

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

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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 CO₂ in the atmosphere and is a topic of ongoing research and debate (U. S. Department of Energy, 1999). Oceanic CO₂ sequestration has been proposed as a method of long-term sequestration of anthropogenic emissions of CO₂. Understanding the fate of CO₂ 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 CO₂ through pipes to ocean depths ranging from 1000 m to 3000 m is a leading candidate for introducing CO₂ into the deep ocean. However, formation of the ice-like CO₂ clathrate hydrate at the interface of CO₂ and seawater complicates the fate of liquid CO₂ injected into the ocean (Holder, et al., 1995). The physical and chemical behavior of CO₂ in the ocean needs to be understood, especially the impact of CO₂ hydrate on the injection and sequestration process.

Formation of CO₂ 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 (L₂) and liquid water (L₁). 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 CO₂ hydrate forms from a two-phase system of either gaseous or liquid CO₂ and water, the hydrate formed was initially less dense than the aqueous solution. This is likely due to occluded bubbles or drops of CO₂ in the hydrate clusters. Such floating hydrate particles will diminish the effectiveness of ocean sequestration of CO₂. However, if CO₂ 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 CO₂ to sink to even greater depths before it dissolves. (Holder, et al., 2001).

In this work, additional experimental single-phase CO₂ 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 CO₂ hydrate (H) and a water-rich liquid (L₁) 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 CO₂ directly into oceans (Brewer, 2000)
- Injection of captured CO₂ into sub-seabed geological formations (Winter & Bergman, 1993)

The ocean represents a large potential sink for sequestration of anthropogenic CO₂ emissions. It is generally accepted that more than 80% of today's anthropogenic CO₂ 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 CO₂ 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 CO₂ from a ship
- Formation of a lake of liquid CO₂ in the deep sea

Most research effort has focused on the introduction of CO₂ by pipeline. The concept is illustrated in Figure 1 below:

If CO₂ 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

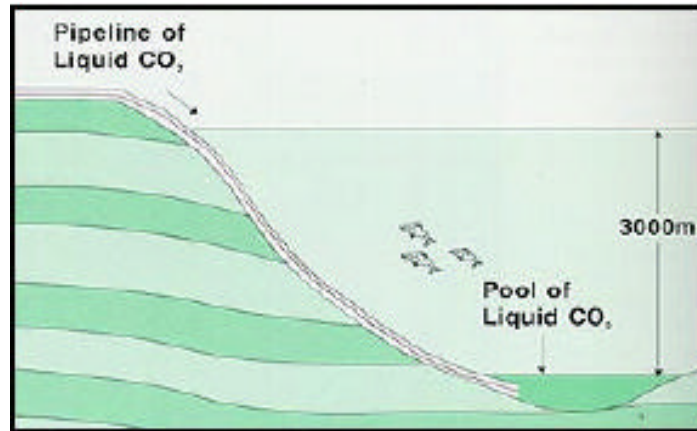


Figure 1 Concept for introducing CO₂ captured from power and industrial plant into deep ocean by land based pipelines.

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 CO₂ 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 CO₂ injected into ocean water is necessary for predicting the behavior of large-scale ocean disposal schemes. The first successful field experiment where CO₂ 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 CO₂ 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 \AA , such as methane, ethane, carbon dioxide and hydrogen sulfide. Structure II is formed with gas molecules somewhat larger ($6 \text{ \AA} < d < 7 \text{ \AA}$), such as propane or iso-butane. Still larger molecules ($7 \text{ \AA} < d < 9 \text{ \AA}$), 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).

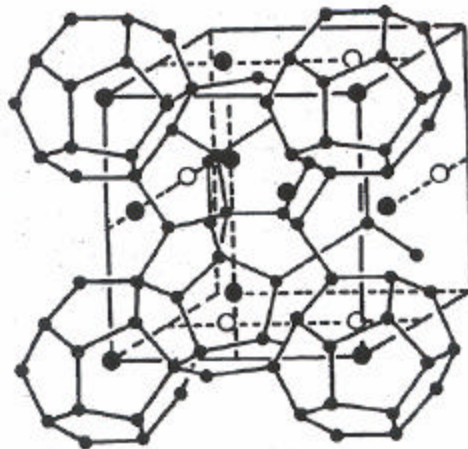
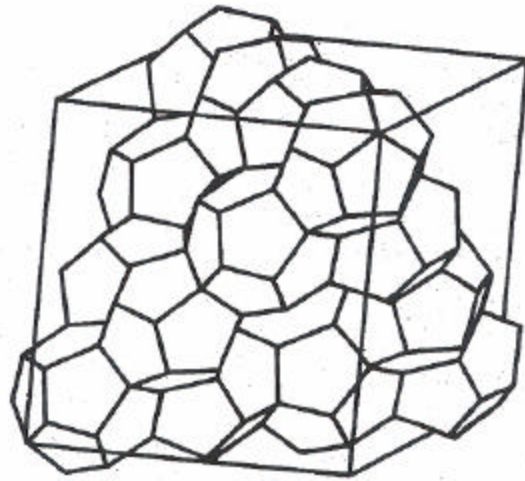


Figure 2 Gas Hydrate Structure I and Structure II

2.4 Formation of CO₂ Hydrate

A considerable amount of research and experimental data in formation of CO₂ hydrate from two-phase system consisting of CO₂ in a separate gas (V) or liquid phase (L₂) and liquid water (L₁) 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 CO₂. Research in formation of hydrate from single-phase is limited in literature. However, the previous research performed at the NETL has demonstrated that if CO₂ 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 cm³ to 40 cm³ 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 CO₂ (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 $\pm 0.2\%$ of reading. Pressure of the viewcell was measured by Heise ATS2000 Digital Pressure Transducer with an accuracy of $\pm 0.02\%$ 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 CO₂ injected through another syringe pump was determined from the volume delivered by using the density for CO₂ 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 CO₂, 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.

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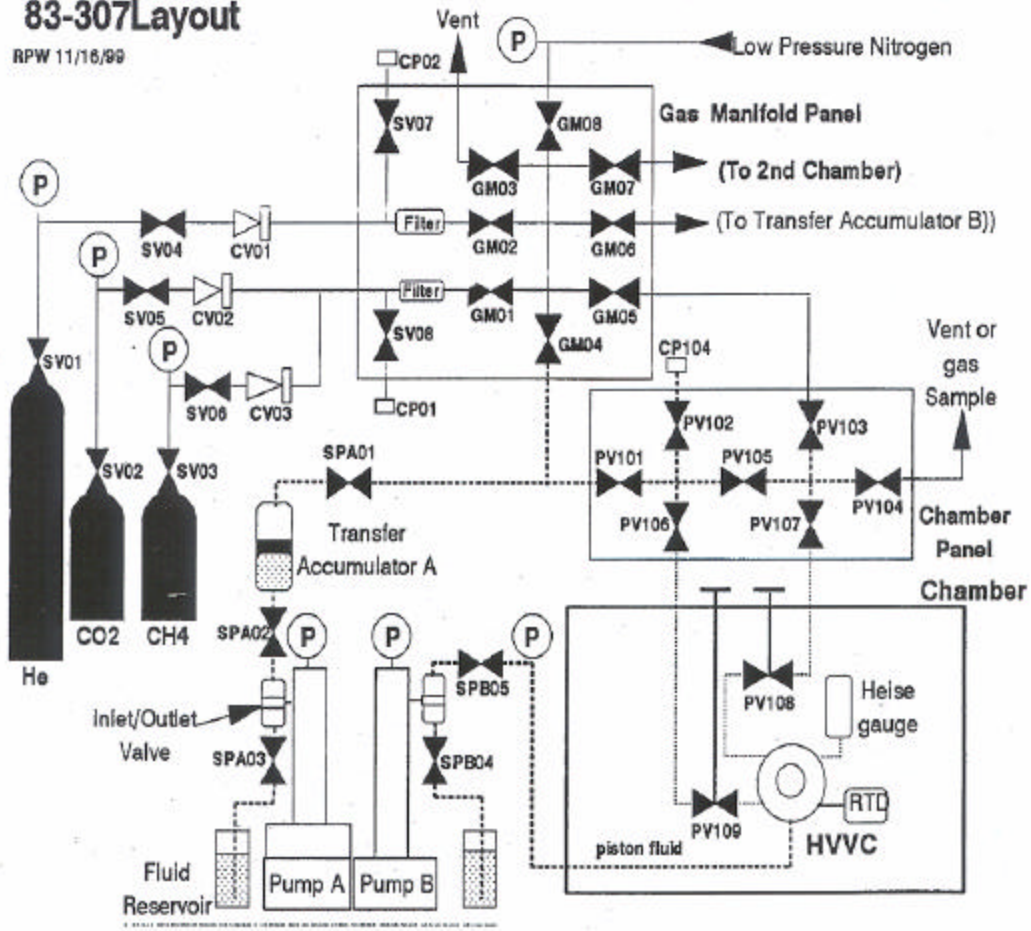


Figure 4 Schematic of Equipment

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 $\pm 2\%$. 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 ($\pm 0.5\text{K}$). 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.

