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The Solubility of Methane, Carbon Dioxide, and Oxygen in Brines From 0° to 300° C

By Stephen D. Cramer

UNITED STATES DEPARTMENT OF THE INTERIOR

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The solubility of methane, carbon dioxide, and oxygen was measured in brines at temperatures from 0° to 300° C as part of Federal Bureau of Mines research on the corrosion of metals in high-temperature geothermal and mineral processing environments. Solubilities were measured by the technique of extracting pure gas, dissolved at pressures where Henry's law was applicable, from known volumes of brine. The results were smoothed with respect to temperature. The solubility, expressed in terms of the Henry's law constant, reaches a maximum at temperatures ranging from 60° to 100° C for methane and oxygen, and from 160° to 170° C for carbon dioxide. The Henry's law constant increases, that is, gases are salted out of the brines, in the presence of dissolved salts. Salting-out coefficients are strongly dependent upon temperature. The temperature dependence of the Henry's law constant for geothermal brines is different from that for sodium chloride brines owing to the more complex chemistry of the geothermal brines. The solubility of oxygen and carbon dioxide in brines exposed to air saturated with water vapor and at a total pressure of 760 mm Hg is reported for temperatures from 0° C to the normal boiling point.

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CONTENTS

	Page
Abstract	1
Introduction	2
Acknowledgment	2
Experimental procedures	3
Theory	4
Results	5
Methane	6
Carbon dioxide	6
Oxygen	6
Discussion	6
Methane	9
Carbon dioxide	11
Oxygen	12
Salting out	13
Summary	14
References	15
Appendix—Nomenclature	17

ILLUSTRATIONS

1. Apparatus used to make solubility measurements by the gas extraction technique 4
2. Standardized residuals for methane-water data 9
3. Standardized residuals for carbon dioxide-water data 9
4. Standardized residuals for oxygen-water data 10
5. Modified Henry's law constant for methane in water and in five brines 10
6. Modified Henry's law constant for carbon dioxide in water and in three brines 11
7. Carbon dioxide solubility in brines exposed to air saturated with water vapor at a total pressure of 760 mm Hg. 12
8. Modified Henry's law constant for oxygen in water and in five brines 12
9. Oxygen solubility in brines exposed to air saturated with water vapor at a total pressure of 760 mm Hg 13
10. Temperature dependence of the salting-out coefficients for methane, carbon dioxide, and oxygen in sodium chloride brines 13

TABLES

1. Concentration of dissolved salts in brines used in solubility measurements 3
2. Composition of geothermal brines 3
3. Mean experimental values of the modified Henry's law constant for methane 6
4. Literature and mean experimental values of the modified Henry's law constant for carbon dioxide 7
5. Mean experimental values of the modified Henry's law constant for oxygen 8
6. Analysis of experimental error 8
7. Solubility constants 9
8. Smoothed values of the modified Henry's law constant for methane 10
9. Smoothed values of the modified Henry's law constant for carbon dioxide 11
10. Carbon dioxide solubility in brines exposed to air saturated with water vapor at a total pressure of 760 mm Hg. 11
11. Smoothed values of the modified Henry's law constant for oxygen 12
12. Oxygen solubility in brines exposed to air saturated with water vapor at a total pressure of 760 mm Hg 13
13. Salting-out coefficient for methane, carbon dioxide, and oxygen 13

THE SOLUBILITY OF METHANE, CARBON DIOXIDE, AND OXYGEN IN BRINES FROM 0° TO 300° C

By Stephen D. Cramer[1]

ABSTRACT

The solubility of methane, carbon dioxide, and oxygen was measured in brines at temperatures from 0° to 300° C as part of Federal Bureau of Mines research on the corrosion of metals in high-temperature geothermal and mineral processing environments. Solubilities were measured by the technique of extracting pure gas, dissolved at pressures where Henry's law was applicable, from known volumes of brine. The results were smoothed with respect to temperature.

The solubility, expressed in terms of the Henry's law constant, reaches a maximum at temperatures ranging from 60° to 100° C for methane and oxygen, and from 160° to 170° C for carbon dioxide. The Henry's law constant increases, that is, gases are salted out of the brines, in the presence of dissolved salts. Salting-out coefficients are strongly dependent upon temperature. The temperature dependence of the Henry's law constant for geothermal brines is different from that for sodium chloride brines owing to the more complex chemistry of the geothermal brines. The solubility of oxygen and carbon dioxide in brines exposed to air saturated with water vapor and at a total pressure of 760 mm Hg is reported for temperatures from 0° C to the normal boiling point.

[1] Chemical engineer, Avondale Research Center, Bureau of Mines, Avondale, Md.

INTRODUCTION

Geothermal and geopressured brines are potentially valuable sources of minerals and energy. This is particularly true of geothermal brines from high-salinity, liquid-dominated reservoirs such as those found in the Salton Sea Known Geothermal Resource Area (KGRA) in the Imperial Valley of California. Reservoir temperatures there can exceed 300° C. Total dissolved solids, consisting largely of alkali and alkaline-earth metal chlorides, can reach 20 to 30 wt-pct. Also present in high- and low-salinity geothermal brines and in geopressured brines are dissolved gases, including carbon dioxide, hydrogen sulfide, ammonia, methane, and hydrogen. While not considered indigenous to such brines, oxygen may enter them during resource recovery plant startup procedures and as a result of pumping and mixing brine streams during process operations.

Dissolved gases can markedly affect physical and chemical processes that occur in geothermal and geopressured brines. For example, gas desorption alters a single-phase flow of brine to a two-phase fluid of very different hydrodynamic properties. Dissolved gases are involved in processes that lead to the formation of complex mineral scales. They can have an important role in complexing metal ions in the brines. They also can promote and accelerate damaging forms of localized corrosion such as crevice corrosion, stress-corrosion cracking, corrosion fatigue, and pitting corrosion. In addition, some brines contain large quantities of dissolved methane and accurate solubility data over a wide range of temperatures are needed to estimate yields for methane recovery operations. As part of Federal Bureau of Mines research on materials of construction for geothermal and mineral processing facilities, the solubility of methane, carbon dioxide, and oxygen in aqueous environments was studied to provide fundamental information for use in these and other scientific and engineering investigations.

The solubility of methane has been measured in pure water at temperatures ranging from the freezing point to 170° C (*2, 4-5, 10, 13-14, 17-18, 22, 24, 34, 48, 50, 57, 60*).[2] Additional measurements have been made in aqueous salt solutions (0*m* to 4*m* dissolved salts; *m* = molal, moles salt dissolved in 1,000 g of water) at temperatures to 125° C (*4-5, 16-18, 34, 50, 57*). Some of these measurements were made at high pressures, 7 to 70 MPa (1,000 to 10,000 psi), typical of natural gas and petroleum reservoirs (*13, 57*) and at slightly lower pressures (*14, 18, 23-24*). Methane and water can form solid methane hydrates at these pressures (*40, 49*), hydrates which have properties consistent with two distinct clathrate hydrate structures (*8-9*) and which maintain orientational short range order through intrashell hydrogen-bonding (*27*).

The solubility of carbon dioxide has been measured in pure water at temperatures ranging from the freezing point to 350° C (*15, 19-21, 42, 45-46, 50-51, 53-54, 65, 67, 72-73, 77*) and in sodium-chloride brines to 500° C (*21, 42, 45-46, 51, 53-54, 65, 67*). Measurements at low temperatures, −5° to 40° C, have focused on the solubility of carbon dioxide in water, sea water, and sea water concentrates (*42, 46, 51, 53, 65, 72*). Measurements at temperatures above 100° C have primarily been concerned with hydrothermal solutions and the role of carbon dioxide in mineral deposition processes (*19-21, 54, 67*). Carbon dioxide forms clathrate hydrates in aqueous solutions, which can markedly affect solution properties (*65-66, 72*).

The solubility of oxygen has been measured in pure water at temperatures ranging from the freezing point up to 343° C (*6-7, 11, 17, 23, 25, 31, 39, 43, 52, 55, 59, 61, 68, 70, 74-76, 78*). Much of this work has focused on the range 0° to 40° C (*7, 17, 31, 39, 52, 68, 74*), which includes most biological and limnological systems. Several measurements have been reported for temperatures above 100° C (*11, 59, 61, 78*). Few studies have been conducted in brines with the exception of measurements in sea water at temperatures from 0° to 40° C (*7, 31, 52, 68, 69*). MacArthur (*44*) reports the solubility of oxygen in aqueous solutions of selected halides at 25° C, and Geffcken (*26*) reports values for 0*m* to 2*m* NaCl solutions at 15° and 25° C. Cramer (*11*) has conducted measurements at temperatures to 270° C in 0*m* to 5.7*m* NaCl aqueous solutions and in a hypersaline geothermal brine.

The present work reports the solubility of methane, carbon dioxide, and oxygen in water, in sodium chloride brines, and in geothermal brines from 0° to 300° C. In part of this work the solubilities of methane and oxygen were measured in pure water for purposes of comparing the data with existing measurements and then to extend the data to higher temperatures. Carbon dioxide solubilities were measured in pure water and in sodium chloride brines primarily in the 40° to 200° C temperature range where data are scarce.

With one exception, all of the solubility measurements were made using the technique of gas extraction (*11, 21, 56-57, 59, 70, 78*) which involves the desorption of gas from a known volume of liquid. This technique is generally applicable at all temperatures and for all combinations of gas and liquid. In the one exception, oxygen solubilities for water and 0.87*m* NaCl at temperatures from 25° to 60° C were measured by the Rideal-Stewart modification of the Winkler titration technique (*1*). The solubility data were then expressed in terms of the Henry's law constant that describes the proportionality between the concentration of gas in the vapor and in the liquid phases (*11, 36, 37, 41,* pp. 242-252, *59*). The Henry's law constant is the most widely used of several parameters for describing the solubility of gases in liquids. Experimental values of the Henry's law constant were then smoothed with respect to temperature by using statistical procedures to fit a smoothing and interpolation formula. This procedure then yielded the smoothed or best estimate of the gas solubilities as a function of temperature. Salting-out effects, that is, the reduction in the solubility of the gas in the presence of dissolved salts, were determined from the smoothed values for water and the sodium-chloride brines using the Setchenow equation (*21, 32, 41,* pp. 584-587, *45, 50, 62-63*). Geothermal brine data were not included in the analysis of salting-out effects because of significant differences from the sodium chloride data.

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The author appreciates the informed and timely advice received from N. A. Gokcen, research supervisor, thermodynamics laboratory, Albany Research Center, Bureau of Mines, Albany, Oreg., concerning the theoretical treatment of the data.

[2] Italic numbers in parentheses refer to items in the list of references preceding the appendix.

