are given in (3.30) and (3.31) (Cφ is neglected in the parameterisation)

$$\beta^0_{CaHCO_3} = -3{,}7313 + 1371{,}42/T - 57330T^{-2} \qquad (3.30)$$

$$\beta^1_{CaHCO_3} = 4{,}3005 - 2819{,}46/T + 483720T^{-2} \qquad (3.31)$$

It should be noticed that in [LI/DUA2008] the coefficient λ(CO_2-$CaHCO_3$) was introduced to account for the influence of CO_2 on $CaHCO_3^+$ concentration. This was done by fitting experimental of calcite solubility data together with the chemical reaction equilibrium constant and the Pitzer activity coefficient. This coefficient is not used in the THEREDA model.

Plummer and Busenberg [PLU/BUS1982] estimated the lgK for $CaCO_3^0$ at 298 K as 3.2±0.07, other data are computed by [DEV/VAN2012]. Sverjensky [SVE/SHO1997] proposed a correlation that allowed calculations of the stability constant of the calcium carbonate ion pair up to 623 K and saturated vapour pressures of water. De Visscher used this correlation and experimental data discussed in [DEV/VAN2012] to fit the stability constant to a 5 coefficient temperature dependent equation:

$$\ln K = A + B/T + C\lg(T) + DT + GT^{-2} \qquad (3.32)$$

This fit is compared with the fit proposed in [PLU/BUS1982] in Figure 3.16.

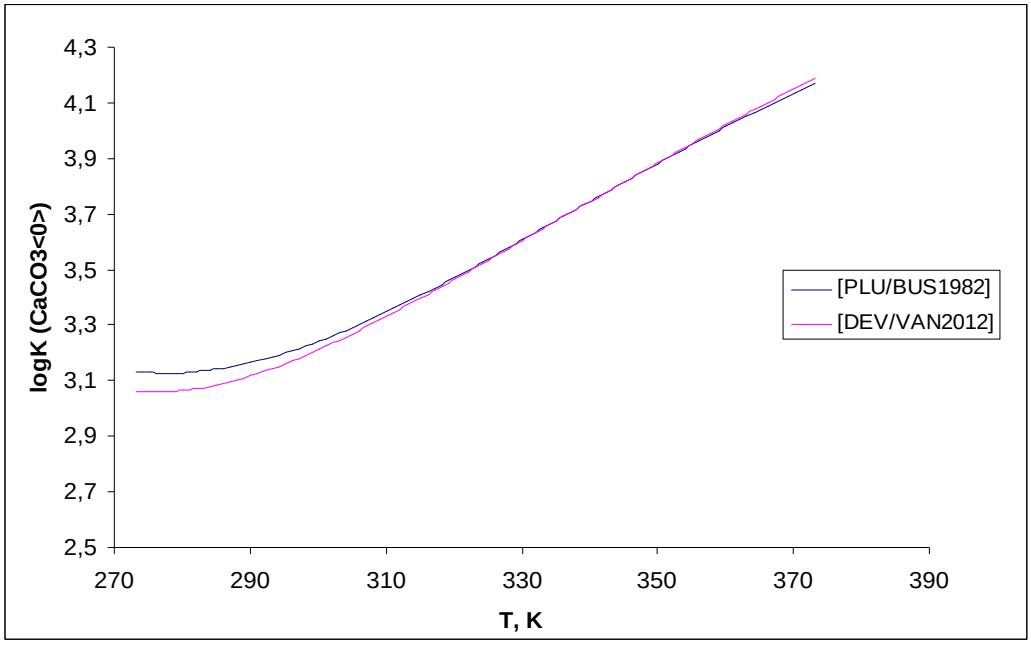

Figure 3.16 **Comparison of the temperature dependence of the stability constant for the ion pair $CaCO_3^0$ between the models of De Visscher and Plummer**

The equation of De Visscher was then refitted in terms of Gibbs formation energy of $CaCO_3^0$ to the form of NEA-equation. Coefficients of the equation on the Figure 3.17 are implemented in THEREDA.

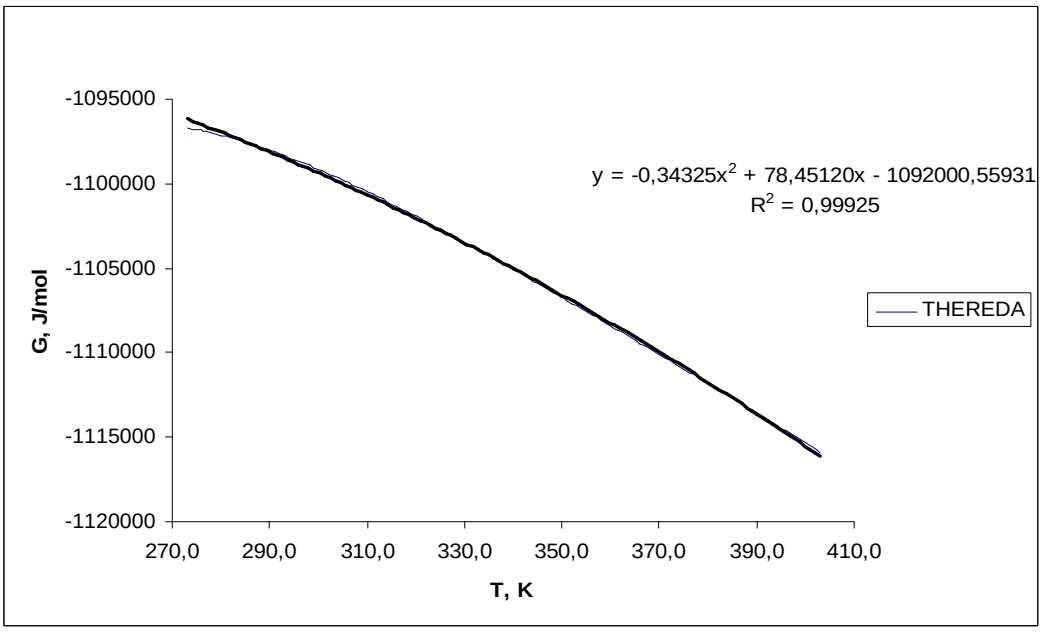

Figure 3.17 **Fit of the formation Gibbs energy of $CaCO_3^0$**

3.8 Solubility of $CaCO_3$ (calcite and aragonite)

Calcium carbonate occurs in various unhydrated and hydrated forms. At least 6 distinct phases have been distinguished nowadays: three anhydrous crystalline polymorphs, calcite, aragonite and vaterite, and three hydrated forms: the crystalline monohydrate, hexahydrate and amorphous calcium carbonate. Calcite and aragonite occur in nature and have been studied thoroughly.

In order to calculate the solubility of calcite and aragonite the standard chemical potential of $CaCO_3$(s) or equilibrium constants as function of temperature and pressure should be acquired. The equilibrium constant of calcite and aragonite are defined for the reaction:

$$CaCO_3(s) \leftrightarrow Ca^{2+} + CO_3^{2-} \qquad (3.33)$$

The equilibrium constant is calculated on the molal scale using the measured solubility and the aqueous model. In this work we analysed the calcite stability constant calculated by Harvie [HAR/MOL1984], Plummer and Busenberg [PLU/BUS1982] and De Visscher [DEV/VAN2012].

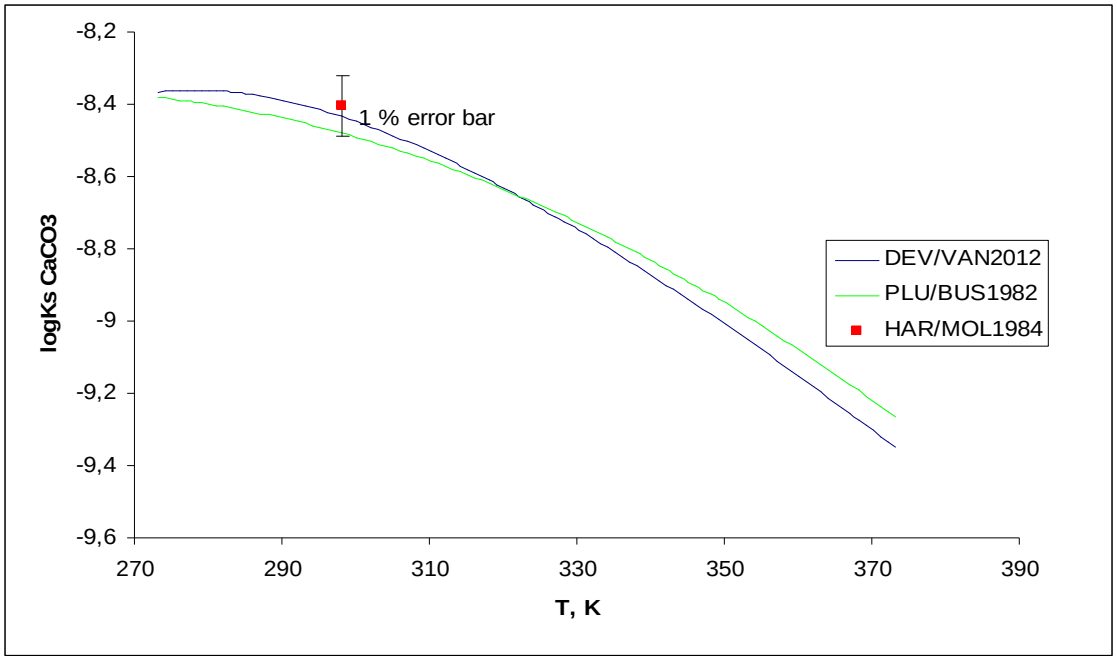

Figure 3.18 **Comparison of the calcite solubility constant calculated by different authors**

As a reference model the regression of De Visscher were chosen. Based on coefficients reported in [DEV/VAN2012] a lgK($CaCO_{3(s)}$) a value of -8,434 at 298.15 K is obtained. This value is in a good agreement with Harvie [HAR/MOL1984] -8,404 at 298.15 K. The equation for lgK_s was refitted in order to calculate the formation Gibbs energy in terms of NEA equation The same procedure were applied for the aragonite. Results of the fit are presented in. Results of the fit and coefficients are presented in Figure 3.19. – 3.20.

