FORMATION OF HYDRATE FROM SINGLE-PHASE AQUEOUS SOLUTIONS

by

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ABSTRACT

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Experimental and theoretical research on the formation of hydrate from single-phase solutions of the hydrate former dissolved in water is described in this work. Two-phase equilibrium between carbon dioxide hydrate (H) and a water-rich liquid (L) are experimentally measured and theoretically described between 273 K and 280 K and at pressures to 60 MPa. Concentrations of carbon dioxide in the water phase ranging between 0.014 and 0.022 were studied. The theoretical and experimental results both indicate that the equilibrium pressure is very sensitive to concentration at all temperatures. These equilibria represent the solubility of carbon dioxide hydrate in a water phase and if a constant aqueous composition LH curve is extrapolated to the three-phase VLH curve, the composition characterizing the LH curve also represents the solubility of carbon dioxide in water at the VLH conditions. Since the solubility of carbon dioxide in water at hydrate- forming conditions is difficult to obtain, this method provides an excellent way of indirectly measuring this three-phase solubility.

DESCRIPTORS

Carbon dioxide solubility     Hydrate formation
Phase equilibrium             Single-phase solution
ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS ............................................................................................................iv

1.0  INTRODUCTION ................................................................................................................... 1

2.0  LITERATURE REVIEW ........................................................................................................ 3
    2.1  CO₂ and carbon sequestration ...........................................................................................3
    2.2  Oceanic Sequestration of CO₂ ..........................................................................................4
    2.3  Nature of Hydrates ............................................................................................................7
    2.4  Formation of CO₂ Hydrate ...............................................................................................9

3.0  DESCRIPTION OF EXPERIMENT ..................................................................................... 10

4.0  RESULTS AND DISCUSSION ............................................................................................ 13
    4.1  Analysis of the Experimental Results .................................................................................13
    4.2  Thermodynamic Models for Hydrate Equilibrium ............................................................16

5.0  SUMMARY AND CONCLUSIONS .................................................................................... 23

APPENDIX ................................................................................................................................24

BIBLIOGRAPHY .........................................................................................................................72
LIST OF TABLES

Table 1 Comparison of experimental data and calculated results by simplified and exact models
................................................................................................................................... 22
LIST OF FIGURES

Figure 1 Concept for introducing CO₂ captured from power and industrial plant into deep ocean by land based pipelines. ..............................................................................................................6

Figure 2 Gas Hydrate Structure I and Structure II.........................................................................................8

Figure 3 Overview of Laboratory Setup ..........................................................................................11

Figure 4 Schematic of Equipment........................................................................................................12

Figure 5 Pressure vs. Temperature history of an experiment in which hydrates were formed and decomposed in a single-phase solution of dissolved CO₂ in water. The trace was preceded as indicated in light arrows.........................................................................................14

Figure 6 dP/dT vs. Temperature for dissociation of CO₂ hydrate in a single-phase solution......15

Figure 7 Comparison of Experimental and Predicted data by using modified models..............20

Figure 8 Hydrate equilibrium temperature vs. Mole fraction of CO₂ at constant pressure ....21

Figure 9 Pressure vs. Mole fraction of CO₂ at constant Temperature .........................................................21
1.0 INTRODUCTION

The potential impact of rising greenhouse gas levels in the atmosphere is a current global concern. Carbon sequestration offers the potential to reduce the buildup of CO$_2$ in the atmosphere and is a topic of ongoing research and debate (U. S. Department of Energy, 1999). Oceanic CO$_2$ sequestration has been proposed as a method of long-term sequestration of anthropogenic emissions of CO$_2$. Understanding the fate of CO$_2$ released into the deep ocean is therefore important to assessing the utility of this strategy for long-term sequestration. The environmental impact and economics are also important and are under investigation (U. S. Department of Energy, 1999).

Direct injection of CO$_2$ through pipes to ocean depths ranging from 1000 m to 3000 m is a leading candidate for introducing CO$_2$ into the deep ocean. However, formation of the ice-like CO$_2$ clathrate hydrate at the interface of CO$_2$ and seawater complicates the fate of liquid CO$_2$ injected into the ocean (Holder, et al., 1995). The physical and chemical behavior of CO$_2$ in the ocean needs to be understood, especially the impact of CO$_2$ hydrate on the injection and sequestration process.

Formation of CO$_2$ hydrate from a single-phase aqueous solution using only the hydrate former dissolved in the aqueous phase is the focus of this work. Generally, in the laboratory, hydrates are formed from two-phase systems consisting of a hydrate former in a separate gas (V) or liquid phase (L$_2$) and liquid water (L$_1$). Information in the literature addressing the formation of hydrate from a single-phase solution of hydrate former dissolved in water is limited (Holder, et al., 2001). Prior work done at the National Energy Technology Laboratory (NETL) has
demonstrated that if CO\textsubscript{2} hydrate forms from a two-phase system of either gaseous or liquid CO\textsubscript{2} and water, the hydrate formed was initially less dense than the aqueous solution. This is likely due to occluded bubbles or drops of CO\textsubscript{2} in the hydrate clusters. Such floating hydrate particles will diminish the effectiveness of ocean sequestration of CO\textsubscript{2}. However, if CO\textsubscript{2} hydrate forms from a single-phase system, the hydrate formed was initially more dense than the aqueous phase. The formation of hydrates could enhance the ocean sequestration effort by causing the CO\textsubscript{2} to sink to even greater depths before it dissolves. (Holder, et al., 2001).

In this work, additional experimental single-phase CO\textsubscript{2} hydrate formation research was performed that compliments and extends previous work (Holder, et al., 2001) and further validates the thermodynamic model (Holder, et al., 1988) which describes the phase equilibrium of hydrate formation. Further modification and improvement to this model were also performed. Two-phase equilibrium between CO\textsubscript{2} hydrate (H) and a water-rich liquid (L\textsubscript{1}) were experimentally measured and theoretically described between 273 K and 280 K and at pressures to 60 MPa.
2.0 LITERATURE REVIEW

2.1 CO₂ and carbon sequestration

Carbon dioxide levels in the atmosphere arising from the combustion of fossil fuel (gas, oil, and coal) and other human activities have increased substantially since the Industrial Revolution, and are expected to continue doing so. Although the long-term consequences of these changes are hotly debated, many scientists agree that rising atmospheric CO₂ concentrations could give a variety of serious environmental problems and CO₂ is quantitatively by far the greatest contributor (64%) to climate forcing among the gases arising from anthropogenic activity (Johnston et al., 1999).

This problem has drawn attention throughout the world. In 1992, 167 nations signed the United Nations Framework Convention on Climate Change, which includes the objective to achieve “stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous interference with the climate system” (Johnston et al., 1999).

Three approaches to manage carbon dioxide were proposed. One is to reduce the need for carbon source energy by improving energy efficiency. Another approach is to increase the use of low-carbon and carbon-free fuels and technologies. The third and newest approach—carbon sequestration, which receives less attention to date than the other two approaches, is truly radical in a technology context. (U. S. Department of Energy, 1999)

Carbon sequestration is to capture and secure storage of carbon that would otherwise be emitted to or remain in the atmosphere. Six scientific/technological focus areas relevant to carbon sequestration were identified in order to achieve carbon emission reductions needed to mitigate the atmospheric CO₂ (U. S. Department of Energy, 1999):
1. Separation and Capture of CO₂

2. Ocean Sequestration

3. Carbon Sequestration in Terrestrial Ecosystems (Soils and Vegetation)

4. Sequestration of CO₂ in Geological Formations

5. Advanced Biological Processes for Sequestration

6. Advanced Chemical Approaches to Sequestration

Approximately 1 billion tones of carbon (GTC)/yr by 2025, and 4 GTC/yr by 2050 need to be sequestered in order to meet the goal adopted by Intergovernmental Panel on Climate Change (IPCC) of stabilizing the atmosphere at about 550 ppm CO₂. (Brewer, 2000) It is clear that advanced CO₂ sequestration is required. “Carbon Sequestration could be a major tool for reducing carbon emissions from fossil fuels. However, much work remains to be done to understand the science and engineering aspects and potential of carbon sequestration options.” (U. S. Department of Energy, 1999)

2.2 Oceanic Sequestration of CO₂

The direct disposal of CO₂ to the deep oceans is one of the approaches that are receiving the greatest focus, as a means of ameliorating greenhouse gas induced climate change (Handa, 1990; Wong & Hirai, 1997; Ormerod, 1996; Ormerod & Angel, 1996). Specifically the proposals fall into three distinct categories: (Johnston, et al., 1999)

- Ocean fertilization, which fertilize open waters to increase primary production and hence to absorb more carbon in fixed form that will eventually be incorporated into the ocean sediments (Coale et al., 1996; Boyd et al., 2000; Markels, 2001)
• Disposal of captured CO$_2$ directly into oceans (Brewer, 2000)

• Injection of captured CO$_2$ into sub-seabed geological formations (Winter & Bergman, 1993)

The ocean represents a large potential sink for sequestration of anthropogenic CO$_2$ emissions. It is generally accepted that more than 80% of today’s anthropogenic CO$_2$ emissions will eventually be absorbed naturally into the oceans, on a time scale of 1000 years. Ocean sequestration strategies attempt to investigate the possibility to speed up this process to reduce the peak of carbon dioxide concentration in the atmosphere and the rate of increase.

Technical approaches to introduce CO$_2$ into oceans include the following three methods (Johnston et al., 1999):

• Introduction by pipeline into deep ocean by dissolution

• Dispersion following discharge of dry-ice blocks or liquid CO$_2$ from a ship

• Formation of a lake of liquid CO$_2$ in the deep sea

Most research effort has focused on the introduction of CO$_2$ by pipeline. The concept is illustrated in Figure 1 below:

If CO$_2$ is introduced into ocean at depths of less than 500m, carbon dioxide exists as a gas at ambient pressures and temperatures, and the bubble plumes created will rise in the seawater with most gas dissolving but some possibly escape to the atmosphere. Optimistically, the retention time of the gas would be relatively short (about 50 years). At depth between 500m and 3000m, carbon dioxide exists as a positively buoyant liquid. It will form a droplet which will probably be which are solid, negatively buoyant, ice-like compounds (Adams et al., 1995). “Retention times
Figure 1 Concept for introducing CO$_2$ captured from power and industrial plant into deep ocean by land based pipelines.

In these cases should be much greater since deep water exchanges with surface water at a much lower rate than surface water interacts with the atmosphere in the upper mixed layer of the sea.” (Johnston et al., 1999) In general, the retention time for disposal of CO$_2$ into the ocean is considered as a function of the depth where it is discharged (Wong & Matear, 1993). There are considerable variations and uncertainty in likely residence times because the models (Bacastow et al., 1993; Ormerod, 1996) used to predict these times depend upon the data used to tune them and upon the accuracy of constant factors describing physical and chemical phenomena. An accurate description of the fate of CO$_2$ injected into ocean water is necessary for predicting the behavior of large-scale ocean disposal schemes. The first successful field experiment where CO$_2$ hydrate was formed in the deep ocean was performed by Monterey Bay Aquarium Research Institute (Brewer et al., 1999). Associated costs of oceanic disposal of CO$_2$ in terms of energy and economic penalties and impacts on the marine environment also need careful investigation and full understanding.
2.3 Nature of Hydrates

Gas hydrates are non-stoichiometric, crystalline molecular complexes formed from water and low molecular weight gases. The water molecules form a lattice structure and the gas molecules occupy the interstitial vacancies of the lattice. There is no chemical association between gas and water molecules. The gas molecules interact with the water molecules through van der Waals type dispersion force. Instead, the water molecules that form the lattice are strongly hydrogen bonded with each other (Holder, et. al., 1988; van der Waals, et. al., 1959; Parrish & Prausnitz, 1972). Although hydrates were first discovered by Davy in 1810, gas hydrates became a subject of investigation after it was been found out that formation of gas hydrates was responsible for the plugging of natural gas process and transportation lines (Hammerschmidt, 1934).

All common natural gas hydrates belong to the three crystal structures: cubic I (sI), cubic structure II (sII), and hexagonal structure (sH). Structure I is formed with gas molecules smaller than $6 \, \text{Å}$, such as methane, ethane, carbon dioxide and hydrogen sulfide. Structure II is formed with gas molecules somewhat larger ($6 \, \text{Å} < d < 7 \, \text{Å}$), such as propane or iso-butane. Still larger molecules ($7 \, \text{Å} < d < 9 \, \text{Å}$), such as iso-pentane or neo-hexane can form structure H when accompanied by smaller molecules such as methane, hydrogen sulfide or nitrogen. Structure I and II are shown in Figure 2 (Sloan, 1998).

At high pressure and low temperature, CO$_2$ and water can form structure I hydrate. The unit cell of the structure I hydrate contains eight cavities, two small and six large, which are constructed from 46 water molecules. Each cavity can at most hold one CO$_2$ molecule. Research in CO$_2$ hydrates formation has been performed in the laboratory at the temperature range from...
151.5 K to 292.7 K and the pressure range from 5.35 kPa to 186.2 kPa (Miller & Smythe, 1970; Takenouchi & Kennedy, 1965; Sloan, 1998).

Figure 2 Gas Hydrate Structure I and Structure II
2.4 Formation of CO$_2$ Hydrate

A considerable amount of research and experimental data in formation of CO$_2$ hydrate from two-phase system consisting of CO$_2$ in a separate gas (V) or liquid phase (L$_2$) and liquid water (L$_1$) have been published (von Stackelberg & Muller, Unruh & Katz, 1949; Takenouchi & Kennedy, 1946; Robinson & Mehta, 1971; Berecz & Balla-Achs, 1983; Ng & Robinson, 1985). Several research results indicate that hydrates formed from two-phase system are initially less dense than water and float. Such floating hydrate particles will diminish the effectiveness of ocean sequestration of CO$_2$. Research in formation of hydrate from single-phase is limited in literature. However, the previous research performed at the NETL has demonstrated that if CO$_2$ hydrate forms from a single-phase system, the hydrate formed was initially more dense than the aqueous phase (Holder, et al., 2001; Warzinski, et al., 2000; Warzinski, et al, 1995). This may have application to carbon sequestration.
3.0 DESCRIPTION OF EXPERIMENT

The experimental observations were made in a high-pressure, variable-volume viewcell (HVVC) of about 10 cm$^3$ to 40 cm$^3$ capacity. A sapphire window permits visual observation of the contents of the HVVC. A small oval-shaped high-density Teflon coated magnetic stirring bar was used to promote mixing within the HVVC. The entire system was enclosed in a temperature programmable environmental chamber that could maintain the temperature of interest to within 0.1 K. Water purified by reverse osmosis and deionization (18 mega ohm-cm) and CO$_2$ (SFC grade, 99.99+% purity) were used in the experiments reported here. Platinum Resistance Temperature Detector (RTD) used in the experiments has an accuracy of ±0.2% of reading. Pressure of the viewcell was measured by Heise ATS2000 Digital Pressure Transducer with an accuracy of ±0.02% of span. Ethylene Propylene Diene Monomer (EPDM) O-ring was used to provide the sealing of the cell.

The HVVC was filled with water injected into the HVVC with a syringe pump. The amount of liquid CO$_2$ injected through another syringe pump was determined from the volume delivered by using the density for CO$_2$ obtained from the IUPAC International Thermodynamic Tables of the fluid state for carbon dioxide at the pressure and the temperature of the laboratory. After dissolution of the added CO$_2$, the system was quickly subcooled to 271 K, and then heated up to 290 K at the rate of 0.3 K/hr. Overview of the laboratory setup and schematic of equipment are shown in Figure 3 and Figure 4, respectively.
Figure 3 Overview of Laboratory Setup
Figure 4 Schematic of Equipment
4.0 RESULTS AND DISCUSSION

4.1 Analysis of the Experimental Results

Five sets of experiments were performed in which CO₂ hydrate was formed from single-phase aqueous solutions. Mole fractions of CO₂ from 0.0160 to 0.020 were studied with accuracy of ±2%. The pressure versus temperature trace for a typical cycle is presented in the Figure 5. Note that this trace is not consistent with the formation of ice. Ice was not observed in these experiments.

Because of metastability in hydrate formation, the hydrate dissociation trace obtained during heating was used to evaluate the equilibrium point. Due to the difficulty in qualifying the equilibrium point from the pressure vs. temperature trace, the slope of dissociation curve vs. temperature was determined as shown in Figure 6. The peak of this curve represents the point of maximum dissociation, but does not represent the equilibrium for the overall CO₂ concentration, because the water phase composition is changed due to removal of CO₂ into the hydrate phase. The minimum in this trace indicates the absence of any further hydrate dissociation and represents a temperature slightly above the equilibrium value. The equilibrium is taken as the midpoint between the peak and the minimum. This produces an estimated uncertainty (±0.5K). Visual observation confirms the selection of this point. The equilibrium point is indicated in the Figure 6. Experiments are continuing at NETL to reduce the uncertainty of this point.

From the experiments, we found out that mixing was a very important factor in obtaining accurate equilibrium data, and the stirring bar played a key role. Different shapes and materials of the stirring bar were tested and it turned out that oval-shaped high-density Teflon coated magnetic stirring bar gave the best performance. We also found out that cooling rate had no
effect on equilibrium and 0.3K/hr of heating rate was satisfactory to obtain accurate equilibrium data.

Figure 5 Pressure vs. Temperature history of an experiment in which hydrates were formed and decomposed in a single-phase solution of dissolved CO$_2$ in water. The trace was preceded as indicated in light arrows.
Figure 6 dP/dT vs. Temperature for dissociation of CO₂ hydrate in a single-phase solution
4.2 Thermodynamic Models for Hydrate Equilibrium

The basic model for hydrate equilibrium used by author is based on the work of van der Waals and Platteeuw (vdWP) (1959) and extended by Parrish and Prausnitz (1972) by using the Kihara potential with modified Kihara parameters. This method was substantially simplified by John and Holder (1981). Bazant and Trout (2001) applied an analytical “inversion” method based on the standard statistical model of vdWP to extract cell potentials directly from experimental data. In this work, the John and Holder model was modified to allow its application to our experimental data.

