Density of Aqueous Solutions of CO_2 *

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Abstract

In this report, we present a numerical representation for the partial molar volume of CO_2 in water and the calculation of the corresponding aqueous solution density. The motivation behind this work is related to the importance of having accurate representations for aqueous phase properties in the numerical simulation of carbon dioxide disposal into aquifers as well as in geothermal applications. According to reported experimental data the density of aqueous solutions of CO_2 can be as much as 2-3 % higher than pure water density. This density variation might produce an influence on the groundwater flow regime. For instance, in geologic sequestration of CO_2, convective transport mixing might occur when, several years after injection of carbon dioxide has stopped, the CO_2-rich gas phase is concentrated at the top of the formation, just below an overlaying caprock. In this particular case the heavier CO_2 saturated water will flow downward and will be replaced by water with a lesser CO_2 content.

1 Introduction

Disposal of CO_2 into geological formations requires, among other conditions, the presence of a regional caprock for confinement. In order to avoid two-phase conditions in the injection line, geological disposal of CO_2 would be made at supercritical conditions. Under such conditions, CO_2 is less dense than water and would have a tendency to migrate to the top of the formation (Pruess and García, 2001). After a relatively long time (decades after ending injection) almost all gas would be stored at the top, underlying the caprock. Because the density of CO_2 saturated water is slightly higher than the density of pure water, density driven flow will occur enhancing the dissolution process by convective mixing. In such flow problems, numerical simulation capabilities that take into account variable density brines are crucial (Oldenburg and Pruess, 1995).

In this report we present a new correlation for the partial molar volume of CO_2 in water and the calculation of the corresponding aqueous solution density. This aqueous phase density correlation is then incorporated into the TOUGH2 Equation-of-State (EOS) module for carbon dioxide ECO2 (under development) (Pruess and García, 2001; Pruess et al., 1999). Currently, the brine density correlation considers only salinity effects with no CO_2 dependency (Battistelli et al., 1997). Figure 1 shows the computed brine density from 10 to 110 ^oC at various salt mass fractions (XNaCl=0.00, 0.05, 0.10 and 0.25) as implemented inside EWASG. The density increase due to salinity is up to almost 20%.

Experimental data for the system H_2O-CO_2 show that the carbon dioxide content produce an increase in aqueous phase density on the order of 2 to 3 %. Because the salinity effect is considerable higher, the dependency on CO_2 content is often ignored. This assumption is perfectly acceptable in geothermal applications. Nevertheless, as discussed before, it can conceal key processes in fluid flow dynamics of carbon dioxide sequestration.

Based on thermodynamic theory (Söhnel and Novotný, 1985; Anderson and Crerar, 1993), the density of aqueous solutions of CO_2 may be expressed as:

$$\rho_{aq} = \rho_1 + M_2 \cdot c - c \cdot \rho_1 \cdot V_\phi \qquad (1)$$

where V_ϕ is the apparent molar volume of dissolved CO_2; M_2 is the molecular weight of CO_2; ρ_1 is the density of pure water and c is the CO_2 concentration

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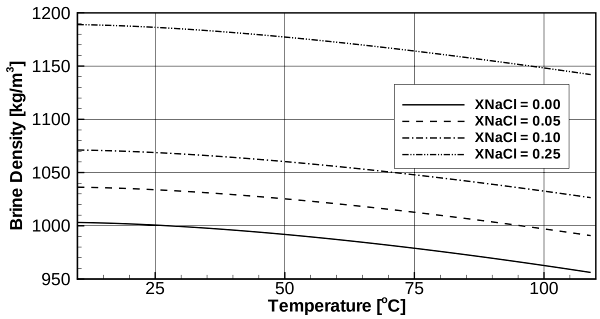

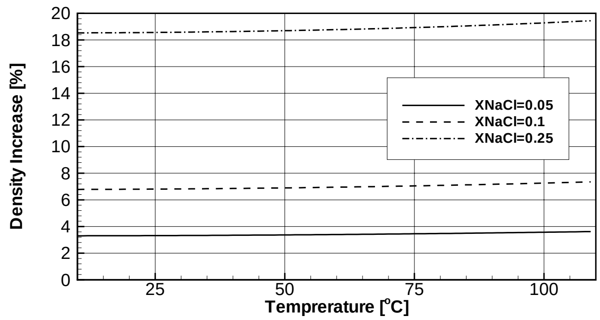

Figure 1: Computed density and density increase of NaCl solutions for salt mass fraction (XNaCl) from 0 to 0.25 using the EWASG correlation.

expressed by the number of moles of solute in 1 m^3 of solution (for details see Appendix A).