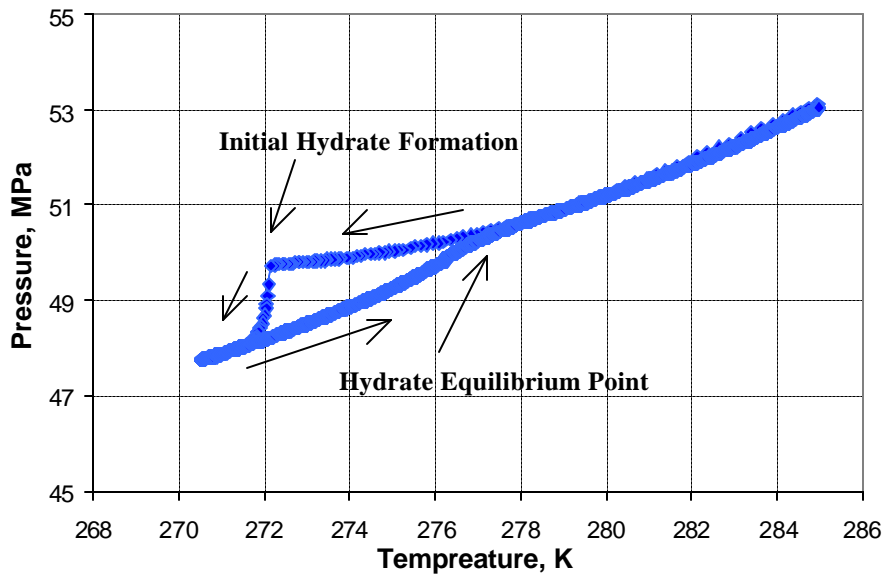


Figure 5 Pressure vs. Temperature history of an experiment in which hydrates were formed and decomposed in a single-phase solution of dissolved CO₂ in water. The trace was preceded as indicated in light arrows.

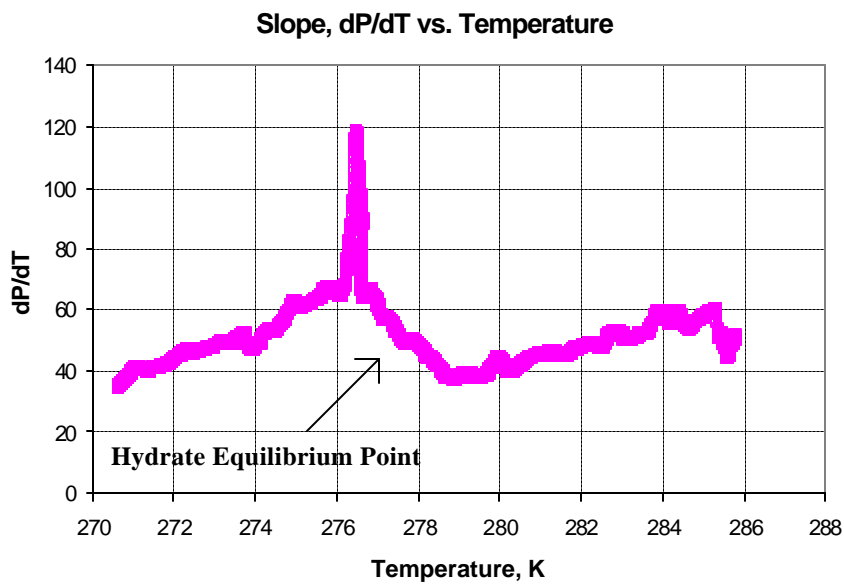


Figure 6 dP/dT vs. Temperature for dissociation of CO_2 hydrate in a single-phase solution

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):

$$\Delta m_H = -RT \sum_{j, cavities} n_j \ln \left(1 - \sum_i q_{ji} \right) \quad (1)$$

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

$$q_{ji} = \frac{C_{ji} f_i}{1 + \sum_i C_{ji} f_i} \quad (2)$$

Where, C_{ji} is the Langmuir constant for species i in cavity j; f_i is the fugacity for the hydrate forming species; θ_{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):

$$\frac{\Delta \mathbf{m}_L}{RT} = \frac{\Delta \mathbf{m}^0}{RT_o} - \int_{T_o}^{T_f} \frac{\Delta h}{RT^2} dT + \int_0^P \frac{\Delta V}{RT} dP - \ln x_w \quad (3)$$

The terms Δh and ΔV 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 $\Delta \mathbf{m}_L(T, P = 0)$, 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:

$$- \sum_{j, \text{cavities}} \mathbf{n}_j \ln \left(1 - \sum_i \mathbf{q}_{ji} \right) = \frac{\Delta \mathbf{m}_L}{RT}(T, P = 0) + \int_0^P \frac{\Delta V}{RT} dP \quad (4)$$

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

$$- \sum_{j, \text{cavities}} \mathbf{n}_j \ln \left(1 - \sum_i \mathbf{q}_{ji}^{VLH} \right) = \frac{\Delta \mathbf{m}_L}{RT}(T, P = 0) + \int_0^{P^{VLH}} \frac{\Delta V}{RT} dP \quad (5)$$

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

$$- \sum_{j, \text{cavities}} \mathbf{n}_j \ln \left(\frac{1 - \sum_i \mathbf{q}_{ji}}{1 - \sum_i \mathbf{q}_{ji}^{VLH}} \right) = \int_{P^{VLH}}^P \frac{\Delta V}{RT} dP \quad (6)$$

Since for single hydrate species,

$$\frac{1 - \mathbf{q}_{ji}}{1 - \mathbf{q}_{ji}^{VLH}} = \frac{1 + C_{ji} f_{ji}^{VLH}}{1 + C_{ji} f_i}$$

The following equation is obtained:

$$\sum_j n_j \ln \left[\frac{\frac{1}{C_{ji} f_i^{VLH}} + \frac{f_i^{sat}}{f_i^{VLH}} \exp \left(\frac{\bar{V}_i (P - P^{sat})}{RT} \right)}{\frac{1}{C_{ji} f_i^{VLH}} + 1} \right] = \frac{\Delta V (P - P^{VLH})}{RT} \quad (7)$$

Where, P^{sat} and f^{sat} are the pressure and corresponding fugacity of the CO₂, which are required to dissolve the experimental levels of CO₂ in the water phase of the given temperature. We use the experimental solubility of CO₂ in water (Kirk-Othmer, 1993) to obtain these values. The exponential term is the Poynting correction (J. M. Prausnitz, 1969) to f^{sat} , giving the fugacity at pressure P. \bar{V}_i is the partial molar volume of CO₂ 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:

$$\text{In some case, } C_{ji} > 9, \quad C_{ji} f_i \gg 1. \quad \frac{f_i^{sat}}{f_i^{VLH}} \approx \frac{P^{sat}}{P^{VLH}}$$

Then, the following equation is obtained:

$$\sum_j n_j \ln \left[\frac{P^{sat}}{P^{VLH}} \exp \left(\frac{\bar{V}_i (P - P^{sat})}{RT} \right) \right] = \frac{\Delta V (P - P^{VLH})}{RT} \quad (8)$$

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.

