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SOLUBILITY OF METHANE IN WATER UNDER NATURAL CONDITIONS A LABORATORY STUDY

FINAL REPORT
FOR THE PERIOD
APRIL 1, 1978 to JUNE 30, 1982

MASTER

CHARLES W. BLOUNT and LEIGH C. PRICE

JUNE 1982

DEPARTMENT OF GEOLOGY
IDAHO STATE UNIVERSITY
POCATELLO, IDAHO 83209
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U.S. DEPARTMENT OF ENERGY
NEVADA OPERATIONS OFFICE
Under CONTRACT No. DE-AS08-78ET12145

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ABSTRACT

The solubility of methane in aqueous solutions has been determined over a broad range of temperature, pressure and salinities. The effect of dissolved carbon dioxide and ethane on methane solubility has been determined at 302°F. Also the solubility of crude oil and water in methane has been determined over a broad range of temperatures and pressures.

The solubility of methane is raised by increasing pressure and temperature (above about 170°F). There is a solubility minimum near 170°F at constant pressure and salinity. Ionic salts effectively salt methane out of solution at all concentrations investigated in this study.

The effect of the addition of small amounts of carbon dioxide or ethane to the gas dissolved in aqueous solutions is to enhance methane solubility compared to solutions without other gases. Higher concentrations of dissolved gases, depending upon the salinity and the gas involved, decrease aqueous methane solubility. The addition of carbon dioxide always increases total gas content even when reducing the concentration of methane. With increasing concentration of ethane in the dissolved gases the total gas content reaches a maximum and then both methane and total gas content decrease.

Comparison of experimental methane solubilities with gas/water ratios, salinities, bottom hole temperatures and pressures of geopressure test wells suggests that some formation fluids may be near saturation, while many others seem to be undersaturated. There are unresolved questions about the effects of other dissolved substances such as bicarbonate ion and higher molecular weight hydrocarbons on aqueous methane solubility.

Petroleum is soluble in methane. Increasing pressure increases the

solubility of crude oil in methane gas. At an elevated pressure, which depends upon the temperature, oil and gas form a single fluid phase.

INTRODUCTION

History of project and previous work

During 1977 the co-principal investigators Drs. Leigh C. Price and Charles W. Blount jointly proposed to systematically determine methane solubility in NaCl solutions at elevated temperatures and pressures appropriate to the geothermal-geopressure resource. This proposal resulted in the issuance of a research contract with D.O.E. on April 1st, 1978.

Previous work on the solubility of methane in water and salt water solutions had been made by a number of investigators over a limited range of physical conditions (Culbertson and McKetta, 1951; Duffy et al, 1961; O'Sullivan and Smith, 1970; Sultanov, 1972; and Price, 1979). Haas (1978) analyzed all previous data, excepting Price (1979), and developed an empirical equation to calculate methane solubilities over a broad range of conditions. This equation was fundamentally an equation for the solubility of methane in pure water with an applied constant salting out or Setschenow constant. Susak and McGee (1980) developed a routine for calculating methane solubilities from Haas's equation using an appropriate programmable calculator. Up to this time no systematic laboratory study had been undertaken to determine methane solubility in NaCl solutions at temperatures above 200°F and at pressures from 2,000 to

22,500 psi.[1]

Proposed studies

Under the initial contract with D.O.E. we proposed to investigate:

1) The solubility of methane in aqueous NaCl solutions at temperatures from 212°F to 464°F with NaCl concentrations up to 25 weight percent at pressures ranging from 2,000 to 22,500 psi.

2) The effect of CO_2 on methane solubility in aqueous solutions.

3) The effect of higher hydrocarbons on methane solubility in aqueous solution.

4) The behavior of these systems at temperatures above 250°C.

During the initial period of study (4/1/78 to 3/27/80) supplies and equipment were procured, personnel trained in the use of high pressure geothermal equipment and the study of solubility of methane in salt water was nearly completed. During this time, D.O.E. expressed an interest in experiments at low temperature and pressure appropriate for the operation of methane gas recovery systems at which point this work was also initiated. Also during this time two pressure vessels failed catastrophically causing damage to laboratory equipment and a delay of several months while new pressure vessels were made and repairs were made to laboratory equipment. Work on the effect of carbon dioxide and of higher molecular weight hydrocarbons was postponed to a later date.

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[1] We have used American units of measurements (temperature in °F, pressure in psi, and methane solubility in SCF/Bbl) rather than metric units throughout this report because the majority of the people who will use these data use American and not metric units. An American petroleum barrel is equal to 42 gallons.

A proposed modification to the original contract was approved on March 27, 1980 where we proposed to investigate:

1) The solubility of methane at low temperatures and pressures.

2) a. The solubility of crude oil in methane in the presence of water.

   b. The solubility of methane and crude oil in water.

Under the modified proposal, a gas chromatograph was purchased, set up and used to analyze gas mixtures obtained from experimental measurements of the solubility of methane in solution containing carbon dioxide and ethane.

Work completed under both phases of the D.O.E. contract is as follows:

1) The solubility of methane in NaCl solutions at temperatures of 212° to 464°F at pressures from 2,000 to 22,500 psi and NaCl concentrations from 0 to 26 weight percent.

2) The solubility of methane in NaCl solutions at temperatures from 77° to 160°F at pressures from 100 to 2,000 psi in 5, 10 and 15 weight percent NaCl solutions. This includes equilibria studies.

3) The solubility of methane in the presence of carbon dioxide in NaCl solutions of 5, 10 and 15 weight percent at 300°F at pressures at 5,000, 13,000 and 22,500 psi (CO_2 concentration ranged from 5 to 90% of the gas dissolved in the aqueous solutions).

4) The effect of dissolved ethane on aqueous methane solubility at 300°F in a 10 weight percent NaCl solution at several pressures.

5) The solubility of crude oil and crude oil distillate fractions in methane in the presence of water.

Measurements of the solubility of methane at temperatures above 464°F were dropped because such data were not considered to be important with respect to the geothermal-geopressure resource and existing laboratory data could be extrapolated into that region. The study of methane solubility in crude oil saturated water was not undertaken because of the need of equipment for other studies and the anticipated experimental difficulties of long equilibration times. We simply did not have enough equipment and personnel to do all of the possible work in the time allocated for the research project.

Under the terms of another ammendment to the contract a third pressure vessel was constructed for use in the solubility studies. Up to that time only two pressure vessels were used for determining methane solubilities at high pressure conditions. The third vessel replaced an unsafe pressure vessel of the same design as those that catastrophically failed.

METHANE SOLUBILITY STUDIES

Equipment

We have measured the solubility of methane in NaCl solutions using hydrothermal solution equipment (HSE) similar to that described by Dickson, Blount, and Tunell (1963) and shown in Figure 1. Experimental solutions were contained in a teflon sample cell sealed and connected to the closure piece of a pressure vessel. The sealed sample cell was installed in a pressure vessel that contained sufficient water to expel air from the vessel when the teflon sample cell was inserted and the vessel closed. A teflon-lined stainless steel tube (sample exit tube) led from the sample cell to a valve block. This tube allowed samples to be withdrawn from the sample cell.

The assembled hydrothermal solution equipment, which contained a chromel-alumel monitoring thermocouple, was then installed in a muffle furnace. The furnace was designed so that the pressure vessel could be rotated back and forth through a 180° arc. Temperatures were controlled by Love[2] proportioning-type temperature controllers to ± 3°F. Temperature measurements were made to ± 3 °F with the aforementioned thermocouple. Pressure measurements were made to ± 45 psi using a Heise precision-type Bourdon gauge.

An air-operated hydraulic pump generated pressures by pumping either distilled water into the pressure vessel or salt solutions into the sample cell. Pressures could also be generated by a separator which pumped methane into the sample cell or pressure vessel. The methane used was of a 99.99 percent purity supplied in a 300 SCF tank at an initial pressure of 2250 psi.

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[2] Use of brand names in this report is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey or the Department of Energy

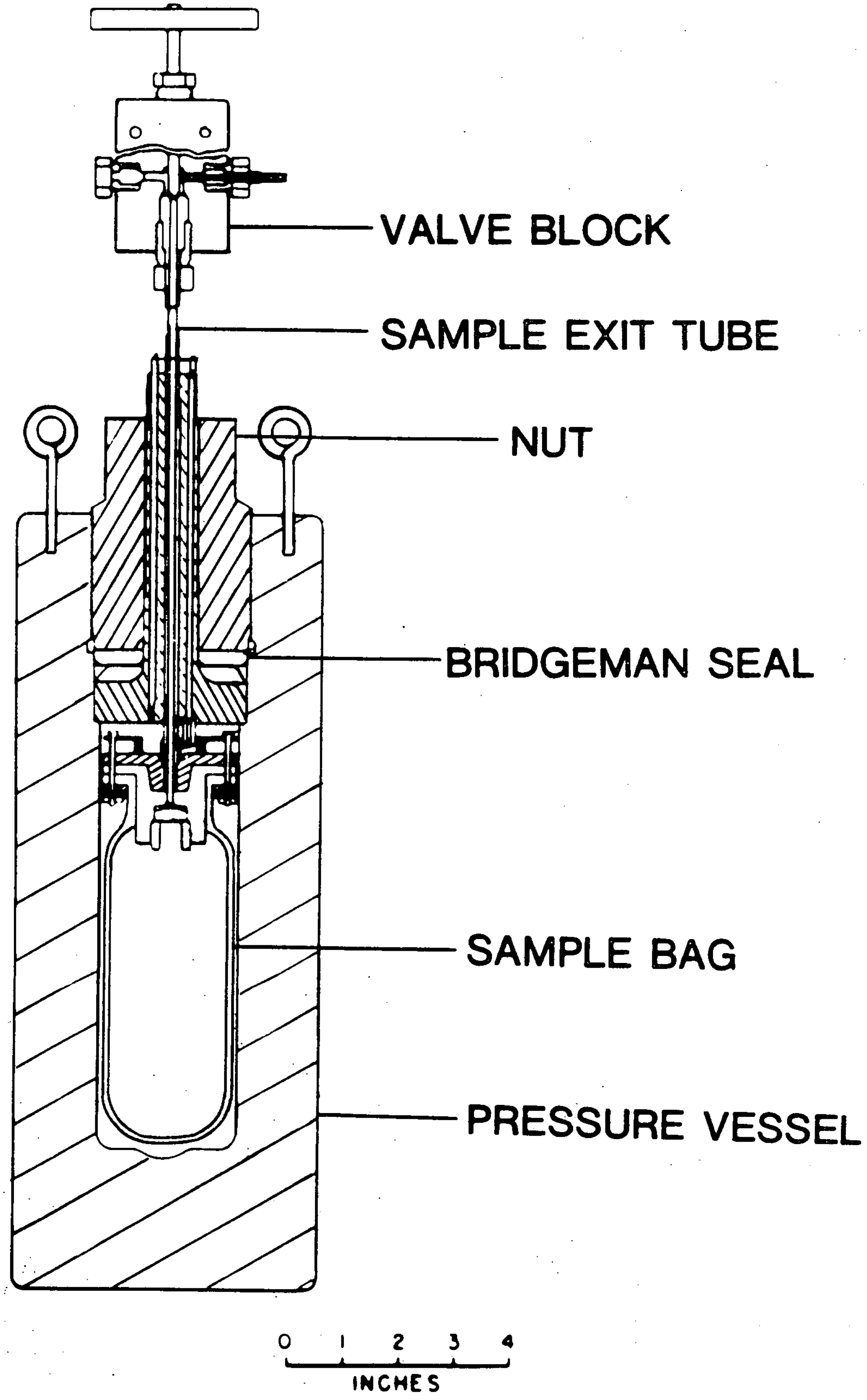


Figure 1

DIAGRAM OF EXPERIMENTAL HSE EQUIPMENT USED IN THIS STUDY

Gas from this tank was allowed to flow into the separator. The tank was then shut off and the methane compressed to the desired pressure by pumping water into the opposite end of the separator. A brass plug separated methane from the water. Salt solutions were gravimetrically prepared using analytical reagent-grade NaCl and distilled water.

Methane and water combine at temperatures below 104°F at high pressures to form a solid hydrate phase which will plug pressure lines. To prevent this, all pressure lines were wrapped with insulation and heated to between 150° and 180°F with electric heating tapes.

The teflon wall of the sample cell was highly permeable to methane, carbon dioxide and ethane and slightly permeable to distilled water. Distilled water from the pressure vessel slowly diffused through the teflon sample cell wall, diluting the concentration of the NaCl solution in the sample cell. The rate of diffusion increased with increasing temperature and with decreasing pressure. At higher temperatures (401 and 464°F), determinations of NaCl concentrations of samples were made frequently to monitor changes in NaCl concentration.

Experimental Procedures

The HSE was heated to the desired temperature while maintaining a pressure of about 4350 psi. Because solutions expand when heated, excess solution was bled from the sample cell during heating to prevent rupture. When the desired temperature was achieved, saline water was bled from the sample cell and replaced by 20 cc of methane at 4,350 psi. Additional methane was pumped into the pressure vessel (outside the sample cell) to saturate the water in the pressure vessel with methane. This was done to prevent large-scale diffusion of methane from the sample cell to the water in the pressure vessel. The HSE was then rocked for a period of 6 to 8 hours. Absorption of methane by the saline solution in the sample cell and the distilled water in the pressure vessel caused the pressure to decrease. More methane was then pumped into the pressure vessel to re-establish the desired pressure. The pressure vessel was rocked for another 6 to 8 hours and then inverted so that the methane gas phase in the sample cell would rise to the end of the cell away from the sample exit tube. Rocking the pressure vessel was a crucial aspect of this study. We found that the uptake of methane in a NaCl solution in a static system could take weeks. This was also true for the uptake of methane in distilled water at pressures of 20,000 psi or greater (Price, 1979). By rocking the system, equilibrium saturation was achieved in a maximum of two days.

Sampling of the saline solution in the sample cell was accomplished as follows. A high-pressure capillary tube was connected to the valve block at the end of the sample exit tube. (A 22-gauge hypodermic needle had been soldered onto the end of this capillary tube). The temperature and pressure of the system in the sample vessel were measured. The pressure of the system was increased by 400 to 600 psi to prevent the system pressure from dropping below the recorded pressure during sampling. The valve block on the sample exit tube was opened slightly until a steady sample flow rate was established. As sample solution came out, methane was injected into the pressure vessel. From 3 to 5 ml of solution were bled from the sample cell before any samples were taken. Duplicate samples (or more if necessary) were taken in sealed round-bottomed flasks, which had Kovar seals attached to them. Brass compression fittings, sealed by a septum at one end, were attached to the Kovar seals. The hypodermic needle was pushed through the septum so that sample solution went into the round-bottom flask. Sample size varied from 3 to 10 ml depending on methane concentration and the size of the flask.

After sampling the pressure was dropped to the desired pressure. The samples in the flasks were then analyzed. Sampling did not cause a significant change in temperature and had no effect on NaCl concentration. Increasing the pressure before sampling did not affect solubilities. Price (1979) had observed that the process of methane dissolution in solution was very slow compared to the rate that methane is evolved from solution following a pressure drop. Thus during sampling it was important to keep the pressure at or above the experimental pressure to prevent methane from exolving from solutions prematurely. Our results confirmed that rapid exsolution also was true in NaCl brines. We used this fact to our advantage in the study. By rocking the pressure vessel we established equilibrium conditions at the highest pressure of interest (22,500 psi). Samples were then taken and the pressure of the system was decreased to the next point of interest, and 3 or 4 hours later, samples could be taken under the new conditions. Thus it was possible to take 2 or 3 measurements every working day. Methane solubilities were determined for a decreasing series of pressures holding the temperature and NaCl concentration as constant as possible.

Methane gas concentrations were calculated from the analysis of samples. The results of the duplicate or triplicate samples taken were usually within ± 5% of the mean or average value. If they failed to agree within ±5%, another set of samples was taken. Usually two or three sets of samples were taken at intervals of time ranging from a few hours to several days. When succeeding sets of samples agreed within the analytical uncertainty the pressure was dropped to the next experimental pressure desired and the sampling process repeated after enough time had passed to permit re-equilibration at the new pressure.

Because sampling depleted the saline solution in the sample cell, occasionally it had to be reloaded, in situ, by injecting salt solution into the cell through the sample valve block. After reloading, the undersaturated saline water was equilibrated by raising the pressure to the desired value and rocking the HSE equipment. When the NaCl content dropped to about ½ weight percent below what was desired, a measured quantity of NaCl solution was reloaded into the sample cell to bring the NaCl concentration back to what was desired.

Analytical Procedures

Sample analyses were made following the procedure of Price (1979). Samples were taken in preweighed round-bottom flasks of known volume. Flasks of 50, 100, and 250 ml were commonly used. Sample flasks were bled to lab pressure just before use. Samples of 3 to 10 grams were injected in the flask through the septum. They were then reweighed and allowed to cool to room temperature. Pressure of gas in the flask was measured to ± 0.05 psi using a precision Bourdon gauge with a range of 15 psi. Usually the pressure of gas was between 3 and 6 psi. At these pressures the ideal gas law can be used to calculate the amount of gas exolved from experimental solutions within the precision of measurements. The appropriate equation used is as follows:

$$n = \frac{(Pm - Pc) \times (Vf - Vs + Vg) \times 1000}{R \times Tp \times Ws}$$

in which n = the moles of gas exolved from a kilogram of solution, Pm = pressure measured on Bourdon gauge, Pc = pressure increase caused by the addition of a volume of fluid to the flask displacing air already in flask, Vf = volume of flask, Vs = volume of sample, Vg = volume of gauge system, R = gas constant, Tp = absolute temperature of room and Ws = weight of sample. The volume of sample is calculated by dividing the weight of solution by the density of NaCl solutions at that concentration. The value of Pc is calculated from the equation:

$$Pc = \frac{Pb(Vf + Vg)}{(Vf + Vg - Vs)}$$

in which Pb is the barometric pressure and the other symbols are the same as described above.

Results in moles/kg. of solution were converted to standard cubic feet per petroleum barrel (SCF/Bbl) using appropriate conversion factors.

In our initial data reporting the effect of solution compression, Pc, had been omitted. The size of this correction varied from sample to sample. It was minimal for those samples where the measured pressure (Pm) was high and small samples had been taken in large flasks. As a result, the data in the Proceedings of the 4th Geothermal Geopressure Conference (Blount, et al, 1979). were higher by 5 to 20% from recalculated values published in the Proceedings of the 5th Geothermal-Geopressure Conference (Price, et al, 1981).

Precision was generally good using the above procedure. On occasion, results were obtained that differed significantly from each other or from what previous systematic behavior suggested they should be. High results could have been due to bubbles of methane gas adhering to the wall of the exit tube or suspended in solution in this tube. Low analyses could have resulted from leakage from the connections around the sample valve block or from the sample flask. Leaks were detected using a soap solution. Such erratic results were discarded and are not included in this report.

Uncertainties in experimental results are nearly ±7% of the value. Uncertainties in the temperature of $\pm 4^{o}$ F would only effect the results by ±1%. Uncertainties in pressure of ±60 psi would result in an uncertainty of about ±2% in the methane concentration. Uncertainties in NaCl concentrations of ±0.1% would affect uncertainties in methane concentrations by about ±0.5%. The combined uncertainties in methane concentration due to uncertanties in temperature, pressure and NaCl concentration are less than ±2½%. Thus the major uncertainty in methane analysis has to be the analytical data. This includes uncertainties on the analytical method and in the method of sampling. No cause for sample analysis variation could be discerned. Part of the uncertainty could be the regression equations used. The equations do not fit experimental results at pressures below 3500 psi. Thus the choice of some different model equation might result in a reduced standard deviation of the residuals. It is unlikely that uncertainties would be reduced to much below ±6%. Examination of the residuals did not suggest any systematic variation that could be eliminated and thereby reduce uncertainties.

DATA ANALYSIS AND MODELING

Experimental measurements of methane solubility were repeated a number of times at the same (or nearly the same) pressure and temperature for a given salinity. Rather than attempt to process thousands of such data points, all the data points for one set of conditions were averaged. This "averaged" value was then taken as the correct solubility measurement for the corresponding pressure, temperature and salinity.

All such averaged values, in SCF/Bbl (standard cubic feet of methane at 25°C, one atmosphere per barrel (42 gallons) of brine) were plotted on a logarithmic scale, versus salinity (grams per liter) on a linear scale for constant temperature and pressure. Figures 2 and 3 are examples. When this was completed, it was evident that some of the values were anomalous. For example, the values obtained in 10.0 percent NaCl solutions at 401° and 464°F were less than those obtained in 15.0 percent NaCl solutions at the same temperatures and pressures. Considering the regularity of methane solubility reduction with increasing NaCl concentration (salting out effect) at all other experimental conditions, the 10.0 percent NaCl data were clearly in error. A careful examination of the laboratory notebooks and files did not offer any explanation for these low values. A possible explanation is that the actual experimental temperatures were lower than the measured temperatures for these data due to thermocouple malfunction. In any case these data (10.0 percent NaCl, 401° and 464°F, at all pressures) were deleted from consideration, as well as occasional other data points which fell far off the linear plots.

After the data were examined, a total of 670 points remained. These raw data are presented in Table A-1 in the appendix. This body of data was statistically analyzed using a Hewlett Packard System 3000 computer and a statistical program termed IDA (interactive data analysis). The mechanics of this are described in Blount et al (1979). Least squares regression

Fig. 2. Aqueous methane solubility as a function of NaCl concentration at a constant pressure of 5,000 psi for various constant temperatures (in °F). The dots are experimentally determined (averaged) data points. The solid lines are values calculated from the equations of Table 1. The dashed lines are values calculated from the equation of Susak and McGee (1980).

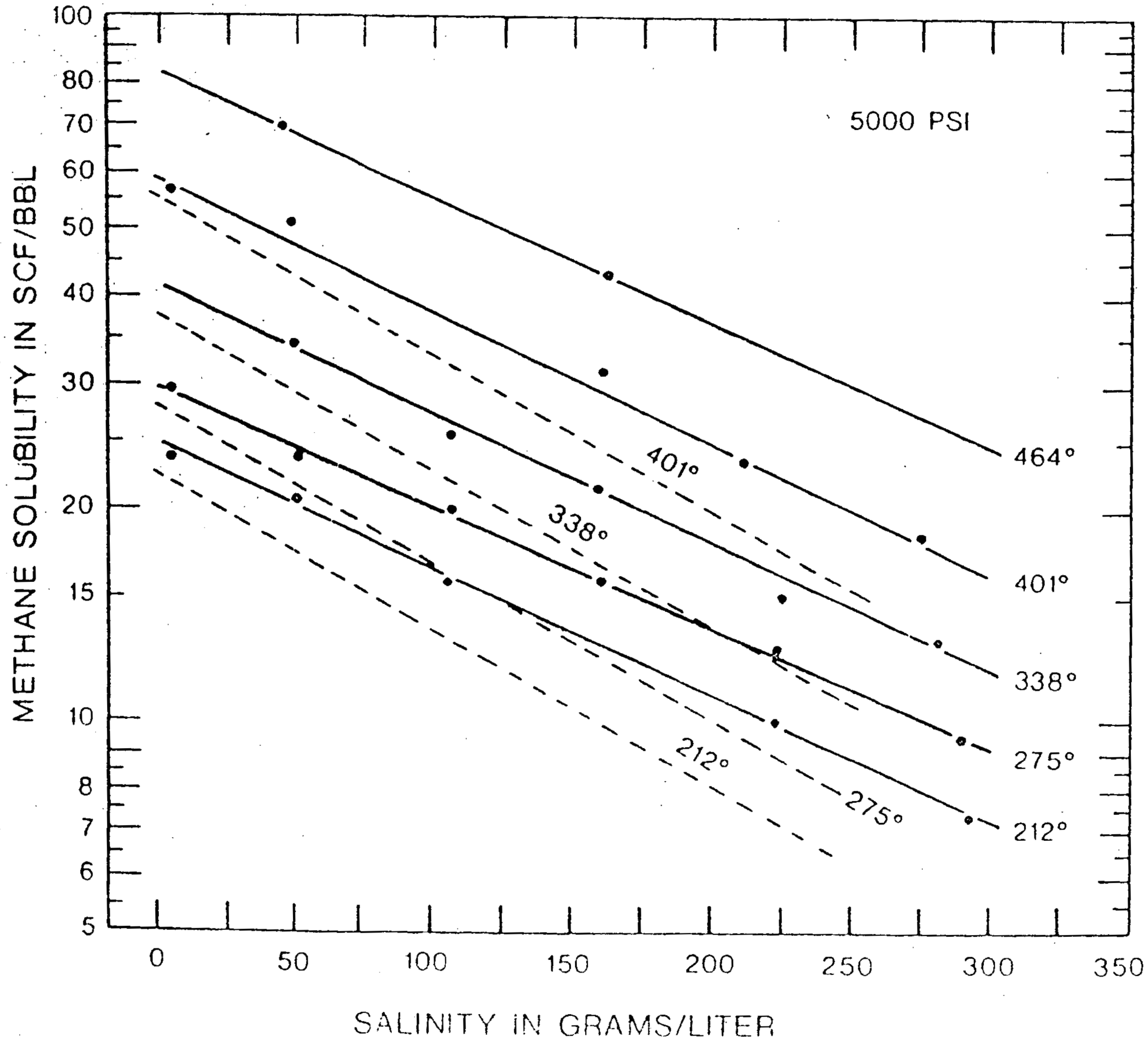
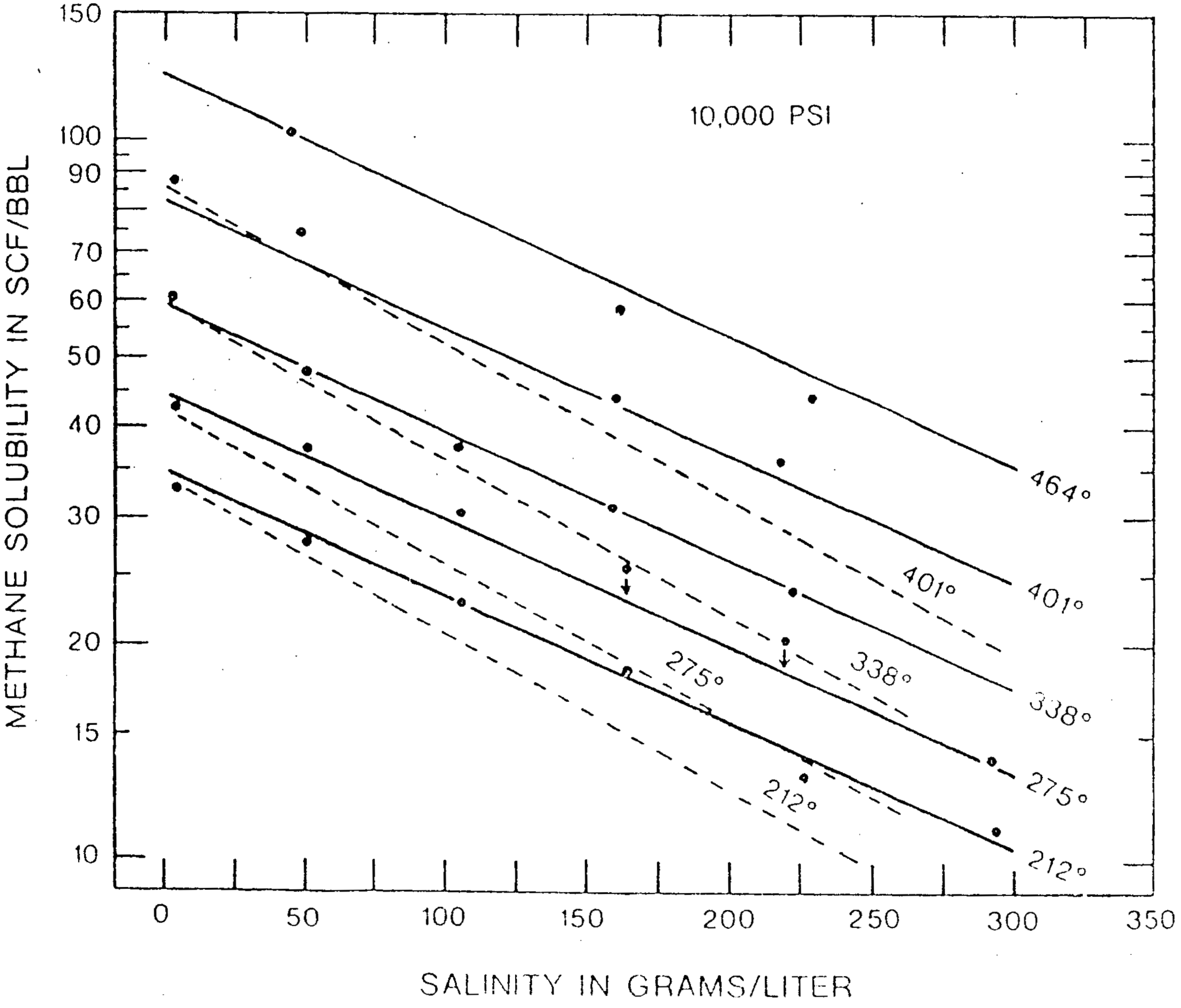


Fig. 3. Aqueous methane solubility as a function of NaCl concentration at a constant pressure of 10,000 psi for various constant temperatures (in °F). The dots are experimentally determined (averaged) data points. The solid lines are values calculated from the equations of Table 1. The dashed lines are values calculated from the equation of Susak and McGee (1980).



equations were derived to best fit the 670 data points. The two "best fit" empirical equations which resulted from this procedure are given in Table 1.

Graphs, such as Figures 2 and 3, at all temperatures and pressures for all experimental and calculated data points, show similar slopes for the salting out coefficient (Setschenow constant). The empirical equations (Table 1) show that methane solubility (on a logarithmic scale) is a linear function of salinity at all temperatures and pressures within the experimental uncertainty. The use of other salinity variables in the equations (Table 1)did not significantly improve the fit of equations to the experimental data. The value of the Setschenow constant was calculated to be 0.1025 (change in $\log_{10}$ of the methane concentration per mole change in the molality of NaCl solutions). The standard error was 0.0047. Over 212^{o} to 464^{o}F there is no apparent effect of temperature on the Setschenow constant. The Setschenow constant at low temperatures (122^{o} and 160^{o}F) was the same as that determined from our measurements at higher temperature within the experimental uncertainty of the measurements (see the section on low pressure-low temperature data).

The empirical equations in Table 1 apply only to calculating methane solubilities at temperatures above 160^{o}F and below 464^{o}F for pressures above 3500 psi. As will be discussed, the equations will give erroneous results at lower pressures and temperatures. Table 2 gives methane solubility values calculated from the equation in Table 1. The values cover the experimental conditions examined in this study: temperature - 212^{o} to 464^{o}F; pressure - 3,500 to 22,500 psi; and salinity - 0 to 300 grams/liter.

Table 1 Equations for the solubility of methane in water and in NaCl solutions for the temperature range 160° to 464°F and the pressure range 3,500 to 22,500 psi. <u>These equations do not apply to lower pressure and temperature conditions</u>.

A. $\log_e CH_4{*} = -1.4053 - 0.002332t + 6.30 \times 10^{-6}t^2 - 0.004038S$
$- 7.579 \times 10^{-6}p + 0.5013 \log_e p + 3.235 \times 10^{-4}\ t \log_e p.$

Standard Deviation of Residuals = 0.0706

Multiple R = 0.9944

B. $\log_e CH_4{*} = -3.3544 - 0.002277t + 6.278 \times 10^{-6}t^2 - 0.004042S$
$+ 0.9904 \log_e p - 0.0311 (\log_e p)^2 + 3.204 \times 10^{-4}\ t \log_e p.$

Standard Deviation of Residuals - 0.0709

Multiple R = 0.9943

$*CH_4$ is in standard cubic feet (SCF) per petroleum barrel (42 gallons) at 25°C (77°F) and one atmosphere.

t is in ° Fahrenheit.

S is salinity in grams per liter.

p is pressure in psi.

All logs are to the base e.

Table 2. Calculated solubility values of methane from equation 1. Pressure (top line) in psi. Methane concentration in SCF/Bbl.

Salinity g/liter	3,500	5,000	7,000	10,000	13,000	16,000	19,000	22,500
				212°F				
0	20.2	24.5	29.25	35.0	39.8	43.8	47.2	50.6
20	18.7	22.6	27.0	32.3	36.7	40.4	43.5	46.7
50	16.5	20.0	23.9	28.6	32.5	35.8	38.6	41.4
100	13.5	16.4	19.5	23.4	26.5	29.2	31.5	33.8
150	11.0	13.4	16.0	19.1	21.7	23.9	25.8	27.6
200	9.02	10.9	13.0	15.6	17.7	19.5	21.0	22.6
250	7.38	8.94	10.7	12.8	14.5	16.0	17.2	18.4
300	6.03	7.30	8.71	10.4	11.8	13.0	14.0	15.1
				275°F				
0	25.0	30.6	36.7	44.3	50.5	55.8	60.4	65.0
20	23.1	28.2	33.9	40.8	46.6	51.5	55.7	60.0
50	20.5	25.0	30.0	36.2	41.3	45.6	49.4	53.1
100	16.7	20.4	24.5	29.6	33.8	37.3	40.4	43.4
150	13.7	16.7	20.0	24.2	27.6	30.5	33.0	35.5
200	11.2	13.6	16.4	19.8	22.5	24.9	27.0	29.0
250	9.12	11.1	13.4	16.1	18.4	20.4	22.0	23.7
300	7.46	9.10	10.9	13.2	15.0	16.6	18.0	19.4
				338°F				
0	32.6	40.0	48.4	58.8	67.5	74.9	81.3	87.8
20	30.0	36.9	44.7	54.3	62.3	69.1	75.0	81.0
50	26.6	32.7	39.6	48.1	55.2	61.2	66.5	71.8
100	21.8	26.7	32.3	39.3	45.1	50.0	54.3	58.6
150	17.8	21.8	26.4	32.1	36.8	40.9	44.4	47.9
200	14.5	17.8	21.6	26.2	30.1	33.4	36.3	39.2
250	11.9	14.6	17.6	21.4	24.6	27.3	29.6	32.0
300	9.7	11.9	14.4	17.5	20.1	22.3	24.2	26.2
				401°F				
0	44.5	55.1	67.2	82.2	94.8	105.7	115.1	124.7
20	41.1	50.8	61.9	75.8	87.5	97.5	106.2	115.0
50	36.4	45.0	54.9	67.2	77.5	86.4	94.1	101.9
100	29.7	36.8	44.8	54.9	63.3	70.6	76.9	83.3
150	24.3	30.1	36.6	44.9	51.8	57.7	62.8	68.1
200	19.9	24.6	30.0	36.7	42.3	47.1	51.3	55.6
250	16.2	20.1	24.5	30.0	34.6	38.5	42.0	45.5
300	13.3	16.4	20.0	24.5	28.2	31.5	34.3	37.2
				464°F				
0	64.0	79.8	97.9	120.7	140.0	156.7	171.3	186.2
20	59.0	73.6	90.3	111.4	129.1	144.5	158.0	171.8
50	52.3	65.2	80.0	98.6	114.4	128.0	140.0	152.2
100	42.7	53.3	65.4	80.6	93.5	104.6	114.4	124.4
150	34.9	43.6	53.4	65.9	76.4	85.5	93.5	101.6
200	28.5	35.6	43.7	53.8	62.4	69.9	76.4	83.0
250	23.3	29.1	35.7	44.0	51.0	57.1	62.4	67.9
300	19.1	13.8	29.2	36.0	41.7	46.7	51.0	55.5

COMPARISON TO PREVIOUS WORK

Published data on the NaCl-H_2O-CH_4 system are limited. Data on the H_2O-CH_4 system are more extensive and will be considered first.

Table 3 compares the data of Sultanov et al (1972) and Price (1979) with our values calculated for their experimental conditions (up to 482°F) using the equations of Table 1. At pressures of 2,000 to 3,000 psi, our calculated values are moderately to substantially higher than their experimental values. At pressures above 3,500 psi, the agreement is good and in some cases exact. The disagreement at low pressures arises from the attempt to model a large amount of data of wide variations in conditions to a single equation. It does not arise from basic errors in the experimental technique.

Plots of methane solubility on a logarithmic scale versus pressure on a logarithmic scale at constant temperature and constant salinity (Fig. 4) are essentially linear above 5,000 psi. However, below 5,000 psi, the plots take on more and more curvature. Below 2,000 psi the curvature becomes extreme (see Culberson and McKetta, 1951, Fig. 1). The bulk of our data were taken above 4,000 psi. Thus the "linear" aspect of most of the data has been superimposed on the lower pressure "curved" portion of the data by the equations of Table 1. This probably could be rectified by modeling the data to a more complex equations. However, because the equation will have mainly higher pressure applications, of a practical nature, we opted to keep it as simple as possible.

The degree of this effect at low pressures is evident in Table 4 which compares the experimental data of Culberson and McKetta (1951) with our calculated values for their experimental conditions. At 160°F and low pressures, our calculated values are much higher than their experimental values, however as pressure increases the difference becomes progressively less. Thus at 330 psi, our calculated value is 60 percent higher than

Fig. 4. Aqueous methane solubility as a function of pressure at a constant NaCl concentration of 160 grams per liter for various constant temperatures in °F. The dots are experimentally determined (averaged) data points. The solid lines are values calculated from the equations of Table 1.

