

The Solubility and Partial Molar Volume of Nitrogen and Methane in Water and in Aqueous Sodium Chloride from 50 to 125° and 100 to 600 Atm¹

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The solubility of nitrogen and of methane in water, 1 *m* NaCl, and 4 *m* NaCl at 51.5, 102.5, and 125.0° has been measured at pressures from 100 to 600 atm using a stirred autoclave and a direct sampling technique. The results for methane in the salt solutions differ from the only previous studies. At the lowest temperature, where the water vapor content of the gas phase can be ignored, $\ln(f/X)$ for the dissolved gas is linear with total pressure, and the isobaric Henry's law applies up to the highest pressure for both gases. At the higher temperatures a curvature develops with rise in temperature, pressure, and, in general, salt concentration, but Henry's law may still apply. The data are interpreted in terms of the partial molar volume of dissolved gas and its variation with pressure, temperature, and salt concentration. Increase in NaCl concentration enhances the temperature coefficient of the partial molar volume of the dissolved gas. It also causes the latter to decrease at 51.5° but, in general, to increase at 102.5 and 125.0°, except at the highest pressure and temperature. Salting-out coefficients are tabulated and found to be nearly the same for both gases, to be approximately independent of pressure, to pass generally through a minimum with rise in temperature, and to show a decrease with increase in salt concentration. At a pressure of 200 atm the solubility of methane in water, 1 *m* NaCl, and 4 *m* NaCl passes through a minimum at 79 ± 2 , 72 ± 3 , and $69 \pm 5^\circ$, respectively.

The solubility of naturally occurring gases such as nitrogen and methane in sodium chloride solution, and its variation with pressure, temperature, and salt concentration is of interest not only to the physical chemist but to the geochemist, for both gases occur associated with brine in the earth's crust and are doubtless transported subterraneously in solution from high to low pressure regions. Very few studies of "permanent" gas in aqueous salt solution at pressures of hundreds of atmospheres have been reported. The most extensive high-pressure solubility data for nitrogen in water are those of Wiebe, Gaddy, and Heins² up to 100° and of Krase and co-workers,^{3,4} but the only studies of its solubility in aqueous sodium chloride at pressures other than atmospheric are from this laboratory: a preliminary one⁵ at 30°, confined to pressures below 70 atm and involving a comparatively inaccurate technique, and an incomplete one⁶ confined to 1 *m* NaCl over a smaller temperature range. The most important measurements for pure methane in water are those of Culberson and McKetta,⁷ while its solubility in aqueous sodium chloride has been determined by Michels, Gerver, and Bijl⁸ up to 220 atm and in this laboratory⁹ at pressures not exceeding 65 atm. The measurements reported in the present paper have an accuracy much greater than that of the last two studies mentioned and extend to pressures of 600 atm. No partial molar volumes of gases dissolved in simple salt solutions appear to be available in the literature.

Experimental Section

The gases were obtained from The Matheson Co., Inc., their purity given as 99.996% for the N₂ and 99.95% for the CH₄. The solubility equilibria were obtained in a 1-gallon, 316 stainless steel stirred, packless autoclave, the temperature of which was controlled to $\pm 0.5^\circ$ by a Minneapolis-Honeywell Electro-Pulse unit and Electronik 18 recorder, except for brief but unavoidable excursions of $\pm 2^\circ$. An iron-constantan thermocouple, calibrated against a certified thermometer, was used to measure the autoclave temperature. The water used was distilled, passed through

(1) Taken from the Ph.D. dissertation of T. D. O. Portions of this paper were presented before the Division of Physical Chemistry at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, and before the Geochemical Society in San Francisco, Calif., Nov 1966.

(2) R. Wiebe, V. L. Gaddy, and C. Heins, Jr., *Ind. Eng. Chem.*, **24**, 97 (1932); *J. Amer. Chem. Soc.*, **55**, 947 (1933).

(3) J. B. Goodman and N. W. Krase, *Ind. Eng. Chem.*, **23**, 401 (1931).

(4) A. W. Saddington and N. W. Krase, *J. Amer. Chem. Soc.*, **56**, 353 (1934).

(5) N. O. Smith, S. Keleman, and B. Nagy, *Geochim. Cosmochim. Acta*, **26**, 921 (1962).

(6) T. D. O'Sullivan, N. O. Smith, and B. Nagy, *ibid.*, **30**, 617 (1966).