For the water species in the hydrate phase, the value of $\Delta \mu_H$ (the chemical potential of water in the hydrate phase) is obtained by using the following equation (Holder, et al., 1988):

$$
\Delta \mu_H = -RT \sum_{j, \text{cavities}} \nu_j \ln \left(1 - \sum_i \theta_{ji}\right)
$$

(1)

Where, $\nu_j$ is the ratio of j-type cavities present to the number of water molecules present in the hydrate phase and

$$
\theta_{ji} = \frac{C_{ji}f_i}{1 + \sum_i C_{ji}f_i}
$$

(2)

Where, $C_{ji}$ is the Langmuir constant for species i in cavity j; $f_i$ is the fugacity for the hydrate forming species; $\theta_{ji}$ is the fraction of j-type cavities, which are occupied by i-type gas molecules. The value of $\Delta \mu_L$ (the chemical potential difference of water in the water-rich phase) is calculated from the following equation (Holder, et al., 1980):
\[
\frac{\Delta \mu}{RT} = \frac{\Delta \mu^0}{RT} - \int \frac{\Delta h}{RT} dT + \int \frac{\Delta V}{RT} dP - \ln x_w \tag{3}
\]

The terms \(\Delta h\) and \(\Delta V\) are the molar enthalpy and volume differences, respectively, between the empty hydrate or liquid water phases.

At equilibrium, \(\Delta \mu_H = \Delta \mu_L\), hydrates can exist.

For the present work, the above models were simplified by omitting the last term in Equation (3), because the concentration of water \((x_w)\) is very close to unity in water-rich solutions. The first two terms on the right represent \(\Delta \mu_L(T, P = 0)\), the chemical potential difference at a fixed temperature and zero pressure. At a fixed temperature, hydrate forms from single-phase solution. The following relationship is obtained:

\[
- \sum_{j, cavities} v_j \ln \left(1 - \sum_i \theta_{ji} \right) = \frac{\Delta \mu_L}{RT}(T, P = 0) + \int_0^P \frac{\Delta V}{RT} dP \tag{4}
\]

When hydrate forms from two-phase solution, the following relation is obtained:

\[
- \sum_{j, cavities} v_j \ln \left(1 - \sum_i \theta_{ji}^{VLH} \right) = \frac{\Delta \mu_L}{RT}(T, P = 0) + \int_0^{P_{VLH}} \frac{\Delta V}{RT} dP \tag{5}
\]

Subtracting equation (5) from equation (4), following equation is obtained:

\[
- \sum_{j, cavities} v_j \ln \left(\frac{1 - \sum_i \theta_{ji}^{VLH}}{1 - \sum_i \theta_{ji}} \right) = \int_{P_{VLH}}^P \frac{\Delta V}{RT} dP \tag{6}
\]

Since for single hydrate species,

\[
\frac{1 - \theta_{ji}^{VLH}}{1 - \theta_{ji}} = \frac{1 + C_{ji} f_{ji}^{VLH}}{1 + C_{ji} f_i}
\]
The following equation is obtained:

\[
\sum_v \ln \left[ \frac{1}{C_{\gamma_j} f_{i}^{\text{VLH}}} + \frac{f_{i}^{\text{sat}}}{f_{i}^{\text{VLH}}} \exp \left( \frac{\bar{V}_{ji} (P - P_{\text{sat}})}{RT} \right) \right] = \frac{\Delta V (P - P_{\text{VLH}})}{RT}
\]  

(7)

Where, \( P_{\text{sat}} \) and \( f_{i}^{\text{sat}} \) are the pressure and corresponding fugacity of the CO\(_2\), which are required to dissolve the experimental levels of CO\(_2\) in the water phase of the given temperature. We use the experimental solubility of CO\(_2\) in water (Kirk-Othmer, 1993) to obtain these values. The exponential term is the Poynting correction (J. M. Prausnitz, 1969) to \( f_{i}^{\text{sat}} \), giving the fugacity at pressure \( P \). \( \bar{V}_{ji} \) is the partial molar volume of CO\(_2\) in liquid water.

Equation (7) can be solved for the pressure. In this approach, reference state properties are not relevant, and the values of the pressures can be easily compared to those obtained in our experiments. Further simplification was also applied as following:

In some case, \( C_{ji} > 9 \), \( C_{ji} f_{i} \gg 1 \),

\[
\frac{f_{i}^{\text{sat}}}{f_{i}^{\text{VLH}}} \approx \frac{P_{\text{sat}}}{P_{\text{VLH}}}
\]

Then, the following equation is obtained:

\[
\sum_v \ln \left[ \frac{P_{\text{sat}}}{P_{\text{VLH}}} \exp \left( \frac{\bar{V}_{ji} (P - P_{\text{sat}})}{RT} \right) \right] = \frac{\Delta V (P - P_{\text{VLH}})}{RT}
\]  

(8)
In this equation, $P$ is the equilibrium pressure for hydrates formed from single-phase solutions. The values of all the other variables can be obtained from either experiments or literature data. Figure 7 presents the comparison of experimental and predicted data that are calculated by equation (7) and (8).

The vertical dash line represents $T=273.15$ K region. The lines for the calculated results obtained by equation (7) are compared to the dash lines obtained by equation (8).

More information can be obtained from Figure 3 as shown in Figure 8 and 9.
Figure 7 Comparison of Experimental and Predicted data by using modified models
Figure 8 Hydrate equilibrium temperature vs. Mole fraction of CO$_2$ at constant pressure

From Figure 8 and 9, it is very clear that for a given CO$_2$ concentration, the higher the pressure that the system can have, the higher the temperature hydrate can form at. For a given
temperature, the higher the concentration of CO$_2$, the lower pressure will be required in order to
form hydrate.

Comparison of experimental data and calculated results by simplified and exact models is
shown below. X is mole fraction of CO$_2$; T$_{exp}$ is the experimental temperature; T$_{sim}$ is the
calculated temperature calculated by simplified model; T$_{exa}$ is the calculated temperature
calculated by exact model.

Table 1 Comparison of experimental data and calculated results by simplified and exact models

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<th>P (MPa)</th>
<th>T$_{exp}$ (K)</th>
<th>T$_{sim}$ (K)</th>
<th>T$_{exa}$ (K)</th>
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</table>
5.0 SUMMARY AND CONCLUSIONS

Formation of CO$_2$ hydrate from single-phase aqueous solutions was performed in this work. The modified and simplified theoretical models can give reasonable prediction of the conditions of hydrate formation equilibria from single-phase aqueous solutions, and will have potential usage in ocean sequestration of CO$_2$. Further investigation of phase equilibrium condition is needed to have better understanding of these phenomena. In addition, the approximations made in the model should be examined and a more rigorous approach taken.
APPENDIX
CALCULATION OF HYDRATE PHASE EQUILIBRIA.
*********************************************************************
THIS PROGRAM CALCULATES PCALC WHEN TENURED PEXP.
LANGMUIR COEFFICIENTS ARE CALCULATED BY USING
Q* CORRELATION METHOD.

25 GASES ARE INCORPORATED INTO THE PROGRAM.
MIXTURES OF UP TO 10 COMPONENTS CAN BE STUDIED.

******** COMMON STATEMENTS ********
PROGRAM HYD
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
IMPLICIT INTEGER (I-N)
CHARACTER*5 YCOMP,YNAME,YNAMEL,YNAMEIM
CHARACTER*4 AQ
DIMENSION YNAME(25)
DIMENSION YCOMP(10)
DIMENSION ICASE(30),ILEN(31)
DIMENSION A(10),SIGMA(10),EPS(10),AMW(10),TC(10),VC(10),PC(10)
DIMENSION ZAA(1,25),AK(25,25)
DIMENSION IISCO(25),PPEXP(100)
DIMENSION KYP(20),NCODE(25)
DIMENSION OMEGA(10),ESTAR(10),C1RKV(10),C2RKV(10),C1RLK(10)
DIMENSION C3PREF(10),C4PREF(10),C1FREF(10),C2FREF(10)
DIMENSION C2FREF(10),C0FREF(10)
DIMENSION XX(13),KK(25),ZA(20),ICODE(10)
DIMENSION YNAMEIM(10)
DIMENSION YNAMEL(10)
COMMON/BKSB/NPT,NSETS,IFLAG
COMMON/BLOCK/ISOLVE
COMMON/AZ/KK,N,MK
COMMON/NC/NCODE,NCOMP
COMMON/DV/PVAP(100),AA(3),AB(3),FSAT(3,100),XY(100)
COMMON /AMOL/MA,ISCODE(10)
COMMON/TEXPT/PEXP(100),X15(100),IS(100),T(100),YEXP(100)
COMMON/SERDAT/T1(100),DT(100),T2(100)
COMMON/FUND/SIGMA,EPS,A
COMMON/XXX/XX,DH
COMMON/COR/EP,DDU,DDH,BETA1,GAMMA
COMMON/VDO/SIGN1,SIGN2
COMMON/BKSA/AK
COMMON/BKSC/IWATER,IPOS,ISTR,IDH
COMMON/PHAS/NVLLH
COMMON/STRUC/NSTRUC
COMMON/IMP/IMPURE,IMCODE,XIMP(100),YCO2(100)
COMMON/SOLUT/XSOLU,ACTIV,YYYCO2
COMMON/SEQ/ISEQ,TMIN,DELT,TMAX,TQL
COMMON/LIQUID/LIQ
*********************************************************************

**** READ IN EACH COMPONENT ****
DATA YNAME/ 'CH4', 'C2H6', 'C2H4', 'C3H8', 'C-C3',
  *'N-C4', 'I-C4', 'C-C4', 'C5H12', 'I-C5', 'NE-C5', 'C-C5',
  *'SF6', 'CIC4', 'TRC4', 'NONE' /
DATA YCOMP/ '*Y-1', '*Y-2', '*Y-3', '*Y-4', '*Y-5', '*Y-6', '*Y-7',
  '*Y-8', '*Y-9', '*Y-10' /
DATA YNAMEL/ 'XL1', 'XL2', 'XL3', 'XL4', 'XL5', 'XL6', 'XL7',
  '*XL8', '*XL9', '*XL0' /
DATA YNAMEIM/ 'MEOH', 'ETOH', 'PROH', 'NACL', 'CACL2', 'KCL',
  *'NH3', 'ETGLY', 'DEGLY', 'TRGLY' /

COMPONENT IDENTIFIERS, WHERE FOLLOWING CODE APPLIES.

**** 1 = METHANE
**** 2 = ETHANE
**** 3 = ETHYLENE
**** 4 = PROPANE
**** 5 = CYCLO -PROPANE
**** 6 = N-BUTANE
**** 7 = ISO-BUTANE
**** 8 = CYCLO-BUTANE
**** 9 = PENTANE
**** 10 = ISO-PENTANE
**** 11 = NEO-PENTANE
**** 12 = CYCLO-PENTANE
**** 13 = WATER
**** 14 = HYDROGEN
**** 15 = CARBON-DI-OXIDE
**** 16 = OXYGEN
**** 17 = NITROGEN
**** 18 = HYDROGEN SULFIDE
**** 19 = XENON
**** 20 = ARGON
**** 21 = KRYPTON
**** 22 = SULFUR HEXAFLOURIDE
**** 23 = CIS-2-BUTENE
**** 24 = TRANS-2-BUTENE
**** 25 = NO COMPONENT PRESENT

IMPURITY IDENTIFIERS, WHERE THE FOLLOWING CODE APPLIES

** 1 = METHANOL
** 2 = ETHANOL
** 3 = PROPAVLON
** 4 = SODIUM CHLORIDE
** 5 = CALCIUM CHLORIDE
** 6 = POTASSIUM CHLORIDE
** 7=AMMONIA
** 8=ETHYLENE GLYCOL
** 9=DIETHYLENE GLYCOL
** 10=TRIETHYLENE GLYCOL

FOLLOWING DATA IS READ FROM FILE FOR12.DAT:
1>ISOLVE=SELECT EQ. OF STATE: 1=PENG ROB. 2=RED. KWONG
2>ISTR=PRINT STRUCTURE DATA: 1=YES, 2=NO
3>ILANG=PRINT LANGMUIR CONSTS.: 1=YES, 2=NO
4>IN=PRINT SWITCH: 1=PRINT COMP. LIST 2=NO COMP LIST
5>NSETS=NUMBER OF ON LINE DATA SETS TO RUN
   =0 IF USES ENTERS HIS OWN EXPT. OR GUESSED DATA
6>IWATER= SWITCH FOR WATER CONTENT CALC FOR 2 & 3 PHASE SYS
   = 0 : DONT PERFORM CALCULATIONS
   = 2 : CALCULATE YH2O AND COMPARE WITH EXPMTL DATA
7>IPOS=COMPONENT POSITION OF WATER I.E. 1,2,0R 3 ...
8>NVLLH=SWITCH FOR QUADRUPLE POINT CALCULATION
   =0 :DONT PERFORM QUAD POINT CALCULATIONS
   =1 :CALCULATE QUADRUPLE POINT. IF NVLLH IS 1 THEN
        NSTRUC SHOULD NOT BE ZERO.
9>NSTRUC=SWITCH FOR CHECKING THE PRESENCE OF 'V L H1 H2' QUAD POINTS
   =1 :ONLY ONE HYDRATE STRUCTURE IS FORMED AND IS THE ONE
        GIVEN IN DATA.
   =2 :CHECK FOR 'V L H1 H2' QUAD POINTS
10>IMPURE=SWITCH FOR CALCULATIONS IN THE PRESENCE IMPURITIES
   =0 :NO IMPURITIES IN WATER
   =1 :IMPURITIES ARE PRESENT (SEE IMPURITY CODES)
11>ISEQ=SWITCH FOR CALCULATING EQUILIBRIUM CURVE BETWEEN TEMPERATURES
    T1(I) AND T2(I) AT INTERVALS OF DT(I)
   =0 :NO SEQUENTIAL CALCULATIONS
   =1 :SEQUENTIAL CALCULATIONS UPTO TEMPERATURE T2(I)
   =2 :SEQUENTIAL CALCULATIONS UPTO THE QUADRUPLE POINT(VLLH)
12>LIQ=SWITCH FOR CALCULATING L1 L2 H EQUILIBRIA ONLY
   =0 :GAS COMPOSITION IS GIVEN
   =1 :LIQUID COMPOSITION IS GIVEN
13>IDH=SWITCH FOR CALCULATING HEAT OF DISSOCIATION
    =0 NO CALCULATIONS PERFORMED
    =1 HEAT OF DISSOCIATION IS CALCULATED

14>MA=NUMBER OF COMPONENTS
15>KK(I)=CODE OF EACH COMPONENT
16>N=NUMBER OF DATA POINTS
17>EXPERIMENTAL HYDRATE CONDITIONS SUCH AS
    P/PSIA, T/DEG.R, Y(I), I=1,MA

* * READ IN OPTION SWITCHES * *

OPEN(12,FILE='TAPE12.DAT',STATUS='OLD')
OPEN(06,FILE='HYDOUT.DAT',STATUS='UNKNOWN')
READ(12,104)AQ
READ(12,200)ISOLVE,ISTR,ILANG,IN
GO TO(90,91),IN
90 CONTINUE
WRITE(06,301)
91 CONTINUE

C
C * * READ IN NUM OF ON LINE SETS TO RUN AND WATER SWITCH * *
C
READ(12,104)AQ
READ(12,302)NSETS,IWATER,NVLLH,NSTRUC,IMPURE,ISEQ,LIQ,IDH
IF(NVLLH.EQ.1.AND.NSTRUC.EQ.0)GO TO 1002
IF(IWATER.NE.0.AND.NVLLH.EQ.1)GO TO 1003
IF(ISEQ.EQ.2.AND.NVLLH.EQ.0)GO TO 1004
IF(LIQ.EQ.1.AND.ISEQ.EQ.1.AND.NVLLH.EQ.1)GO TO 1005
IF(LIQ.EQ.1.AND.ISEQ.EQ.2)GO TO 1006
IFLAG=1

C
C * * SET CONDITIONS FOR USER'S EXPT OR GUESSED DATA * *
C
IF(NSETS.NE.0)GO TO 56
ILEN(1)=0
ICASE(1)=1
IFLAG=0

C NSETS=1
GO TO 57

C
C 56 READ(12,104)AQ
C
C * * READ IN CODES FOR ON LINE DATA SETS TO BE RUN * *
C
DO 51 I=1,NSETS
READ(12,202)ICASE(I)
51 CONTINUE
READ(12,104)AQ

C ILEN(1)=0

C
C * * READ IN TOTAL NUMBER OF ON LINE DATA SETS * *
C * * PRESENT IN FOR12.DAT
C
READ(12,202)NTSETS
READ(12,104)AQ
NTSETS=NTSETS+1

C
C * * READ IN LENGTH OF EACH DATA ON LINE DATA SET * *
C
DO 50 I=2,NTSETS
READ(12,202)ILEN(I)
50 CONTINUE
READ(12,104)AQ

C
C * * CONVERT ILEN VALUES TO CUMULATIVE VALUES * *
C
DO 55 I=2,NTSETS
ILEN(I)=ILEN(I)+ILEN(I-1)
55 CONTINUE
IMOVE=ILEN(ICASE(I))

* * MOVE THROUGH FOR12.DAT AND GET DESIRED DATA * *

DO 983 IJK=1,NSETS
IF(IMOVE.EQ.0)GO TO 54
IF(IJK.EQ.1)GO TO 65
IMOVE=ILEN(ICASE(IJK)) - ILEN(ICASE(IJK-1)+1)
IF(IMOVE.EQ.0)GO TO 54