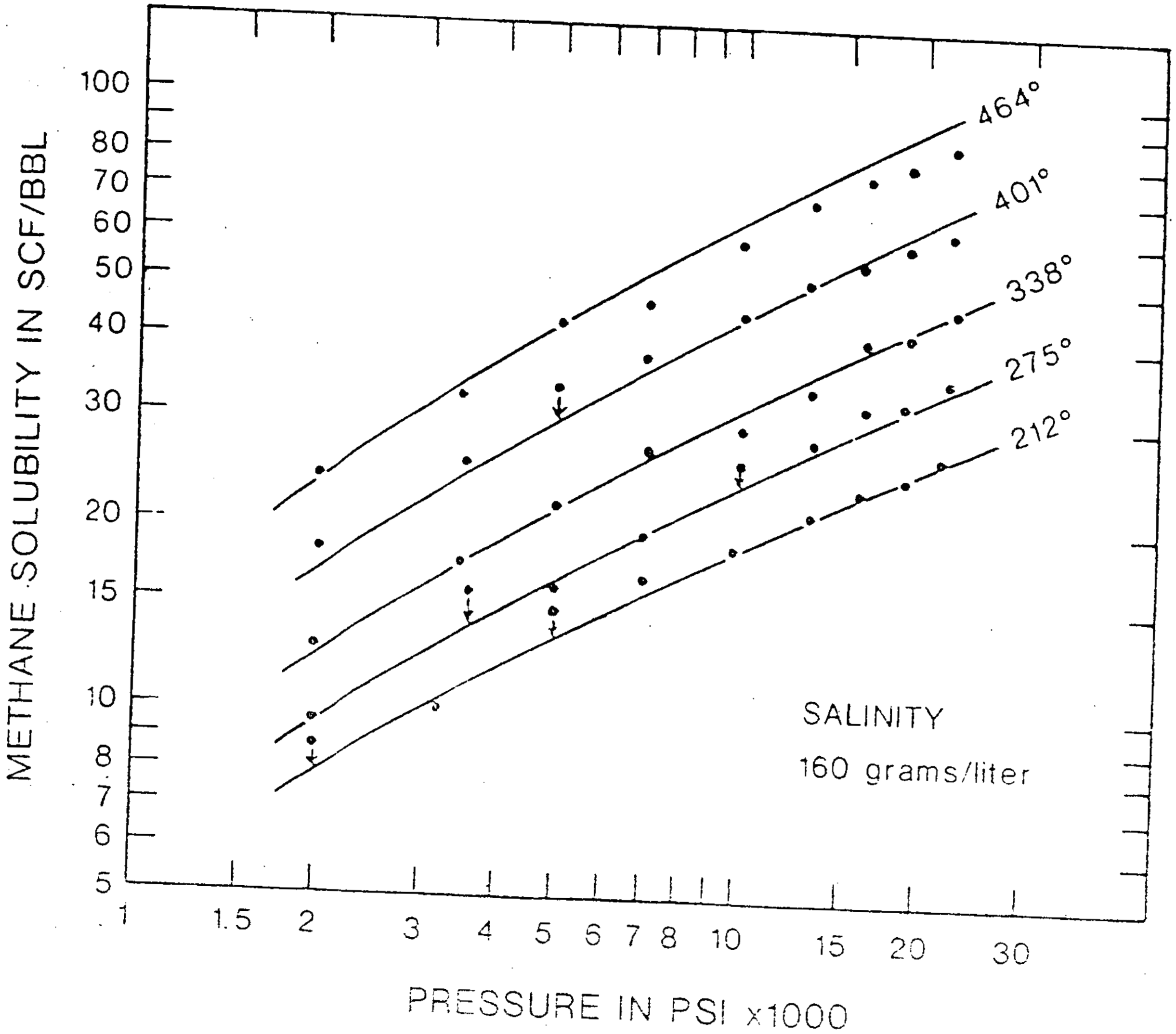


Fig. 5. Comparisons of methane solubility in distilled water from different studies. Crosses are 302°F (150°C) data from Sultanov et al (1972, Table 3, this study). Solid dots are 309°F (154°C) data from Price (1979, Table 3, this study). Circled dots are interpolated 302°F data from Culberson and McKetta (1951), the trend of which is traced by the dashed line. The solid lines are values calculated from the equations of Table 1 (this paper) for constant temperatures of 302°F (150°C) and 309°F (154°C). The bold faced arrows at 3,600 psi show the lower pressure limit to which the equations of Table 1 apply.

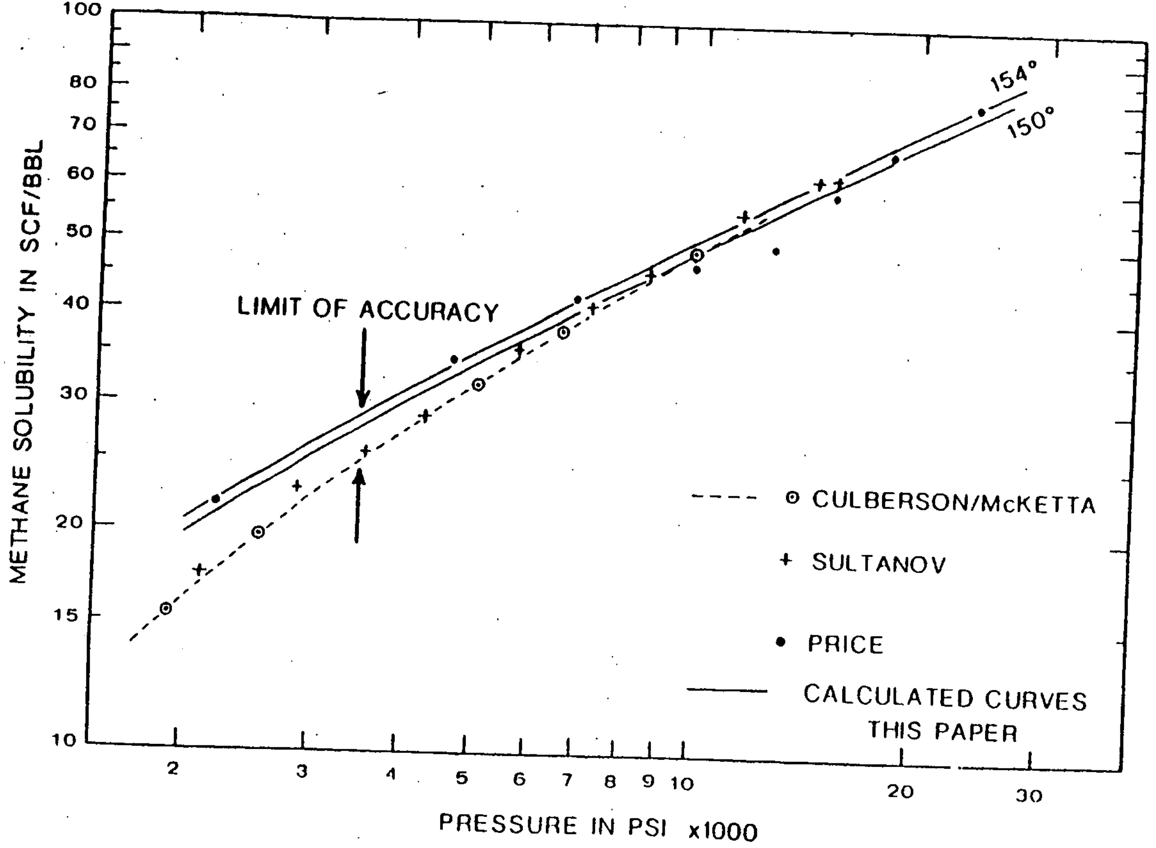


Table 3. Comparison of interpolated (calculated) methane solubility data of this study with experimental data of Sultanov et al (1972) and Price (1979). SCF/Bbl; standard cubic feet of methane per barrel of water at 25°C and one atmosphere.

Pressure bars	Pressure (psi)	This study	Price (1979)
309°F (154°C)			
152.0	2,205	21.9	21.8
320.2	4,645	33.9	34.4
468.1	6,790	41.8	42.0
672.9	9,760	50.7	46.7
873.6	12,670	57.7	49.8
1,052.1	15,260	63.5	58.8
1,259.0	18,260	69.2	67.4
1,639.5	23,780	78.4	78.8
403°F (206°C)			
160.2	2,323	35.0	30.8
294.4	4,270	51.0	48.1
546.3	7,923	73.0	72.4
948.6	13,759	98.6	98.1
1,303.5	18,906	116.2	116.5
1,630.7	23,652	129.9	127.0
1,924.6	27,915	140.9	143.5
430°F (221°C)			
367.6	5,331	67.8	62.9
628.0	9,109	92.4	101.7
873.6	12,670	110.9	116.4
1035.6	15,020	121.4	131.4
1,236.9	17,940	133.3	135.3
1,415.5	20,530	142.9	139.4
452°F (234°C)			
148.9	2,160	44.0	34.9
207.8	3,014	54.5	54.8
277.6	4,027	65.4	64.0
471.3	6,836	90.0	108.2
596.9	8,658	103.2	117.3
781.2	11,330	120.0	140.0
933.5	13,540	132.4	150.8
1,081.8	15,690	143.3	161.9
1,087.3	15,770	143.7	159.2
1,325.8	19,230	159.6	169.3
1,471.3	21,340	168.4	172.1
1,643.0	23,830	178.2	181.0

Pressure bars	Pressure (psi)	This study	Sultanov et al (1972)
302°F (150°C)			
147.1	2,133	20.8	17.5
196.2	2,845	24.8	22.9
245.2	3,556	28.2	25.9
294.2	4,267	31.4	29.0
392.2	5,689	36.8	35.9
490.3	7,112	41.5	41.3
588.4	8,534	45.8	45.9
748.6	11,380	51.8	55.2
980.4	14,220	59.3	61.4
1,078.7	15,645	62.1	62.1
392°F (200°C)			
147.1	2,133	31.4	26.7
196.2	2,845	37.6	35.2
245.2	3,556	43.1	43.6
294.2	4,267	48.1	49.8
392.2	5,689	56.9	61.4
490.3	7,112	64.7	68.3
588.4	8,534	71.6	76.1
748.6	11,380	81.7	91.6
980.4	14,220	94.2	101.8
1,078.7	15,645	99.0	105.7
482°F (250°C)			
147.1	2,133	52.2	35.1
196.2	2,845	63.1	50.5
245.2	3,556	72.8	61.6
294.2	4,267	81.7	79.2
392.2	5,689	97.5	101.8
490.3	7,112	111.5	120.6
588.4	8,534	124.1	135.6
748.6	11,380	142.6	161.7
980.4	14,220	165.7	180.7
1,078.7	15,645	174.6	185.5

their experimental value. By 1,880 psi the difference has declined to 9 percent; and within experimental error at 2,555 psi, the two values are equal. The agreement of the 160°F data above 2,555 psi for the two studies suggests that our equations are valid to 160°C, although we did not take experimental data below 212°F. At all other temperatures, at pressures above 3,500 psi, the agreement between the two studies is very good (Table 4), although our calculated values are consistently slightly higher than the experimental values of Culberson and McKetta (1951).

In Figure 5, data from three studies are visually compared in the 302° to 309°F (150° to 154°C) range. Above 6,000 psi the data from all three studies overlie each other within experimental error.

The only experimental data for the system $NaCl-CH_4-H_2O$ remotely comparable to this work, is that of O'Sullivan and Smith (1970). They give methane solubility data for pure water, 1m NaCl, and 4m NaCl solutions between 122° to 257°F (50° to 125°C) at 2,940 psi (200 atm). Unfortunately, the pressure they used (2,940 psi) is outside the realm that we consider valid for our equation. As expected, our calculated data are higher than their experimental data at temperatures above 158°F (70°C) and the difference increases with increase in temperature (Fig. 6, Table 5. However, we do not believe that our calculated data are valid, as: 1) They lie outside the boundary conditions for our equation, and 2) The calculated data exhibit a solubility minimum at temperatures below 122°F (50°C) (Fig. 6). In contrast, the data of O'Sullivan and Smith (1970), Culberson and McKetta (1951) as well as experimental low pressure-low temperature methane solubility data we have taken, all exhibit the solubility minimum at about 160° to 175°F.

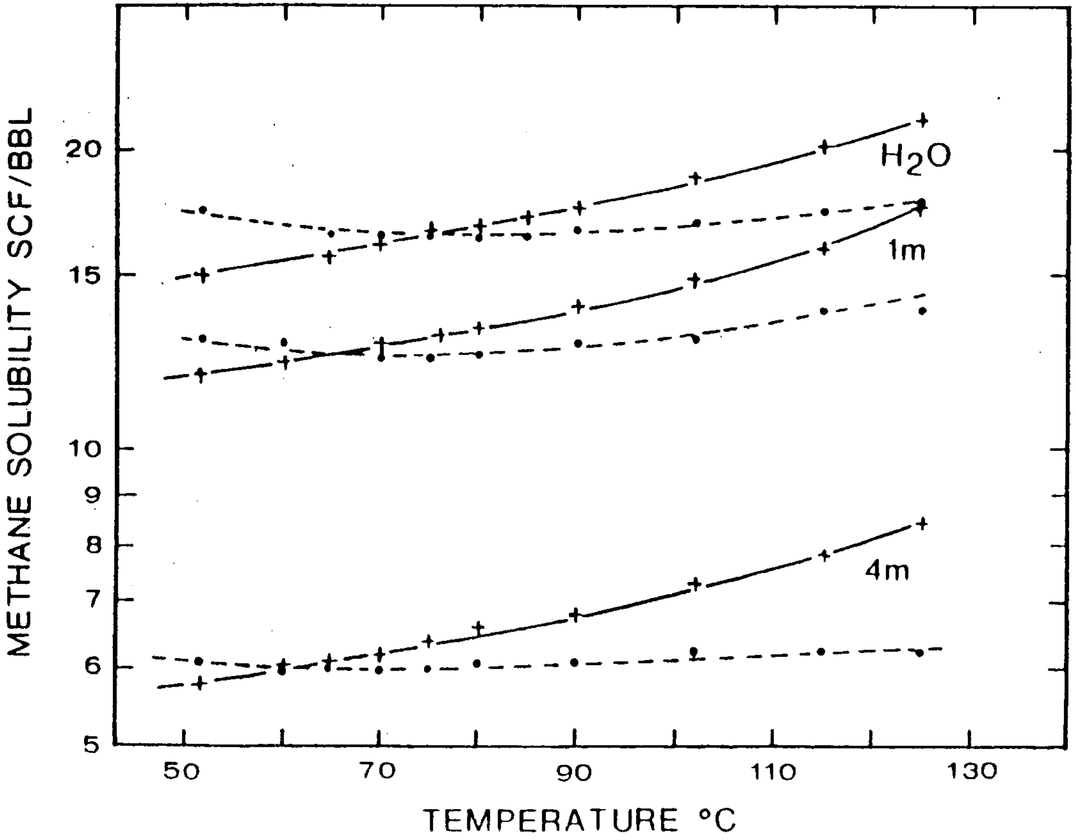
Table 4. Comparison of interpolated (calculated) methane solubility data of this study with experimental data of Culberson and McKetta (1951). Their solubility values-MF x 10^3 (mole fraction) converted to SCF/Bbl by dividing by the conversion factor 0.0001312. SCF/Bbl is standard cubic feet of methane per barrel of water at 25°C and one atmosphere.

Pressure	Pressure	McKetta and Culberson (1951)		This study
(bars)	(psi)	MF x 10^3	SCF/Bbl	SCF/Bbl
160°F (71°C)				
22.8	330	.340	2.59	4.2
32.2	467	.470	3.58	5.3
45.4	659	.632	4.82	6.6
65.0	943	.909	6.93	8.3
91.0	1,320	1.183	9.02	10.2
129.6	1,880	1.500	11.43	12.5
176.2	2,555	1.924	14.66	14.9
243.7	3,535	2.385	18.17	17.8
339.6	4,925	2.770	21.11	21.1
449.9	6,525	3.420	26.07	24.3
566.7	8,220	3.750	28.58	27.2
680.2	9,865	4.240	32.32	29.7
(220°F (104°C)				
174.8	2,535	1.980	15.09	17.3
246.1	3,570	2.510	19.13	21.0
342.3	4,965	3.140	23.93	25.1
449.9	6,525	3.610	27.52	28.9
564.7	8,190	4.080	31.10	32.5
680.8	9,875	4.510	34.38	35.6
(280°F (138°C)				
171.0	2,480	2.346	17.88	21.0
245.1	3,555	3.015	22.98	25.9
343.0	4,975	3.805	29.00	31.3
449.1	6,525	4.490	34.22	36.2
570.2	8,270	5.180	39.48	41.0
678.1	9,835	5.740	43.75	44.9
340°F (171°C)				
177.9	2,580	3.025	23.06	27.5
246.8	3,580	3.835	29.23	33.4
347.8	5,045	4.875	37.16	40.8
449.9	6,525	5.95	45.35	47.1
566.0	8,210	6.80	51.83	53.4
689.1	9,995	7.75	59.07	59.3

Table 5. Comparison of interpolated (calculated) methane solubility data of this study with experimental data of O'Sullivan and Smith (1970). Their solubility values MF x 10^4 (mole fraction) were converted to SCF/Bbl (standard cubic feet of methane per barrel of water or brine at 25°C and one atmosphere) by dividing MF x 10^4 by the appropriate conversion factors - 0.0001312 for pure water; 0.0001317 for 1m NaCl; and 0.0001328 for 4m NaCl.

T°C	Pressure		Pure water			1m NaCl			4m NaCl		
	bars	psi	O'Sullivan and Smith MF x 10^4	O'Sullivan and Smith SCF/Bbl	This Paper SCF/Bbl	O'Sullivan and Smith MF x 10^4	O'Sullivan and Smith SCF/Bbl	This paper SCF/Bbl	O'Sullivan and Smith MF x 10^4	O'Sullivan and Smith SCF/Bbl	This paper SCF/Bbl
51.5	197.3	2,940	22.79	17.37	15.0	16.95	12.87	11.8	8.05	6.06	5.8
60.0	197.3	2,940				16.57	12.58	12.2	7.92	5.96	6.0
65.0	197.3	2,940	21.51	16.40	15.7				7.96	5.99	6.1
70.0	197.6	2,944	21.44	16.34	16.1	16.25	12.34	12.7	7.91	5.96	6.2
75.0	197.6	2,944	21.36	16.28	16.5	16.30	12.38	13.0	7.97	6.00	6.4
80.0	197.6	2,944	21.33	16.26	16.8	16.40	12.45	13.3	8.03	6.05	6.6
85.0	198.0	2,950	21.48	16.37	17.1						
90.0	198.0	2,950	21.72	16.55	17.5	16.74	12.71	13.8	8.08	6.08	6.8
102.5	198.3	2,955	22.05	16.81	18.7	16.93	12.85	14.8	8.26	6.22	7.3
115.0	200.0	2,980	22.76	17.35	20.2	17.47	13.27	15.9	8.22	6.19	7.8
125.0	201.3	2,999	23.21	17.69	21.5	17.52	13.30	17.8	8.25	6.21	8.4

Fig. 6. Comparison of experimental aqueous methane solubility data of O'Sullivan and Smith (1970, dots and dashed lines) with values (crosses, solid lines) calculated from the equations of Table 1 (this paper). Data are for distilled water, 1 m NaCl (5.85 weight percent), 4 m NaCl (23.4 weight percent) at a constant pressure of 2,950 psi (200 atm) as a function of temperature in °C. Data from Table 5.



Susak and McGee (1980) have published tables of methane solubility from 77° to 662°F (25° to 350°C), 1,000 to 20,000 psi, and from 0 to 20 weight percent NaCl, based on the equations of Haas (1978), using an assumed Setschenow (salting-out) coefficient of 0.129. This differs considerably from our experimentally determined value of 0.1025. Because Susak and McGee (1980) appear to have overestimated the effect of increasing salt concentration on methane solubility, it is not surprising to find that their calculated values are less than our experimentally determined as well as our calculated values (Figures 2 and 3). The agreement is fair between the calculated values of Susak and McGee (1980) and our calculated values for the H_2O-CH_4 system (zero salinity, Figures 2 and 3).

Although we did not collect data above 464°F in this study, we used the equations of Table 1 to calculate values equivalent to the high temperature data of Sultanov et al (1972, 572°, 626°, 662°, and 680°F) and Price (1979, 536°, 558°, 601°, and 669°F). We found that our calculated values at pressures lower than 5,000 psi were much higher than the experimentally determined values of both studies. From this, we concluded that the equations of Table 1 are not valid at pressures below 5,000 psi and temperatures above 482° F. At pressures above 5,000 psi our calculated values show good (±10 percent) agreement with the experimental data of Price (1979) for his 536°, 558°, and 601°F isotherms (the experimental data of that study were within ±7 percent). However, there is a systematic trend between the two studies. Over 6,000 to 14,000 psi, our calculated values are less than the experimental values of Price (1979). The two data sets have the same values between 14,000 to 16,000 psi, and above 16,000 psi our calculated values are higher than those of Price (1979). The agreement between our calculated values and Price's (1979) 601°F isotherm was not good, our values being 3 percent higher at 6,200 psi but systematically increasing to 25 percent higher by 24,600 to 28,600 psi.

The agreement of our calculated values with the higher-temperature experimental data of Sultanov et al (1972) is not good, except for their 572°F isotherm at pressures above 7,000 psi. Over this range, our calculated values are 10 to 13 percent lower than their experimental values. Our calculated data is 25 to 60 percent lower than the experimental data of Sultanov et al (1972) for their 626°, 662° and 680°F isotherms above 7,000 psi. Price (1979) had previously contended that the higher temperature data of Sultanov et al (1972) were in error (too high). The extrapolated data of this study seem to support his conclusion.

Two conclusions result from these comparisons of high temperature data:

1) The equations of Table 1 are apparently valid (can be extrapolated to) temperatures of 601°F at pressures above 5,000 psi.
2) The data of Sultanov et al (1972) made up a major portion of the data base for the equations that Haas, 1978 (and therefore Susak and McGee, 1980) derived to calculate methane solubility over a wide range of conditions. The higher temperature portion of the Sultanov et al (1972) data appears questionable.

STUDIES RELATED TO EXSOLUTION AND THE DETERMINATION OF EQUILIBRIUM

Valid aqueous methane solubility data depends upon the attainment of a real equilibrium between a gas phase and the aqueous solution for the system studied. Our measurements were performed at essentially isothermal and isosalinity conditions. The sampling process did not change temperature or salinity of experimental solutions. The concentration of methane dissolved in solutions depended upon the pressure and either the time required for the exsolution of methane from oversaturated solutions or the uptake of methane by undersaturated solutions.

Measurements of the rate of methane uptake by aqueous solutions in a static system in which gas and solution were not mixed together was very slow. Methane concentraions were still going up after several weeks at experimental conditions. Very long times would be required to saturate solutions using this procedure. In order to saturate solutions more rapidly we rocked pressure vessel and furnace together after setting the pressure to the highest value to be used for the proposed series of experimental measurements (19,000 to 22,500 psi) by pumping methane into the pressure vessel. All of the previous experimental work had shown that the solubility of methane invariably increases with increasing pressure. Generally two to three days of rocking were required to saturate solutions at this initial high pressure. Several samples were taken at these conditions. Two experimental checks could be made to determine if the solutions had been saturated. If additional rocking did not result in the uptake of more methane, this would suggest that our solutions were nearly saturated. If the concentration of methane decreased when we dropped the pressure on the system then we have at least come close to saturation at the higher pressure. The final check, so to speak, was to examine the solubility data following a series of pressure drops. If all of this data showed a systematic trend of solubility vs pressure, it is likely that we had reached saturation from an undersaturated condition at the highest pressure.

The vast majority of our solubility data was taken following a drop in pressure. Thus most of our data was approached from conditions of supersaturation. In contrast to the slow rate of methane uptake by undersaturated solutions, the exsolution of methane from oversaturated solutions proved to be a very rapid process. Samples taken only 10 minutes after a drop in pressure were just slightly above those taken after 1 hour or more. Analyses of samples taken after 3 or 4 hours following a decrease in pressure agreed with analyses at the same pressure taken 12, 24 or 48 hours later. At low temperature and pressure exsolution seems to be slower. A series of analyses on solutions at 122°F in 15 weight percent NaCl continued to decrease in methane content over a 4 hour period. Samples were not taken until at least 4 hours had elapsed since the pressure had been dropped.

Our experience with the rapid speed of methane exsolution and the slowness of methane uptake in static systems showed that it was very important to maintain pressure during sampling at a value that exceeded the experimentally desired pressure. If the pressure had dropped below the desired pressure exsolution of dissolved methane would have occured. The solutions would then be undersaturated when the desired pressure was reestablished.

LOW PRESSURE-LOW TEMPERATURE DATA

Aqueous methane solubilities were measured at pressures from 125 to 2,000 psi, at 77°, 122° and 160°F in NaCl solutions of 5, 10 and 15 weight percent (salinities of 52, 107 and 167 grams per liter). Solubilities at these conditions were low (between 0.3 and 10 SCF/Bbl). Since standard deviations for repeated measurements ranged from 0.2 to 0.5 SCF/Bbl, analytical uncertainties for these conditions were usually between ±10 and ±25 percent of the mean values of repeated measurements.

The first step in the analysis of these data was the averaging of values taken at the same experimental conditions. These averaged data were plotted against pressure on log-log graph paper at constant salinity and temperature. Curves were then drawn through the data along each isotherm for each NaCl concentration. Some data were obviously in error (for the most part high) and were rejected. The remaining solubility data were next plotted versus salinity at constant temperature and pressure on semi-logarithmic graph paper with solubility on the logarithmic scale. The solubility of methane, thus plotted, decreased linearly with increasing NaCl concentration. The slopes of the different isobaric and isothermal lines were essentially equal which strongly suggests that the Setschenow constant did not change with pressure or temperature. Calculated values for the Setschenow constant, at these low temperatures and pressures, were equal (within experimental uncertainty) to that previously determined at high temperature and pressure. A few additional spurious data points were also rejected at this point. The low pressure-low temperature solubility data of this study are thus based on 129 samples taken at 34 different experimental pressure, temperature and salinity conditions (Table A-2, appendix).

Aqueous methane solubility at 77°, 122° and 160°F are illustrated in

Figures 7, 8 and 9 where the solubility values of Culberson and McKetta (1951) are plotted at zero salinity. Methane solubilities measured in NaCl solutions of 52, 107 and 167 g/l salinity agree with the data of Culberson and McKetta (1951), when values of this study are extrapolated to zero salinity using the value for the Setschenow determined during this study. The slopes of the lines representing plots of methane solubility versus salinity at low pressures and temperatures as determined by O'Sullivan and Smith (1970) agree well with the slopes of the lines based on the data obtained in this study. Duffy et al (1961) determined methane solubilities at 77°F as a function of pressure in NaCl solutions of varied concentrations. Interpolated solubility values from their data are in good agreement with our data at 500 psi but are definately lower than our 250 psi data. The data of Duffy et al (1961) generally agree with the data of Culberson and McKetta (1951) in pure water at pressures above 250 psi however at lower pressures the data of Duffy et al (1961) are also lower than those of Culberson and McKetta (1951).

Graphically interpolated methane solubilities (Table 6) obtained from the low pressure-low temperature empirical data (Table A-2, appendix) were used to construct Figures 10 and 11. Here, methane solubilities in NaCl solutions with salinities of 52 and 107 g/liter are plotted on a semi-logarithmic scale versus temperature on an arithmetic scale at constant pressure. The resulting curves show a minimum near 175°F. We took a limited amount of low pressure methane solubility data at temperatures above 212°F. We also took some low pressure methane solubility data on brines from the Pleasant Bayou No. 2 well. These brines had a salinity near 130 g/liter so these data were extrapolated to a lower salinity using the previously determined Setschenow constant of 0.1025. These extrapolated data agree well with our methane solubility data in NaCl

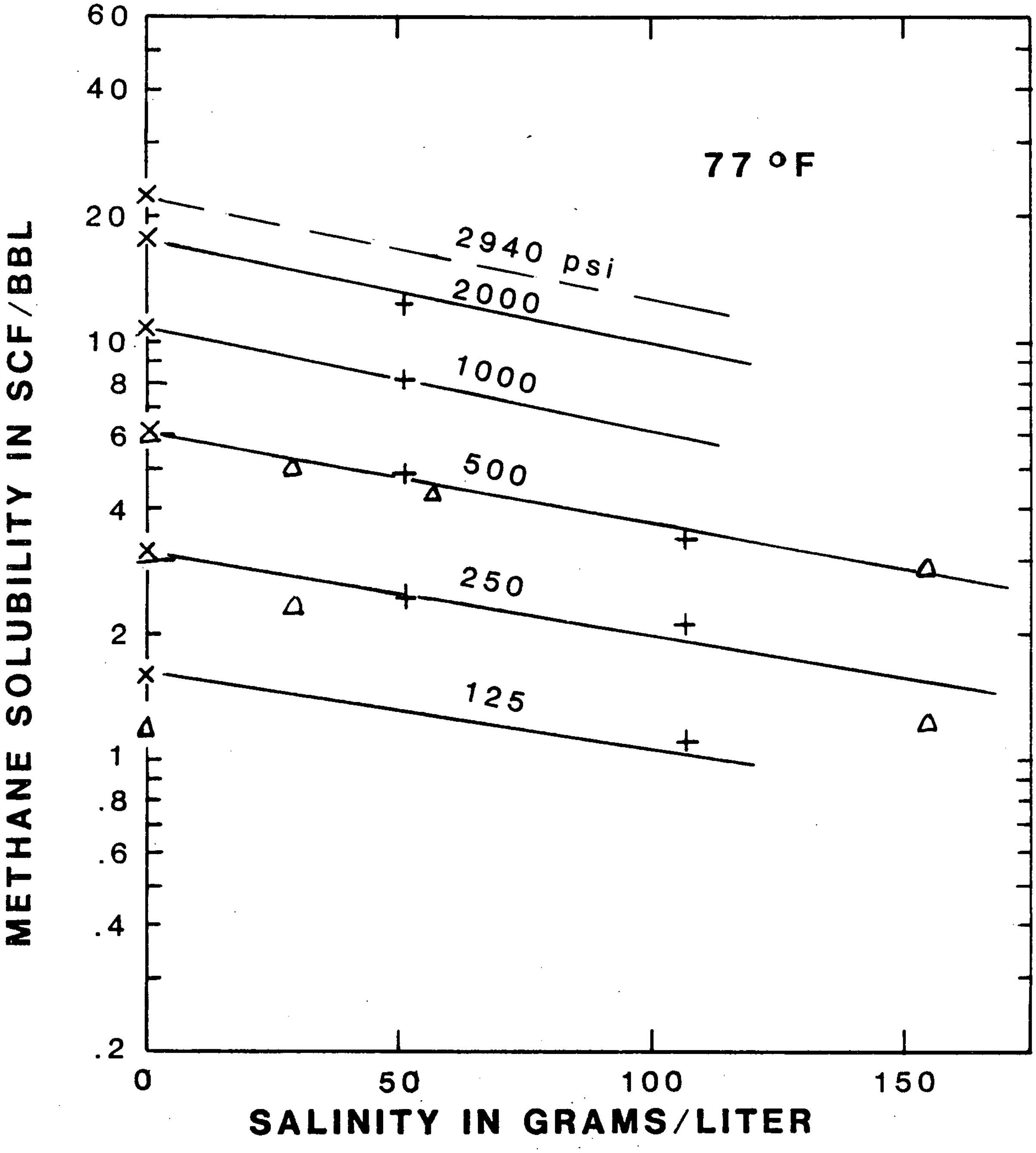


Figure 7 Aqueous methane solubility at 77°F as a function of NaCl concentration at constant (low) pressures. Crosses (+) are data from this study, X's are data from Culbertson and McKetta (1951), and triangles(Δ) are data from Duffy et al (1961).

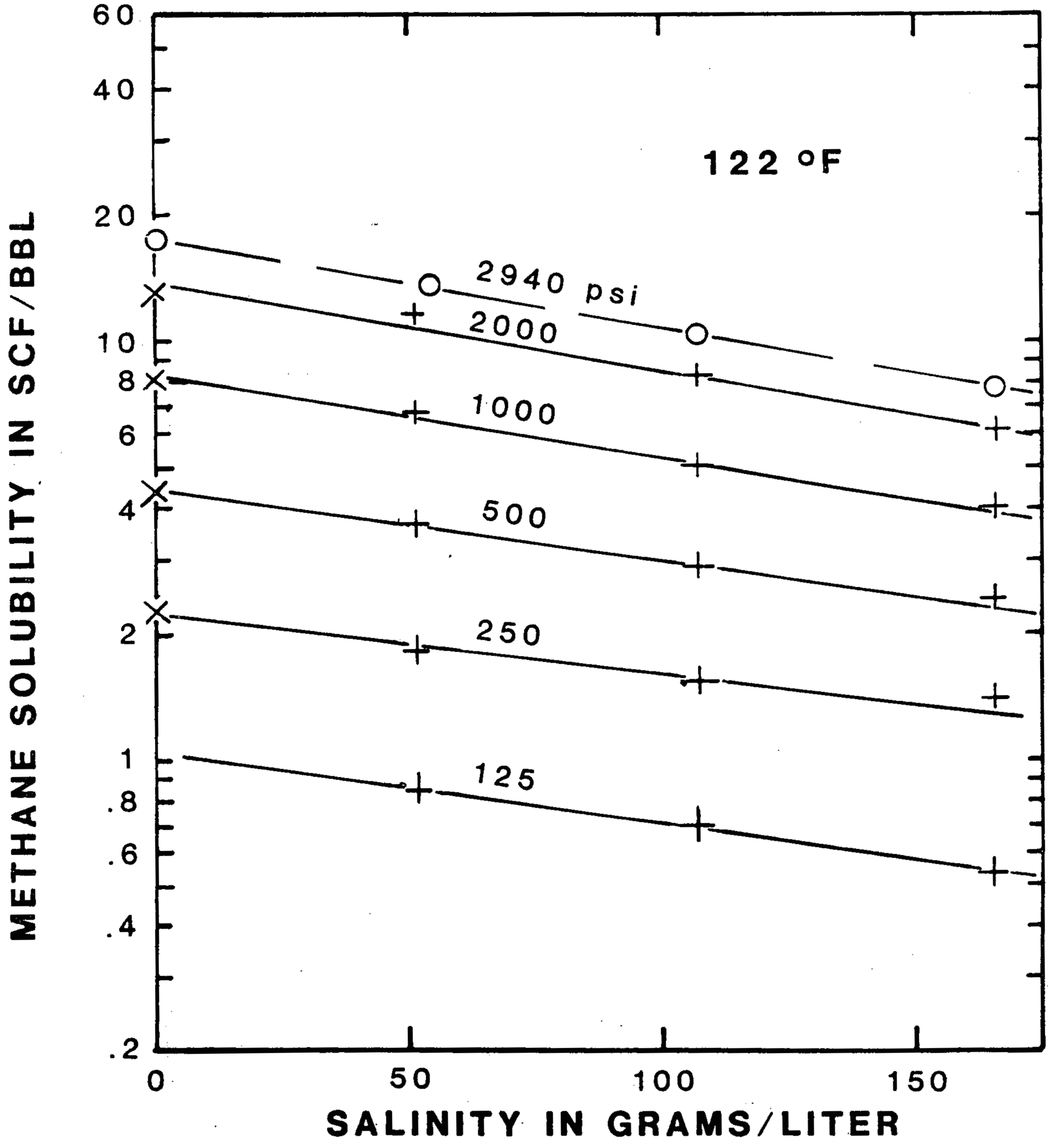


Figure 8 Aqueous methane solubility at 122°F as a function of NaCl concentration at constant (low) pressures. Crosses (+) are data from this study. Circles are data from O'Sullivan and Smith (1970). X's are data from Culbertson and McKetta (1951).

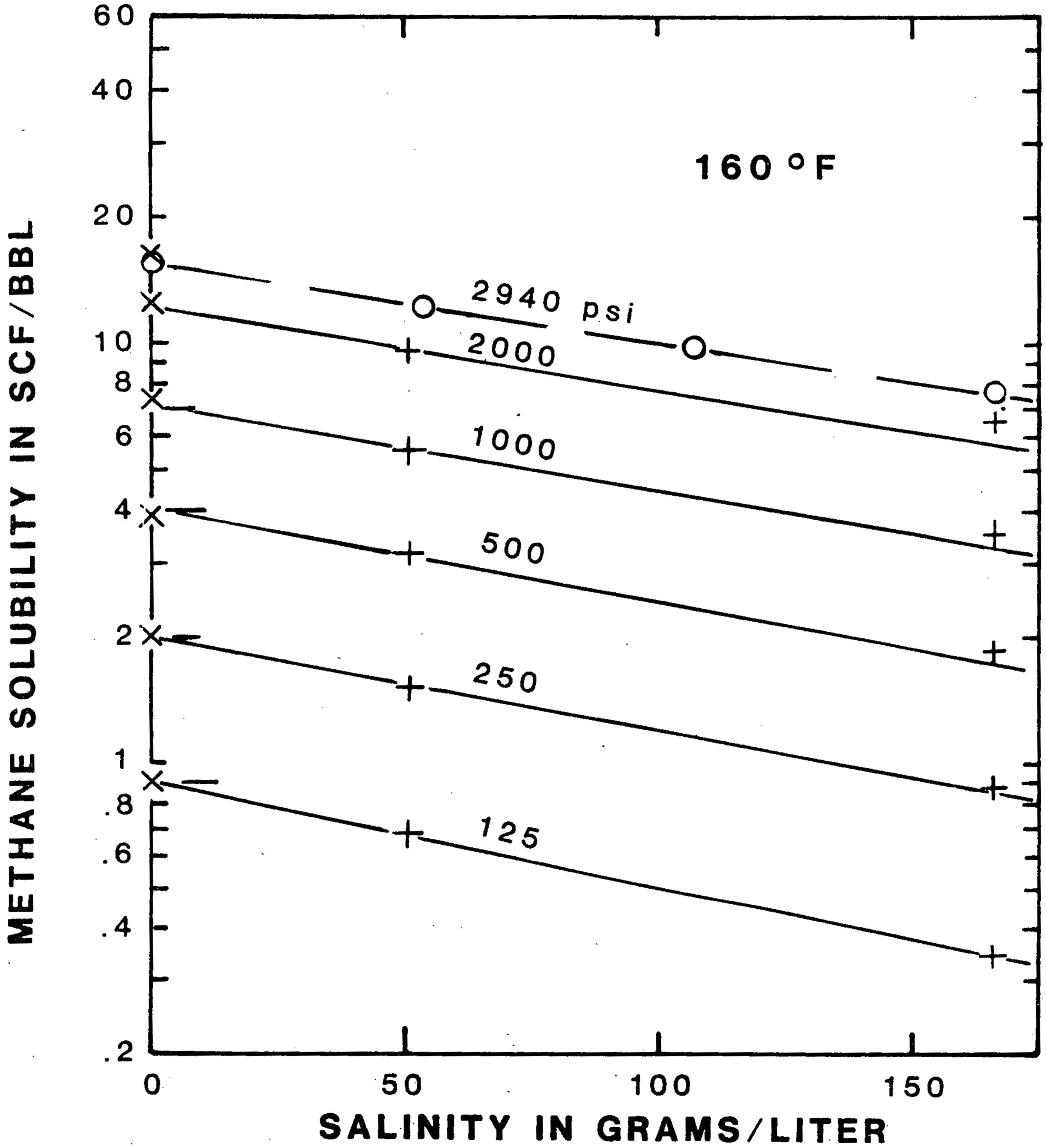


Figure 9 Aqueous methane solubility at 160°F as a function of NaCl concentration at various (low) pressures. Crosses (+) are data from this study. Circles are data from O'Sullivan and Smith (1970). X's are data from Culbertson and McKetta (1951).