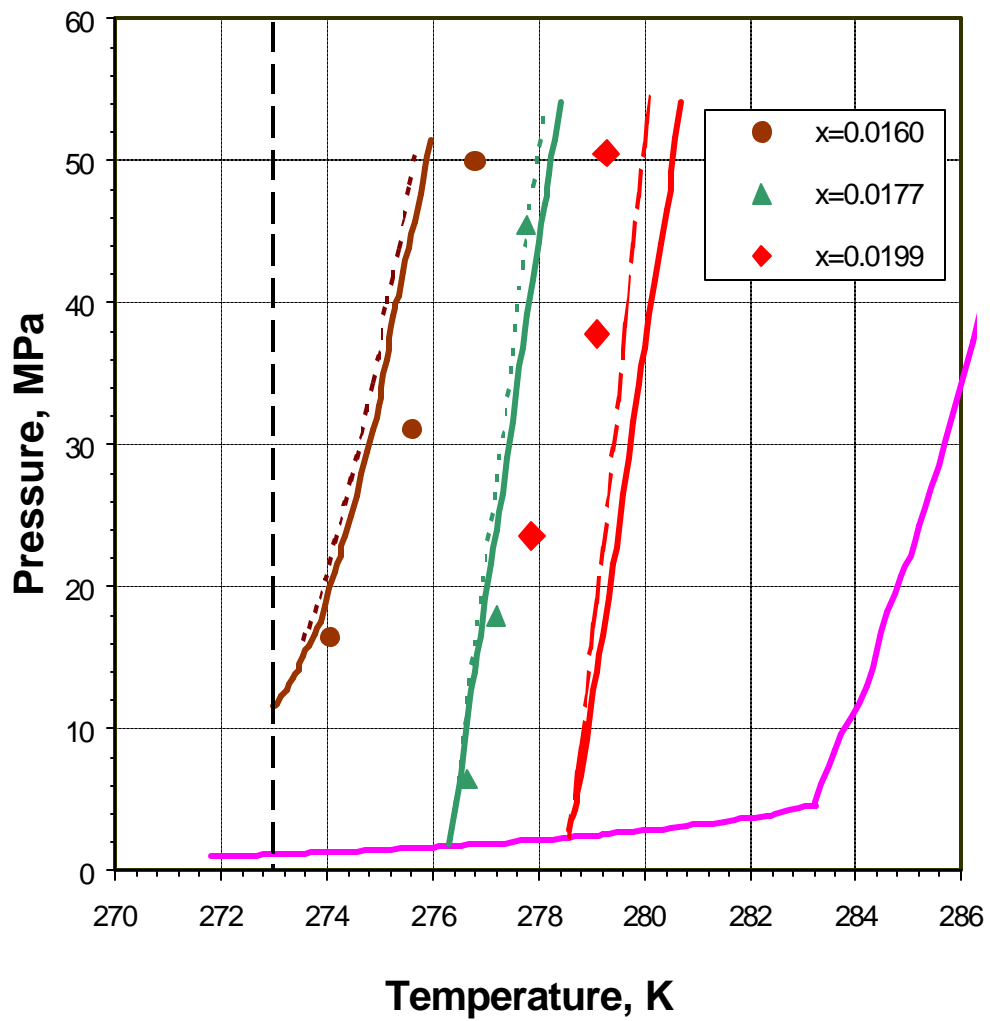


Figure 7 Comparison of Experimental and Predicted data by using modified models

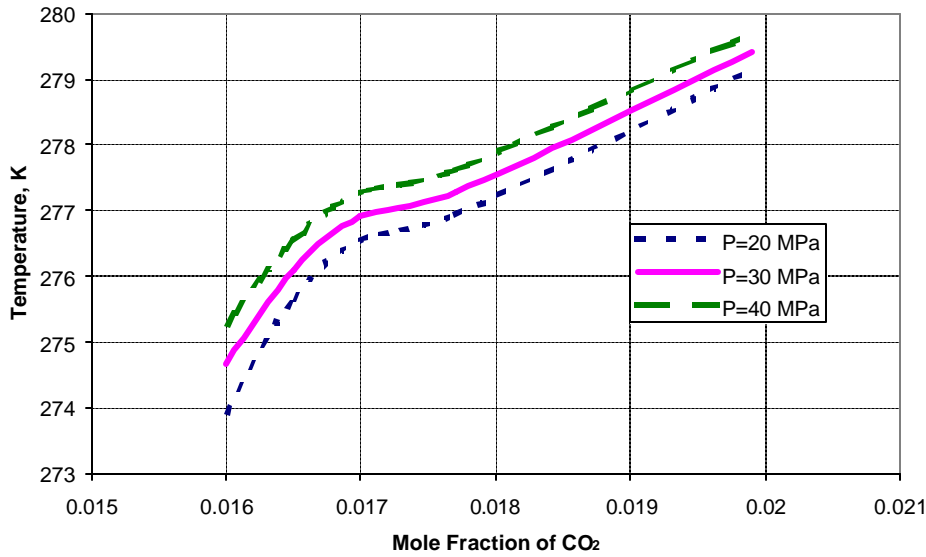


Figure 8 Hydrate equilibrium temperature vs. Mole fraction of CO₂ at constant pressure

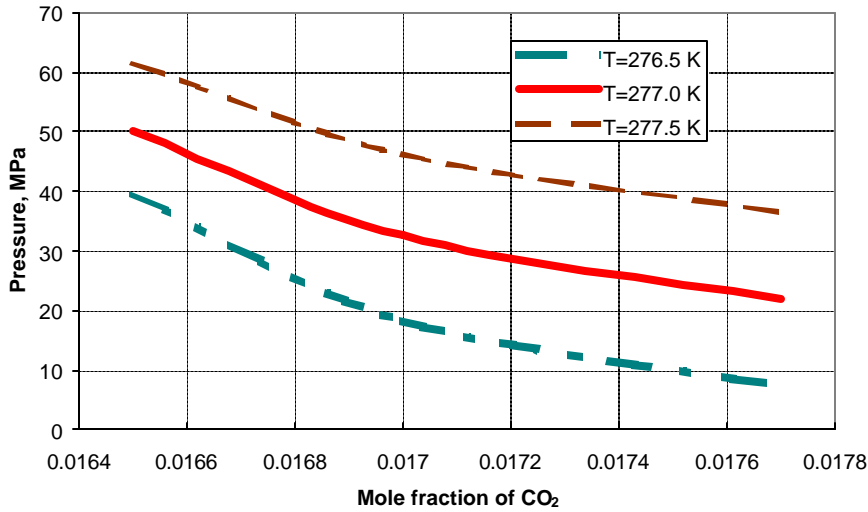


Figure 9 Pressure vs. Mole fraction of CO₂ at constant Temperature

From Figure 8 and 9, it is very clear that for a given CO₂ 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 CO₂, 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 CO₂; 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

X	P (MPa)	T _{exp} (K)	T _{sim} (K)	T _{exa} (K)
0.0199	50.58	279.3	280.0	280.6
	37.87	279.1	279.6	280.1
	23.58	277.9	279.2	279.6
0.0177	45.26	277.8	277.8	278.0
	18.00	277.2	277.1	277.1
	6.65	276.5	276.6	276.6
0.0160	50.01	276.8	275.7	275.8
	31.14	275.6	274.6	274.7
	16.47	274.0	273.6	273.7

5.0 SUMMARY AND CONCLUSIONS

Formation of CO₂ 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 CO₂. 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

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C *****
C
C CALCULATION OF HYDRATE PHASE EQUILIBRIA.
C *****
C THIS PROGRAM CALCULATES PCALC WHEN TENURED PEXP.
C LANGMUIR COEFFICIENTS ARE CALCULATED BY USING
C Q* CORRELATION METHOD.
C
C
C 25 GASES ARE INCORPORATED INTO THE PROGRAM.
C MIXTURES OF UP TO 10 COMPONENTS CAN BE STUDIED.
C
C *****      COMMON STATEMENTS      *****
C
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), C1RKL(10)
DIMENSION C3FREF(10), C4FREF(10), C1FREF(10), C2RKL(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), PSAT(3,100), XY(100)
COMMON /AMOL/MA, ISCODE(10)
COMMON/TEXPT/PEXP(100), X(15,100), 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 SH, DDU, DDH, BETA1, GAMMA
COMMON/VDO/SIGH1, SIGH2
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
C *****
C
C ***** READ IN EACH COMPONENT *****
C

```


C ** 7=AMMONIA
C ** 8=ETHYLENE GLYCOL
C ** 9=DIETHYLENE GLYCOL
C ** 10=TRIETHYLENE GLYCOL
C
C
C
C
C
C
C FOLLOWING DATA IS READ FROM FILE FOR12.DAT:
C 1>ISOLVE=SELECT EQ. OF STATE: 1=PENG ROB. 2=RED. KWONG
C 2>ISTR=PRINT STRUCTURE DATA: 1=YES, 2=NO
C 3>ILANG=PRINT LANGMUIR CONSTS.: 1=YES, 2=NO
C 4>IN=PRINT SWITCH: 1=PRINT COMP. LIST 2=NO COMP LIST
C 5>NSETS=NUMBER OF ON LINE DATA SETS TO RUN
C =0 IF USES ENTERS HIS OWN EXPT. OR GUESSED DATA
C 6>I WATER= SWITCH FOR WATER CONTENT CALC FOR 2 & 3 PHASE SYS
C = 0 : DONT PERFORM CALCULATIONS
C = 1 : CALCULATE YH2O GIVEN P
C = 2 : CALCULATE YH2O AND COMPARE WITH EXPMTL DATA
C 7>IPOS=COMPONENT POSITION OF WATER I.E. 1,2,OR 3 ...
C 8>NVLLH=SWITCH FOR QUADRUPLE POINT CALCULATION
C =0 :DONT PERFORM QUAD POINT CALCULATIONS
C =1 :CALCULATE QUADRUPLE POINT. IF NVLLH IS 1 THEN
C NSTRUC SHOULD NOT BE ZERO.
C 9>NSTRUC=SWITCH FOR CHECKING THE PRESENCE OF 'V L H1 H2' QUAD POINTS
C =1 :ONLY ONE HYDRATE STRUCTURE IS FORMED AND IS THE ONE
C GIVEN IN DATA.
C =2 :CHECK FOR 'V L H1 H2' QUAD POINTS
C 10>IMPURE=SWITCH FOR CALCULATIONS IN THE PRESENCE IMPURITIES
C =0 :NO IMPURITIES IN WATER
C =1 :IMPURITIES ARE PRESENT (SEE IMPURITY CODES)
C 11>ISEQ=SWITCH FOR CALCULATING EQUILIBRIUM CURVE BETWEEN TEMPERATURES
C T1(I) AND T2(I) AT INTERVALS OF DT(I)
C =0 :NO SEQUENTIAL CALCULATIONS
C =1 :SEQUENTIAL CALCULATIONS UPTO TEMPERATURE T2(I)
C =2 :SEQUENTIAL CALCULATIONS UPTO THE QUADRUPLE POINT(VLLH)
C 12>LIQ=SWITCH FOR CALCULATING L1 L2 H EQUILIBRIA ONLY
C =0 :GAS COMPOSITION IS GIVEN
C =1 :LIQUID COMPOSITION IS GIVEN
C 13>IDH=SWITCH FOR CALCULATING HEAT OF DISSOCIATION
C =0 NO CALCULATIONS PERFORMED
C =1 HEAT OF DISSOCIATION IS CALCULATED
C
C 14>MA=NUMBER OF COMPONENTS
C 15>KK(I)=CODE OF EACH COMPONENT
C 16>N=NUMBER OF DATA POINTS
C 17>EXPERIMENTAL HYDRATE CONDITIONS SUCH AS
C P/PSIA,T/DEG.R,Y(I),I=1,MA
C
C * * READ IN OPTION SWITCHES * *
C
C OPEN(12,FILE='TAPE12.DAT',STATUS='OLD')
C OPEN(06,FILE='HYDOUT.DAT',STATUS='UNKNOWN')
C READ(12,104)AQ
C READ(12,200)ISOLVE,ISTR,ILANG,IN
C 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
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
C
C