2 Experimental Data and Preliminary Correlations

A large number of data exist on the solubility of CO_2 in water (Scharlin (1996) and Drummond (1981)). In spite of their significance, there is limited experimental data on densities of the aqueous system H_2O-CO_2-NaCl. Usually, there is two sets of data, one for the system H_2O-NaCl and another for the system H_2O-CO_2. Because the effect of salinity on density is considerably higher than the effect of carbon dioxide, the latter is often ignored. The most significant investigations of partial molar volume of CO_2 and density of aqueous solutions of CO_2 along with experimental conditions are listed in Table 1.

The data collected indicate that CO_2 saturated water is heavier than pure water below 300 ^{o}C and down to at least 5 ^{o}C. Some measurements were done at CO_2 saturation, while others were for very low mole fraction. Apparent molar volumes for data sets reporting only densities and solubilities were calculated using the theory presented in Appendix A.

Table 1: Experimental data for partial molar volume and density of aqueous solutions for the system CO_2-H_2O.

NP *	T [^oC]	P [MPa]	Reference
24	5-20	6.4-29.5	Teng et al. (1997)
14	25-300	20-35	Hnědkovský et al. (1996)
5	274-297	19.6-29.4	Malinin (1974)
8	25-100	1.96	Ellis and McFadden (1972)
1	5-40	NR **	Parkinson and Nevers (1969)
1	25	NR **	Moore et al. (1982)

* Number of points used in this study
** Not reported

Experimental results show that the partial molar volume (approximated here as the apparent molar volume) is weakly dependent on CO_2 mole fraction (Parkinson and Nevers, 1969) and, for temperatures below 300^oC is independent of pressure (Malinin, 1974). Salinity effects on partial molar volume of CO_2 in water are not considered in this study. There are limited data that consider salinity. Malinin (1974) presented several data points for solutions of 1 M NaCl at high temperatures and pressures. His findings showed that the salinity effects are weak and within experimental uncertainty.

2.1 Previous Work

There are correlations available for the partial molar volume as a function of temperature. Most of these representations consider a polynomial fit as follows:

$$V_\phi = a + bT + cT^2 + dT^3 + eT^4 \tag{2}$$

Table 2 summarizes the different fits for Equation 2 found in the literature as well as other types of correlations.

2.2 Novel Correlation

The fit to Equation 2 proposed in this study considers 53 data points (See Figure 2). The following equation adequately represents the data with an $R^2 = 0.98$.

$$\begin{aligned} V_\phi =& 37.51 - 9.585 * 10^{-2}T \\ &+ 8.740 * 10^{-4}T^2 - 5.044 * 10^{-7}T^3 \end{aligned} \tag{3}$$

Equation 3 and 1 were used to compute densities of aqueous solutions of CO_2 at a pressure of 100 bar

Table 2: Correlations used by other authors for partial molar volume of CO_2 in water.

a	b	c	d	e	Reference
37.36	$-7.109 * 10^{-2}$	$-3.812 * 10^{-5}$	$+3.296 * 10^{-6}$	$-3.702 * 10^{-9}$	Andersen et al. (1992) *
1799.36	-17.8218	0.0659297	$-1.0579 * 10^{-4}$	$+6.200 * 10^{-8}$	Enick and Klara (1990) **
35.663	$-5.960 * 10^{-2}$	$+6.308 * 10^{-4}$			Jonathan Ennis-King[1] *
37.51	$-9.585 * 10^{-2}$	$+8.740 * 10^{-4}$	$-5.044 * 10^{-7}$		This work *
$V_\phi = e^{154.7881 - \frac{3582.452}{T} - 26.7757773 log(T) + 0.045234908 T}$					Iglesias and Moya (1992) ***

* Equation 2 V_ϕ is in $cm^3/mole$ and T is in degrees Celsius
** Equation 2 V_ϕ is in $cm^3/mole$ and T is in degrees Kelvin
*** V_ϕ is in $cm^3/mole$ and T is in degrees Kelvin
[1] Personal Communication