Table 6 Graphically interpolated solubility data for methane in NaCl solutions at low pressures and temperatures from the experimental data of Table A-2 (appendix) Values in parenthesis are extrapolated values.

		Methane Solubility in SCF/Bbl			
Temp. °F	Press. psi	Salinity 0 g/liter	Salinity 52 g/liter	Salinity 107 g/liter	Salinity 167 g/liter
77	2,940	22.5	(16.7)	(12.0)	--
	2,000	17.9	13.0	(9.6)	--
	1,000	10.8	8.1	(5.8)	--
	500	6.1	4.7	3.6	--
	250	3.2	2.5	1.9	--
	125	1.6	1.3	1.0	--
122	2,940	17.4	13.7	10.4	8.8
	2,000	10.3	10.8	8.2	6.2
	1,000	8.3	6.5	5.0	4.0
	500	4.4	3.6	2.9	2.4
	250	2.2	1.9	1.5	1.3
	125	(1.0)	0.85	0.69	0.54
160	2,940	15.3	12.5	9.8	7.7
	2,000	12.4	9.8	7.6	5.8
	1,000	7.2	5.6	4.3	3.4
	500	4.0	3.2	2.4	1.8
	250	2.0	1.6	1.2	0.88
	125	0.90	0.68	0.48	0.35

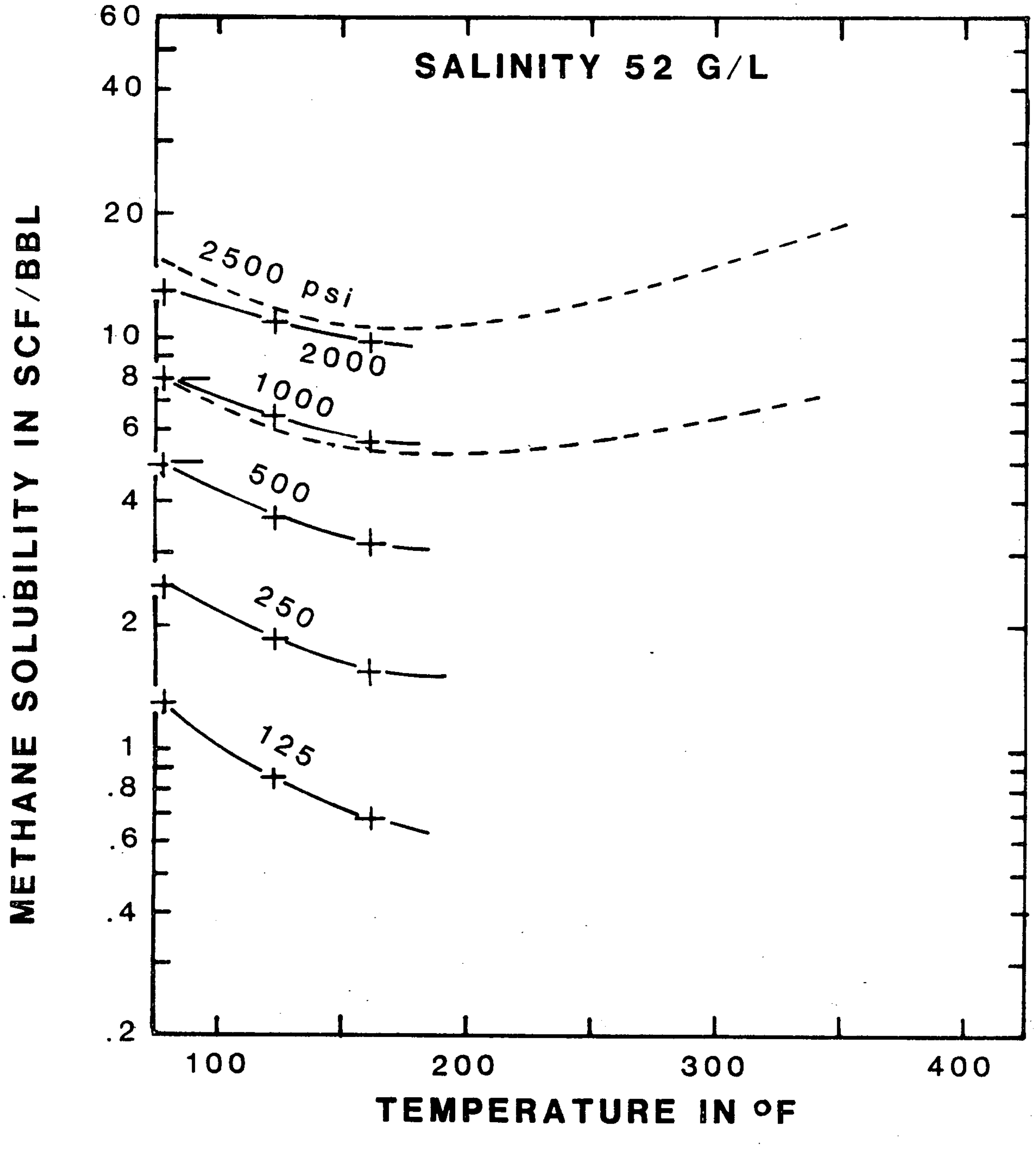


Figure 10 Constant pressure curves (isobars) of low pressure-low temperature aqueous methane solubility versus temperature at constant NaCl salinity of 52 grams/liter. Dashed lines represent methane solubilities calculated from equations by Haas (1978) and Susak and McGee (1980). Crosses are experimental data from this study.

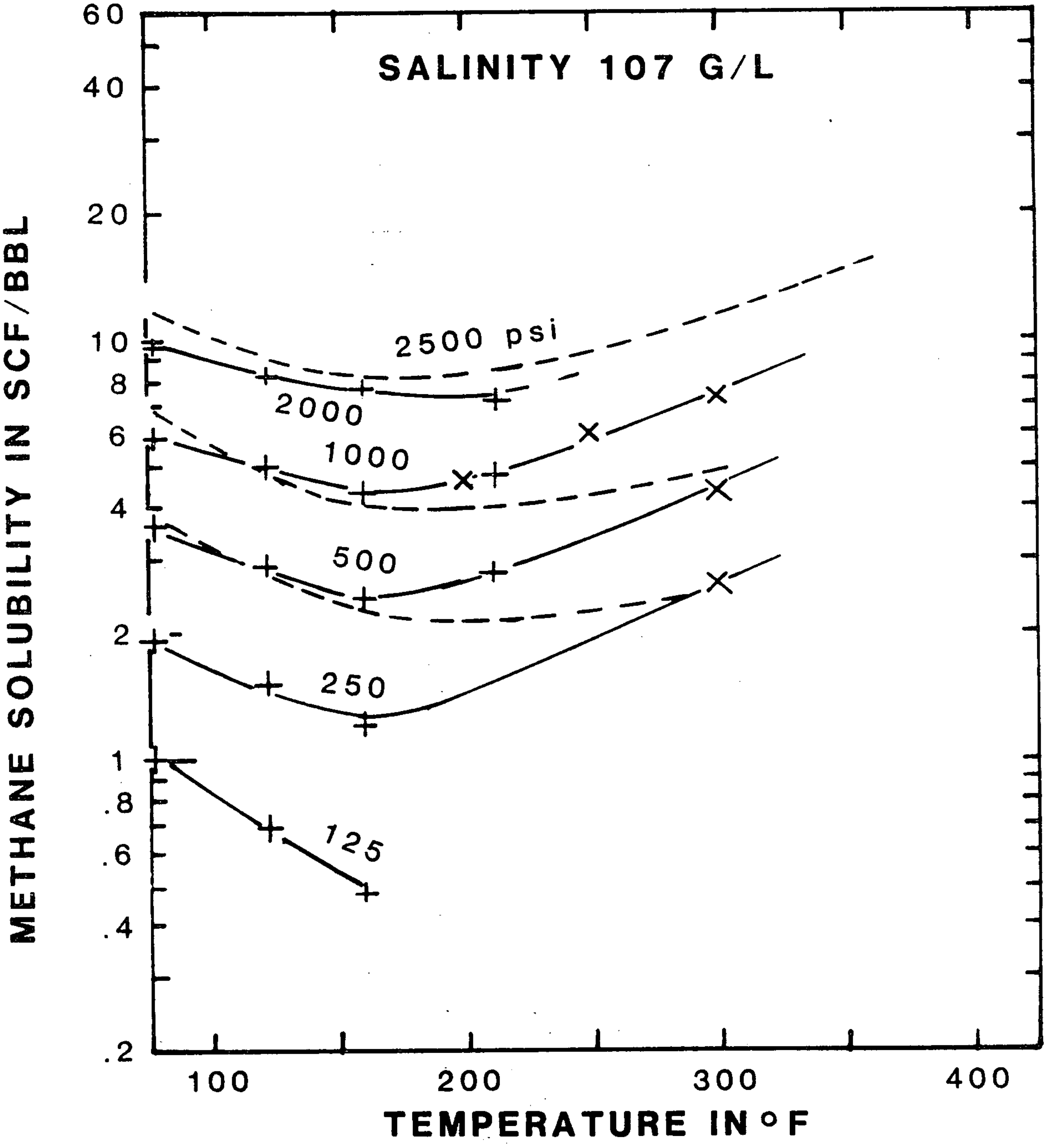


Figure 11 Constant pressure curves (isobars) of low pressure-low temperature aqueous methane solubility versus temperature at constant NaCl salinity of 107 grams/liter. Dashed lines represent methane solubilities calculated from equations by Haas (1978) and Susak and McGee (1980). Crosses are experimental data from this study. X's are Pleasant Bayou data extrapolated to a salinity of 107 g/l using a Setschenow constant of 0.1025.

solutions with a salinity of 107 g/liter. Solubilities calculated from the equation of Susak and McGee (1980) result in values significantly lower than our measured values at temperatures above 175°F but their calculated values agree well with our measured values below that temperature. In general, our low pressure-low temperature laboratory methane solubility data agree well with the data of previous studies and is in sharp disagreement with the values calculated from our equations modeling the high pressure-high temperature data (Table 1). This reinforces our earlier conclusion that these equations are invalid at temperatures below 160°F and at pressures below 3,500 psi.

EFFECTS OF CO_2 ON METHANE SOLUBILITY

Equipment and Experimental Procedures

The equipment used to study the effect of carbon dioxide on methane solubility is the same as previously described. The sample cell and pressure vessel were injected with carbon dioxide-methane mixtures instead of pure methane; however, it was not possible to maintain constant carbon dioxide concentrations. During sampling either methane or a methane-carbon dioxide mixture was injected into the pressure vessel to maintain constant pressure. As the teflon sample cell was permeable to gases, when methane was pumped into the pressure vessel some of it migrated into the sample cell causing a relative decrease in the carbon dioxide concentration. If a methane-carbon dioxide mixture was pumped into the pressure vessel, the result was to raise the amount of carbon dioxide in solution. The ratio between carbon dioxide and methane in the gas phase in contact with solutions was very much less than this ratio in the aqueous solution. One measurement showed that a gas phase with 2 percent carbon dioxide and 98 percent methane was in contact with a solution with a dissolved gas composed of 80 percent carbon dioxide and 20 percent methane. Carbon dioxide is a polar molecule that interacts chemically with water to produce a number of unionized and ionized substances such as H_2CO_3 and HCO_3^-. Thus the aqueous solubility of carbon dioxide is far greater than methane at the same temperature, pressure and salinity. For example according to the data of Todheide and Frank (1963) the solubility of carbon dioxide at 22,5000 psi and 302°F is about 400 SCF/Bbl as compared to 75 SCF/Bbl for methane at the same conditions.

The emphasis of this aspect of the study was to determine the effects that carbon dioxide has on the aqueous solubility of methane. Because of the many variables to be considered (methane concentration, temperature, pressure, salinity and carbon dioxide concentration) a complete study of this system would require a large amount of time. Because of limited time and equipment, we decided to study the system at 302°F at three pressures, two salinities, and a range of aqueous carbon dioxide concentrations (1 to 80 mole percent). A total of 84 data points were taken at 27 experimental conditions (Table A-3).

Analytical Procedures

Gas samples were collected and total gas content quantitatively analyzed as previously described. To minimize the amount of carbon dioxide retained by the aqueous solution at laboratory conditions, a quantity of solid monochloroacetic acid sufficient to reduce the pH of solutions to around 3.0 was placed in the empty sample flask. Since laboratory air contains carbon dioxide, the sample flasks were vacuum evacuated and back filled with nitrogen at laboratory pressure. The ratio of carbon dioxide to methane (expressed as mole percent carbon dioxide) was determined by quantitative gas chromatography. The instrumental conditions for this analysis are described in Appendix B. Gases of known composition (Matheson Corp.) were used to calibrate the gas chromatograph.

Data Presentation

The methane-carbon dioxide aqueous solubility data are given in Table A-3 and in Figures 12 and 13. The aqueous methane solubility data in 0 percent carbon dioxide was obtained from the empirical equations of Table 1.

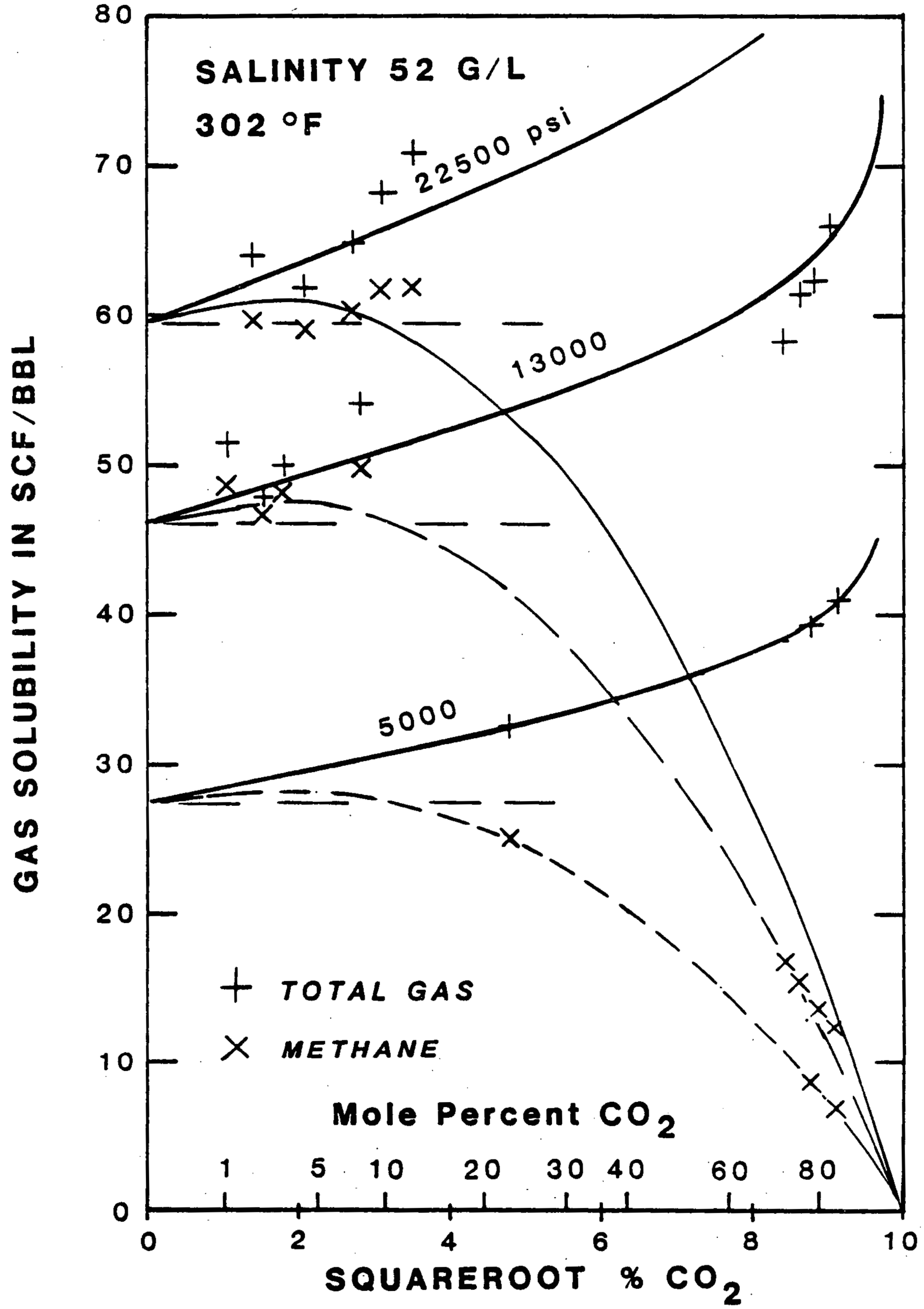


Figure 12 Solubility of methane and total gas (methane and carbon dioxide) as a function of the percentage of CO_2 in gases dissolved in a solution of 52 grams of NaCl per liter at 302°F. Heavy curves represent total gas content of solutions containing both CO_2 and methane at the designated pressure. Dashed horizontal lines are the methane solubility values for CO_2 free brines at the pressure of the joining total gas curves. Thin curves represent methane concentrations in the presence of varying amounts of CO_2 at the pressure of the total gas curve that they join at 0 percent CO_2.

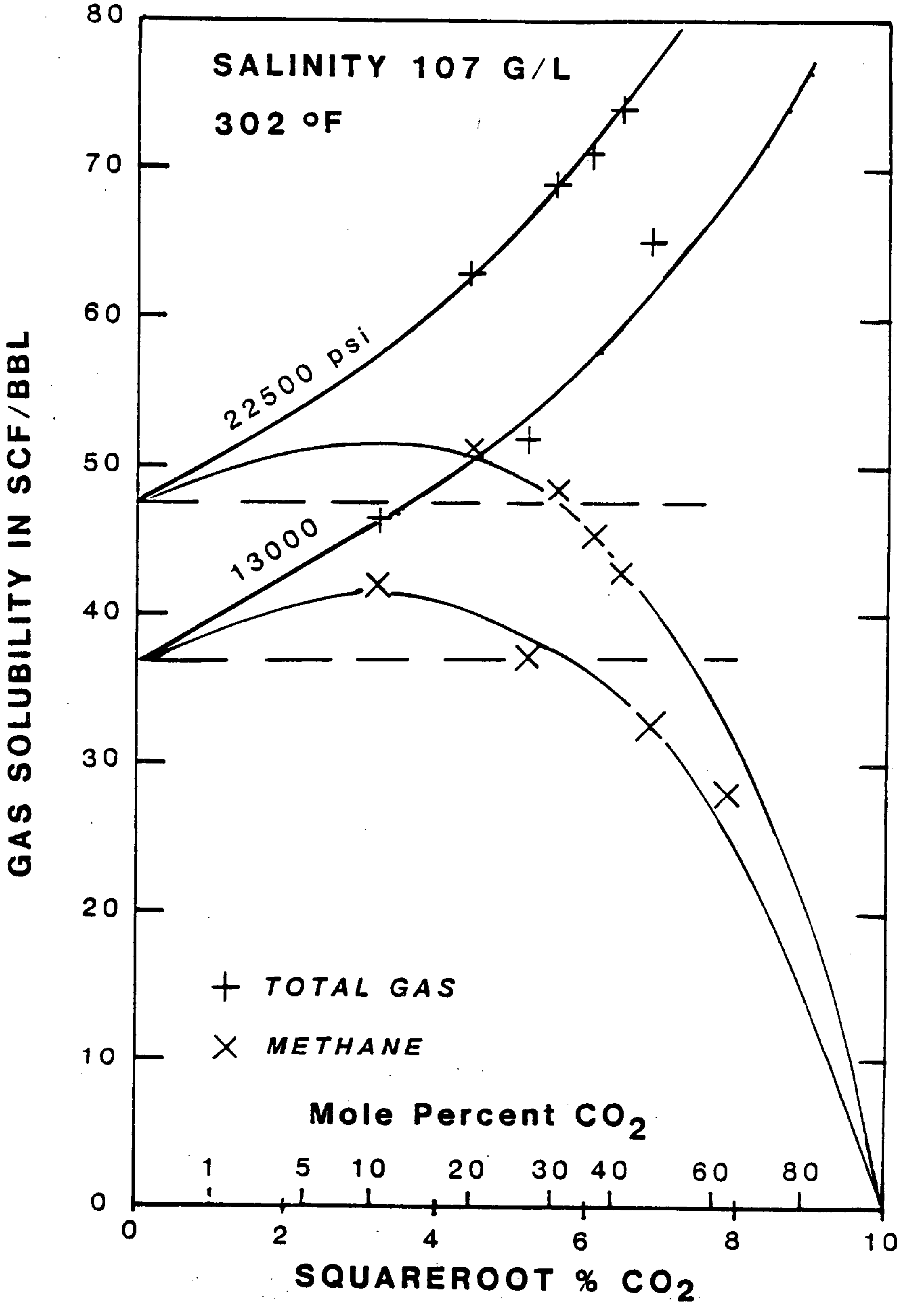


Figure 13 Solubility of methane and total gas (methane and carbon dioxide) as a function of the percentage of CO_2 in gases dissolved in a solution of 107 grams of NaCl per liter at 302°F. Heavy curves represent total gas content of solutions containing both CO_2 and methane at the pressure designated. Dashed horizontal lines are the methane solubility values for CO_2 free brines at the pressure of the joining total gas curves. Thin curves represent methane concentrations in the presence of varying amounts of CO_2 at the pressure of the total gas curve that they join at 0 percent CO_2.

Table 7 Graphically interpolated values for the solubility of methane and carbon dioxide in NaCl solutions at 302°F obtained from the experimental data of Table A-3 (appendix). Salinity is in grams of NaCl per liter of solution.

Pressure psi	Salinity g/liter	Percent CO_2 in dissolved gases 0		5	10	20	30	40	60	80
22,500	52	59.6	A	64.0	65.8	68.5	70.8	73.0	77.5	83.4
			B	60.8	59.2	54.8	49.6	43.8	31.0	16.7
			C	102	99	92	83	73	52	28
13,000	52	46.1	A	49.8	51.1	53.5	54.8	56.2	59.7	64.5
			B	47.3	46.0	42.8	38.4	33.7	23.9	12.9
			C	102	100	93	83	73	52	28
5,000	52	27.6	A	29.7	30.6	32.0	33.2	34.2	36.8	39.8
			B	28.2	27.5	25.6	23.2	20.5	14.7	8.0
			C	102	100	93	84	74	53	29
22,500	107	47.7	A	54.0	57.0	63.0	68.5	73.8	82.5	105
			B	51.3	51.3	50.4	47.9	44.3	33.0	21.0
			C	108	108	106	100	93	69	44
13,000	107	36.9	A	43.2	45.8	50.0	53.5	59.0	67.0	76.0
			B	41.0	41.2	40.0	37.4	35.4	27.0	15.0
			C	111	112	108	101	96	73	41

A	Total gas in SCF/Bbl.
B	Methane in SCF/Bbl.
C	Methane percentage compared to methane at 0 percent CO_2.

Graphically interpolated values from experimental data (Table A-3, appendix) for the solubility of methane at CO_2 concentrations of 5, 10, 20, 30, 40, 60 and 80 mole percent are presented in Table 7.

Several effects are produced by increasing the concentration of CO_2 in solution (Fig. 12 and 13). First, a small smount of CO_2 causes a slight increase in the concentration of methane. At higher CO_2 concentrations CO_2 salts methane out of solution as the total gas concentration approaches the saturation concentration for CO_2. The total gas curves should show a sharp upward inflection in the region of 90 to 95 mole percent CO_2 (See discussion page 42 this text). It is evident (Fig. 12 and 13) that increasing pressure markedly increases total gas solubility. Salinity has a significant influence on the effects of CO_2 on aqueous methane solubility. In a NaCl solution with a salinity of 52 g/liter methane solubility decreases below the value for solutions without CO_2, when CO_2 makes up more than 10 mole percent of the gas in solution. In a NaCl solution with a salinity 107 g/liter this occurs when CO_2 makes up more than 30 mole persent of the gas in solution. At this time, we only have data for 302°F, thus the effect of temperature on the CO_2 effect is not known.

The fact that carbon dioxide in high concentrations suppresses aqueous methane solubility has application to the geopressured resource. As sediment-burial temperatures increase to 360°F, we can expect increasing amounts of carbon dioxide to be dissolved in the sandstone pore waters of the Late Tertiary Gulf Coast sequences. Over the temperature range 212°F to 360°F, the main products from the thermal cracking of kerogen are CO_2, H_2O and N_2 with very little methane or higher molecular-weight hydrocarbons being formed. Only by 360°F (corresponding to vitrinite reflectances of 0.8 to 1.0) are significant amounts of methane thermally generated. The data of Huc and Hunt (1980 - uncorrected log temperatures) in the Tertiary offshore Texas, Brown (1979 - analyses of Pleasant Bayou fine-grained sediments), laboratory experiments of Ishiwatari et al (1977) and unpublished data of L. C. Price (organic thermal diagenisis laboratory experiments) all support this conclusion. Based on the above, as well as on a large amount of other laboratory and field data, we can expect that above 212°F in the Tertiary Gulf Coast the shale (and associated sand) pore-waters will have greater and greater concentrations of carbon dioxide in them, from the progressive thermal breakdown of kerogen with increasing temperature. This expectation is verified by limited field data from the geopressured wells thus far studied (Table 8). There are two reversals (Fairfax-Sutter and Pleasant Bayou) in the trend of increasing mole percent CO_2 and absolute CO_2 solubility (SCF/Bbl) versus increasing temperature. However these two wells have brine concentrations much higher than the other four wells. It is possible that for iso-salinity conditions, the CO_2 solubility data of these two wells would fall within the trend defined by the other four wells. It can be argued that the increase in these CO_2 solubility values is due to the increase in the solubility of CO_2 in water from the increased pressure and temperature of burial. However the data of Takenouchi and Kennedy (1964) suggest that the lower brine concentration waters of Table 8 would be undersaturated with respect to CO_2. The trend in these two CO_2 solubility parameters (Table 8) versus temperature is much more likely due to a supply effect, from the thermal breakdown of kerogen.

Tentative conclusions can be drawn from consideration of the above:

1) The amount of CO_2 dissolved in geopressured brines is much greater than originally suspected. These high values only have become apparent from recent analyses due to the institution (by Phil Randolph of IGT) of acid liberation of CO_2 from the separator brine samples.

Table 8 Mole percent CO_2 of the total dissolved gas (column 3) and as absolute concentration (column 4) dissolved in brines for various geothermal wells. Fairfax-Sutter data from McCoy and Hartsock (1979). All other data, personal communs. of Chris Hayden, Institute of Gas Technology (IGT), Chicago, Ill., July, 1981. Salinity for Pleasant Bayou from Bebout et al (1979). The Fairfax - Sutter, Riddle and Leer CO_2 concentrations were originally reported for non-acid liberation of the separator brine. An additional 3.0 SCF/Bbl of CO_2 was added to the original CO_2 was added to the original CO_2 data for these wells. This correction factor personal commun. of Chris Hayden, Institute of Gas Technology, Chicago, Ill. July 27, 1981.

Well	Temp. °F	Mole % CO_2	CO_2 SCF/Bbl	Salinity mg/L
Leer	260	18.3	7.0	15,000
Fairfax-Sutter	270	18.4	4.8	190,900
Prairie Canal	294	17.0	7.6	44,000
Riddle	300	28.9	15.4	32,000
Pleasant Bayou	308	22.9	6.8	120,000
Crown Zellarbach	327	38.0	14.8	18.200

2) CO_2 in high concentrations in brines can drastically reduce methane solubility. Because of this effect, waters which appear to be undersaturated with respect to methane, actually may be at or above saturation. An example of this is the Riddle well which had a "best guess" gas/water ratio of 50 SCF/Bbl (Personal communication, Chris Hayden, Institute of Gas Technology, Chicago, IL, July 1981) of which 68.9 mole percent of the gas was CH_4 (34.4 SCF/Bbl of CH_4) and 28.8 mole percent of the gas was CO_2. From the equation of Table 1, 34.7 SCF/Bbl of methane would be expected for the reservoir conditions (300°F, 6,627 psi, 32,000 mg/L), and after the CO_2 salting out effect is corrected for (Fig. 6), we could expect 28.8 SCF/Bbl of CH_4. It would appear that there could be a small amount of excess (free) gas in this well. However other wells of Table 8 appear undersaturated after similar calculations are made. It appears that before we have a better knowledge of all the controlling parameters of aqueous methane solubility, no conclusions regarding methane saturation of geopressured brines or the presence or absence of free gas may be conclusively drawn.

3) At the initiation of substantial methane generation in the fine-grained rocks of the Tertiary Gulf Coast (about 360°F), there may be such a high concentration of CO_2 in the sand and shale waters that this methane may immediately form a free gas phase.

EFFECT OF ETHANE ON METHANE SOLUBILITY

The equipment and procedures used to determine the effect of ethane on methane solubility were identical to those used for the CO_2 aspect of the study except that gas mixtures were not used for pressuring the sample vessel. A small amount of ethane was injected into the pressure vessel then additional methane was injected. We prepared known gas mixtures for gas chromatographic standards by vacuum evacuating a flask of known volume and filling it with methane at room temperature and barometric pressure. Ethane gas was then injected into the flask to raise the pressure to a predetermined value above the barometric pressure. The ratio of gases was computed using the ideal gas law, barometric pressure for methane and the measured overpressure for ethane. We encountered some difficulty in getting reproducible results on the gas chromatograph probably due to injection techniques. Analytical conditions are listed in Appendix B.

While the present work is only a beginning, some interesting relationships surfaced based on 26 measurements at 9 different experimental conditions. The original experimental results are given in Table A-4, Appendix. Smoothed and graphically interpolated values from the data of Table A-4 are given in Table 9. Average experimental results obtained at the 9 experimental conditions are illustrated in Figure 14. At low concentrations, ethane salts methane into solution. Above 6 to 8 mole percent ethane of the dissolved gas in solution, methane is strongly salted out by ethane. In contrast to the effect of CO_2 on aqueous methane solubility, the total gas concentration of solutions containing ethane is less than that of methane alone when ethane exceeds

10 mole percent of the gas dissolved in solution. This is a significant departure from the solubility behavior of low molecular weight hydrocarbons observed by Amirajatari and Campbell (1972).

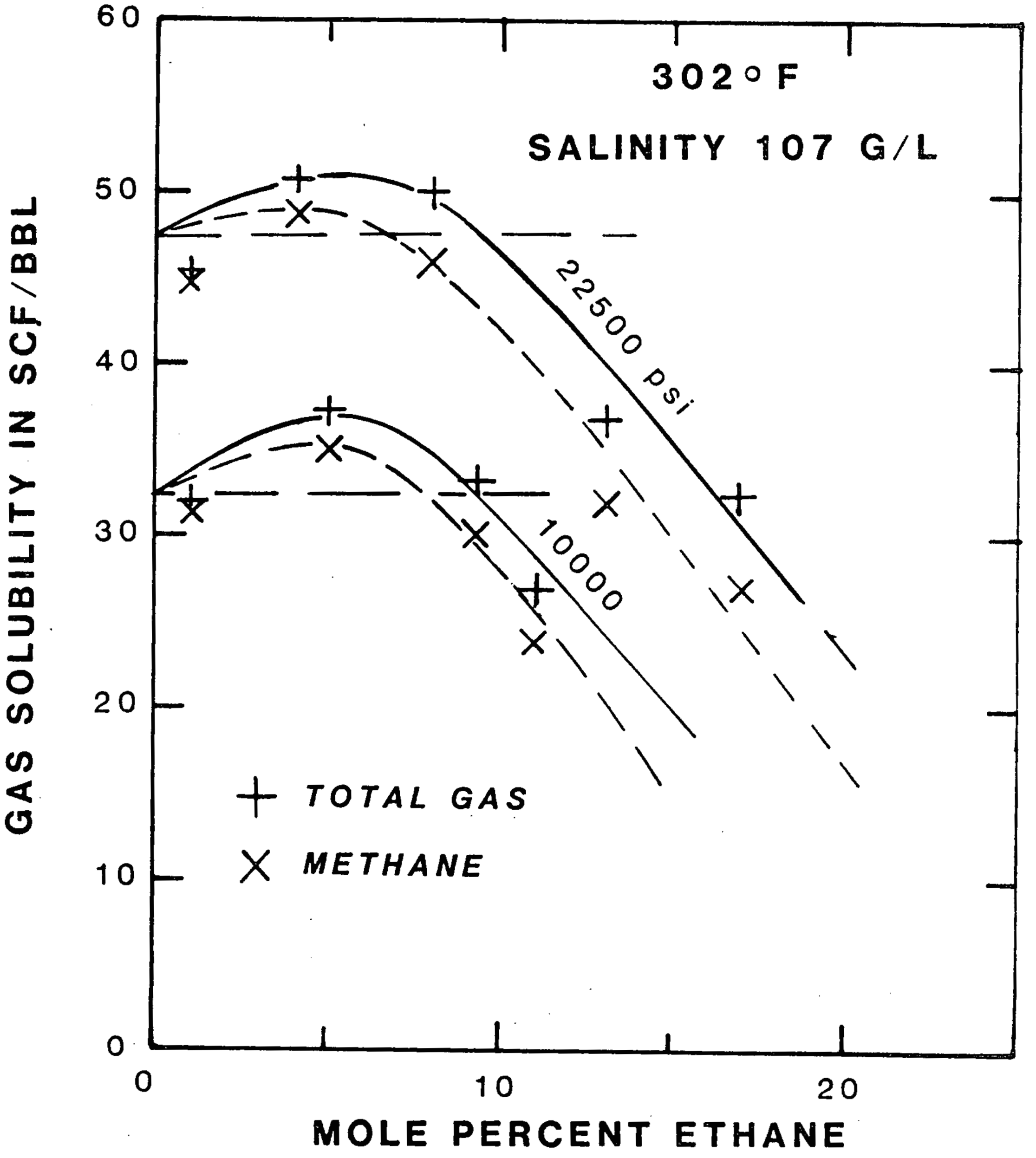


Figure 14 Solubility of methane and total gas (methane and ethane) as a function of the percentage of ethane in gases dissolved in a solution of 107 grams of NaCl per liter at 302°F. Solid curves represent total gas content of solutions containing both methane and ethane. Dashed horizontal lines are the methane solubility values for ethane free brines at the pressure of the joining total gas curve. Short dashed curves represent methane concentrations in the presence of varying amounts ao ethane at the pressure of the total gas curve that they join at 0 percent ethane.

Table 9 Smoothed values for the solubility of methane and total gas (methane and ethane) at 302°F in aqueous NaCl solutions at a salinity of 107 g/liter.

	Pressure	Percent ethane in dissolved gas							
	psi	0	2.5	5.0	7.5	10.0	12.5	15.0	20.0
Total Gas	22,500	47.7	50.0	51.0	50.0	46.0	41.5	35.0	21.0
Methane		47.7	48.8	48.4	46.2	41.4	36.3	29.8	16.6
Total Gas	10,000	32.3	35.5	37.0	35.5	31.0	25.5	19.5	--
Methane		32.3	34.6	35.2	32.8	27.9	22.3	16.6	--

SOLUBILITY OF CRUDE OIL AND WATER IN METHANE

Introduction

The following is a brief description of a research study on the solubility of crude oil in methane gas in the presence of water. A detailed report is presented in Appendix C of this report.

Equipment

Equipment for this part of the study was supplied by the U.S. Geological Survey. A number of stainless steel pressure vessels were used without liners. The vessels had pressure connections at both ends so that fluids or gas could be pumped into or out of the vessel. These vessels were placed in rocking furnaces so that they could be rocked to speed up the attainment of equilibrium between oil, water and gas.