```

```

57     IMOVE=ILEN(ICASE(1))
C
C     * * MOVE THROUGH FOR12.DAT AND GET DESIRED DATA * *
C
      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
C
65     DO 53 I=1,IMOVE
      READ(12,104)AQ
104    FORMAT(A4)
      53    CONTINUE
      54    IMOVE=1000
C
C
      READ(12,202) MA
C
C     ** 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
C
C     ** CHECK FOR PRESENCE OF CO2 WITH INHIBITOR **
C
      DO 1060 JJ=1,MA
      IF(KK(JJ).EQ.15)JJ1=JJ
1060   CONTINUE
C     *****      READ IN NUMBER OF DATA POINTS      *****
C
186    READ(12,305) N
      NPT=N
C
C     CHECK FOR HEAT OF DISSOCIATION CALCULATIONS
C
      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),
1      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)
341 CONTINUE
GO TO 12
327 CONTINUE
C CHECK FOR WATER CALCULATION
IF(IWATER.EQ.0.OR.IWATER.EQ.1)GO TO 67
C
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
C
C 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)
C
C ** CHECK FOR PRESENCE OF CO2 WITH IMPURITY **
C
C 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
C ** CHECK WHETHER SEQUENTIAL CALCULATION IS REQUIRED **
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
C
12 CONTINUE
C
C ***** WRITE OUT ALL INPUT DATA *****
DO 978 I=1,MA
C
WRITE(06,310) I,YNAME(KK(I))
978 CONTINUE
IF(IMPURE.EQ.1)WRITE(6,344)YNAMEIM(IMCODE)
IF(IFLAG.NE.0)GO TO 58
WRITE(06,105)(YCOMP(I),I=1,MA)
GO TO 59
58 IF(LIQ.EQ.0)WRITE(06,101)(YCOMP(I),I=1,MA)
IF(LIQ.EQ.1)WRITE(06,101)(YNAMEL(I),I=1,MA)

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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
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
C  983  CONTINUE
C
C
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,I1,6X,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,I1,4X,10(F7.4,1X))
103  FORMAT(4X,'PSIA',7X,'DEG.R',/,100('-'),//)
105  FORMAT(100('-'),/,6X,'INPUT HYDRATE DATA

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```

A WITH INITIAL PRESSURE GUESSED',
B/,100('-'),/, 'PRESSURE', 3X, 'TEMPERATURE',
C2X, 'STRUCTURE', 10(8X,A5))
200  FORMAT(5(I1,1X))
202  FORMAT(I2)
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('*'),
*   1X,'18 = HYDROGEN SULFIDE',/,20X,5('*'),1X,'19 = XENON',/,20X,
*   5('*'),1X,'20 = ARGON',/,20X,5('*'),1X,'21 = KRYPTON',/,
*   20X,5('*'),1X,'22 = SULFUR HEXAFLOURIDE',/,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(I2)
306  FORMAT(10X,5(2X,E12.5),/,10X,5(2X,E12.5),/,10X,5(2X,E12.5),/
1   ,10X,5(2X,E12.5))
307  FORMAT(10X,6(2X,E12.5),/,10X,6(2X,E12.5),/,10X,6(2X,E12.5),/,
1   10X,6(2X,E12.5),/,12X,E12.5)
308  FORMAT(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)
GO TO 1000
1003  WRITE(6,823)
GO TO 1000
1004  WRITE(6,833)
GO TO 1000
1005  WRITE(6,843)
GO TO 1000
1006  WRITE(6,853)
*1000  END
1000  stop
end
C
C

```

```

C
C
C *****
C      SUBROUTINE FUN(NN,XX,FF)
C *****
C
C      THIS PROGRAM CALCULATES THE DIFFERENCES BETWEEN
C      EXPERIMENTAL AND THEORETICAL HYDRATE FORMING
C      CONDITIONS. THE CALCULATED HYDRATE FORMING CONDITIONS
C      DEPEND UPON THE CHOICE OF KIHARA PARAMETERS
C      , SIGMA AND EPSILON, FOR THE VARIOUS COMPONENTS IN
C      THE GAS PHASE.
C
C
C      HYDRATE PHYSICAL PROPERTIES ARE ASSIGNED. SUBROUTINE DATA
C      IS CALLED TO READ GAS PROPERTIES. SUBROUTINE HYDRAT IS
C      CALLED TO CALCULATE HYDRATE FORMING CONDITIONS OR SUB-
C      ROUTINE QUAD IS CALLED FOR QUADRUPLE POINT CALCULATIONS
C      OR FOR SEQUENTIAL CALCULATIONS.
C
C
C ***** COMMON STATEMENTS *****
C      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C      DIMENSION ICODE(10)
C      DIMENSION KK(10),XA(11)
C      DIMENSION XX(13),PCALC(100),SS(100),AXC(10,2),Y(10)
C      DIMENSION ERROR(100)
C      DIMENSION A(10),SIGMA(10),EPS(10)
C      DIMENSION Y3(100)
C      DIMENSION ERR(100),SW(100)
C      DIMENSION XL(10)
C      DIMENSION NCODE(10)
C      DIMENSION GAMMA1(2)
C      DIMENSION ZZV(100)
C      COMMON/BKSB/NPT,NSETS,IFLAG
C      COMMON/STAT/SS
C      COMMON/NC/NCODE,NCOMP
C      COMMON/AMOL/MA,ISCODE(10)
C      COMMON/FUND/SIGMA,EPS,A
C      COMMON/TEXPT/PEXP(100),X(15,100),IS(100),T(100),YEXP(100)
C      COMMON/SERDAT/T1(100),DT(100),T2(100)
C      COMMON/DHDATA/DU(2),DH(2)
C      COMMON/AZ/KK,N,MK
C      COMMON/JK/JCHK
C      COMMON/BEGA/BETA1,GAMMA1
C      COMMON/COR/EP SH,DDU,DDH,BETA,GAMMA
C      COMMON/VDO/SIGH1,SIGH2
C      COMMON/BKSC/IWATER,IPOS,ISTR,IDH
C      COMMON/HO/YH3
C      COMMON/X/XL
C      COMMON/PHAS/NVLLH
C      COMMON/STRUC/NSTRUC
C      COMMON/IMP/IMPURE,IMCODE,XIMP(100),YCO2(100)
C      COMMON/SOLUT/XSOLU,ACTIV,YYYCO2
C      COMMON/TBLOC/ITAG
C      COMMON/SEQ/ISEQ,TMIN,DELT,TMAX,TQL
C      COMMON/LIQUID/LIQ