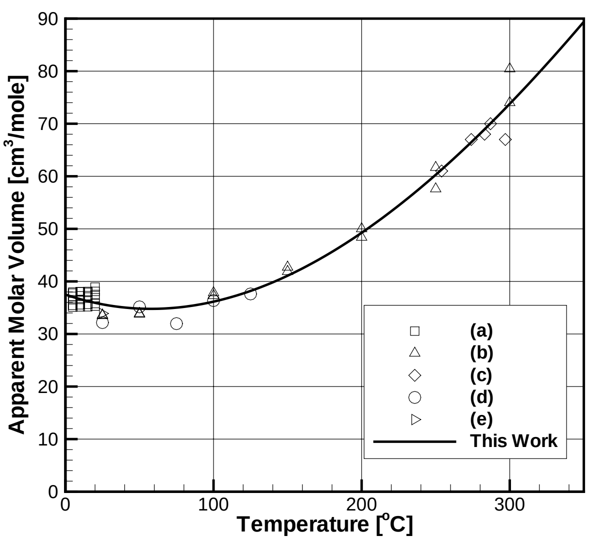

Figure 2: Fit of Partial Molar Volume Vs. Temperature. (a) Teng et al Teng et al. (1997), (b) Hnedkosky et al Hnědkovský et al. (1996), (c)Malinin Malinin (1974), (d) Ellis and McFadden Ellis and McFadden (1972), (e)Moore et al Moore et al. (1982)

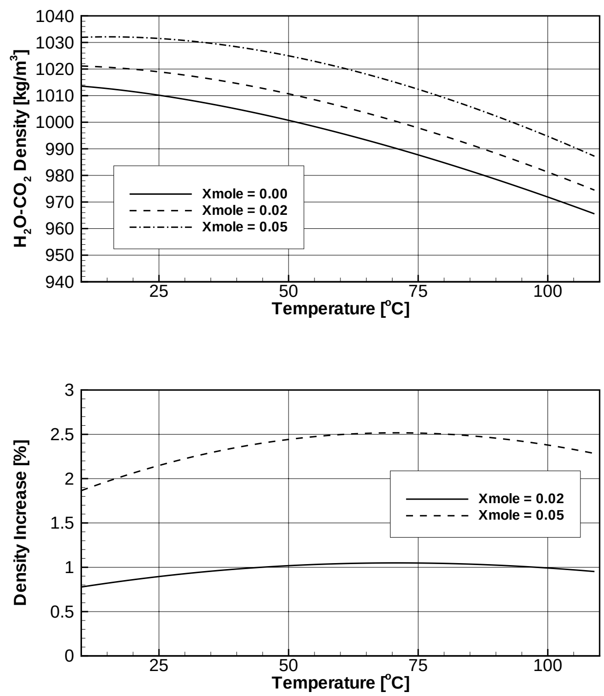

Figure 3: Computed density of aqueous solutions of CO_2 (P=100 bar)

for mole fractions (Xmole) of 0.02 and 0.05 (Figure 3). A maximum density increase of 2.5 % is obtained for a solution with a CO_2 mole fraction of 0.05.

As expected according Equation 1, the density variation of the aqueous solutions of CO_2 is nearly linear with respect to CO_2 mole fraction (See Figure 4). Figure 5 and 6 show a comparison between the measured and predicted values of the partial molar volume of CO_2 in water and the density of aqueous solutions of CO_2, respectively. Predicted values using Equation 3 agree very well with the measured data.

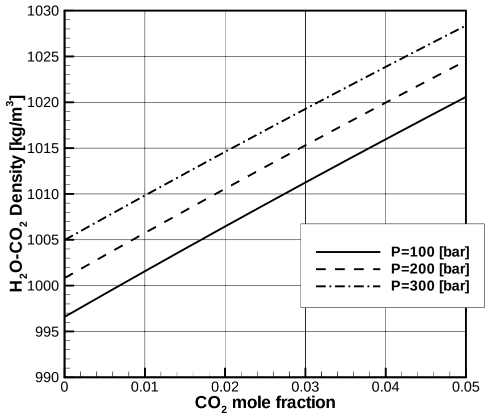

Figure 4: Computed density of aqueous solutions of CO_2 (P=100 bar)