Experimental Procedures

Pressure vessels were loaded and heated to the experimental temperature. Methane, water and oil were added according to the planned experiment. Pressure could be established by pumping gas or water into the vessel. The vessel was then rocked for a period of time and then set vertical to allow the gas, oil and water to separate into layers. The gas layer was then sampled in large round bottom flasks similar to the procedure used for sampling methane saturated aqueous solutions. In contrast, however, gas samples expand greatly, therefore large flasks are needed to avoid blowing them up. Pressure was maintained in the pressure vessel by pumping distilled water into the bottom of the vessel. Thus repeated samples could be taken until the gas phase was depleted. Then methane could be pumped into the vessel and the experiment continued. In this way the solubilities of crude oil and water in methane gas were determined at 50, 100, 150, 200 and 250°C as a function of pressure. Experiments were generally performed at high pressure initially, then after a series of samples were taken at that pressure that showed good agreement, the pressure was then reduced and another series of samples taken. Experimental samples consisted of crude oil, the asphaltic fraction of crude oil and tar.

Experimental Results

The following description is a brief summary of the experimental results of the experimental studies. A detailed description is given in Appendix C of this report.

Experimental studies conducted during this project include the following:

1) Solubility of crude oil and water in a pure methane gas phase as a function of pressure until co-solubility was reached. Co-solubility is attained when the crude oil and methane gas cease to exist as separate phases. At low pressure, the methane gas dissolves some crude oil and the crude oil dissolves some methane gas. As pressure increases, the solubility of each increases in the other until they become equal at some high pressure. A total of 60 data points were obtained at various pressures at 50, 100, 150, 200 and 250°C. In general, the pressure at which co-solubility is reached decreases with increasing temperature. The results suggest that methane gas could dissolve and carry a large amount of crude oil from deep source areas (high temperature and pressure conditions) up to shallower sands where the crude oil could exolve from the gas at conditions of lower temperature and pressure.

2) Further experiments of the above type were conducted on an asphaltic fraction of the crude oil. This material has a boiling point below

240°C at 6 microns pressure and corresponds roughly to C_{38} to C_{50} carbon numbers. Twenty-eight data points were taken on this material at various pressures at temperatures of 50, 150, and 250°C.

3) The solubility of tar was also determined at 250°C as a function of pressure by eight data points. This material had a boiling point above 266°C at 6 microns pressure.

4) The effect of carbon dioxide on the solubility of crude oil in methane was briefly examined.

In the above studies, samples of the solute crude oil, asphalt and tar fractions were taken for qualitative analysis. Gas chromatography was performed on over 50 crude oil samples. The purpose was to examine the changes in the carbon number distribution of the solute crude oil as a function of pressure and temperature. Compound class analysis (saturated and aromatic hydrocarbons and N-S-O bearing compounds) was performed on the C_{15}+ fraction of about 25 of the crude oil solute samples. The purpose was to examine the change in compound class distribution as a function of pressure and temperature. Compound class distribution analyses have been performed on solute samples of the asphalt samples for the 50 and 150°C runs. The purpose was to determine changes in the distribution of saturated and aromatic hydrocarbons, N-S-O bearing compounds, and asphaltenes as a function of pressure and temperature.

DISCUSSION

The solubility data for methane in aqueous NaCl solutions provides a large amount of basic data at this time. There are still remaining questions to be answered before it will be possible, at least in some situations, to conclude whether particular sandstone pore waters are saturated with methane or not. These questions are:

1) The effect of carbon dioxide.
2) The effect of brine composition.
3) The effect of other dissolved higher molecular weight hydrocarbons.

The effect of carbon dioxide is complex. Salinity appears to influence the point at which additional carbon dioxide suppresses aqueous methane solubility. Carbon dioxide is more effective in salting out methane from solution at low salinities than at high salinities.

The effect of brine composition is almost unknown and since sandstone (and shale) pore waters are chemically complex, this effect could have a strong control on aqueous methane solubility in natural brines. We made a limited study of methane solubility in brine from the Pleasant Bayou No. 2 well (Table 10, Column 3) and compared the experimental data to methane solubilities calculated from the empirical equation (Table 10, Column 4). The calculated solubilities agree with the experimentally measured solubilities within the uncertainty in the data, however there is a slight tendency toward lower solubilities in Pleasant Bayou brine. There are several problems with this comparison. It should be noted that when we received them, the Pleasant Bayou brines contained a reddish-brown precipitate (probably iron oxide) which contained to form with time, so that this brine certainly had changed from its original composition.

Table 10. Solubility of methane in Pleasant Bayou brine at various temperatures and pressures, as well as calculated values (Table 1) for an equivalent NaCl concentration (130,000 mg/l).

[NA, not applicable]

Temperature °F	Pressure psi	Experimental solubility SCF/Bbl	Calculated solubility SCF/Bbl
201.6	12,016	20.4	21.9
196.3	9,126	19.8	18.8
198.2	5,076	13.4	14.0
198.2	2,021	8.3	8.5
198.7	1,059	4.2	NA
248.1	12,024	24.8	25.8
248.0	11,950	24.1	25.7
248.0	11,893	25.2	25.7
249.8	9,083	22.3	22.5
250.3	5,018	17.5	16.5
248.9	2,060	9.9	10.0
250.3	2,002	9.4	9.9
250.3	1,001	5.7	NA
301.1	12,300	29.3	32.6
301.1	12,040	27.2	32.2
302.8	9,040	25.0	28.0
299.5	5,076	19.6	20.1
301.1	2,002	12.2	11.9
299.7	1,004	7.7	NA
301.1	507	3.9	NA
301.3	260	3.4	NA
300.2	104	1.3	NA

A question of considerable importance is the role of dissolved carbonate species in solution as compared to dissolved carbon dioxide gas which has a significantly greater effect on methane solubility than does an equivalent concentration of ionic species. Should HCO_3^- and other ionic or neutral dissolved substances be treated or considered as equivalent CO_2 gas or as an increase in salinity? Also the relative percentage of each ionic (or neutral) species will change with changes in pH, salinity, pressure and temperature. We have no insight into the mechanics of this system yet.

The presence of higher molecular weight hydrocarbons probably has a significant effect on the solubility of methane in brines based on the behavior of similar systems (Price, 1982). While methane is the dominant gas in natural brines other hydrocarbon gases are also present. The cumulative effect of these probably is to lower the solubility of methane in natural brines. Although there is great uncertainty about the application of the results of our methane solubility studies to determine if test well brines are saturated with methane, these data have revealed problem areas that need further research.

Data for a number of test wells from the geopressured program are given in Table 11. Sources of data for this compilation include correspondence from Mr. Keith Westhusing (formerly with the Department of Energy in Houston), a report by Mr. Philip Randolf (presented at the 5th Geopressured-Geothermal Conference) and final reports supplied by Eaton Operating Company. There is uncertainty in the values for CO_2 percentage and total measured gas in this table. Column six is the quantity of methane that saturated brines should contain at the conditions of temperature, pressure and salinity for the reservoir of each well. These saturation values were calculated from Table 1. The measured

Table 11 Comparison of analyses of geopressured brines (observed aqueous methane solubilities) with calculated solubility data for methane in aqueous NaCl solutions. Numbers in well designation column are references.

Well designation (and references)	Physical conditions	Type of gases	Percent of gas	Gas measured SCF/Bbl	Gas calc. equation Table 1	Percent saturation of brine
Edna DelCambre	238°F	All gases	100	22		
No. 1	11,012 psi	CH_4	92.8	20.4	25.4	80-88
Sand No. 3	113.3 g/liter	C_2H_6	4	0.9		
(1)		CO_2	1	0.2		
		Balance	2.2	0.5		
Pleasant Bayou	280°F	All gases	100	24.7		
No. 2	11,400 psi	CH_4	85.5	21.1	27.9	76-82
(1)	135 g/liter	C_2H_6	3.1	0.8		
		CO_2	11.3	2.5		
		Balance	.1	0.3		
Fairfax	270°F	All gases	100	22.8		
Foster Sutter	12,230 psi	CH_4	89.6	20.4	22.2	92-100
No. 2	191 g/liter	C_2H_6	1.8	0.4		
(1)		CO_2	7.9	1.8		
		Balance	0.7	0.2		
Beulah Simon	285°F	All gases	100	24.3		
Southport	13,100 psi	CH_4	91	22.1	35.3	63-69
Exploration No. 2	100 g/liter	C_2H_6	2.3	0.6		
(1)		CO_2	5.1	1.2		
		Balance	1.6	0.4		
Crown Zellerbach	330°F	All gases	100	34.7		
Well No. 2	10,114 psi	CH_4	66	22.8	50.1	
lower zone	31.7 g/liter	C_2H_6	3.4	1.2	x.75=	
(2)(6)		CO_2	29.4	10.2	37.5	61-66
		Balance	1.2			

Table 11 (continued)

Well designation (and references)	Physical conditions	Type of gases	Percent of gas	Gas measured SCF/Bbl	Gas calc. equation Table 1	Percent saturation of brine
Prairie Canal	294°F	All gases	100	42.1		
Well No. 1	12,942 psi	CH_4	84	35.4	45.9	
(3)(6)	43.4 g/liter	C_2H_6	2.3	1.0	x.93=	
		CO_2	13.5	5.7	42.7	82.9-
		Balance	0.2	0.1		88
Saldana	300°F	All gases	100	49.2		
Well No. 2	6,627 psi	CH_4	79.2	39	37.5	
(4)(6)	12.8 g/liter	C_2H_6	3.9	1.9	x.83=	
		CO_2	16.5	8.1	31	130+
		Balance	0.4	.2		
		prob. more CO_2				
P. R. Girouard	274°F	All gases	100	40		
Well No. 1	13,203	CH_4	91.3	36.5	46.1	
(5)(6)	23.5 g/liter	C_2H_6	2.4	1.0	x.96=	
		CO_2	6.0+	2.4	44.2	82-
		Balance	0.3	0.1		87
Lear G. M.	260°F	All gases	100	35		
Koelemay	9,449 psi	CH_4	83.9	29.4	38.1	
Well No. 1	15.0 g/liter	C_2H_6	4.7	1.6	x.94=	
(6)		CO_2	7.5+	2.6	35.7	82-
		Balance				88
Sweet Lake	299°F	All gases	100	23.7		
5th Sand.	12,053 psi	CH_4	88	20.9	27.7	
(7)	165 g/liter	C_2H_6	1.7	0.4		
		CO_2	9.9	2.3		75-
		Balance	0.4	0.1		83

References: (1) Letter from Keith Westhusing; (2-5) Eaton Operating Company (1981); (2) Final Report Crown Zellerbach Well No. 2; (3) Final Report Prairie Canal Well No. 1; (4) Final Report Saldana Well No. 2; (5) Final Report Girouard Well No. 1; (6) Raymond (1981); (7) Karkalits and Hankins (1981).

quantity of methane (Column 5) exceeds the calculated methane solubility in only one well. Part of the produced gas of this well was thought to be from a free gas phase. All other well brines contain less methane than the concentration predicted from the equations in Table 1. In some of these wells, the gas concentration reported is from "flare line analysis" and some additional gases obviously remained in solution. Under most operating conditions only about 2 SCF of methane should remain in solution, however in some cases considerable CO_2 could remain in solution (Caption, Table 8).

The effect of CO_2 in suppressing methane solubility would not seem to be such a large factor for high salinity wells such as the Edna DelCambre, Pleasant Bayou, Fairfax Foster, Beulah Simon, and Sweet Lake. Among these wells the Fairfax Foster seems to be closest to saturation. While the Beulah Simon well would seem to be well below saturation. Some of the low salinity wells have high carbon dioxide contents (especially the Crown Zellerbach and Saldana wells). Extrapolation of the data for the CO_2 effect on methane solubility at low salinities suggests that the saturation concentration of methane would be 75 to 80 percent of the solubility in CO_2 free solutions[1]. Even correcting for the effect results in a predicted CH_4 content that exceeds the measured methane content in these geopressure well tests. Only for the Saldana well does measured methane exceed calculated.

Most of the wells of Table 11 have a measured methane concentration between 80 and 90 percent of the predicted methane concentration. Either these wells are slightly undersaturated with methane or, if they are indeed saturated, some other unknown factor(s) must be reducing the observed methane concentration

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[1] A tentative procedure for estimating the effect of CO_2 on methane solubility is given in Appendix D.

very uniformly below the predicted value. In all wells the ethane concentration is below that needed to suppress methane concentration.

There are too many unknowns at this time, to be able to conclude if these well brines are methane saturated or not. Ethane plus CO_2 may have a combined effect on the suppression of methane solubility especially at low salinities. The effect produced by dissolved higher hydrocarbons also is probably significant. Also the roles of solution composition, especially of the carbonate species, are not understood.

Correlations between results of laboratory solubility measurements and the results of well tests need much closer co-ordination. Flare line gas flows give values that depend on separator pressure, temperature and fluid composition and dynamic solution kinetics. Solubility data should be compared on the basis of total gas content of the well brines with appropriate data about gas composition. This is not an easy task considering the high flow rates and the dynamics of a well under test conditions. Some of the uncertainties of test well results is indicated by the poor agreement between some well data in Tables 8 and 11 supplied by different sources.

RECOMMENDATIONS

1. The effect of carbon dioxide on the aqueous solubility of methane should be examined further to determine the effect of temperature variation on this system.
2. Direct reconstitution studies should be carried out using brines from the various geothermal tests as they become available, to ascertain if the brines are methane saturated in nature. Carbon dioxide should be progressively added to these systems and samples taken and analyzed for methane saturation up to the carbon dioxide level found in nature for that sample.
3. Low temperature-low pressure measurements of aqueous methane solubility should not be examined further unless there is an important (currently unknown) engineering need for such data.
4. Because the empirical equations developed in this paper to calculate aqueous methane solubility apparently can be extrapolated to 601°F at pressures above 5,000 psi, there appears to be no need to take aqueous methane solubility data above 464°F.
5. Further critical research should focus on the effects of ionic species, especially the effects of CO_2 dissociation, on aqueous methane solubility.
6. The effect of higher molecular weight hydrocarbons (C_6+) on methane solubility must be examined to fully understand the system.

CONCLUSIONS

1) The previously reported aqueous methane solubility data of Blount et al (1979) are incorrect due to an error in the experimental procedure.
2) New data as well as the older corrected data has been modeled into an equation which computes aqueous methane solubilities over a broad range of conditions: 160° to 464°F at pressures above 3,500 psi, 464° to 601°F at pressures above 5,000 psi, all for salinities of 0 to 25 weight percent NaCl.
3) Calculated data from this study by in large agree with previous experimental work within the limits of the equation of this study.
4) Calculated data from this study do not agree with the high temperature (626°, 662°, and 690°F isotherms) of Sultanov et al (1972). This agrees with an earlier observation (Price, 1979) that the high temperature data of Sultanov et al (1972) appear to be too high and in error.
5) The results of low temperature low pressure methane solubility determinations of this study agree very well with the previous results of Culbertson and McKetta (1950), Duffy et al (1961) and O'Sullivan and Smith (1970).
6) The calculated data of this study do not agree with the calculated data of Haas (1978) or Susak and McGee (1980). This is not surprising as the salting out coefficient they assumed (0.129) is not in agreement with our experimentally measured value: 0.1025. Also a large part of their data base was made up of the data of Sultanov et al (1972), the higher temperature portion of which we find questionable.
7) The effect that brine composition has on the aqueous solubility of methane is an unknown.
8) At 300°F and a salinity of 52g NaCl/liter, increasing CO_2 concentration up to 10 mole percent of the dissolved gas in solution enhances aqueous methane

solubility. When CO_2 makes up more than 10 mole percent of the dissolved gas in solution, methane solubility is decreased by increasing CO_2 content. This effect is considerable at CO_2 contents of 40 mole percent or greater. The effect of increasing salinity to 107 g/liter is to permit up to 30 mole percent CO_2 in the dissolved gas before additional CO_2 causes a suppression of methane solubility to a value below that observed in the absence of CO_2.

9) In Tertiary Gulf Coast sediments it is expected that carbon dioxide will make up an increasing amount of the dissolved gas in sand and shale pore waters (greater than 40 mole percent) with increasing depth of burial from the early diagenesis of the kerogen in shales.

10) In theory, at the onset of significant methane generation (burial temperatures of about 360°F) Gulf Coast sand and shale pore waters could have such high concentrations of carbon dioxide, that the newly generated methane would immediately form a free gas phase.

11) Comparison of our calculated methane solubility data with observed (but questionable) methane concentration values from nature shows that most geothermal-geopressured brines contain between 80 and 90 percent of the predicted methane concentration. Only the Saldana well contained more methane than the predicted value.

12) At this point we do not understand the controlling parameters (other than pressure, temperature and salinity) of aqueous methane solubility well enough to be able to ascertain if Gulf Coast geopressured brines are saturated or undersaturated with respect to methane. Thus from solubility considerations alone, we are not able to say if we are dealing with a free gas phase or not at the temperature and pressure conditions of the present and past DOE geopressured tests. A tighter cooperation between laboratory and field studies will be necessary in the future to speak to this problem.

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APPENDICES

A. Tables of experimental data.

   1. Original empirical data of aqueous methane solubility as determined in this study.

   2. Original empirical data for the solubility of methane in NaCl solutions at low temperature and pressure.

   3. Original empirical data for the solubility of methane and carbon dioxide at 302°F in aqueous NaCl solutions.

   4. Original empirical data for the solubility of methane and ethane at 302°F in aqueous NaCl solutions at a salinity of 107 g/liter.

B. Gas chromatographic analysis conditions.

C. Results of study of petroleum solubility in methane.

D. Estimation of effect of CO_2 on methane solubility.

Table A-1

ORIGINAL EMPIRICAL DATA OF AQUEOUS METHANE SOLUBILITY AS DETERMINED IN THIS STUDY

NUMBER	TDEGF	PSI	SAL	SCF
1.0	212.4	22364.9	.0	48.8
2.0	212.4	22364.9	.0	49.8
3.0	212.4	22335.9	.0	52.5
4.0	211.1	19101.5	.0	48.7
5.0	211.1	19101.5	.0	47.7
6.0	211.1	19101.5	.0	48.0
7.0	211.1	19101.5	.0	49.8
8.0	211.1	19101.5	.0	49.3
9.0	212.4	16026.7	.0	43.4
10.0	212.4	16026.7	.0	43.6
11.0	212.4	16084.7	.0	45.5
12.0	212.4	16084.7	.0	43.2
13.0	212.0	16128.2	.0	44.4
14.0	212.0	16128.2	.0	45.2
15.0	213.8	13169.4	.0	40.9
16.0	213.8	13169.4	.0	41.0
17.0	212.0	10239.7	.0	35.4
18.0	212.0	10239.7	.0	35.5
19.0	212.4	7106.9	.0	30.5
20.0	212.4	5003.8	.0	25.8
21.0	212.4	5003.8	.0	24.3
22.0	212.4	3524.4	.0	19.7
23.0	212.4	3524.4	.0	18.7
24.0	212.4	2175.6	.0	14.8
25.0	212.4	2175.6	.0	15.0
26.0	213.4	22538.9	3.2	48.5
27.0	213.4	19000.0	3.2	47.9
28.0	213.4	19000.0	3.2	46.2
29.0	212.4	16055.7	3.2	42.2
30.0	212.4	16055.7	3.2	43.0
31.0	212.4	13227.5	3.2	39.1
32.0	212.4	13227.5	3.2	39.2
33.0	212.4	10007.6	3.2	33.8
34.0	212.4	10007.6	3.2	32.0
35.0	213.4	7063.4	3.2	30.4
36.0	213.4	5105.3	3.2	23.6
37.0	213.4	5105.3	3.2	23.6
38.0	212.9	3640.5	3.2	18.9
39.0	212.9	3640.5	3.2	20.1
40.0	212.9	2146.6	3.2	16.6
41.0	212.9	2146.6	3.2	13.7
42.0	212.9	2219.1	3.2	14.2
43.0	212.9	2219.1	3.2	15.1
44.0	212.4	19420.6	51.1	38.0
45.0	212.4	19420.6	51.1	35.3
46.0	212.0	19420.6	51.1	35.9
47.0	212.0	19420.6	51.1	37.6
48.0	212.0	16026.7	51.1	33.4
49.0	212.0	13111.4	51.1	32.3
50.0	212.0	13111.4	51.1	32.6

Table A-1

ORIGINAL EMPIRICAL DATA OF AQUEOUS METHANE SOLUBILITY AS DETERMINED IN THIS STUDY

NUMBER	TDEGF	PSI	SAL	SCF
51.0	212.0	13111.4	51.1	32.9
52.0	211.5	10181.7	51.1	28.5
53.0	211.5	10181.7	51.1	26.1
54.0	211.1	7222.9	51.1	23.9
55.0	211.1	7222.9	51.1	24.1
56.0	212.0	5032.8	51.1	20.6
57.0	212.0	5032.8	51.1	20.7
58.0	212.0	3596.9	51.1	17.0
59.0	212.0	3596.9	51.1	17.4
60.0	213.8	16186.2	106.0	28.7
61.0	213.8	13213.0	106.0	25.4
62.0	213.8	13213.0	106.0	25.7
63.0	212.0	22509.9	106.5	34.4
64.0	212.0	22509.9	106.5	33.8
65.0	212.0	22509.9	106.5	34.1
66.0	212.0	22509.9	106.5	33.8
67.0	212.0	22393.9	106.5	34.6
68.0	212.0	22393.9	106.5	34.9
69.0	212.9	19043.5	106.5	32.1
70.0	212.9	19043.5	106.5	31.7
71.0	212.4	15359.5	106.5	29.3
72.0	212.4	15359.5	106.5	30.0
73.0	212.9	15272.5	106.5	28.6
74.0	212.9	15272.5	106.5	29.4
75.0	212.9	13242.0	106.5	25.8
76.0	212.9	13242.0	106.5	26.1
77.0	212.9	12908.4	106.5	26.3
78.0	212.9	12908.4	106.5	27.1
79.0	212.0	10181.7	106.5	24.1
80.0	212.0	10181.7	106.5	23.7
81.0	212.0	10094.6	106.5	21.8
82.0	212.0	10094.6	106.5	22.7
83.0	212.9	7164.9	106.5	20.6
84.0	212.9	7164.9	106.5	18.8
85.0	212.9	7077.9	106.5	19.6
86.0	212.9	7077.9	106.5	19.9
87.0	212.4	5163.4	104.0	18.2
88.0	212.4	5163.4	104.0	17.5
89.0	212.4	5119.8	105.0	15.8
90.0	212.4	5119.8	105.0	18.0
91.0	212.9	3669.5	105.0	13.7
92.0	212.0	3698.5	105.0	14.3
93.0	212.4	3640.5	105.0	13.4
94.0	212.4	3640.5	105.0	13.0
95.0	212.0	2059.5	105.0	9.7
96.0	212.0	2059.5	105.0	9.1
97.0	211.5	21842.7	166.3	26.8
98.0	211.5	21842.7	166.3	26.1
99.0	211.1	22103.8	166.3	27.3
100.0	211.1	19087.0	166.3	24.5

Table A-1

ORIGINAL EMPIRICAL DATA OF AQUEOUS METHANE SOLUBILITY AS DETERMINED IN THIS STUDY

NUMBER	TDEGF	PSI	SAL	SCF
101.0	211.1	19087.0	166.3	24.4
102.0	210.6	16157.2	166.3	23.1
103.0	211.5	13314.5	166.3	20.3
104.0	211.5	13314.5	166.3	20.7
105.0	211.5	13198.5	163.5	22.6
106.0	211.5	13198.5	163.5	20.5
107.0	211.5	13372.5	163.5	22.6
108.0	211.5	13372.5	163.5	21.3
109.0	210.6	9993.1	164.6	17.6
110.0	210.6	9993.1	164.6	18.1
111.0	212.0	9833.6	163.5	20.5
112.0	212.0	9833.6	163.5	17.6
113.0	212.4	9935.1	163.5	17.5
114.0	212.4	9935.1	163.5	19.8
115.0	210.9	7208.4	164.6	15.4
116.0	209.8	7106.9	163.5	17.3
117.0	209.8	7106.9	163.5	16.6
118.0	209.8	7106.9	163.5	17.0
119.0	209.8	7106.9	163.5	17.0
120.0	211.5	7034.3	163.5	16.4
121.0	211.5	7034.3	163.5	16.0
122.0	211.5	5018.3	163.5	14.5
123.0	211.5	5018.3	163.5	14.5
124.0	210.9	3205.3	163.5	9.8
125.0	210.9	3205.3	163.5	9.7
126.0	211.1	1914.5	163.5	8.6
127.0	211.1	1914.5	163.5	8.5
128.0	211.1	1972.5	163.5	8.6
129.0	211.1	1972.5	163.5	8.6
130.0	211.5	22466.4	227.6	17.9
131.0	211.5	22466.4	227.6	18.6
132.0	211.5	22466.4	227.6	20.9
133.0	211.5	22466.4	227.6	19.6
134.0	211.5	22437.4	227.6	20.7
135.0	211.5	22437.4	227.6	19.4
136.0	211.5	17462.6	227.6	18.2
137.0	211.5	17462.6	227.6	18.1
138.0	211.5	15345.0	227.6	17.7
139.0	210.6	15519.1	227.6	18.4
140.0	210.6	15519.1	227.6	19.1
141.0	211.1	16302.3	227.6	16.9
142.0	210.6	16360.3	227.6	16.0
143.0	210.6	16360.3	227.6	16.8
144.0	210.6	13285.5	227.6	14.7
145.0	210.6	13517.5	227.6	14.1
146.0	210.6	13517.5	227.6	15.5
147.0	210.2	9746.6	227.6	13.0
148.0	210.6	10181.7	227.6	12.2
149.0	210.6	10181.7	227.6	13.7
150.0	210.2	7280.9	225.1	11.4

Table A-1

ORIGINAL EMPIRICAL DATA OF AQUEOUS METHANE SOLUBILITY AS DETERMINED IN THIS STUDY

NUMBER	TDEGF	PSI	SAL	SCF
151.0	210.2	7280.9	225.1	11.9
152.0	210.6	5047.3	225.1	12.0
153.0	210.2	5366.4	223.7	10.0
154.0	210.6	5395.4	223.7	8.6
155.0	210.6	5395.4	223.7	9.5
156.0	210.6	3596.9	223.7	8.1
157.0	210.6	3596.9	223.7	8.4
158.0	210.6	3596.9	223.7	10.5
159.0	210.6	3567.9	223.7	8.1
160.0	210.2	2117.6	223.7	6.5
161.0	210.2	2117.6	223.7	6.2
162.0	213.4	22219.8	293.5	12.4
163.0	212.9	19000.0	293.5	13.7
164.0	212.9	19000.0	293.5	14.3
165.0	212.9	19000.0	293.5	14.0
166.0	212.9	19000.0	293.5	13.9
167.0	212.9	19000.0	293.5	14.7
168.0	212.9	15997.7	293.5	10.4
169.0	212.9	15997.7	293.5	13.2
170.0	212.9	13067.9	293.5	11.1
171.0	212.9	13067.9	293.5	12.2
172.0	214.2	13169.4	294.6	10.7
173.0	214.2	13169.4	294.6	11.4
174.0	213.4	13111.4	294.6	11.8
175.0	213.4	13111.4	294.6	12.5
176.0	213.8	10239.7	294.6	11.2
177.0	213.8	10239.7	294.6	10.9
178.0	213.4	7193.9	294.6	8.7
179.0	213.4	7193.9	294.6	9.1
180.0	213.8	5177.9	294.6	7.7
181.0	213.8	5177.9	294.6	7.3
182.0	214.2	3625.9	294.6	5.9
183.0	214.2	3625.9	294.6	6.7
184.0	213.4	2045.0	294.6	5.1
185.0	213.4	2045.0	294.6	4.9
186.0	213.4	2045.0	294.6	4.5
187.0	213.4	2045.0	294.6	4.9
188.0	272.8	22495.4	3.2	60.6
189.0	272.8	22495.4	3.2	60.4
190.0	272.8	19203.0	3.2	59.8
191.0	272.8	19203.0	3.2	53.3
192.0	273.2	19217.5	3.2	56.4
193.0	273.2	19217.5	3.2	56.4
194.0	272.8	16186.2	3.2	53.6
195.0	272.8	16186.2	3.2	49.0
196.0	273.2	13169.4	3.2	47.5
197.0	273.2	13169.4	3.2	49.3
198.0	273.2	10399.2	3.2	44.8
199.0	273.2	10399.2	3.2	40.6
200.0	272.3	10384.7	3.2	43.2

Table A-1

ORIGINAL EMPIRICAL DATA OF AQUEOUS METHANE SOLUBILITY AS DETERMINED IN THIS STUDY

NUMBER	TDEGF	PSI	SAL	SCF
201.0	272.3	10384.7	3.2	40.6
202.0	273.7	7222.9	3.2	33.9
203.0	272.8	7266.4	3.2	33.0
204.0	272.8	7266.4	3.2	35.3
205.0	273.2	7629.0	3.2	35.8
206.0	273.2	7629.0	3.2	34.8
207.0	274.1	5148.8	3.2	30.6
208.0	273.2	5163.4	3.2	28.2
209.0	273.7	5134.3	3.2	28.6
210.0	273.7	5134.3	3.2	31.1
211.0	273.2	3625.9	3.2	23.5
212.0	273.2	3625.9	3.2	25.2
213.0	274.1	2248.1	3.2	18.4
214.0	274.1	2248.1	3.2	20.6
215.0	275.0	16128.2	51.1	48.9
216.0	274.5	16186.2	51.1	45.7
217.0	274.5	16186.2	51.1	48.2
218.0	275.0	13154.9	51.1	40.3
219.0	275.0	13242.0	51.1	41.3
220.0	275.0	13242.0	51.1	38.8
221.0	274.5	10326.7	51.1	36.9
222.0	274.5	10326.7	51.1	38.5
223.0	272.8	7034.3	51.1	29.4
224.0	272.8	7034.3	51.1	28.1
225.0	272.0	7034.3	51.1	28.8
226.0	272.0	7034.3	51.1	29.8
227.0	272.8	5061.8	51.1	23.8
228.0	272.8	5061.8	51.1	23.9
229.0	272.8	3567.9	51.1	20.0
230.0	272.8	3567.9	51.1	20.1
231.0	272.3	2016.0	51.1	13.2
232.0	272.3	2016.0	51.1	12.7
233.0	275.0	19014.5	106.0	36.5
234.0	275.0	19014.5	106.0	36.8
235.0	275.0	16273.3	106.0	32.4
236.0	275.0	16273.3	106.0	31.9
237.0	275.0	16157.2	106.0	34.1
238.0	275.0	16157.2	106.0	37.2
239.0	275.0	16128.2	106.0	38.4
240.0	275.0	16128.2	106.0	37.9
241.0	275.5	13169.4	106.0	31.6
242.0	273.2	13372.5	106.0	29.6
243.0	273.2	13372.5	106.0	30.6
244.0	274.5	13096.9	106.0	29.9
245.0	274.5	13096.9	106.0	29.7
246.0	274.5	13256.5	106.0	32.2
247.0	276.8	13082.4	106.0	31.3
248.0	276.8	13082.4	106.0	31.9
249.0	276.8	10312.2	106.0	30.7
250.0	276.8	10312.2	106.0	30.2

Table A-1

ORIGINAL EMPIRICAL DATA OF AQUEOUS METHANE SOLUBILITY AS DETERMINED IN THIS STUDY

NUMBER	TDEGF	PSI	SAL	SCF
251.0	274.1	7222.9	106.0	25.2
252.0	274.1	7222.9	106.0	25.0
253.0	274.5	7425.9	106.0	25.9
254.0	274.5	7425.9	106.0	26.7
255.0	274.5	5279.4	106.0	19.0
256.0	274.1	3596.9	106.0	16.7
257.0	274.1	3596.9	106.0	15.4
258.0	274.1	3625.9	106.0	17.1
259.0	274.1	3625.9	106.0	16.0
260.0	275.9	19043.5	105.0	36.7
261.0	276.4	19130.5	105.0	37.2
262.0	276.4	19130.5	105.0	36.7
263.0	276.8	15939.7	105.0	33.9
264.0	276.8	15939.7	105.0	35.1
265.0	277.0	13024.4	105.0	29.5
266.0	277.0	13024.4	105.0	29.7
267.0	277.2	13154.9	105.0	30.3
268.0	277.2	13154.9	105.0	29.5
269.0	276.8	13125.9	105.0	30.1
270.0	277.2	7019.8	107.0	22.7
271.0	277.2	7063.4	107.0	24.4
272.0	277.2	7063.4	107.0	22.8
273.0	277.2	5018.3	107.0	19.4
274.0	277.2	5018.3	107.0	19.7
275.0	276.8	5148.8	107.0	20.8
276.0	276.8	5148.8	107.0	20.7
277.0	276.8	5148.8	107.0	20.7
278.0	276.8	3684.0	107.0	15.5
279.0	277.0	3364.9	107.0	15.8
280.0	277.0	3364.9	107.0	16.1
281.0	277.0	2016.0	106.8	11.2
282.0	277.0	2016.0	106.8	11.2
283.0	271.0	2016.0	106.8	10.7
284.0	271.0	2016.0	106.8	10.2
285.0	275.0	22538.9	163.5	35.7
286.0	275.0	22538.9	163.5	34.8
287.0	275.0	22277.8	161.7	34.0
288.0	275.0	22350.4	161.7	36.0
289.0	275.0	22437.4	161.7	35.6
290.0	275.0	19029.0	161.7	34.4
291.0	275.0	19203.0	161.7	31.2
292.0	275.0	19203.0	161.7	32.0
293.0	275.0	16157.2	160.7	31.0
294.0	275.0	16157.2	160.7	32.7
295.0	275.9	13227.5	163.5	26.0
296.0	275.5	12850.4	160.7	27.5
297.0	275.0	13024.4	160.7	29.1
298.0	275.0	13024.4	160.7	27.9
299.0	275.9	10210.7	163.5	24.8
300.0	275.0	10181.7	163.5	24.4

Table A-1

ORIGINAL EMPIRICAL DATA OF AQUEOUS METHANE SOLUBILITY AS DETERMINED IN THIS STUDY

NUMBER	TDEGF	PSI	SAL	SCF
301.0	275.0	10181.7	163.5	27.1
302.0	275.5	10152.7	160.7	27.2
303.0	275.5	10152.7	160.7	24.0
304.0	275.0	7135.9	160.7	19.2
305.0	275.0	7135.9	160.7	19.2
306.0	275.5	5163.4	160.3	16.3
307.0	275.5	5090.8	160.3	15.9
308.0	275.5	5090.8	160.3	15.8
309.0	275.0	3567.9	159.7	12.3
310.0	274.5	3625.9	163.9	12.4
311.0	274.5	3655.0	163.9	15.6
312.0	275.0	2146.6	163.9	9.4
313.0	275.0	2146.6	163.9	8.7
314.0	274.5	2291.6	163.9	8.6
315.0	274.5	2291.6	163.9	10.6
316.0	275.0	19087.0	224.3	24.5
317.0	275.0	19087.0	224.3	24.6
318.0	275.0	19232.0	224.3	22.5
319.0	274.5	19174.0	224.3	23.6
320.0	273.7	19072.5	227.8	23.5
321.0	273.7	19072.5	227.8	22.6
322.0	273.7	19072.5	227.6	22.1
323.0	273.7	19072.5	227.6	24.6
324.0	273.7	16041.2	227.1	22.4
325.0	273.7	16070.2	225.7	23.8
326.0	273.7	16070.2	225.7	23.2
327.0	273.7	13024.4	225.4	19.5
328.0	273.7	13024.4	225.4	21.6
329.0	273.7	10065.6	223.7	21.4
330.0	273.7	10065.6	223.7	22.0
331.0	273.7	10080.1	222.6	20.9
332.0	273.7	10080.1	222.6	18.9
333.0	273.7	10094.6	221.3	21.2
334.0	273.7	10109.1	219.9	18.9
335.0	273.7	10109.1	219.9	18.9
336.0	273.7	7135.9	218.6	16.4
337.0	272.3	7193.9	224.3	15.9
338.0	272.3	7193.9	224.3	16.6
339.0	273.7	4873.3	224.3	14.2
340.0	273.2	4931.3	224.3	12.4
341.0	273.2	4931.3	224.3	12.1
342.0	273.7	3596.9	223.7	9.1
343.0	273.7	3596.9	223.7	9.5
344.0	273.7	2175.6	223.2	7.1
345.0	273.7	2175.6	222.6	9.0
346.0	273.7	2175.6	222.6	8.4
347.0	273.7	2161.1	222.6	7.2
348.0	273.7	2161.1	222.6	6.9
349.0	275.9	22640.4	295.2	21.6
350.0	275.9	22640.4	295.1	21.6