```



```

COMMON/ZV/ZV
COMMON/HEAT/DDELH(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(NSTRUC.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)

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```

          EPS(I)=(EPS(I)*EPSH)**0.5
          SIGMA(I)=0.5*(SIGMA(I)+SIGH1)
901      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)
846      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)
9        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
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)

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```

DO 952 K=1,N
WRITE(6,953)T(K),PCALC(K)
952 CONTINUE
962 CONTINUE
C
C * * FORMAT STATEMENTS * *
C
778 FORMAT(///20X,'CALCULATED RESULTS'//1X,'TEMPERATURE',3X,
1 'PRESSURE',4X,'DELTA 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,'STRUC',5X,'LIQUID COMP
1 OSITION'/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,'STRUC',5X,'VAPOR COMP
1 OSITION'/6X,'(K)',7X,'(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)',6X,':',7X,'(K)',8X,'(KPA)',8X,'X1',7X,'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('-'),/)
951 FORMAT(///,20X,'CALCULATED RESULTS',/,20X,
A 10('-'),1X,7('-'),//,21X,'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(///20X,'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)',
A9X,'(KPA)',9X,'H2O',14X,':',6X,'(KPA)',10X,'H2O'/)
104 FORMAT(///20X,'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'
A/7X,'(K)',7X,'(KPA)',9X,'H2O',15X,'H2O',16X,':',5X,'(KPA)',
A11X,'H2O'/)
960 RETURN
END
C
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'

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C      AND BUBBLE POINT CURVE TO GET 'V L1 L2 H';
C      AND 'V L1 H1' AND 'V L1 H2'
C      CURVES TO GET THE 'V L1 H1 H2' POINT.
C
C      THIS SUBROUTINE IS ALSO CALLED FOR SEQUENTIAL CALCULATIONS
C      AT SPECIFIC INTERVALS.
C
C      IST0=STRUCTURE AT STARTING TEMP T0
C      IST2=STRUCTURE BEYOND THE QUAD POINT
C      ID=VARIABLE INDICATING WHETHER VLH1H2 QUAD POINT HAS BEEN
C      CALCULATED. 0--NOT CALCULATED; 1--CALCULATED.
C      ITAG=VARIABLE INDICATING WHICH FUGACITY COEFFICIENTS ARE
C      REQUIRED FROM SUBROUTINE PHIMIX. 0--ONLY VAPOR
C      1--VAPOR AND LIQ; 2--LIQUID ONLY.
C
C      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C      DIMENSION Y(15),XL(10)
C      DIMENSION PH(2),PRESS(2),ISCHEC(2),PBD(2),TQ(60),PQ(60)
C      DIMENSION PLP2(60)
C      DIMENSION PLP1(60)
C      DIMENSION NCODE(10)
C      COMMON/STRUC/NSTRUC
C      COMMON/PHAS/NVLLH
C      COMMON/X/XL
C      COMMON/NC/NCODE,NCOMP
C      COMMON/TBLOC/ITAG
C      COMMON/SEQ/ISEQ,TMIN,DELT,TMAX,TQL
C      COMMON/LIQUID/LIQ
C      COMMON/CRITCL/NCRIT,TCRIT
C      COMMON/HEAT/DDELH(100),DELH
C      COMMON/BKSC/IWATER,IPOS,ISTR,IDH
C      COMMON/ZV/ZV
C      COMMON/HELP/IST0,IST2,ISLOW,N0,NQ
C      DOUBLE PRECISION YNEW(100)
C
C
C      T0=T
C      ITER=0
C      DTQ=1.0
C      DTH=1.0
C      N0=1
C      AXC=0
C      NQ=N0
C      ID=0
C      IDEW=0
C      M=1
C      IF(NVLLH.NE.0)GO TO 107
C
C      IF NVLLH IS ZERO THEN NO QUAD POINTS ARE REQUIRED BUT THIS
C      SUBROUTINE HAS BEEN CALLED FOR SEQUENTIAL CALCULATIONS.
C
C      THH=TMAX+2.*DELT
C      TQL=TMAX+2.*DELT
C      IF(LIQ.EQ.1)TQL=TMIN-2*DELT
C      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.N0)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((NSTRUC.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(NSTRUC.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)

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      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(NSTRUC.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)

```

```

257     CONTINUE
        IF(NSTRUC.EQ.2)IS=IST0
C
C     ** CHECK FOR HEAT OF DISSOCIATION CALCULATIONS **
C
        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
14     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.THH)IS=IST2
        IF(NSTRUC.EQ.2.AND.T.LT.THH.AND.(T+DELT).GT.THH)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.TQL.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))
C
        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)

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120   T=T0
      GO TO 800
151   WRITE(6,100)
      GO TO 800
152   TQL=TQL/1.8
      PQL=PQL*6.8948
      WRITE(6,154)TQL,PQL
      GO TO 800
853   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)

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C          *****
C          PROGRAM FOR CALCULATION OF THE DISSOCIATION PRESSURES
C          OF GAS HYDRATES FROM METHANE, ETHANE, AND PROPANE
C          BY JERRY HOLDER, CHEMICAL ENGINEERING U. MICH.
C
C          THE DISSOCIATION PRESSURE IS THAT PRESSURE AT WHICH
C          THE CHEMICAL POTENTIAL OF WATER IN THE HYDRATE IS
C          EXACTLY EQUAL TO THE CHEMICAL POTENTIAL OF THE WATER
C          IN THE WATER PHASE.  THE CHEMICAL POTENTIAL OF THE
C          HYDRATED WATER IS CALCULATED USING THE THEORY DEVELOPED
C          BY VAN DER WAALS WHICH ASSUMES 1) THERE IS ONE MOLECULE
C          OF GAS PER HYDRATE CAVITY, 2) ONLY THE TRANSLATIONAL
C          PARTITION FUNCTION IS AFFECTED IN THE ENCAGED STATE
C          3) ONLY FIRST NEIGHBOR INTERACTIONS ARE IMPORTANT.
C          THE KIHARA POTENTIAL MODEL IS USED.
C
C          THE UPDATED Q* VERSION INCLUDES 2ND AND 3RD SHELL
C          CONTRIBUTIONS AND SHELL ASPHERICITY.
C
C          THIS SUBROUTINE ALSO CALCULATES WATER CONTENT AND
C          HEAT OF DISSOCIATION.
C
C          *** LIST OF VARIABLES ***
C
C          AR, BR, CR - CONSTANTS FOR CALCULATING THE DISSOCIATION
C                     PRESSURE OF THE REFERENCE HYDRATE. THESE ARE
C                     FROM FITTED DATA.
C          C          - THE SO CALLED LANGMUIR ADSORPTION CONSTANTS
C                     WHICH SPECIFY THE RELATIVE AMOUNT OF GAS IN
C                     A GIVEN TYPE OF CAVITY. SUBSCRIPTS I,J REFER
C
C          DH          - DIFFERENCE IN ENTHALPY BETWEEN THE OCCUPIED AND
C                     UNOCCUPIED HYDRATE.
C          DU          - DIFFERENCE IN CHEM. POTENTIAL (AS DH)
C          DV          - DIFFERENCE IN MOLAR VOLUME
C          P0          - DISSOCIATION PRESSURE OF REFERENCE HYDRATE
C                     AT 273 DEG K
C          PR          - DISSOCIATION PRESSURE OF REF. HYD. AT T
C          T           -TEMPERATURE( DEG K)
C                     (NOTE THAT T IS CHANGED FROM R TO K )
C          VM          - NUMBER OF MOLECULES OF WATER PER CAVITY
C          VY(I,J)     - FRACTION OF CAVITIES I OCCUPIED BY MOLECULE J
C          XU(I)       - MOLE FRACTION OF GAS I IN THE GAS PHASE
C          ZMU,ZMOLD, ETC. - CHEMICAL POTENTIAL DIFFERENCES.
C
C          *****      COMMON STATEMENTS      *****
C
C          IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C          external psat
C          DIMENSION KK(10)
C          DIMENSION XX(13)
C          DIMENSION XL(10),PHIL(10)
C          DIMENSION XU(10),PHI(10),XS(10),VY(10,2),VM(2),
2 C(10,2),NCODE(10),SCC(2)
C          DIMENSION XXMAX(10),XXMIN(10),B2(10)
C          DIMENSION XW(10)

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```

PSAVE=P
P=P/14.696
IF( IS.EQ.1) GO TO 11
C
C   *** DATA FOR STRUCTURE II
C
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
C
C   *** DATA FOR STRUCTURE I ***
C
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
C
C   *** LANGMUIR CONSTANTS
C
12  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
C
C   AT ZERO DEGREES CENTIGRADE
C
    ZMUTPR=DU/273.15
    ZMOLD=ZMUTPR
    AH=2616.398+DH
    TO=273.15
C
C   *** ENTHALPIC CHANGE OF CHEMICAL POTENTIAL WITH
C   TEMPERATURE (WATER PHASE)
C
C ***** ALPHA, BETA, AND GAMMA ARE PARAMETERS *****
C ***** 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

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      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.
C      ZM=HINT+ZMOLD
C      ZMUTPR=T*ZM
C      We know that ZMUTPR is the liquid phase chemical potential
C      Instead of having the program calculate the pressure point where
C      the liquid phase chemical potential and the hydrate phase chemical
C      potentials intersect, we need to calculate the plain hydrate and
C      liquid potential. We also need to print out ZMUPTR since it is
C      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
C      P1=1
C      P2=2
C      DO 30 JJ=1,2000
C      DMU1=0.0
C      DMU2=0.0
C      DO 28 JJJ=1,2
C      P=P1
C      P3=P
C      IF (P.GT.PSATD) P3=PSATD
C      IF(JJJ.EQ.2) P=P2
C      *** GET THE FUGACITY COEFFICIENTS( PHI IS RETURNED)
C
C
C      CALL PHIMIX(XU,14.696*P3,1.8*T,PHI)
C      IF(NCRIT.EQ.1)GO TO 821
C      IF(ITAG.NE.2)GO TO 481
C      DO 44 LI=1,NCOMP
C      PHI(LI)=PHIL(LI)
C 44  CONTINUE
C      X1=0.0
C      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)

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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)*P3*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)ZMUPT
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   ZMUA1=ZMUA-1.987*T*DLOG(1.0-X1)
C 147 DMU1=DMU2
C   DMU2=DMU
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.).LT..001.AND.ABS(DMU).LT.1.) GO TO 35
IF(ABS(DMU).LT..0005) GO TO 35
28 CONTINUE
IF(ABS((P1-P2)/P2).LT.1.E-5) P2= P2+1.0
IF(ABS(DMU2-DMU1).LT. .001) GO TO 29
P3=P1-(P2-P1)/(DMU2-DMU1)*DMU1
IF(P3.LE.0.0) P3=0.01
IF(P3.GT.2.E4) P3=2.E4
C   P1=P3
C 29 P3=P1+3
29 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)TTO
      WRITE(6,8885)ACTIV
      WRITE(6,8886)ZMU
      WRITE(6,8887)ZMUA
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)
C 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
C      ** HEAT OF DISSOCIATION CALCULATIONS **
C
      JACKQ=JACKQ+1
      IF(JACKQ.EQ.2) 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./(VVY(1)*2.+VVY(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) VVY(1)
C WRITE(6,7783) VVY(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
DO 144 J=1,NCOMP
XHYD(J)=(VY(NCODE(J),1)*VM(1)+VY(NCODE(J),2)*VM(2))/COMSUM
144 CONTINUE
C WRITE(7,1020)T,(VY(NCODE(J),1),VY(NCODE(J),2),J=1,MA)
1020 FORMAT(' T (K)',4X,'HYDRATE COMPOSITION'/9X,'XH1 XH2'/
1F6.2,4X,10(F6.4))
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
C WRITE(06,1008)PHI(I),(C(I,J),J=1,2)
C1008 FORMAT(5X,1F,10X,2F)
158 CONTINUE
C