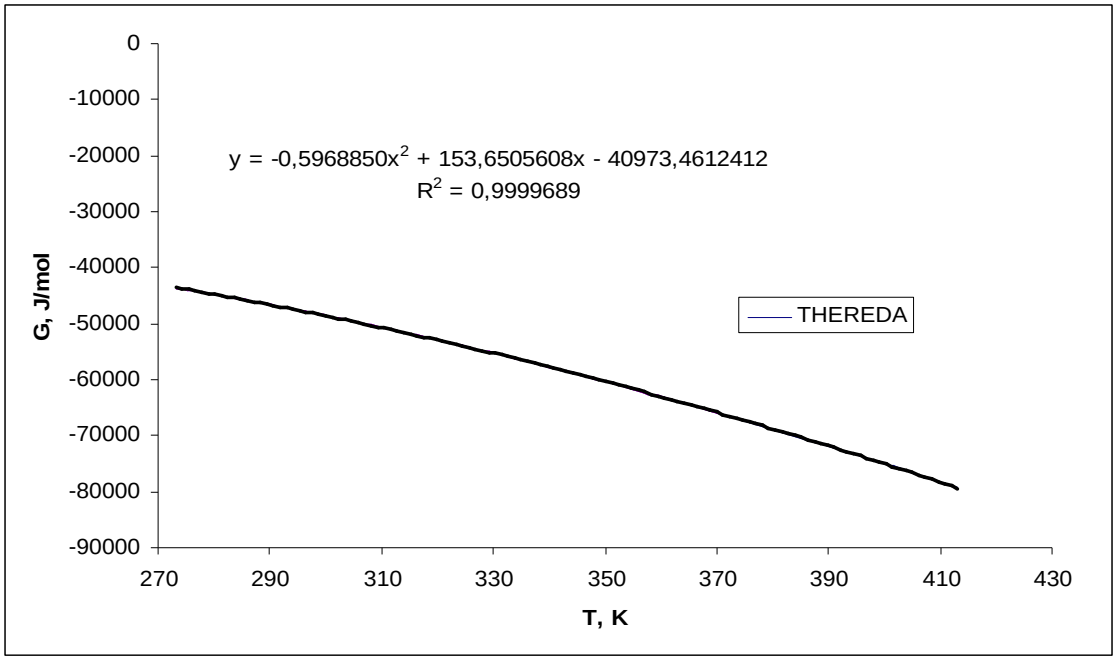

Figure 3.19 **Gibbs formation energy of calcite derived from [DEV/VAN2012] fit**

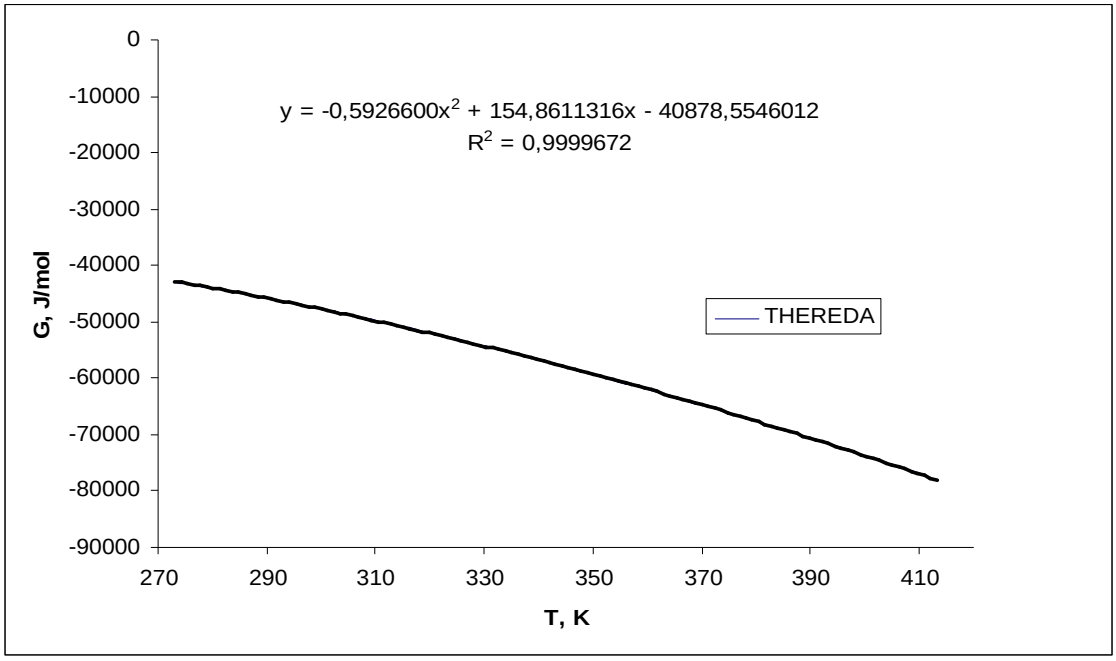

Figure 3.20 **Gibbs formation energy of aragonite derived from [DEV/VAN2012] fit**

3.8.1 System $CaCO_3$(calcite)+H_2O+CO_2

The calcite solubility data can be classified into two categories, those with CO_2 saturated and those with CO_2 unsaturated. The extensive experimental data with CO_2 saturated include those of Miller [MIL1952], Plummer and Busenberg [PLU/BUS1982], Segnit [SEG1962], Wolf [WOL1989]. Miller [MIL1952] summarized most of early data and carried out the first thorough experimental study at temperatures up to 373.15 K and with partial pressure of CO_2 of 1 bar. The THEREDA model agrees well with most of the experimental data of [MIL1952] and [PLU/BUS1982] (see Figure 3.21-3.23). High temperature data of Ellis [ELI1959], [ELI1963] have not been considered in this work since they are not in the range of THEREDA region of interest. But at 373.15 K they agree with the model as well. At pressures above 1 bar the THEREDA model agree with the [LI/DUA2008] model. Both models disagree with data from Miller at high pressure (see Figure 3.21). The errors of calculations do not exceed those obtained with [LI/DUA2008] model and since Miller's data do not corresponds well with Plummer and Busenberg data at 1 bar it was assumed that some errors were done in calculation partial CO_2 pressure by these authors.

The solubility of calcite has also been measured in CO_2 unsaturated aqueous solutions. But these data are usually outside the THEREDA pressure region, except for

data of Weyl [WEY1959] who measured calcite solubility at very low CO_2 molalities and temperatures 273-353 K. Agreement of our model with these data is shown on Figure 3.23.

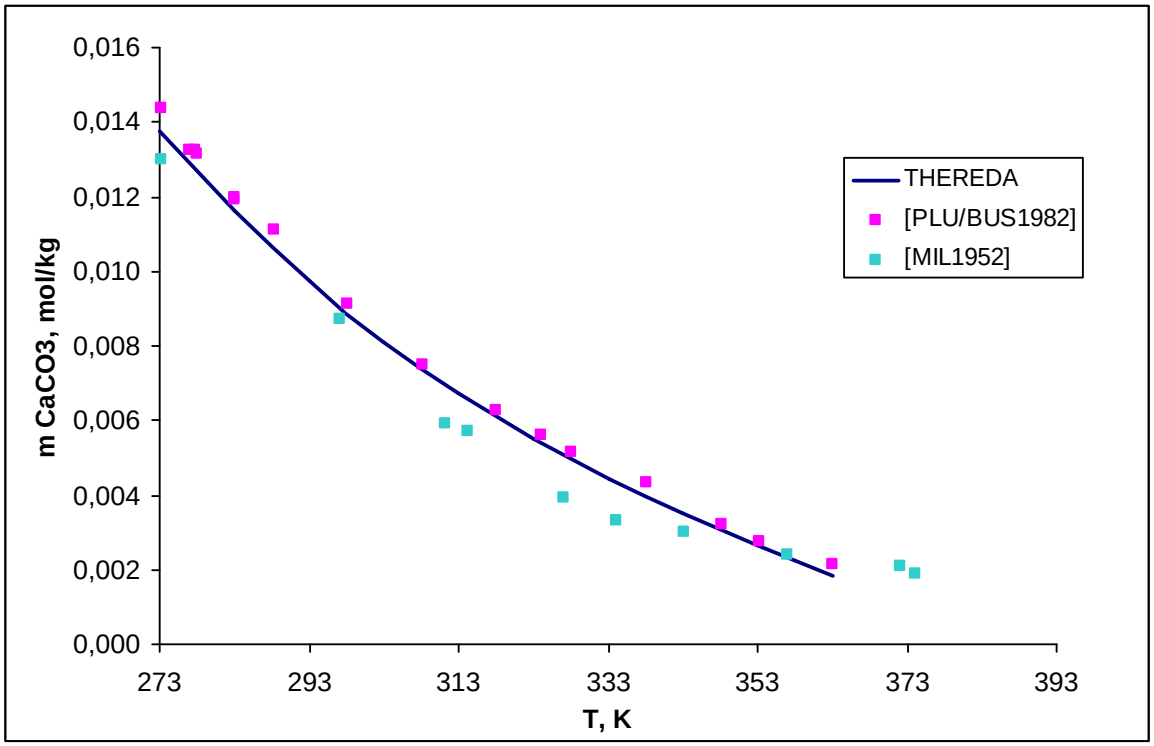

Figure 3.21 **The solubility of calcite at temperatures from 273 to 373 K and 1 bar CO_2 partial pressure**