EXPERIMENTAL PROCEDURES

The solubility of methane, carbon dioxide, and oxygen was measured in demineralized water and in sodium chloride and geothermal brines. Table 1 gives the concentration of dissolved salts in these solutions. East Mesa geothermal brine (EMGB) is a low-salinity brine obtained as an unflashed sample from geothermal well Mesa 6-1 (*3*). (Unflashed brine has not lost water by evaporation during sampling. It has essentially the same composition as the brine in the reservoir.) Prior to use, the brine from Mesa 6-1 was stored at room temperature and no attempt was made to retain dissolved gases. Salton Sea geothermal brine (SSGB) is a synthetic brine based on Helgeson's analysis of unflashed hypersaline brine from geothermal well IID-2 (*35*). Both geothermal wells are located in the Imperial Valley of California, with Mesa 6-1 in the East Mesa geothermal field and IID-2 in the Salton Sea geothermal field. Detailed compositions for the two geothermal brines are given in table 2. The pH (measured at 25° C) of unflashed EMGB is 5.6 to 6.0 while that of SSGB is 4.6 (*58*). For experimental purposes the pH of these brines was adjusted to neutral by the addition of NaOH. The pH of the "as-prepared" sodium-chloride brines was neutral. In preliminary measurements, the solubility of carbon dioxide in water at 80° C was not sensitive to pH over the range 1 to 7. This is to be expected since more than 99 pct of the carbon dioxide in solution is in the molecular form and only a small amount is hydrolyzed to form carbonic acid and its ionization products (*20, 47, 53*).

The sodium-chloride brines and the synthetic SSGB were prepared from reagent grade chemicals dissolved in demineralized water. The synthetic SSGB brine was prepared from chloride salts of the constituent metal ions, sodium silicate, sodium sulfide, and sodium metaborate, in accordance with the composition given in table 2. Certain minor constituents, however, precipitated from the synthetic brine during its preparation. For example, marked reductions were observed in the concentration of Fe, Zn, Pb, B, and SiO_2 in samples of the "as-prepared" brine at 25° C. Acidifying the brine to pH 1.7 increased the concentration of these elements to the levels shown in table 4 except for Fe and SiO_2, which remained at about half their nominal value. Heating the "as-prepared" brine to 200° C followed by cooling to 25° C precipitated the Fe, Mg, SiO_2, and sulfur. However, these changes did not significantly affect the total concentration of dissolved solids in the synthetic brine since most of the solids were soluble alkali and alkaline-earth metal chlorides. Because of overdilution of the stock solutions used in preparing the synthetic brine, the concentration of salts in SSGB for the methane solubility measurements, table 1, is 17 pct lower than that specified in table 2 or used in the carbon dioxide and oxygen solubility measurements. This does not mean that the methane solubility values measured in SSGB are in error, but simply that they were determined in a brine that was dilute compared to the composition given in table 2. This fact is reflected in the concentrations given in table 1. The methane data can be extrapolated to the higher concentration of the SSGB brine used in the oxygen and carbon dioxide measurements by using the Setchenow equation (*21, 32, 41, 45, 50, 62-63*).

Table 1.—Concentration of dissolved salts in brines used for solubility measurements

Brine	Molality, *m*	Molarity, *M*	Ionic strength[1]
Methane:			
NaCl-1	.81	.79	.81
NaCl-2	1.95	1.86	1.95
NaCl-3	3.18	2.97	3.18
NaCl-4	4.70	4.26	4.70
SSGB[2]	4.05	3.55	6.18
Carbon Dioxide:			
NaCl-1	.50	.49	.50
NaCl-2	1.95	1.86	1.95
SSGB	4.87	4.19	7.34
Oxygen:			
NaCl-1	.87	.85	.87
NaCl-2	2.97	2.78	2.97
NaCl-3	5.69	5.09	5.69
EMGB	.57	.56	.60
SSGB	4.87	4.19	7.34

[1] Based on molal concentrations.
[2] Overdilution of a stock solution resulted in a 17-pct lower concentration of dissolved salts than that used for CO_2 and O_2 solubility measurements.
NOTE.—Composition of SSGB and EMGB is given in table 2.

Except for the several oxygen solubility values reported earlier that were obtained using the Rideal-Stewart modification of the Winkler technique (*11*), the solubilities of methane, carbon dioxide, and oxygen were determined from pressure-volume-temperature (PVT) measurements using the technique of gas extraction.[3] The apparatus for this technique is shown in figure 1 and consists of (1) a high-pressure, high-temperature section for dissolving the gas in the brine, (2) a heat exchanger for cooling (or heating) samples of gas-saturated brine to room temperature, and (3) a low-pressure, constant-temperature section for making PVT measurements on collected gas and liquid samples.

The following procedure was used to measure solubilities by the gas extraction technique. The 2-liter, type 316 stainless steel stirred reactor, fitted with a heat- and chemical-resistant glass liner, was filled two-thirds full with brine. The reactor was then sealed, stirring of the brine at 60 rpm was begun, and the brine was deaerated by evacuating

[3] Z. Ambrus, R. E. Brown, S. Cunningham, and W. D. Riley, Avondale (Md.) Research Center, assisted with these measurements.

Table 2.—Composition of geothermal brines, parts per million by weight

Constituent	EMGB[1]	SSGB[2]	Constituent	EMGB[1]	SSGB[2]
Ammonium ion	3.9	[3]	Magnesium	22	10
Barium	58	250	Manganese	.9	1,370
Boron	27	390	Potassium	1,430	16,500
Bromine	35	[3]	Rubidium	1.7	70
Calcium	1,370	28,800	Silica	101	400
Cesium	4	20	Silver	.04	[4]<1
Chlorine	18,000	155,000	Sodium	11,000	53,000
Copper	.05	[4]3	Strontium	226	440
Fluorine	1.5	[3]	Sulfate ion	16	[3]
Iron	.2	2,000	Sulfur	[3]	30
Lead	.3	80	Zinc	.02	500
Lithium	55	210			

[1] Reference 3. [3] Not determined.
[2] Reference 35. [4] Not included in synthetic brine.

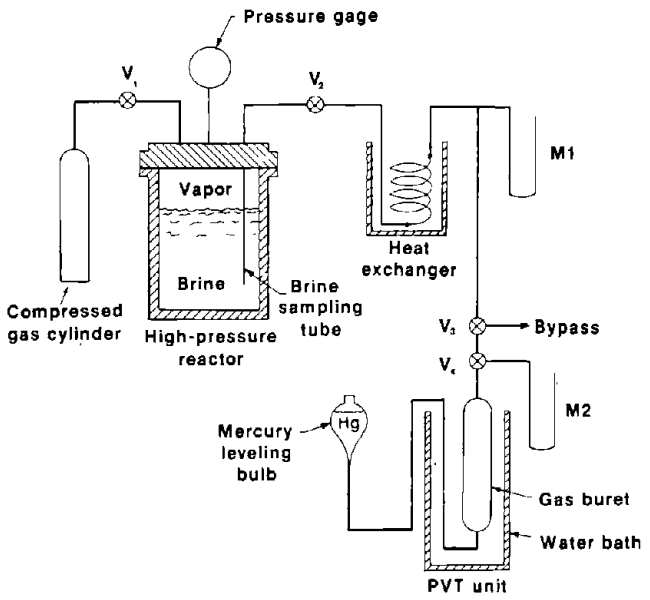


Figure 1.—Apparatus used to make solubility measurements by the gas extraction technique.

the reactor to the vapor pressure of the brine for at least 3 minutes. The temperature of the reactor was then adjusted (by either heating or cooling) to the test temperature, which ranged from 0° to 310° C. Upon reaching thermal equilibrium, 99.5 pct pure gas was injected into the reactor and allowed to distribute at a fixed partial pressure between the vapor and liquid phases. This was done by using gas (from a regulated supply) at a pressure in excess of the brine vapor pressure to yield a specific gas overpressure. The regulated gas supply was open to the reactor throughout the test to prevent changes in the gas partial pressure due to equilibration of the gas between the two phases or due to liquid volume changes during sampling. Equilibration of the gases occurred within 5 hours at 150° C and above, and 24 hours at lower temperatures. Equilibration times were determined at several temperatures by measuring the solubility of each gas as a function of time. These equilibration times were in general agreement with those reported by others (*13, 18-19, 21, 45, 48, 53, 55, 57, 65-66, 68*). Maximum gas partial pressures for methane were 2.9 MPa (420 psi) at the lower temperatures to 4.5 MPa (650 psi) at the higher temperatures. The corresponding values for carbon dioxide were 1.8 MPa (260 psi) and 3.1 MPa (450 psi) and for oxygen were 4.3 MPa (630 psi) and 5.2 MPa (750 psi). The total pressure, P, of the vapor phase, that is, the sum of the gas partial pressure and the vapor pressure of the brine, is tabulated in tables 3 through 5 along with the experimental solubility results for methane, carbon dioxide, and oxygen, respectively.

After chemical and thermal equilibrium had been attained, a sample of gas-saturated brine was extracted from the reactor through the sampling tube. Sampling flow rates were low, 25 to 50 ml/min, and there was negligible decrease in the reactor pressure while sampling. The sample flowed through the heat exchanger and was cooled (or heated) from the reactor temperature to near room temperature. The first 25 to 50 ml of each sample was discharged through the bypass valve to flush the sampling lines. A sample was then collected over mercury in the gas buret at atmospheric pressure. Because of the sizable drop in pressure from the reactor to the gas buret, much of the dissolved gas was extracted from the brine, and separate gas and liquid sample fractions formed in the gas buret. The total amount of gas dissolved in the brine sample at the reactor conditions was then calculated from the gas fraction in the gas buret by the ideal gas law, and from the small amount of gas that remained dissolved in the liquid fraction (at the gas buret temperature of 32.8° C) by Henry's law. Generally, four to eight measurements of the gas solubility were made at each test temperature with 15 to 30 minutes elapsing between each measurement.