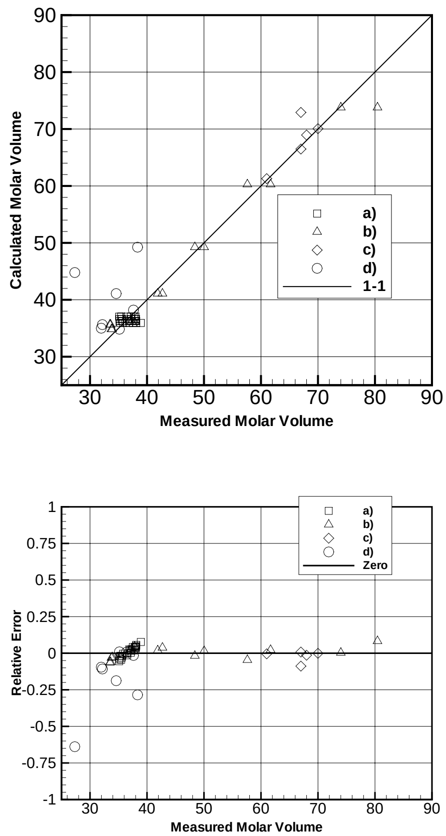

Figure 5: Comparison between measured and predicted partial molar volume of CO_2 in water

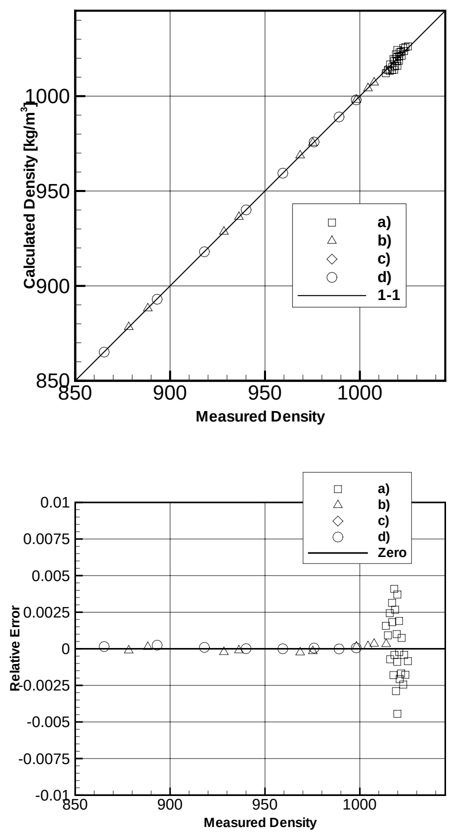

Figure 6: Comparison between measured and predicted density of aqueous solution of CO_2

3 TOUGH2-ECO2 Implementation

The proposed new formulation for the partial molar volume of CO_2 in water and the corresponding aqueous solution density is incorporated into the TOUGH2 Equation-of-State module ECO2 through the new subroutine COCO2. Only few changes are required in the rest of the module. Calls to subroutine COCO2 require the following arguments: aqueous phase temperature and pressure, CO_2 and Salt mass fractions, and brine density:

```
CALL COCO2(TX,PL,XG,XSA,DB)
```

The CO_2 dependency on brine density can be turned on through parameter specification in data block `SELEC`. A description of additional **SELEC**tion options is provided in Pruess et al. (1999).

IE(9) Allows to select brine density as a function of CO_2 content
0: Brine density independent of CO_2 content
1: Full dependence

The beta version of subroutine COCO2 is presented in Appendix B.

4 Nomenclature

c	molarity of solution (moles/m^3)
M	molecular weight (kg/mol)
m	molality of the solution expressed in moles of solute in 1 kg of solvent (mol/kg)
n_i	number of moles of the i-th component in the mixture (mol)
P	pressure (Pa)
T	temperature (^{o}C)
V	volume (m^3)
$\overline{V}_i$	partial molar volume of the i-th component (m^3/mol)
V_m	molar volume (m^3/mol)
V_ϕ	apparent molar volume of dissolved CO_2 (m^3/mol)
x_i	molar fraction
ρ	density of the solution (kg/m^3)
ρ_1	density of water (kg/m^3)

Subscripts

aq	aqueous phase
s	mixture
1	solvent (H_2O)
2	solute (CO_2)

Superscripts

o	at infinite dilution

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References

Andersen, G., Probst, A., Murray, L., and Butler, S. (1992). An accurate PVT model for geothermal fluis as represented by H_2O-CO_2-NaCl mixtures. *Proceedings, Seventeenth Workshop on Geothermal Reservoir Engineering*, 17:239–248. Stanford University, Stanford, California, January 29-31, 1992.

Anderson, G. M. and Crerar, D. A. (1993). *Thermodynamics in Geochemistry: The Equilibrium Model*. Oxford University Press.