(7) O. L. Culberson and J. J. McKetta, *Trans. Am. Inst. Mech. Engr.*, **192**, 223 (1951); *J. Petrol. Technol.*, **2**, 319 (1950).

(8) A. Michels, J. Gerver, and A. Bijl, *Physica*, **3**, 797 (1936).

(9) J. R. Duffy, N. O. Smith, and B. Nagy, *Geochim. Cosmochim. Acta*, **24**, 23 (1961).

an ion-exchange column, and N_2 or CH_4 bubbled through it overnight. The salt solutions were prepared in a similar manner using Baker Analyzed Reagent grade NaCl previously dried at 115° . They were made up by weight, but analyzed after a run by evaporation to dryness, as a check. The water, or solution, was transferred to the autoclave by suction, flushed with N_2 or CH_4 at atmospheric pressure to remove any residual air, saturated with the gas at 50–100 atm, the pressure reduced, and the system again flushed. Gas was again admitted and the pressure and temperature brought to the desired values. High pressures were attained by means of a 1.5-hp compressor and compression cylinder. The pumping liquid was water, saturated with the gas being studied. Autoclave pressure was measured with a precision Heise-Bourdon gauge, 0 to 15,000 psi with an accuracy of $\pm 0.05\%$, calibrated frequently with a dead-weight tester and found to exhibit a hysteresis of about 0.1%. It is estimated that the maximum possible error in the pressures quoted in the tables is 0.5 atm below 100 atm and 1 atm at 600 atm. All connecting tubing ($1/8$ in. i.d. except for the sampling tubes which were $1/16$ in.) and valves were of stainless steel. At least 8 hr was allowed for the attainment of equilibrium, and the same results were obtained when approached from higher and lower pressures. When equilibrium had been reached, 15–30 ml of saturated liquid sample was withdrawn at the rate of 0.5–1 ml/min into an evacuated, calibrated, water-jacketed buret system using mercury as leveling fluid and similar to that used elsewhere,² whereupon the gas flashed out of solution giving two phases in the burets. The first sample was always discarded. Results were found to be independent of the rate of sample withdrawal. During the sampling the equilibrium pressure in the autoclave was maintained by admitting more gas from the compression cylinder. By manipulation of the leveling bulbs mercury was cascaded through the liquid phase until no more gas bubbles were seen. Since at no time had the pressure in the burets exceeded 0.05 atm it was assumed that only a negligible amount of gas remained in solution. The pressure in the burets was now raised to atmospheric, and the volumes of the liquid and gas phases and the temperature and atmospheric pressure recorded. After correcting for aqueous pressure¹⁰ and meniscus curvature, the number of moles of gas was calculated from the gas volume with the aid of tables of molar volume.¹¹ The number of moles of liquid was calculated from its volume, composition, and density.¹⁰ For each pressure three or more separate samples were withdrawn for analysis and the results averaged. Their average deviation was about 0.4%. The pressure was changed to a new value without replacing the liquid contents of the autoclave, the volume of which was never allowed to be less than 1500 cc. Measurements were made in this way for water, 1 *m* NaCl, and

4 *m* NaCl at 51.5, 102.5, and 125.0° . These isothermal runs were supplemented by isobaric ones; the solubility of methane (only) in the same three liquids was measured at a number of temperatures under an estimated fixed partial pressure of methane of 200 atm in an effort to study quantitatively the effect of dissolved salt on the temperature of minimum solubility.

Results and Discussion

The results of the isothermal work are given in Table I, where P is total pressure (atm) and X_2 is mole frac-

Table I: Solubility of N_2 and CH_4 in H_2O , 1.000 *m* NaCl, and 4.00 *m* NaCl (Mole Fraction of Dissolved Gas $\times 10^4$)