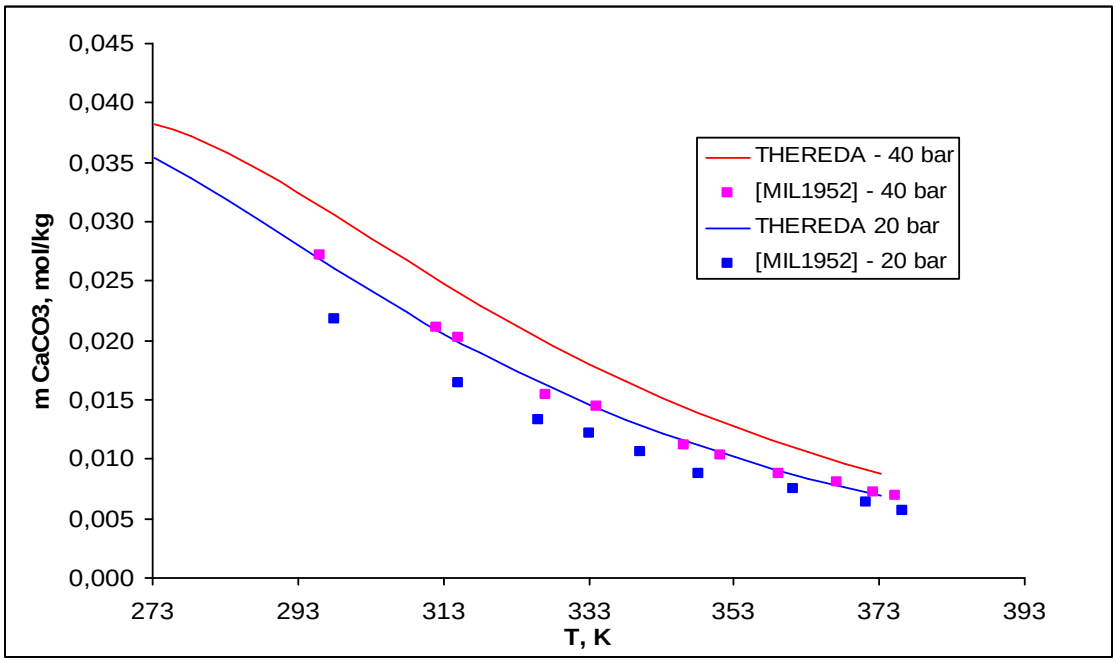

Figure 3.22 **The solubility of calcite at temperatures from 273 to 373 K and CO_2 partial pressures of 20 and 40 bar**

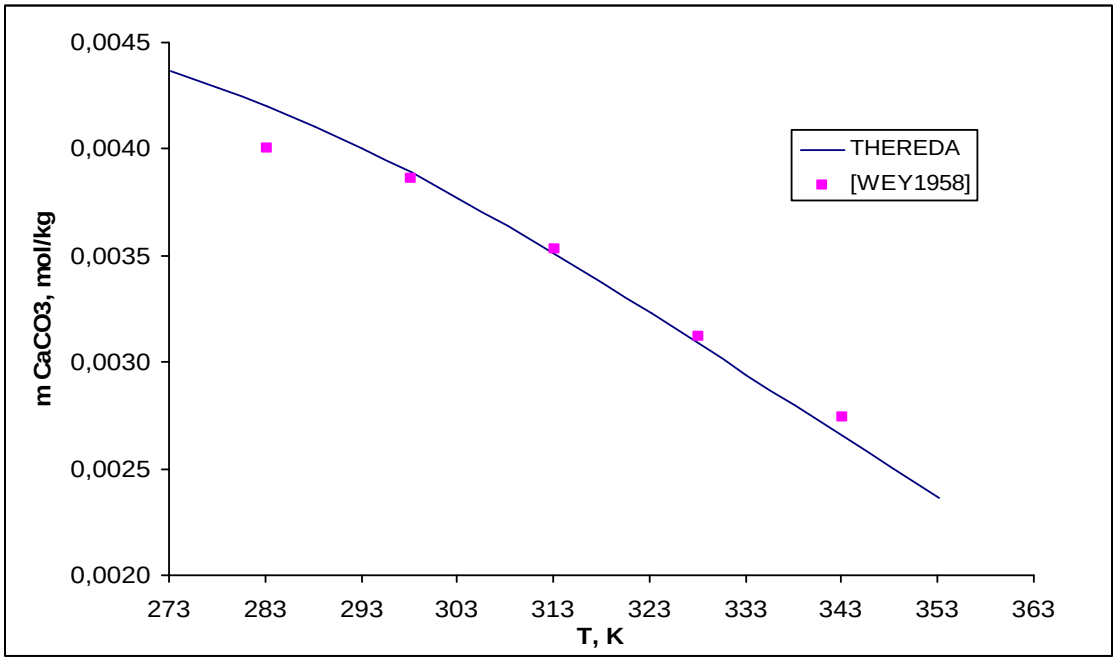

Figure 3.23 **The solubility of calcite at temperatures from 273 to 353 K at 0.0074 m of CO_2**

De Visscher and Vanderdeelen [DEV/VAN2012] analyzed all available literature for the calcite solubility and considered 36 references for the evaluation. It should be mentioned that De Visscher also noted that Miller [MIL1952] solubility's at 1 bar CO_2 and mid-range temperatures were too low. As a result of evaluation a regression based on the empirical equation (3.34) was proposed.

$$\lg S = A + B\lg(P_{CO_2}) + CP_{CO_2} + DTP_{CO_2} + E/T + F\lg(T) \qquad (3.34)$$

The standard deviation between the solubilities and the model prediction is 0.039 in lg scale [DEV/VAN2012].

We compared finally our model with tentative calculations done by De Visscher [DEV/VAN2012] and experimental data at 373.15 K. Our model shows good agreement with both experimental data and De Visscher fit (Figure 3.24).

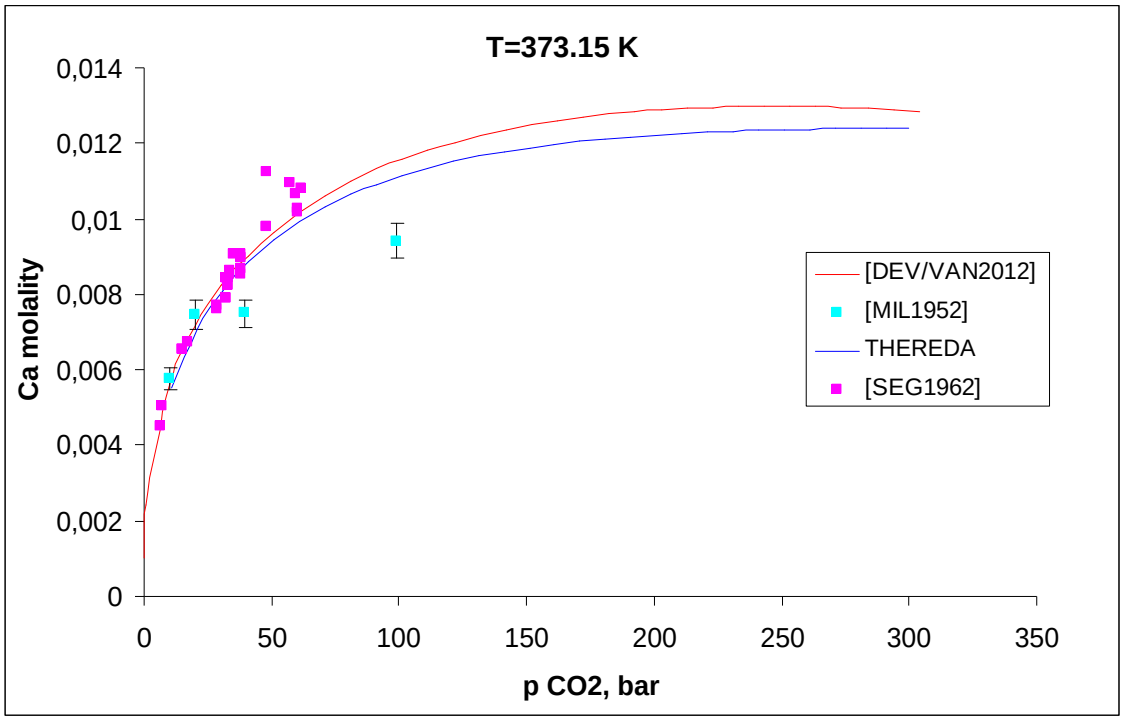

Figure 3.24 **The solubility of calcite at a of 373 K as function of p(CO_2).**

3.8.2 System $CaCO_3$(calcite)+H_2O

De Visscher evaluated 13 publications where the system $CaCO_3$-H_2O was investigated in absence of additional CO_2. Additional data were aquired from Berendsen [BER1934], who studied the solubility of calcite in CO_2-H_2O solutions from 373 K and up to 573 K. From Figure 3.25 one can see that above 323 K agreement with experimental data is weak. Extrapolation of the model shows that it predicts a maximum in the solubility at 393 K which corresponds well with experimental data. According to [DEV/VAN2012] the possibility of an overestimation of the solubility cannot be excluded due to the small crystals with increased solubility.

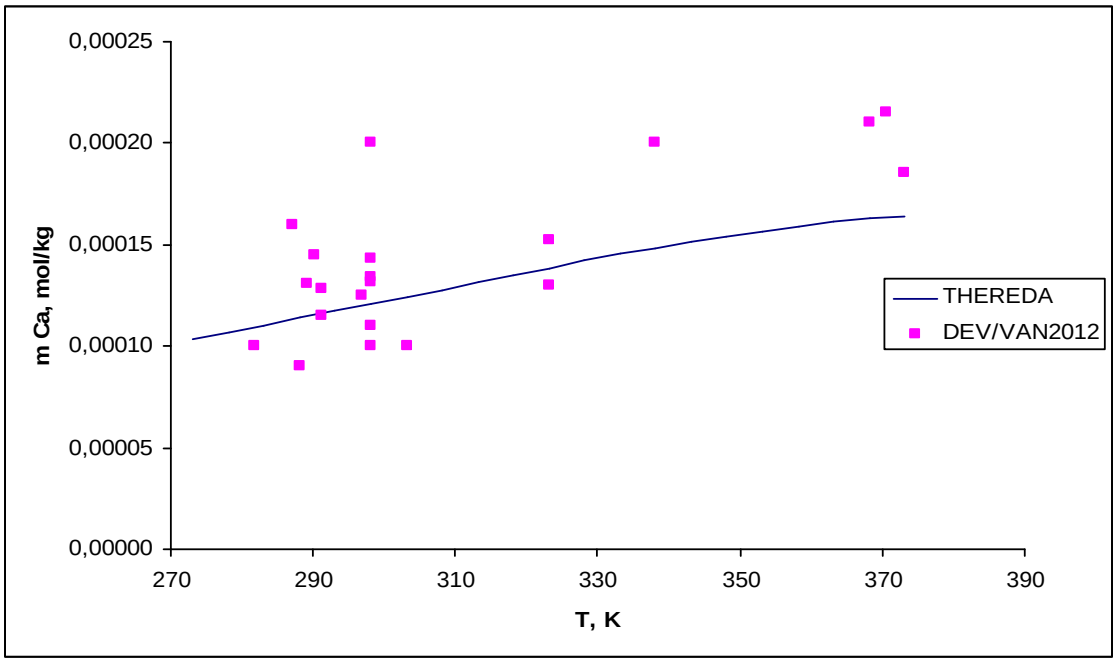

Figure 3.25 **The solubility of calcite in the system $CaCO_3$-H_2O measured and predicted with our model (closed system, no additional CO_2)**

3.9 Solubility of $CaCO_3$ in electrolyte solutions

The solubility of $CaCO_3$ depends on the concentration of dissolved CO_2, the concentration of which is a function of temperature, pressure and molality of electrolyte. By adding an electrolyte in the aqueous solution the activity of all species in the solution will be affected. Experimental data are available for the systems $CaCO_3$-H_2O-CO_2-NaCl, $CaCO_3$-H_2O-CO_2-$MgCl_2$, $CaCO_3$-H_2O-CO_2-$CaCl_2$, $CaCO_3$-H_2O-CO_2-KCl, $CaCO_3$-H_2O-CO_2-Na_2SO_4, $CaCO_3$-H_2O-CO_2-Na_2CO_3. The most intensively studied system is $CaCO_3$-H_2O-CO_2-NaCl. For this system Pitzer coefficients have been de-

rived from solubility data consistent with THEREDA-DB to describe the solubility in the complete T-P-range considered in this project.