```

```

C      * * CALCULATIONS TO DETERMINE THE WATER CONTENT OF A GAS * *
C      * * IN EQUILIBRIUM WITH THE HYDRATE * *
C      * * TEMP(R) AND PRESSURE(PSIA) * *
C      * * IWATER = 0 : DONT PERFORM CALCULATIONS * *
C      * * IWATER = 1 : CALCULATE YH2O
C      * * IWATER = 2 : CALCULATE YH2O AND COMPARE WITH EXPMTL DATA * *
C      * * * *
C
C      IF(IWATER.EQ.0)GO TO 821
C
C      * * PH=3-PHASE PRESSURE * *
C      * * P =2-PHASE PRESSURE * *
C
C
C      PH=P
C      P=PSAVE
C      PSW=PSAT(T)
C      IF(IS.EQ.1)VHYD=22.6
C      IF(IS.EQ.2)VHYD=22.9
C      IF(T.LT.491.67)VH2O=19.6
C      IF(T.GE.491.67)VH2O=18.0
C      FWSAT=PSW*(1-X1)*EXP(0.0014926491/T*VH2O*(PH-PSW))
C      FWSATP=FWSAT*EXP(0.0014926491/T*VHYD*(P-PH))
C      CALL PHIMIX(XU,P,T,PHI)
C      T=T/1.8
C      P=P/14.696
C      ZWAT=0.0
C      DO 127 I=1,2
C      CCC=0.0
C      DO 126 II=1,NCOMP
C      CCC=CCC+C(II,I)*XU(II)*PHI(II)*P
126    CONTINUE
C      ZW=VM(I)*DLOG(1+CCC)
127    ZWAT=ZWAT+ZW
C
C      DO 23 I=1,NCOMP
C      XUSTOR(I)=XU(I)
23    CONTINUE
C      ICOUN=1
C      COUNT=1
C      MA=MA+1
C      NCOMP=NCOMP+1
C      IPOS=MA
C      NW=1
C      PHI(IPOS)=1.0
C      PHIX=1.0
C**
C      IF(14.696*P.GT.PH)GO TO 618
C      GO TO 835
C
C      ** 2-PHASE WATER CONTENT CALCULATION **
618    ZMUP=0.0
C      GO TO 85
85    FWP=FWSATP*DEXP(ZMU/(1.987*T)-ZWAT)
C
C      * * CALCULATE A TEST VALUE OF YH2O * *
C      T=1.8*T

```



```

      P=14.696*P
C
815      YH20N=FWP/(PHI(IPOS)*P)
      IF(YH20.GT.0.05.OR.YH20.LT.0.0)GO TO 800
      GO TO 801
800      WRITE(6,803)ICOUN,YH20
      YH20=0.05
C
C
C
801      XU(IPOS)=YH20N
      CALL NORMW(NCOMP,IPOS,XU)
      YH20=YH20N
807      CALL PHIMIX(XU,P,T,PHI)
      YH20N=FWP/(PHI(IPOS)*P)
      ICOUN=ICOUN+1
      IF(ABS((YH20N-YH20)/YH20N).GT.1.E-3.AND.ICOUN.LT.30)GO TO 801
      XU(IPOS)=YH20N
C
C ** 3-PHASE WATER CONTENT CALCULATION **
835      DO 825 I=1,MA
      XW(I)=XU(I)
825      CONTINUE
809      YH3=FWSAT/(PHIX*PH)
      IF(ABS(YH3-XW(IPOS)).LT.1.E-7)GO TO 819
      XW(IPOS)=YH3
      CALL NORMW(NCOMP,IPOS,XW)
      CALL PHIMIX(XW,PH,T,PHI)
      COUNT=COUNT+1
      IF(COUNT.GT.30)GO TO 818
      PHIX=PHI(IPOS)
      GO TO 809
818      WRITE(6,828)
819      P2P=P*6.8948
      PH3P=PH*6.8948
      TK=T/1.8
      IF(ICOUN.GE.30)WRITE(6,810)
      IF(P.GT.PH)GO TO 845
      WRITE(6,823)
      GO TO 812
845      IF(IWATER.EQ.2)GO TO 812
      WRITE(6,811)TK,P2P,XU(IPOS),PH3P,YH3
C
812      P=PH
      NCOMP=NCOMP-1
      MA=MA-1
      NW=0
821      RETURN
C      * * FORMAT STATEMENTS * *
C
828      FORMAT(' 3 PHASE WATER CALCULATIONS NOT CONVERGED')
803      FORMAT('0',T20,'* * YH20 DEFAULTS TO A VALUE OF 0.05 ON'
A , ' ITERATION# ',I2, / ,1X,T20,'* * FROM A PREVIOUS'
B , ' VALUE OF YH20 = ',E10.3)
810      FORMAT('0',T20,'* * WATER CONTENT EQUILIBRIUM
C CALCULATIONS HAVE NOT CONVERGED * * ')
811      FORMAT(5X,F7.3,2X,F9.3,2X,F15.9,8X,': ',3X,F9.3,2X,F15.9)