65 DO 53 I=1,IMOVE
READ(12,104)AQ
104 FORMAT(A4)
53 CONTINUE
54 IMOVE=1000

READ(12,202)MA

** CHECK WHETHER IMPURITY CALCULATION IS REQUIRED **
IF(IMPURE.EQ.1)GO TO 185
READ(12,308) (KK(I),I=1,MA)
GO TO 186
185 READ(12,309)(KK(I),I=1,MA),IMCODE

** CHECK FOR PRESENCE OF CO2 WITH INHIBITOR **
DO 1060 JJ=1,MA
IF(KK(JJ).EQ.15)JJ1=JJ
1060 CONTINUE

********** READ IN NUMBER OF DATA POINTS **********

186 READ(12,305) N
NPT=N

CHECK FOR HEAT OF DISSOCIATION CALCULATIONS

IF(IDH.EQ.0) GO TO 327
IF(ISEQ.EQ.1) GO TO 378
IF(IMPURE.EQ.1) GO TO 326
DO 328 I=1,N
READ(12,329) PEXP(I),T(I),IS(I),(X(J,I),J=1,MA)
328 CONTINUE
GO TO 12

378 CONTINUE
IF(IMPURE.EQ.0) GO TO 675
DO 468 I=1,N
READ(12,969) PEXP(I),T1(I),DT(I),T2(I),IS(I),(X(J,I),J=1,MA),XIMP(I)
468 CONTINUE
GO TO 12

675 CONTINUE
DO 8132 I=1,N
READ(12,968) PEXP(I),T1(I),DT(I),T2(I),IS(I),(X(J,I),J=1,MA)
8132 CONTINUE
GO TO 12

326 CONTINUE
DO 341 I=1,N
READ (12,330) PEXP(I),T(I),IS(I),(X(J,I),J=1,MA),XIMP(I)
CONTINUE
GO TO 12
327 CONTINUE
C CHECK FOR WATER CALCULATION
IF (IWATER.EQ.0.OR.IWATER.EQ.1) GO TO 67
C
********** READ IN N DATA POINTS **********
DO 123 I=1,N
READ (12,100) PEXP(I),T(I),IS(I),(X(J,I),J=1,MA),YEXP(I)
123 CONTINUE
GO TO 12
67 IF (IMPURE.EQ.0) GO TO 567
C **CHECK WHETHER SEQUENTIAL CALCULATION WITH IMPURITIES IS REQUIRED**

IF (IMPURE.EQ.1.AND.ISEQ.EQ.0) GO TO 569
DO 221 I=1,N
READ (12,181) PEXP(I),T1(I),DT(I),T2(I),IS(I),(X(J,I),J=1,MA)
1,XIMP(I)
YCO2(I)=X(JJ1,I)
221 CONTINUE
GO TO 12
569 DO 222 I=1,N
READ (12,111) PEXP(I),T(I),IS(I),(X(J,I),J=1,MA),XIMP(I)
YCO2(I)=X(JJ1,I)
222 CONTINUE
GO TO 12
567 IF (ISEQ.EQ.0) GO TO 568
DO 240 I=1,N
READ (12,180) PEXP(I),T1(I),DT(I),T2(I),IS(I),(X(J,I),J=1,MA)
240 CONTINUE
GO TO 12
568 DO 122 I=1,N
READ (12,100) PEXP(I),T(I),IS(I),(X(J,I),J=1,MA)
122 CONTINUE
C
12 CONTINUE
C
******* WRITE OUT ALL INPUT DATA *******
DO 978 I=1,MA
WRITE (06,310) I,YNAME(KK(I))
978 CONTINUE
WRITE (06,310) I,YNAME(KK(I))
59 WRITE(06,103)
   IF(IMPURE.EQ.0)GO TO 182
   DO 95 I=1,N
   IF(ISEQ.EQ.1.OR.ISEQ.EQ.2)T(I)=T1(I)
   WRITE(6,112) PEXP(I),T(I),IS(I),(X(J,I),J=1,MA),XIMP(I)
95   CONTINUE
   GO TO 97
182   DO 94 I=1,N
   IF(ISEQ.EQ.1.OR.ISEQ.EQ.2)T(I)=T1(I)
   WRITE(6,102) PEXP(I),T(I),IS(I),(X(J,I),J=1,MA)
94   CONTINUE
97   WRITE(6,315)
C
C       CALL FUN TO EVALUATE PCALC AS A FUNCTION
C       OF TEMPERATURE AND MOLE FRACTION.
C
C
CALL FUN(NN,XX,FF)
XX(1)=SIGH1
XX(2)=SIGH2
XX(3)=EPSH
XX(4)=DDU
XX(5)=DDH
XX(6)=BETTA1
XX(7)=GAMMA
IF(ILANG.NE.1)GO TO 983
   WRITE(06,812) XX(1),XX(3),XX(4),XX(5),XX(6),XX(7),XX(2)
C
C
983   CONTINUE
C
C
C
C
C
C       *******    THE FOLLOWING ARE FORMAT STATEMENTS  ONLY  *******
309   FORMAT(1(/),11(I2,1X))
968   FORMAT(4(F5.0,1X),I1,1X,9(F5.0,1X))
969   FORMAT(4(F5.0,1X),I1,1X,9(F5.0,1X))
344   FORMAT(' IMPURITY',A15,' PRESENT IN WATER')
112   FORMAT(3X,2(F10.3,4X),4X,11,6X,11(F6.4,2X))
853   FORMAT(' ERROR IN INPUT DATA ISEQ=2 AND LIQ=1')
843   FORMAT(' ERROR IN INPUT DATA LIQ=1 ISEQ=1 NVLLH=1')
833   FORMAT(' ERROR IN INPUT DATA ISEQ=2 NVLLH=0')
823   FORMAT(' ERROR IN INPUT DATA NVLLH=1 AND WATER CALCULATION')
803   FORMAT(' ERROR IN INPUT DATA NVLLH=1 AND NSTRUC=0')
100   FORMAT(2(F5.0,1X),I1,1X,10(F5.0,1X))
111   FORMAT(2(F5.0,1X),I1,1X,11(F5.0,1X))
180   FORMAT(4(F5.0,1X),I1,1X, 9(F5.0,1X))
181   FORMAT(4(F5.0,1X),I1,1X, 9(F5.0,1X))
101   FORMAT(100(’-’),//,30X,’EXPERIMENTAL HYDRATE DATA’,
     *,100(’-’),//,4X,’PRESSURE’,3X,’TEMPERATURE’,
     *2X,’STRUCTURE’,4X,10(A5,3X))
102   FORMAT(3X,2(F10.3,4X),4X,11,4X,10(F7.4,1X))
103   FORMAT(4X,’PSIA’,7X,’DEG.R’,//,100(’-’),//)
105   FORMAT(100(’-’),//,6X,’INPUT HYDRATE DATA

31
A WITH INITIAL PRESSURE GUESSED',
B/'100 ('-'),/'PRESSURE',3X,'TEMPERATURE',
C2X,'STRUCTURE',10(8X,A5))

200   FORMAT(5(I1,1X))
202   FORMAT(12)
301   FORMAT(20X,5('*'), 1X, '1 = METHANE'/,20X,5('*'),1X, '2 = ETHANE'
     * ,/20X,5('*'),1X, '3 = ETHYLENE'/,20X,5('*'),1X, '4 = PROPANE
     * ,/20X,5('*'),1X, '5 = CYCLO-PROPANE',/20X,5('*'),1X,
     * '6 = N-BUTANE
     * ,/20X,5('*'),1X, '7 = ISO-BUTANE',/20X,5('*'),1X,
     * '8 = CYCLO-BUTANE
     * ,/20X,5('*'),1X, '9 = PENTANE',/20X,5('*'),1X, '10 = ISO-PENTANE
     * ,/20X,5('*'),1X, '11 = NEO-PENTANE',/20X,5('*'),1X,'12 =
     * CYCLO-PENTANE
     * ,/20X,5('*'),1X, '13 = WATER',/20X,5('*'),1X,
     * '14 = HYDROGEN',/20X,5('*'),1X,
     * '15 = CARBON-DI-OXIDE',/20X,5('*'),1X,
     * '16 = OXYGEN',/20X,5('*'),1X, '17 = NITROGEN',/20X,5('*'),
     * '18 = HYDROGEN SULFIDE',/20X,5('*'),1X, '19 = XENON',/20X,
     * 5('*'),1X, '20 = ARGON',/20X,5('*'),1X, '21 = KRYPTON',/
     * 20X,5('*'),1X, '22 = SULFUR HEXAFLUORIDE',/20X,5('*'),1X,'23 =
   CIS-2-BUTENE',/20X,5('*'),1X, '24 = TRANS-2-BUTENE',/20X
     * ,5('*'),1X, '25 = NO COMPONENT',///)
302   FORMAT(8(I1,1X))
330   FORMAT(2(F5.0,1X),I1,1X,11(F5.0,1X))
329   FORMAT(2(F5.0,1X),I1,10(F5.0,1X))
305   FORMAT(12)
306   FORMAT(10X,5(2X,E12.5),/10X,5(2X,E12.5),/10X,5(2X,E12.5),/
     110X,5(2X,E12.5))
307   FORMAT(10X,6(2X,E12.5),/10X,6(2X,E12.5),/10X,6(2X,E12.5),/
     110X,6(2X,E12.5),/10X,6(2X,E12.5),/
308   FORMAT(1(1/),10(I2,1X))
310   FORMAT(10X, 'COMPONENT',I2,'=',A5)
315   FORMAT(100('-'),/)
812   FORMAT(///,25('*'),5X,'VALUES USED TO CALCULATE PRESSURES',
   15X,25('*'),///, 'SIGMA,H2O SC..............',F10.5,/
   2' EPSILON,H2O .................',F10.5,/, 
   3' DELTA U ....................',F10.5,/, 
   4' DELTA H .....................',F10.5,/, 
   5' BETA .........................',F10.5,/, 
   6' GAMMA ........................',F10.5,/, 
   7' SIGMA  H2O LC .............',F10.5,///)
GO TO 1000
1002   WRITE(6,803)
1003   WRITE(6,823)
1004   WRITE(6,833)
1005   WRITE(6,843)
1006   WRITE(6,853)
*1000   END
1000   STOP
end
C
C
SUBROUTINE FUN(NN,XX,FF)

THIS PROGRAM CALCULATES THE DIFFERENCES BETWEEN EXPERIMENTAL AND THEORETICAL HYDRATE FORMING CONDITIONS. THE CALCULATED HYDRATE FORMING CONDITIONS DEPEND UPON THE CHOICE OF KIHARA PARAMETERS, SIGMA AND EPSILON, FOR THE VARIOUS COMPONENTS IN THE GAS PHASE.

HYDRATE PHYSICAL PROPERTIES ARE ASSIGNED. SUBROUTINE DATA IS CALLED TO READ GAS PROPERTIES. SUBROUTINE HYDRAT IS CALLED TO CALCULATE HYDRATE FORMING CONDITIONS OR SUBROUTINE QUAD IS CALLED FOR QUADRUPLE POINT CALCULATIONS OR FOR SEQUENTIAL CALCULATIONS.

********** COMMON STATEMENTS **********
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION ICODE(10)
DIMENSION KK(10),XA(11)
DIMENSION XX(13),PCALC(100),SS(100),AXC(10,2),Y(10)
DIMENSION ERROR(100)
DIMENSION A(10),SIGMA(10),EPS(10)
DIMENSION Y3(100)
DIMENSION ERR(100),SW(100)
DIMENSION XL(10)
DIMENSION NCODE(10)
DIMENSION GAMMA1(2)
DIMENSION ZZV(100)
COMMON/BKSB/NPT,NSETS,IFLAG
COMMON/STAT/SS
COMMON/NC/NCODE,NCOMP
COMMON/AMOL/MA,ISCODE(10)
COMMON/FUND/SIGMA,EPS,A
COMMON/TEXPT/PEXP(100),X(15,100),IS(100),T(100),YEXP(100)
COMMON/SERDAT/T1(100),DT(100),T2(100)
COMMON/DHDATA/DU(2),DH(2)
COMMON/AZ/KK,N,MK
COMMON/JK/JCHK
COMMON/BEGA/BETA1,GAMMA1
COMMON/COR/EPH,DDU,DDH,BETA,GAMMA
COMMON/VDO/SIGH1,SIGH2
COMMON/BKSC/IWATER,IPOS,ISTR,IDH
COMMON/HO/YH3
COMMON/X/XL
COMMON/PHAS/NVLLH
COMMON/STRUC/NSTRUC
COMMON/IMP/IMPURE,IMCODE,XIMP(100),YCO2(100)
COMMON/SOLUT/XSOLU,ACTIV,YYYCO2
COMMON/TBLOC/ITAG
COMMON/SEQ/ISEQ,TMIN,DELT,TMAX,TQL
COMMON/LIQUID/LIQ
COMMON/ZV/ZV
COMMON/HEAT/DELH(100),DELH
C
***********************************************************************
IF(IWATER.EQ.0)GO TO 105
IF(IWATER.EQ.1)GO TO 102
WRITE(6,104)
GO TO 105
102    WRITE(6,103)
105    CONTINUE
N=NPT
SUM=0.0
WSUM=0.0
IF(ISEQ.EQ.1.OR.ISEQ.EQ.2)GO TO 80
IF(NVLLH.EQ.0)GO TO 80
IF(NSTRUCT.EQ.2)GO TO 845
IF(LIQ.EQ.0)WRITE(6,201)
IF(LIQ.EQ.1)WRITE(6,2011)
GO TO 80
845    WRITE(6,202)
80     CONTINUE
DO 9 K=1,N
C
REFERENCE PARAMETERS FOR STRUCTURE I AND II
SIGH1=3.56438
SIGH2=SIGH1
EPSH=102.13357
DU(2)=222.371
DDU=DU(2)
DH(2)=300.984
DDH=DH(2)
BETA1=0.0
BETA=BETA1
GAMMA1(2)=-0.00045
GAMMA=GAMMA1(2)
4    CONTINUE
SIGH1=3.56438
SIGH2=SIGH1
EPSH=102.13357
DU(1)=267.74141
DDU=DU(1)
DH(1)=301.32093
DDH=DH(1)
BETA1=0.0
BETA=BETA1
GAMMA1(1)=-0.00145
GAMMA=GAMMA1(1)
3    CONTINUE
DO 10 KI=1,MA
Y(KI)=0.0
10    CONTINUE
DO 101 I=1,MA
Y(I)=X(I,K)
101   CONTINUE
XSOLU=XIMP(K)
YYYCO2=YCO2(K)
CALL DATA(Y,XA,T(K))
DO 901 I=1,MA
708    Y(I)=XA(I)
901    CONTINUE
EPS(I) = (EPS(I) * EPSH) ** 0.5
SIGMA(I) = 0.5 * (SIGMA(I) + SIGH1)

CONTINUE

PCALC(K) = PEXP(K)
IF (NVLLH.EQ.0 .AND. ISEQ.EQ.0) GO TO 79
IF (ISEQ.EQ.0) GO TO 846
T(K) = T1(K)
TMIN = T1(K)
DELT = DT(K)
TMAX = T2(K)

CALL QUAD(T(K), PCALC(K), Y, IS)
GO TO 9

79 ITAG = 0
IF (LIQ.EQ.1) ITAG = 2
CALL HYDRAT(T(K), PCALC(K), Y, AXC, IS(K))
Y3(K) = YH3
DDELH(K) = DELH
ZZV(K) = ZV
PCALC(K) = PCALC(K) * 6.8948
PEXP(K) = PEXP(K) * 6.8948
T(K) = T(K) / 1.8
IF (IWATER.EQ.1) GO TO 9
IF (IWATER.EQ.2) GO TO 905
ERROR(K) = ABS(PCALC(K) - PEXP(K)) * 100.0 / PEXP(K)
SS(K) = (1.0 - PCALC(K) / PEXP(K)) ** 2
SUM = SUM + SS(K)
GO TO 9

905 ERR(K) = ABS(Y(IPOS) - YEXP(K)) * 100.0 / YEXP(K)
SW(K) = (1.0 - Y(IPOS) / YEXP(K)) ** 2
WSUM = WSUM + SW(K)
WRITE(6,909) T(K), PEXP(K), Y(IPOS), YEXP(K), ERR(K), PCALC(K), Y3(K)

CONTINUE
IF (NVLLH.NE.0) GO TO 960
IF (ISEQ.NE.0) GO TO 960
IF (IWATER.EQ.2) GO TO 906
IF (IWATER.EQ.1) GO TO 960
FF = SUM / N
FF = (FF ** 0.5) * 100.0
IF (IFLAG.EQ.0) GO TO 950
IF (IDH.EQ.0) GO TO 435
IF (IDH.EQ.1) WRITE(6,778)
DO 434 K = 1, N
WRITE(6,779) T(K), PCALC(K), DDELH(K), ZZV(K), (X(J,K), J = 1, MA)
434 CONTINUE

CONTINUE
435 CONTINUE
IF (IDH.EQ.1) GO TO 962
WRITE(06,902)
DO 913 K = 1, N
WRITE(06,900) T(K), PEXP(K), PCALC(K), ERROR(K), IS(K)
913 CONTINUE
WRITE(6,206) FF
GO TO 960