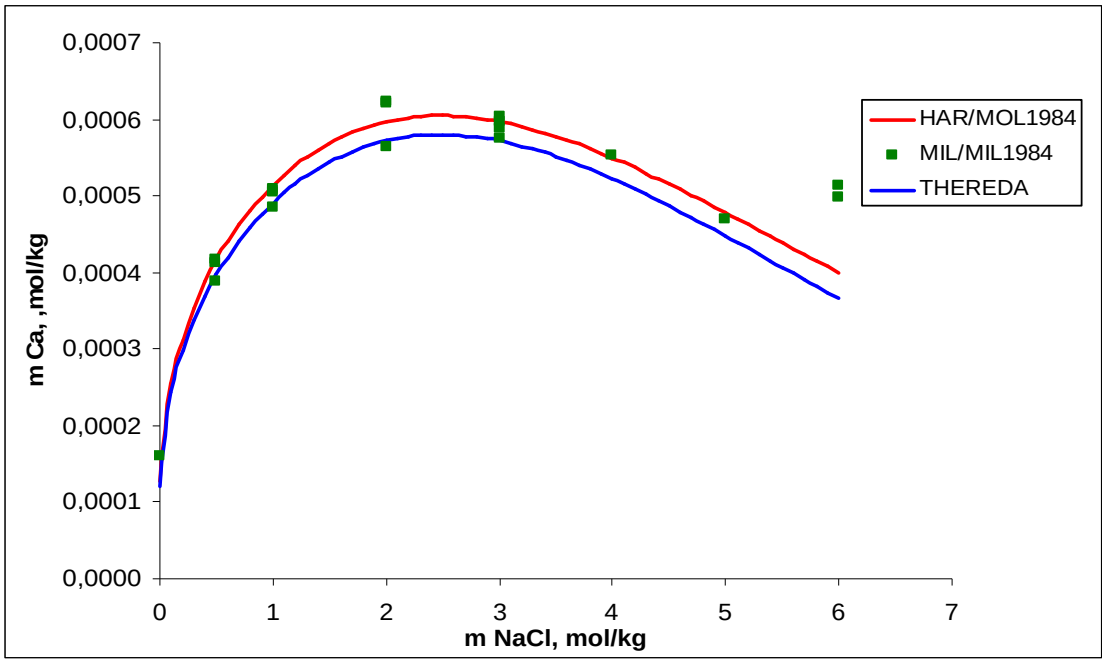

Figure 3.26 **The solubility of calcite in NaCl solutions at 298,15 K as function of NaCl molality (closed system, no additional CO_2)**

4 Literature

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Appendix 1

CHEMAPP datafile (“poli2CaC.dat”)

```
Parameter File for ChemApp - 2012-08-19 14:10:39
 7   2   4  10  12
 EA                        H                         O
 Ca                        C                         Na
 Cl
 0.00055                   1.0079                   15.9994
 40.0780                   12.0107                  22.9898
 35.4530
 7   1   2   3   4   5   6   7
 7   1   2   3   4   5   6   7
 GAS
 IDVT
 H2
   1  1    0.0    2.0    0.0    0.0    0.0    0.0    0.0
  393.15000     0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
0.000000     0.000000     0.000000     0.000000
 O2(g)
   1  1    0.0    0.0    2.0    0.0    0.0    0.0    0.0
  393.15000     0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
0.000000     0.000000     0.000000     0.000000
 H2O(g)
   1  1    0.0    2.0    1.0    0.0    0.0    0.0    0.0
  393.15000     -179019.12     -480.51629      57.283556     -.47821718E-01
0.24314485E-04 0.00000000     0.00000000
0.000000     0.000000     0.000000     0.000000
 CO2(g)
   1  1    0.0    0.0    2.0    0.0    1.0    0.0    0.0
  373.15000     -356914.28      77.815737     0.00000000     -.68388780
0.00000000     0.00000000      2.3100000
  304.100      73.8000      93.9000     0.239000
 AQUEOUS
 PIMZ
 H2O
   1  1   0.00    0.0    2.0    1.0    0.0    0.0    0.0    0.0
  393.15000     -237140.32     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
 H<+>
   1  1   1.00   -1.0    1.0    0.0    0.0    0.0    0.0    0.0
  393.15000     0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
 OH<->
   1  1  -1.00    1.0    1.0    1.0    0.0    0.0    0.0    0.0
  373.15000      740775.86     -24698.726      4264.4300     -8.4313800
0.32320000E-02 -34104000.     0.00000000
 Ca<2+>
   1  1   2.00   -2.0    0.0    0.0    1.0    0.0    0.0    0.0
  393.15000     -552806.15     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
 CO3<2->
   1  1  -2.00    2.0    0.0    3.0    0.0    1.0    0.0    0.0
  393.15000     -527899.77     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
 Ca(CO3)<0>
   1  1   0.00    0.0    0.0    3.0    1.0    1.0    0.0    0.0
  393.15000     -1092000.6      78.451200     0.00000000     -.34325000
0.00000000     0.00000000     0.00000000
 CO2<0>
   1  1   0.00    0.0    0.0    2.0    0.0    1.0    0.0    0.0
  393.15000     -390674.39      274.41952     0.00000000     -.86816000
0.00000000     0.00000000      5.5700000
 HCO3<->
   1  1  -1.00    1.0    1.0    3.0    0.0    1.0    0.0    0.0
  393.15000     -579358.49      99.102380     0.00000000     -.41700000
0.00000000     0.00000000      2.7500000
 Na<+>
   1  1   1.00   -1.0    0.0    0.0    0.0    0.0    1.0    0.0
```

```
 298.15000     -261952.89     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
Cl<->
  1  1  -1.00    1.0    0.0    0.0    0.0    0.0    0.0    1.0
 298.15000     -131218.37     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           beta0 (Ca<2+> HCO3<->)
  4   8   0  11402.672     -31.023894     0.00000000     0.00000000
0.00000000     -476670.28     0.00000000
  2           beta0 (Ca<2+> OH<->)
  3   4   0  3451.9555     -13.145695     0.00000000     0.21956428E-02
0.00000000     0.00000000     0.00000000
  2           beta0 (Ca<2+> Cl<->)
  4  10   0  4353540.3     -108709.06      18529.345     -34.897528
0.12265717E-01 -.19099769E+09 0.00000000
  2           beta0 (H<+> Cl<->)
  2  10   0  82323.710     -2375.0146      416.28386     -.90651573
0.35612776E-03 -2918607.0     0.00000000
  2           beta0 (Na<+> Cl<->)
  9  10   0 -25462.111      1099.6802     -202.87548     0.55401345
-.25795426E-03 0.00000000     0.00000000
  2           beta0 (Na<+> CO3<2->)
  5   9   0 0.00000000     0.33174855     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           beta0 (Na<+> HCO3<->)
  8   9   0 0.00000000     0.23031165     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           beta0 (Na<+> OH<->)
  3   9   0 -822.20764      6.2229969     0.00000000     -.87123620E-02
0.00000000     0.00000000     0.00000000
  2           beta1 (Ca<2+> HCO3<->)
  4   8   1 -23442.400      35.756507     0.00000000     0.00000000
0.00000000      4021889.9     0.00000000
  2           beta1 (Ca<2+> Cl<->)
  4  10   1 0.00000000      28.923303     0.00000000     -.12818310
0.26432309E-03 0.00000000     0.00000000
  2           beta1 (H<+> Cl<->)
  2  10   1  1577997.9     -38153.644      6456.0799     -11.610315
0.38843862E-02 -71498556.     0.00000000
  2           beta1 (Na<+> Cl<->)
  9  10   1 -54041.201      2457.9038     -457.39015      1.2911265
-.59926869E-03 0.00000000     0.00000000
  2           beta1 (Na<+> OH<->)
  3   9   1 -1713.7182      9.9959374     0.00000000     -.10773978E-01
0.00000000     0.00000000     0.00000000
  2           beta1 (Na<+> CO3<2->)
  5   9   1 0.00000000      11.548841     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           beta1 (Na<+> HCO3<->)
  8   9   1 0.00000000     0.34172595     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           beta1 (Ca<2+> OH<->)
  3   4   1 0.00000000     -1.9148293     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           beta2 (Ca<2+> OH<->)
  3   4   2 0.00000000     -47.558940     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           cphi (Ca<2+> Cl<->)
  4  10   3 -411152.18      10286.769     -1753.9742      3.3097027
-.11656019E-02  18003065.     0.00000000
  2           cphi (Na<+> Cl<->)
  9  10   3 -45899.952      1148.2943     -195.95545     0.37254307
-.13275686E-03  2032924.9     0.00000000
  2           cphi (Na<+> CO3<2->)
  5   9   3 0.00000000     0.36583800E-01 0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           cphi (Na<+> OH<->)
  3   9   3  143.84132     -.75771374     0.00000000     0.98332891E-03
0.00000000     0.00000000     0.00000000
  2           theta (Ca<2+> H<+>)
  2   4   0 0.00000000     0.80536520     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           theta (Cl<-> CO3<2->)
  5  10   0 0.00000000     -.16629000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           theta (Cl<-> HCO3<->)
```

```
  8  10   0 0.00000000     0.24943500     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           theta (Na<+> Ca<2+>)
  4   9   0  18850.732     -673.92309      116.52582     -.17687864
0.00000000     0.00000000     0.00000000
  2           theta (Na<+> H<+>)
  2   9   0 -33.709125     0.40022484     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           theta (OH<-> Cl<->)
  3  10   0 -410.41491     0.91863338     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           theta (CO3<2-> HCO3<->)
  5   8   0 0.00000000     -.33258000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           theta (OH<-> CO3<2->)
  3   5   0 0.00000000     0.83145000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           lambda (CO2<0> Ca<2+>)
  7   4   0 0.00000000      2.4043400     0.00000000     -.23600000E-02
0.00000000     0.00000000     0.00000000
  2           lambda (CO2<0> Cl<->)
  7  10   0 0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           lambda (CO2<0> Na<+>)
  7   9   0 -15409.477      278.07641     -45.034547     0.68442914E-01
-.20740000E-04  1118850.0     0.00000000
  3           psi (Ca<2+> Cl<-> OH<->)
  3   4  10  816.46667     -6.8203133     0.00000000     0.12635402E-01
0.00000000     0.00000000     0.00000000
  3           psi (Ca<2+> H<+> Cl<->)
  2   4  10  164.76428     -1.7327846     0.14272742     0.89866093E-03
0.00000000     0.00000000     0.00000000
  3           psi (Cl<-> CO3<2-> Na<+>)
  5   9  10 0.00000000     0.70673250E-01 0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  3           psi (Cl<-> HCO3<-> Na<+>)
  8   9  10 0.00000000     -.12471750     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  3           psi (CO3<2-> HCO3<-> Na<+>)
  5   8   9 0.00000000     0.16629000E-01 0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  3           psi (Na<+> Ca<2+> Cl<->)
  4   9  10 -51450.000      2513.9506     -475.27103      1.4455000
-.72523628E-03 0.00000000     0.00000000
  3           psi (Na<+> Ca<2+> OH<->)
  3   4   9 0.00000000      42293.593     -9944.2321      62.672124
-.48585601E-01 0.00000000     0.00000000
  3           psi (Na<+> Cl<-> OH<->)
  3   9  10 0.00000000     -30.043804      6.8878390     -.39341128E-01
0.28052686E-04 0.00000000     0.00000000
  3           psi (Na<+> H<+> Cl<->)
  2   9  10  29.874381     -.12107707     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  3           psi (OH<-> CO3<2-> Na<+>)
  3   5   9 0.00000000     -.14134650     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  3           psi (Cl<-> CO2<0> Na<+>)
  7   9  10 0.00000000     -.69837600E-01 0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  0
Aragonite
  1  1    0.0    0.0    3.0    1.0    1.0    0.0    0.0
 373.15000     -1121584.5      154.86113     0.00000000     -.59266000
0.00000000     0.00000000     0.00000000
Calcite
  1  1    0.0    0.0    3.0    1.0    1.0    0.0    0.0
 373.15000     -1121679.4      153.65056     0.00000000     -.59688500
0.00000000     0.00000000     0.00000000
Portlandite
  1  1    0.0    2.0    2.0    1.0    0.0    0.0    0.0
 393.15000     -1027086.8      7181.2509     -1394.5143      4.8035731
-.25896965E-02 0.00000000     0.00000000
Halite
  1  1    0.0    0.0    0.0    0.0    0.0    1.0    1.0
 393.15000      7502194.1     -201321.25      34480.308     -66.765887
0.24075243E-01 -.33942512E+09 0.00000000
```