```

```

351  FORMAT(/,18X,'CODE #',5X,'A(I)',8X,'SIGMA(I)',8X,'EPS(I)',/)
352  FORMAT(5X,I5,3F10.3)
823  FORMAT(5X,' PRESSURE IS NOT IN 2 PHASE REGION')
C
END
C
C
C
C *****
SUBROUTINE NORMW(NCOMP,IPOS,XU)
C *****
C * * THIS SUBROUTINE NORMALIZES THE VECTOR XU * *
C * * WITHOUT CHANGING THE VALUE OF XU(IPOS) * *
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION XU(10)
COMMON/STOR/XUSTOR(10)
C
SUM=1.0-XU(IPOS)
DO 1 I=1,NCOMP
IF(I.EQ.IPOS)GO TO 1
XU(I)=XUSTOR(I)*SUM
1 CONTINUE
C
RETURN
END
C
C *****
DOUBLE PRECISION FUNCTION PSAT(TR)
C *****
C * * FUNCTION TO CALCULATE THE SATURATION PRESSURE OF * *
C * * WATER USING THE CORRELATION DEVELOPED BY KEENAN * *
C * * KEYES AND MOORE P(PSIA), T(R) * *
C * * A CORRELATION TO CALCULATE THE VAPOR PRESSURE * *
C * * FOR ICE WAS ALSO USED BASED ON THE DATA FROM * *
C * * PERRY'S 5'TH ED. 3-205 * *
C *****
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION F(8),A1(7),B1(7),TREF(8)
C
DATA F/-741.9242,-29.721,-11.55286,-0.8685635,
A0.1094098,0.439993,0.2520658,0.05218684/
C
DATA A1/1.110788E-11,4.813026E-12,1.053791E-12,
A6.92593447E-14,2.289828E-15,4.697288E-18,4.261011E-22/
C
DATA B1/0.046341356,0.048066983,0.0512724161,
A0.0572912243,0.06528872,0.08110062,0.108179821/
C
DATA TREF/492.0,484.0,475.0,451.0,426.0,394.0,
A344.0,300/
C
C * * CRITICAL PROPERTIES FOR WATER * *
C
T1=374.136

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```

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
IF(TR.LT.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
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
30 FORMAT(1X,T20,' * * TEMP BELOW TABLE FOR FUNCT. PSAT
A: T(R)= ',E12.5)
C
C
40 RETURN
END
C
C
C *****
DOUBLE PRECISION FUNCTION CC(T,IS,IC,I,J)
*****
C
C
C
C
C THIS FUNCTION CALCULATES LANGMUIR CONSTANTS FOR HYDRATE
C FORMATION FROM C1,C2,OR C3 USING THE SPHERICALLY SYMETRIC
C KIHARA POTENTIAL FUNCTION. THIS PROGRAM CALLS ON THE
C FUNCTION OMEGA WHICH GIVES THE POTENTIAL AS A FUNCTION OF
C POSITION. GAUSSIAN INTEGRATION (C&W PAGE 100) IS USED
C TO INTEGRATE OMEGA OVER THE CELL VOLUME.
C OMEGA IS A FUNCTION THAT CALCULATES THE
C SMOOTHED CELL POTENTIAL AS A SUM OF
C CONTRIBUTIONS OF THE FIRST,SECOND AND
C THIRD SHELLS.
C THE VARIABLES ARE
C IS- CODE FOR WHICH HYDRATE STRUCTURE(I OR II) IS FORMED
C IC= CODE FOR WHICH CAVITY IS UNDER CONSIDERATION
C A= CORE RADIUS FOR THE MOLECULE,C1...C3
C T=TEMPERATURE
C EPS= EPSILON, DEPTH OF INTERMOLECULAR POTENTIAL WELL, ERG
C R= RADIAL POSITION OF THE ENCLOSED MOLECULE
C RR =FIRST SHELL RADIUS.
C RR2=SECOND SHELL RADIUS

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```

C      RR3=THIRD SHELL RADIUS.
C      Z=FIRST SHELL COORDINATION NUMBER
C      Z2=SECOND SHELL COORDINATION NUMBER.
C      Z3=THIRD SHELL COORDINATION NUMBER.
C
C      REF: PARRISH AND PRAUSNITZ, I&EC PROC. DES & DEV, 11(1), P26(1972)
C
C
C      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C      EXTERNAL OMEGA
C      COMMON /SIG/ SIGMA, EPS, RR, Z, A, TT, RR2, Z2, RR3, Z3
C      COMMON /AMOL/MA, ISCODE(10)
C      COMMON /RRR/ R
C      COMMON/FUND/SSIG(10), EEPS(10), AA(10)
C      COMMON/AFACT/OM(10)
C      COMMON/ID/II, JJ, ISS
C      CC=0.0
C      II=I
C      JJ=IC
C      ISS=IS
C      WRITE(06, 51) II, JJ, ISS, CC
51      FORMAT(4X, 3I2, 5X, E15.5)
C      PI=3.14159
C      QSTAR=1.0
C      IF(IS.EQ.1.AND.ISCODE(J).EQ.3)RETURN
C      IF(IC.EQ.1.AND.ISCODE(J).EQ.2)RETURN
C      IF(IC.EQ.1.AND.ISCODE(J).EQ.3)RETURN
C      IF(ISCODE(J).EQ.4)RETURN
C      TT=T
C      A=AA(I)
C      SIGMA=SSIG(I)-A
C      EPS=EEPS(I)
C      WRITE(06, 1031) SIGMA, EPS, A
1031      FORMAT(5X, 3E15.5)
C      ***CHECK FOR WHICH STRUCTURE IS FORMED***
C      IF(IS.EQ.2) GO TO 6
C      ***CHECK FOR WHICH CAVITY IS OCCUPIED****
C      IF(IC.EQ.2) GO TO 5
C      RR=3.875
C      Z=20.
C      RR2=6.593
C      Z2=20.0
C      RR3=8.056
C      Z3=50.0
C      GO TO 8
C      ***STRUCTURE I CAVITY II
5      RR=4.152
C      Z=21.
C      RR2=7.078
C      Z2=24.0
C      RR3=8.285
C      Z3=50.0
C      GO TO 8
6      CONTINUE
C      ***CHECK FOR CAVITY, STRUCTURE II***
C      IF(IC.EQ.2) GO TO 7

```

```

C      ***STRUCTURE II, CAVITY I***
      RR=3.87
      Z=20.
      RR2=6.667
      Z2=20.0
      RR3=8.079
      Z3=50.0
      GO TO 8
C      ***STRUCTURE II, CAVITY II***
7     RR=4.703
      Z=28.
      RR2=7.464
      Z2=28.0
      RR3=8.782
      Z3=50.0
8     CONTINUE
C
C      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.
C      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
C      WRITE(6,552)(FORM,QSTAR)
C552   FORMAT(1X,1F,2X,1F)
      RETURN
      END
C
C
C
C      *****
      SUBROUTINE CUBEQN(A,Z,MTYPE)
      *****
C
C      THIS SUBROUTINE FINDS THE THREE ROOTS OF THE CUBIC
C      EQUATION GENERATED BY THE EQUATION OF STATE.
C
C
C      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)
      BETOV2=BET/2.
      ALFOV3=ALF/3.
      CUAOV3=ALFOV3**3
      SQBOV2=BETOV2**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
C
C
C
C
C
C
C

```

*****
SUBROUTINE DATA(Y, XA, T)
*****

```

THIS SUBROUTINE READS THERMODYNAMIC DATA FOR THE GASES,
CALCULATES MIXTURE CRITICAL PROPERTIES, FREEZING POINT
DEPRESSIONS, AND ACTIVITY COEFFICIENTS FOR WATER IN
THE PRESENCE OF INHIBITORS.

```

      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION A(10),SIGMA(10),EPS(10)
      DIMENSION NCODE(10),KK(10)

```

```

DIMENSION ZAA(1,25),AA(10,25)
DIMENSION IISCO(25)
DIMENSION Y(25),XA(25),ZA(20)
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)
COMMON /PVTIJ/ OMEGA, PCIJ, TCIJ
COMMON /AMOL/MA,ISCODE(10)
COMMON /AZ/KK,N,MK
COMMON /COEFF/ C0FREF, C1FREF, C2FREF, C3FREF, C4FREF,
2 C0HNRV, C1HNRV, C2HNRV, C3HNRV, C4HNRV, C5HNRV,
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/OM(10)
COMMON/FUND/SIGMA, EPS, A
COMMON/BKSA/AK
COMMON/BKSC/IWATER, IPOS, ISTR
COMMON/IMP/IMPURE, IMCODE, XIMP(100), YCO2(100)
COMMON/SOLUT/XSOLU, ACTIV, YYYCO2
COMMON/TFREEZ/TT0
COMMON/AWAT/ANN(25,25)
IF(IWATER.EQ.0)GO TO 508
MA=MA+1
KK(MA)=13
508 CONTINUE
DATA X1OLD/1./
OPEN(10,FILE='TAPE10.DAT',STATUS='OLD')
I=1
DO 96 I2=1,25
IF(IWATER.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)

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```

      READ(10,307)(ZAA(1,J),J=19,24)
      READ(10,307)(ZAA(1,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(I2)
      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(IWATER.NE.0)GO TO 826
      IF(Y(I).LT.1.E-5) GO TO 10
826     J=J+1
      JJ=JJ+1
      NCODE(J)=I

```



```

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

```

```

      TT0=0.0
507   IF(IMPURE.EQ.0.OR.XSOLU.EQ.0.0)GO TO 509
      T=T/1.8
C
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
1      **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.+
1      (-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)
1*XSOLU**2.+(183.219)*XSOLU**3.)/(0.082*T))
C
C   ** CORRECTION FACTOR FOR SYSTEMS CONTAINING CO2 **
C
      ACTIV=(1-0.30*YYYCO2*XSOLU)*ACTIV
C
C   ** FREEZING POINT DEPRESSIONS **
C
      IF(IMCODE.EQ.1)TT0=-0.13171+105.59*XSOLU+161.82*XSOLU**2
1      -70.233*XSOLU**3
      IF (IMCODE.EQ.2)TT0=-0.33398+109.91*XSOLU+308.25*XSOLU**2
1      -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
1      +8884.6*XSOLU**3
      IF(IMCODE.EQ.5)TT0=0.12618+207.67*XSOLU+6510.4*XSOLU**2
1      +4113.4*XSOLU**3
      IF(IMCODE.EQ.6)TT0=0.0085870+185.53*XSOLU-65.062*XSOLU**2
1      +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
1      +1857.6*XSOLU**3
      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
C   *****
C   DOUBLE PRECISION FUNCTION DEL(N)
C   *****
C
C   THE DEL FUNCTIONS EVALUATE DEL OF THE KIHARA FUNCTION FOR
C   THE 1ST, 2ND AND 3RD SHELLS OF WATER.
C
C   IMPLICIT DOUBLE PRECISION (A-H,O-Z)
COMMON /SIG/ SIGMA,EPS,RR,Z,A,T,RR2,Z2,RR3,Z3
COMMON /RRR/ R