906 YFF = WSUM / N
YFF = (YFF ** 0.5) * 100.0
WRITE(6,908) YFF
GO TO 960

950 WRITE(6,951)
DO 952 K=1,N
WRITE(6,953)T(K),PCALC(K)
952 CONTINUE
962 CONTINUE
C
C     * * FORMAT STATMENTS * *
C
778 FORMAT(///20X,'CALCULATED RESULTS'/1X,'TEMPERATURE',3X,
1 'PRESSURE',4X,'DELT A H',13X,'Y-1',5X,'Y-2',5X,'Y-3'
2 /5X, '(K)', 8X, ' (KPA)', 5X, ' (KJ/MOLE)', 5X, ' Z', '/80 ('-')
779 FORMAT(2X,F6.2,5X,F8.2,6X,F6.2,4X,F6.4,2X,10(F6.4,2X))
909 FORMAT(5X,F7.3,2X,F9.3,1X,F15.9,1X,F15.9,3X,F6.1,4X,':',2X,
AF9.3,1X,F15.9)
206 FORMAT(///,3X,'AVERAGE ERROR IS',3X,F6.2,'%')
201 FORMAT(///20X,'CALCULATED RESULTS'/18X,'V L1 L2 H QUADRUPLE
1 POINTS'/70 ('-')/5X,'TEMP',7X,'PRESS',5X,'STRUCT',5X,'LIQUID COMP
10SION'/6X, '(K)', 7X, ' (KPA)', 16X, 'WATER FREE'/70 ('-')/
2011 FORMAT(///20X,'CALCULATED RESULTS'/18X,'V L1 L2 H QUADRUPLE
1 POINTS'/70 ('-')/5X,'TEMP',7X,'PRESS',5X,'STRUCT',5X,'VAPO R COMP
10SION'/6X, '(K)', ' (KPA)', 16X, '10X/70 ('-')/
202 FORMAT(///,20X,'CALCULATED RESULTS',/3X,'V H1 H2 L1 QUADRUPLE
1 POINTS',3X,';','3X,'V L1 L2 H QUADRUPLE POINTS',/3X,28 ('-'),3X
2',';','3X,28 ('-')',/2X,'STRUCT',3X,'TEMP',8X,'PRESS',6X,':',6X,'TEMP
3',8X,'PRESS',7X,'LIQUID COMPOSITION',/2X,'BELOW',5X,'(K)',8X, '(K
4PA)',8X,';','7X, '(K)', '8X, '(KPA)', 8X, 'X1', 'X2', '/1X,'QUAD PT',
526X, ':', '30X,'WATER FREE',/3X,28 ('-'),3X,: '3X,28 ('-')//
900 FORMAT(1X,4(F10.3,2X),8X,I1)
902 FORMAT(///,20X,'CALCULATED RESULTS',/20X,10 ('-'),
*1X,7 ('-'),/6X,'TEMP',8X,'PEXP',7X,'PCALC',7X,
*'ERROR',7X,'STRUCTURE',6X, '(K)', 9X, ' (KPA)', 6X,
*' (KPA)', '/80 ('-'),//
911 FORMAT(///,20X,'CALCULATED RESULTS',/20X,
A 10 ('-'),1X,7 ('-'),/6X,'TEMP',7X,
B 'PCALC',/21X, '(K)', 8X, '(KPA)', /18X,21 ('-'),
C //
953 FORMAT(19X,F10.3,2X,F10.3)
908 FORMAT(' AVERAGE ERROR IN YH2O CALCULATION',F8.2)
103 FORMAT('CALCULATED RESULTS'/20X,18 ('-')//10X,'2-PHASE',
A45X,'3-PHASE'/4X,36 ('-'),14X,22 ('-')/5X,'TEMP',6X,'PRESS',
A10X,' Y-2PHASE',10X,: '9X,'PRESS',5X,'Y-3PHASE'/5X,'(K)',
104 FORMAT('CALCULATED RESULTS'/20X,18 ('-')//20X,'2-PHASE',
A50X,'3-PHASE'/5X,60 ('-'),7X,25 ('-')/6X,'TEMP',7X,'PRESS',8X,
A'YCALC',12X,'YEXP',8X,'ERROR',4X,':',4X,'PRESS',10X,'Y-3PHASE'
A11X,'H20//')
960 RETURN
END
C
C
C  ******************************************** ***********
SUBROUTINE QUAD(T,P,Y,IS)
C  *******************************************************
C
C THIS SUBROUTINE CALCULATES QUADRUPLE POINTS BY FINDING THE
C POINT OF INTERSECTION OF 'V L1 H' AND DEW POINT CURVES TO
C GET THE 'V L1 L2 H' POINT ; OR INTERSECTION OF 'L1 L2 H'
AND BUBBLE POINT CURVE TO GET 'V L1 L2 H';
AND 'V L1 H1' AND 'V L1 H2'
CURVES TO GET THE 'V L1 H1 H2' POINT.

THIS SUBROUTINE IS ALSO CALLED FOR SEQUENTIAL CALCULATIONS AT SPECIFIC INTERVALS.

IST0=STRUCTURE AT STARTING TEMP T0
IST2=STRUCTURE BEYOND THE QUAD POINT
ID=VARIABLE INDICATING WHETHER VLH1H2 QUAD POINT HAS BEEN CALCULATED. 0--NOT CALCULATED; 1--CALCULATED.
ITAG=VARIABLE INDICATING WHICH FUGACITY COEFFICIENTS ARE REQUIRED FROM SUBROUTINE PHIMIX. 0--ONLY VAPOR
1--VAPOR AND LIQ; 2--LIQUID ONLY.

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION Y(15),XL(10)
DIMENSION PH(2),PRESS(2),ISCHEC(2),PBD(2),TQ(60),PQ(60)
DIMENSION PLP2(60)
DIMENSION PLP1(60)
DIMENSION NCODE(10)
COMMON/STRUC/NSTRUC
COMMON/PHAS/NVLLH
COMMON/X/XL
COMMON/NC/NCODE,NCOMP
COMMON/TBLOC/ITAG
COMMON/SEQ/ISEQ,TMIN,DELT,TMAX,TQL
COMMON/LIQUID/LIQ
COMMON/CRTICL/NCRIT,TCRTI
COMMON/HEAT/DDDELH(100),DELH
COMMON/BKSC/IWATER,IPOS,ISTR,IDH
COMMON/ZV/ZV
COMMON/HELP/IST0,IST2,ISLOW,N0,NQ
DOUBLE PRECISION YNEW(100)

T0=T
ITER=0
DTQ=1.0
DTH=1.0
N0=1
AXC=0
NQ=N0
ID=0
IDEW=0
M=1
IF(NVLLH.NE.0)GO TO 107

IF NVLLH IS ZERO THEN NO QUAD POINTS ARE REQUIRED BUT THIS SUBROUTINE HAS BEEN CALLED FOR SEQUENTIAL CALCULATIONS.

THH=TMAX+2.*DELT
TQL=TMAX+2.*DELT
IF (LIQ.EQ.1) TQL=TMIN-2*DELT
GO TO 10
107 DO 105 K=1,2
17 IF(NSTRUC.EQ.2.AND.ID.EQ.0)GO TO 101
PRESS(K) = P
ITAG = 0
IF (LIQ .EQ. 1) ITAG = 2
CALL HYDRAT(T, PRESS(K), Y, AXC, IS)
IF (NCRIT .EQ. 1) GO TO 801
GO TO 103

101 DO 102 IQ = 1, 2
IS = IQ
PH(IS) = P
ITAG = 0
CALL HYDRAT(T, PH(IS), Y, AXC, IS)
IF (NCRIT .EQ. 1) GO TO 801

102 CONTINUE
C
C ** CHECK WHICH STRUCTURE IS FORMED AT TEMP T **
IF (PH(2) .LT. PH(1)) IS = 2
IF (PH(1) .LT. PH(2)) IS = 1
IF (PH(1) .EQ. PH(2)) GO TO 130
ISCHEC(K) = IS
16 PRESS(K) = PH(IS)
C
C ** IST0 IS THE STRUCTURE FORMED AT THE STARTING TEMP (GIVEN TEMP) **
IF (NQ .EQ. NO) IST0 = IS
NQ = NQ + 1
103 CONTINUE
CALL BUBDEW(T, PBD(K), Y)
IF (LIQ .EQ. 1) GO TO 140
IF (PBD(K) .GE. PRESS(K)) GO TO 150
IDEW = IDEW + 1
IF (IDEW .GT. 5) T = T - 1.0
IF (IDEW .LT. 5) T = T - 0.4
IF (IDEW .GT. 20) GO TO 152
GO TO 107
140 IF (PBD(K) .LT. PRESS(K)) GO TO 150
IDEW = IDEW + 1
IF (IDEW .LE. 2) T = T + 0.2
IF (IDEW .GT. 2) GO TO 110
GO TO 107
150 TCOMP = T
IF ((NISTRUC .EQ. 1) .OR. ID .EQ. 1) .AND. ABS(TQL - T) .LT. 5.0) GO TO 45
IF (LIQ .EQ. 0) T = T + 1.0
IF (LIQ .EQ. 1) T = T - 1.0
IF (LIQ .EQ. 0) DTQ = 1.0
IF (LIQ .EQ. 1) DTQ = -1.0
GO TO 105
45 IF (LIQ .EQ. 0) T = T + 0.05
IF (LIQ .EQ. 1) T = T - 0.1
IF (LIQ .EQ. 0) DTQ = 0.05
IF (LIQ .EQ. 1) DTQ = -0.1
105 CONTINUE
IF (NISTRUC .EQ. 1) GO TO 106
IF (ID .EQ. 1) GO TO 106
IF (ISCHEC(1) .EQ. ISCHEC(2)) GO TO 106
T = T - 3
GO TO 107
106 AMH = (DLOG(PRESS(2)) - DLOG(PRESS(1))) / DTQ
CH = DLOG(PRESS(2)) - AMH * (T - DTQ)
AML = (DLOG(PBD(2)) - DLOG(PBD(1))) / DTQ
CL = DLOG(PBD(2)) - AML * (T - DTQ)
TQL = (CH - CL) / (AML - AMH)
PQL = EXP(AMH * TQL + CH)
IF (NSTRUCT.EQ.1) GO TO 109
IF (ID.EQ.1) GO TO 182
IF (T.EQ.(T0+1)) PQLOW = PQL
IF (PQL.GT.PQLOW) GO TO 113
PQLOW = PQL
ISLOW = IS

113
TQ(M) = TQL
PQ(M) = PQL
PLP1(M) = PRESS(1)
PLP2(M) = PRESS(2)
IF (IS.NE.IST0) GO TO 111
IF (T.GT.TQL) GO TO 120
M = M + 1
IF (M.EQ.50) GO TO 112
GO TO 107

C ** IF IST0.ISLOW NO VLHH PRESENT **

111
IF (IST0.EQ.ISLOW) GO TO 114
IST2 = IS
AM1 = (DLOG(PLP2(M-1)) - DLOG(PLP1(M-1))) / DTH
AM2 = (DLOG(PLP2(M)) - DLOG(PLP1(M))) / DTH
C1 = DLOG(PLP2(M-1)) - AM1 * (T - 3)
C2 = DLOG(PLP2(M)) - AM2 * (T - 1)
THH = (C1 - C2) / (AM2 - AM1)
PHH = EXP(AM2 * THH + C2)

182
ID = 1
IF (ABS(TQL-TCOMP).LE.0.1) GO TO 181
ITER = ITER + 1
IF (ITER.GT.500) GO TO 151
T = (TQL+TCOMP) / 2.0
GO TO 107

181
CONTINUE
IF (ISEQ.EQ.1.OR.ISEQ.EQ.2) GO TO 10
THH = THH/1.8
TQL = TQL/1.8
PHH = PHH*6.8948
PQL = PQL*6.8948
WRITE(6,203) IST0, THH, PHH, TQL, PQL, (XL(I), I=1, NCOMP)
GO TO 120

114
WRITE(6,117)
TQ(1) = TQ(1)/1.8
PQ(1) = PQ(1)*6.8948
WRITE(6,118) IST0, TQ(1), PQ(1), (XL(I), I=1, NCOMP)
GO TO 120

109
IF (ABS(TQL-TCOMP).LE.0.1) GO TO 110

455
ITER = ITER + 1
IF (ITER.GT.500) GO TO 151
T = (TQL+TCOMP) / 2.0
IF (LIQ.EQ.1) T = TCOMP
GO TO 107

110
IF (ISEQ.EQ.0) GO TO 104

10
T = TMIN-DELT
DO 257 J = 1, NCOMP
YNEW(J) = Y(J)

39
CONTINUE
IF(NSTRUC.EQ.2)IS=IST0

** CHECK FOR HEAT OF DISSOCIATION CALCULATIONS **

IF(LIQ.EQ.0.AND.IDH.EQ.0)WRITE(6,250)
IF(LIQ.EQ.1)WRITE(6,2501)
IF(IDH.EQ.1)WRITE(6,886)
ITAG=0
IF(T.GT.TQL)ITAG=2
IF(ISEQ.EQ.2)TMAX=TQL
IF(ISEQ.EQ.2.AND.LIQ.EQ.1)GO TO 853
DO 91 I=1,100
T=T+DELT
IF(T.GT.TMAX)GO TO 120
CALL HYDRAT(T,P,YNEW,AXC,IS)
TT=T/1.8
PP=P*6.8948
IF(IDH.EQ.0) GO TO 14
WRITE(6,885) TT,PP,DELH,ZV,(YNEW(N),N=1,NCOMP)
GO TO 8567

CONTINUE
IF(T.LT.TQL)WRITE(6,904)TT,PP,IS,(YNEW(N),N=1,NCOMP)
IF(T.GT.TQL)WRITE(6,904)TT,PP,IS,(XL(N),N=1,NCOMP)
8567 CONTINUE
TTHH=THH/1.8
PPHH=PHH*6.8948
IF(NSTRUC.EQ.2.AND.(T+DELT).GT.TTHH)IS=IST2
IF(NSTRUC.EQ.2.AND.T.LT.TTHH.AND.(T+DELT).GT.TTHH)WRITE(6,153)
1TTHH,PPHH
IF((T+DELT).GE.TQL)GO TO 191
GO TO 91
191 PPQL=PQL*6.8948
TTQL=TQL/1.8
IF(T.LT.TQL.AND.(T+DELT).GE.TQ AND.ISEQ.NE.2)WRITE(6,71)TTQL
1,PPQL
IF(T.LT.TQL.AND.(T+DELT).GE.TQL.AND.ISEQ.EQ.2)WRITE(6,72)TTQL
1,PPQL
ITAG=2
IF(LIQ.NE.0)GO TO 91
DO 53 J=1,NCOMP
Y(J)=XL(J)
53 CONTINUE
91 CONTINUE
WRITE(6,123)
GO TO 120
104 TQL=TQL/1.8
PQL=PQL*6.8948
WRITE(6,444)(XL(I),I=1,NCOMP)
WRITE(6,444)(Y(J),J=1,NCOMP)
444 FORMAT(' XL=',10(4X,F6.3))

WRITE(6,119)TQL,PQL,IS,(XL(I),I=1,NCOMP)
GO TO 120
112 WRITE(6,121)
GO TO 114
130 WRITE(6,108)PH(1)

40
T=T0
GO TO 800
WRITE(6,100)
GO TO 800
TQL=TQL/1.8
PQL=PQL*6.8948
WRITE(6,154)TQL,PQL
GO TO 800
WRITE(6,823)
DO 258 I=1,NCOMP
Y(I)=YNEW(I)
258 CONTINUE

C ---------FORMATS-----------------
885 FORMAT(1X,F6.2,3X,F8.2,4X,F7.3,5X,F6.4,4X,10(F6.4,2X))
886 FORMAT(///25X,'CALCULATED RESULTS',///3X,'TEMP',4X,'PRESSURE'
2 ,3X,'DELTA H',8X,'Z',10X,'GAS COMPOSITION',/4X,'(K)',6X,'(KPA)'
3 ,4X,'(KJ/MOLE)',15X,'Y-1',5X,'Y-2',5X,'Y-3'/80('('')
121 FORMAT(' NOT CONVERGED IN QUAD, PROBABLY NO V L H1 H2 EXISTS')
100 FORMAT(' QUADRUPLE POINT CALCULATIONS NOT CONVERGED IN QUAD'
1. INITIAL TEMP MAY NOT BE IN RANGE.')
119 FORMAT(4X,F6.2,5X,F9.2,4X,I1,5X,10(F6.4,5X))
C901 FORMAT(2F,I,'FOR901!')
118 FORMAT(4X,I1,35X,F6.2,5X,F8.2,5X,10(F6.4,5X))
203 FORMAT(4X,I1,5X,F6.2,5X,F8.2,5X,':',5X,F6.2,5X,F8.2,5X,10(F6.4
1,5X))
123 FORMAT(1X,40(' -'))
250 FORMAT(///20X,'CALCULATED RESULTS'/20X,10(' -'),1X,7(' -')/10X,
1'TEMP',10X,'PRESS',4X,'STRUCTURE',8X,'GAS COMPOSITION',/11X,
1'(K)',10X,'(KPA)',16X,'Y 1',4X,'Y 2',4X,'Y 3'/5X,60(' -'))
2501 FORMAT(///20X,'CALCULATED RESULTS'/20X,10(' -'),1X,7(' -')/10X,
1'TEMP',10X,'PRESS',7X,'STRUCTURE',5X,'LIQ COMPOSITION',/11X,
1'(K)',10X,'(KPA)',16X,'XL1',5X,'XL2',5X,'XL3'/5X,60(' -'))
904 FORMAT(9X,F6.2,8X,F8.2,6X,I3,3X,10(F6.4,2X))
108 FORMAT(' QUAD PT AT PRESS=',F10.2)
117 FORMAT(' V L H1 H2 EQUILIBRIUM NOT PRESENT')
153 FORMAT(9X,F6.2,8X,F8.2,2X,'QUADRUPLE POINT V L H1 H2')
71 FORMAT(9X,F6.2,8X,F8.2,2X,'QUADRUPLE POINT V L1 L2 H'//53X,
1'LIQUID COMPOSITION'/48X,'X 1',6X,'X 2',6X,'X 3'/)
72 FORMAT(9X,F6.2,8X,F8.2,2X,'QUADRUPLE POINT V L1 L2 H'/)
154 FORMAT(' NOT CONVERGED DUE TO TEMP CROSSING QUAD POINT'/' TQL='
1,F6.2,2X,'PQL=',F8.2)
823 FORMAT(' ERROR IN INPUT DATA ISEQ=2 AND LIQ=1')
843 FORMAT(' QUAD POINT NOT CALCULATED'/' VAPOR IS'
1 CLOSE TO CRITICAL'/' CRITICAL TEMP OF MIX=',F6.2,'K'/)
C -----------------------------
GO TO 800
801 TCRIT=TCRIT/1.8
WRITE(6,843)TCRIT
800 RETURN
END
C *********************************************************************
C
C
C
C
C *********************************************************************

SUBROUTINE HYDRAT(T,P,XU,VY,IS)
**PROGRAM FOR CALCULATION OF THE DISSOCIATION PRESSURES**
**OF GAS HYDRATES FROM METHANE, ETHANE, AND PROPANE**
**BY JERRY HOLDER, CHEMICAL ENGINEERING U. MICH.**

THE DISSOCIATION PRESSURE IS THAT PRESSURE AT WHICH
THE CHEMICAL POTENTIAL OF WATER IN THE HYDRATE IS
EXACTLY EQUAL TO THE CHEMICAL POTENTIAL OF THE WATER
IN THE WATER PHASE. THE CHEMICAL POTENTIAL OF THE
HYDRATED WATER IS CALCULATED USING THE THEORY DEVELOPED
BY VAN DER WAALS WHICH ASSUMES 1) THERE IS ONE MOLECULE
OF GAS PER HYDRATE CAVITY, 2) ONLY THE TRANSLATIONAL
PARTITION FUNCTION IS AFFECTED IN THE ENCAGED STATE
3) ONLY FIRST NEIGHBOR INTERACTIONS ARE IMPORTANT.
THE KIHARA POTENTIAL MODEL IS USED.