Trona
```
  1  1    0.0    5.0    8.0    0.0    2.0    3.0    0.0
 298.15000     -2380892.8     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
```
Thermonatrite
```
  1  1    0.0    2.0    4.0    0.0    1.0    2.0    0.0
 298.15000     -1286181.9     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
```
Pirssonite
```
  1  1    0.0    4.0    8.0    1.0    2.0    2.0    0.0
 298.15000     -2659525.9     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
```
Natron
```
  1  1    0.0   20.0   13.0    0.0    1.0    2.0    0.0
 298.15000     -3427876.9     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
```
Nahcolite
```
  1  1    0.0    1.0    3.0    0.0    1.0    1.0    0.0
 298.15000     -851090.50     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
```
Na2(CO3):7H2O(cr)
```
  1  1    0.0   14.0   10.0    0.0    1.0    2.0    0.0
 298.15000     -2714383.5     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
```
Ca2Cl2(OH)2:H2O(cr)
```
  1  1    0.0    4.0    3.0    2.0    0.0    0.0    2.0
 393.15000     -2079470.0      14792.224     -3037.5181      12.059186
-.64205121E-02 0.00000000     0.00000000
```
Ca4Cl2(OH)6:13H2O(cr)
```
  1  1    0.0   32.0   19.0    4.0    0.0    0.0    2.0
 303.15000     -6979327.4      200912.76     -45011.753      232.19010
-.13906309     0.00000000     0.00000000

##########################################
# Date: 2012-08-19
# Time: 14:10:39
##########################################
```