THEORY

In the simplest process, the dissolution of a gas in a liquid involves the relocation of gas molecules, A, from the vapor phase into the solution phase. This is described by the reversible dissolution reaction

$$A\ (\text{vapor}) \rightleftharpoons A\ (\text{solution}).$$

At equilibrium, the relative amounts of A in two phases is defined by the equilibrium constant

$$K = a_g/\bar{f}_g, \qquad (1)$$

where a_g is the activity of the gas in the solution, and $\bar{f}_g$ is the fugacity of the gas in the vapor phase. This relationship is more commonly described in terms of the Henry's law constant (*28*, pp. 240-241, *36, 41*, pp. 232-240, 242-252, *59*)

$$k^\circ = \frac{1}{K} = \bar{f}_g/a_g. \qquad (2)$$

At the temperatures and relatively low pressures used in the present work, the solubility of methane, carbon dioxide, and oxygen in pure water has been shown to follow Henry's law (*21, 57, 59, 77-78*). By assuming that the vapor behaves as an ideal solution, $\bar{f}_g$ can be determined from the fugacity of the pure gas, f_g°, and the mole fraction of the gas in the vapor phase, y, using the Lewis and Randall rule (*41*, pp. 294-296, *64*, pp. 341-357)

$$\bar{f}_g = y f_g^\circ. \qquad (3)$$

In this equation, f_g° is evaluated at the temperature and ***total*** pressure, P, of the vapor phase (*29*). The fugacity of the pure gas can be computed from P using the fugacity coefficient, ϕ_g, (*64*, pp. 144-147, 409-412)

$$f_g^\circ = \phi_g P, \qquad (4)$$

where ϕ_g, like f_g°, is evaluated at the temperature and ***total*** pressure of the vapor phase. Ideally, the mole fraction, y, is found by analysis of the vapor phase constituents. This was not done in the present work and it was necessary to estimate y from the pressure data using Dalton's law. The total pressure of the vapor phase is equal to the partial pressure of the gas, P_g, plus the water vapor pressure of the brine, $P_{w,T}$. At the pressures used in this study, y is then given by

$$y = \frac{P_g}{P} = \frac{P - P_{w,T}}{P} \qquad (5)$$

Combining equations 3, 4, and 5 yields

$$\bar{f}_g = \phi_g P_g, \quad (6)$$

indicating that the fugacity of the gas in the vapor phase is proportional to the gas partial pressure and that deviations from ideal gas behavior are expressed through ϕ_g, which is evaluated at the total pressure of the systems, P.

The activity of the gas in solution, a_g, is typically defined at low pressures as (*41*, pp. 242-252)

$$a_g = \gamma x_g, \quad (7)$$

where x_g is the mole fraction of the dissolved gas and γ is the activity coefficient. Since the solution is a mixed solvent consisting of water and the ionic species produced by dissolved salts, the mole fraction of gas in solution is defined as

$$x_g = \frac{m_g}{m_g + \sum_j m_j \sum_i \nu_{ij} + \frac{1{,}000}{M}}, \quad (8)$$

where m_g = molality of dissolved gas,
m_j = molality of j-th salt,
ν_{ij} = moles i-th ionic species per mole of the j-th salt,
and M = molecular weight of solvent, that is, water.

Substituting equations 6 and 7 into equation 2 yields

$$k^\circ = \phi_g P_g / \gamma x_g. \quad (9)$$

One can extract from this equation a modified Henry's law constant that is composed of readily determined quantities

$$k = \phi_g P_g / x_g. \quad (10)$$

For an ideal solution, the activity coefficient in equation 9 is unity and $k = k^\circ$.

The change in the standard Gibbs energy for the gas in passing from the vapor phase into solution, ΔG_s°, is (*64*, pp. 404-409)

$$\Delta G_s^\circ = G_b^\circ - G_v^\circ = RT \ln k^\circ. \quad (11)$$

Since ΔG_s° is independent of pressure and of the concentration of dissolved salts and gases, k° is uniquely defined for each temperature. When the solution is ideal, as in dilute solutions of a gas in pure water, $k = k^\circ$. However, with the addition of salt to form a brine, the gas may be "salted out" due to an increase in the activity of the gas in the brine. The equation most commonly used to describe the effect of dissolved salts on the solubility of a gas is that attributed to Setchenow (*41*, pp. 584-587, *63*),

$$\log \gamma = \log \frac{k}{k^\circ} = k_s m_s, \quad (12)$$

where k is the modified Henry's law constant for the brine and k° is the Henry's law constant for water, m_s is the molality of dissolved salts in the brine, and k_s is the salting-out coefficient.

Many industrial and natural aqueous systems are open to the atmosphere. The equilibrium concentration of gases dissolved in open systems can be an important variable in determining their physical, chemical, and electrochemical properties. Equilibrium concentrations are readily computed from a knowledge of the Henry's law constant and the physical properties of the system. At atmospheric pressure, P_a, the partial pressure of a gas in dry air at temperature T is

$$P_{g,T} = (P_a - P_{w,T})y, \quad (13)$$

where y is the mole fraction (equivalent to volume fraction) of gas in dry air, and $P_{w,T}$ is the vapor pressure of water over the brine at the same temperature. Typical values of y are: oxygen, 0.2093 (*68*); carbon dioxide, 0.00033 (*71*). $P_{w,T}$ can be computed using the reference substance technique (*33*) which gives the temperature of pure water having the same vapor pressure as that of the brine. Steam tables or the formula of Keenan and Keyes (*38*) can be used to compute the vapor pressure of pure water at this temperature.

For dilute solutions of gas where $m_g << (\sum_j m_j \sum_i \nu_{ij}) + 55.49$), equation 8 can be rearranged to give the moles of gas dissolved in 1,000 g of water as

$$m_g = \left(\sum_j m_j \sum_i \nu_{ij} + 55.49\right) x_g. \quad (14)$$

Equations 10 and 13 are combined with equation 14 to eliminate x_g. The factor $1{,}000/(1{,}000 + m_s M_s)$ converts equation 14 to a basis of 1,000 g of solution. Thus, the concentration of dissolved gas, expressed in parts per million, in brine exposed to air saturated with water vapor is given by

$$C = \frac{\left(\sum_j m_j \sum_i \nu_{ij} + 55.49\right)(P_a - P_{w,T})\,\phi_g y\, M_g}{\left(1{,}000 + \sum_j m_j M_j\right) k_T} \cdot 10^6. \quad (15)$$

At atmospheric pressure $\phi_g = 1$ and, for 1 – 1 electrolytes, such as sodium chloride, $(\sum_j m_j \sum_i \nu_{ij}) = 2m_s$. At $P_{w,T} = P_a$, that is, the boiling point, C = 0. Equilibrium concentrations of dissolved gas are typically computed from equation 15 for a total pressure, P_a, of one atmosphere, that is, 14.696 psia or, equivalently, 0.101 MPa or 760 mm Hg, and reported in tabular form for temperatures between the normal freezing and boiling points.

RESULTS

Experimental values of the Henry's law constant were computed using the modified Henry's law constant defined by equation 10. The gas partial pressure in this computation was calculated as the difference between the reactor pressure and the vapor pressure of water over the brine. This latter value was estimated using the reference substance technique (*33*) to compute the temperature of pure water having the same vapor pressure as that of the brine. Water vapor pressures were computed using the formula of Keenan and Keyes (*38*). The reference substance technique, derived for NaCl solutions, was also used for the mixed-chloride geothermal brines since their major constituent is sodium chloride. Fugacity coefficients were obtained from a generalized chart using the reduced

Table 3.—Mean experimental values of the modified Henry's law constant, k, for methane

P, MPa	T, °C	k, MPa	P, MPa	T, °C	k, MPa	P, MPa	T, °C	k, MPa
	Water			NaCl-1—Continued			NaCl-3—Continued	
3.0	4.5	2,580	8.7	240.6	3,400	5.7	203.7	7,430
3.0	12.6	3,430	10.3	264.0	2,450	6.8	205.3	10,870
NAp	[1]25.0	[1]4,550		NaCl-2		7.3	225.1	7,160
NAp	[1]37.8	[1]5,360	2.3	0.5	5,530	9.4	256.0	5,670
1.1	42.0	5,800	2.7	5.0	5,870	11.3	269.5	5,250
1.1	61.0	6,260	2.3	12.6	7,080	10.8	271.5	5,050
NAp	[1]71.1	[1]6,900	2.6	13.0	6,060	12.4	295.6	3,410
1.1	90.4	6,610	2.3	26.3	8,230		NaCl-4	
NAp	[1]104.4	[1]7,320	1.9	47.5	10,530	2.4	3.5	17,560
1.2	111.0	6,310	2.3	78.0	11,770	2.3	13.3	14,650
NAp	[1]137.8	[1]6,320	4.6	102.0	12,260	3.7	31.7	23,560
1.1	159.3	4,890	3.5	131.9	10,450	3.9	61.6	23,360
NAp	[1]171.1	[1]5,040	4.4	161.8	8,620	5.5	89.5	28,150
5.7	184.3	4,050	7.1	205.2	6,770	5.4	112.6	21,110
7.2	187.7	3,990	8.9	224.6	5,330	4.7	115.7	27,470
6.9	193.3	3,120	8.1	244.9	3,820	4.7	146.9	20,110
6.9	210.7	3,080	10.1	271.4	3,180	3.7	159.4	18,710
6.9	239.7	2,580	11.9	301.1	2,070	5.8	204.8	15,400
10.5	264.4	2,040		NaCl-3		8.2	241.1	10,240
8.0	269.2	2,240	3.3	3.5	8,160	10.9	287.9	6,740
12.0	281.0	1,780	2.4	12.5	8,860		SSGB	
13.3	300.0	1,130	2.5	12.5	9,090	2.6	4.5	12,490
	NaCl-1		4.1	24.5	13,390	2.7	12.5	13,160
1.9	3.0	3,620	3.1	45.7	15,590	2.7	16.0	12,920
2.2	13.0	4,190	1.1	60.2	17,330	1.1	45.3	17,990
3.3	20.0	5,640	3.4	61.8	14,290	1.1	60.2	17,630
4.1	41.6	7,120	3.3	61.9	15,350	1.1	88.1	18,000
2.7	73.3	8,400	2.4	75.4	17,160	1.1	121.7	16,790
3.0	100.4	9,260	4.0	88.8	16,300	2.7	166.8	16,450
3.0	124.6	7,870	5.2	111.9	15,920	5.3	204.3	13,180
6.3	146.0	8,150	4.3	134.4	14,870	6.4	233.0	9,200
5.0	174.5	6,440	5.5	162.2	12,870	10.5	268.0	6,320
5.5	191.6	5,350	6.8	180.7	11,200	12.7	301.0	4,830

NAp Not applicable. [1] Reference 14.

properties of the gases and a reduced compressibility factor of 0.27 (*64*, pp. 144-147, 409-412). The mole fraction of the gas dissolved in the brine was calculated using equation 8.

The four to eight experimental values of the modified Henry's law constant measured at each temperature were averaged to yield the mean experimental value. Mean experimental values of the modified Henry's law constant as a function of temperature are tabulated in tables 3, 4, and 5 for methane, carbon dioxide, and oxygen, respectively. The total pressure of the vapor phase for each set of experimental measurements is included with these values.