Table A-1

ORIGINAL EMPIRICAL DATA OF AQUEOUS METHANE SOLUBILITY AS DETERMINED IN THIS STUDY

NUMBER	TDEGF	PSI	SAL	SCF
351.0	275.9	19217.5	295.1	19.3
352.0	275.9	19217.5	295.1	19.1
353.0	275.9	16273.3	294.4	18.9
354.0	275.9	16273.3	294.4	17.7
355.0	277.3	13067.9	293.6	15.6
356.0	277.3	13067.9	293.6	15.2
357.0	277.7	10167.2	293.0	13.8
358.0	277.7	10167.2	293.0	14.0
359.0	276.8	7150.4	292.1	11.6
360.0	276.8	7150.4	292.1	11.4
361.0	276.4	5163.4	291.5	9.5
362.0	276.4	5163.4	291.5	9.4
363.0	276.8	2262.6	286.0	6.3
364.0	276.8	2262.6	286.0	5.8
365.0	335.1	22538.9	3.0	80.9
366.0	335.1	22538.9	3.0	91.5
367.0	335.8	22277.8	3.0	89.9
368.0	335.8	22277.8	3.0	82.9
369.0	335.8	21842.7	3.0	89.4
370.0	335.8	22596.9	3.0	80.6
371.0	335.8	22596.9	3.0	85.9
372.0	336.2	22800.0	3.0	83.6
373.0	336.2	22771.0	3.0	94.9
374.0	336.2	22771.0	3.0	92.9
375.0	336.2	18332.8	3.0	80.2
376.0	336.2	18332.8	3.0	85.8
377.0	336.2	17926.7	3.0	87.4
378.0	335.8	19217.5	3.0	84.7
379.0	335.8	16360.3	3.0	73.0
380.0	335.8	16360.3	3.0	78.8
381.0	336.6	13169.4	3.0	72.8
382.0	336.6	13169.4	3.0	71.4
383.0	336.6	10225.2	3.0	59.2
384.0	335.8	10268.7	3.0	58.6
385.0	336.2	10167.2	3.0	63.3
386.0	337.5	5076.3	3.0	46.3
387.0	337.5	5076.3	3.0	44.9
388.0	336.2	3625.9	3.1	31.8
389.0	336.2	3625.9	3.1	32.5
390.0	336.2	3640.5	3.1	35.3
391.0	336.2	3640.5	3.1	37.4
392.0	340.3	18347.3	51.1	63.7
393.0	340.3	18347.3	51.1	63.8
394.0	340.3	17984.7	51.1	63.4
395.0	340.3	17984.7	51.1	66.2
396.0	340.0	15649.6	51.0	60.6
397.0	340.0	15649.6	51.0	62.0
398.0	340.7	12821.4	50.7	53.0
399.0	340.7	12821.4	50.7	56.1
400.0	340.0	9775.6	50.4	49.5

Table A-1

ORIGINAL EMPIRICAL DATA OF AQUEOUS METHANE SOLUBILITY AS DETERMINED IN THIS STUDY

NUMBER	TDEGF	PSI	SAL	SCF
401.0	340.0	9775.6	50.4	45.2
402.0	340.0	6773.3	50.0	38.2
403.0	340.0	6773.3	50.0	40.1
404.0	339.1	4800.8	49.7	35.5
405.0	339.1	4800.8	49.7	33.2
406.0	339.1	4800.8	49.7	33.4
407.0	338.9	3553.4	49.5	27.4
408.0	338.9	3553.4	49.5	28.2
409.0	339.3	1958.0	49.5	18.8
410.0	339.3	1958.0	49.5	18.0
411.0	339.4	19043.5	104.6	46.9
412.0	339.8	19072.5	104.6	51.5
413.0	339.8	19072.5	104.6	52.4
414.0	339.8	16157.2	104.6	46.8
415.0	339.8	16157.2	104.6	45.6
416.0	339.8	16026.7	104.6	45.8
417.0	339.8	16026.7	104.6	44.9
418.0	339.8	16026.7	104.6	47.6
419.0	339.8	16026.7	104.6	47.6
420.0	339.8	13024.4	104.6	40.7
421.0	339.8	13024.4	104.6	41.7
422.0	338.4	13024.4	104.6	41.7
423.0	338.4	13024.4	104.6	43.3
424.0	339.8	10007.6	106.0	37.8
425.0	339.8	10007.6	106.0	39.0
426.0	339.8	10036.6	106.0	36.4
427.0	339.8	7048.8	106.0	29.6
428.0	339.8	7019.8	106.0	28.7
429.0	339.8	7019.8	106.0	29.8
430.0	339.8	6990.8	106.0	29.2
431.0	339.8	6990.8	106.0	29.0
432.0	339.8	5047.3	106.0	24.2
433.0	339.8	5047.3	106.0	25.9
434.0	339.8	5250.4	106.0	25.6
435.0	339.8	5250.4	106.0	23.9
436.0	339.8	3553.4	106.0	21.1
437.0	339.8	3553.4	106.0	19.6
438.0	339.8	3567.9	104.0	22.5
439.0	339.8	3567.9	104.0	20.0
440.0	339.8	2001.5	104.0	17.2
441.0	339.8	2001.5	104.0	16.7
442.0	339.8	2001.5	104.0	13.9
443.0	339.8	2001.5	104.0	15.6
444.0	338.0	22567.9	163.9	46.3
445.0	338.0	22567.9	163.9	45.6
446.0	338.0	22582.4	162.1	46.0
447.0	338.0	22582.4	162.1	44.4
448.0	338.4	19072.5	163.4	42.1
449.0	338.4	19072.5	163.4	41.0
450.0	336.2	16099.2	159.8	39.8

Table A-1

ORIGINAL EMPIRICAL DATA OF AQUEOUS METHANE SOLUBILITY AS DETERMINED IN THIS STUDY

NUMBER	TDEGF	PSI	SAL	SCF
451.0	336.2	16099.2	159.8	41.8
452.0	338.4	13096.9	157.8	32.9
453.0	338.4	13096.9	157.8	33.1
454.0	336.2	10297.7	159.5	29.8
455.0	336.2	10297.7	159.5	27.5
456.0	336.2	7164.9	159.5	26.8
457.0	336.2	7164.9	159.5	26.3
458.0	336.2	5105.3	159.5	21.7
459.0	336.2	5105.3	159.5	21.5
460.0	336.2	3553.4	159.5	17.1
461.0	336.2	3553.4	159.5	17.6
462.0	337.1	2059.5	159.5	13.2
463.0	337.6	2016.0	159.5	12.4
464.0	337.6	2016.0	159.5	12.4
465.0	338.4	22538.9	224.3	38.2
466.0	338.4	22538.9	224.3	37.6
467.0	338.4	22335.9	224.3	39.0
468.0	338.4	22335.9	224.3	39.2
469.0	338.0	19087.0	223.7	34.3
470.0	338.0	19087.0	223.7	31.9
471.0	337.6	16026.7	223.5	30.1
472.0	338.0	16070.2	223.5	29.4
473.0	338.0	16070.2	223.5	31.5
474.0	338.0	13082.4	223.7	28.1
475.0	338.0	13096.9	223.7	29.0
476.0	338.0	13096.9	223.7	30.4
477.0	337.6	10065.6	223.5	23.3
478.0	338.4	10051.1	223.5	23.3
479.0	338.4	10051.1	223.5	23.4
480.0	335.8	7034.3	220.4	19.4
481.0	338.0	7092.4	220.4	21.2
482.0	338.0	7092.4	220.4	20.7
483.0	338.0	5177.9	226.5	15.2
484.0	338.0	5032.8	226.5	14.6
485.0	338.0	5032.8	226.5	15.1
486.0	338.0	3625.9	220.4	12.8
487.0	338.0	3625.9	220.4	11.9
488.0	338.4	2262.6	226.5	9.6
489.0	338.4	2277.1	226.5	9.5
490.0	338.0	22480.9	289.9	29.3
491.0	338.0	22480.9	289.9	28.5
492.0	339.8	21552.6	289.9	29.1
493.0	338.0	19232.0	287.2	26.9
494.0	338.0	19232.0	287.2	27.1
495.0	338.0	16258.8	284.5	26.3
496.0	338.0	16258.8	284.5	25.2
497.0	338.0	13256.5	283.0	23.1
498.0	338.0	13256.5	283.1	21.4
499.0	338.0	13256.5	283.1	21.7
500.0	338.0	13256.5	283.1	22.5

Table A-1

ORIGINAL EMPIRICAL DATA OF AQUEOUS METHANE SOLUBILITY AS DETERMINED IN THIS STUDY

NUMBER	TDEGF	PSI	SAL	SCF
501.0	338.9	10210.7	283.1	20.2
502.0	338.9	10210.7	283.1	19.3
503.0	339.4	7251.9	283.1	15.0
504.0	339.4	7251.9	283.1	15.7
505.0	339.4	5163.4	282.1	12.9
506.0	339.4	5163.4	282.1	13.6
507.0	338.9	3538.9	282.1	10.5
508.0	338.9	3538.9	282.1	10.8
509.0	401.0	22451.9	3.1	125.1
510.0	401.5	22742.0	3.5	122.6
511.0	401.5	22742.0	3.5	125.9
512.0	401.5	19406.1	3.5	114.4
513.0	401.5	19406.1	3.5	123.7
514.0	400.5	19319.1	3.5	119.4
515.0	400.5	19319.1	3.5	122.0
516.0	401.9	16418.3	3.5	108.1
517.0	401.9	16360.3	3.5	114.9
518.0	401.9	16360.3	3.5	111.6
519.0	401.9	13140.4	3.5	96.3
520.0	401.9	13140.4	3.5	98.5
521.0	401.5	10355.7	3.5	86.0
522.0	401.2	10268.7	3.5	91.5
523.0	400.8	10326.7	3.5	87.4
524.0	400.8	10326.7	3.5	85.0
525.0	398.8	7309.9	3.5	79.2
526.0	398.8	7309.9	3.5	80.0
527.0	398.3	5206.9	3.5	56.8
528.0	398.3	5206.9	3.5	56.6
529.0	398.1	3655.0	3.5	43.6
530.0	398.1	3655.0	3.5	43.8
531.0	397.2	2059.5	3.5	36.8
532.0	397.2	2059.5	3.5	33.1
533.0	401.9	19246.5	49.8	96.7
534.0	401.9	19377.1	49.4	96.1
535.0	401.5	19522.1	49.3	92.5
536.0	401.5	19522.1	49.3	93.5
537.0	401.5	16070.2	49.2	87.3
538.0	401.5	16244.3	49.0	94.9
539.0	401.5	16244.3	49.0	91.0
540.0	401.5	13227.5	49.0	90.6
541.0	401.5	13227.5	49.0	84.6
542.0	401.5	9978.6	49.0	75.4
543.0	401.5	9978.6	49.0	73.9
544.0	401.9	7193.9	48.8	53.6
545.0	401.9	7193.9	48.8	55.6
546.0	402.3	7513.0	48.8	57.6
547.0	401.0	4873.3	46.8	47.7
548.0	401.0	4916.8	46.8	51.0
549.0	401.0	4960.3	46.8	52.8
550.0	401.0	4960.3	46.8	53.1

Table A-1

ORIGINAL EMPIRICAL DATA OF AQUEOUS METHANE SOLUBILITY AS DETERMINED IN THIS STUDY

NUMBER	TDEGF	PSI	SAL	SCF
551.0	401.4	3553.4	46.3	41.0
552.0	401.4	3553.4	46.3	43.0
553.0	401.4	2161.1	46.3	27.2
554.0	401.4	2161.1	46.3	27.8
555.0	404.6	22277.8	161.7	59.6
556.0	404.6	22277.8	161.7	60.5
557.0	404.6	22292.3	161.7	60.8
558.0	404.6	22292.3	161.7	61.2
559.0	404.6	18854.9	161.7	57.4
560.0	404.6	18854.9	161.7	58.3
561.0	404.6	15968.7	161.7	55.1
562.0	404.6	15968.7	161.7	52.9
563.0	404.2	12966.4	161.7	52.1
564.0	403.7	12951.9	161.7	49.3
565.0	404.2	10123.7	161.7	45.3
566.0	404.2	10123.7	161.7	43.7
567.0	404.2	7005.3	161.7	38.7
568.0	404.2	7005.3	161.7	37.2
569.0	404.2	5076.3	161.7	31.9
570.0	404.2	5076.3	161.7	35.2
571.0	404.2	3567.9	161.7	25.4
572.0	404.2	3567.9	161.7	25.0
573.0	404.2	2074.0	161.7	19.5
574.0	404.2	2074.0	161.7	17.2
575.0	402.4	22480.9	221.0	47.4
576.0	402.4	22480.9	221.0	50.4
577.0	401.9	19217.5	221.0	47.0
578.0	401.9	19087.0	216.0	46.9
579.0	401.9	19087.0	216.0	46.1
580.0	402.4	15635.1	212.6	42.2
581.0	402.4	15635.1	212.6	45.9
582.0	402.4	13169.4	212.3	35.8
583.0	402.4	13169.4	212.3	36.4
584.0	401.9	13067.9	211.5	36.4
585.0	401.9	13067.9	211.5	37.0
586.0	401.9	10384.7	219.7	34.7
587.0	402.4	10428.2	218.6	36.1
588.0	402.4	10428.2	218.6	36.0
589.0	402.4	7092.4	216.0	28.1
590.0	402.4	7092.4	216.0	25.1
591.0	402.4	4989.3	211.5	23.0
592.0	402.4	4989.3	211.5	20.6
593.0	401.9	3509.9	207.0	17.9
594.0	401.9	3509.9	207.0	17.4
595.0	398.8	22683.9	281.7	44.4
596.0	398.8	22567.9	281.7	41.2
597.0	398.8	22567.9	281.7	41.6
598.0	399.2	22451.9	281.7	42.6
599.0	398.8	22219.8	281.7	44.9
600.0	398.8	22219.8	281.7	46.0

Table A-1

ORIGINAL EMPIRICAL DATA OF AQUEOUS METHANE SOLUBILITY AS DETERMINED IN THIS STUDY

NUMBER	TDEGF	PSI	SAL	SCF
601.0	398.8	22596.9	281.7	42.9
602.0	398.8	22596.9	281.7	44.7
603.0	399.2	19362.6	281.7	38.4
604.0	399.2	19362.6	281.7	41.7
605.0	399.2	16273.3	281.7	38.4
606.0	399.2	16273.3	281.7	35.7
607.0	398.8	13198.5	281.7	33.1
608.0	398.8	13198.5	281.7	32.7
609.0	398.3	10268.7	273.7	29.6
610.0	398.3	10268.7	273.7	29.3
611.0	398.3	7106.9	273.7	24.1
612.0	398.3	5163.4	255.8	18.4
613.0	398.3	5163.4	255.8	17.1
614.0	398.8	5453.4	249.1	19.3
615.0	398.8	5453.4	249.1	19.2
616.0	398.3	3684.0	243.6	15.2
617.0	398.3	3684.0	243.6	14.3
618.0	462.2	18942.0	47.7	135.2
619.0	462.2	19145.0	47.6	150.3
620.0	462.2	19145.0	47.6	141.3
621.0	462.2	19217.5	47.5	137.7
622.0	462.2	15968.7	47.4	126.6
623.0	462.2	15968.7	47.4	122.0
624.0	462.2	13329.0	46.3	127.1
625.0	462.2	13329.0	46.3	124.6
626.0	462.2	13575.6	46.1	107.3
627.0	462.2	14213.7	45.8	118.9
628.0	462.2	14503.8	45.8	117.8
629.0	462.2	14503.8	45.8	119.4
630.0	462.2	9572.5	45.8	101.5
631.0	462.2	9572.5	45.8	101.0
632.0	462.2	7396.9	45.3	92.4
633.0	462.2	7396.9	45.3	84.7
634.0	462.2	5018.3	45.1	74.7
635.0	462.2	5221.4	44.0	67.6
636.0	462.2	5308.4	43.7	67.8
637.0	462.2	5308.4	43.7	67.9
638.0	460.4	3567.9	43.7	62.3
639.0	460.4	3567.9	43.7	54.0
640.0	460.4	2030.5	43.2	41.4
641.0	460.4	2030.5	43.2	37.0
642.0	460.4	2045.0	43.2	35.1
643.0	461.8	19203.0	158.4	78.7
644.0	461.8	19203.0	158.4	78.2
645.0	462.2	16171.7	158.4	74.2
646.0	462.2	16171.7	158.4	74.4
647.0	461.3	13169.4	158.4	65.9
648.0	461.3	13169.4	158.4	69.7
649.0	461.8	9964.1	161.9	58.1
650.0	461.8	9964.1	161.9	57.7

Table A-1

ORIGINAL EMPIRICAL DATA OF AQUEOUS METHANE SOLUBILITY AS DETERMINED IN THIS STUDY

NUMBER	TDEGF	PSI	SAL	SCF
651.0	461.8	7077.9	161.9	47.0
652.0	461.8	7077.9	161.9	44.2
653.0	459.5	5003.8	161.9	42.8
654.0	459.5	5003.8	161.9	43.1
655.0	461.8	3509.9	161.9	31.7
656.0	461.8	3509.9	161.9	32.5
657.0	461.8	3451.9	161.9	32.0
658.0	461.8	3451.9	161.9	31.7
659.0	462.2	19232.0	253.8	59.4
660.0	462.2	19232.0	253.8	58.4
661.0	464.0	16331.3	253.2	52.7
662.0	464.0	16331.3	253.2	59.7
663.0	464.0	15867.2	250.4	54.2
664.0	464.0	15867.2	250.4	52.4
665.0	464.0	13140.4	248.3	51.8
666.0	464.0	13140.4	248.3	52.8
667.0	464.0	13256.5	243.6	50.9
668.0	464.0	13256.5	243.6	51.0
669.0	464.0	10297.7	229.4	44.0
670.0	464.0	10297.7	229.4	42.7

Temerature in ^{O}F.
Psi is absolute
Salinity in grams/liter.
SCF at 25^{O}C (77^{O}F)

Table A-2 Empirical data for the solubility of methane in NaCl solutions at low temperature and pressure

NUMBER	TDEGF	PSI	SAL	SCF
1	75.0	1922	52	11.5
2	75.0	1015	52	8.2
3	75.0	1010	52	8.0
4	74.0	1005	52	8.3
5	74.0	1005	52	8.1
6	74.5	510	52	4.6
7	74.5	510	52	4.3
8	75.0	510	52	5.4
9	74.5	505	52	4.4
10	74.5	505	52	5.6
11	74.5	258	52	2.4
12	74.5	258	52	2.1
13	74.0	255	52	3.1
14	74.0	249	52	2.2
15	74.0	249	52	2.4
16	124.5	2045	52	11.4
17	124.5	2045	52	10.7
18	124.5	2031	52	10.1
19	124.5	2031	52	10.9
20	124.5	1033	52	6.8
21	124.5	1033	52	6.8
22	124.0	355	51	2.4
23	124.0	355	51	2.4
24	124.0	154	51	0.9
25	124.0	154	51	1.3
26	120.0	150	52	0.8
27	120.0	130	52	0.9
28	120.0	130	52	1.0
29	120.0	130	52	0.7
30	120.0	130	52	0.8
31	157.0	1976	46	9.0
32	157.0	1976	46	10.1
33	156.5	1044	46	6.0
34	156.5	1044	46	5.1
35	155.5	540	46	3.3
36	155.5	251	49	1.9
37	155.5	251	49	1.7
38	156.0	261	49	1.5
39	156.0	261	49	1.6
40	156.0	240	49	1.4
41	156.0	240	49	1.3
42	156.0	149	49	0.8
43	156.0	149	49	0.8
44	78.5	500	105	3.4
45	78.5	500	105	3.4
46	78.0	496	105	3.3
47	78.0	496	105	3.3
48	78.0	312	105	2.6
49	78.0	312	105	2.5
50	78.0	125	105	0.8

Table A-2 continued

NUMBER	TDEGF	PSI	SAL	SCF
51	78.0	125	105	1.1
52	78.0	125	105	0.7
53	78.0	125	105	1.4
54	78.0	125	105	1.5
55	78.0	125	105	1.3
56	120.5	2010	107	8.5
57	120.5	2010	107	8.5
58	120.5	2000	107	8.1
59	120.5	2000	107	8.3
60	120.0	1040	106	5.7
61	120.0	1040	106	5.4
62	122.0	1000	106	5.1
63	122.0	1000	106	5.4
64	122.0	1000	107	5.2
65	120.0	500	107	3.0
66	120.0	500	107	2.9
67	120.0	500	107	3.0
68	122.5	500	107	3.0
69	123.0	500	107	2.6
70	123.0	500	107	2.5
71	123.0	133	107	0.7
72	123.0	133	107	0.7
73	123.0	130	107	0.6
74	123.0	130	107	1.0
75	120.5	2000	166	6.1
76	120.5	2000	166	6.5
77	120.5	2000	166	5.9
78	120.5	2000	166	6.4
79	121.0	2000	166	5.8
80	121.0	2000	166	6.2
81	120.0	1000	166	4.1
82	120.0	1000	166	3.9
83	121.5	1000	166	4.4
84	121.5	1000	166	4.1
85	121.5	1000	163	4.2
86	123.0	500	163	2.4
87	123.0	500	163	2.6
88	123.0	500	163	2.4
89	123.0	500	163	2.3
90	121.5	250	163	1.5
91	121.5	250	163	1.4
92	121.5	250	163	1.5
93	121.5	250	163	1.4
94	121.5	250	163	1.5
95	122.0	130	163	0.5

Table A-2 continued

NUMBER	TDEGF	PSI	SAL	SCF
96	122.0	125	166	0.53
97	122.0	125	166	0.51
98	161.0	2000	166	6.4
99	161.0	2000	166	6.7
100	161.0	2000	166	6.6
101	160.0	1002	166	3.5
102	160.0	1002	166	3.5
103	158.5	1000	166	4.0
104	158.5	1000	166	3.7
105	158.5	1008	166	3.7
106	158.5	1008	166	3.1
107	158.0	505	166	1.9
108	158.0	505	166	1.8
109	158.0	500	166	1.9
110	158.0	128	166	0.2
111	159.0	125	166	0.6
112	159.0	125	166	0.2
113	159.0	125	166	0.2
114	159.0	125	166	0.5
115	212.0	2010	107	8.2
116	212.0	2010	107	8.1
117	212.0	2000	107	7.7
118	212.0	2000	107	7.7
119	212.0	2006	107	8.3
120	212.0	1010	107	4.7
121	212.0	1010	107	4.1
122	212.0	1006	107	4.6
123	212.0	1006	107	4.5
124	212.0	500	107	2.7
125	212.0	500	107	2.4
126	212.0	500	107	2.2
127	212.0	500	107	2.2
128	212.0	500	107	2.7

Temperature in ^{o}F.
Psi is absolute.
Salinity in grams/liter.
SCF at 25^{o}C (77^{o}F).

Table A-3 Original empirical data for the solubility of methane and carbon dioxide at 302°F in aqueous NaCl solutions. The symbol σ is the standard deviation for averaged experimental data.

Experimental Results							Averaged Experimental Data			
Cond.	Temp. °F	Pressure psi	Salinity g/l	Total Gas SCF	% CO_2	CH_4 SCF	Total Gas	% CO_2	CO_2 SCF	CH_4 SCF
1-1	303	22,340	52	71.2	12.8	62.0	70.8	12.6	8.9	61.8
2	"	"	"	74.1	12.7	64.7	σ3.3		σ.4	σ2.5
3	"	"	"	71.5	13.3	62.0				
4	302	22,470	"	66.2	11.5	58.6				
2-1	303	22,600	"	67.9	9.9	61.2	68.5	9.8	6.7	61.8
2	"	"	"	69.0	9.6	62.3				
3-1	302	22,610	"	65.6	7.5	60.7	64.9	7.3	4.7	60.1
2	"	"	"	64.3	7.4	59.6				
3	303	22,510	"	64.7	7.0	60.1				
4-1	305	22,610	"	61.8	4.5	59.0	61.8	4.5	2.8	59.0
5-1	303	22,460	"	69.1	2.3	67.5	64.1	2.1	1.3	62.8
2	"	22,540	"	58.7	1.9	57.6	σ4.0			σ3.8
3	"	"	"	61.9	2.0	60.6				
4	302	22,570	"	64.7	2.1	63.4				
5	"	"	"	66.2	2.0	64.9				
6-1	302	12,760	"	67.0	82.0	12.1	66.1	81.5	53.7	12.3
2	"	"	"	68.4	81.0	13.0				
3	"	13,050	"	62.9	81.0	12.0				
7-1	"	"	"	62.4	79.0	13.1	62.2	78.0	48.5	13.7
2	"	"	"	62.5	79.0	13.1	σ0.9			
3	"	"	"	63.2	78.0	13.9				
4	"	13,020	"	61.7	78.0	13.6				
5	"	"	"	60.8	77.0	14.0				
6	"	13,050	"	62.9	77.0	14.5				
8-1	"	13,020	"	61.6	75.0	15.4	61.6	75.0	46.2	15.4

Table A-3 (continued, page 2)

Experimental Results							Averaged Experimental Data			
Cond.	Temp. °F	Pressure psi	Salinity g/l	Total Gas SCF	% CO_2	CH_4 SCF	Total Gas	% CO_2	CO_2 SCF	CH_4 SCF
9-1	302	13,020	52	51.1	72.0	16.6	58.5	71.5	41.8	16.7
2	"	13,000	"	57.7	73.0	15.6				
3	"	"	"	58.0	70.0	17.4				
4	"	12,910	"	59.1	71.0	17.1				
10-1	303	13,110	"	57.5	8.2	52.8	54.2	8.2	4.4	49.8
2	"	"	"	54.4	8.4	49.8				
3	"	13,080	"	50.8	8.0	46.7				
11-1	303	13,050	"	48.9	3.7	47.0	50.0	3.3	1.7	48.3
2	"	13,080	"	48.8	3.0	47.4				σ2.0
3	"	"	"	52.9	3.2	51.2				
4	"	"	"	49.2	3.4	47.5				
12-1	303	"	"	47.8	2.4	46.6	47.8	2.4	1.2	46.6
13-1	"	13,110	"	51.9	1.3	51.2	50.2	1.15	0.6	48.9
2	"	12,970	"	48.4	1.0	47.9				
14-1	300	5,030	"	42.6	84.0	6.8	41.1	83.5	34.3	6.8
2	"	"	"	39.6	83.0	6.7				
15-1	303	"	"	40.6	78.0	8.9	39.2	77.5	30.4	8.8
2	"	"	"	38.2	79.0	8.0				
3	"	5,000	"	39.6	77.0	9.1				
4	"	"	"	38.6	76.0	9.2				
16-1	302	5,060	"	33.8	25.0	25.3	32.7	23.0	7.5	25.1
2	"	"	"	32.1	23.0	24.7				
3	"	5,000	"	32.3	21.0	25.5				

Table A-3 (continued, page 3)

Experimental Results							Averaged Experimental Data			
Cond.	Temp. ^{o}F	Pressure psi	Salinity g/l	Total Gas SCF	% CO_2	CH_4 SCF	Total Gas	% CO_2	CO_2 SCF	CH_4 SCF
17-1	305	22,553	107	72.7	42.0	43.2	73.4	42.0	30.8	42.6
2	"	"	"	71.4	42.0	41.4				
3	"	"	"	74.9	42.0	43.5				
4	"	"	"	74.6	42.0	43.2				
18-1	299	22,480	105	74.6	36.4	47.4	71.8	37.2	26.7	45.1
2	"	"	"	71.6	39.0	43.7	σ2.2	σ1.0		σ1.4
3	298	22,470	"	71.6	37.5	44.8				
4	"	"	"	72.2	37.5	45.1				
5	300	22,500	"	68.4	36.5	43.7				
6	"	"	"	72.0	36.5	45.8				
19-1	300	"	"	67.6	30.0	47.4	69.3	30.0	20.8	48.5
2	301	"	"	73.9	29.0	52.2				
3	300	22,520	"	68.3	30.5	47.5				
4	"	"	"	67.6	30.5	47.0				
20-1	"	22,500	107	64.5	20.5	51.2	63.8	20.1	12.8	51.0
2	"	"	"	66.1	21.0	52.2				
3	301	"	"	63.1	19.2	51.0				
4	"	"	"	61.4	19.6	49.4				
21-1	302	"	"	54.7	12.1	45.2	53.9	12.3	6.6	47.3
2	"	"	"	53.1	12.5	45.2				
22-1	"	"	103	50.0	9.6	45.4	49.9	9.4	4.6	45.2
2	"	"	"	49.7	9.2	45.0				
23-1	301	22,520	"	46.4	3.1	45.4	46.5	3.25	1.3	45.2
2	"	"	"	46.6	3.4	45.0				

Table A-3 (continued, page 4)

Experimental Results							Averaged Experimental Data			
Cond.	Temp. °F	Pressure psi	Salinity g/l	Total Gas SCF	% CO_2	CH_4 SCF	Total Gas	% CO_2	CO_2 SCF	CH_4 SCF
24-1	301	13,080	106	64.3	48.1	33.3	64.8	48.2	31.2	33.5
2	"	"	"	65.2	48.3	33.7				
25-1	"	13,020	"	75.6	62.1	28.7	75.0	62.0	46.5	28.5
2	"	"	"	74.3	61.9	28.3				
26-1	"	13,000	107	52.9	28.9	37.6	51.8	27.3	14.8	37.0
2	"	"	"	53.4	27.6	38.7				
3	"	"	"	50.9	26.0	37.7				
4	"	"	"	49.9	26.8	36.5				
27-1	"	13,040	"	44.4	10.1	39.9	46.5	10.1	4.7	41.8
2	"	"	"	46.9	11.2	41.7				
3	"	13,000	"	48.1	9.8	43.4				
4	"	"	"	46.7	9.6	42.2				

Table A-4 Empirical data for the solubility of methane and ethane at 302°F in aqueous NaCl solutions at a salinity of 107 grams/liter.

Sample number	Temp. $^{\circ}$F	Pressure psi	Salinity g/l	% C_2H_6	Total Gas SCF/Bbl	CH_4 SCF/Bbl
1	301	22,500	107	0.9	44.8	44.4
2	"	"	"	1.1	45.1	44.6
3	"	"	"	3.8	49.5	47.6
4	"	"	"	3.9	52.1	50.1
5	"	"	"	4.5	51.1	48.8
6	"	"	"	4.5	50.46	48.19
7	302	"	"	7.8	50.8	46.8
8	"	"	"	8.4	49.2	45.1
9	"	"	"	12.7	38.5	33.6
10	"	"	"	13.7	35.1	30.3
11	"	"	105	14.9	34.2	29.1
12	"	"	"	15.1	34.4	29.2
13	"	"	"	17.2	31.9	26.4
14	"	"	"	20.0	29.6	23.7
15	"	10,000	"	0.9	30.2	30.0
16	"	"	"	1.5	33.7	33.2
17	"	"	"	3.9	35.2	33.8
18	"	"	"	4.2	35.2	33.7
19	"	"	107	6.0	38.6	34.5
20	"	"	"	6.3	39.1	36.6
21	"	"	"	9.2	34.2	31.0
22	"	"	"	9.4	32.2	29.2
23	"	"	"	10.6	30.6	27.3
24	"	"	"	10.9	29.2	26.0
25	"	9,980	"	11.2	25.2	22.3
26	"	"	"	11.3	22.7	20.2

APPENDIX B

Gas Chromatographic Analysis Conditions

Instrumentation:

Hewlett-Packard Model 5840A Gas Chromatograph

Methane-Carbon dioxide Analysis:

Column - Stainless steel, 6 feet by 1/8 inch packed with Spherocarb 80/100 mesh.
Carrier Gas - Helium at 20 ml/min.
Detector - Thermal Conductivity.
Injection Temperature - 250°C.
Oven Temperature - 60°C.
Detector Temperature - 300°C.

Analysis - Area integration by HP 5840 microprocessor.

Methane-Ethane Analysis:

Column - Stainless steel, 6 feet by 1/8 inch packed with Carbosieve B 80/100 mesh.
Other analytical conditions were the same as for the methane-carbon dioxide analysis (above).

APPENDIX C

SOLUBILITY OF CRUDE OIL IN METHANE AS A FUNCTION OF PRESSURE AND TEMPERATURE[1]

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[1]Partially supported by DOE (contract DE-AS08-78ET12145). This article is dedicated to Hollis Hedberg and Stefano Neglia, both early proponents.

CONTENTS

Appendix

ABSTRACT

The solubility of a 44° API (0.806 specific gravity) whole crude oil has been measured in methane with water present at temperatures of 50° to 250°C and pressures of 740 to 14,852 psi, as have the solubilities of two high molecular weight petroleum distillation fractions at temperatures of 50° to 250°C and pressures of 4,482 to 25,266 psi. Both increases in pressure and temperature increase the solubility of crude oil and petroleum distillation fractions in methane, the effect of pressure being greater than that of temperature. Unexpectedly high solubility levels (0.5 to 1.5 grams of oil per liter of methane -at laboratory temperature and pressure) were measured at moderate conditions (50° to 200°C and 5,076 to 14,504 psi). Similar results were found for the petroleum distillation fractions, one of which was the highest molecular weight material of petroleum (material boiling above 266°C at 6 microns pressure). Unexpectedly mild conditions (100°C-15,200 psi; 200°C-7,513 psi) resulted in cosolubility of crude oil and methane. Under these conditions, samples of the gas-rich phase could give solubility values of 4 to 5 g/L, or greater.

Qualitative analyses of the crude-oil solute samples showed that at low pressure and temperature equilibration conditions, the solute condensate would be enriched in C_5 to C_{15} range hydrocarbons and in saturated hydrocarbons in the C_{15+} fraction. With increases in temperature and especially pressure, these tendencies were reversed, and the solute condensate became identical to the starting crude oil.

The data of this study, compared to that of previous studies, shows that methane, with water present, has a much greater carrying capacity for crude oil than in dry systems. The presence of water also drastically lowers the temperature and pressure conditions required for cosolubility.

The data of this and/or previous studies demonstrate that the addition of carbon dioxide, ethane, propane, or butane to methane also has a strong positive effect on crude oil solubility, as does the presence of fine grained rocks.

The n-paraffin distributions (as well as the overall composition) of the solute condensates are controlled by the temperature and pressure of solution and exsolution, as well as by the composition of the original starting material. It appears quite possible that primary migration by gaseous solution could "strip" a source rock of crude-oil like components leaving behind a bitumen totally unlike the migrated crude oil. The data of this study demonstrate previous criticisms of primary petroleum migration by gas solution are invalid; that primary migration by gaseous solution cannot occur based on the inadequacey of methane to dissolve sufficient volumes of crude oil or to dissolve the highest molecular weight components of petroleum (tars and asphaltenes).

INTRODUCTION

Of the different processes which lead to the accumulation of commercial oil deposits, the primary migration of petroleum is still considered by most investigators to be the least understood. It is an area where, speculative hypothesis far outweigh hard data -a situation best summed up by S. L. Clemens′ a.k.a. Mark Twain (1883, p. 174) quote "There is something fascinating about science. One gets such wholesale returns of conjecture out of such a trifling investment of fact."

Here we present data from a solubility study of crude oil (and high molecular weight petroleum distillation fractions) in methane in the presence of water. These data allow a more solid appraisal (Price and Wenger, 1982), than heretofore has been possible, of the feasibility of gaseous solution as a mechanism of primary petroleum migration. Here gaseous solution is taken as the solution of the components of a crude oil into a free methane gas phase in the pores of fine grained rocks and the movement of that phase from those rocks to a carrier system or directly to a reservoir-trap system.

Primary petroleum migration by gaseous solution has been championed previously by Sokolov (1948), Sokolov et al (1963), Neglia (1979) and Hedberg (1980). The mechanism has been criticized on an unsubstantiated assumption that a methane gas phase cannot dissolve the highest molecular weight (tar and asphalt) components of a crude oil (Uspenskii, 1962; Sokolov et al, 1963; Welte, 1965; Cordell, 1972; Price, 1976; Tissot and Welte, 1978, and others. McAuliffe (1980, p. 97) noted, "However it is doubtful that gas can contain the heavier hydrocarbons and N-S-O compounds in high-molecular weight crude oil fractions." Data of this paper reply to that criticism. McAuliffe (1978) and Hunt (1979) have criticized this migration mechanism on the basis that the crude oil to gas ratios of many producing fields negate the possibility of primary migration by gaseous solution. Data of this paper also reply partially to that criticism. Other criticisms of this mechanism are discussed elsewhere (Price and Wenger, 1982), as is the relation of these laboratory data to the natural system.

PRESENTATION OF DATA

Quantitative Solubility Data

The solubility of the Spindle field whole crude oil is given in Figure 1 and Table 1 (see appendix for a description of the crude oil). Obvious breaks in slope occur in the 50° and 100°C curves. As shown by qualitative analysis of the solute hydrocarbons (Table 2, discussed below), the lower pressure

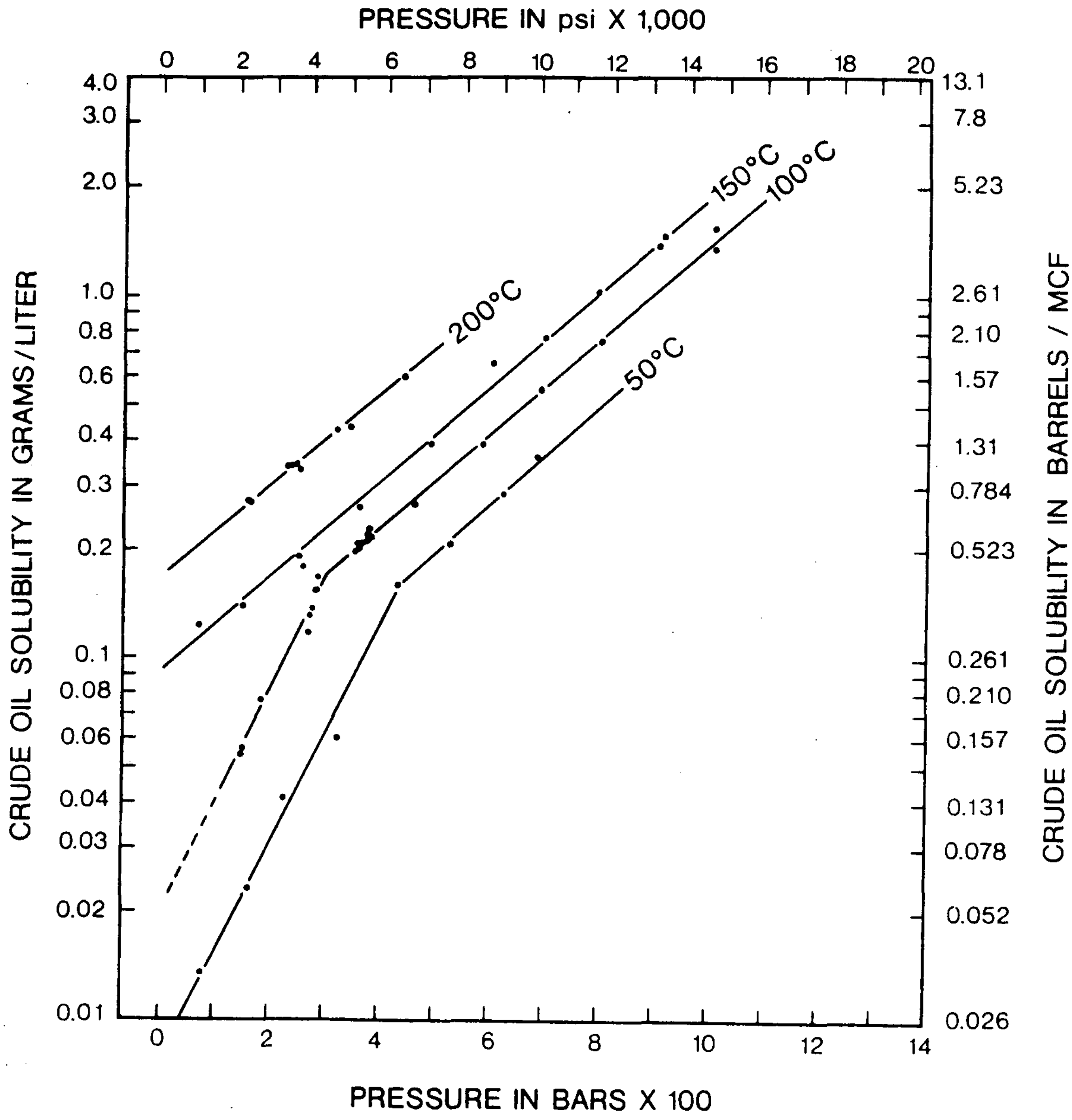

Figure 1.--Solubility of Spindle field whole crude oil (see appendix for description) in pure methane as a function of pressure for different isotherms. The solubility scale of the left hand side of the figure, grams of crude oil per liter of methane (at 25°C and one atmosphere), is accurate. The scale on the right hand side is only an approximation for descriptive purposes as a constant API gravity of 35° (.850 specific gravity) was assumed for all crude oil solute samples for ease of calculation. This assumption is invalid for the lower pressure-temperature samples which would have much higher API (lower specific) gravities than the assumed value. Therefore solubility values on the volumetric scale (Bbls/MCF) at lower pressures and temperatures would actually be slightly higher than those shown. For higher temperature and pressure samples this approximation is likely close to reality. The recovered volumes of most crude oil solute samples prevented determination of their API (specific) gravities. Data from Table 1.