P , atm	H_2O		1 <i>m</i> NaCl		4 <i>m</i> NaCl	
	X_{N_2}	X_{CH_4}	X_{N_2}	X_{CH_4}	X_{N_2}	X_{CH_4}
51.5°						
100.0	7.99	14.27	5.93	10.76
200.0	14.54	22.79	10.76	16.95	5.00	8.05
300.0	20.17	28.7	14.97	21.38	7.00	9.97
400.0	24.9	33.4	18.60	25.0	8.78	11.54
500.0	29.2	37.3	22.16	27.9	10.34	13.03
600.0	33.5	40.9	25.3	30.7	11.79	14.44
102.5°						
101.0	7.77	13.55	6.03
201.0	14.47	22.05	11.13	16.93	5.23	8.26
302.0	20.05	28.7	15.38	22.19	7.31	10.79
403.0	25.2	33.3	19.20	25.7	8.99	12.11
503.0	29.8	38.5	22.52	28.9	10.47	13.19
604.0	33.7	41.9	26.0	32.0	12.05	14.33
125.0°						
103.0	8.08	14.34	6.32	10.58
204.0	14.92	23.21	11.02	17.52	5.67	8.25
305.0	20.47	29.6	15.33	22.23	7.40	10.05
405.0	25.7	34.3	18.83	26.0	9.21	11.64
507.0	30.6	39.6	22.31	29.4	10.41	13.22
608.0	35.1	43.0	25.5	32.5	12.27	14.38

tion of dissolved gas. X_2 was calculated for the salt solutions as if the salt were *undissociated*. The solubilities for nitrogen in water agree with those of Wiebe, *et al.*,² within about 1.5% at 51.5° and 1.8% at 102.5° . The values for methane in water differ from those interpolated from the work of Culberson and McKetta⁷ by about 1% at 51.5° , 1.5% at 102.5° , and 8% at 125.0° . The results for methane in both water and salt solution differ seriously from those of Michels, *et al.*,⁸ obtained by an inaccurate pressure decline technique.

In determining the extent to which Henry's law applies for each of the systems at each temperature it may be noted that P/X_2 increases with P even at 51.5° where the partial pressure of water, p_{H_2O} , contributes negligibly to P . At larger pressures the condition of

(10) "International Critical Tables," Vol. 3, McGraw-Hill Publications, New York, N. Y., 1928.

(11) F. Din, "Thermodynamic Functions of Gases," Vol. 3, Butterworth and Co. Ltd., London, 1961.

constant *total* pressure, which is inherent in Henry's law, becomes important. In addition, fugacity should be used in place of partial pressure of permanent gas. Krichevsky and Kasarnovsky,¹² and later Kobayashi and Katz,¹⁸ showed that by combining Henry's law

$$f_2 = kX_2(T, P \text{ constant}) \quad (1)$$

(where f_2 is the fugacity of the solute gas and X_2 its mole fraction) with other thermodynamic relations, and assuming \bar{V}_2 , the partial molar volume of dissolved gas, to be independent of P

$$\ln (f_2/X_2) = \ln k^* + (P\bar{V}_2/RT) \quad (2)$$

where k^* is the limiting value of f_2/X_2 as P is reduced indefinitely, or the Henry's law constant. Although this result is correct, both pairs of investigators derived it by arguments involving the mutual cancellation of errors. In ref 12 an essential part of the derivation is the use of the approximation $d\mu_2 = RT d \ln X_2$ (where μ_2 is chemical potential), which implies the absence of any dependence of μ_2 on P . It is this very dependence that forms the basis for the article. In ref 13 $d\mu_2 = \bar{V}_2 dP$, valid only for fixed composition, is equated to $d\mu_2 = RT d \ln f_2$ and integrated, and then the concentration is permitted to vary. These difficulties can be avoided as follows. Since $\mu_2 = \mu_2(T, P, X_2)$, $d\mu_2 = (\partial\mu_2/\partial X_2)_{T,P} dX_2 + \bar{V}_2 dP$. At any one temperature, however, $d\mu_2 = RT d \ln f_2$ so $(\partial\mu_2/\partial X_2)_{T,P} = RT(\partial \ln f_2/\partial X_2)_{T,P}$. Moreover, by eq 1, valid only for $dT = dP = 0$, $(\partial \ln f_2/\partial X_2)_{T,P} = 1/X_2$ or $(\partial\mu_2/\partial X_2)_{T,P} = RT/X_2$. It follows that for isothermal changes $RT d \ln f_2 = (RT/X_2) dX_2 + \bar{V}_2 dP = RT d \ln X_2 + \bar{V}_2 dP$ or

$$[\partial \ln (f_2/X_2)/\partial P]_T = \bar{V}_2/RT \quad (3)$$

Integration between $P = P^*$, a very small pressure (where $X_2 = X_2^*$, $f_2 = f_2^*$) and $P = P$ (where $X_2 = X_2$, $f_2 = f_2$), assuming \bar{V}_2 independent of P , yields eq 2. Thus when the isobaric Henry's law holds and \bar{V}_2 is independent of P a plot of $\ln (f_2/X_2)$ vs. P is linear with a slope of \bar{V}_2/RT and an intercept of $\ln k^*$. It is to be noted also that if the isobaric Henry's law holds, \bar{V}_2 must be independent of X_2 at constant total pressure and equal to the value at infinite dilution, \bar{V}_2^0 . Experimentally, however, it is virtually impossible to separate the effects of the variables X_2 and P on \bar{V}_2 .