METHANE

Mean experimental values of the modified Henry's law constant for methane dissolved in water and five brines are given in table 3. Six additional values, computed from published data (*14*) on the solubility of methane in water at temperatures from 25° to 171.1° C and pressures to 6.9 MPa (1,000 psi), are included in this table and were used later when the pure water data were smoothed. Prior to inclusion of these data in table 3, it was necessary to correct the higher temperature literature values for the vapor pressure of water.

CARBON DIOXIDE

Carbon dioxide solubility measurements in water and in sodium chloride brines were made primarily in the temperature range 40° to 200° C where data are scarce. Prior work has indicated that the solubility of carbon dioxide has a minimum in this temperature range (*21*). Another purpose of these measurements was the initial determination of the solubility of carbon dioxide in a hypersaline geothermal brine such as SSGB, and the comparison of these results with those from NaCl brines. Literature and mean experimental values of the modified Henry's law constant for water and three brines are given in table 4. Most of the data for water and the two sodium chloride brines were obtained from the literature and the original sources are cited in table 4. In all cases the literature values were obtained from tabular data rather than graphical materials. Before using these values it was necessary to correct the carbon dioxide concentration to the mole fraction defined by equation 8 since concentrations were generally reported in the literature as the mole ratio of carbon dioxide to water. This correction was significant for the data from the more concentrated salt solutions. The published values were then recomputed in terms of the modified Henry's law constant given by equation 10. Both the experimental and the literature values were used later in smoothing the carbon dioxide data with respect to temperature.

OXYGEN

Mean experimental values of the modified Henry's law constant for oxygen dissolved in water and five brines are given in table 5. Included in the values for water and NaCl-1 are several measurements made by the Rideal-Stewart modification of the Winkler titration technique at temperatures from 25° to 60° C.

DISCUSSION

The experimental error in the determination of the modified Henry's law constant by the gas extraction technique includes errors due to the cyclic fluctuation of independent variables about preset values, such as reactor

Table 4.—Literature and mean experimental values of the modified Henry's law constant, k, for carbon dioxide

P, MPa	T, °C	k, MPa	Reference
	Water		
NAp	0	79	65
NAp	0	72.9	53
NAp	0	68.9	77
NAp	.2	73.8	46
NAp	.7	75	42
NAp	4	85.2	42
NAp	5	95	65
NAp	10	118	65
NAp	10	105	53
NAp	10.2	106	42
NAp	13.3	130	50
NAp	18	147	73
NAp	20	145	53
NAp	20	144	42
NAp	25	206	65
NAp	25	162	54
NAp	25	171	45
NAp	25	166	53
NAp	25	166	46
NAp	25	166	77
NAp	25.8	184	50
NAp	30	188	53
NAp	30	188	42
NAp	31	203	73
0.8	33	206	(1)
NAp	34.6	229	50
NAp	35	243	15
NAp	35	212	53
NAp	38	225	53
NAp	40	244	46
NAp	40	271	15
NAp	50	287	54
NAp	50	324	15
NAp	50	296	45
NAp	50	291	77
NAp	50	302	73
NAp	51.1	323	50
NAp	63.1	394	50
NAp	72.4	448	50
NAp	75	455	15
NAp	75	426	45
NAp	75	395	77
NAp	75	428	73
NAp	78.7	457	50
NAp	100	547	54
NAp	100	563	15
NAp	100	522	77
NAp	100	534	73
NAp	120	581	15
2.0	126.3	602	(1)
2.0	132.5	617	(1)
2.8	146	565	(1)
NAp	150	727	67
NAp	150	670	54
3.1	153.5	580	(1)
NAp	177	699	21
4.1	198.1	537	(1)
NAp	200	623	67
NAp	200	629	54
NAp	202	628	21
NAp	204	618	21
5.8	213.1	484	(1)
NAp	229	598	21
NAp	229	577	21
NAp	235	628	21
NAp	250	510	67
NAp	250	501	54
NAp	261	496	21
NAp	261	496	21
NAp	265	496	21
NAp	265	486	21
NAp	300	358	54
NAp	300	339	67
NAp	309	365	21
NAp	309	365	21
NAp	309	385	21
NAp	334	304	21
NAp	334	304	21
	NaCl-1		
NAp	0	84.9	42
NAp	0	85.4	53
NAp	2	91.4	42
NAp	4	98.3	42
NAp	5	103.2	53
NAp	6	105	42
NAp	8	113	42
NAp	10	121	42
NAp	10	122.3	53
NAp	12	129	42
NAp	14	137	42
NAp	15	144	53
NAp	16	146	42
NAp	18	154	42
NAp	20	163	42
NAp	20	166	53
NAp	22	171	42
0.8	23.6	199	(1)
NAp	24	180	42
NAp	25	190	46
NAp	25	191	53
NAp	25	187	54
NAp	26	189	42
NAp	28	199	42
NAp	30	209	42
NAp	30	217	53
NAp	35	242	53
NAp	38	258	53
NAp	50	328	54
1.7	73.7	499	(1)
NAp	100	616	54
2.1	123.6	645	(1)
NAp	150	752	54
NAp	176	711	21
NAp	176	752	21
NAp	200	712	54
NAp	236	660	21
NAp	236	660	21
NAp	250	577	54
NAp	286	536	21
NAp	286	536	21
NAp	300	422	54
NAp	309	485	21
NAp	309	464	21
NAp	309	464	21
	NaCl-2		
NAp	0.2	133	46
NAp	25	273	46
1.9	25.2	329	(1)
NAp	40	393	46
1.3	52.9	514	(1)
1.2	57.2	506	(1)
1.5	74.7	637	(1)
1.4	82.1	647	(1)
.9	84.8	820	(1)
1.9	97.4	939	(1)
1.7	128.4	1,060	(1)
2.1	144.3	1,037	(1)
NAp	176	1,042	21
NAp	176	1,010	21
NAp	199	1,010	21
NAp	199	1,020	21
NAp	228	955	21
NAp	228	989	21
6.2	238.6	928	(1)
NAp	282	891	21
NAp	306	836	21
NAp	306	879	21
NAp	306	825	21
NAp	330	603	21
	SSGB		
1.8	4.9	363	(1)
1.8	5.0	333	(1)
1.5	11.7	392	(1)
1.2	26.4	575	(1)
1.9	39	670	(1)
1.7	60.4	951	(1)
2.1	75.4	1,144	(1)
2.1	97	1,506	(1)
2.2	124.2	1,622	(1)
2.2	137.1	2,109	(1)
1.5	156.3	1,938	(1)
2.5	159	1,833	(1)
3.9	199.8	1,702	(1)
4.9	228.6	2,081	(1)
5.9	249.2	2,182	(1)

NAp Not applicable. [1] Present study.

temperature and pressure, and the random errors that normally occur in the measurement of any experimental variables, such as the gas and liquid sample volumes. An analysis of the error in the Henry's law constant involved first defining the error in terms of the independent variable x_i. This was done using the total differential

$$dk = \sum_{i=1}^{N} \frac{\partial k}{\partial x_i} dx_i. \quad (16)$$

The total differential was then divided by the Henry's law constant, k, to give the relative error, (dk/k), in the Henry's law constant. This quantity was then squared. Since the x_i variables are independent, the time average of cross products $x_i x_j$ $(i \neq j)$ is zero. Individual terms were maximized to give a worst-case estimate of the relative error, E, in the Henry's law constant

$$E^2 = \max \left[\frac{dk}{k}\right]^2 = \sum_{i=1}^{N} \max \left[\left(\frac{1}{k}\frac{\partial k}{\partial x_i}\right) dx_i\right]^2 \quad (17)$$

The maximum error, max $[dx_i]$, in each variable was obtained from careful analysis of the operating data for the apparatus used in measuring the gas solubility. These values are listed in table 6. They were then inserted into equation 17 and the contribution of each variable to the relative error, E, as given by the term in brackets, was determined (table 6). Squaring these contributions and summing them, as required by equation 17, and then taking the square root yielded a relative error, E, for the modified Henry's law constant of 5.8 pct.

The mean experimental values of the modified Henry's law constant (and appropriate literature values) given in tables 3, 4, and 5 for methane, carbon dioxide, and oxygen, respectively, were fit by the least-squares procedure to the smoothing and interpolation formula

$$R \ln k = (\Delta\alpha - \Delta S_o) + \frac{\Delta H_o}{T} - \Delta\alpha \ln T - \Delta\beta T - \Delta\lambda T^2 \quad (18)$$

where ΔS_o and ΔH_o are constants of integration, T is the absolute temperature in kelvin, k is in MPa, and R is

Table 5.—Mean experimental values of the modified Henry's law constant, k, for oxygen

P, MPa	T, °C	k, MPa
	Water	
2.5	3.0	2,530
3.4	6.5	2,920
3.5	7.5	3,330
3.5	13.7	3,670
3.0	19.0	4,060
3.1	22.4	4,630
2.9	24.3	4,310
4.2	28.5	4,980
.1	32.0	5,110
.1	42.0	5,250
.1	42.5	5,270
4.2	49.6	6,480
.1	50.0	5,650
.1	51.0	5,830
4.3	60.7	7,340
4.0	71.8	7,060
4.0	75.2	7,060
4.0	90.2	7,270
4.1	100.2	7,520
4.2	114.6	7,500
4.0	122.9	6,910
5.1	140.2	6,890
5.1	165.2	5,880
4.7	187.9	4,380
6.7	240.7	2,940
12.3	288.0	1,350
	NaCl-1	
2.6	1.5	4,020
3.1	6.7	4,980
3.7	13.5	5,090
2.6	20.2	5,680
3.8	30.2	7,020
.1	42.0	7,510
.1	42.5	7,520
3.8	49.6	8,060
.1	50.0	8,010
.1	51.0	7,760
.1	61.5	8,100
3.8	62.9	8,920
3.5	70.2	8,630
4.1	84.0	9,440
4.1	99.0	9,580
4.1	125.0	8,570
4.1	150.7	7,790
5.7	166.8	6,790
5.7	202.9	6,140
6.7	241.2	3,720
8.9	257.3	3,500
12.9	285.9	2,270
	NaCl-2	
2.8	1.5	10,020
3.4	7.5	10,260
3.4	11.8	11,240
3.1	19.0	11,780
3.0	23.5	12,140
4.3	27.4	12,770
4.3	49.6	14,550
4.3	59.1	15,950
3.9	75.2	14,730
4.0	95.7	14,290
4.0	117.4	12,210
6.9	137.4	12,790
6.9	157.5	13,180
6.9	185.2	9,450
6.7	240.5	6,720
6.6	240.7	6,890
8.5	269.6	4,960
12.3	296.2	4,040
	NaCl-3	
2.8	3.0	20,290
3.5	7.4	22,770
3.6	13.7	22,980
4.6	26.3	23,690
4.6	47.9	26,160
4.6	59.1	26,290
4.6	73.5	26,950
4.3	84.1	26,520
4.3	95.2	28,390
4.3	110.7	24,800
3.7	117.4	23,900
4.3	128.5	23,940
5.5	165.7	16,490
5.1	187.9	14,720
5.7	207.9	14,690
6.1	241.8	19,900
8.6	259.8	9,890
8.1	270.0	10,250
10.6	289.0	8,160
	EMGB	
4.2	2.3	3,650
3.1	6.8	3,870
3.6	13.5	4,340
7.3	46.5	7,260
7.2	60.7	7,480
3.5	79.2	7,880
3.5	99.8	7,870
3.9	106.0	8,700
2.9	118.0	7,570
3.3	155.0	6,140
4.0	200.6	4,340
4.4	202.0	4,660
5.2	222.0	3,790
	SSGB	
3.9	1.8	12,410
3.2	7.5	14,640
3.4	12.0	15,990
3.1	19.0	15,900
3.9	21.3	18,020
4.0	28.5	18,640
4.1	47.9	18,030
4.1	61.3	19,770
3.9	76.8	19,770
3.9	94.0	19,770
3.7	123.5	17,760
5.7	137.9	15,670
5.8	150.2	14,490
5.7	152.4	13,870
5.1	187.9	11,100
6.1	230.1	9,360
8.5	272.4	6,100
10.8	286.5	7,200
12.1	310.0	5,630