Appendix 2

CHEMAPP datafile ("OZ3CARB8.DAT") tested for the system Na^{+}-Ca^{++}-Cl^{-}-CO_3^{2-}-CO_2-H_2O

```
oz3carb8.dat 18.10.2013
 10   2   4  20  63
 H                        O                        S
 Cl                       Na                       K
 Mg                       Ca                       EA
 C
 1.0079                  15.9994                  32.0660
 35.4527                 22.9898                  39.0983
 24.3050                 40.0800                  0.00055
 12.0110
 7   1   2   3   4   5   6   7
 7   1   2   3   4   5   6   7
 GAS
 IDVT
 H2O
   1  1    2.0    1.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
  393.15000      58121.200     -480.51629      57.283556     -.47821718E-01
0.24314485E-04 0.00000000     0.00000000
0.000000     0.000000     0.000000     0.000000
 H2
   1  1    2.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
  393.15000     0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
0.000000     0.000000     0.000000     0.000000
 O2
   1  1    0.0    2.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
  393.15000      228570.00     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
0.000000     0.000000     0.000000     0.000000
 CO2
   1  1    0.0    2.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    1.0
  400.00000     -66154.819      77.815737     0.00000000     -.68388780
0.00000000     0.00000000      2.3100000
 304.100      73.8000      93.9000     0.239000
 AQ
 PITZ
 Water
   1  1   0.00    2.0    1.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
  393.15000     0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
 Na+
   1  1   1.00    0.0    0.0    0.0    0.0    1.0    0.0    0.0    0.0   -1.0    0.0
  393.15000     0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
 K+
   1  1   1.00    0.0    0.0    0.0    0.0    0.0    1.0    0.0    0.0   -1.0    0.0
  393.15000     0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
 Mg++
   1  1   2.00    0.0    0.0    0.0    0.0    0.0    0.0    1.0    0.0   -2.0    0.0
  393.15000     0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
 Ca++
   1  1   2.00    0.0    0.0    0.0    0.0    0.0    0.0    0.0    1.0   -2.0    0.0
  393.15000     0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
 Cl-
   1  1  -1.00    0.0    0.0    0.0    1.0    0.0    0.0    0.0    0.0    1.0    0.0
  393.15000     0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
 SO4--
   1  1  -2.00    0.0    4.0    1.0    0.0    0.0    0.0    0.0    0.0    2.0    0.0
  393.15000     0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
 KMgSO4+
   1  1   1.00    0.0    4.0    1.0    0.0    0.0    1.0    1.0    0.0   -1.0    0.0
```

```
 393.15000      103945.00     -300.00000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
CaSO4
  1  1   0.00    0.0    4.0    1.0    0.0    0.0    0.0    0.0    1.0    0.0    0.0
 393.15000     0.00000000      215.43333     0.00000000     -.66666666
0.00000000     0.00000000     0.00000000
KCaSO4+
  1  1   1.00    0.0    4.0    1.0    0.0    0.0    1.0    0.0    1.0   -1.0    0.0
 393.15000      15957.550     -77.000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
H+
  1  1   1.00    1.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0   -1.0    0.0
 393.15000     0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
OH-
  1  1  -1.00    1.0    1.0    0.0    0.0    0.0    0.0    0.0    0.0    1.0    0.0
 393.15000      977916.17     -24698.726      4264.4288     -8.4313792
0.32319570E-02 -34104000.     0.00000000
HSO4-
  1  1  -1.00    1.0    4.0    1.0    0.0    0.0    0.0    0.0    0.0    1.0    0.0
 393.15000     -253892.51      10767.946     -1961.9057      4.7438017
-.21397000E-02 0.00000000     0.00000000
MgOH+
  1  1   1.00    1.0    1.0    0.0    0.0    0.0    0.0    1.0    0.0   -1.0    0.0
 393.15000      444044.08     -5495.0390      798.74121     0.00000000
-.52773000E-03 -24391000.     0.00000000
CO3--
  1  1  -2.00    0.0    3.0    0.0    0.0    0.0    0.0    0.0    0.0    2.0    1.0
 373.15000     0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
HCO3-
  1  1  -1.00    1.0    3.0    0.0    0.0    0.0    0.0    0.0    0.0    1.0    1.0
 373.15000     -124637.00      2321.2100     -368.73139     0.00000000
0.00000000     0.00000000     0.00000000
MgCO3
  1  1   0.00    0.0    3.0    0.0    0.0    0.0    0.0    1.0    0.0    0.0    1.0
 373.15000     -62354.566      1601.2591     -254.00140     0.00000000
0.00000000     0.00000000     0.00000000
CaCO3
  1  1   0.00    0.0    3.0    0.0    0.0    0.0    0.0    0.0    1.0    0.0    1.0
 373.15000     -86916.811      2181.9003     -342.50139     0.00000000
0.00000000     0.00000000     0.00000000
MgC2O6--
  1  1  -2.00    0.0    6.0    0.0    0.0    0.0    0.0    1.0    0.0    2.0    2.0
 373.15000     -21940.000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
CO2
  1  1   0.00    0.0    2.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    1.0
 393.15000     -99914.934      274.41952     0.00000000     -.86816000
0.00000000     0.00000000      5.5700000
  2          Na_Cl
  2   6   1 -54041.201      2457.9038     -457.39015      1.2911265
-.59926869E-03 0.00000000     0.00000000
  2          Na_Cl
  2   6   0 -25462.111      1099.6802     -202.87548     0.55401345
-.25795426E-03 0.00000000     0.00000000
  2          Na_Cl
  2   6   3 -45899.952      1148.2943     -195.95545     0.37254307
-.13275686E-03  2032924.9     0.00000000
  2          K_Cl
  3   6   1  932830.10     -23314.148      3977.0052     -7.5427738
0.26933085E-02 -41129020.     0.00000000
  2          K_Cl
  3   6   0 -6306.3515      222.30674     -39.129576     0.83743510E-01
-.31261673E-04 0.00000000     0.00000000
  2          K_Cl
  3   6   3  758.86535     -27.481697      4.8759814     -.10792744E-01
0.41215609E-05 0.00000000     0.00000000
  2          Na_SO4
  2   7   1 -419312.40      14159.515     -2420.4091      3.5104303
0.00000000     0.00000000     0.00000000
  2          Na_SO4
  2   7   0  8747.1895     -369.16438      65.313121     -.10779428
0.00000000     0.00000000     0.00000000
  2          Na_SO4
  2   7   3 -4109.7040      150.03581     -25.943605     0.38925801E-01
```

```
0.00000000     0.00000000     0.00000000
  2           K_SO4
  3   7   1  212990.82     -10996.509      2100.2948     -6.6658450
0.34806007E-02 0.00000000     0.00000000
  2           K_SO4
  3   7   0 -117355.18      5026.8850     -923.37731      2.4195104
-.10484916E-02 0.00000000     0.00000000
  2           K_SO4
  3   7   3  80534.975     -3479.5464      640.13439     -1.6880766
0.73687326E-03 0.00000000     0.00000000
  2           Mg_Cl
  4   6   1  10304.061     -61.221074     0.00000000     0.13631309
0.00000000     0.00000000     0.00000000
  2           Mg_Cl
  4   6   0 -79.776859      4.3283687     0.00000000     -.37941201E-02
0.00000000     0.00000000     0.00000000
  2           Mg_Cl
  4   6   3  104.16596     -.37703367     0.00000000     0.23750150E-03
0.00000000     0.00000000     0.00000000
  2           Mg_SO4
  4   7   1  463762.41     -15568.528      2834.7684     -7.6738503
0.39107196E-02 -15128800.     0.00000000
  2           Mg_SO4
  4   7   0  1375417.8     -32487.368      5474.7848     -9.6435732
0.31820206E-02 -64422337.     0.00000000
  2           Mg_SO4
  4   7   2 0.00000000      110733.56     -26548.943      182.29787
-.15895679     0.00000000     0.00000000
  2           Mg_SO4
  4   7   3  20686.481     -609.69496      105.63881     -.20174451
0.57701105E-04 -564154.80     0.00000000
  2           Ca_Cl
  5   6   1 0.00000000      28.923303     0.00000000     -.12818310
0.26432309E-03 0.00000000     0.00000000
  2           Ca_Cl
  5   6   0  4353540.3     -108709.06      18529.345     -34.897528
0.12265717E-01 -.19099769E+09 0.00000000
  2           Ca_Cl
  5   6   3 -411152.18      10286.769     -1753.9742      3.3097027
-.11656019E-02  18003065.     0.00000000
  2           Ca_SO4
  5   7   1 -667136.20      29847.346     -5532.6031      15.299141
-.69979612E-02 0.00000000     0.00000000
  2           Ca_SO4
  5   7   0  459602.04     -20546.038      3807.3626     -10.403044
0.46689217E-02 0.00000000     0.00000000
  2           Ca_SO4
  5   7   2 0.00000000     -1894.9632     0.00000000      4.8340222
0.00000000     0.00000000     0.00000000
  2           Na_K
  2   3   0 0.00000000     -.10013923     0.00000000     0.12290221E-05
0.00000000     0.00000000     0.00000000
  2           Na_Mg
  2   4   0 0.00000000     -.52666917     0.00000000     0.37185214E-02
0.00000000     0.00000000     0.00000000
  2           Na_Ca
  2   5   0  18850.732     -673.92309      116.52582     -.17687864
0.00000000     0.00000000     0.00000000
  2           K_Mg
  3   4   0 -8718.5630      48.878184     0.00000000     -.65859402E-01
0.00000000     0.00000000     0.00000000
  2           K_Ca
  3   5   0 0.00000000     0.96114464     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           Mg_Ca
  4   5   0 -39790.104      1873.7785     -351.39622      1.0251090
-.49490787E-03 0.00000000     0.00000000
  2           Cl_SO4
  6   7   0  5109.4482     -33.382704     0.00000000     0.55045510E-01
0.00000000     0.00000000     0.00000000
  3           Na_K_Cl
  2   3   6 0.00000000     -.65700641E-01 0.00000000     0.17016509E-03
0.00000000     0.00000000     0.00000000
  3           Na_K_SO4
  2   3   7 0.00000000     -.96064034     0.00000000     0.29431371E-02
0.00000000     0.00000000     0.00000000
```

```
  3           Na_Mg_Cl
  2   4   6 0.00000000     -22.252401      5.1456209     -.30585246E-01
0.21980779E-04 0.00000000     0.00000000
  3           Na_Mg_SO4
  2   4   7 -612.64839      3.8646778     0.00000000     -.64885494E-02
0.00000000     0.00000000     0.00000000
  3           Na_Ca_Cl
  2   5   6 -51450.000      2513.9506     -475.27103      1.4455000
-.72523628E-03 0.00000000     0.00000000
  3           Na_Ca_SO4      Fit2
  2   5   7  4500.0000     -243.33791      46.939769     -.15750618
0.84974384E-04 0.00000000     0.00000000
  3           K_Mg_Cl
  3   4   6  2761.3428     -20.016637     0.00000000     0.44709652E-01
-.31026497E-04 0.00000000     0.00000000
  3           K_Mg_SO4
  3   4   7  42872.031     -1663.2380      297.57900     -.66110952
0.23252540E-03 0.00000000     0.00000000
  3           K_Ca_Cl
  3   5   6 -225.12943     0.39599739     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  3           Mg_Ca_Cl
  4   5   6 -10.368957     -136.44495      32.410612     -.21338692
0.17257193E-03 0.00000000     0.00000000
  3           Mg_Ca_SO4
  4   5   7 -21402.093      451.11022     -66.594222     0.00000000
0.00000000     0.00000000     0.00000000
  3           Na_Cl_SO4
  2   6   7 -1067.0003      7.1618153     0.00000000     -.11978664E-01
0.00000000     0.00000000     0.00000000
  3           K_Cl_SO4
  3   6   7 -1715.9433      10.712108     0.00000000     -.16625208E-01
0.00000000     0.00000000     0.00000000
  3           Mg_Cl_SO4
  4   6   7 -5570.4817      48.515243     0.00000000     -.13697473
0.12345121E-03 0.00000000     0.00000000