Battistelli, A., Calore, C., and Pruess, K. (1997). The simulator TOUGH2/EWASG for modelling geothermal reservoirs with brines and non-condensible gas. *Geothermics*, 26(4):437–464.

Drummond, S. E. (1981). *Boiling and Mixing of Hydrothermal Fluids: Chemical Effects on Mineral Precipitation*. PhD thesis, Pennsylvania State University.

Ellis, A. and McFadden, I. (1972). Partial molal volumes of ions in hydrothermal solutions. *Geochimica et Cosmochimica Acta*, 36:413–426.

Enick, R. M. and Klara, S. M. (1990). CO_2 solubility in water and brine under reservoir conditions. *Chem. Eng. Comm.*, 90:23–33.

Hnědkovský, L., Wood, R. H., and Majer, V. (1996). Volumes of aqueous solutions of CH_4, CO_2, H_2S, and NH_3 at temperatures from 298.15 K to 705 K and pressures to 35 Mpa. *J. chem. Thermodynamics*, 28:125–142.

Iglesias, E. R. and Moya, S. L. (1992). An accurate formulation of the solubility of CO_2 in water for geothermal applications. *Proceedings, Seventeenth Workshop on Geothermal Reservoir Engineering*, 17:231–238. Stanford University, Stanford, California, January 29-31, 1992.

Malinin, S. (1974). Thermodynamics of the H_2O-CO_2 system. *Geochemistry International*, 11:1060–1085.

Moore, J. C., Battino, R., Retitic, T. R., Handa, P., and Wilhelm, E. (1982). Partial molar volumes of "gases" at infinite dilution in water at 298.15 k. *J. Chem. Eng. Data*, 27:22–24.

Oldenburg, C. M. and Pruess, K. (1995). Dispersive transport dynamics in a strongly coupled groundwater-brine flow system. *Water Resources Research*, 31(2):289–302.

Parkinson, W. and Nevers, N. D. (1969). Partial molal volume of carbon dioxide in water solutions. *Industrial and Engineering Chemistry Fundamentals*, 8(4):709–713.

Prausnitz, J. M., Lichtenthaler, R. N., and de Azevedo, E. G. (1986). *Molecular Thermodynamics of Fluid-Phase Equilibria*. Prentice-Hall, second edition.

Pruess, K. and García, J. E. (2001). Multiphase flow dynamics during CO_2 disposal into saline aquifers. *Environmental Geology*, Submitted(Submitted).

Pruess, K., Oldenburg, C., and Moridis, G. (1999). TOUGH2 User's Guide Version 2.0. Technical Report LBL-43134, Lawrence Berkeley National Laboratory.

Scharlin, P. (1996). *Carbon Dioxide in Water and Aqueous Electrolyte Solutions*, volume 62 of *Solubility Data Series*. Oxford University Press, International Union of Pure and Applied Chemestry, Oxford, UK.

Söhnel, O. and Novotný, P. (1985). *Densities of Aqueous Solutions of Inorganic Substances*. Elsevier: New York.

Teng, H., Yamasaki, A., Chum, M.-K., and Lee, H. (1997). Solubility of liquid CO_2 in water at temperatures from 278 K to 293 K and pressures from 6.44 MPa to 29.49 MPa and densities of the corresponding aqueous solutions. *J. Chem. Thermodynamics*, 29:1301–1310.

A Density of Binary Aqueous Solutions

The partial molar volume is an important thermodynamic quantity since: (1) its value may be used to correct Henry's constant when the gas pressure is large (Prausnitz et al., 1986) and; (2) the knowledge of its value can be used to estimate the density of the solution. In this appendix we present an overview of theory related to partial molar volumes and estimation of the corresponding binary aqueous solutions density. For additional details the reader is referred to Prausnitz et al. (1986) and Anderson and Crerar (1993).

The definition of a partial molar property is applicable only to extensive properties differentiated at constant temperature and pressure. The total volume of a system with j-components can be expressed by the relation:

$$V = \sum_{i=1}^{j} n_i \overline{V_i} \tag{4}$$

where

$$\overline{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{5}$$

is the partial molar volume of the i-th component.