Table 6.—Analysis of experimental error

Variable	Maximum error, max [dx]	Contribution to relative error, pct
Reactor pressure	0.068 MPa	1.4
Reactor temperature	2° C	4.2
Sample volume:		
Liquid fraction	0.4 ml	2.6
Gas fraction	0.4 ml	2.6
Gas buret temperature	2° C	.6
Atmospheric pressure	1 mm Hg	.3
Brine concentration	0.2*m*	.5

1.9872 cal/K-mole. This formula is based upon the following empirical equation describing the temperature dependence of the heat capacity (*28*, pp. 77-86, 180-183, *30*, *68*, pp. 144-147, 409-412):

$$C_p = \alpha + 2\beta T + 6\lambda T^2. \qquad (19)$$

For the simple gas dissolution reaction given earlier, the difference between the heat capacity of the gas in solution and that in the vapor phase is

$$\Delta C_p = C_{p,b} - C_{p,v}$$
$$= \Delta\alpha + 2\Delta\beta T + 6\Delta\lambda T^2 \qquad (20)$$

where $\Delta\alpha$, $\Delta\beta$, and $\Delta\lambda$ are the differences in the corresponding terms for the gas in the solution and in the vapor phases. Equation 18 provides the analytical basis for computing the thermodynamic quantities related to the dissolution of gas in solutions (*28*, pp. 77-86, 180-183, *36*). The solubility constants ΔS_o, ΔH_o, $\Delta\alpha$, $\Delta\beta$, and $\Delta\lambda$ are tabulated in table 7 for methane, carbon dioxide, and oxygen. The standard error of the estimate for the data smoothed using equation 18 is given in table 7 and ranges from 5.1 to 10.5 pct for methane, 3.4 to 7.7 pct for carbon dioxide, and 4.0 to 6.0 pct for oxygen. The error term used in computing the standard error of the estimate was $(\hat{k}_i - k_i)/\hat{k}$, where k_i is the i-th experimental value and $\hat{k}_i$ is the smoothed value of the modified Henry's constant. These values of the standard error agree well with the estimated experimental error, 5.8 pct. They indicate that deviations from the smoothed curves are primarily due to errors in measuring the independent variables given in table 6.

Using the methane-water, carbon dioxide-water, and oxygen-water data sets as examples, an analysis of residuals was performed to obtain yet another measure "goodness of fit" for equation 18. Letting

$$y = \ln k\,, \qquad (21)$$

the i-th residual was defined as

$$\epsilon_i = \hat{y}_i - y_i\,, \qquad (22)$$

where y_i is the experimental value and $\hat{y}_i$ is the smoothed value. The standard error of the estimate based on logarithmic values of the modified Henry's law constant is given by

$$s^2 = \frac{\sum_{i=1}^{N} \epsilon_i^2}{N-5} \qquad (23)$$

and the standardized residual is given by ϵ_i/s. Plots of standardized residuals versus $\hat{y}$, e.g., the smoothed value of

Table 7.—Solubility constants

Brine	ΔS_o, cal/K-gmole	ΔH_o, cal/gmole	$\Delta\alpha$, cal/K-gmole	$\Delta\beta$, cal/K^2-gmole	$\Delta\lambda$, cal/K^3-gmole	Standard error of the estimate, pct
			METHANE			
Water	−38.5406	−11,122.8	−14.2643	0.207386	-1.15047×10^{-4}	9.0
NaCl-1	−14.6677	−7,559.5	−13.0949	.127904	$-.50054 \times 10^{-4}$	5.2
NaCl-2	.1949	−5,841.0	−14.2558	.109012	$-.35958 \times 10^{-4}$	5.1
NaCl-3	−33.0603	−7,841.5	−9.6622	.130809	$-.61361 \times 10^{-4}$	9.1
NaCl-4	.0733	−4,420.1	−12.7811	.095976	$-.35585 \times 10^{-4}$	10.5
SSGB	9.7367	−1,389.8	−8.5243	.014526	$.25353 \times 10^{-4}$	5.8
			CARBON DIOXIDE			
Water	−19.7341	−10,071.9	−13.1511	0.147353	-0.72233×10^{-4}	6.7
NaCl-1	−14.4692	−9,798.3	−14.2502	.150530	$-.75883 \times 10^{-4}$	3.4
NaCl-2	−20.9874	−10,230.9	−14.2357	.171026	$-.97707 \times 10^{-4}$	5.9
SSGB	−17.3455	−7,562.5	−10.7513	.121501	$-.70492 \times 10^{-4}$	7.7
			OXYGEN			
Water	−21.1537	−7,561.7	−10.6578	0.107708	-0.32942×10^{-4}	6.0
NaCl-1	−22.2338	−5,916.3	−7.9075	.081094	$-.22453 \times 10^{-4}$	4.7
NaCl-2	−12.6251	−3,888.2	−8.1155	.070532	$-.23145 \times 10^{-4}$	5.5
NaCl-3	−8.0613	−5,224.7	−13.7075	.140559	$-.79595 \times 10^{-4}$	5.3
EMGB	−11.4186	−9,290.6	−18.8512	.208580	-1.17803×10^{-4}	4.0
SSGB	32.1306	−5,575.1	−25.7905	.205121	-1.18354×10^{-4}	5.9

In k, are given in figures 2 through 4. These figures show that the standardized residuals are independent of $\hat{y}$ and are approximately normally distributed about $\epsilon/s = 0$. This is another indication of a good fit of the data. The relatively fewer residuals at low values of $\hat{y}$ for methane and oxygen simply reflects the fewer solubility measurements that were made at high temperatures.

METHANE

Smoothed values of the modified Henry's law constant, k, were generated from equation 18 for water and each of the brines and are tabulated in table 8 for temperatures from 0° to 300° C. The results of Culberson and McKetta (*14*) were included in smoothing the data for water. The value of k for water at 25° C, 4,330 MPa, compares well with values computed from the results of Arnold (*2*), 4,160 MPa; Frolich (*23*), 4,590 MPa; Duffy (*18*), 4,270 MPa, and Culberson and McKetta (*14*), 4,550 MPa. It is appreciably higher than values computed from the results of Franks (*22*), 3,960 MPa, and McAuliffe (*48*), 3,700 MPa. At 51.5° C, the value of k for water, 6,030 MPa, is in experimental agreement with the value computed from the results of Morrison and Billet (*50*), 5,870 MPa, and marginally so with the value reported by O'Sullivan and Smith (*57*), 5,510 MPa.

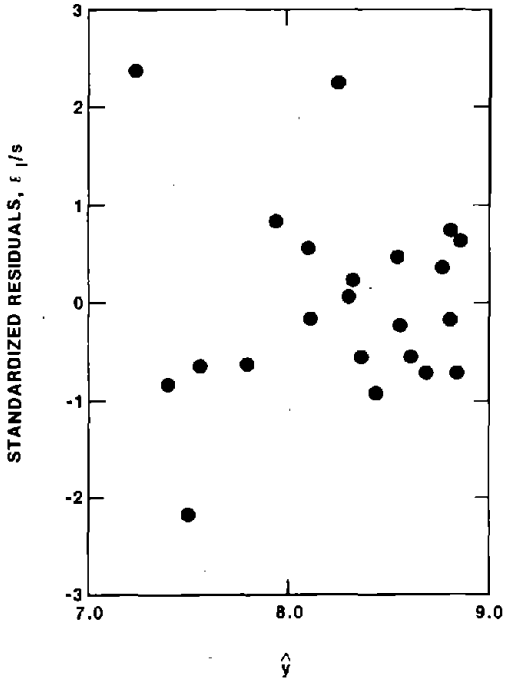


Figure 2.—Standardized residuals for methane-water data.

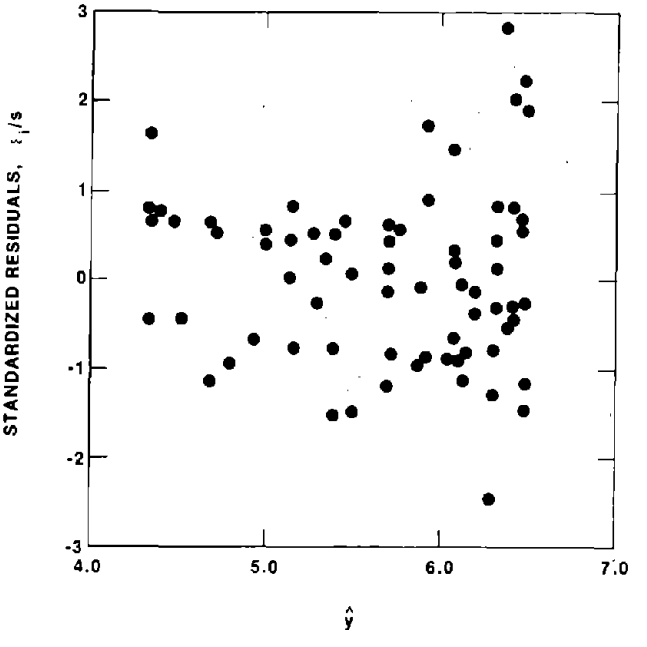


Figure 3.—Standardized residuals for carbon dioxide-water data.