THE UPDATED Q* VERSION INCLUDES 2ND AND 3RD SHELL
CONTRIBUTIONS AND SHELL ASPHERICITY.

THIS SUBROUTINE ALSO CALCULATES WATER CONTENT AND
HEAT OF DISSOCIATION.

*** LIST OF VARIABLES ***

AR, BR, CR - CONSTANTS FOR CALCULATING THE DISSOCIATION
PRESSURE OF THE REFERENCE HYDRATE. THESE ARE
FROM FITTED DATA.

C - THE SO CALLED LANGMUIR ADSORPTION CONSTANTS
WHICH SPECIFY THE RELATIVE AMOUNT OF GAS IN
A GIVEN TYPE OF CAVITY. SUBSCRIPTS I,J REFER

DH - DIFFERENCE IN ENTHALPY BETWEEN THE OCCUPIED AND
UNOCCUPIED HYDRATE.

DU - DIFFERENCE IN CHEM. POTENTIAL (AS DH)

DV - DIFFERENCE IN MOLAR VOLUME

P0 - DISSOCIATION PRESSURE OF REFERENCE HYDRATE
AT 273 DEG K

PR - DISSOCIATION PRESSURE OF REF. HYD. AT T

T - TEMPERATURE( DEG K)

VM - NUMBER OF MOLECULES OF WATER PER CAVITY

VY(I,J) - FRACTION OF CAVITIES I OCCUPIED BY MOLECULE J

XU(I) - MOLE FRACTION OF GAS I IN THE GAS PHASE

ZMU, ZMOL, ETC. - CHEMICAL POTENTIAL DIFFERENCES.

***** COMMON STATEMENTS *****

IMPLICIT DOUBLE PRECISION (A-H,O-Z)

external psat
DIMENSION KK(10)
DIMENSION XX(13)
DIMENSION XL(10), PHIL(10)
DIMENSION XU(10), PHI(10), XS(10), VY(10,2), VM(2),
2 C(10,2), NCODE(10), SCC(2)
DIMENSION XXMAX(10), XXMIN(10), B2(10)
DIMENSION XW(10)
DIMENSION GAMMA1(2)
DIMENSION XHYD(10)
DIMENSION VVY(2)
COMMON /PVDATA/ DV,AR,CR
COMMON/AZ/KK,N,MK
COMMON/AMOL/MA,ISCODE(10)
COMMON/NC/NCODE,NCOMP
COMMON/MAMI/XXMAX,XXMIN
COMMON /HYD/ IHYD
COMMON/FUND/SIGMA(10),EPS(10),A(10)
COMMON/DHDATA/HDU(2),HDH(2)
COMMON/JK/JCHK
COMMON/VDO/SIGH1,SIGH2
COMMON/BEGA/BETA1,GAMMA1
COMMON/BKSC/IWATER,IPOS,ISTR,IDH
  COMMON/TBLOC/ITAG
  COMMON/HO/YH3
  COMMON/SOLUT/XSOLU,ACTIV,YYYCO2
  COMMON/IMP/IMPURE,IMCODE,XIMP(100),YCO2(100)
  COMMON/TFREEZ/TT0
  COMMON/ZV/ZV
  COMMON/X/XL
  COMMON/PH/PHIL
  COMMON/WATER/NW
  COMMON/STOR/XUSTOR(10)
  COMMON/CRTLC/NCRTLC,TCRTLC
  COMMON/HEAT/DDELH(100),DELA
  COMMON/HELP/IST0,IST2,ISLOW,NQ,N0

C
C       **************************************************
C
C
C      * * CHECK IF STRUCTURE DATA IS TO BE PRINTED * *
C
JACKQ=0
C Saturation pressure is in atmospheres. Partial molar volume is in ml/mole. Saturation pressure is the pressure at which a given mole fraction of gas is dissolved in the liquid.
PSATD=30.30
PMOLVOL=35.

17 CONTINUE
  IF(ITAG.NE.2)GO TO 40
  DO 43 I=1,NCOMP
    XL(I)=XU(I)
43 CONTINUE
40 IF(ISTR.NE.1)GO TO 260
  WRITE(06,351)
  DO 258 I=1,MA
    WRITE(06,352)KK(I),A(I),SIGMA(I),EPS(I)
258 CONTINUE
C
260 DO 5 I=1,NCOMP
  DO 5 J=1,2
    VY(I,J)=0.0
5 T=T/1.8
PSAVE=P
P=P/14.696
IF( IS.EQ.1) GO TO 11

*** DATA FOR STRUCTURE II ***

VM(1)=0.11765
VM(2)=0.058823
DV=4.99644
IF(T.LE.(273.15-TT0)) DV=DV-1.6
DU=HDU(2)
DH=HDH(2)
GAMMA=GAMMA1(2)
GO TO 12

*** DATA FOR STRUCTURE I ***

11 VM(1)=2./46.
VM(2)=6./46.
DU=HDU(1)
DH=HDH(1)
DV=4.5959
GAMMA=GAMMA1(1)
IF(T.LE.(273.15-TT0)) DV=DV-1.6

*** LANGMUIR CONSTANTS ***

DO 15 K=1,NCOMP
   DO 15 J=1,2
      J5=J
      K5=K
      K1=K
   777 CONTINUE
      C(K,J)=CC(T,IS,J5,K5,K1)
15 CONTINUE

AT ZERO DEGREES CENTIGRADE

ZMUTPR=DU/273.15
ZMOLD=ZMUTPR
AH=2616.398+DH
TO=273.15

*** ENTHALPIC CHANGE OF CHEMICAL POTENTIAL WITH TEMPERATURE (WATER PHASE) ***

***** ALPHA, BETA, AND GAMMA ARE PARAMETERS *****
***** IN THE ENTHALPIC INTEGRAL *****

IF(T.GT.273.1.AND.T.LT.273.2) GO TO 8999
ALPHA=DH
BETA=BETA1
IF(T.LT.(273.15-TT0)) GO TO 8998
ALPHA=ALPHA-1436.0+9.054*273.15+0.021163*(273.15**2)
BETA=BETA+9.054+0.042326*273.15
GAMMA=GAMMA-0.021163
8998 CONTINUE
HINT=ALPHA*(1./T-1./273.15)+BETA*DLOG(T/273.15)
* +GAMMA*(T-273.15)
GO TO 9988
8999 HINT=0.0
9988 CONTINUE
C
C
C       *** VOLUMETRIC CHANGE OF CHEMICAL POTENTIAL WITH
C       TEMPERATURE (DP=DP/DT*DT)
C       GAUSSIAN INTEGRATION IS USED.
ZM=HINT+ZMOLD
ZMUTPR=T*ZM
C
We know that ZMUTPR is the liquid phase chemical potential
Instead of having the program calculate the pressure point where
the liquid phase chemical potential and the hydrate phase chemical
potentials intersect, we need to calculate the plain hydrate and
liquid potential. We also need to print out ZMUPTR since it is
the liquid phase potential.
C       **** NEWTONS METHOD IS USED TO FIND THE PRESSURE AT
C            WHICH THE CHEMICAL POTENTIAL OF THE HYDRATED
C            AND LIQUID WATER ARE THE SAME (FOR THE SPECIFIED
C            TEMPERATURE).
C
C
P1=1
P2=2
DO 30 JJ=1,2000
DMU1=0.0
DMU2=0.0
C DO 28 JJJ=1,2
P=P1
P3=P
IF (P.GT.PSATD) P3=PSATD
C IF(JJJ.EQ.2) P =P2
C *** GET THE FUGACITY COEFFICIENTS( PHI IS RETURNED)
C
CALL PHIMIX(XU,14.696*P3,1.8*T,PHI)
IF(NCRIT.EQ.1)GO TO 821
IF(ITAG.NE.2)GO TO 481
C        DO 44 LI=1,NCOMP
C        PHI(LI)=PHIL(LI)
44     CONTINUE
X1=0.0
GO TO 56
481    X1=0.0
IF(T.LT.(273.15-TT0)) GO TO 56
DO 55 J7=1,NCOMP
KJ=NCODE(J7)
Y7=XU(J7)
PHI7=PHI(J7)
CALL SOL7(KJ,Y7,PHI7,P3,T,X6)
X1=X1+X6
55 CONTINUE
56 CONTINUE
IF(ABS(P).LT. .1) P=P+.1
ZMUA=ZMUTPR+DV/41.2929*(P)
ZMUA = ZMUA - 1.987 * T * DLOG(1 - X1)
C
WRITE (6, 8890) ZMUA
ZMU = 0.0
DO 27 I = 1, 2
CCC = 0.0
DELTAP = 0
IF (P.GT.PSATD) DELTAP = P - PSATD
DO 26 II = 1, NCOMP
FUGAC = PHI (II) * P^3 * DEXP (PMOLVOL * DELTAP / (82.1 * T))
CCC = CCC + C(II, I) * XU(II) * FUGAC
WRITE (6, 5000) FUGAC
WRITE (6, 5001) PSATD
5000 FORMAT (5X, 'FUGACITY=', F10.5)
5001 FORMAT (5X, 'PSAT=', F10.5)
C Need to obtain exact value of R with more precision than 82
26 CONTINUE
SCC(I) = CCC
C
C *** POTENTIAL DIFFERENCE OF HYDRATE WATER
C
IF (CCC.GT.-0.9) GO TO 461
WRITE (6, 457) CCC, C(1, 1), XU(1), PHI(1), P
457 FORMAT (5F10.2)
461 CONTINUE
ZMUTP = 1.987 * T * DLOG(1 + CCC) * VM(I)
C
WRITE (6, 8891) ZMUTP
27 ZMU = ZMUTP + ZMU
C
DMU = ZMUA - ZMU
C
IF (IMPURE.EQ.0.OR.T.LT.(273.15 - TT0).OR.XSOLU.EQ.0.0) GO TO 148
C
DMU = DMU - 1.987 * T * DLOG (ACTIV * (1.0 - XSOLU - X1))
C GO TO 147
C 148 DMU = DMU - 1.987 * T * DLOG (1.0 - X1)
C
ZMU1 = ZMUA - 1.987 * T * DLOG (1.0 - X1)
C
147 DMU1 = DMU2
C
DMU2 = DMU
C
C
C *** CHECK TO SEE IF CHEMICAL POTENTIALS ARE EQUAL
C
IF NOT, EXTRAPOLATE (OR INTERPOLATE) TO A NEW PRESSURE
C
IF (ABS (P2/P1 - 1.0).LT. .001.AND. ABS (DMU).LT. .1) GO TO 35
C IF (ABS (DMU).LT. .0005) GO TO 35
28 CONTINUE
C IF (ABS ((P1 - P2) / P2).LT.1.E-5) P2 = P2 + 1.0
C IF (ABS (DMU2 - DMU1).LT. .001) GO TO 29
C P3 = P1 - (P2 - P1) / (DMU2 - DMU1) * DMU1
C IF (P3.LE.0.0) P3 = 0.01
C IF (P3.GT.2.E4) P3 = 2.0E4
C P1 = P3
C 29 P3 = P1 + 3
P2 = P1 + 2
Pold = P1
P1 = P1 + 1
P = P1
WRITE (6, 8880) T
WRITE (6, 8881) Pold
WRITE (6, 8882) X1
WRITE (6, 8883) XSOLU
C WRITE(6,8884) TT0
WRITE(6,8885) ACTIV
WRITE(6,8886) ZMU
WRITE(6,8887) ZMU
30 CONTINUE
GO TO 45
IHYD=IS
P=P1
WRITE(6,505) DMU, IS,XU(1),T
505 FORMAT(' FAILED TO CONVERGE IN HYDRATE',/,'6X,
2 'DIFFERENCE IN CHEMICAL POTENTIAL OF WATER',/,
3 'IN THE HYDRATE AND WATER PHASES IS',2X,
4 E9.2/', 'STRUCTURE IS',I4,2F10.5)
35 CONTINUE
8880 FORMAT(5X,'T=',F10.5)
8881 FORMAT(5X,'P=',F10.5)
8882 FORMAT(5X,'X1=',F10.5)
8883 FORMAT(5X,'XSOLU=',F10.5)
8884 FORMAT(5X,'TTO=',F10.5)
8885 FORMAT(5X,'ACTIV=',F10.5)
8886 FORMAT(5X,'ZMU=',F10.5)
8887 FORMAT(5X,'ZMUA=',F10.5)
C 8888 FORMAT(5X,'XU(1)=',F10.5)
C 8889 FORMAT(5X,'XU(2)=',F10.5)
8890 FORMAT(5X,'Chemical potential of liquid phase =',F10.5)
8891 FORMAT(5X,'Chemical potential of the hydrate phase =',F10.5)
C *** CALCULATE FRACTIONAL OCCUPANCY OF THE CAVITY
C
DO 45 I=1,2
DO 45 J=1,NCOMP
IF(ABS(1+SCC(I)).LT.1.E-4) WRITE(6,9876) SCC(I)
9876 FORMAT(' ERROR IN LANGMUIR CALCULATION',F10.7)
VY(NCODE(J),I) = C(J,I)*XU(J)*PHI(J)*P/(1+SCC(I))
45 CONTINUE
IF(IDH.EQ.0) GO TO 46
C ** HEAT OF DISSOCIATION CALCULATIONS **
C
JACKQ=JACKQ+1
IF(JACKQ.EQ.1) GO TO 412
PH1=P
TH1=T
T=T+0.01
T=T*1.8
P=P*14.696
GO TO 17
412 CONTINUE
JACKQ=0
VVY(1)=0.0
VVY(2)=0.0
DO 7 J=1,NCOMP
DO 7 I=1,2
VVY(I)=VVY(I)+VY(NCODE(J),I)
7 CONTINUE
IF(IS.EQ.1) GO TO 717
HN=136./(VVY(1)*16.+VVY(2)*8.)
DV1=DV
GO TO 718

717   HN=46./((VY(1))*2.+VY(2)*6.)
718   CONTINUE

C    WRITE(6,7777) ZV
C    WRITE(6,7778) T
C    WRITE(6,7779) TH1
C    WRITE(6,7780) P
C    WRITE(6,7781) PH1
C    WRITE(6,7782) VY(1)
C    WRITE(6,7783) VY(2)
C    WRITE(6,7784) HN
C    WRITE(6,7785) DV1

7777  FORMAT(' ZV=',F10.5)
7778  FORMAT(' T=',F10.5)
7779  FORMAT(' TH1=',F10.5)
7780  FORMAT(' P=',F10.5)
7781  FORMAT(' PH1=',F10.5)
7782  FORMAT(' VY(1)=',F10.5)
7783  FORMAT(' VY(2)=',F10.5)
7784  FORMAT(' HN=',F10.5)
7785  FORMAT(' DV=',F10.5)

DELHH=ZV*82.05*T**2*((DLOG(P/PH1))/(T-TH1))
DELH2=HN*DV*T*((P-PH1)/(T-TH1))
DELH=DELHH-DELH2
DELH=DELH/9869.2
DELHH=DELHH/9869.2
DELH2=DELH2/9869.2

C    WRITE(6,7786) DELHH
C    WRITE(6,7787) DELH2
C    WRITE(6,7788) DELH

7786  FORMAT(' DELH1=',F10.3)
7787  FORMAT(' DELH2=',F10.3)
7788  FORMAT(' DELH=',F10.3)

T=TH1
P=PH1

46   CONTINUE
COMSUM=0.0
DO 143 J=1,NCOMP
COMSUM=COMSUM+VY(NCODE(J),1)*VM(1)+VY(NCODE(J),2)*VM(2)
143   CONTINUE

C    WRITE(6,7786) DELHH
C    WRITE(6,7787) DELH2
C    WRITE(6,7788) DELH

700   T=T*1.8
P=P*14.696

13   CONTINUE

C    WRITE(06,1005)
1005  FORMAT(/,14X,'PHI(I)',20X,'LANGMUIR COEFFICIENTS'/,14X,5('-'),20X,21('-'))
DO 158 I=1,NCOMP
XHYD(J)=(VY(NCODE(J),1)*VM(1)+VY(NCODE(J),2)*VM(2))/COMSUM
158   CONTINUE

C    WRITE(7,1020)T,(VY(NCODE(J),1),VY(NCODE(J),2),J=1,MA)
1020  FORMAT(' T (K)',4X,'HYD RATE COMPOSITION'/9X,'XH1   XH2'/1F6.2,4X,10(F6.4))
* * CALCULATIONS TO DETERMINE THE WATER CONTENT OF A GAS * *
* * IN EQUILIBRIUM WITH THE HYDRATE * *
* * TEMP(R) AND PRESSURE(PSIA) * *
* * IWATER = 0 : DONT PERFORM CALCULATIONS * *
* * IWATER = 1 : CALCULATE YH2O * *
* * IWATER = 2 : CALCULATE YH2O AND COMPARE WITH EXPMTL DATA * *
* *
IF(IWATER.EQ.0)GO TO 821