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```

D=(1.-R/RR-A/RR)
DD=(1.+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
C *****
DOUBLE PRECISION FUNCTION DEL2(N)
*****
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/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
C *****
DOUBLE PRECISION FUNCTION DEL3(N)
*****
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/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
C *****
DOUBLE PRECISION FUNCTION GAUSS(A,B,M,FUNCTN)
*****
C ****REF: CARNAHAN,LUTHER AND WILKES:APP. NUMERICAL METH'S.
C ****WILEY & SONS, INC.(1969).
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

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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
C      C=(B-A)/2.
C      D=(B+A)/2.
C
C      *** ACCUMULATE THE SUM IN THE MPOINT FORMULA
C      SUM=0.
C      DO 5 J=JFIRST,JLAST
C      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)
C      2 + FUNCTN( -Z(J)*C +D))
C
C      *** MAKE INTERVAL CORRECTION AND RETURN ****
C      GAUSS=C*SUM
2100 FORMAT('   GAUSS;      ',1G10.5)
C      RETURN
C      END
C
C
C
C      *****
C      DOUBLE PRECISION FUNCTION OMEGA(R)
C      *****
C
C      THIS FUNCTION EVALUATES THE CELL POTENTIAL( SPHERICALLY
C      SYMETRIC KIHARA) WITH THE RADIAL POSITION, R, OF THE
C      MOLECULE IN THE CAVITY AS THE INDEPENDENT VARIABLE.
C
C      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C      COMMON /SIG/ SIGMA, EPS, RR, Z, A, T, RR2, Z2, RR3, Z3
C      COMMON /RRR/ ZZ
C      ZZ=R
C      OMEGA=2.*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)))
C      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)))
C      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)))
C      OMEGA=OMEGA+OMEGA2+OMEGA3
C      OMEGA=-OMEGA/T
C      IF(ABS(OMEGA).GT. 170.) OMEGA=ABS(OMEGA)/OMEGA*170.
C      IF (OMEGA.LE.-60.) OMEGA=-60.
C      OMEGA=DEXP(OMEGA)*R*R
2300 FORMAT('   OMEGA;      ', 1G10.5)
C      RETURN
C      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
C      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C      DIMENSION PVAP(10)
C      DIMENSION TCIJ(10,10), PCIJ(10,10), PC(10), TC(10), VC(10), OMEGA(10)
C      DIMENSION NCODE(10)

```

```

COMMON/PVTIJ/OMEGA,PCIJ,TCIJ
COMMON/NC/NCODE,NCOMP
COMMON/PVT/RT,TC,PC,VC,NSOLV
DO 401 I=1,NCOMP
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
C *****
C SUBROUTINE BUBDEW(T,P,Y)
C *****
C
C THIS SUBROUTINE CALCULATES THE DEW POINT PRESSURE IF LIQ=0 AND
C BUBBLE POINT PRESSURE IF LIQ=1
C
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C DIMENSION XL(10),Y(10),V(10),PHIL(10)
C DIMENSION PHI(10),PVAP(10)
C DIMENSION NCODE(10)
C DIMENSION ZK(10),ZCN(10)
C COMMON/X/XL
C COMMON/PH/PHIL
C COMMON/NC/NCODE,NCOMP
C COMMON/TBLOC/ITAG
C COMMON/LIQUID/LIQ
C COMMON/HELP/IST0,IST2,ISLOW

C
C
C ITAG=1
C ITER=0
C CALL VAPRES(PVAP,T)
C SFRAC=0
C IF(LIQ.EQ.1)GO TO 8000
C ** DEW POINT CALCULATIONS **
C DO 280 I=1,NCOMP
C FRAC=Y(I)/PVAP(I)
C SFRAC=SFRAC+FRAC
280 CONTINUE
C MAKE AN INITIAL ESTIMATE OF PRESSURE
C P=1/SFRAC
288 S=0
C DO 201 I=1,NCOMP
C XL(I)=Y(I)*P/PVAP(I)
C S=S+XL(I)
201 CONTINUE
C DO 222 I=1,NCOMP
C XL(I)=XL(I)/S
222 CONTINUE
206 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=FRAC+SFRAC
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)
23    CONTINUE
205    RETURN
      END
C
C
C *****
C   SUBROUTINE PHIMIX(Y,P,T,PHI)
C *****
C
C   ** THIS SUBROUTINE IS TAKEN DIRECTLY FROM PRAUSNITZ
C      AND CHUEH'S BOOK "COMPUTER CALCULATIONS FOR MULTI
C      COMPONENT VAPOR LIQUID EQUILIBRIA"(1968) PRENTICE HALL
C
C   THIS SUBROUTINE CALCULATES THE FUGACITY COEFFICIENTS FOR
C   EACH COMPONENT FROM THE EQUATION OF STATE.
C
C   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/CRITCL/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
      I1=I+1
      DO 100 J=I1,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)

```



```

100 CONTINUE
110 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)
C
C           CALCULATE VAPOR MOLAR VOLUME FOR MIXTURE
C
    A(1)=1.
    A(2)=-1.
    PBRT=P*BMRKV/RT
    ABRT=AMRKV/(BMRKV*10.72999*T**1.5)
    A(3)=PBRT*(ABRT-1.-PBRT)
    A(4)=-ABRT*(PBRT**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
C
C           CALCULATE FUGACITY COEFFICIENTS WITH THE
C           MODIFIED REDLICH-KWONG EQUATION OF STATE
C
    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-QBVB)-DLOG(ZV)
    IF(PHI(I).LT.170.0) GO TO 27
    WRITE(6,28) QVVB, BRKV(I), Q1VB, AIRKV(I), Q2RTB, QVBV,
2 QARTB, QBVB, ZV
28 FORMAT(9F10.5)
27 CONTINUE
    PHI(I)=DEXP(PHI(I))
160 CONTINUE
    RETURN
C
C ***** CALCULATE FUGACITY COEFFICIENTS USING PENG *****
C ***** ROBINSON EQUATION OF STATE *****
C
200 BC=0.0
    BCX=0.0
    DO 201 I=1, NCOMP
    AKK=0.37464+1.54226*OMEGA(I)-0.26992*OMEGA(I)**2

```

```

      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)
1)))**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)
203  CONTINUE
202  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=-AP/(2.828427*B)*(2.0*F3/AC-BTC(I)/BC)
F3=F3*DLOG((ZV+2.414*B)/(ZV-0.414*B))
PHI(I)=DEXP(F1+F2+F3)
207 CONTINUE
  IF(NVLLH.EQ.0.OR.ITAG.EQ.0)GO TO 810
288 APX=ACX*P/(10.73*T)**2.
  BX=BCX*P/(10.73*T)
  A(1)=1
  A(2)=BX-1
  A(3)=APX-3.0*BX**2.-2.*BX
  A(4)=BX**3.+BX**2.-APX*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)
217 DO 218 I=1,NCOMP
  F1=BTC(I)/BCX*(ZL-1.0)
  F2=-DLOG(ZL-BX)
  F3=0.0
  DO 219 K=1,NCOMP
  F3=F3+XL(K)*AY(K,I)
219 CONTINUE
  F3=-APX/(2.828427*BX)*(2.0*F3/ACX-BTC(I)/BCX)
  F3=F3*DLOG((ZL+2.414*BX)/(ZL-0.414*BX))
  PHIL(I)=DEXP(F1+F2+F3)
218 CONTINUE
810 RETURN
C
  END
C
C
C
C *****
C SUBROUTINE YLIMIT(RLIMIT)
C *****
C
C ..... COPIED FROM W. R. PARRISH'S THESIS(BERKLEY)
C
C THIS SUBROUTINE CALCULATES THE UPPER LIMIT OF
C INTEGRATION IN THE SMOOTH CELL LANGMUIR CONSTANT
C EXPRESSION.
C
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
COMMON /SIG/ SIGMA,EPS,RR,Z,A,T,RR2,Z2,RR3,Z3
CA=A/RR
CHECK=0.0
RCA=SIGMA/RR*1.122462
S=1-0.98*(SIGMA/(2*(RR-A)))
IF(S.LT.0.4) S=0.4
RCA6=RCA**6
RCA12=RCA**12

```

```

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
DA11=UM11*UM+UP11*UP
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(DS.LE.0) DS=S*1.05
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

C
C
C *****
C REVISED SOLUBILITY SUBROUTINE
C
C SUBROUTINE SOL7(JK,Y7,PHI7,P,T,X6)
C *****
C
C THIS SUBROUTINE CALCULATES THE SOLUBILITIES OF
C THE GASES IN WATER USING KRICHEVSKY-KASARNOVSKY
C EXPRESSIONS FOR EACH GAS.
C
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C DIMENSION A(25),B(25),C(25),D(25)
C DIMENSION VBAR(25),NCODE(25)
C COMMON/NC/NCODE,NCOMP
C
C P IS IN ATM. AND T IS IN K
C
C 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/1.0,1.0,1.0,1.0,760.0,
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
C
  IF(JK.EQ.20.OR.JK.EQ.21.OR.JK.EQ.14.OR.JK.EQ.11.
AOR.JK.EQ.22)GO TO 10
  IF(JK.EQ.8.OR.JK.EQ.9.OR.JK.EQ.10.OR.JK.EQ.12.
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

```

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