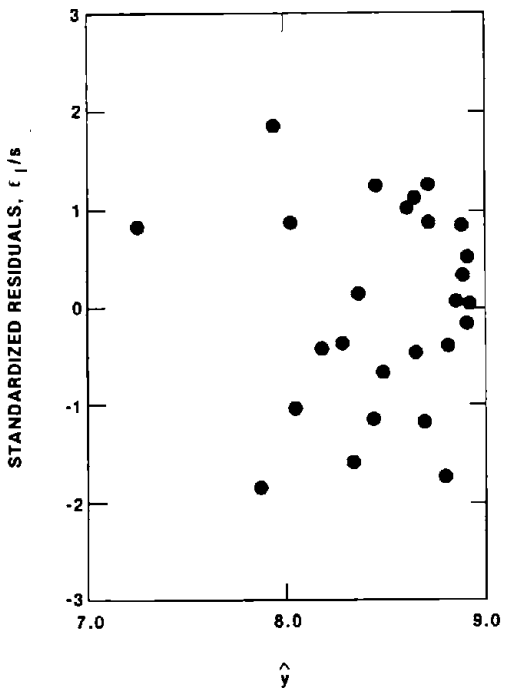


Figure 4.—Standardized residuals for oxygen-water data.

Smoothed values of the modified Henry's law constant are plotted in figure 5 as a function of reciprocal temperature. Values for water reported by O'Sullivan and Smith (*57*) and computed from the results of Culberson and McKetta (*14*) are included in this figure to illustrate the agreement with selected literature values. The curve for water is 7 to 12 pct higher than the values of O'Sullivan and Smith (*57*) and as much as 10 pct lower than the values of Culberson and McKetta (*14*). The deviation of the Culberson and McKetta data from this curve increases with increasing temperature. While the differences between the selected literature values and the smoothed data for water are at, or slightly larger than, the standard error of the estimate, an average of the literature values corrected for temperature would be in excellent agreement with the smoothed data.

Maximums in the curves occurred at the following temperatures: water, 89° C; NaCl-1, 96° C; NaCl-2, 92° C; NaCl-3, 89° C; NaCl-4, 83.5° C; and SSGB, 96° C. The average of these temperatures was 91° C. The maximums for the sodium-chloride solutions appear to decrease with increasing salinity. Maximums in the data of O'Sullivan and Smith (*57*) occurred at lower temperatures, 69° to 79° C, for brines up to 4*m* NaCl. Using the transformation $dT = -T^2d(1/T)$, the partial molal heat of solution can be shown to equal

$$\Delta\bar{H}_s = \frac{R\,\partial \ln k}{\partial(1/T)} \qquad (24)$$

At the maximums in the curves, where the slope is zero, $\Delta\bar{H}_s$ is also zero, and no heat is given up to or absorbed from the surroundings when the gas is dissolved. At lower temperatures ΔH_s is negative and the dissolution reaction is exothermic; at higher temperatures it is positive and the reaction is endothermic.

In figure 5, the curve of the Henry's law constant for SSGB is much flatter in the temperature range 40° to 200° C than the neighboring curves for NaCl-3 and NaCl-4. Explanations for this behavior would appear related to the more complex chemistry of the geothermal brine (*12*). Morrison and Billett (*50*) and Malinin and Savelyeva (*45*) have measured the salting-out coefficient for gases in a number of aqueous alkali and alkaline-earth metal chloride

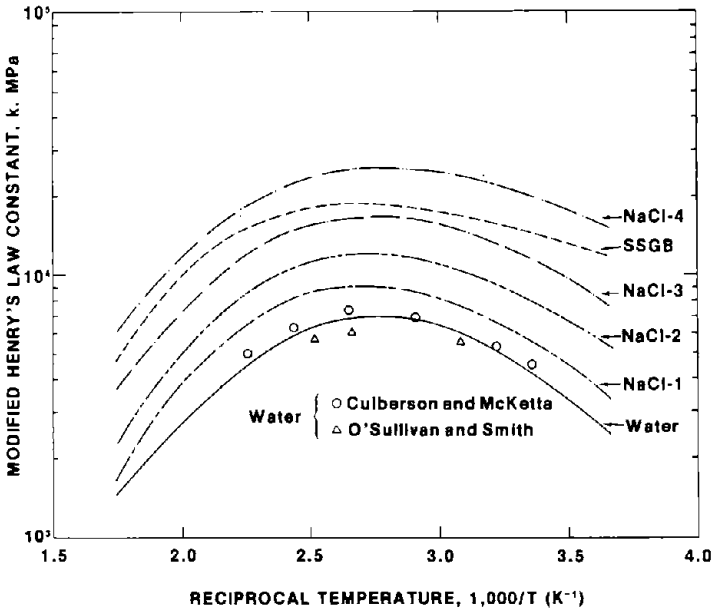


Figure 5.—Modified Henry's law constant for methane in water and in five brines.

Table 8.—Smoothed values of the modified Henry's law constant, k, for methane, megapascals

T, °C	Water	NaCl-1	NaCl-2	NaCl-3	NaCl-4	SSGB
0	2,460	3,400	5,320	7,550	14,970	11,680
20	3,950	5,140	7,540	10,840	19,170	14,090
40	5,370	6,810	9,540	13,760	22,500	16,120
60	6,420	8,120	11,020	15,830	24,620	17,610
80	6,940	8,880	11,810	16,830	25,440	18,470
100	6,930	9,050	11,900	16,810	25,090	18,670
120	6,510	8,700	11,380	15,970	23,810	18,260
140	5,850	7,990	10,420	14,570	21,890	17,310
160	5,070	7,060	9,210	12,890	19,600	15,960
180	4,290	6,040	7,910	11,120	17,190	14,340
200	3,580	5,040	6,620	9,410	14,810	12,560
220	2,950	4,120	5,430	7,860	12,580	10,760
240	2,430	3,310	4,370	6,500	10,570	9,010
260	2,010	2,630	3,480	5,340	8,810	7,390
280	1,670	2,070	2,730	4,380	7,290	5,940
300	1,400	1,620	2,130	3,590	6,000	4,690

solutions. Their data show a strong dependence of the salting-out coefficient on the cation and indicates the effect of temperature on the salting-out coefficient is cation dependent. Thus, in mixed-chloride solutions such as geothermal brines, where substantial quantities of metal chloride salts other than sodium chloride are present, the solubility curves for sodium chloride brines and for geothermal brines may very well differ in the ways observed here.

CARBON DIOXIDE

Smoothed values of the modified Henry's law constant, k, were generated from equation 18 for water and each of the brines and are tabulated in table 9 for temperatures from 0° to 300° C. The smoothed value generated from equation 18 for water at 25° C, 171.2 MPa, agrees within the experimental error with the results of Naumov (*54*), 162 MPa; Malinin and Savelyeva (*45*), 171 MPa; Murray and Riley (*53*), 166 MPa; Markham and Kobe (*46*), 166 MPa; and Zelvinskii (*77*), 166 MPa. The value from Stewart and Munjal (*65*) for 25° C, 206 MPa, was much higher. Ellis (*20*) has shown that the percentage of dissolved carbon dioxide that hydrolyzes to form carbonic acid and which can dissociate to form bicarbonate and carbonate ions is very small, no more than 1 pct of the total carbon dioxide present at temperatures up to 200° C. This appears to explain why the solubility of carbon dioxide measured in preliminary experiments in acidified sodium chloride solutions (pH~1) was identical to that in neutral solutions (pH~7). The small amount of concentrated hydrochloric acid required to acidify the solutions had no effect on the measured solubility, as has been shown elsewhere (*53*).

Smoothed values of the Henry's law constant are plotted in figure 6 as a function of reciprocal temperature. The low standard error of the estimate given in table 7 for water, NaCl-1, and NaCl-2 indicates a good fit of the data. Maximums in the curves occurred at the following temperatures: water, 156° C; NaCl-1, 162 C; and NaCl-2, 168 C. The average of these temperatures is 162° C. The curve for SSGB in figure 6 is very different from these three curves. There is no maximum, suggesting that the partial molal heat of solution is exothermic up to at least 250° C, the highest temperature where measurements were made. While this result was not expected, it does fit a pattern for carbon dioxide. With increasing salinity, the maximums occur at increasing temperatures and the slope of the high-temperature portion of the curves tends to decrease. There is some evidence that the solubility of carbon dioxide in sea water (and, by extension, brackish water) is the same as in sodium-chloride solutions of similar chlorinity ("Buch's assumption") at temperatures below 30° C (*42*). However,

Table 9.—Smoothed values of the modified Henry's law constant, k, for carbon dioxide, megapascals

T, °C	Water	NaCl-1	NaCl-2	SSGB
0	76.8	85.4	134.1	294.1
20	149.0	164.4	251.1	490.6
40	245.4	269.8	401.5	727.1
60	354.6	389.8	566.7	981.6
80	461.3	508.3	725.1	1,231
100	551.6	610.3	858.5	1,456
120	616.1	685.9	956.6	1,645
140	651.3	731.1	1,017	1,794
160	658.8	746.9	1,042	1,902
180	643.5	737.9	1,041	1,975
200	611.5	710.5	1,019	2,021
220	568.9	670.8	985.9	2,048
240	521.1	624.4	947.2	2,062
260	472.1	575.6	908.1	2,071
280	424.7	527.7	872.4	2,082
300	380.6	482.7	842.9	2,100

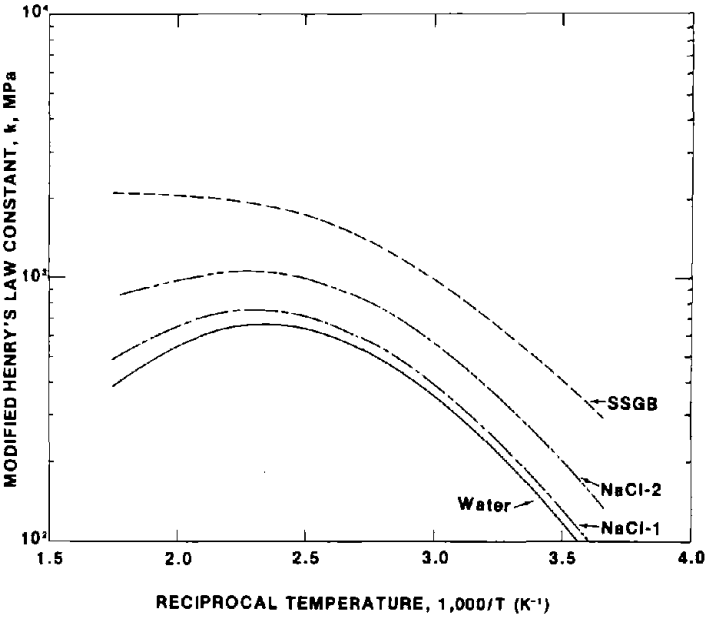


Figure 6.—Modified Henry's law constant for carbon dioxide in water and in three brines.