In practice, the apparent molar quantities are more easy to be determined, and the partial molar quantities are calculated from these. For binary solutions the apparent molar volume, V_ϕ, is defined as:

$$V_\phi = \frac{V - n_1 V_{m,1}}{n_2} \tag{6}$$

As illustrated in Figure 7, the apparent molar volume is the volume that should be attributed to the solute in the solution if one assumes that the solvent contributes the same volume it has in its pure state. Alternatively,

$$V = n_1 V_{m,1} + n_2 V_\phi \tag{7}$$

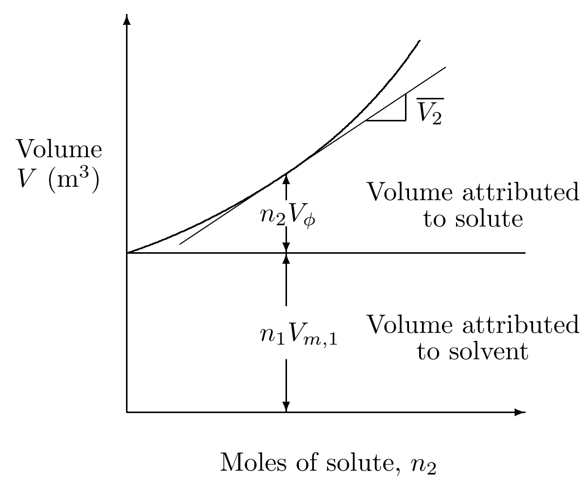

Figure 7: Total volume of a solution as a function of solute concentration showing the difference between partial molar volume and apparent molar volume. Adapted from Anderson and Crerar (1993).

Dividing Equation 7 by $(n_1 + n_2)$ we obtain:

$$V_m = x_1 V_{m,1} + x_2 V_\phi \tag{8}$$

The apparent molar volume V_ϕ can be seen (Figure 8) to be the intercept on the solute axis.

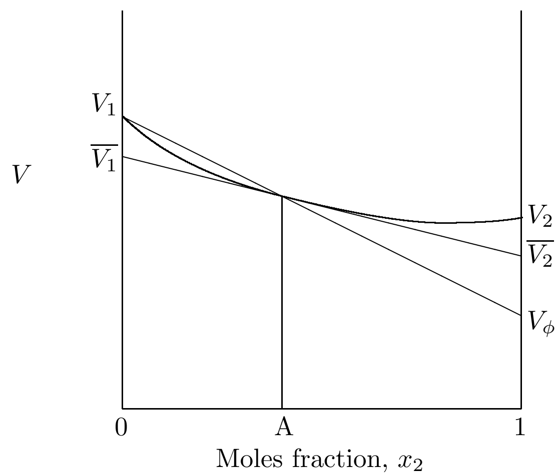

Figure 8: Molar volume of a binary solution versus mole fraction showing the difference between partial molar volume and apparent molar volume for solution at composition A. Adapted from Anderson and Crerar (1993)

The partial molar volume of solute and solvent in a binary solution can be obtained from V_ϕ as:

$$\overline{V}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1} = V_\phi + n_2 \left(\frac{\partial V_\phi}{\partial n_2}\right)_{T,P,n_1} \tag{9}$$

at infinite dilution (i.e. $n_2 \to 0$) the following relation holds

$$\overline{V}_2^o = V_\phi^o \tag{10}$$

i.e. the partial molar volume of a solute at infinite dilution is equal to its apparent molar volume at infinite dilution.

The apparent partial molar volume can be expressed in terms of densities and molecular weights (Teng et al., 1997).

$$V_\phi = \frac{1}{n_2}\left(\frac{n_1 M_1 + n_2 M_2}{\rho} - n_1 \frac{M_1}{\rho_1}\right) \tag{11}$$

If the composition is expressed by the number of moles of solute in 1 kg of solvent (i.e. $n_2 = m\, n_1 = 1/M_1$), we obtain:

$$V_\phi = \frac{\rho_1 - \rho}{m \rho \rho_1} + \frac{M_2}{\rho} \tag{12}$$

Or, if the composition is expressed by the number of moles of solute in 1 m^3 of solution (i.e. $n_2 = c\, n_1 = (\rho - cM_2)/M_1$):

$$V_\phi = \frac{\rho_1 - \rho}{c \rho_1} + \frac{M_2}{\rho_1} \tag{13}$$

Either Equation 12 or 13 can be used to obtain an expression for aqueous density. From equation 13

$$\rho_{aq} = \rho_1 + M_2 \cdot c - c \cdot \rho_1 \cdot V_\phi \tag{14}$$

Or from equation 12:

$$\rho = \frac{1 + m M_2}{m V_\phi + \frac{1}{\rho_1}} \tag{15}$$

where m can be expressed in terms of mol fractions $(x_1,\ x_2)$ as:

$$m = \frac{1}{M_1\left(\frac{1}{x_2} - 1\right)} = \frac{x_2}{M_1 x_1} \tag{16}$$

$$x_2 = \frac{m M_1}{1 + m M_1} \tag{17}$$

Replacing equation 16 into equation 15

$$\rho = \frac{1 + \frac{x_2 M_2}{M_1 x_1}}{\frac{x_2 V_\phi}{M_1 x_1} + \frac{1}{\rho_1}} \tag{18}$$

After further simplification we obtain an alternative equation for the aqueous phase density

$$\frac{1}{\rho} = \frac{x_2 V_\phi}{M_T} + \frac{M_1 x_1}{\rho_1 M_T} \tag{19}$$

where $M_T = M_1 x_1 + M_2 x_2$

A.1 Ideal Solutions

For an *ideal solution*, the partial molar volumes of the species in solution are equal to the molar volumes of pure species at the same temperature and pressure. In this event, the total volume becomes:

$$V = n_1 V_{m,1} + n_2 V_{m,2} \tag{20}$$

Expressing the molar volumes in terms of densities ($V_{m,i} = \frac{M_i}{\rho_i}$):

$$V = n_1 \frac{M_1}{\rho_1} + n_2 \frac{M_2}{\rho_2} \tag{21}$$

$$\frac{n_1 M_1 + n_2 M_2}{\rho} = n_1 \frac{M_1}{\rho_1} + n_2 \frac{M_2}{\rho_2} \tag{22}$$

Dividing Equation 22 by the total mass:

$$\frac{1}{\rho} = \frac{X_1}{\rho_1} + \frac{X_2}{\rho_2} \tag{23}$$

Where $X_i = \frac{n_1 M_i}{n_1 M_1 + n_2 M_2}$ is the mass fraction of specie i.

B Subroutine COCO2

(inc)(line)

```
      C
      SUBROUTINE COCO2(TX,PX,XG,XSA,DBJ)
      C      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/GASLAW/R,AMS,AMA,CVNCG
      COMMON/EOSG/ZA,AMSALT,GAST
      COMMON/EOSEL/IE(16),FE(512)
      COMMON/VISWAT/DW0
      COMMON/KONIT/KON,DELT,IGOOD
      SAVE ICALL
      DATA ICALL/0/
      ICALL=ICALL+1
      IF(ICALL.EQ.1) WRITE(11,899)
  899 FORMAT(6X,'COCO2    0.9      19 September 2001',6X,
      X'DENSITY OF AQUEOUS PHASE AS FUNCTION OF T, P',
      X' AND CO2 MOLE FRACTION')
      C
      C-----WHEN IE(9)>1 INCLUDE CO2 MOLE FRACTION DEPENDENCY.
      C
      DBC=DBJ
      C      Compute effective molecular weight
      EMW=(1.0-XG)/((1.0-XG-XSA)/AMS+XSA/AMSALT)
      C      Compute mole fraction.
      XMG=XG/(XG+AMA*(1.-XG)/EMW)
      C      Correlation for partial molar volume JULIO GARCIA (2001)
      IF(IE(9).EQ.1) THEN
         VPH=37.51-9.585E-2*TX+8.740E-4*TX*TX-5.044E-7*TX*TX*TX
      END IF
      C      Unit Conversion
      VPHI=VPH/1000000.
      TOTM=(1.0-XMG)*EMW+XMG*AMA
      DBINV=(XMG*VPHI/TOTM)+(EMW*(1.0-XMG))/(DBC*TOTM)
      DBJ=1./DBINV
      C-----IDEAL SOLUTIONS
      C      Partial molar volumes of species in solution are
      c      equal to molar volumes of pure species.
      c      To be included only for testing purposes...
      C      Get pure CO2 density at saturated conditions
      c      Calculate TOT1 and TOT2 and evaluate density of aqueous solution
      C      DBINV1=TOT1/DBC+TOT2/DCO2
      C      DB2=1./DBINV1
      IF (IGOOD.NE.0) RETURN
      C-----Viscosity OF CO2 SATURATED AQUEOUS PHASE
      C      There are few data points for this. To be included in a
      C      next version if COCO2.
      RETURN
      END
```