  3           Ca_Cl_SO4
  5   6   7 0.00000000     -.14900000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           H_Cl
 11   6   0  82323.710     -2375.0146      416.28386     -.90651573
0.35612776E-03 -2918607.0     0.00000000
  2           H_Cl
 11   6   1  1577997.9     -38153.644      6456.0799     -11.610315
0.38843862E-02 -71498556.     0.00000000
  2           H_SO4
 11   7   0  151460.01     -4701.6130      844.52129     -2.1902487
0.10838151E-02 -5395166.6     0.00000000
  2           H_SO4
 11   7   3  103446.52     -3223.8018      576.78543     -1.4186518
0.62360134E-03 -3684995.5     0.00000000
  2           H_HSO4
 11  13   0 -31421.386      981.52779     -175.19474     0.43247963
-.19952910E-03  1119306.6     0.00000000
  2           H_HSO4
 11  13   1 0.00000000      1.6836341     0.00000000     0.13309668E-01
-.22320422E-04 0.00000000     0.00000000
  2           Na_HSO4
  2  13   0 -3724.1209      217.94920     -41.577711     0.12602265
-.59157789E-04 -88.482036     0.00000000
  2           Na_HSO4
  2  13   1  2348.1658     -182.23809      26.217169     0.15587374
-.23977321E-03  60.242074     0.00000000
  2           Na_HSO4
  2  13   3  788.46323     -45.762693      8.8024500     -.27760766E-01
0.13426776E-04  15.486435     0.00000000
  2           K_HSO4
  3  13   0 0.00000000     -.24943200E-02 0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           K_HSO4
  3  13   1 0.00000000     0.10000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           K_HSO4
  3  13   3  59.245579     -.62531422     0.00000000     0.19011374E-02
-.15271059E-05 0.00000000     0.00000000
  2           Ca_HSO4
```

```
  5  13   0  8215.3451     -350.78892      63.391964     -.11894779
0.00000000     0.00000000     0.00000000
  2           Ca_HSO4
  5  13   1 0.00000000      763.79753     -158.54199     0.53383464
0.00000000     0.00000000     0.00000000
  2           Mg_HSO4
  4  13   0 -1921426.5      34662.806     -5437.9751      5.0741461
0.00000000     0.11169814E+09 0.00000000
  2           Mg_HSO4
  4  13   1 0.00000000      14.375598     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           Mg_HSO4
  4  13   3 -465546.43      9120.2080     -1453.4742      1.4929710
0.00000000      24652196.     0.00000000
  2           Na_H
  2  11   0 -33.709125     0.40022484     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           K_H
  3  11   0 -464.57567      1.6860501     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           Mg_H
  4  11   0 0.00000000      4.2947604     0.00000000     -.26032434E-01
0.48461074E-04 0.00000000     0.00000000
  2           Ca_H
  5  11   0 0.00000000     0.80535551     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           SO4_HSO4
  7  13   0  1006551.8     -23650.785      3979.7223     -6.9341019
0.22484754E-02 -47426103.     0.00000000
  3           Na_H_Cl
  2  11   6  29.874381     -.12107707     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  3           K_H_Cl
  3  11   6  362.85837     -6.6788799     0.93012480     0.17664588E-03
0.00000000     0.00000000     0.00000000
  3           Mg_H_Cl
  4  11   6 -11285.199      509.21801     -94.030605     0.24337017
-.92902114E-04 -280.06282     0.00000000
  3           Ca_H_Cl
  5  11   6  164.76428     -1.7327846     0.14272742     0.89866093E-03
0.00000000     0.00000000     0.00000000
  3           Na_H_SO4
  2  11   7  20.611548     0.39593495E-01 0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  3           K_H_SO4
  3  11   7 -336.45625      1.0798498     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  3           Na_H_HSO4
  2  11  13 0.00000000     -.12166387     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  3           K_H_HSO4
  3  11  13 0.00000000     -320.57603      74.097326     -.43801465
0.32417929E-03 0.00000000     0.00000000
  3           Mg_H_HSO4
  4  11  13 0.00000000     -.14799632     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  3           Na_SO4_HSO4
  2   7  13  165.43522     -.85954991     0.00000000     0.11677977E-02
0.00000000     0.00000000     0.00000000
  3           Ca_SO4_HSO4
  5   7  13 -14603.328      375.08184     -60.564905     0.58214430E-01
0.00000000     0.00000000     0.00000000
  3           Ca_Cl_HSO4
  5   6  13 0.00000000      1463.1182     -338.98520      1.9992081
-.14379755E-02 0.00000000     0.00000000
  2           Na_OH
  2  12   0 -822.20764      6.2229969     0.00000000     -.87123620E-02
0.00000000     0.00000000     0.00000000
  2           Na_OH
  2  12   1 -1713.7182      9.9959374     0.00000000     -.10773978E-01
0.00000000     0.00000000     0.00000000
  2           Na_OH
  2  12   3  143.84132     -.75771374     0.00000000     0.98332891E-03
0.00000000     0.00000000     0.00000000
  2           K_OH
  3  12   0  1222.3097     -4.9108674     0.00000000     0.65508157E-02
```

```
0.00000000     0.00000000     0.00000000
  2           K_OH
  3  12   1 -17885.577      105.24053     0.00000000     -.14243722
0.00000000     0.00000000     0.00000000
  2           K_OH
  3  12   3 -185.54625      1.1384805     0.00000000     -.16813132E-02
0.00000000     0.00000000     0.00000000
  2           Ca_OH
  5  12   0  3451.9555     -13.145695     0.00000000     0.21956428E-02
0.00000000     0.00000000     0.00000000
  2           Ca_OH
  5  12   1 0.00000000     -1.9148293     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           Ca_OH
  5  12   2 0.00000000     -47.558940     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           MgOH_Cl
  6  14   0 0.00000000     -.83144100     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           MgOH_Cl
  6  14   1 0.00000000      13.785275     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           OH_Cl
  6  12   0 -410.41491     0.91863338     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           OH_SO4
  7  12   0 0.00000000     -2.7916115      1.2081932     -.18892988E-01
0.16245222E-04 0.00000000     0.00000000
  3           Na_K_OH
  2   3  12 -1530.0743      9.0785682     0.00000000     -.13340636E-01
0.00000000     0.00000000     0.00000000
  3           Na_Ca_OH
  2   5  12 0.00000000      42293.593     -9944.2321      62.672124
0.48585601E-01 0.00000000     0.00000000
  3           Na_Cl_OH
  2   6  12 0.00000000     -30.043804      6.8878390     -.39341128E-01
0.28052686E-04 0.00000000     0.00000000
  3           K_Cl_OH
  3   6  12 -14.168745     -.29432043E-01 0.00000000     0.16811406E-03
0.00000000     0.00000000     0.00000000
  3           Ca_Cl_OH
  5   6  12  816.46667     -6.8203133     0.00000000     0.12635402E-01
0.00000000     0.00000000     0.00000000
  3           Na_SO4_OH
  2   7  12 -21.239122     -.39060745     0.00000000     0.12283477E-02
0.00000000     0.00000000     0.00000000
  3           K_SO4_OH
  3   7  12 -349.95986      1.0928628     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  3           Mg_MgOH_Cl
  4   6  14 0.00000000     0.23280320     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  3           psi     Na_OH_CO3
  2  12  15 0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           beta0   Na_HCO3
  2  16   0 0.00000000     -.77378420E-01 0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           beta1   Na_HCO3
  2  16   1 -350.37300     -20.213800     -1.6194900     0.15376900
-.15617900E-03  14151.700     0.00000000
  2           beta0   Na_MgC2O6
  2  19   0 0.00000000     -19.731260     0.00000000     0.11949413
-.17543400E-03 0.00000000     0.00000000
  2           beta1   Na_MgC2O6
  2  19   1 0.00000000     -54.611160     0.00000000     0.43350670
-.16984104E-03 0.00000000     0.00000000
  2           cphi    Na_MgC2O6
  2  19   3 0.00000000     0.43235000E-01 0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           beta0   Na_CO3
  2  15   0 0.00000000     0.98688629     0.00000000     -.13679840E-02
0.00000000     0.00000000     0.00000000
  2           beta1   Na_CO3
  2  15   1 0.00000000     -1788.5200      365.75400     -.96277100
-.40047000E-07 0.00000000     0.00000000
```

```
  2           cphi    Na_CO3
  2  15   3 0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           theta   OH_CO3
 12  15   0 0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           theta   HCO3_CO3
 16  15   0 0.00000000     -.18023053     0.00000000     0.74289247E-03
0.00000000     0.00000000     0.00000000
  2           beta0   Mg_HCO3
  4  16   0 0.00000000     0.27438000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           beta1   Mg_HCO3
  4  16   1 0.00000000      7.0673300     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           beta0   HCO3_Ca
 16   5   0 0.00000000      2.3280000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           beta1   HCO3_Ca
 16   5   1 0.00000000      2.4940000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  3           psi     Na_HCO3_Cl
  2  16   6 0.00000000     -.11889700     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           lambda Na_CO2
  2  20   0 -15409.477      278.07641     -45.034547     0.68442914E-01
-.20740000E-04  1118850.0     0.00000000
  2           lambda Mg_CO2
  4  20   0 0.00000000      1.5220000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           lambda Ca_CO2
  5  20   0 0.00000000      2.4043400     0.00000000     -.23600000E-02
0.00000000     0.00000000     0.00000000
  2           lambda Cl_CO2
  6  20   0 0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  2           lambda H_CO2
 11  20   0 0.00000000     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  3           psi Na_CO2_Cl
  2  20   6 0.00000000     -.69800000E-01 0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
  0
anhy
  1  1    0.0    4.0    1.0    0.0    0.0    0.0    0.0    1.0    0.0    0.0
 393.15000     -1634543.8      80144.232     -15209.016      47.389963
-.24985450E-01 0.00000000     0.00000000
arc
  1  1    0.0    4.0    1.0    0.0    0.0    2.0    0.0    0.0    0.0    0.0
 393.15000     -107917.59      691.72159     0.00000000     -1.5035715
0.95079820E-03 0.00000000     0.00000000
astra
  1  1    8.0   12.0    2.0    0.0    2.0    0.0    1.0    0.0    0.0    0.0
 393.15000     -139697.38      890.67259     0.00000000     -1.5665144
0.00000000     0.00000000     0.00000000
bisch
  1  1   12.0    6.0    0.0    2.0    0.0    0.0    1.0    0.0    0.0    0.0
 393.15000      4095895.4     -195408.93      36798.927     -109.70474
0.53992175E-01 0.00000000     0.00000000
carn
  1  1   12.0    6.0    0.0    3.0    0.0    1.0    1.0    0.0    0.0    0.0
 393.15000      31505.274     -2025.8582      399.74737     -.92070257
0.00000000     0.00000000     0.00000000
eps
  1  1   14.0   11.0    1.0    0.0    0.0    0.0    1.0    0.0    0.0    0.0
 393.15000     0.00000000     -146.69220     0.00000000     0.60554922
-.78595383E-03 0.00000000     0.00000000
gips
  1  1    4.0    6.0    1.0    0.0    0.0    0.0    0.0    1.0    0.0    0.0
 393.15000     -2531757.3      124418.55     -23616.970      73.665316