Murray and Riley (*53*) determined that "Buch's assumption" led to values 2 to 3 pct higher than their measured values at temperatures between 16° and 30° C. It is clear from figure 6 that the solubility of carbon dioxide in complex brines, such as SSGB, is not equivalent to that in sodium-chloride brines and "Buch's assumption" is not generally applicable.

The solubility of carbon dioxide, in parts per billion, in brines exposed to air saturated with water vapor at a total pressure of 760 mm Hg (0.101 MPa) is given in table 10 and plotted in figure 7 as a function of temperature. Temperatures range from 0° C to the normal boiling point of the

Table 10.—Carbon dioxide solubility in brines exposed to air saturated with water vapor at a total pressure of 760 mm Hg, parts per billion

(Basis: 0.033 vol-pct carbon dioxide in dry air)

T, °C	Water	NaCl-1	NaCl-2	SSGB
0	1,056	941	582	253
5	877	763	488	219
10	737	659	414	192
15	625	560	354	169
20	535	480	306	149
25	462	415	266	133
30	402	361	233	119
35	351	316	206	107
40	309	278	182	97
45	272	245	162	87
50	240	216	144	78
55	211	190	128	71
60	185	167	113	64
65	161	146	100	57
70	138	125	86	50
75	116	105	74	44
80	94	86	61	37
85	72	66	48	31
90	49	46	35	24
95	25	25	21	17
100	0	2	6	9
101	[1]	[1]	3	8
102	[1]	[1]	[1]	6
103	[1]	[1]	[1]	4
104	[1]	[1]	[1]	3
105	[1]	[1]	[1]	1

[1] Temperature exceeds the normal boiling point.

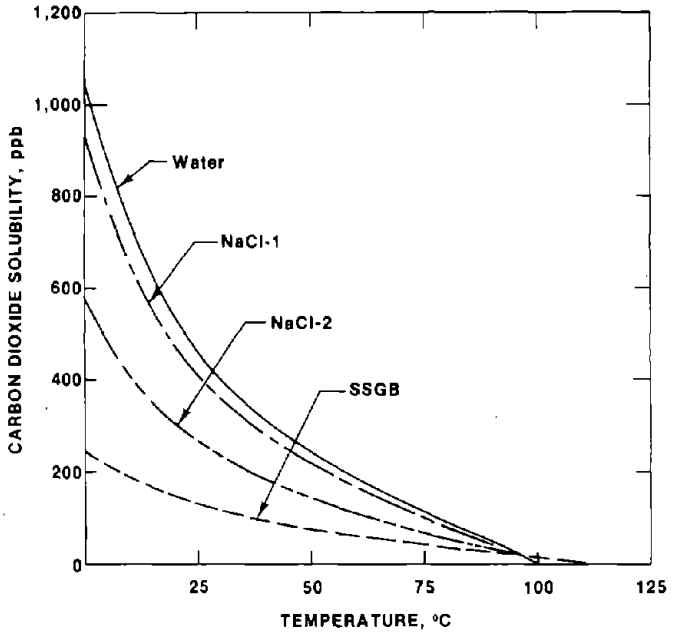


Figure 7.—Carbon dioxide solubility in brines exposed to air saturated with water vapor at a total pressure of 760 mm Hg.

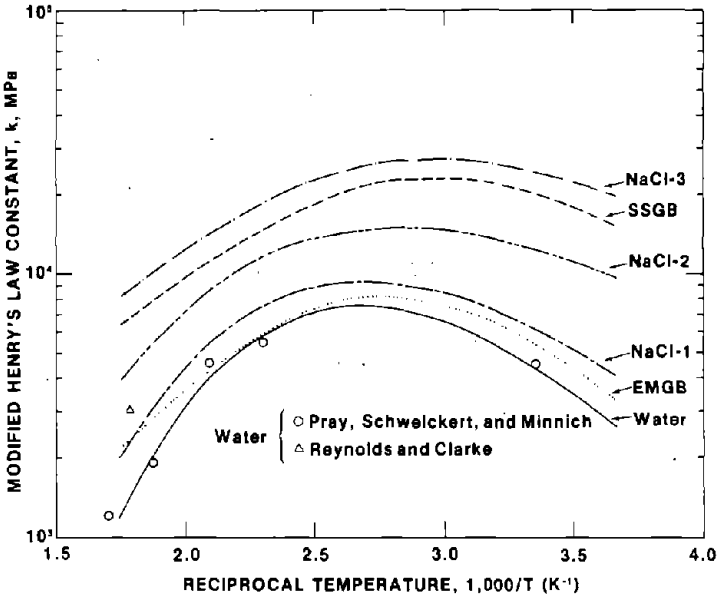


Figure 8.—Modified Henry's law constant for oxygen in water and in five brines.

brines. It is interesting to note that at temperatures in the neighborhood of 100° C, the concentration of dissolved carbon dioxide is higher in the brines than in water and increases with increasing salinity rather than decreases, as occurs at lower temperatures. This behavior is due solely to the suppression of the brine vapor pressure with increase in total dissolved salts and the relative effect of the reduced water vapor pressure on the carbon dioxide partial pressure. This same effect is shown in the atmospheric pressure solubility results presented later for oxygen.

OXYGEN

Smoothed values of the modified Henry's law constant, k, were generated from equation 18 for water and the five brines and are tabulated in table 11 for temperatures from 0° to 300° C. The smoothed value of k for pure water at 25° C is 4,410 MPa, and compares well with values reported by Pray (*59*), 4,520 MPa; or computed from the results of Orcutt and Seevers (*56*), 4,480 MPa; MacArthur (*44*), 4,420 MPa; and Carpenter (*7*), 4,410 MPa. At 38° C, the smoothed value of k is 5,310 MPa; that computed from the results of Van Slyke and Neill (*70*) was 5,420 MPa.

Table 11.—Smoothed values of the modified Henry's law constant, k, for oxygen, megapascals

T, °C	Water	NaCl-1	NaCl-2	NaCl-3	EMGB	SSGB
0	2,620	4,130	9,810	19,900	3,340	15,360
20	4,040	5,780	11,970	23,900	5,040	19,290
40	5,450	7,300	13,600	26,390	6,560	21,870
60	6,600	8,450	14,560	27,310	7,630	22,920
80	7,320	9,130	14,870	26,880	8,120	22,610
100	7,540	9,310	14,590	25,470	8,070	21,330
120	7,310	9,040	13,860	23,460	7,620	19,460
140	6,730	8,430	12,810	21,170	6,910	17,350
160	5,940	7,600	11,580	18,840	6,100	15,250
180	5,060	6,650	10,270	16,620	5,280	13,290
200	4,190	5,680	8,970	14,600	4,520	11,570
220	3,370	4,760	7,740	12,830	3,860	10,110
240	2,660	3,910	6,610	11,300	3,280	8,890
260	2,070	3,170	5,590	10,020	2,820	7,910
280	1,580	2,540	4,700	8,960	2,440	7,140
300	1,190	2,010	3,930	8,090	2,140	6,560

Smoothed values of the modified Henry's law constant are plotted in figure 8 as a function of reciprocal temperature. The few data reported for pure water at high temperatures are also plotted. The results of Pray (*59*) show excellent agreement with the smoothed values and the differences are only slightly larger than the standard estimate of the error for water given in table 7. The value of the Henry's law constant computed from the results of Reynolds and Clarke (*61*) for 287.8° C is a factor of two higher than the corresponding value from the smoothed curve and would indicate that these results are in error. Maximums in the curves occurred at the following temperatures: water, 96° C; EMGB, 88° C; NaCl-1, 97° C; NaCl-2, 80° C; SSGB, 65° C; and NaCl-3, 63° C. The average of these temperatures is 82° C. They appear to decrease with increasing salinity of the brines.

At temperatures above approximately 60° C, the curves for EMGB and SSGB are different from those for water and sodium chloride, figure 8. For example, both have maximums at lower temperatures than the neighboring curves for sodium-chloride brines. They exhibit less curvature at high temperatures than the curves for water and sodium chloride. Such behavior, as noted earlier, appears related to the more complex chemistry of the geothermal brines.

Many industrial and natural processes occur where brines are exposed to air at atmospheric pressure, for example, in caustic soda and chlorine production and in the recovery of minerals from sea water and from geothermal brines. Table 12 gives the solubility of oxygen, in parts per million, in water and five brines exposed to air saturated with water vapor at a total pressure of 760 mm Hg (0.101 MPa). Temperatures range from 0° C to the normal boiling point of the brines. For pure water, the solubility results agree reasonably well with those reported by Truesdale (*68*). For example, at 0°, 25° and 40° C the values from table 12 are 14.29, 8.29, and 6.41 ppm while the corresponding literature

values are 14.16, 8.11, and 6.59 ppm. The solubilities from table 12 are plotted in figure 9 versus temperature. The increase in solubility with increase in dissolved salt concentration in the vicinity of 100° C, noted earlier for carbon dioxide, is readily apparent in this figure.

Table 12.—Oxygen solubility in brines exposed to air saturated with water vapor at a total pressure of 760 mm Hg, parts per million

(Basis: 20.93 vol-pct oxygen in dry air)

T, °C	Water	NaCl-1	NaCl-2	NaCl-3	EMGB	SSGB
0	14.29	8.89	3.60	1.70	11.05	2.23
5	12.61	8.07	3.39	1.61	9.79	2.08
10	11.23	7.37	3.21	1.53	8.77	1.95
15	10.08	6.77	3.05	1.46	7.92	1.84
20	9.11	6.25	2.91	1.40	7.21	1.75
25	8.29	5.79	2.78	1.35	6.61	1.67
30	7.58	5.40	2.66	1.30	6.10	1.60
35	6.96	5.04	2.55	1.26	5.66	1.54
40	6.41	4.71	2.44	1.22	5.26	1.48
45	5.91	4.40	2.34	1.18	4.90	1.43
50	5.45	4.11	2.24	1.14	4.57	1.37
55	5.01	3.83	2.13	1.10	4.25	1.32
60	4.58	3.54	2.01	1.06	3.93	1.26
65	4.15	3.24	1.88	1.01	3.61	1.20
70	3.71	2.93	1.74	.95	3.27	1.12
75	3.24	2.59	1.58	.88	2.89	1.04
80	2.73	2.21	1.39	.80	2.48	.94
85	2.17	1.79	1.17	.71	2.00	.82
90	1.54	1.30	.91	.59	1.46	.67
95	.82	.75	.61	.45	.83	.50
100	0	.11	.25	.28	.08	.29
101	(1)	(1)	.17	.25	(1)	.24
102	(1)	(1)	.09	.21	(1)	19
103	(1)	(1)	.01	.17	(1)	14
104	(1)	(1)	(1)	.13	(1)	.08
105	(1)	(1)	(1)	.08	(1)	03

[1] Temperature exceeds the normal boiling point.