* * PH=3-PHASE PRESSURE * *
* * P =2-PHASE PRESSURE * *

PH=P
P=PSAVE
PSW=PSAT(T)
IF(IS.EQ.1)VHYD=22.6
IF(IS.EQ.2)VHYD=22.9
IF(T.LT.491.67)VH2O=19.6
IF(T.GE.491.67)VH2O=18.0
FWSAT=PSW*(1-X1)*EXP(0.0014926491/T*VH2O*(PH-PSW))
FWSATP=FWSAT*EXP(0.0014926491/T*VHYD*(P-PH))
CALL PHIMIX(XU,P,T,PHI)
T=T/1.8
P=P/14.696
ZWAT=0.0
DO 127 I=1,2
CCC=0.0
DO 126 II=1,NCOMP
CCC=CCC+C(II,I)*XU(II)*PHI(II)*P
126 CONTINUE
ZW=VM(I)*DLOG(1+CCC)
127 ZWAT=ZWAT+ZW
DO 23 I=1,NCOMP
XUSTOR(I)=XU(I)
23 CONTINUE
ICOUN=1
COUNT=1
MA=MA+1
NCOMP=NCOMP+1
IPOS=MA
NW=1
PHI(IPOS)=1.0
PHIX=1.0

** 2-PHASE WATER CONTENT CALCULATION **
618 ZMUP=0.0
GO TO 85
85 FWP=FWSATP*DEXP(ZMU/(1.987*T)-ZWAT)

** CALCULATE A TEST VALUE OF YH2O **
T=1.8*T

49
P = 14.696 * P

C
815   \text{YH20} = \frac{\text{FWP}}{\phi(i) \times P}
\text{IF}(\text{YH20} \text{GT} 0.05 \text{OR} \text{YH20} \text{LT} 0.0) \text{GO TO 800}
\text{GO TO 801}

800   \text{WRITE}(6,803) \text{ICOUN, YH20}
\text{YH20} = 0.05

C
C
801   \text{XU(i)} = \text{YH20}
\text{CALL NORMW(NCOMP, IPOS, XU)}
\text{YH20} = \text{YH20}

807   \text{CALL PHIMIX(XU, P, T, PHI)}
\text{YH20} = \frac{\text{FWP}}{\phi(i) \times P}
\text{ICOUN = ICOUN+1}
\text{IF}(|(\text{YH20} - \text{YH20})/\text{YH20}1.E-3 \text{AND} \text{ICOUN}1.30) \text{GO TO 801}
\text{XU(i)} = \text{YH20}

C
C ** 3-PHASE WATER CONTENT CALCULATION **
835   \text{DO 825 I = 1, MA}
\text{XW(I) = XU(I)}

825   \text{CONTINUE}

809   \text{YH3} = \frac{\text{FWSAT}}{\phi(i) \times PH}
\text{IF}(|\text{ABS}(\text{YH3} - \text{XW(i)})1.E-7) \text{GO TO 819}
\text{XW(i)} = \text{YH3}
\text{CALL NORMW(NCOMP, IPOS, XW)}
\text{CALL PHIMIX(XW, PH, T, PHI)}
\text{COUNT = COUNT+1}
\text{IF}(|\text{COUNT}1.30) \text{GO TO 818}
\text{PHIX = PHI(i) \times P}
\text{GO TO 809}

818   \text{WRITE}(6,828)

819   \text{P2P} = P \times 6.8948
\text{PH3P} = PH \times 6.8948
\text{TK} = T/1.8
\text{IF}(|\text{ICOUN}1.30) \text{WRITE}(6,810)
\text{IF}(\text{P.GT.PH}) \text{GO TO 845}
\text{WRITE}(6,823)
\text{GO TO 812}

845   \text{IF}(I \text{WATER.EQ.2)GO TO 812}
\text{WRITE}(6,811)TK, P2P, XU(i), PH3P, YH3

C
812   \text{P = PH}
\text{NCOMP = NCOMP-1}
\text{MA = MA-1}
\text{NW = 0}

821   \text{RETURN}
C
* * FORMAT STATEMENTS * *
C
828   \text{FORMAT(' 3 PHASE WATER CALCULATIONS NOT CONVERGED')}
803   \text{FORMAT('0',T20,'* * YH20 DEFAULTS TO A VALUE OF 0.05 ON'
\text{A ',', ' iteration# ',I2, '/',1X,T20,'* FROM A PREVIOUS'
\text{B ',', ' VALUE OF YH20 = ',E10.3)
810   \text{FORMAT('0',T20,'* WATER CONTENT EQUILIBRIUM'
\text{C CALCULATIONS HAVE NOT CONVERGED * * ')}
811   \text{FORMAT(5X,F7.3,2X,F9.3,2X,F15.9,8X,:3X,F9.3,2X,F15.9)}
**FORMAT(/,18X,'CODE #',5X,'A(I)',8X,'SIGMA(I)',8X,'EPS(I)'),/)
FORMAT(5X,IS,3F10.3)
FORMAT(5X,'PRESSURE IS NOT IN 2 PHASE REGION')

END

************************************************************
SUBROUTINE NORMW(NCOMP,IPOS,XU)
************************************************************
* * THIS SUBROUTINE NORMALIZES THE VECTOR XU * *
* * WITHOUT CHANGING THE VALUE OF XU(IPOS) * *
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION XU(10)
COMMON/STOR/XUSTOR(10)

SUM=1.0-XU(IPOS)
DO 1 I=1,NCOMP
   IF(I.EQ.IPOS)GO TO 1
   XU(I)=XUSTOR(I)*SUM
1  CONTINUE
RETURN
END

************************************************************
DOUBLE PRECISION FUNCTION PSAT(TR)
************************************************************
* * FUNCTION TO CALCULATE THE SATURATION PRESSURE OF * *
* * WATER USING THE CORRELATION DEVELOPED BY KEENAN * *
* * KEYES AND MOORE P(PSIA), T(R) * *
* * A CORRELATION TO CALCULATE THE VAPOR PRESSURE * *
* * FOR ICE WAS ALSO USED BASED ON THE DATA FROM * *
* * PERRY'S 5TH ED. 3-205 * *
************************************************************
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION F(8),A1(7),B1(7),TREF(8)

DATA F/-741.9242,-29.721,-11.55286,-0.8685635,
0.1094098,0.439993,0.2520658,0.05218684/
DATA A1/1.110788E -11,4.813026E-12,1.053791E-12,
6.92593447E-14,2.289828E-15,4.697288E-18,4.261011E-22/
DATA B1/0.046341356,0.048066983,0.0512724161,
0.0572912243,0.06528872,0.08110062,0.108179821/
DATA TREF/492.0,484.0,475.0,451.0,426.0,394.0,
A344.0,300/

* * CRITICAL PROPERTIES FOR WATER * *
T1=374.136
P1 = 220.88

C
C

C = TR / 1.8 - 273.15
AK1 = 1800.0 / TR

C
C

* * CHECK IF LIQ. WATER OR ICE IS PRESENT * *

C
C

IF (TR < 492.0) GO TO 2
P = 0
DO 1 J = 1, 8
1 P = P + F(J) * (0.65 - 0.01 * C) ** (J - 1)
P = P1 * DEXP (AK1 * 1.E-5 * (T1 - C) * P) / 10.0
PSAT = P * 145.03894
GO TO 40

C
C

* * CORRELATION FOR VAPOR PRESS. OF ICE * *
C
C

2 DO 10 I = 1, 7
IF (TR .LE. TREF(I) .AND. TR .GT. TREF(I + 1)) GO TO 20
10 CONTINUE
WRITE (6, 30) TR
20 PSAT = A1(I) * DEXP (B1(I) * TR)

C
C

30 FORMAT (1X, T20, ' * * TEMP BELOW TABLE FOR FUNCT. PSAT
A: T(R) = ', E12.5)
C
C

40 RETURN
END

C
C

**************************************************************************
DOUBLE PRECISION FUNCTION CC(T, IS, IC, I, J)
**************************************************************************

C
C

THIS FUNCTION CALCULATES LANGMUIR CONSTANTS FOR HYDRATE
FORMATION FROM C1, C2, OR C3 USING THE SPHERICALLY SYMETRIC
KIHARA POTENTIAL FUNCTION. THIS PROGRAM CALLS ON THE
FUNCTION OMEGA WHICH GIVES THE POTENTIAL AS A FUNCTION OF
POSITION. GAUSSIAN INTEGRATION (C&W PAGE 100) IS USED
TO INTEGRATE OMEGA OVER THE CELL VOLUME.
OMEGA IS A FUNCTION THAT CALCULATES THE
SMOOTHED CELL POTENTIAL AS A SUM OF
CONTRIBUTIONS OF THE FIRST, SECOND AND
THIRD SHELLS.
THE VARIABLES ARE
IS- CODE FOR WHICH HYDRATE STRUCTURE (I OR II) IS FORMED
IC= CODE FOR WHICH CAVITY IS UNDER CONSIDERATION
A= CORE RADIUS FOR THE MOLECULE, C1...C3
T= TEMPERATURE
EPS= EPSILON, DEPTH OF INTERMOLECULAR POTENTIAL WELL, ERG
R= RADIAL POSITION OF THE ENCLOSED MOLECULE
RR = FIRST SHELL RADIUS.
RR2= SECOND SHELL RADIUS
RR3=THIRD SHELL RADIUS.
Z=FIRST SHELL COORDINATION NUMBER
Z2=SECOND SHELL COORDINATION NUMBER.
Z3=THIRD SHELL COORDINATION NUMBER.

REF: PARRISH AND PRAUSNITZ, I&EC PROC. DES & DEV, 11(1), P26 (1972)

IMPLICIT DOUBLE PRECISION (A-H, O-Z)
EXTERNAL OMEGA
COMMON /SIG/ SIGMA, EPS, RR, Z, A, TT, RR2, Z2, RR3, Z3
COMMON /AMOL/ MA, ISCODE (10)
COMMON /RRR/ R
COMMON /FUND/ SSIG (10), EEPS (10), AA (10)
COMMON /AFACT/ OM (10)
COMMON /ID/ II, JJ, ISS
CC=0.0
II=I
JJ=IC
ISS=IS

WRITE (06, 51) II, JJ, ISS, CC
51 FORMAT (4X, 3I2, 5X, E15.5)
PI=3.14159
QSTAR=1.0
IF (IS.EQ.1.AND.ISCODE (J).EQ.3) RETURN
IF (IC.EQ.1.AND.ISCODE (J).EQ.2) RETURN
IF (IC.EQ.1.AND.ISCODE (J).EQ.3) RETURN
IF (ISCODE (J).EQ.4) RETURN
TT=T
A=AA(I)
SIGMA=SSIG(I) - A
EPS=EEPS(I)
WRITE (06, 1031) SIGMA, EPS, A
1031 FORMAT (5X, 3E15.5)

***CHECK FOR WHICH STRUCTURE IS FORMED***
IF (IS.EQ.2) GO TO 6

***CHECK FOR WHICH CAVITY IS OCCUPIED****
IF (IC.EQ.2) GO TO 7

***STRUCTURE I CAVITY II
RR=4.152
Z=21.
RR2=7.078
Z2=24.0
RR3=8.285
Z3=50.0
GO TO 8

***CHECK FOR CAVITY, STRUCTURE II***
IF (IC.EQ.2) GO TO 7
***STRUCTURE II, CAVITY I***
RR=1.87
Z=20.
RR2=6.667
Z2=20.0
RR3=8.079
Z3=50.0
GO TO 8

***STRUCTURE II, CAVITY II***
RR=4.703
Z=28.
RR2=7.464
Z2=28.0
RR3=8.782
Z3=50.0
CONTINUE

EVALUATE THE INTEGRAL AND RETURN THE VALUE OF C
CALL YLIMIT(B)
C=GAUSS(0.,B,10,OMEGA)
PI=3.14159
CC=C*4.*PI/T/1.38/9.869/10.

QSTAR CORRELATIONS.
FORM=(SIGMA*OM(I)/(RR-A))*(EPS/273.15)
IF(IS.EQ.1.AND.IC.EQ.1)QSTAR=DEXP(-35.3446*(FORM**0.973))
IF(IS.EQ.1.AND.IC.EQ.2)QSTAR=DEXP(-14.1161*(FORM**0.8266))
IF(IS.EQ.2.AND.IC.EQ.1)QSTAR=DEXP(-35.3446*(FORM**0.973))
IF(IS.EQ.2.AND.IC.EQ.2)QSTAR=DEXP(-782.8469*(FORM**2.3129))
CC=CC*QSTAR

WRITE(6,552)(FORM,QSTAR)
C552 FORMAT(1X,1F,2X,1F)
RETURN

END

******************************************************************************
SUBROUTINE CUBEQN(A,Z,MTYPE)
******************************************************************************

THIS SUBROUTINE FINDS THE THREE ROOTS OF THE CUBIC
EQUATION GENERATED BY THE EQUATION OF STATE.

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION A(4),Z(3),B(3)
B(1)=A(2)/A(1)
B10V3=B(1)/3.0
B(2)=A(3)/A(1)
B(3)=A(4)/A(1)
ALF=B(2)-B(1)*B10V3
BET=2.*B10V3**3-B(2)*B10V3+B(3)
BETOVB2=BET/2.
ALFOV3=ALF/3.
CUAOV3=ALFOV3**3
SQBOV2=BETOVB2**2
DEL=SQBOV2+CUAOV3
IF(DEL) 40,20,30
20  MTYPE=0
   GAM=DSQRT(-ALFOV3)
IF(BET) 22,22,21
21  Z(1)=-2.*GAM-B10V3
   Z(2)=GAM-B10V3
   Z(3)=Z(2)
   GO TO 50
22  Z(1)=2.*GAM-B10V3
   Z(2)=-GAM-B10V3
   Z(3)=Z(2)
   GO TO 50
30  MTYPE=1
   EPS=DSQRT(DEL)
   TAU=-BETOV2
   RCU=TAU+EPS
   SCU=TAU-EPS
   SIR=1.
   SIS=1.
   IF(RCU) 31,32,32
31  SIR=-1.
32  IF(SCU) 33,34,34
33  SIS=-1.
34  R=SIR*(SIR*RCU)**.333333
   S=SIS*(SIS*SCU)**.333333
   Z(1)=R+S-B10V3
   Z(2)=-(R+S)/2.-B10V3
   Z(3)=0.866025*(R-S)
   GO TO 50
40  MTYPE=-1
   QUOT=SQBOV2/CUAOV3
   ROOT=DSQRT(-QUOT)
IF(BET) 42,41,41
41  PEI=(1.570796+DATAN(ROOT/DSQRT(1.-ROOT**2)))/3.
   GO TO 43
42  PEI=DATAN(DSQRT(1.-ROOT**2)/ROOT)/3.
43  FACT=2.*DSQRT(-ALFOV3)
   Z(1)=FACT*DCOS(PEI)-B10V3
   Z(2)=FACT*DCOS(PEI+2.094395)-B10V3
   Z(3)=FACT*DCOS(PEI+4.188790)-B10V3
50  RETURN
END
C
C
C
C       **************************************************
SUBROUTINE DATA(Y,XA,T)
C       **************************************************
C
C       THIS SUBROUTINE READS THERMODYNAMIC DATA FOR THE GASES,
C       CALCULATES MIXTURE CRITICAL PROPERITES, FREEZING POINT
C       DEPRESSIONS, AND ACTIVITY COEFFICIENTS FOR WATER IN
C       THE PRESENCE OF INHIBITORS.
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION A(10),SIGMA(10),EPS(10)
DIMENSION NCODE(10),KK(10)