Table 1.--Solubility of the Spindle whole crude oil, and water, in methane in grams per liter of gas at 25°C and one atmosphere. Bars may be converted to psi by multiplying by 14.504 and to atmospheres by multiplying by 1.0132.

Temperature in °C	Pressure in bars	Oil/Gas in g/L	Water/Gas in g/L	Percent water
50.0	79	0.0136	0.00156	10.3
50.0	166	0.0232	0.00172	6.89
50.6	227	0.0407	0.00168	3.25
50.6	324	0.0597	0.00138	2.25
49.2	433	0.159	0.00217	1.35
49.2	529	0.207	0.00078	0.38
49.4	626	0.284	0.00288	1.00
49.8	688	0.360	0.00210	0.58
49.4	807	0.669	0.00238	0.35
99.2	71	0.0430	0.00386	8.23
98.9	145	0.0528	0.00390	6.88
100.0	150	0.0542	0.00835	13.3
99.8	153	0.0560	0.00950	14.5
100.6	183	0.0768	0.00892	9.62
100.6	186	0.0763	0.00957	11.1
100.8	271	0.117	0.00681	5.52
100.8	273	0.131	0.00388	2.87
100.2	276	0.135	0.00316	2.28
99.8	284	0.155	0.00320	2.02
99.0	288	0.166	0.00498	2.92
100.0	355	0.196	0.00671	3.30
100.0	360	0.207	0.00951	4.39
99.8	364	0.201	0.01060	5.04
99.8	366	0.208	0.01070	4.9
100.0	377	0.219	0.00305	1.37
100.6	377	0.212	0.00356	1.66
100.0	384	0.227	0.00214	0.93
100.0	385	0.217	0.00349	1.58
100.0	466	0.267	0.00614	2.25
99.2	588	0.393	0.01030	2.55
99.8	695	0.558	0.01300	2.27
99.8	811	0.757	0.00394	0.52
99.4	1008	1.542	0.00652	0.42
99.4	1010	1.362	0.00404	0.29
99.2	1024	1.360	0.00574	0.42
150.6	73	0.123	0.0204	14.2
148.9	153	0.137	0.0143	9.45
150.2	255	0.190	0.0072	3.65
150.2	262	0.177	0.0078	4.22
150.2	364	0.261	0.0081	3.02
150.5	495	0.391	0.0099	2.47
150.6	610	0.653	0.0109	1.65
150.8	700	0.740	0.0114	1.51
150.8	705	0.770	0.0118	1.50
149.4	772	0.816	0.0153	1.50
150.0	798	1.03	0.0158	1.51
150.0	909	1.39	0.0127	0.90
150.2	918	1.46	0.0102	1.50
205.0	160	0.270	0.0438	6.17
205.0	165	0.269	0.0315	10.5
199.0	234	0.339	0.0197	5.49
199.0	240	0.340	0.0205	5.69
204.0	251	0.324	0.0300	8.47
204.2	255	0.330	0.0405	10.9
199.8	320	0.410	0.0171	4.00
199.4	321	0.403	0.0281	6.52
199.8	323	0.411	0.0252	5.78
204.8	346	0.434	0.0323	6.94
204.8	445	0.591	0.0307	4.93
251.1	51	1.12	0.612	35.2
248.9	90	0.699	0.209	23.0
250.2	161	0.489	0.130	21.0
251.1	259	0.507	0.094	15.7
251.1	352	0.572	0.084	12.8
251.3	452	0.828	0.088	9.59
251.1	510	1.15	0.081	6.57

Table 2.--Qualitative analyses of Spindle whole crude oil solute samples. Analytical methods given in appendix. Bars may be converted to psi by multiplying by 14.504 and to atmospheres by multiplying by 1.0132.

		Normalized Carbon Number Distribution in percent								C_{15+} Compound Distribution in percent		
Temperature in °C	Pressure in bars	C_1-C_{10}	C_{10}-C_{15}	C_{15}-C_{20}	C_{20}-C_{25}	C_{25}-C_{30}	C_{30+}	C_1-C_{15}	$\frac{C_{25}+}{C_1-C_{15}}$	Saturates	Aromatics	N-S-O's
49.4	327	33.60	53.55	11.27	1.59	---	---	87.15	0	---	---	---
49.2	356	40.67	44.00	11.72	2.93	0.69	---	84.67	0.008	---	---	---
49.2	413	35.48	47.28	11.82	4.05	1.37	---	82.76	0.017	---	---	---
49.2	433	28.92	50.80	15.36	3.95	0.97	---	79.71	0.012	94.80	4.81	0.38
49.2	529	31.32	38.06	18.25	8.47	2.19	1.70	69.39	0.056	---	---	---
49.5	621	27.08	38.16	20.80	8.68	3.39	1.59	65.24	0.076	95.37	4.35	0.27
49.5	626	25.82	37.62	20.36	9.10	4.09	3.01	63.44	0.112	---	---	---
49.8	688	20.47	37.18	22.77	10.75	5.24	3.38	57.65	0.150	---	---	---
49.4	729	29.02	34.18	20.19	9.57	4.13	2.91	63.20	0.111	94.16	5.07	0.77
49.4	807	17.20	30.14	22.04	13.91	8.25	8.47	47.33	0.353	91.30	6.66	1.94
98.3	249	35.81	51.52	9.92	2.23	0.57	---	87.32	0.006	---	---	---
97.8	343	36.08	45.81	13.51	3.16	1.08	---	82.25	0.013	94.71	4.67	0.62
100.0	360	34.26	38.82	19.06	5.39	1.99	0.48	73.08	0.034	---	---	---
99.2	468	36.30	39.22	16.57	5.30	1.81	0.80	75.52	0.035	94.11	5.24	0.65
99.2	588	29.13	31.40	18.75	18.75	5.50	5.30	60.53	0.178	92.78	5.82	1.40
100.0	700	15.49	33.44	21.69	13.03	7.94	8.41	48.93	0.334	89.65	8.67	1.68
99.8	701	17.88	25.97	19.62	12.91	8.99	14.63	43.86	0.538	---	---	---
99.4	702	16.88	27.98	19.39	12.96	9.10	13.69	44.86	0.508	---	---	---
99.8	811	18.71	27.77	19.27	13.08	8.83	12.34	46.47	0.456	86.80	10.63	2.57
99.4	1008	19.51	25.66	18.46	13.11	8.61	14.64	45.17	0.515	---	---	---
149.8	76	49.36	40.80	6.73	2.25	0.77	---	90.25	0.008	---	---	---
150.2	151	35.57	45.36	14.69	3.03	1.35	---	80.93	0.017	---	---	---
150.2	255	38.57	41.91	12.62	4.70	2.20	---	80.48	0.027	---	---	---
150.2	364	34.00	43.53	15.33	4.81	2.01	0.32	77.53	0.030	92.26	6.64	1.10
150.5	495	31.76	33.44	20.12	8.57	3.81	2.20	65.00	0.092	94.56	4.32	1.12
150.6	610	17.93	32.35	21.68	12.81	7.51	7.52	50.28	0.299	---	---	---
150.2	635	21.42	26.81	18.90	12.25	8.15	12.55	48.15	0.430	88.07	9.00	2.93
150.0	798	18.27	26.75	19.57	12.57	9.28	13.56	45.02	0.507	86.08	10.98	2.94
150.0	909	20.59	26.22	19.07	12.76	8.12	13.24	46.81	0.456	---	---	---
205.8	88	59.48	33.71	5.60	1.01	0.20	---	93.19	0.002	---	---	---
204.8	163	38.76	45.23	12.04	3.51	0.46	---	83.98	0.006	94.04	4.89	1.07
203.3	197	38.52	45.70	12.98	2.46	0.34	---	84.22	0.004	94.07	5.17	0.76
199.4	247	24.53	53.56	16.58	3.98	1.03	0.31	78.34	0.017	---	---	---
205.8	340	38.14	37.41	15.77	5.51	2.08	1.05	75.59	0.041	94.26	4.90	0.84
205.2	458	23.83	30.14	24.57	12.21	6.81	2.38	54.03	0.170	---	---	---
204.0	468	10.94	28.46	21.56	14.55	10.28	14.21	39.40	0.622	---	---	---
205.8	609	19.31	26.95	19.78	12.97	8.82	12.18	46.25	0.454	---	---	---
206.1	620	15.12	28.85	14.76	14.77	10.50	16.00	43.97	0.603	82.66	13.72	3.62
251.1	63	34.61	54.93	10.27	1.91	---	---	89.54	0	---	---	---
248.9	90	38.44	49.34	10.44	1.77	---	---	87.79	0	95.36	3.77	0.87
250.2	161	38.63	44.36	13.42	3.03	0.55	---	82.99	0.007	94.53	4.86	0.61
251.1	259	30.79	41.48	17.37	6.26	2.57	1.52	72.28	0.057	93.48	5.89	0.63
251.1	352	14.40	43.78	23.52	10.64	4.63	3.02	58.13	0.132	93.91	5.18	0.91
251.3	452	14.87	31.77	22.21	13.09	9.26	9.00	46.64	0.392	91.74	6.63	1.43
251.1	510	8.58	21.72	16.36	12.90	9.78	8.94	30.30	0.618	88.79	8.43	2.78
251.1	523	10.94	26.61	21.24	14.39	9.93	14.59	39.85	0.615	---	---	---
Spindle Crude Oil		29.30	23.32	17.03	11.13	7.29	11.94	52.62	0.3521	86.99	10.89	2.12
Kimball Crude Oil										86.87	9.88	3.25

samples of the 50° and 100°C isotherms were composed almost entirely of C_4-C_{10} or C_4-C_{15} hydrocarbons. Thus these breaks in slope were actually experimental artifacts, caused by a depletion of the lowest molecular weight hydrocarbons in the hydrocarbon reservoir in the pressure vessel, at a crude oil solubility level of roughly 0.16 g/L. Crude oil solubility data at 250°C (Fig. 2, Table 1) plot as a hyperbolic curve as a function of pressure, with a minimum at around 2,900 psi.* Again this behavior was due to selective solution (Table 2) of the lower molecular weight hydrocarbons (C_4 to C_{15}) at lower pressusres, and a depletion of those hydrocarbons in the hydrocarbon reservoir of the presssure vessel.

The extremely high solubilities (1.0 gram/liter and higher) that we measured for moderate temperatures (50° to 150°C) and pressures (10,150 to 14,500 psi) were surprising and unexpected. With water present in the system, as would be the case in nature, methane exhibits an extreme carrying capacity for crude oil.

Cosolubility was encountered for the 100°, 150°, and 200°C isotherms at pressures slightly higher (435 to 870 psi) than the highest pressure points shown for each isotherm (Fig. 1). The relatively mild conditions (100°C, 15,230 psi; 150°C, 13,634 psi; and 200°C, 7,513 psi-we found that as temperature increased, lower pressures were required for cosolubility) at which we encountered cosolubility were surprising, and again testify to an extreme carrying capacity that methane has for crude oil at elevated

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*We have given pressures here in the non-metric psi (pounds per square inch) as most of the people who will use these data employ that unit of measurement. An exception to this is in our tables of original data where the data were given in our laboratory unit of measurement, bars. Bars may be converted to psi by multiplying by 14.504 and to atmospheres by multiplying by 1.0132. Data of other investigators discussed here was also converted to psi from their original unit of measurement.

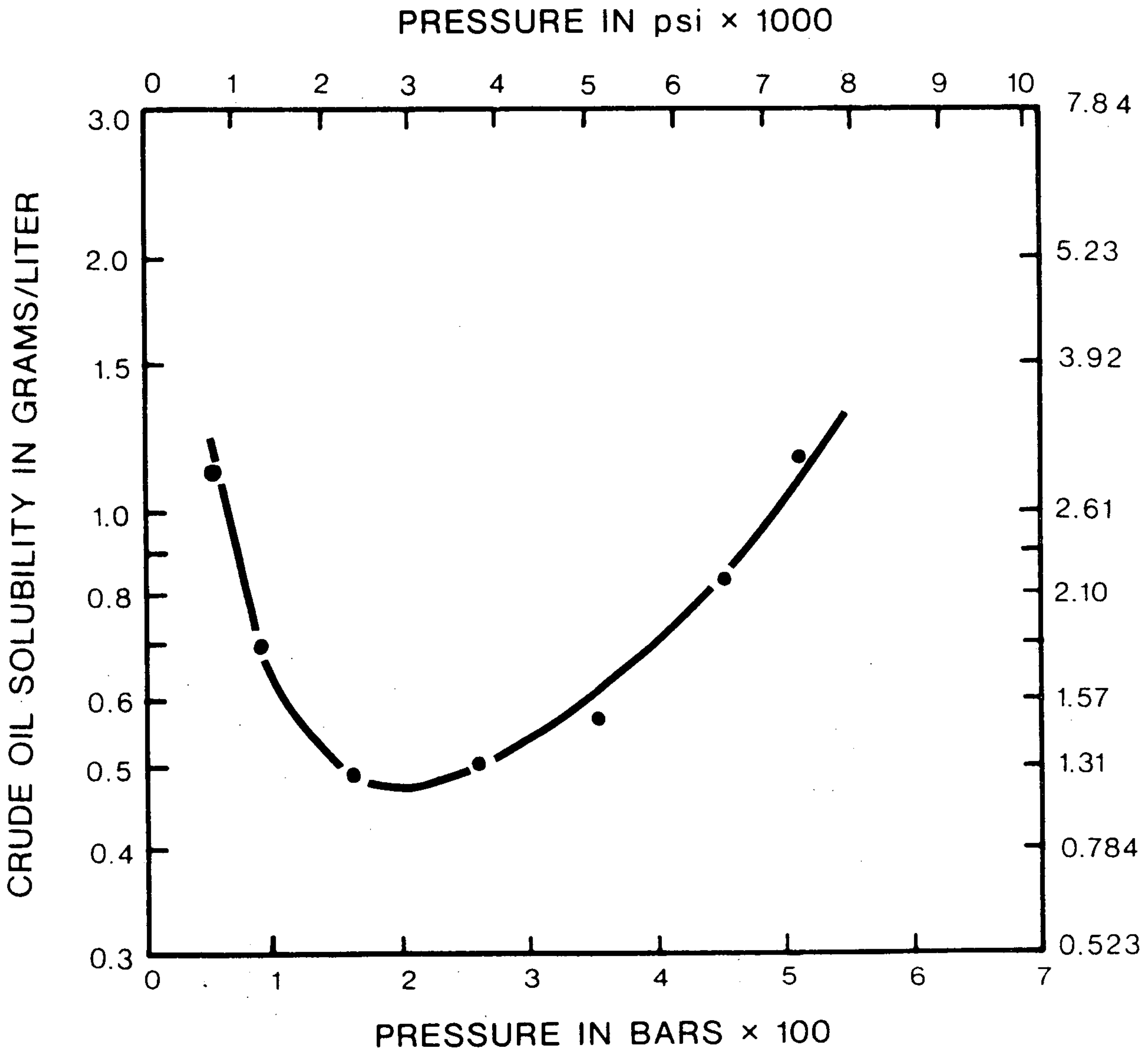

Figure 2.--Solubility of Spindle field whole crude oil (see appendix for description) in pure methane as a function of pressure at 250°C. The solubility scale of the left hand side of the figure, grams of crude oil per liter of methane (at 25°C and one atmosphere), is accurate. The scale on the right hand side is only an approximation for descriptive purpose as a constant API gravity of 35° (.850 specific gravity) was assumed for all crude oil solute samples for ease of calculation. See discussion in the figure 1 caption. Data from Table 1.

temperature and pressure. At pressures in excess of critical pressure, crude oil and methane became a one phase system and under this condition, in our tests for cosolubility (see appendix), we recorded solubility values as high as 4 to 5 grams/liter (oil to gas).

An arithmetic plot of crude oil solubility versus pressure (not shown) revealed a significant break in slope for the 50^{o}, 100^{o} and $150^{o}C$ isotherms at around 8,700 psi, where the effect of pressure on increasing crude oil solubility became dominant. Isobaric arithmetic plots of crude oil solubility versus temperature (not shown) demonstrated that increases in temperature had a smaller effect on increasing crude oil solubility than did increases in pressure.

The effect of adding carbon dioxide to the methane was examined for one data point (Table 3) to verify the results of a previous study (Zaks, 1952). We found, as Zaks (1952) did, that the addition of carbon dioxide to methane significantly increased the solute capacity of methane. Unfortunately however, time limitations prevented detailed examination of the carbon dioxide influence.

The solubility of the twelfth (F-12) distillation fraction (material distilled off at $215^{o}C$, 6 microns pressure, roughly C_{31} to C_{47}) in methane gas as a function of pressure for three different isotherms 50^{o}, 150^{o}, and $250^{o}C$ is given in Figure 3 and Table 4. Pressure increases, at all temperatures, drastically increased the solubility of this distillation fraction, literally hundreds of times. With this fraction pressure was also more dominant than temperature in increasing crude oil solubility. However here, the effect of temperature on increasing crude oil solubility was much more pronounced than it was for the whole crude oil. The high solubilities measured for this high molecular weight fraction were unexpected. The solubility of the fifteenth

Table 3.--Comparison of the solubility of the Spindle whole crude oil and water in pure methane and in a mixture of 71.8 percent methane and 28.2 percent carbon dioxide in grams per liter of gas at 25°C and one atmosphere. The oil/gas solubility value for the pure methane is from figure 1, and the water/gas solubility value from figure 5. Bars may be converted to psi by multiplying by 14.504 and to atmospheres by multiplying by 1.0132.

Temperature in °C	Presssure in bars	Oil/Gas in g/L	Water/Gas in g/L	Percent water
28.2 Percent Carbon Dioxide				
102.2	416	0.405	0.00977	2.36
Pure Methane				
100	416	0.237	0.006	2.45

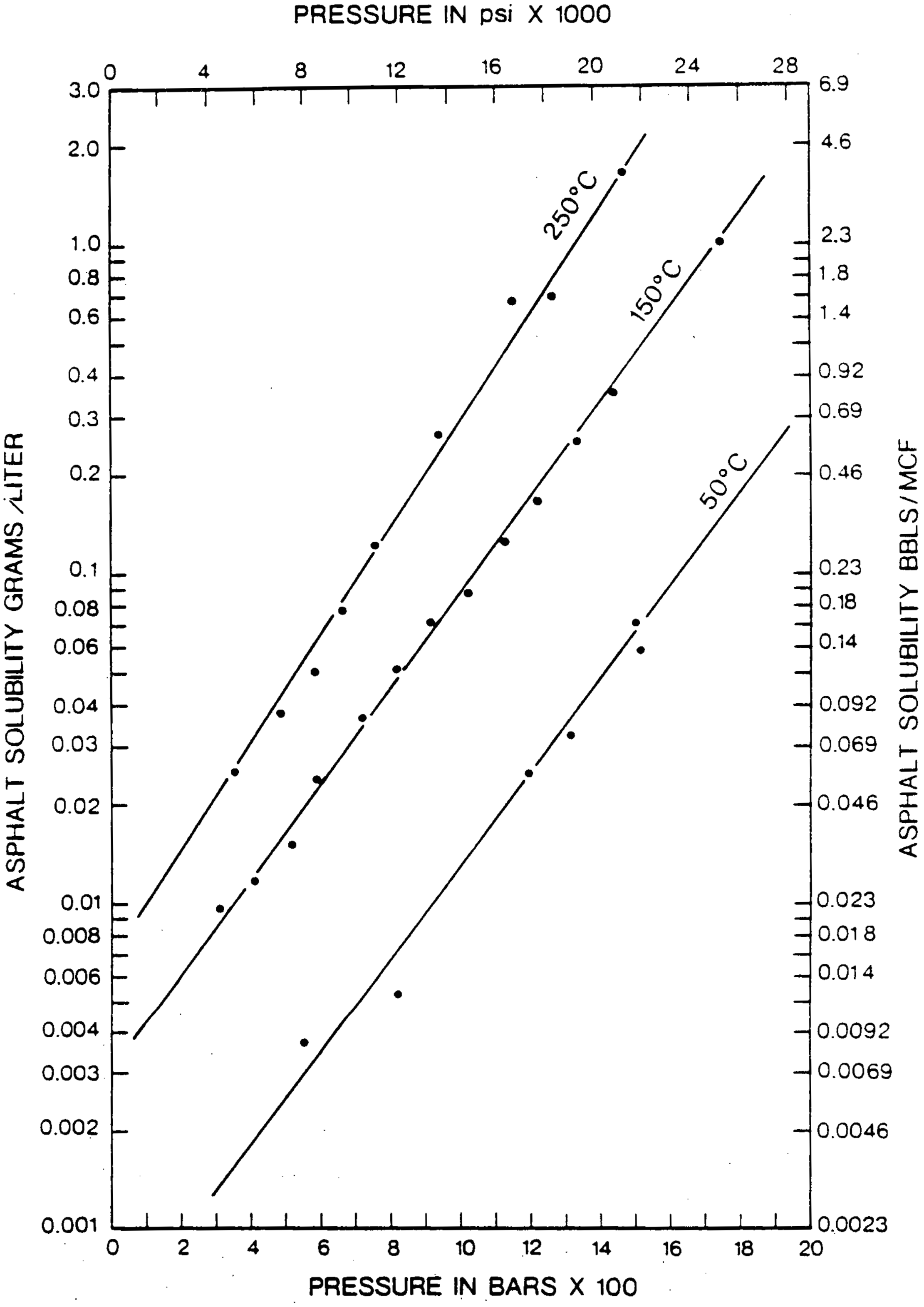

Figure 3.--Solubility of the twelfth distillation fraction (F-12) of the Kimball field crude oil (see appendix for description) in pure methane as a function of pressure at three different isotherms. The left hand solubility scale (grams of asphalt per liter of methane at 25^{o}C and one atmosphere) is valid. The solubility scale on the right hand side (Bbls/MCF) is only an approximation for descriptive purposes. See discussion in the figure 1 caption. In the case of the F-12 fraction a constant API gravity of 15^{o} (.966 specific gravity) was assumed. Data from Table

Table 4.--Solubility of the twelfth (F-12) distillation fraction (material boiling below 215°C at 6 microns pressure) of the Kimball crude oil, and water, in methane in grams per liter of gas at 25°C and one atmosphere. Bars may be converted to psi by multiplying by 14.504 and to atmospheres by multiplying by 1.0132.

Temperature in °C	Presssure in bars	Oil/Gas in g/L	Water/Gas in g/L	Percent water
50.0	545	0.00371	0.00278	42.9
50.0	817	0.00534	0.00666	55.0
50.0	1195	0.0248	0.00276	10.2
49.4	1314	0.0324	0.00163	4.78
50.2	1501	0.0711	0.00599	7.77
49.8	1514	0.0586	0.00413	6.58
152.5	309	0.0972	0.00769	44.2
151.8	412	0.0130	0.00716	35.5
152.5	520	0.0151	0.00525	25.8
152.5	617	0.0238	0.00396	14.3
152.8	723	0.0365	0.00185	4.83
152.8	819	0.0513	0.00379	6.87
152.8	924	0.0713	0.00301	4.05
152.8	1025	0.0874	0.00352	3.87
152.5	1127	0.126	0.00363	2.80
152.5	1221	0.164	0.00348	2.08
152.5	1333	0.254	0.00512	1.98
152.5	1438	0.357	0.00626	1.72
152.0	1742	1.00	0.0190	1.80
251.3	357	0.0248	0.0826	76.9
251.3	487	0.0374	0.0643	63.2
250.2	586	0.0498	0.0574	53.5
251.1	663	0.0768	0.0545	41.5
250.8	759	0.122	0.0389	24.3
251.8	909	0.266	0.0468	14.9
250.6	1150	0.672	0.0802	10.7
250.6	1265	0.686	0.0804	10.5
248.3	1465	1.65	0.074	4.30

(F-15) distillation fraction (material boiling above 266°C at 6 microns pressure, roughly C_{47+}) is given in Figure 4 and Table 5 for 250°C as a function of pressure. Again increases of pressure had a strong positive effect on increasing the gaseous solubility of even tar.

Figure 5 gives the solubility of water in the methane gas phase for the 100°, 150°, 200°, and 250°C isotherms as a function of pressure. Although the data show scatter; for all temperatures, with increase in pressure, water becomes less soluble in methane.

Qualitative Solubility Data

Qualitative analyses performed on solute samples of the crude oil and petroleum distillation fractions (see appendix for methods) revealed that temperature, and especially pressure, controlled the molecular weight (carbon number) distributions of the solute hydrocarbons (Table 2 and Fig. 6). At low pressures and low temperatures the lower molecular weight (C_1 to C_{15}) hydrocarbons made up almost all of the solute sample. At any given pressure, as temperature increased from 50° to 250°C, the C_{15+} material became more dominant as the C_1 to C_{15} material decreased in abundance (column 9, Table 2). This demonstrates that methane, at high temperatures, has an increased carrying capacity for higher molecular weight hydrocarbons compared to low temperatures.

However, pressure has an even greater effect than temperature on increasing the average molecular weight of the solute hydrocarbons. At any given temperature, as pressure increased, the C_1 to C_{15} hydrocarbons decreased from between 87 to 90 percent at low pressures to between 40 to 45 percent at high pressures (column 9, Table 2). At the same time, the C_{30+} material increased from zero to between 8 to 16 percent (column 8, Table 2). This

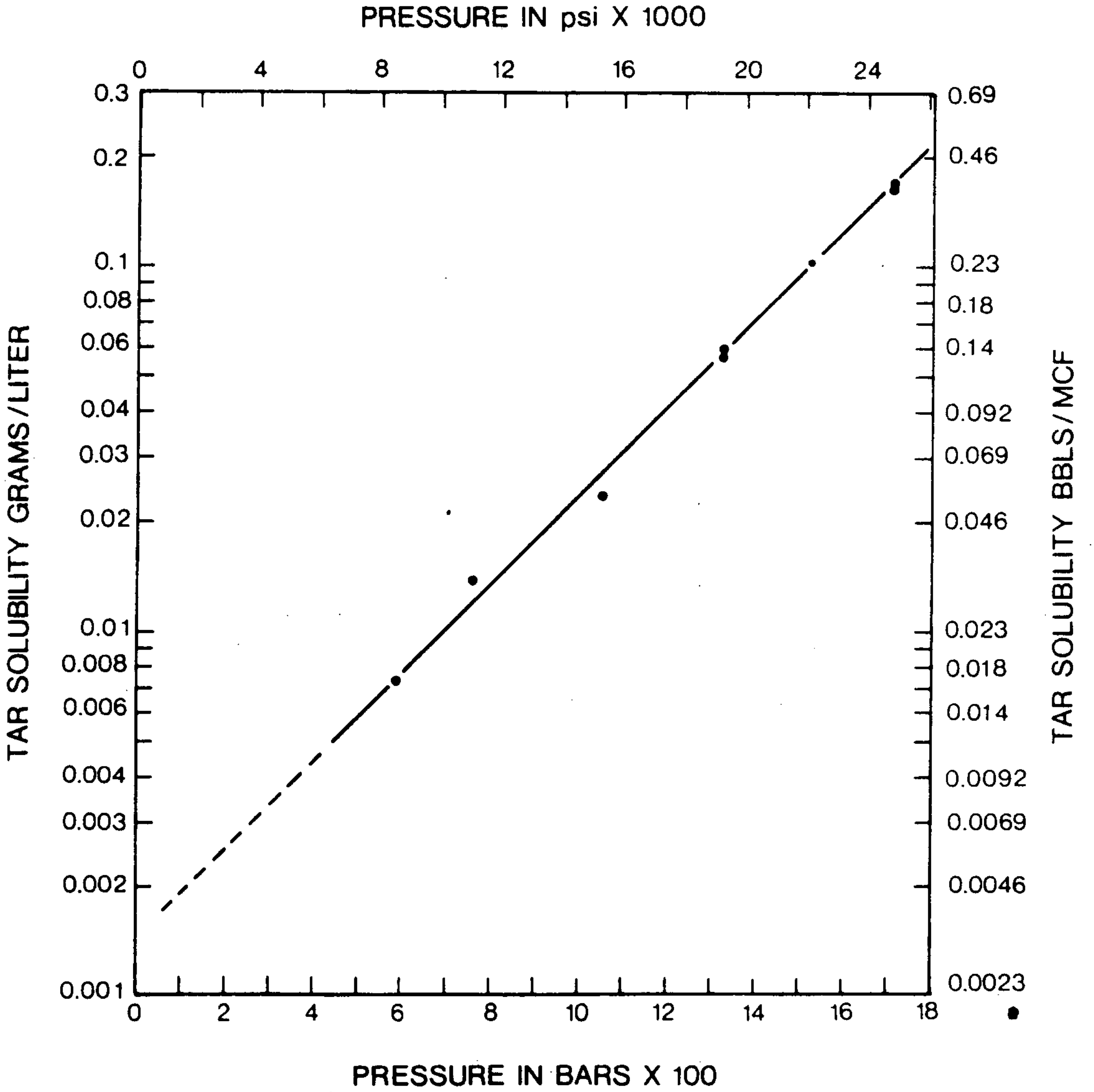

Figure 4.--Solubility of the fifteenth distillation fraction (F-15) of the Kimball field crude oil (see appendix for description) in pure methane as a function of pressure at 250°C. The left hand solubility scale (grams of asphalt per liter of methane at 25°C and one atmosphere) is valid. The solubility scale on the right hand side (Bbls/MCF) is only an approximation for descriptive purposes. See discussion in the Figure 1 caption. In the case of the F-15 fraction, a constant API gravity of 7.5° (1.015 specific gravity) was assumed. Data from Table 5.

Table 5.--Solubility of the fifteenth (F-15) distillation fraction (material boiling above 266°C at 6 microns pressure) of the Kimball crude oil, and water, in methane in grams per liter of gas at 25°C and one atmosphere. Bars may be converted to psi by multiplying by 14.504 and to atmospheres by multiplying by 1.0132.

Temperature in °C	Presssure in bars	Oil/Gas in g/L	Water/Gas in g/L	Percent water
248.3	582	0.00738	0.0141	65.6
248.0	759	0.0140	0.0305	68.6
247.8	1056	0.0197	0.0252	56.2
249.0	1323	0.0321	0.0232	41.9
248.5	1328	0.0430	0.0178	29.3
248.5	1335	0.0412	0.0215	34.4
249.2	1527	0.107	0.0179	14.3
250.6	1720	0.166	0.0213	11.3
248.3	1723	0.163	0.0269	14.2

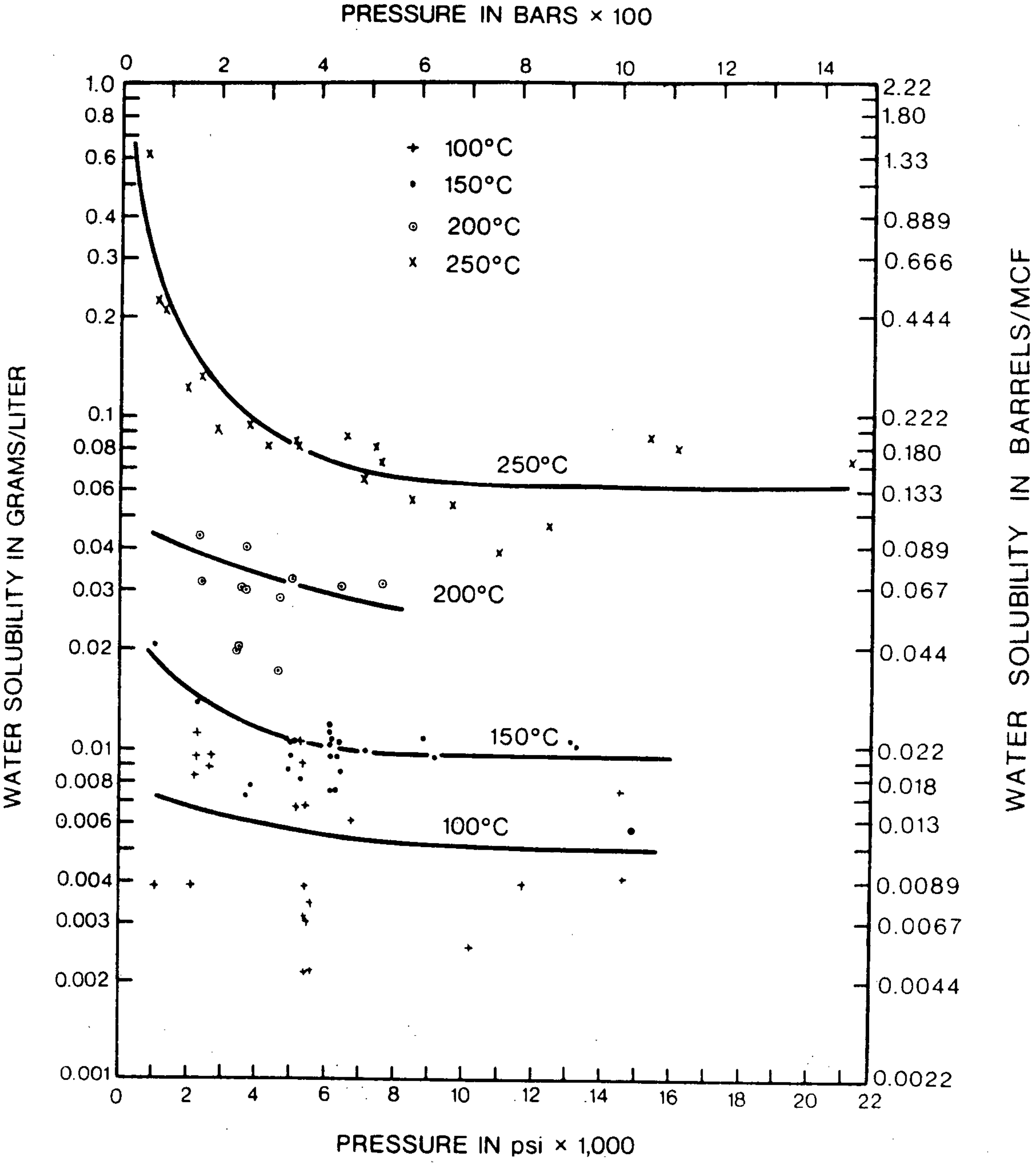

Figure 5.--Solubility of water in pure methane at four different isotherms as a function of pressure. The solubility scales on both sides of the figure are accurate. (Water has a constant density of 1.00 gram/cc). Data from Tables 1, 4 and 5 as well as unpublished data from equilibrium approach studies.

overall carbon number shift is displayed in a plot of the percentage of the C_{25+} compounds divided by the percentage of C_1 to C_{15} compounds for solute crude oil samples from the 50°, 150°, and 250°C runs (Fig. 7). For all three temperatures, this ratio changed from zero at low pressures to between 0.35 to 0.60 at high pressures. Another manifestation of this shift in carbon number distribution was seen in the comparison of the original Spindle field crude oil (line 47, Table 2) to any of the solute samples. This showed that the solute samples became more crude oil like with increase of either pressure or temperature.