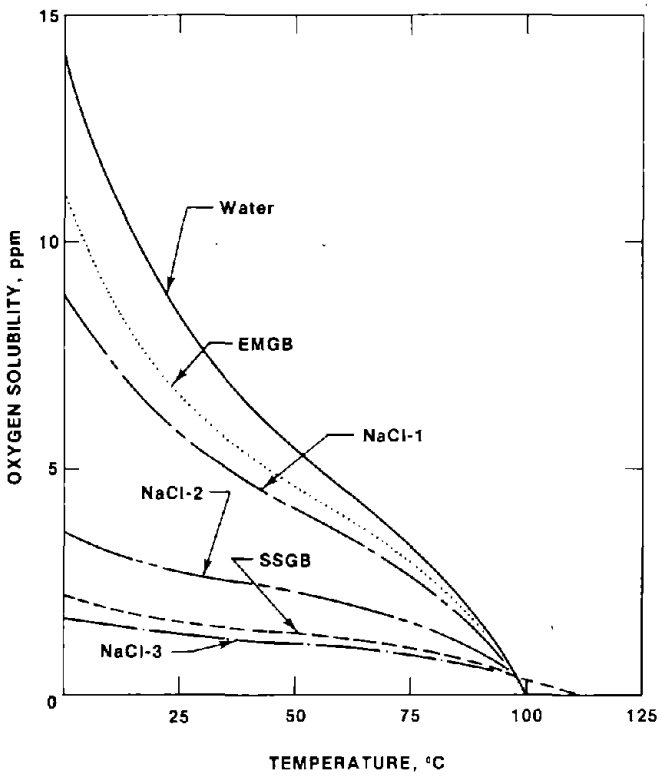


Figure 9.—Oxygen solubility in brines exposed to air saturated with water vapor at a total pressure of 760 mm Hg.

SALTING OUT

The effect of salting out is clearly evident by the higher values of the Henry's law constant for solutions containing dissolved salts. The salting-out coefficient, k_s, was computed by a least squares fit of equation 12 to the smoothed values of the Henry's law constants for water and the sodium chloride brines. This method of computing k_s is different from that described in the literature (*21, 45, 54, 57*) where individual values of k_s are computed for each solution concentration. Values obtained by the least squares procedure are reported in table 13 and plotted in figure 10 as a function of temperature for methane, carbon dioxide, and oxygen. The values from the present study for methane at

Table 13.—Salting-out coefficient, k_s molality^{-1}

T, °C	Methane	Carbon Dioxide	Oxygen
0	0.165	0.120	0.162
20	.141	107	.141
40	.127	098	.124
60	.119	.093	.110
80	.116	.089	.100
100	.116	.088	.093
120	.118	.089	.089
140	.122	.092	.087
160	.126	.096	.088
180	.130	.101	.091
200	.134	108	.096
220	.138	.116	.104
240	.137	.124	.113
260	.136	134	.125
280	.133	145	.139
300	.128	156	.155

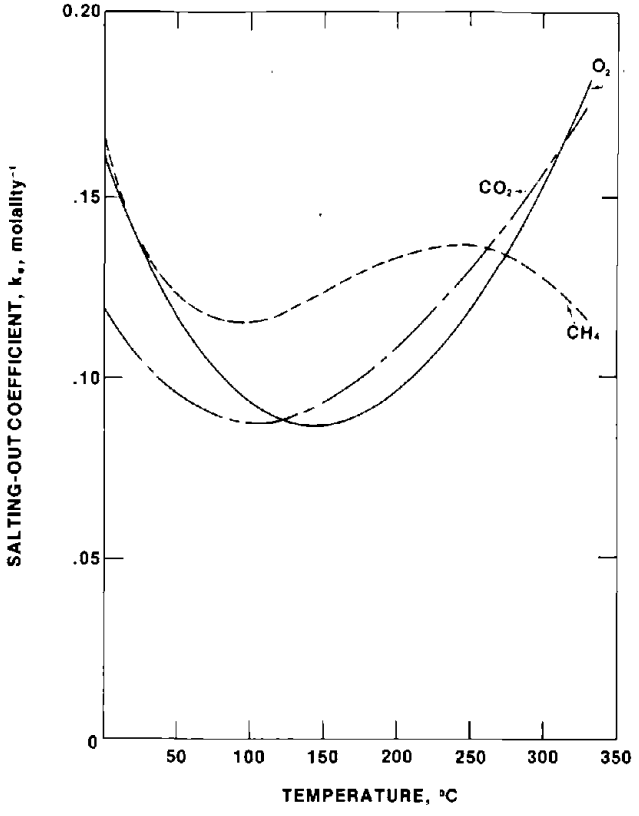


Figure 10.—Temperature dependence of the salting-out coefficients for methane, carbon dioxide, and oxygen in sodium chloride brines.

50°, 100°, and 125° C are 0.122, 0.116, and 0.119 (molality)$^{-1}$ and compare well with the values of O'Sullivan and Smith (*57*) for 1*m* NaCl at 51.5°, 102.5° and 125° C of 0.128, 0.115, and 0.122 (molality)$^{-1}$. The values of Morrison and Billet (*50*) for 1*m* NaCl at 47.3° and 71.6° C of 0.111 and 0.102 (molality)$^{-1}$ are substantially lower than these values, as are the corresponding values of O'Sullivan and Smith (*57*) for 4*m* NaCl. For oxygen, the value from the present study value at 25° C is 0.123 (molality)$^{-1}$ and is larger than that computed from the sea water results of Green (*32*) of 0.113 (molality)$^{-1}$. It is, however, in good agreement with the value of 0.137 (molality)$^{-1}$ computed by a least squares fit of MacArthur's data (*44*) for 0*m* to 5*m* sodium chloride brines. The values for carbon dioxide at 50°, 100°, 200°, and 300° C of 0.095, 0.088, 0.108, and 0.156 (molality)$^{-1}$ are similar to those measured by Ellis and Golding (*21*) for 1*m* NaCl of 0.095, 0.078, 0.089, and 0.176 (molality)$^{-1}$. The differences that occur are found in the mid- and high-temperature range where substantially fewer data were used by Ellis and Golding to obtain values for the salting-out coefficient. Minimums in the salting-out coefficient for methane, carbon dioxide, and oxygen occur at 90° 100°, and 140° C respectively. These temperatures do not correlate with the average temperatures at which the maximum value of Henry's law constant occurred, 91°, 162°, and 82° C.

SUMMARY

The solubility of methane, carbon dioxide, and oxygen was measured in water, sodium chloride brines, and geothermal brines at temperatures from 0° to 300° C as part of Federal Bureau of Mines research on the corrosion of metals in high-temperature geothermal and mineral processing environments. The results, expressed as the Henry's law constant, were smoothed with respect to temperature to give an analytical expression for numerical interpolation and for computation of the thermodynamic functions describing the dissolution of gases in liquids. The results extend the known solubility values to much higher temperatures and expand them to include geothermal brines and substantially more concentrated sodium chloride brines.

Curves of Henry's law constant versus temperature for individual brines exhibit maximums in the temperature range of 60° to 100° for methane and oxygen. Curves for carbon dioxide are distinguished from these by maximums at higher temperatures, 155° to 170° C, and by a more gradual change in the slope of the curves with temperature at the higher temperatures. The curve describing the solubility of carbon dioxide in a hypersaline geothermal brine did not have a maximum. This suggests a fundamental difference between the solubility of carbon dioxide and that of the other two gases in brines related to the effect of temperature on the dissolution process.

The temperature dependence of the Henry's law constant for geothermal brines appears to be significantly different from that for sodium chloride brines of comparable salinity. This would appear related to the more complex chemistry of the geothermal brines and specifically due to the presence, in significant concentrations, of a variety of single and multivalent cations. It can be reconciled by the concept that the salting-out coefficient is dependent on the nature of the cations in solution. Salting-out coefficients computed from the water and sodium-chloride data were strongly dependent on temperature. The coefficients for methane, carbon dioxide, and oxygen exhibited a minimum in the temperature range 90° to 140° C.

The solubility of carbon dioxide and oxygen in water and brines exposed to air saturated with water vapor at a total pressure of 760 mm Hg (0.101 MPa) was computed for temperatures from 0° C to the normal boiling point. These values are reported as parts per million of oxygen and parts per billion of carbon dioxide in tabular and graphical form. Dry air containing 20.93 vol-pct oxygen and 0.033 vol-pct carbon dioxide was assumed for these computations.

Smoothed values of the modified Henry's law constants, atmospheric solubilities, and salting-out coefficients were compared with published values. These comparisons were generally excellent over the more limited range of temperature and salinity where results are reported in the literature.

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APPENDIX—NOMENCLATURE

a = Activity
C = Concentration of dissolved gas, parts per million
C_p = Heat capacity
E = Relative error in Henry's law constant, equation 17
f = Fugacity; $f°$, pure component; $\bar{f}$, vapor phase
$G°$ = Standard Gibbs energy
ΔG_s° = Gibbs energy of solution at standard conditions, equation 11
ΔH_o = Solubility constant, equation 18
$\Delta \bar{H}_s$ = Partial molal heat of solution, equation 24
$k°$ = Henry's law constant, equation 2
k = Modified Henry's law constant, equation 10; $\hat{k}$, smoothed value
k_s = Salting-out coefficient, equation 12
K = Equilibrium constant for dissolution reaction, equation 1
m = Molality; m_s, molality of dissolved salt
M = Molecular weight
P = Pressure; P_a, atmospheric pressure
R = Gas constant
s = Standard error of estimate, equation 23
ΔS_o = Solubility constant, equation 18
T = Absolute temperature, kelvins
x = Mole fraction in solution phase; x_i, independent variable, in equations 16 and 17
y = Mole fraction in vapor phase; also ln k in equations 21 and 22
$\Delta\alpha$ = Solubility constant, equation 18
$\Delta\beta$ = Solubility constant, equation 18
$\Delta\lambda$ = Solubility constant, equation 18
ϵ = Residual, equation 22
γ = Activity coefficient
ϕ = Fugacity coefficient
ρ = Density

Subscripts

b = Brine
g = Gas
w = Water
v = Vapor
T = Temperature

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