C
C
C
C
C
C
C
DIMENSION ZAA(1,25), AA(10,25)
DIMENSION IISCO(25)
DIMENSION Y(25), XA(25), ZA(20)
DIMENSION XIC(10), TCIJ(10,10), PCIJ(10,10), VCIJ(10,10),
PC(10), TC(10), VC(10), OMEGA(10), ESTAR(10), C1RKV(10), C2RKV(10),
C1RKL(10), C2RKL(10), AMW(10), C0FREF(10), C1FREF(10),
C2FREF(10), C3FREF(10), C4FREF(10), TS(10,10),
AK(25,25), DVR(25,25), DTR(25,25)
COMMON /PVTIJ/ OMEGA, PCIJ, TCIJ
COMMON /AMOL/ MA, ISCODE(10)
COMMON /AZ/ KK, N, MK
COMMON /COEFF/ C0FREF, C1FREF, C2FREF, C3FREF, C4FREF,
2 C0HNRY, C1HNRY, C2HNRY, C3HNRY, C4HNRY, C5HNRY,
3 C0ALFS, C1ALFS, C2ALFS, C3ALFS, C4ALFS, C5ALFS
COMMON /PVT/ RT, TC, PC, VC, NSOLV
COMMON /NC/ NCODE, NCOMP
COMMON /ACTVTY/ TS, ESTAR
COMMON /VOL/ DVR, DTR, C1RKL, C2RKL
COMMON /PHMX/ C1RKV, C2RKV
COMMON /AFACT/ OMEGA(10)
COMMON /FUND/ SIGMA, EPS, A
COMMON /BKSA/ AK
COMMON /BKSC/ I WATER, IPOS, ISTR
COMMON /IMP/ IMCODE, XIMP(100), YCO2(100)
COMMON /SOLUT/ XSOLU, ACTIV, YYYYCO2
COMMON /TFREEZ/ TT0
COMMON /AWAT/ ANN(25,25)
IF (I WATER.EQ.0) GO TO 508
MA=MA+1
KK(MA)=13
508 CONTINUE
DATA X10LD/1./
OPEN (10, FILE = 'TAPE10.DAT', STATUS = 'OLD')
I=1
DO 96 I2=1, 25
IF (I WATER.EQ.0) GO TO 51
IF (I2 .NE. 13) GO TO 51
READ (10, 306) A(MA), SIGMA(MA), EPS(MA), AMW(MA), TC(MA)
READ (10, 306) VC(MA), PC(MA), OMEGA(MA), ESTAR(MA), C1RKV(MA)
READ (10, 306) C2RKV(MA), C1RKL(MA), C2RKL(MA), C0FREF(MA), C1FREF(MA)
READ (10, 306) C2FREF(MA), C3FREF(MA), C4FREF(MA)
READ (10, 307) (AK(MA, J), J= 1, 6)
READ (10, 307) (AK(MA, J), J= 7, 12)
READ (10, 307) (AK(MA, J), J=13, 18)
READ (10, 307) (AK(MA, J), J=19, 24)
READ (10, 307) (AK(MA, J), J=25, 25)
OM(MA)=OMEGA(MA)
READ (10, 308) ISCODE(MA)
GO TO 96
51 IF (I2 .EQ. KK(I)) GO TO 95
READ (10, 306) (ZA(J), J= 1, 5)
READ (10, 306) (ZA(J), J= 6, 10)
READ (10, 306) (ZA(J), J=11, 15)
READ (10, 306) (ZA(J), J=16, 20)
READ (10, 307) (ZAA(1,J), J= 1, 6)
READ (10, 307) (ZAA(1,J), J= 7, 12)
READ (10, 307) (ZAA(1,J), J=13, 18)
READ (10, 307) (ZAA(I,J), J=19, 24)
READ (10, 307) (ZAA(I,J), J=25, 25)
READ (10, 308) IISCO(I)
GO TO 96
95 READ (10, 306) A(I), SIGMA(I), EPS(I), AMW(I), TC(I)
READ (10, 306) VC(I), PC(I), OMEGA(I), ESTAR(I), C1RKV(I)
READ (10, 306) C2RKV(I), C1RKL(I), C2RKL(I), C0FREF(I), C1FREF(I)
READ (10, 306) C2FREF(I), C3FREF(I), C4FREF(I)
READ (10, 307) (AK(I,J), J= 1, 6)
READ (10, 307) (AK(I,J), J= 7, 12)
READ (10, 307) (AK(I,J), J=13, 18)
READ (10, 307) (AK(I,J), J=19, 24)
READ (10, 307) (AK(I,J), J=25, 25)
OM(I)=OMEGA(I)
READ (10, 308) ISCODE(I)
I=I+1
96 CONTINUE
REWIND (UNIT=10)
CLOSE (UNIT=10)
C 306 FORMAT (10X, 5(2X,E12.5),/,, 10X, 5(2X,E12.5),/,, 10X, 5(2X,E12.5),/,
C 1 , 10X,5 (2X, E12.5))
C 307 FORMAT (10X, 6(2X,E12.5),/,, 10X, 6(2X,E12.5),/,, 10X, 6(2X,E12.5),/,,
C 1 10X,6 (2X, E12.5),/,, 12X, E12.5)
306 FORMAT (5(E12.5,1X))
307 FORMAT (6(E12.5, 1X))
308 FORMAT (12)
K=1
DO 106 I=1, MA
DO 107 J=1, 25
IF (J.NE.KK(K+1)) GO TO 107
AA(I,K+1)=AK(I,J)
K=K+1
107 CONTINUE
K=I+1
106 CONTINUE
DO 108 I=1, MA
DO 109 J=1, MA
AK(I,J)=0.0
AK(I,J)=AA(I,J)
109 CONTINUE
108 CONTINUE
DO 6 I=1, MA
DO 6 J=1, MA
AK(J,I)=AK(I,J)
DVR(I,J)=DVR(J,I)
DTR(I,J)=DTR(J,I)
TS(I,J)=TS(J,I)
6 CONTINUE
RT=10.73*T
J=0
JJ=1
DO 10 I=1, MA
IF (I.WATER.NE.0) GO TO 826
IF (Y(I).LT.1.E-5) GO TO 10
826 J=J+1
JJ=JJ+1
NCODE(J)=J
\[ XA(J) = Y(I) \]
NCOMP = J

10 CONTINUE
DO 20 I = 1, NCOMP
EPS(I) = EPS(NCODE(I))
SIGMA(I) = SIGMA(NCODE(I))
A(I) = A(NCODE(I))
ISCODE(I) = ISCODE(NCODE(I))
OM(I) = OM(NCODE(I))
PC(I) = PC(NCODE(I))
TC(I) = TC(NCODE(I))
VC(I) = VC(NCODE(I))
OMEGA(I) = OMEGA(NCODE(I))
ESTAR(I) = ESTAR(NCODE(I))
C1RKV(I) = C1RKV(NCODE(I))
C2RKV(I) = C2RKV(NCODE(I))
C1RKL(I) = C1RKL(NCODE(I))
C2RKL(I) = C2RKL(NCODE(I))
C0FREF(I) = C0FREF(NCODE(I))
C1FREF(I) = C1FREF(NCODE(I))
C2FREF(I) = C2FREF(NCODE(I))
C3FREF(I) = C3FREF(NCODE(I))
C4FREF(I) = C4FREF(NCODE(I))
TCIJ(I, I) = TC(NCODE(I))
AMW(I) = AMW(NCODE(I))
20 CONTINUE
IF (NCOMP .EQ. 1) GO TO 22
C IF (IWATER .NE. 0 .AND. (NCOMP - 1) .EQ. 1) GO TO 22
NCOMP1 = NCOMP - 1
DO 21 I = 1, NCOMP1
I1 = I + 1
DO 21 J = I1, NCOMP
TS(I, J) = TS(NCODE(I), NCODE(J))
TS(J, I) = TS(I, J)
DVR(I, J) = DVR(NCODE(I), NCODE(J))
DVR(J, I) = DVR(I, J)
DTR(I, J) = DTR(NCODE(I), NCODE(J))
DTR(J, I) = DTR(I, J)
AK(I, J) = AK(NCODE(I), NCODE(J))
ZC(I, J) = .291 - .04*(OMEGA(I) + OMEGA(J))
ZC(J, I) = ZC(I, J)
TCIJ(I, J) = (TC(I) * TC(J))**.5*(1. - AK(I, J))
TCIJ(J, I) = TCIJ(I, J)
VCIJ(I, J) = (.5*VC(I)**.3333333+VC(J)**.3333333)**3
VCIJ(J, I) = VCIJ(I, J)
PCIJ(I, J) = ZC(I, J)*10.73*TCIJ(I, J)/VCIJ(I, J)
PCIJ(J, I) = PCIJ(I, J)
21 CONTINUE
22 CONTINUE
DO 31 I3 = 1, NCOMP
DO 31 I4 = 1, NCOMP
ANN(I3, I4) = AK(I3, I4)
31 CONTINUE
IF (IWATER .EQ. 0) GO TO 507
MA = MA - 1
NCOMP = NCOMP - 1
ACTIV = 1.0
58
TT0=0.0
507 IF(IMPURE.EQ.0.OR.XSOLU.EQ.0.0) GO TO 509
  T=T/1.8
C ** ACTIVITY COEFFICIENT OF WATER **
C IF(IMCODE.EQ.1) ACTIV=DEXP(-0.90634*XSOLU**2+1.95522*XSOLU**3)
IF(IMCODE.EQ.2) ACTIV=DEXP(5.77435*XSOLU**2)
IF(IMCODE.EQ.3) ACTIV=DEXP(-0.90634*XSOLU**2+1.95522*XSOLU**3)
IF(IMCODE.EQ.4) ACTIV=DEXP(-0.29965*XSOLU**2-172.56293*XSOLU**3)
IF(IMCODE.EQ.5) ACTIV=DEXP(-199.63879*XSOLU**2+3869.86893*XSOLU**3)
1
IF(IMCODE.EQ.6) ACTIV=DEXP(-239.55098*XSOLU**2+9683.44617*XSOLU**3)
1
IF(IMCODE.EQ.7) ACTIV=DEXP((10.44*T-3535.34)*XSOLU**2.+
(-32.19*T+10888.7)*XSOLU**3.)/(0.082*T)
IF(IMCODE.EQ.8) ACTIV=DEXP(-1.84825*XSOLU**2+4.26904*XSOLU**3)
IF(IMCODE.EQ.9.OR.IMCODE.EQ.10) ACTIV=DEXP((( -64.2019)*XSOLU**2.+
1*XSOLU**3.)/(0.082*T))
C ** CORRECTION FACTOR FOR SYSTEMS CONTAINING CO2 **
C ACTIV=(1-0.30*YYYCO2*XSOLU)*ACTIV
C ** FREEZING POINT DEPRESSIONS **
C IF(IMCODE.EQ.1) TT0= -0.13171+105.59*XSOLU+161.82*XSOLU**2
-70.233*XSOLU**3
IF(IMCODE.EQ.2) TT0=-0.33398+109.91*XSOLU+308.25*XSOLU**2
-745.82*XSOLU**3
IF(IMCODE.EQ.3) TT0=-1.1132+161.707*XSOLU-101.0468*XSOLU**2.
IF(IMCODE.EQ.4) TT0=-0.083176+197.62*XSOLU-175.14*XSOLU**2
+8884.6*XSOLU**3
1
IF(IMCODE.EQ.5) TT0=0.12618+207.67*XSOLU+6510.4*XSOLU**2
+4113.4*XSOLU**3
IF(IMCODE.EQ.6) TT0=0.0085870+185.53*XSOLU-65.062*XSOLU**2
+494.73*XSOLU**3
IF(IMCODE.EQ.7) TT0=0.0460878+163.998*XSOLU+941.4078*XSOLU**2.
IF(IMCODE.EQ.8) TT0=-0.019306+104.71*XSOLU+64.867*XSOLU**2
+1857.6*XSOLU**3
1
IF(IMCODE.EQ.9.OR.IMCODE.EQ.10) TT0= -0.11843+110.2595*XSOLU+
1126.4329*XSOLU**2.
  T=T*1.8
509 RETURN
END
C
C **********************************************
DOUBLE PRECISION FUNCTION DEL(N)
**********************************************
C THE DEL FUNCTIONS EVALUATE DEL OF THE KIHARA FUNCTION FOR
C THE 1ST, 2ND AND 3RD SHELLS OF WATER.
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
COMMON /SIG/ SIGMA,EPS,RR,Z,A,T,RR2,Z2,RR3,Z3
COMMON /RRR/ R
D = (1.0 - R/RR - A/RR)
DD = (1.0 + R/RR - A/RR)
D = 1.0/D**N - 1.0/DD**N
DEL = D/N
2000 FORMAT('   DEL;   ', 1G10.5)
RETURN
END

C
C
C

***********************************************************************
DOUBLE PRECISION FUNCTION DEL2(N)
***********************************************************************
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
COMMON/SIG/SIGMA,EPS,RR,Z,A,T,RR2,Z2,RR3,Z3
COMMON/RRR/R
D = (1.0 - R/RR2 - A/RR2)
DD = (1.0 + R/RR2 - A/RR2)
D = 1.0/D**N - 1.0/DD**N
DEL2 = D/N
RETURN
END

C
C
C

***********************************************************************
DOUBLE PRECISION FUNCTION DEL3(N)
***********************************************************************
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
COMMON/SIG/SIGMA,EPS,RR,Z,A,T,RR2,Z2,RR3,Z3
COMMON/RRR/R
D = (1.0 - R/RR3 - A/RR3)
DD = (1.0 + R/RR3 - A/RR3)
D = 1.0/D**N - 1/DD**N
DEL3 = D/N
RETURN
END

C
C
C

****************************************************
DOUBLE PRECISION FUNCTION GAUSS(A,B,M,FUNCTN)
****************************************************
C     ****REF: CARNAHAN,LUTHER AND WILKES:APP. NUMERICAL METH'S.
C
C     FORMULA TO COMPUTE THE INTEGRAL OF FUNCTN(X) BETWEEN THE
C     INTEGRATION LIMITS A AND B.
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION NPOINT(7), KEY(8),Z(24),WEIGHT(24)
EXTERNAL FUNCTN
C
C     **PRESET NPOINT,KEY,Z,AND WEIGHT ARRAYS
DATA NPOINT /2,3,4,5,6,10,15/
DATA KEY / 1,2,4,6,9,12,17,25 /
WEIGHT(1) = 1.0
WEIGHT(2) = 0.888888889
WEIGHT(3) = 0.555555556
WEIGHT(4) = 0.652145155
WEIGHT(5) = 0.347854845
WEIGHT(6) = 0.568888889
WEIGHT(7) = 0.478628671
WEIGHT(8) = 0.236926885
WEIGHT(9) = 0.467913935
WEIGHT(10) = 0.360761573
WEIGHT(11) = 0.171324493
WEIGHT(12) = 0.295524225
WEIGHT(13) = 0.269266719
WEIGHT(14) = 0.219086363
WEIGHT(15) = 0.149451349
WEIGHT(16) = 0.066671344
WEIGHT(17) = 0.202578242
WEIGHT(18) = 0.198431485
WEIGHT(19) = 0.186160000
WEIGHT(20) = 0.166269206
WEIGHT(21) = 0.139570678
WEIGHT(22) = 0.107159221
WEIGHT(23) = 0.070366047
WEIGHT(24) = 0.030753242

Z(1) = 0.577350269
Z(2) = 0.0
Z(3) = 0.774596669
Z(4) = 0.339981044
Z(5) = 0.861136312
Z(6) = 0.0
Z(7) = 0.538469310
Z(8) = 0.906179846
Z(9) = 0.238619186
Z(10) = 0.661209387
Z(11) = 0.932469514
Z(12) = 0.148874339
Z(13) = 0.433395394
Z(14) = 0.679409568
Z(15) = 0.865063367
Z(16) = 0.973906529
Z(17) = 0.0
Z(18) = 0.2011941
Z(19) = 0.3941513
Z(20) = 0.5709722
Z(21) = 0.7244177
Z(22) = 0.848206583
Z(23) = 0.937273392
Z(24) = 0.987992518

C *** FIND SUBSCRIPT OF FIRST Z AND WEIGHT VALUE ***
DO 1 I=1,7
IF(M.EQ.NPOINT(I)) GO TO 2
1 CONTINUE
C *** INVALID M USED ***
GAUSS=0.
RETURN

C
C *** SET UP INITIAL PARAMETERS ***
2 JFIRST=KEY(I)
JLAST=KEY(I+1)-1
C = (B - A) / 2.
D = (B + A) / 2.

C
C *** ACCUMULATE THE SUM IN THE MPOINT FORMULA
SUM = 0.
DO 5 J = JFIRST, JLAST
IF (Z(J) .EQ. 0.0) SUM = SUM + WEIGHT(J) * FUNCTN(D)
5 IF (Z(J) .NE. 0.0) SUM = SUM + WEIGHT(J) * (FUNCTN(Z(J) * C + D) + FUNCTN(-Z(J) * C + D))
C
C *** MAKE INTERVAL CORRECTION AND RETURN ****
GAUSS = C * SUM
2100 FORMAT(' GAUSS; ', 1G10.5)
RETURN
END
C
C C
C
C       **********************************************
DOUBLE PRECISION FUNCTION OMEGA(R)
C       **********************************************
C
C     THIS FUNCTION EVALUATES THE CELL POTENTIAL (SPHERICALLY
C     SYMMETRIC KIHARA) WITH THE RADIAL POSITION, R, OF THE
C MOLECULE IN THE CAVITY AS THE INDEPENDENT VARIABLE.
C
IMPLICIT DOUBLE PRECISION (A - H, O - Z)
COMMON /SIG/ SIGMA, EPS, RR, Z, A, T, RR2, Z2, RR3, Z3
COMMON /RRR/ ZZ
ZZ = R
OMEGA = 2.0 * Z * EPS * (SIGMA ** 12 / RR ** 11 / R * (DEL(10) + A / RR * DEL(11))
1 - SIGMA ** 6 / RR ** 5 / R * (DEL(4) + A / RR * DEL(5)))
OMEGA2 = 2.0 * Z2 * EPS * (SIGMA ** 12 / RR2 ** 11 / R * (DEL2(10) + A / RR2 * DEL2(11))
1 - SIGMA ** 6 / RR2 ** 5 / R * (DEL2(4) + A / RR2 * DEL2(5)))
OMEGA3 = 2.0 * Z3 * EPS * (SIGMA ** 12 / RR3 ** 11 / R * (DEL3(10) + A / RR3 * DEL3(11))
1 - SIGMA ** 6 / RR3 ** 5 / R * (DEL3(4) + A / RR3 * DEL3(5)))
OMEGA = OMEGA + OMEGA2 + OMEGA3
OMEGA = -OMEGA / T
IF (ABS(OMEGA) .GT. 170.) OMEGA = ABS(OMEGA) / OMEGA * 170.
IF (OMEGA .LE. -60.) OMEGA = -60.
OMEGA = DEXP(OMEGA) * R * R
2300 FORMAT(' OMEGA; ', 1G10.5)
RETURN
END
C
C C
C
C       ****************************************************
SUBROUTINE VAPRES(PVAP,T)
C       ****************************************************
C
C       THIS SUBROUTINE IS CALLED BY BUBDEW. IT CALCULATES THE VAPOR PRESSURE
C OF EACH COMPONENT USING RIEDEL'S CORRELATION.
C
IMPLICIT DOUBLE PRECISION (A - H, O - Z)
DIMENSION PVAP(10)
DIMENSION TCIJ(10,10), PCIJ(10,10), PC(10), TC(10), VC(10), OMEGA(10)
DIMENSION NCODE(10)
COMMON/PVT/I\_J/\_OMEGA,PCI\_J,TC\_J
COMMON/N\_C/N\_CODE,N\_COMP
COMMON/PVT/RT,TC,PC,VC,NSOLV
DO 401 I=1,N\_COMP
TR=T/TC(I)
IF(TR.GT.1.0)GO TO 400
B=36.\_TR-35.-TR\_6.0+42.*DLOG(\_TR)
ALFAC=5.\_808+4.\_93*\_OMEGA(I)
RES=0.\_118*B-7.*DLOG10(\_TR)+(ALFAC-7.)*(0.\_036*B-DLOG10(\_TR))
PVAP(I)=PC(I)/10.**(RES)
GO TO 401
400 PVAP(I)=PC(I)
401 CONTINUE
RETURN
END