The percentages of the different compound classes (saturated hydrocarbons, aromatic hydrocarbons, and N-S-O bearing compounds) in the C_{15+} fraction of the solute samples varied slightly with temperature and more significantly with pressure. At low pressure, especially at low temperature, the saturated hydrocarbons were preferentially taken into solution over the aromatic hydrocarbons and N-S-O bearing compounds (columns 11 through 13, Table 2) compared to the original crude oil (line 47, Table 2). At temperatures of 100°C or greater, with increase in pressure, the percentage of the saturated hydrocarbons in the C_{15+} fraction of the solute samples decreased from between 96 to 95 percent to between 88 to 82 percent, as the percentages of both the aromatic hydrocarbons and N-S-O bearing compounds increased. At constant pressure, at pressures less than about 5,800 psi, increase in temperature had no discernable effect on compound class changes in the C_{15+} fraction of the solute samples. However at pressures in excess of about 5,800 psi, at constant pressure, with increases in temperature the percentage of the saturated hydrocarbons decreased as the percentages of aromatic hydrocarbons and N-S-O bearing compounds increased. This resulted in the C_{15+} solute material coming to more resemble the original crude oil

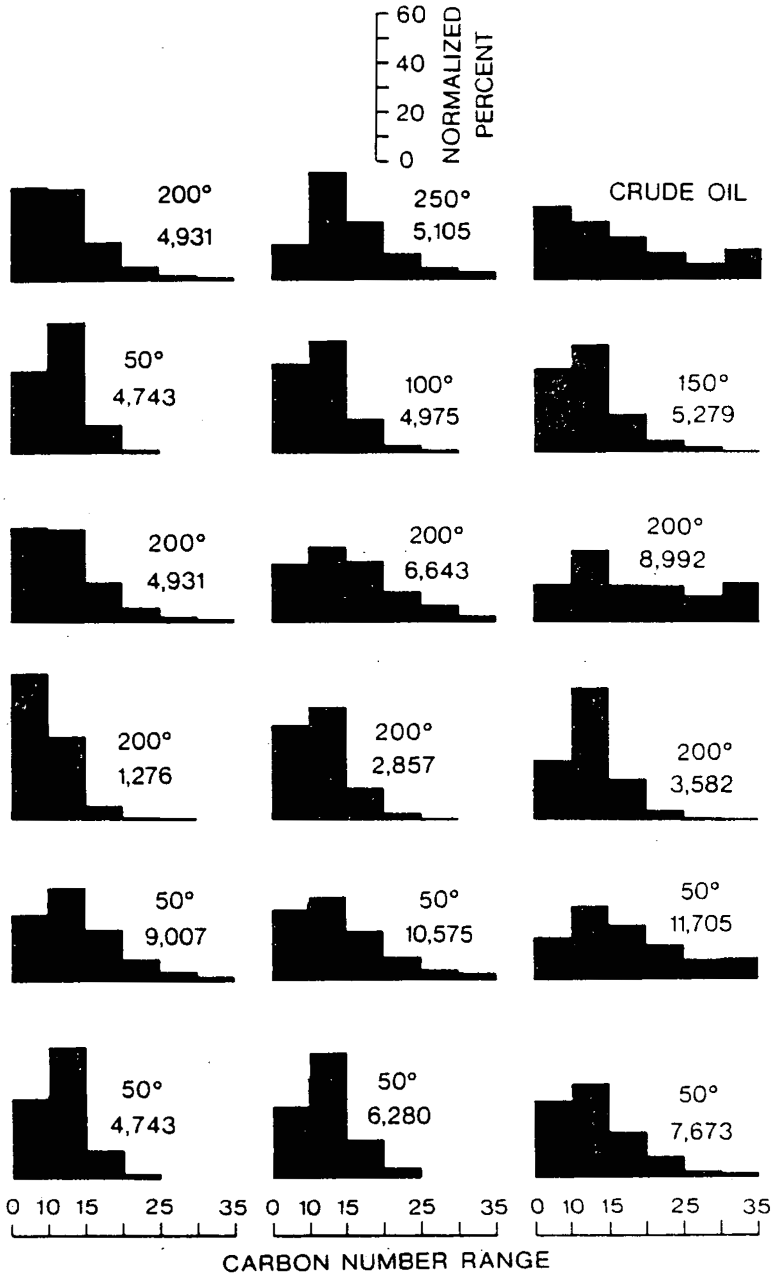

Figure 6.--Plot of carbon number distribution of various Spindle field crude oil solute samples equilibrated at different pressures and temperatures. The left hand most bar of every bar graph represents compounds with carbon numbers of 0 to 10, which in reality were largely C_4 to C_{10} compounds. All other bars are increments of five carbon numbers. The bottom two lines of bar graphs show the influence of pressure on solute composition as a function of pressure at a constant temperature of 50°C. The middle two lines of bar graphs show the influence of pressure on solute composition at a constant temperature of 200°C. The top two lines of bar graphs (five samples) show the influence of temperature on solute composition at a roughly constant pressure of 4,743 to 5,279 psi. The carbon number distribution of the original Spindle whole crude oil is shown in the upper right hand corner of the figure.

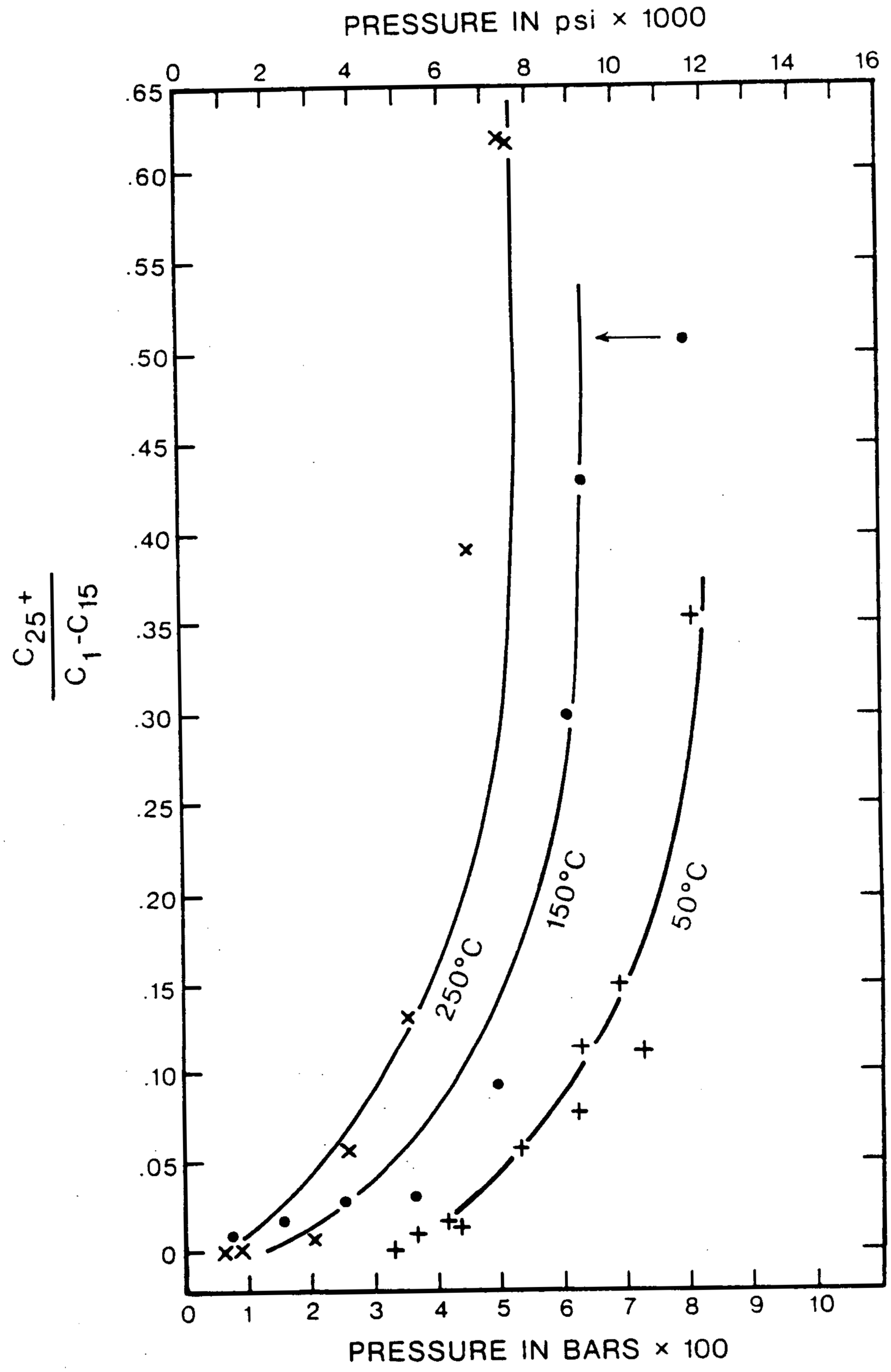

Figure 7.--Plot of C_{25}+/C_{1-15} ratio for solute samples of the Spindle whole crude oil equilibrated at different pressures at three different isotherms (50°, 100°, and 150°C). This ratio is the percentage of compounds with carbon numbers of C_{25} or greater (C_{25+}) divided by the percentage of compounds with carbon number between C_1 to C_{15}. Data from Table 2.

(columns 11 to 13 and line 47, Table 2).

Changes in the carbon number distribution of the solute crude oil samples as a result of changes in temperature and presssure are most evident in the gas chromatograms of the solute samples (Fig. 8). Due mainly to the high pressures, the 50°C-11,705 psi, 100°C-11,763 psi, and 200°C-8,833 psi solute samples all closely resemble the starting crude oil despite large differences in temperature. The pressure effect on the qualitative aspects of gas solution is most evident in the 50°C-11,705 psi solute sample. In spite of the low temperature, the carbon number distribution (lines 10 and 47, Table 2) and overall appearance (Fig. 8) of this sample is quite similar to the original oil. Even considering the small differences in the compound class distributions, and percentages of C_{30+} material, the close similarity at this low temperature was suprising. The 100°C-3,612 psi, and 250°C-914 psi samples demonstrate the other endpoint. Although the temperatures of these two samples were higher than the 50°C-11,705 psi sample, the low pressures prevented significant solution of any C_{18+} material. These two samples are equivalent to high API gravity condensates found in the natural system. The temperature effect on the qualitative aspects of gas solution is also apparent with these two samples. In spite of the large pressure differential (914 versus 3,612 psi) the lower pressure 250°C solute sample was almost identical in composition (lines 11 and 39, Table 2) and appearance (Fig. 8) to the much higher pressure 100°C solute sample.

The 250°C-3,757 psi, and 150°C-7,180 psi solute samples are examples between the high and low pressure cases. These samples were equilibrated at temperatures and pressures which resulted in a transition from gas-condensate characteristics to crude-oil characteristics. Significant amounts of C_{20+} material were present in both samples, which still do not, however, totally

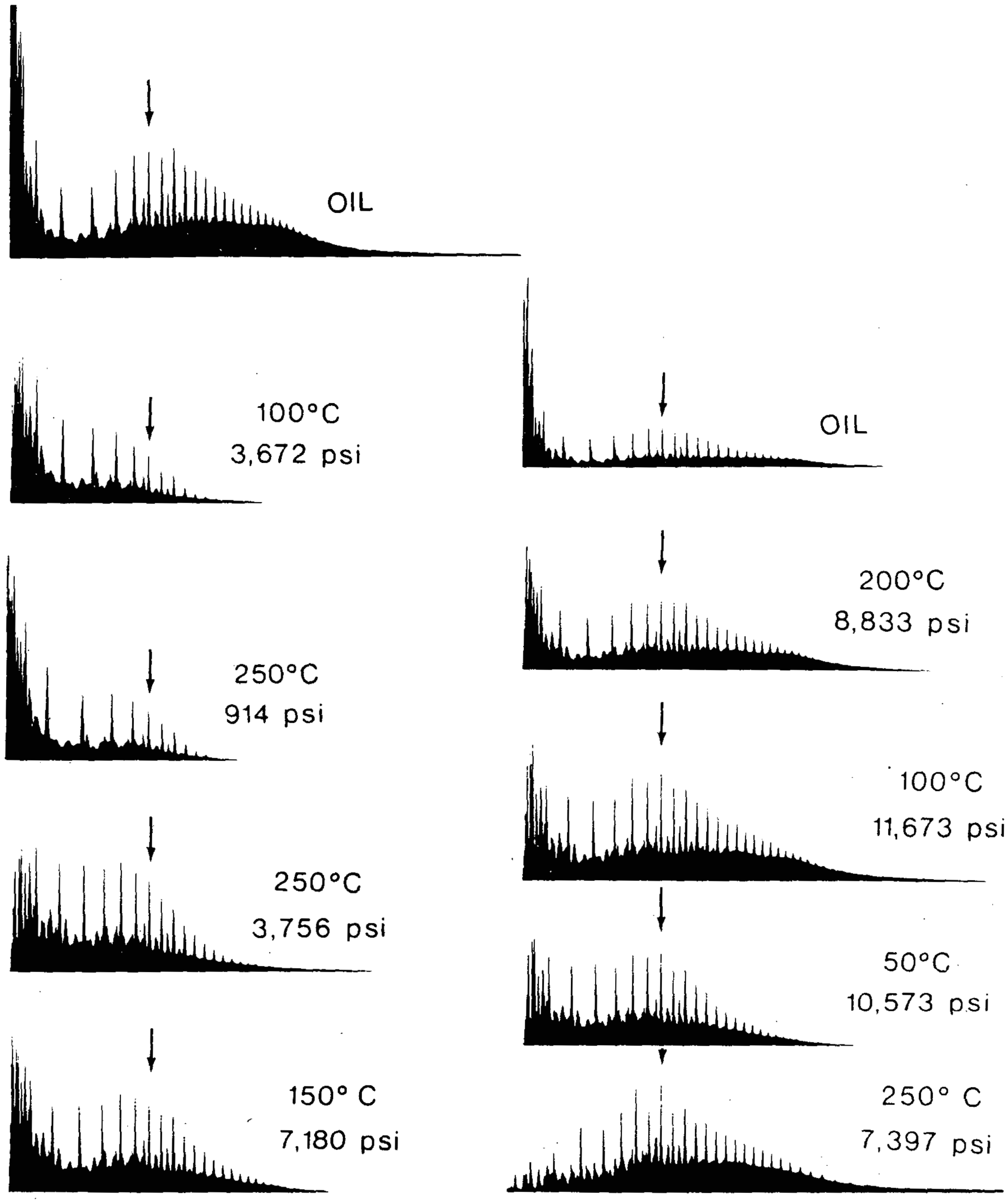

Figure 8.--Gas chromatograms of solute samples of the Spindle crude oil equilibrated under the conditions shown above each chromatogram. Two chromatograms of different attenuations of the original Spindle crude oil are also given. The C-15 n-paraffin is designated in each chromatogram by the arrow.

resemble the starting material. Whereas the starting crude oil had 30.36 percent of C_{20+} material, the 250°C-3,757 psi solute sample had only 10.35 percent and the 150°C-7,180 psi sample only 14.58 percent.

The 250°C-7,397 psi sample (Fig. 8) is an example of another control, besides temperature and presssure, on the qualitative aspects of gas solution of crude oil and that is the composition of the starting material. In this case the crude oil reservoir in the pressure vessel had been largely depleted in C_4 to C_7 material. The pressure and temperature at which this sample was equilibrated, were such that if more lower molecular weight material were present to be dissolved, it would have been dissolved. However, this was not the case, and the result was a sample depleted in C_4 to C_7 material compared to a "normal" solute sample.

Crude oil n-paraffin distributions have been used to type oils into families as well as match oils to source rocks. However, in this study, the n-paraffin distribution of the solute crude oil was very dependent on the sample equilibration pressure and temperature, as well as on the composition of the original starting material (Fig. 9). On the topmost set of four curves of Figure 9, the equilibration conditions (100°C-11,763 psi, 150°C-9,210 psi, and 200°C-8,833 psi) were such that, disregarding minor differences in the lowest carbon number range, the n-paraffin distributions of the three samples of solute crude oil were very close to the original crude oil. In these cases, the temperature-pressure conditions were high enough such that all molecular weight ranges of the crude oil were taken into solution in the same proportion as they were present in the starting material. However this was not the case in the middle set of curves, where equilibration conditions (150°C-1,044 psi, 200°C-2,364 psi, 250°C-914 psi and 2,944 psi) were milder. Because of the lower equilibration pressures, the higher molecular weight n-

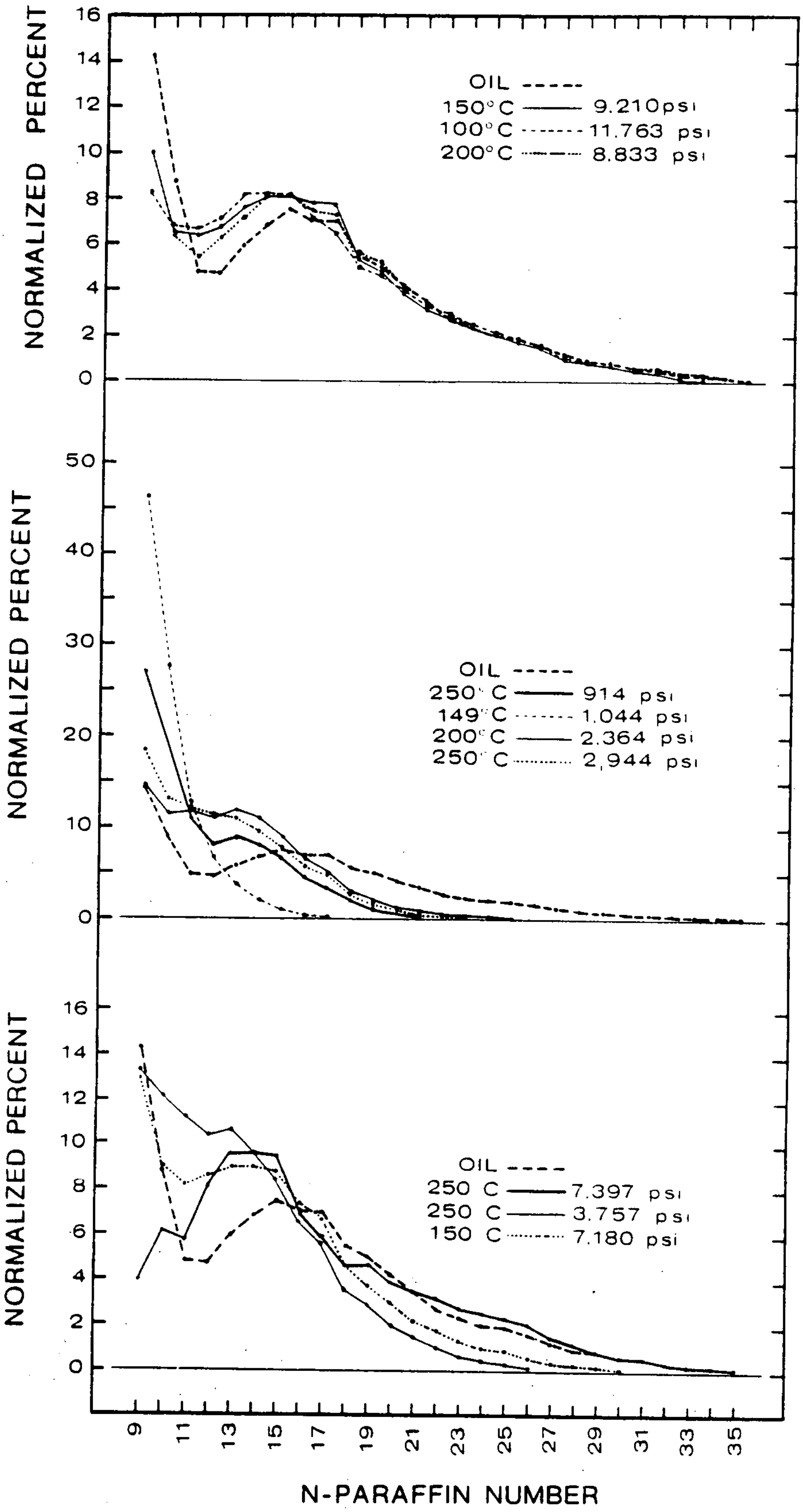

Figure 9.--Plots of the normalized percent of the n-paraffins of solute samples of the Spindle crude oil as well as that of the original crude oil. The scale on the middle set of curves is different than that of the upper and lower set of curves.

paraffins were not taken into solution by the gas phase. The equilibration conditions (150°C-7,180 psi, 250°C-3,757 psi) for two of the samples in the bottom set of curves are such that a greater percentage of the higher molecular weight n-paraffins were dissolved by the gas. Thus the resulting n-paraffin distributions of these two samples were more like, but still significantly different, from the starting crude oil.

The n-paraffin distribution of the 250°C-7,397 psi solute sample, in the bottom set of curves, Figure 9, demonstrates the control that the original starting material has on the material taken into gas solution. The equilibration pressure and temperature of this sample were high enough such that its n-paraffin distribution should match that of the original material. However previous depletion of the C_4 to C_{10} hydrocarbons from the pressure vessel, resulted in a difference between the n-paraffin distribution of this solute sample and the starting crude oil.

Qualitative analyses were also performed on solute samples of the F-12 and F-15 distillation fractions (Table 6). The F-12 solute samples at 50°C show an enrichment in the NSO compounds at all pressures compared to the original fraction (10 to 22 percent versus 7 percent). Saturated hydrocarbons increase, with increase in pressure, from 56 percent at 817 bars (11,850 psi), to values ranging around that of the original fraction. There is no definite trend in the aromatic hydrocarbon fraction. At 150°C, at all pressures, the percentages of the NSO compounds in the F-12 solute samples are roughly equal to that of the original fraction. The percentage of the aromatic fraction is quite variable with no trends. Like the 50°C F-12 solute samples, there is a trend for the percentage of the saturated hydrocarbons in the 150°C solute samples to increase with increase in pressure from a value much lower than that of the original fraction (37 versus 68 percent) at low pressure to high

Table 6.--Qualitative analyses of solute samples of the twelfth, F-12 (material boiling below 215°C at 6 microns vacuum, carbon number range C_{31} to C_{47}) and fifteenth, F-15, (material boling above 266°C at 6 microns vacuum) distillation fractions of the Kimball field crude oil. The F-12 fraction contains no asphaltenes. Analytical methods given in appendix. Bars may be converted to psi by multiplying by 14.504 and to atmospheres by multiplying by 1.0132.

		Normalized Percent			
Temperature in °C	Presssure in bars	Saturated hydrocarbons	Aromatic hydrocarbons	N-S-O bearing compounds	Asphaltenes
		Twelfth Distillation Fraction			
Original	Fraction	68.25	27.22	7.43	
152.5	122	36.74	51.70	11.56	
152.5	309	67.57	25.31	7.12	
152.8	723	70.26	23.25	6.49	
152.5	1127	81.33	13.20	5.46	
152.5	1127	83.25	11.42	5.33	
152.5	1438	72.60	20.21	7.19	
50.0	817	55.85	26.99	17.16	
46.4	1314	73.07	10.40	16.53	
49.8	1514	63.20	14.04	22.76	
50.00	1820	64.18	24.92	10.90	
250.0	74	38.38	41.03	20.59	
250.8	135	43.52	34.20	22.28	
251.3	487	44.75	41.01	14.24	
250.8	759	36.93	42.18	20.88	
250.6	1060	43.50	34.90	21.60	
248.3	1465	42.57	43.87	13.56	
		Fifteenth Distillation Fraction			
Original	Fraction	11.80	33.53	34.77	19.90
255.8	512	20.50	22.98	42.24	14.28
248.0	759	19.36	37.99	24.76	17.89
249.0	1056	31.59	49.37	18.27	0.77
248.5	1323	35.60	43.00	20.46	0.94
249.2	1527	34.60	28.80	21.19	15.41
248.0	1720	26.53	45.11	21.25	7.11
248.0	1796	23.84	44.19	25.15	6.82

percentages (up to 83 percent) at higher pressures. At 250°C, the F-12 solute samples are noticeably richer in aromatic hydrocarbons than the starting material (34 to 44 percent versus 27 percent) as well as NSO compounds (14 to 22 percent versus 7 percent). The percentage of saturated hydrocarbons in the solute samples are quite depressed, compared to the starting fraction (37 to 43 percent versus 68 percent). The apparent tendency of the F-12 solute samples at 50°C and 150°C to be depleted in saturated hydrocarbons at the lowest pressures is opposite of the behavior of the Spindle whole crude oil, which was enriched in saturated hydrocarbons at low pressures. We do not understand nor have an explanation for this behavior, although it probably reflects the complexity of crude oil and the system we studied. The depletion of the saturated hydrocarbons in the F-12 solute samples at all pressures at 250°C is also unexpected and inexplicable.

Solute samples of the F-15 fraction show apparent random compositional variation at 250° as a function of pressure although some trends are present. All solute samples show a definite enrichment in saturated hydrocarbons compared to the original starting material (19 to 37 percent versus 12 percent). This is expected based on the compositional behavior of the Spindle field whole crude oil solute samples (Table 2) and makes the compositional behavior of the F-12 fraction at 250°C even more puzzling. Most of the F-15 solute samples show a depletion of aromatic hydrocarbons and NSO compounds compared to the original sample. The asphaltenes, with the exception of two samples, always make up significant concentrations in the solute samples. The two exceptions to this, the 1056 bar (15,316 psi) and 1323 bar (19,189 psi) samples, are probably artifacts from sample work up and/or qualitative sample analyses. (The F-15 fraction is an obsidian-like tar which was quite difficult to work with.) The significant percentages of the asphaltenes (7 to 18 percent) in most of the F-15 solute samples demonstrate the ability of methane to dissolve even the highest molecular weight material in crude oil.

Comparison to and Previous Work

Most previous work in this area has been performed by Russian investigators, much of which has not been translated. Chilingar and Adamson (1964) reviewed the earlier Russian work and their discussion has been largely paraphrased here. Kapelyushnikov (1954) examined the system oil, gas (unspecified composition) and water (brines) to 100°C and 7,345 psi. He found, as did this study that in addition to dissolving crude oil components, the gas also dissolved (and transported) water and salts (the solution of salts was not examined in this study). He also found, as we did, that the tars and asphaltenes were the last components of a crude oil to be dissolved, and the first to exsolve with decrease of pressure or temperature. Kapelyushnikov (1954) also found that the presence of fine-grained rocks decreased the critical pressure of oil-gas mixtures (i.e.-increased the solubility of crude oil in the gas phase at a given pressure and temperature). Chilingar and Adamson (1964) experimentally duplicated this using clays. Kovalev (1960) reported that the presence of ethane, propane, and/or butane (alone or in combination) in the gas phase, greatly increased crude oil solubility. For example at 100°C-4,409 psi, when the amount of heavier gases was increased from 32 to 47 percent, crude oil solubility was increased 250 percent. Zaks (1952) found that pure carbon dioxide had a much greater carrying capacity for crude oil than a mixture of methane (30 percent) and carbon dioxide (70 percent). We also found that the addition of carbon dioxide to methane increased the solubility of crude oil in the gas phase.

Gerber and Dvali (1961) extracted bitumen from fine grained sediments with pure carbon dioxide at pressures of 2,845 to 5,689 psi and temperatures of 40°C to 90°C. They found, even under these mild conditions, that the tars, asphaltenes, and porphyrins were taken into solution as well as large amounts of petroleum-like bitumen. Gerber et al (1972), in a later study, extracted two limestones, a marl, and three "combustible" (oil?) shales with a natural gas mixture (70 percent methane, 20 to 25 percent propane, and 5 to 10 percent ethane, butane, nitrogen and carbon dioxide), as well as with pure propane, at temperatures of 100° to 130°C and pressures of 1,469 to 4,409 psi). Water was not present in their experiments. The natural gas mixture removed up to 2 kg of bitumen per cubic meter of compressed gas whereas the pure propane removed up to 4 kg/m^3 (compressed gas). The first gases which passed through the rocks were enriched in lower molecular weight saturated hydrocarbons. With time, the absolute amount of solute bitumen in the gas decreased, while its composition became more aromatic and tarry.

Zhuze et al (1962) equilibrated condensates and petroleum with natural gases (89 to 92 percent methane, the remainder being ethane, propane, butane, nitrogen and carbon dioxide) in systems without water at temperatures and pressures of 70° to 150°C and 4,531 to 10,287 psi. They found, at low temperatures and pressures, that compared to the starting material, the solute "condensate" was enriched in saturated hydrocarbons and impoverished in both aromatic hydrocarbons and non-hydrocarbons. We recorded the same results in this study (Table 2). They also found, as we did, as system temperature and pressure increased, that the composition of the solute material more and more approached that of the starting material. Also they found, as we did, that with increase in system temperture and pressure, not only did the amount of solute material increase, but also the solute specific gravity and its molecular weight range.

A notable difference between our results and theirs, was the conditions needed for critical pressure (co-solubility). Whereas they estimated at 150°C, pressures of 16,165 to 17,364 psi would be necessary for cosolubility, we encountered cosolubility at this temperature at (9,210 psi). At 70°C and 10,287 psi, their solute condensate contained only 22 percent of the components of starting material. At 49°C and 11,705 psi, our solute condensate was very close to our starting material, and at 99°C and 10,167 psi, identical. At 150°C and 10,287 psi, their solute condensate contained only 39 percent of the components of the starting material, whereas we encountered cosolubility at 150°C at 9,210 psi. In our studies, we used pure methane gas, whereas Zhuze et al (1962) used natural gases which contained significant percentages of hydrocarbon gases besides methane, which if anything would give their gas a much greater carrying capacity for crude oil than ours. However, our experiments were carried out with water present, whereas those of Zhuze et al (1962) were done in dry systems. The large differences between the two studies, in regards to the pressures and temperatures needed for cosolubility, then must have been due to a significant and unsuspected positive influence of water on gas solution.

Chilingar and Adamson (1964) found that the presence of water increased the critical pressure (decreased the solubility) of light hydrocarbons (benzene, hexane and cyclohexane) in methane. This is opposite of the influence that we propose water has on the solubility, in methane, of the higher molecular weight material in crude oil. Analagous aqueous solubility behavior (Price, 1981), as a function of solute-hydrocarbon molecular weight, was found in the system water-petroleum-gas (the gas was either methane or carbon dioxide). In that study, the presence of either gas decreased the aqueous solubility of lower molecular weight hydrocarbons, whereas at the same temperature and pressure, the aqueous solubility of the higher molecular weight hydrocarbons was increased. We believe that the same behavior is present in the gas phase of this system as was present in the aqueous phase of the system.

Previous quantitative measurements of crude oil solubility in petroleum gases (Sokolov, 1948; Zaks, 1952; Kapelyushnikov, 1954; Zhuze and Ushkevich, 1959; Sokolov and Mironov, 1962; Sokolov et al, 1963; and Zhuze et al, 1962, 1968) were not made under uniform conditions. These experiments, depending on the investigators, were carried out in dry systems, with pure methane or with gas mixtures, with and without clay present, and with different starting crude oils. All these parameters affect the solubility behavior of crude oil in a gas phase. Therefore direct comparison of the data of previous studies with each other or with the data of this study loses meaning. However the data of Table 7 and Figure 10 show that our solubility data are consistently higher than the values reported in previous studies. This, we believe is, due to the fact that we carried out our experiments in the presence of water, whereas the previous studies were carried out in dry systems. Had we used gas mixtures instead of pure methane, our solubility values would have been even higher.

DISCUSSION

The solubility values reported for the tar (F-15) distillation fraction of this study (Fig. 4) were for pure methane. The presence of higher molecular weight hydrocarbon gases, carbon dioxide, or clay in the system would have resulted in the measurement of higher solubility values for that fraction. We did not measure the solubility of the F-15 fraction in methane

Table 7.--Comparison of previous gas solution data with interpolated data of this study. Pressures from previous studies were converted to bars from atmospheres. Our value for 200°C, 987 bars (Stepnovo field; Zhuze et al, 1968) was extrapolated from the 200°C curve of figure 1, as these conditions were in our field of cosolubility. Solubility values of previous studies which were given in kilograms (or grams) of condensate per cubic meter of gas at reduced conditions were changed to grams of condensate per liter of gas (reduced conditions). Do is ditto.

Field and (authors)	Temperature in °C	Pressure in bars	Reported Solubility grams/liter	Solubility this study grams/liter
Stepnovo Zhuze et al (1962)......	120	691	0.344	0.64
Stepnovo Zhuze et al (1968)......	140	790	0.680	0.95
Do..................	150	395	0.147	0.303
Do..................	150	691	0.462	0.738
Do..................	160	888	0.820	1.43
Do..................	200	987	0.874	3.05
Kum-Dag	100	395	0.109	0.225
(West and East Fields	100	691	0.281	0.550
Combined 1 to 1)	150	395	0.145	0.301
Zhuze et al (1968)	150	691	0.360	0.742
West Kum-Dag	100	395	0.127	0.225
Sokolov et al (1963)	100	691	0.315	0.550
Do..................	150	395	0.155	0.301
Do..................	150	691	0.397	0.742
East Kum-Dag	100	395	0.094	0.225
Sokolov et al (1963)	100	691	0.271	0.550

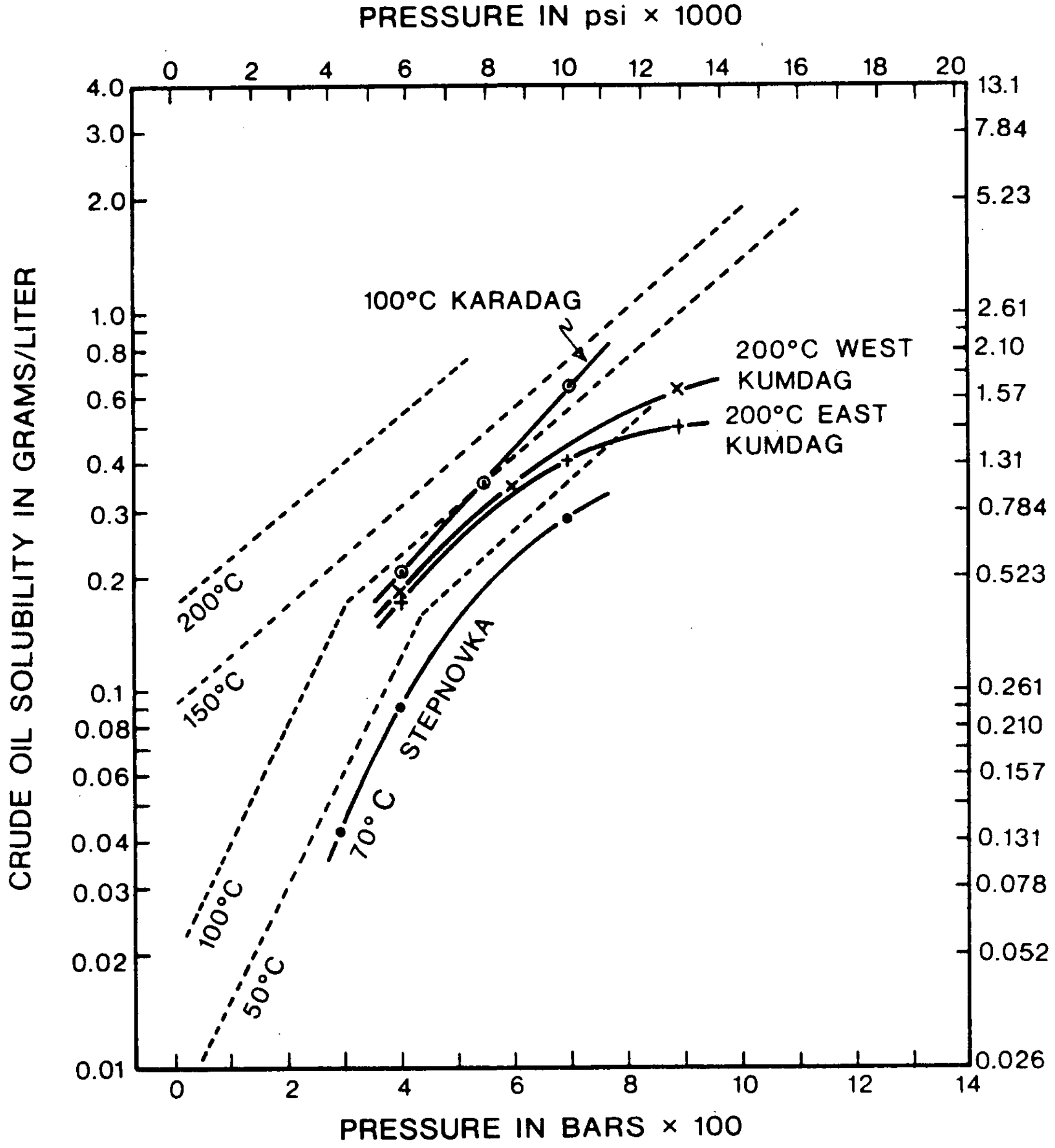

Figure 10.--Comparison of previously published gas solution data with the data for this study. The dashed lines are the 50°, 100°, 150°, and 200°C data of this study (curves of figure 1, without data points). The 200°C West Kum-Dag and 200°C East Kum-Dag data are from Sokolov et al (1963). The 70°C Stepnovka data are from Zhuze et al (1968), and the 100°C Karadag data are from Zhuze et al (1962). The original data of those authors were given in pressures of atmospheres and solubilities in kilograms (or grams) of condensate per cubic meter of gas at reduced conditions. These units were converted to pressure in bars and solubility in grams of condensate/liter of gas.

at 150°C. However based upon other data of this study as well as other data from previous studies, it can safely be assumed that at 150°C, at high pressures, with other gases present, methane would have an adequate carrying capacity for this fraction (F-15) to account for the amounts of this fraction found in a typical 35° to 40° API gravity crude oil.