-.38445596E-01 0.00000000     0.00000000
glas
  1  1    0.0   16.0    4.0    0.0    2.0    6.0    0.0    0.0    0.0    0.0
 393.15000     0.00000000     -817.57188     0.00000000      3.7356571
-.49701770E-02 0.00000000     0.00000000
glaub
```

```
  1  1    0.0    8.0    2.0    0.0    2.0    0.0    0.0    1.0    0.0    0.0
 393.15000     -158818.59      3748.4395     -581.93164     0.00000000
0.00000000     0.00000000     0.00000000
goerg
  1  1    2.0   25.0    6.0    0.0    0.0    2.0    0.0    5.0    0.0    0.0
 393.15000     -511049.22      11427.174     -1789.8090     0.00000000
0.00000000     0.00000000     0.00000000
hal
  1  1    0.0    0.0    0.0    1.0    1.0    0.0    0.0    0.0    0.0    0.0
 393.15000      7895365.4     -201321.25      34480.308     -66.765887
0.24075243E-01 -.33942512E+09 0.00000000
halb
  1  1    1.0 4.5000    1.0    0.0    0.0    0.0    0.0    1.0    0.0    0.0
 393.15000     -4030000.0      196701.57     -37230.085      114.27014
-.58574910E-01 0.00000000     0.00000000
hexa
  1  1   12.0   10.0    1.0    0.0    0.0    0.0    1.0    0.0    0.0    0.0
 393.15000     0.00000000     -103.65534     0.00000000     0.49632963
-.85078345E-03 0.00000000     0.00000000
kain
  1  1   22.0   27.0    4.0    4.0    0.0    4.0    4.0    0.0    0.0    0.0
 393.15000     -44652402.      2201390.7     -417522.56      1298.1013
-.67259605     0.00000000     0.00000000
kies
  1  1    2.0    5.0    1.0    0.0    0.0    0.0    1.0    0.0    0.0    0.0
 393.15000     0.00000000      96.355347     0.00000000     -.20228530
-.43189700E-03 0.00000000     0.00000000
labil
  1  1    4.0   14.0    3.0    0.0    4.0    0.0    0.0    1.0    0.0    0.0
 393.15000     -127642.37      3041.3789     -477.51957     0.00000000
0.00000000     0.00000000     0.00000000
lang
  1  1    0.0   12.0    3.0    0.0    0.0    2.0    2.0    0.0    0.0    0.0
 393.15000     0.12102524E+09 -2978817.1      506347.42     -941.62365
0.32892000     -.53836929E+10 0.00000000
leo
  1  1    8.0   12.0    2.0    0.0    0.0    2.0    1.0    0.0    0.0    0.0
 393.15000      79692.252     -1064.9813     0.00000000      3.8277529
-.47217095E-02 0.00000000     0.00000000
loew
  1  1   30.0   67.0   13.0    0.0   12.0    0.0    7.0    0.0    0.0    0.0
 393.15000     -424299.63      3324.1295     0.00000000     -7.0849414
0.00000000     0.00000000     0.00000000
mir
  1  1   20.0   14.0    1.0    0.0    2.0    0.0    0.0    0.0    0.0    0.0
 393.15000     0.00000000     -538.44215     0.00000000      2.5452016
-.27438983E-02 0.00000000     0.00000000
nona
  1  1    0.0   40.0   10.0    3.0   21.0    0.0    1.0    0.0    0.0    0.0
 393.15000     -3057443.5      26617.009     0.00000000     -75.451500
0.69148869E-01 0.00000000     0.00000000
penta
  1  1    6.0   27.0    6.0    0.0    2.0    0.0    0.0    5.0    0.0    0.0
 393.15000     -453127.22      10465.790     -1646.4830     0.00000000
0.00000000     0.00000000     0.00000000
poly
  1  1    4.0   18.0    4.0    0.0    0.0    2.0    1.0    2.0    0.0    0.0
 393.15000     0.00000000     -683.25031     0.00000000      3.0031109
-.54298021E-02 0.00000000     0.00000000
schoen
  1  1   12.0   14.0    2.0    0.0    0.0    2.0    1.0    0.0    0.0    0.0
 393.15000     -29989.906      17.604758     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
syl
  1  1    0.0    0.0    0.0    1.0    0.0    1.0    0.0    0.0    0.0    0.0
 393.15000     -162523.39      5834.9036     -1043.2716      2.6401379
-.12970464E-02 0.00000000     0.00000000
syn
  1  1    2.0    9.0    2.0    0.0    0.0    2.0    0.0    1.0    0.0    0.0
 393.15000      59721313.     -2893908.7      546617.83     -1662.2185
0.83970094     0.00000000     0.00000000
tach
  1  1   24.0   12.0    0.0    6.0    0.0    0.0    2.0    1.0    0.0    0.0
 393.15000     -480.87492     -19188.229      4771.0017     -33.744579
0.27039713E-01 0.00000000     0.00000000
then
```

```
  1  1    0.0    4.0    1.0    0.0    2.0    0.0    0.0    0.0    0.0    0.0
 393.15000     -74836.784      1781.8866     -271.69788     0.39034146E-01
0.00000000     0.00000000     0.00000000
vant
  1  1    0.0   16.0    4.0    0.0    6.0    0.0    1.0    0.0    0.0    0.0
 393.15000     -56967.899      612.34379     0.00000000     -1.4982407
0.00000000     0.00000000     0.00000000
nasesq
  1  1    1.0    8.0    2.0    0.0    3.0    0.0    0.0    0.0    0.0    0.0
 393.15000      4712442.1     -220547.46      41204.588     -116.35523
0.52353556E-01 0.00000000     0.00000000
merc
  1  1    1.0    4.0    1.0    0.0    0.0    1.0    0.0    0.0    0.0    0.0
 393.15000     -814526.58      15529.133     -2368.0462     0.00000000
0.27372940E-02  37827600.     0.00000000
ksesq
  1  1    1.0    8.0    2.0    0.0    0.0    3.0    0.0    0.0    0.0    0.0
 393.15000     -4881800.0      222927.83     -41527.894      116.55633
-.53585020E-01 0.00000000     0.00000000
mise
  1  1    6.0   28.0    7.0    0.0    0.0    8.0    0.0    0.0    0.0    0.0
 393.15000     -20309.179     0.00000000     0.00000000     -.98371727
0.17754310E-02 0.00000000     0.00000000
NaHS1
  1  1    3.0    5.0    1.0    0.0    1.0    0.0    0.0    0.0    0.0    0.0
 298.15000     -4696.4858     -39915.835      9446.2676     -61.269017
0.49214710E-01 -179.36619     0.00000000
port
  1  1    2.0    2.0    0.0    0.0    0.0    0.0    0.0    1.0    0.0    0.0
 393.15000     0.00000000      7181.2509     -1394.5143      4.8035731
-.25896965E-02 0.00000000     0.00000000
OxchlorA
  1  1   32.0   19.0    0.0    2.0    0.0    0.0    0.0    4.0    0.0    0.0
 393.15000     0.00000000      200912.76     -45011.753      232.19010
-.13906309     0.00000000     0.00000000
OxchlorB
  1  1    4.0    3.0    0.0    2.0    0.0    0.0    0.0    2.0    0.0    0.0
 393.15000     0.00000000      14792.224     -3037.5181      12.059186
-.64205121E-02 0.00000000     0.00000000
bruc
  1  1    2.0    2.0    0.0    0.0    0.0    0.0    1.0    0.0    0.0    0.0
 393.15000      127348.81     -99.376187     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
Mgoxychlor
  1  1   11.0    7.0    0.0    1.0    0.0    0.0    2.0    0.0    0.0    0.0
 298.15000      148656.37     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
MgSO4
  1  1    0.0    4.0    1.0    0.0    0.0    0.0    1.0    0.0    0.0    0.0
 298.15000      500000.00     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
MgCl2
  1  1    0.0    0.0    0.0    2.0    0.0    0.0    1.0    0.0    0.0    0.0
 298.15000      500000.00     0.00000000     0.00000000     0.00000000
0.00000000     0.00000000     0.00000000
CaCO3monohyd
  1  1    2.0    4.0    0.0    0.0    0.0    0.0    0.0    1.0    0.0    1.0
 298.15000      6110.1000     -165.95200     0.24521500E-03 0.00000000
0.00000000     0.00000000     0.00000000
Aragonit
  1  1    0.0    3.0    0.0    0.0    0.0    0.0    0.0    1.0    0.0    1.0
 400.00000     -117454.00      2678.5700     -428.91100     0.00000000
0.00000000     0.00000000     0.00000000
Calcit
  1  1    0.0    3.0    0.0    0.0    0.0    0.0    0.0    1.0    0.0    1.0
 400.00000     -117727.00      2685.2000     -430.45500     0.00000000
0.00000000     0.00000000     0.00000000
Vaterit
  1  1    0.0    3.0    0.0    0.0    0.0    0.0    0.0    1.0    0.0    1.0
 373.15000     -113768.00      2245.9600     -353.80100     0.00000000
0.00000000     0.00000000     0.00000000
Artinit
  1  1    8.0    8.0    0.0    0.0    0.0    0.0    1.0    0.0    0.0    1.0
 348.15000      46634.400      1388.1900     -238.11600     0.00000000
0.00000000     0.00000000     0.00000000
Dolomit
```

```
  1  1    0.0    6.0    0.0    0.0    0.0    0.0    1.0    1.0    0.0    2.0
 373.15000     -224721.00      5174.0600     -839.43700      0.00000000
0.00000000     0.00000000     0.00000000
Eitelit
  1  1    0.0    6.0    0.0    0.0    2.0    0.0    1.0    0.0    0.0    2.0
 348.15000     -172420.00      4752.7800     -759.37000      0.00000000
0.00000000     0.00000000     0.00000000
Gaylussit
  1  1   10.0   11.0    0.0    0.0    2.0    0.0    0.0    1.0    0.0    2.0
 348.15000     -31110.000     -76.230300     0.47584400E-04 0.00000000
0.00000000     0.00000000     0.00000000
Huntit
  1  1    0.0   12.0    0.0    0.0    0.0    0.0    3.0    1.0    0.0    4.0
 373.15000      941926.00     -19711.200      2801.8800      0.00000000
0.00000000     0.00000000     0.00000000
Hydromagnesit
  1  1   10.0   18.0    0.0    0.0    0.0    0.0    5.0    0.0    0.0    4.0
 348.15000     -196536.00      8701.9600     -1446.2500      0.00000000
0.00000000     0.00000000     0.00000000
Ikait
  1  1   12.0    9.0    0.0    0.0    0.0    0.0    0.0    1.0    0.0    1.0
 298.15000     -38500.000      3.1000000     -.21300000E-10 0.00000000
0.00000000     0.00000000     0.00000000
Magnesit_nat
  1  1    0.0    3.0    0.0    0.0    0.0    0.0    1.0    0.0    0.0    1.0
 373.15000     -102280.00      748.61800     -109.90300      0.00000000
0.00000000     0.00000000     0.00000000
Lansfordit
  1  1   10.0    8.0    0.0    0.0    0.0    0.0    1.0    0.0    0.0    1.0
 298.15000     -103761.00      2179.1700     -338.32200      0.00000000
0.00000000     0.00000000     0.00000000
Natron
  1  1   20.0   13.0    0.0    0.0    2.0    0.0    0.0    0.0    0.0    1.0
 303.15000     -314335.00      9686.3591     -1663.3500       2.7825353
0.00000000     0.00000000     0.00000000
Pirssonit
  1  1    4.0    8.0    0.0    0.0    2.0    0.0    0.0    1.0    0.0    2.0
 323.15000     -233513.00      4881.6200     -749.53300      0.00000000
0.00000000     0.00000000     0.00000000
Nesquehonit
  1  1    6.0    6.0    0.0    0.0    0.0    0.0    1.0    0.0    0.0    1.0
 343.15000     -72500.400      1973.1500     -321.34100      0.00000000
0.00000000     0.00000000     0.00000000
NaHCO3
  1  1    1.0    3.0    0.0    0.0    1.0    0.0    0.0    0.0    0.0    1.0
 373.15000     -165581.00      2870.3600     -442.46800      0.00000000
0.00000000     0.00000000     0.00000000
Na2CO3
  1  1    0.0    3.0    0.0    0.0    2.0    0.0    0.0    0.0    0.0    1.0
 393.15000     -588798.95      24275.246     -4399.0717       10.732585
-.46961801E-02 0.00000000     0.00000000
Na2CO3monoH
  1  1    2.0    4.0    0.0    0.0    2.0    0.0    0.0    0.0    0.0    1.0
 393.15000     -527680.88      23710.607     -4396.6639       12.239537
-.59711468E-02 0.00000000     0.00000000
Na2CO3hepta
  1  1   14.0   10.0    0.0    0.0    2.0    0.0    0.0    0.0    0.0    1.0
 373.15000     -157428.92      4031.7424     -666.13526      0.94643065
0.00000000     0.00000000     0.00000000
Trona
  1  1    5.0    8.0    0.0    0.0    3.0    0.0    0.0    0.0    0.0    2.0
 393.15000     -223552.00      4058.5500     -619.09200      0.00000000
0.00000000     0.00000000     0.00000000
Wegscheiderit
  1  1    3.0   12.0    0.0    0.0    5.0    0.0    0.0    0.0    0.0    4.0
 393.15000     -502982.00      9127.0500     -1413.9600      0.00000000
0.00000000     0.00000000     0.00000000

########################################
# 12.10.2013 last change
########################################
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