C

*** SUBROUTINE BUBDEW(T,P,Y) ***

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION XL(10),Y(10),V(10),PHIL(10)
DIMENSION PHI(10),PVAP(10)
DIMENSION N\_CODE(10)
DIMENSION ZK(10),ZCN(10)
COMMON/X/XL
COMMON/PH/PHIL
COMMON/N\_C/N\_CODE,N\_COMP
COMMON/T\_BLOC/ITAG
COMMON/L\_IQUID/L\_IQ
COMMON/H\_HELP/IST0,IST2,ISLOW

ITAG=1
ITER=0
CALL VAPRES(PVAP,T)
SFRAC=0
IF(L\_IQ.EQ.1)GO TO 8000

** DEW POINT CALCULATIONS **
DO 280 I=1,N\_COMP
FRAC=Y(I)/PVAP(I)
SFRAC=SFRAC+FRAC
280 CONTINUE

MAKE AN INITIAL ESTIMATE OF PRESSURE
P=1/SFRAC
S=0
DO 201 I=1,N\_COMP
XL(I)=Y(I)*P/PVAP(I)
S=S+XL(I)
201 CONTINUE
DO 222 I=1,N\_COMP
XL(I)=XL(I)/S
222 CONTINUE
CALL PHIMIX(Y,P,T,PHI)
SUM=0.0
DO 202 I=1,NCOMP
  ZK(I)=PHIL(I)/PHI(I)
  ZCN(I)=Y(I)/ZK(I)
  SUM=SUM+ZCN(I)
202   CONTINUE
DO 203 I=1,NCOMP
  XL(I)=ZCN(I)/SUM
203   CONTINUE
PNEW=P/SUM
IF(ABS(SUM-1.0).LT.0.0001)GO TO 205
P=PNEW
ITER=ITER+1
IF(ITER.GT.100)GO TO 207
GO TO 206
207 WRITE(6,208)
208   FORMAT(' FAILED TO CONVERGE IN BUBDEW')
GO TO 205

C ** BUBBLE POINT CALCULATIONS **
C   HERE XL IS SET EQUAL TO Y BECAUSE THE VALUES OF Y COMING IN
C       ARE LIQUID COMPOSITION
8000   DO 101 I=1,NCOMP
     XL(I)=Y(I)
101   CONTINUE
DO 102 I=1,NCOMP
  FRAC=XL(I)*PVAP(I)
  SFRAC=SFRAC+FRAC
102   CONTINUE
C       MAKE AN INITIAL ESTIMATE OF PRESSURE
P=SFRAC
S=0
DO 103 I=1,NCOMP
  Y(I)=XL(I)*PVAP(I)/P
  S=S+Y(I)
103   CONTINUE
DO 104 I=1,NCOMP
  Y(I)=Y(I)/S
104   CONTINUE
105   CALL PHIMIX(Y,P,T,PHI)
SUM=0.0
DO 106 I=1,NCOMP
  ZK(I)=PHIL(I)/PHI(I)
  ZCN(I)=ZK(I)*XL(I)
  SUM=SUM+ZCN(I)
106   CONTINUE
DO 107 I=1,NCOMP
  Y(I)=ZCN(I)/SUM
107   CONTINUE
PNEW=P*SUM
IF(ABS(SUM-1.0).LT.0.0001)GO TO 225
P=PNEW
ITER=ITER+1
IF(ITER.GT.100)GO TO 207
GO TO 105
C   INTERCHANGE XL AND Y VALUES AGAIN BY STORING Y VALUES IN V
225   DO 23 I=1,NCOMP
     V(I)=Y(I)
Y(I) = XL(I)
XL(I) = V(I)
CONTINUE
RETURN

***********************************************************************
SUBROUTINE PHIMIX(Y,P,T,PHI)
***********************************************************************

** THIS SUBROUTINE IS TAKEN DIRECTLY FROM PRAUSNITZ AND CHUEH'S BOOK "COMPUTER CALCULATIONS FOR MULTI COMPONENT VAPOR LIQUID EQUILIBRIA" (1968) PRENTICE HALL

THIS SUBROUTINE CALCULATES THE FUGACITY COEFFICIENTS FOR EACH COMPONENT FROM THE EQUATION OF STATE.

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION NCODE(10)
DIMENSION X(11),TCIJ(10,10),ZC(10,10),PCIJ(10,10),VCIJ(10,10),
2 PC(10),TC(10),VC(10),OMEGA(10),ESTAR(10),C1RKV(10),C2RKV(10),
3 C1RKL(10),C2RKL(10),AMW(10),C0FREF(10),C1FREF(10),
4 C2FREF(10),C3FREF(10),C4FREF(10),TS(10,10),
5 AK(25,25),DVR(25,25),DTR(25,25)
DIMENSION PHIL(10)
DIMENSION XL(10)
COMMON/BLOCK/ISOLVE
COMMON /PHMX/ C1RKV, C2RKV
COMMON /PVTIJ/ OMEGA, PCIJ, TCIJ
COMMON /PVT/ RT, TC, PC, VC, NSOLV
COMMON/NC/NCODE,NCOMP
COMMON/AFACT/OM(10)
COMMON/BKSA/AK
COMMON/X/XL
COMMON/PHAS/NVLLH
COMMON/PH/PHIL
COMMON/TBLOC/ITAG
COMMON/ZV/ZV
COMMON/WATER/NW
COMMON/AWAT/ANN(25,25)
COMMON/CRIPTCL/NCRIT,TCRIT
COMMON/LIQUID/LIQ
DIMENSION Y(10),PHI(10),Z(3),ARKV(10,10),
2 BRKV(10),AIRKV(10),A(4),AMWT(10,10)
DIMENSION AA(25),BTC(25),AY(25,25)
IF(ISOLVE.EQ.1)GO TO 200
DO 100 I=1,NCOMP
ARKV(I,I)=C1RKV(I)*10.73**2*TC(I)**2.5/PC(I)
BRKV(I)=C2RKV(I)*10.73*TC(I)/PC(I)
IF(I.EQ.NCOMP) GO TO 110
II=I+1
DO 100 J=II,NCOMP
ARKV(I,J)=(C1RKV(I)+C1RKV(J))*0.5*10.73**2*TCIJ(I,J)
1**2.5/PCIJ(I,J)
ARKV(J,I)=ARKV(I,J)
CONTINUE
CONTINUE
AMRKV=0.
BMRKV=0.
DO 120 I=1,NCOMP
AIRKV(I)=0.
BMRKV=BMRKV+Y(I)*BRKV(I)
DO 120 J=1,NCOMP
AIRKV(I)=AIRKV(I)+Y(J)*ARKV(I,J)
120 AMRKV=AMRKV+Y(I)*Y(J)*ARKV(I,J)

CALCULATE VAPOR MOLAR VOLUME FOR MIXTURE

A(1)=1.
A(2)=-1.
PBRRT=P*BMRKV/RT
ABRT=AMRKV/(BMRKV*10.72999*T**1.5)
A(3)=PBRRT*(ABRT-1.-PBRRT)
A(4)=-ABRT*(PBRRT**2)
CALL CUBEQN(A,Z,MTYPE)
IF(MTYPE)130,140,140
130 AMAX1=Z(1)
IF(AMAX1.LT.Z(2)) AMAX1=Z(2)
IF(AMAX1.LT.Z(3)) AMAX1=Z(3)
ZV=AMAX1
GO TO 150
140 ZV=Z(1)
150 VV=ZV*RT/P

CALCULATE FUGACITY COEFFICIENTS WITH THE MODIFIED REDLICH-KWONG EQUATION OF STATE

QVVB=DLOG(VV/(VV-BMRKV))
Q1VB=1./(VV-BMRKV)
Q2RTB=2./(10.73*T**1.5*BMRKV)
QVBV=DLOG((VV+BMRKV)/VV)
QARTB=AMRKV/(10.73*T**1.5*BMRKV**2)
QBVB=BMRKV/(VV+BMRKV)
DO 160 I=1,NCOMP
PHI(I)=QVVB+BRKV(I)*Q1VB-AIRKV(I)*Q2RTB*QVBV+2 BRKV(I)*QARTB*(QVBV-QVBV)-DLOG(ZV)
IF(PHI(I).LT.170.0) GO TO 27
WRITE(6,28) QVVB,BRKV(I),Q1VB,AIRKV(I),Q2RTB,QVBV,QARTB,QBVB,ZV
28 FORMAT(9F10.5)
27 CONTINUE
160 CONTINUE
RETURN

****** CALCULATE FUGACITY COEFFICIENTS USING PENG ROBINSON EQUATION OF STATE ******

BC=0.0
BCX=0.0
DO 201 I=1,NCOMP
AKK=0.37464+1.54226*OMEGA(I)-0.26992*OMEGA(I)**2
201 CONTINUE
ATC=52.643367*TC(I)**2/PC(I)
IF(NW.EQ.0)GO TO 211
DO 81 I1=1,NCOMP
AK(I1,NCOMP)=ANN(I1,NCOMP)*(0.4605*P/T-0.2237)
AK(NCOMP,I1)=AK(I1,NCOMP)
81 CONTINUE
IF(I.LT.NCOMP)GO TO 211
IF((T/TC(I)).LT.0.85)ALPHA=(1.0085677+0.82154*(1.-DSQRT(T/TC(I))**0.5)
IF((T/TC(I)).GE.0.85)GO TO 211
GO TO 212
211 ALPHA=(1.0+AKK*(1.0-DSQRT(T/TC(I))))**2
212 AA(I)=ATC*ALPHA
BTC(I)=0.834794*TC(I)/PC(I)
BC=BC+Y(I)*BTC(I)
BCX=BCX+XL(I)*BTC(I)
201 CONTINUE
AC=0.0
ACX=0.0
DO 202 I=1,NCOMP
DO 203 J=1,NCOMP
AY(I,J)=(1.0-AK(I,J))*DSQRT(AA(I)*AA(J))
AC=AC+Y(I)*Y(J)*AY(I,J)
ACX=ACX+XL(I)*XL(J)*AY(I,J)
202 CONTINUE
203 CONTINUE
NCRIT=0
IF(LIQ.EQ.1)GO TO 809
IF(NVLLH.EQ.0)GO TO 809
TCRIT=(AC/BC)/63.061506
IF((T/TCRIT).GT.0.97)GO TO 808
GO TO 809
808 NCRIT=1
GO TO 810
809 CONTINUE
IF(ITAG.EQ.2)GO TO 288
AP=AC*P/(10.73*T)**2
B=BC*P/(10.73*T)
A(1)=1
A(2)=B-1
A(3)=AP-3.0*B**2-2.0*B
A(4)=B**3+B**2-AP*B
CALL CUBEQN(A,Z,MTYPE)
IF(MTYPE)204,205,205
204 AMAX1=Z(1)
IF(AMAX1.LT.Z(2))AMAX1=Z(2)
IF(AMAX1.LT.Z(3))AMAX1=Z(3)
ZV=AMAX1
GO TO 206
205 ZV=Z(1)
206 DO 207 I=1,NCOMP
F1=BTC(I)/BC*(ZV-1.0)
F2=-DLOG(ZV-B)
F3=0.0
DO 208 K=1,NCOMP
F3=F3+Y(K)*AY(K,I)
208 CONTINUE
F3 = \frac{-AP}{(2.828427 \times B) \times (2.0 \times F3 / AC - BTC(I) / BC)}
F3 = F3 \times DLOG((ZV + 2.414 \times B) / (ZV - 0.414 \times B))
PHI(I) = DEXP(F1 + F2 + F3)

207  CONTINUE
IF(NVLLH.EQ.0.OR.ITAG.EQ.0)GO TO 810
288  APX = ACX \times P / (10.73 \times T)^{**2.}
BX = BCX \times P / (10.73 \times T)
A(1) = 1
A(2) = BX - 1
A(3) = APX - 3.0 \times BX^{**2} - 2.0 \times BX
A(4) = BX^{**3} - BX^{**2} - APX \times BX
CALL CUBEQN(A,Z,MTYPE)
IF(MTYPE)214,215,216
214  AMINI = Z(1)
IF(AMINI.GT.Z(2).AND.Z(2).GT.0)AMINI = Z(2)
IF(AMINI.GT.Z(3).AND.Z(3).GT.0)AMINI = Z(3)
ZL = AMINI
GO TO 217
215  ZL = Z(2)
GO TO 217
216  ZL = Z(1)
DO 218 I = 1, NCOMP
F1 = BTC(I) / BCX \times (ZL - 1.0)
F2 = -DLOG(ZL - BX)
F3 = 0.0
DO 219 K = 1, NCOMP
F3 = F3 + XL(K) \times AY(K,I)
219  CONTINUE
F3 = \frac{-APX}{(2.828427 \times BX) \times (2.0 \times F3 / ACX - BTC(I) / BCX)}
F3 = F3 \times DLOG((ZL + 2.414 \times BX) / (ZL - 0.414 \times BX))
PHIL(I) = DEXP(F1 + F2 + F3)
218  CONTINUE
810  RETURN
DO 2 N=1,20
IF( S.GT.1. OR S.LE.0.) GO TO 6
UM=1./(1.-S-CA)
UP=1./(1.+S-CA)
UM5=UM**5
UP5=UP**5
DA4=UM5+UP5
DA5=UM5*UM+UP5*UP
DB6=DA4+CA*DA5
UM11=UM**11
UP11=UP**11
DA10=UM11+UP11
DB12=DA10+CA*DA11
DB=RCA12*DB12-2.*RCA6*DB6
A10=UM11/UM-UP11/UP
A11=UM11-UP11
B12=A10/10.+CA*A11/11
A4=UM5/UM-UP5/UP
A5=UM5-UP5
B6=A4/4.+CA*A5/5.
B=RCA12*B12-2.*RCA6*B6
W=Z*EPS/(2.*S*T)*B
DWY=-W/S+Z*EPS*DB/(2.*S*T)
DS=S-(W-10.)/DWY
IF(ABS((DS-S)/DS).LT.01) GO TO 3
IF(DS.LE.0) CHECK=CHECK+1
IF(CHECK.GT.5) GO TO 6
2 S=DS
3 RLIMIT=S*RR
RETURN
6 CONTINUE
WRITE(6,100)SIGMA,EPS,A,RR,Z,T,S
100   FORMAT(' ','BLOW UP ON Y-LIMIT',7F10.5)
RETURN
END

***********************************************************************
REVISED SOLUBILITY SUBROUTINE

SUBROUTINE SOL7(JK,Y7,PHI7,P,T,X6)
***********************************************************************

THIS SUBROUTINE CALCULATES THE SOLUBILITIES OF
THE GASES IN WATER USING KRICHEVSKY-KASARNOVSKY
EXPRESSIONS FOR EACH GAS.

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION A(25),B(25),C(25),D(25)
DIMENSION VBAR(25),NCODE(25)
COMMON/NC/NCODE,NCOMP

P IS IN ATM. AND T IS IN K

DATA A/-15.826227,-18.400368,-18.057885,-20.958631,
A   -67.557,-22.150557,-20.108263,0.0,0.0,0.0
A   ,-868.764,0.0,0.0,-357.802,-14.283146,
C   -17.160634,-17.934347,-15.103508,-17.979226,
D   -336.76,-270.967,-877.845,-20.108263,
E   -20.108263,0.0/
C
DATA B/1559.0631,2410.4807,2627.6108,3109.3918,
A   9177.534,3407.2181,2739.7313,0.0,0.0,0.0
B   ,43323.6,0.0,0.0,13897.5,2050.3269,1915.144,
C   1933.381,2603.9795,2530.0405,16170.1,
D   15992.9,42051.0,2739.7313,2739.7313,0.0/
C
DATA C/0.0,0.0,0.0,0.0,0.072775,
A   0.0,0.0,0.0,0.0,0.0,
B   122.986,0.0,0.0,52.2871,0.0,
C   0.0,0.0,0.0,0.0,46.2117,
D   33.2892,125.018,0.0,0.0,0.0/
C
DATA D/1.0,1.0,1.0,1.0,1.0,760.0,
A   1.0,1.0,1.0,1.0,1.0,
B   0.0,1.0,0.0,-0.029836,1.0,
C   1.0,1.0,1.0,1.0,-0.00608793,
D   0.0260485,0.0,1.0,1.0,1.0/
C
DATA VBAR/32.0,32.0,60.0,13*32.0,
A   32.8,8*32.0/
C
AOR.JK.EQ.22)GO TO 10
AOR.JK.EQ.6.OR.JK.EQ.7)GO TO 20
XO=D(JK)*DEXP(A(JK)+B(JK)/T+C(JK)*T)
GO TO 30
10  XO=DEXP((A(JK)+B(JK)/T+C(JK)*DLOG(T)+
AD(JK)*T)/1.987)
30  F=P*Y7*PHI7
    X6=F*XO*DEXP(-1.0*VBAR(JK)*(P-1.0)/(82.06*T))
    IF(X6.GT.0.05)GO TO 40
    GO TO 50
40   CONTINUE
C
WRITE(6,200)JK,X6
X6=0.05
GO TO 50
C
20   WRITE(6,100)JK
20       X6=0.0
50   RETURN
100  FORMAT(1X,T20,' * * COMPONENT# ',I3,' NOT YET
A AVAILABLE IN SOL7 * * ')}
200  FORMAT(1X,T20,' * * COMPONENT# ',I3,' HAS DEFAULTED
A TO X6 = 0.05 FROM X6 = ',E15.5,' * * ')
C
END
BIBLIOGRAPHY
BIBLIOGRAPHY


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