The Spindle field crude oil used in this study has a rather high saturated to aromatic hydrocarbon ratio (7.99). In spite of this high ratio, we saw (Table 2) a tendency under some conditions for methane to preferentially take up saturated hydrocarbons. This same tendency was also reported by Zhuze et al (1962, 1968) and Gerber et al (1972). An informative experiment, which we did not carry out, would be to equilibrate a methane rich gas (natural gas) with a starting material quite unlike a crude oil (such as the extract of a humic coal, which would be rich in N-S-O bearing compounds, and asphaltenes and would have a low saturated to aromatic hydrocarbon ratio), and determine if a more "typical" crude oil would be "stripped" from the original material by gas solution. Much of the data from this and previous gas solution studies suggest that this would be the case.

Hunt (1979, p. 215) in discussing migration by gas solution stated "Gas-phase migration------may explain the presence of aromatic rich condensates in the Pleistocene of the Gulf Coast. When gas is passed through oil, it tends to concentrate more aromatics in the gas phase." Hunt gave no reference to a study which documented this "tendency". On the other hand data from this study as well as previous studies have shown the opposite tendency - i.e., the saturated hydrocarbons tend to be concentrated in the gas phase. Price (1981) showed that up to 275°C, water preferentially takes aromatic hydrocarbons into solution over saturated hydrocarbons. An extensive testing program of the geopressured-geothermal resource has been carried out on the Gulf Coast in which large amounts (5,000 to 30,000 bbls/day) of brine were produced from sandstones at moderate depths (3,000 to 4,000 km) through surface separators to try to recover the dissolved methane. In some cases, in addition to the methane, samples of a small amount of condensate or crude oil like material also have been recovered. Compositional analyses (Price and Wenger, 1982) of the lightest samples show that some of them are almost entirely composed of light aromatic hydrocarbons, which due to the decrease in temperature in the surface separator, exsolved from solution from the brines. The presence of aromatic rich condensates in the Pleistocene of the Gulf Coast, the Alberta basin, the Beaufort basin, the East Turkmen basin, and most probably many other localilties, is likely due to primary migration of the condensate hydrocarbons, and gases, by aqueous molecular solution over the temperature range 200° to 275°C. There is no evidence to link these condensates to migration by gas solution, as Hunt (1979) proposes.

Kapelyushnikov (1954) and Chilingar and Adamson (1964) reported that the presence of rock or clay in the system crude oil-methane, increased crude-oil solubility in the methane gas phase. Chilingar and Adamson (1964) attributed the effect to adsorption. Because two different research groups have reported this same phenomena, it cannot be easily attributed as an artifact from experimental procedure. We certainly have no explanation or even insight as to why the presence of claystone should result in this behavior. Nor do we understand how adsorption would be a contributary factor.

The crude-oil solute molecular compositional data of this paper (Table 2) have application to hydrocarbon phase behavior in deep reserviors as well as to the field of hydrocarbon production engineering. Clearly, in the past, there has been an overwhelming opinion that methane, even under conditions encountered in deep, high pressure-high temperature reservoirs, would not take up the higher molecular weight components of petroleum (Uspenskii, 1962; Sokolov et al, 1963; Welte, 1965; Cordell, 1972; Price, 1976; Tissot and Welte, 1978; McAuliffe, 1978, 1980; Hunt, 1979). For example, Uspenskii (1962, p. 802) commenting on the solubility data of crude oil in methane of Zhuze et al (1962) stated--"These data show that the gas phase of petroleum-condensate deposits lying at a depth of 6,000-7,000 meters must contain condensates vaporizing within a broad temperature range and approaching petroleum in specific gravity and molecular weight. The principal difference between condensate and petroleum in this case will be the lower content of "tar" in the condensate and almost complete absence of asphaltenes."

Neglia, (1979, p. 579) has provided the only evidence from the natural system, of which we are aware, that the high molecular weight material of petroleum can be dissolved in methane in his discussion of the Malossa field, Po Valley, Italy-"PVT analyses prove that Malossa is a condensate field with heavy liquid components dissolved in the gaseous phase. The decrease of bottom-hole pressure causes separation of asphalt, the melting point of which is around 120°C. The asphalt tends to plug the production tubing; a squeeze of solvent is needed every 2 months to dissolve the deposits of asphalt and clean the well." Hunt (1979, p. 213) after considering Neglia's (1979) conclusions on the Malossa field noted, "The data of Rzasa and Katz (1950) indicate that hydrocarbons through C_{18} would be dissolved in the gas phase under these conditions." Hunt's conclusions here are in error, as asphalt which melts at 120°C has a carbon number much greater than C_{18}.

Hunt's, and other's, beliefs in this matter probably are due to two main reasons. Firstly, phase behavior studies, such as those of Rzasa and Katz (1950) for the most part have been carried out with methane as the only component in the gas phase (see Standing, 1977). The substantial effects that water, carbon dioxide, and the hydrocarbon gases ethane through butane have on the methane-crude oil system went unnoticed through years of experimental measurements by petroleum engineers, who in efforts to minimize the degrees of freedom for these systems did not fully delineate all the controlling parameters. Thus experiments were designed which suggested a behavior of the methane-crude oil system different from its behavior in nature. These experiments thus supported the incorrect belief that methane rich natural gas could not dissolve the higher molecular weight components of crude oil.

The second reason that the methane-crude oil system has been misinterpreted for so many years lies, we believe, in its sensitivity to pressure, as evidenced by the data of Tables 1 and 2. In the production of a deep, high presssure, high temperature hydrocarbon reservoir, the hydrocarbon fluids will suffer a substantial pressure decline in the well bore and even in the reservoir. This will cause separation of the higher molecular weight components from the gas phase, before the separator is encountered. Thus it appears that the hydrocarbon reservoir is a two phase system, when in reality it is probably a one phase (very pressure sensitive) system. If the pressure decline in the reservoir was substantial, during early production, it is conceivable that a significant exsolution of the higher molecular weight components could occur in the reservoir. This material would then be lost to production forever.

CONCLUSIONS AND SUMMARY

1) Methane, in systems with water, has substantial carrying capacities for all components of petroleum.

2) At low pressures and temperatures, the lower molecular weight (C_5 to C_{15}) saturated hydrocarbons are taken into gaseous solution in preference to aromatic hydrocarbons and higher molecular weight saturated hydrocarbons, and in extreme preference to the high boiling distillation fractions of petroleum which are composed of tars, resins, and asphaltenes. As temperature and pressure increase, even at moderate conditions (100°C, 10,150 psi), all components of crude oil become quite soluble in a methane gas phase-even the tars and asphaltenes. Indeed, the composition of the solute material in the gas phase becomes an exact compositional match of the starting material. Increases in pressure have a greater effect on increasing petroleum solubility in methane than do increases in temperature.

3) The presence of water in the methane gas phase, as would be found in the natural system, has a large and previously unreported positive influence on the solution of all components of petroleum in methane, but especially on the solution of the highest molecular weight material of petroleum.

4) Increases in carbon dioxide concentration in the gas phase drastically increase gas-phase petroleum solubility (Zaks, 1952; and this study).

5) The presence of ethane through butane in the gas phase increases gas-phase petroleum solubility (Kovalev, 1960, and Gerber et al, 1965).

6) The presence of fine-grained rocks in hydrocarbon gas-petroleum systems, decreases the critical pressure of these systems-increases petroleum solubility in the gas phase (Kapelyushnikov, 1954; and Chilingar and Adamson, 1964).

7) We have measured high to extreme solubilities of crude oil, and high boiling distillation fractions of crude oil, in a pure methane gas phase in the presence of water. Cosolubility was encountered in these crude oil-methane-water systems under relatively mild conditions (100°C, 15,230 psi; 150°, 13,364 psi; 200°C, 7,513 psi). Had these systems been examined with the other variables present which have a positive effect on crude oil-gas solution (the presence of carbon dioxide, ethane through butane, or claystones), even higher solubililties and lower pressure-temperature conditions for cosolubility would have been encountered than those reported in this study.

8) The data of this study show that two previous criticisms of gas solution as an agent of primary petroleum migration are invalid: 1) That the highest molecular weight components of petroleum (tars, asphaltenes etc.) are not soluble enough in a methane rich gas phase to account for petroleum deposits, and 2) the associated gas of many oil deposits is too low to have allowed primary migration by gaseous solution.

APPENDIX

Experimental Techniques

Materials

The crude oil used was from the Spindle field, Weld County, Colorado (Denver basin). The 44° API (0.806 specific) gravity oil is produced from the Cretaceous Sussex Sandstone at 1,443 m. Petroleum distillation fractions were derived from the crude oil of the Kimball field, Kimball County, Nebraska (Denver basin). This 35° API (0.850 specific) gravity oil is produced from the Cretaceous "J" sand at 1,989 m. The original distillation of this oil, done at the Marathon Oil Co. Research Laboratory, Littleton, Colorado, resulted in eleven separate distillation fractions plus a C_{31+} residue. (The first through eleventh distillation fractions were used in a another solution study, Price, 1981). The C_{31+} residue was vacuum distilled by J. E. Dooley, at the then ERDA Research Center, Bartlesville, Oklahoma, into 3 fractions leaving a residue (here termed F-15) boiling above 266°C at 6 microns pressure. This residue plus the first fraction taken by Mr. Dooley (F-12, boiling below 215°C at 6 microns -carbon number range C_{31} to C_{47}) were used in this study. Methane (99.99 percent pure) was obtained from Matheson* in 300 SCF tanks at 2,250 psi. Distilled-deionized water was used for all procedures.

Mallinckrodt reagent grade tetrahydrofuran (THF) was used as a solvent to prepare the samples taken from the pressure vessels for quantitative analysis. This cyclic aliphatic ether is cosoluble with both water and petroleum. Butylated hydroxytoluene (0.025 percent) was present in the THF to

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*Use of specific brand name does not necessarily constitute endorsement of the product by the U.S. Geological Survey.

prevent peroxide formation. Because THF is extremely hydroscopic, a layer of 3 angstrom molecular sieve (8-12 mesh beads) was added to the reagent bottle to remove any water which the THF would take up from the air.

Containment Vessels and Support Equipment

All systems were contained in 300 ml pressure vessels (321 stainless steel) sealed by Bridgeman seals (Fig. 11). These vessels were heated in large diameter (10.4 cm) muffle furnaces (Fig. 12). Temperatures were maintained to ± 1.5°C by Love temperature controllers and measured by chromel-alumel thermocouples using a potentiometer, galvanometer, standard cell and an electronic ice-point reference (Kaye Instruments). Pressures were generated by a Teledyne-Sprague air-actuated hydraulic pump which could either pump water into the pressure vessel or, by means of a separator, methane or petroleum (Fig. 12). A separator is a stainless steel cylinder, with a polished bore, sealed at both ends, and fitted with a (sliding) brass plug guided by one or more rubber o-rings. The separator is filled with methane or petroleum with the plug at one end and the gas or fluid is then compressed to the desired pressure by pumping water into the other end. Pressures were monitored by 0-50,000 psi Ashcroft gauges, and measured by a 2500 bar Heise gauge.

Round bottom flasks (usually 1,000 or 2,000 ml), whose volumes had been accurately measured, served as sample flasks (Price, 1979). The flasks were sealed by attaching brass compression fittings to the metal end of glass to metal (Kovar) seals which were attached to the round bottoms at the glass end. A septum placed in the compression fitting and held in place by a ferrule and nut made the flask gas tight and allowed sample access by means of hypodermic needles.

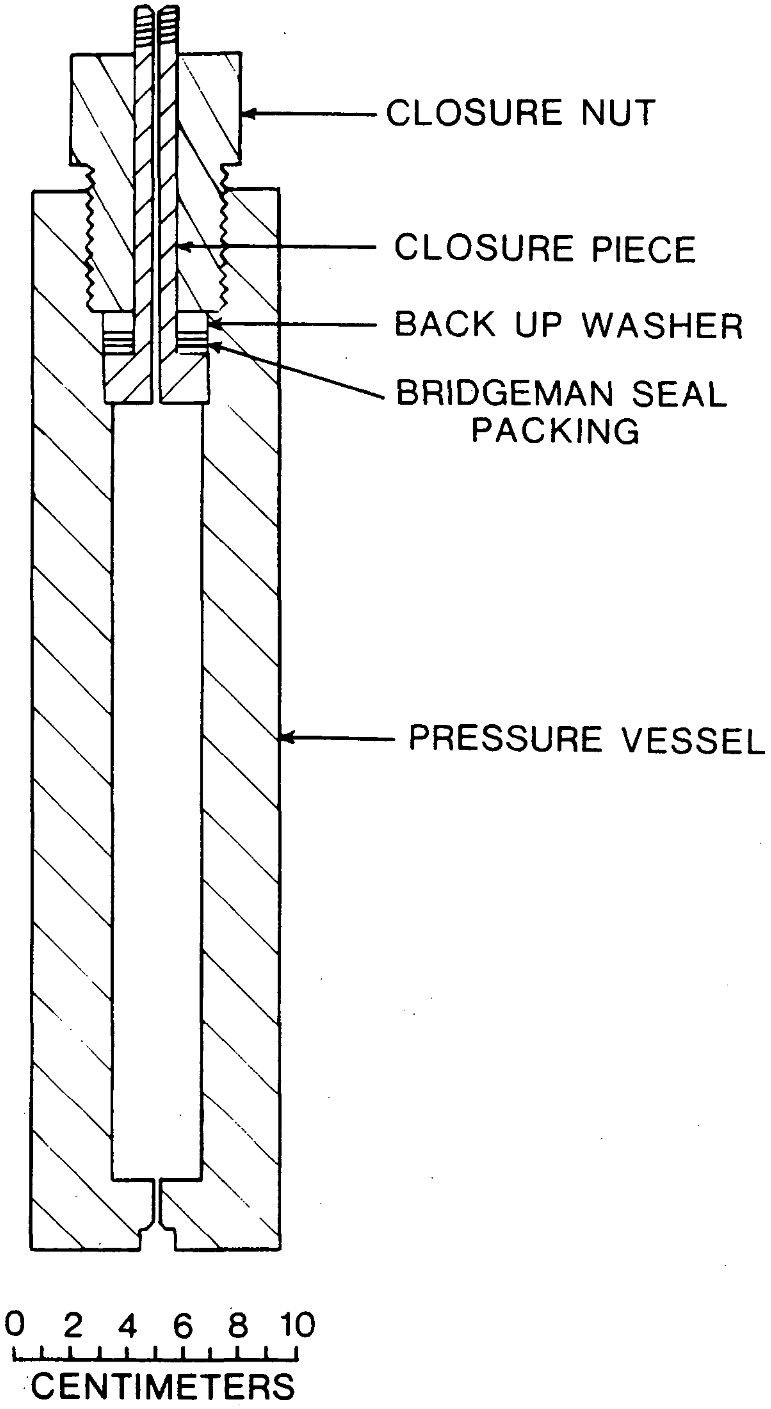

Figure 11.--Diagram of the pressure vessels used in this study. The vessels were sealed by tightening the large closure nut which exerted pressure through the back up washer to the Bridgeman seals (washers). This pressure caused these slightly convex washers to flatten out, which exerted lateral pressures on sides of the pressure vessel which made the seal.

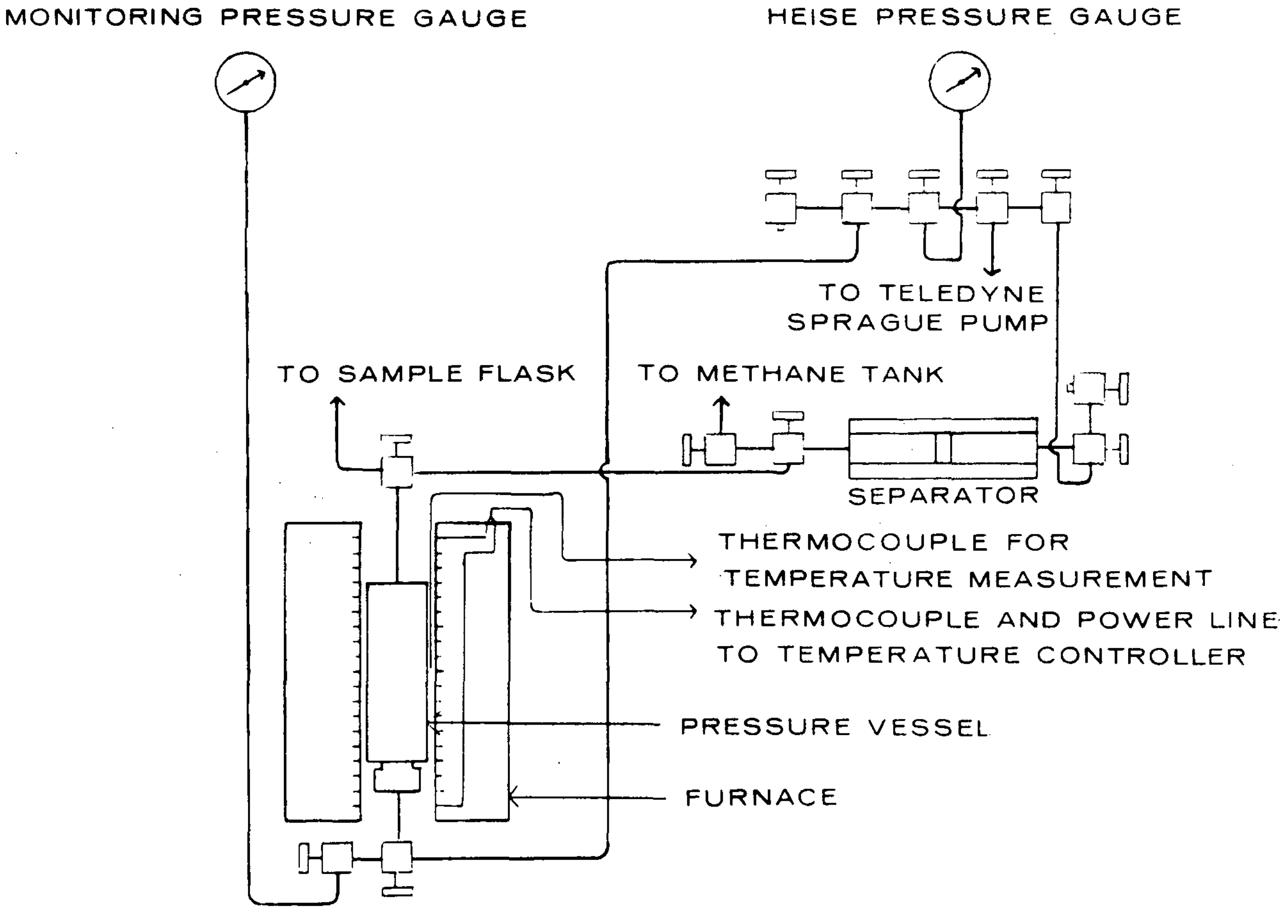

Figure 12.--Diagram of pressure vessel, furnace and support equipment. High pressure valves (shown) isolated the various components as well as the pressure vessel.

Sampling

A high pressure capillary (0.48 mm I.D.) line (the sample line) with a 22 gauge hypodermic needle silver soldered on its end, was attached to a valve block. The valve block in turn was attached to a large inside diameter (2.34 mm) high pressure line (sample exit tube) attached to the top of the pressure vessel. When the pressure vessel (autoclave) was in an upright position, inside the vessel, a methane rich phase (the phase of interest) over laid a petroleum-rich phase which in turn was over water. The sample exit tube, valve block, and in the case of petroleum distillation fractions, the sample line, were all heated to the temperature of the pressure-vessel to help prevent exsolution of liquids from the gas phase during sampling.

Methane and water form a hydrate phase at high pressures, below 40°C, which plugs lines and cannot be dislodged by even extreme pressure differentials (Price, 1979). Therefore all "support" capillary lines carrying methane to or from the autoclave were heated to 50°C to 60°C, to prevent hydrate formation, by wrapping them with electrical heating tape and asbestos cloth.

Once the system of interest in the autoclave had reached equilibrium, a slight decrease in pressure during sampling would cause immediate exsolution of liquids from the gas phase, and therefore erroneous results. Thus, before sampling, the autoclave was slightly overpressured (40 to 90 bars) by pumping water into the bottom of the autoclave, and during sampling (a five minute process) this slight overpressure was maintained. Equilibrium studies (discussed below) showed that if the furnace and autoclave were static, equilibrium approach from undersaturation was very slow. Thus this slight overpressuring for short times did not affect equilibrium solubility values.

Before sampling, the sealed round-bottom sample-flasks were vacuum evacuated and filled with methane at laboratory pressure and temperature. (If the sample flasks, before sampling, contained air and not methane, bouyancy introduced errors into subsequent calculations). The flasks were then tared on a top loading balance to 0.001 g. Before sampling, a sufficient bleed was taken from the autoclave to remove any petroleum-rich phase or water which had lodged in the sample exit tube during rocking (see below). A needle on the end of the sample line allowed sample access to the sample flask through the sample-flask septum. All water and petroleum carried in the gas phase exsolved in the sample flask from the pressure-temperature drop caused by sampling.

After sampling, the flask was reweighed and allowed to come to room temperature. The excess pressure generated by the methane was then measured with a Matheson 0 to 15 or 0 to 30 psi Bourdon tube test gauge (accurate to 0.25 percent at full scale). A hypodermic needle silver soldered onto the end of the gauge allowed access to the sample flask. With knowledge of the sample-flask volume and the volume of the Bourdon tube in the gauge, ideal gas calculations gave the number of moles and therefore the sample weight of the methane. Subtraction of the sample-flask tare weight and the methane weight from the sample flask weight after sampling gave the weight of the liquids in the sample (water and petroleum).

Crude oil samples for <u>qualitative</u> analyses were taken in 2,000 or 5,000 ml round bottom flasks sealed by a septum (to prevent loss of C_4-C_{10} range hydrocarbons). The round bottom falsks contained about five ml of distilled water. After a sample was taken, oil, exsolved from the gas phase would form an immiscible layer on the water. The crude-oil sample was recovered by pouring the liquids into a two dram vial, and suspending the sample flask over the vial for complete drainage. The vial was sealed by a tin-lined screw cap and the samples were frozen until analysis.

At low pressures, and therefore low oil solubilities, multiple gas samples had to be taken. This was done by vacuum evacuating the sample flask before sampling, which allowed a larger volume of gas to be taken. The sample flask was then chilled with ice to promote total exsolution of all light hydrocarbons from the gas phase. The excess gas pressure was bled from the sample flask with a needle and another sample was taken. The process was repeated as necessary. Because of extremely low solubilities (Fig. 1), no qualitative samples were recovered at the lowest pressures.

Qualitative samples of the two distillation fractions were taken directly into eight-dram vials, as loss of light hydrocarbons was not a problem.

Equilibrium Attainment

The muffle furnaces, which contained the autoclaves, could be mechanically rocked through a 60° arc from horizontal for mixing of the different phases. A 40 gram stainless-steel ball (used at the suggestion of Ralph Simon, Chevron Oil Field Research Center, La Habra, CA) inside the autoclave also aided in mixing the three phases. Equilibrium approach studies were carried out without rocking (static muffle furnace), with rocking and with rocking with a steel ball. Without rocking, equilibrium was not achieved after 168 hours. With rocking but without the stainless steel ball, equilibrium would be achieved between 25 to 31 hours. With rocking and with the ball, equilibrium was achieved between 5 to 10 hours. Equilibrium approach from oversaturation (exsolution due to pressure decrease) yielded the same solubility values as approach from undersaturation.

All solubility data for the formal study were approached from undersaturation by increase of pressure, with 24 hours of rocking for the crude oil and 48 hours of rocking for the petroleum distillation fractions. Before sampling, the furnace and autoclave were set vertically stationary for one hour after rocking to allow liquids to settle away from the exit tube. Two studies showed that after one hour, the length of time of sampling after rocking had no detectable effect on the solubility values. Sample size also had no effect on solubility values.

For any isothermal run with petroleum, samples were taken with increasing pressure until a condition of "limited" cosolubility was reached. Here most (roughly carbon number C_{40} or less) of the compounds in the petroleum phase became cosoluble with the gas phase. Once this condition was reached, further measurements had no meaning as any solubility number could be manufactured by varying the gas-oil ratio of the total system. Cosolubility was apparent by a large positive deviation in a linear plot of crude-oil solubility (on the logarithmic scale) versus pressure (arithmetic scale) at constant temperature. This deviation could be caused by either cosolubility or loss of the gas-rich phase from too much oil in the system. When such a deviation occurred, the system was tested to determine which cause was responsible by adding methane to the system to form a gas rich phase if possible. After equilibration, the system was sampled. This process was repeated several times in an attempt to achieve a constant solubility value which indicated that a petroleum-saturated gas-rich phase existed. If, on the other hand, solubility values continued to decline as more methane was added to the system, it was assummed that cosolubillity had occurred and that a one-phase mixture existed.

In all solubility studies with the crude oil, the petroleum "reservoir" was removed from the autoclave regularly by purging the system with water or methane, and new crude oil was injected. This prevented strong preferential depletion of the lower molecular weight fractions of the crude oil which could change the solubililty values.

Quantitative Analyses

After a sample was taken, and the round-bottom sample flask was reweighed and its overpressure measured, the excess methane was bled from the sample flask by means of a hypodermic needle. The sample flask was then opened and rinsed five times with five ml each of tetrahydrofuran (THF), which quantitatively dissolved all water and hydrocarbons in the sample flask. The successive rinses of THF with dissolved crude oil and water were transferred to 50 ml hypodermic vials. Tuf-Bond discs (Pierce Chemical Co.) were used to seal the vials with an aluminum cap which was crimped on the top of the vial. The discs were constructed of a layer of silicone rubber bonded to a thin layer of teflon. The teflon side contacted the solvent. Other septa (butyl rubber, silicone rubber, neoprene, etc.) were unsatisfactory, as they were permeable to water and allowed the very hydroscopic THF to take up substantial water from the air, which led to erroneous data. Contact of rinse THF with air was minimized due to the hydroscopic nature of the former. THF solvent blanks were prepared in the same fashion as the samples, every three samples. These provided background levels of solvent-water concentrations which were subtracted from the water concentrations in the samples.

The hypodermic vial was tared to five places with cap and septum, before adding the five rinses (with sample liquids) to it. Water concentrations in the hypodermic vials were determined using the Aquatest IV (Photovolt Corp.). This is an automatic analyzer which determines water concentration in any organic solvent based upon a quantitative electronic titration which generates Karl Fischer reagent. Before analyses with the Aquatest IV, the vial was reweighed (to five places) to determine the weight of fluids in the vial. The sealed hypodermic vial was then pierced and a 250 μl to 2.0 ml syringe was used to withdraw a sample of THF from the vial. Sample size was dependent on expected water concentration, small concentrations necessitated sample sizes up to 1.5 ml, while sample sizes of 150 μl could be used with high water concentrations. After sample withdrawal, the syringe was sealed and weighed on an analytical balance. After injecting the sample into the Aquatest unit, the syringe was reweighed, the difference between the two weighings being the weight of sample injected. The Aquatest read out water concentrations for each analyses in ppm (by weight). Multiplying these numbers by the weight of the liquids in the hypodermic vial, gave the absolute weight of the water in each sample. By subtracting this number and the weight of the methane from the total sample weight, the weight of the liquid hydrocarbon fraction was determined by difference. Usually quantitative analyses by difference are undesireable. However in this case, except at lower pressures, the petroleum or distillation fraction made up most (90 to 99 percent) of the total sample weight (Tables 1, 4 and 5). Therefore even moderate errors (which we do not believe were present) in the determination of methane or water weights, would have resulted in only small errors in petroleum weights. When petroleum made up only a small percentage of the total sample weight (not the case for most samples) larger errors could be introduced. The limit of detection for petroleum using this analysis was about 0.005 g/L.

Qualitative Hydrocarbon Analyses

Crude oil solute samples were qualitatively analyzed for carbon number distribution, using a Hewlett Packard 5740 gas chromatograph with dual flame ionization detectors. Column conditions were 1.6 mm I.D. X 45.8 m open column coated with SE-30. The oven temperature was programmed at 15°C per minute from 60° to 300°C with a variable upper temperature limit interval (0 to 16 minutes, dependent on the amount of high molecular weight material in each sample). Detector and injection port temperatures were 300°C. Sample sizes varied from 0.2 to 1.5 microliters, dependent on the percentage of C_4-C_9 hydrocarbons in the sample. The chromatograph was equipped with a Hewlett Packard 7127-A strip chart recorder with a mechanical Disc Integrator. Carbon numbers were identified using the n-paraffins in each sample as internal standards. The percentage of each carbon number range in a given sample was determined by dividing the number of Disc Integrator counts for that carbon number range by the total number of counts for the entire sample. Verticals from the midpoint of the respective n-paraffins to the integrator trace, allowed determination of the counts corresponding to that respective carbon number range.

The C_{13+} fraction of crude oil solute samples and solute samples of petroleum-distillation fractions were analyzed for compound class distribution by high performance liquid chromatography. One to two hundred milligram aliquots of crude oil qualitative samples (dependent upon carbon number distribution) were evaporated to constant weight (roughly C_{13+}) by nitrogen evaporation, and then dissolved in 1.5 ml of hexane for injection onto the high performance liquid chromatograph (HPLC). The HPLC consisted of Constametric I and II pumps controlled by a Gradient Master (Laboratory Data Control, LDC), a loop injector (Model U6K, Waters Associates), a Spectromonitor I UV-Vis detector (LDC), a flame ionization detector model LCM-2 (Pye-Unicam), and a backflush valve model 70-10 (Rheodyne, Inc.). The Whatman column was 10 μm I.D., 250 mm long, preceded by a 2.2 mm I.D. by 70 mm long guard column, packed with Whatman 10 μm PAC.

The column was equilibrated with hexane, previously passed through Super I alumina W200 basic (ICN Pharmaceuticals, Inc.) to remove water and impurities. The hexane, with dissolved oil, was injected onto the column at 3 ml/minute. On injection, a two minute gradient, curve 5, was initiated to yield a mobile phase of 90/10-hexane/dichloromethane. During this time, the saturated hydrocarbons and alkyl-substituted monoaromatics eluted, followed by the di-, tri- and poly-cyclic aromatics. Compound class detection was by a flame ionization detector and a UV detector at 254 or 300 nm, dependent on aromatic compound concentration. On complete elution of the aromatic fraction, column flow was reversed, and a two minute gradient, curve 1, was initiated to 100 percent dichloromethane, to elute the NSO fraction. The column was cleaned with tetrahydrofuran, acetonitrile, and methanol.

After fractionation by HPLC, the weights of the saturated and aromatic hydrocarbons were gravimetrically determined after solvent evaporation with nitrogen without a heating bath to constant weight (C_{13+}). The NSO fraction weights for most of the samples could not be gravimetrically determined due to their low amounts. The weights of such samples were determined by peak-height measurement from the HPLC flame detector. A linear plot of peak heights versus known weights of NSO fractions, served as an index.

The petroleum distillation fractions (F_{12} and F_{15}) were qualitatively analyzed differently. The THF and water were removed by evaporation from the quantitative samples in the hypodermic vials. The F_{12} samples were redissolved in hexane and filtered into a tared 3 dram vial to remove solid particulate matter. The samples were then blown down to dryness with nitrogen in a heated water bath and a sample weight was taken. The material was redissolved in hexane in a 10 ml volumetric flask and enough liquid was pipetted for the HPLC for a 80 to 100 mg sample weight. The F_{15} samples, after hypodermic vial evaporation, were dissolved in pentane (for deasphaltening) and filtered into a tared three dram vial to remove solid particulate matter and the asphaltenes. The asphaltenes were remobilized into a tared 3 dram vial by dichloromethane which was removed by evaporation to give an asphaltene weight. The pentane in the other 3 dram vial was removed by evaporation, and the same procedure as used with the F_{12} fraction, was then followed.

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APPENDIX D

Estimation of the effect of CO_2 on methane solubility

The effect of carbon dioxide on aqueous methane solubility was determined at pressures of 5000, 13000 and 22500 psi at 302°F in NaCl solutions with salinities of 52 and 107 grams per liter. In Table 7 (along the horizontal lines designated by "C") the percentage of methane (as compared to carbon dioxide free brines) in solutions containing different amounts of carbon dioxide was reported. Carbon dioxide is expressed as percentages of total dissolved gases. In Figure D-1 the interpolated concentration of carbon dioxide for specific methane percentages were plotted along the appropriate salinity lines for a pressure of 13000 psi. Carbon dioxide values were plotted on a scale that is equal to the square root of the carbon dioxide content. Contours representing equal percentage values for methane were drawn between the salinities and extrapolated to zero salinity. The 100 percent line represents the locus of points (combinations of salinities and carbon dioxide concentrations) that separates conditions where methane solubility is suppressed from the conditions where methane solubility is enhanced (compared to methane solubilities in carbon dioxide free solutions under the same conditions. The different percentage contours indicate the amount of methane contained in saturated solutions compared to carbon dioxide free solutions.

From the contours in Figure D-1, it is apparent that carbon dioxide suppresses methane solubility greatest at low salinities and high carbon dioxide concentrations. The addition of carbon dioxide at low to intermediate concentrations at high salinity can enhance methane concentrations.

The carbon dioxide content and salinity of a number of geopressure test wells are also plotted on Figure D-1. For example, "CZ" represents the Crown Zellerbach well No. 2 (CO_2 content of about 29 mole percent of the dissolved gases and a salinity of 31.7 grams/liter, see Table 11). Under these conditions saturation with methane would be predicted when the methane content reached 75 percent of that predicted using equations in Table 1 and the physical conditions listed in Table 11. The solubility of methane predicted in this way was 37.5 scf per barrel. The measured content of 22.9 scf is well below the predicted value. This suggests that the Crown Zellerbach well may be undersaturated.

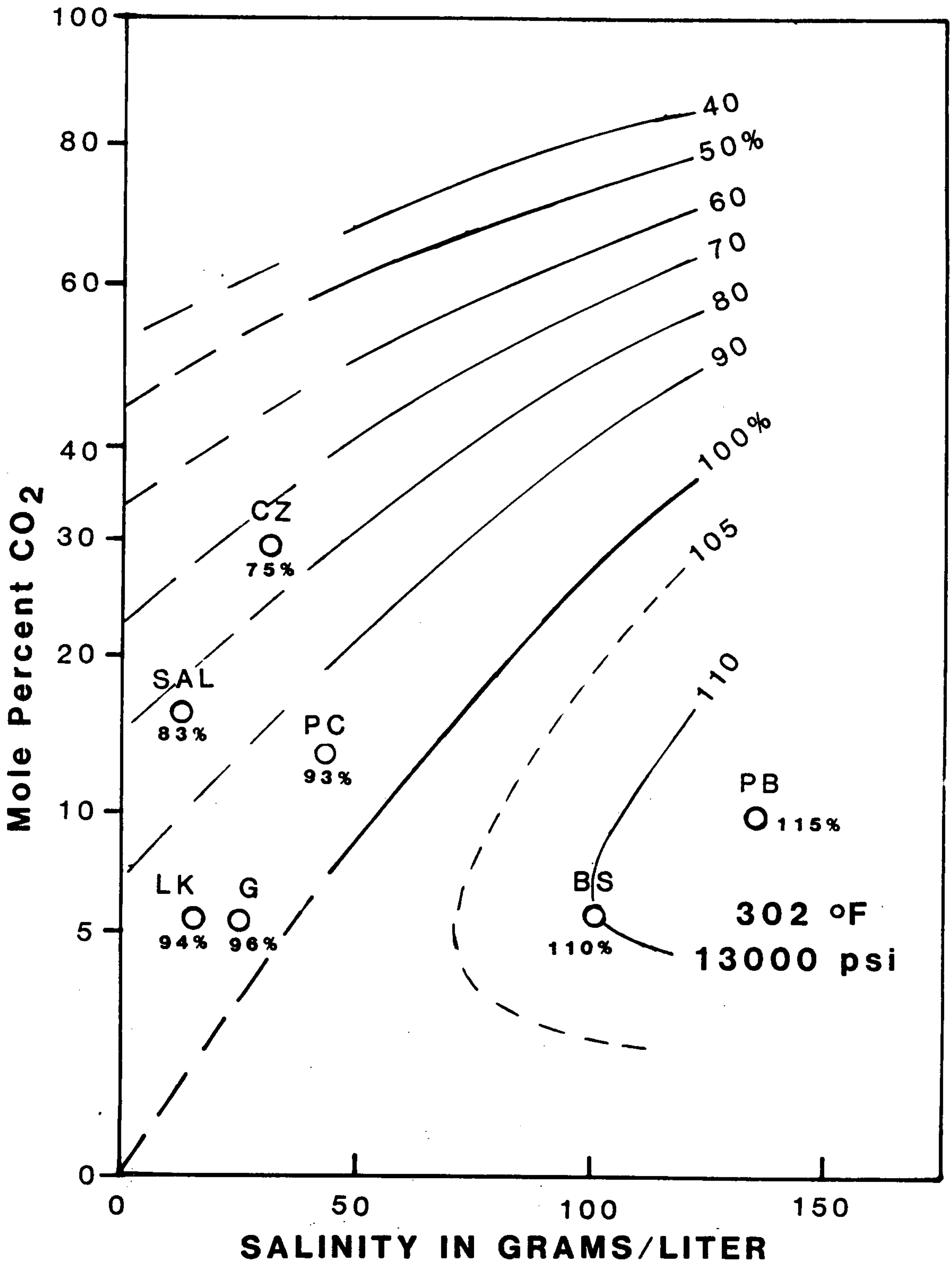

Figure D-1 Contours representing the percentage amount of methane contained in solutions at the indicated salinity and mole percent of carbon dioxide of gases dissolved in solution compared to methane solubility values in CO_2 free solutions at the same salinity, temperature and pressure. The circles represent the compositional position of geopressured test wells as follows: CZ = Crown Zellerbach, SAL = Saldana, PC = Praire Canal, LK = Lear Koelemay, G = Girouard, BS = Beulah Simon, and PB = Pleasant Bayou.