At 51.5° the gas phase is essentially pure nitrogen (or methane) so the gas partial pressure is given by P , from which f_{N_2} and f_{CH_4} can be determined by reference tables.^{11,14} Figure 1 is a plot of $\ln (f_2/X_2)$ vs. P . The lines are straight within experimental error. The evidence is strong, therefore, that at this temperature Henry's law holds for all three solvents up to 600 atm for both gases and that \bar{V}_2 is independent of P .

At the higher temperatures, however, it is possible only to estimate the fugacities. The gas phase now has a water vapor content that cannot be ignored,

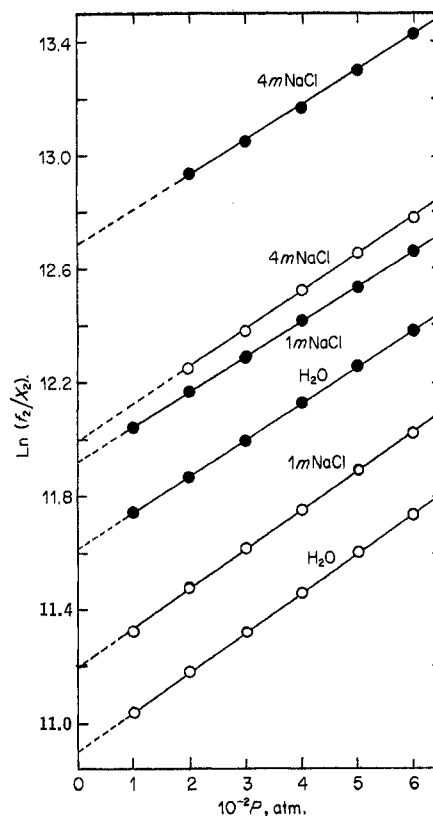


Figure 1. Solubility of N_2 and of CH_4 in H_2O , 1 *m* NaCl, and 4 *m* NaCl at 51.5°: ●, N_2 ; ○, CH_4 .

but the analyses of previous investigators do not always agree, as comparisons of the data for nitrogen^{4,15,16} and methane^{16,17} show. The Gibbs-Poynting equation, $(\partial \ln p_{H_2O}/\partial P)_T = \bar{V}_2/RT$, cannot be relied upon to give a quantitative answer because of the nonideality of the gas-water vapor mixture.¹⁸ Even when the gas-phase composition is known, there is still the problem of finding the fugacity of the permanent gas. The Lewis and Randall rule¹⁹ can be used but is not reliable, again because of gas mixture nonideality. Nevertheless the fugacities at 102.5 and 125.0° were estimated by finding them for the pure gas at the same pressure and temperature^{11,14} and multiplying these by the mole fraction of water as given in the literature.^{4,16,17} This mole fraction is greatest for the highest temperatures and the lowest pressures, being 0.030 for methane at 125.0° and 103.0 atm. The fugacity of pure methane under

(12) I. R. Krichevsky and J. S. Kasarnovsky, *J. Amer. Chem. Soc.*, **57**, 2168 (1935).

(13) R. Kobayashi and D. L. Katz, *Ind. Eng. Chem.*, **45**, 440 (1953).

(14) W. E. Deming and L. E. Shupe, *Phys. Rev.*, **37**, 638 (1931).

(15) E. P. Bartlett, *J. Amer. Chem. Soc.*, **49**, 65 (1927).

(16) M. Rigby and J. M. Prausnitz, *J. Phys. Chem.*, **72**, 330 (1968).

(17) R. H. Olds, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **34**, 1223 (1942).

(18) N. O. Smith, *J. Chem. Educ.*, **40**, 317 (1963).

(19) G. N. Lewis and M. Randall, "Thermodynamics," rev. by K. S. Pitzer and L. Brewer, McGraw-Hill Publications, New York, N. Y., 1961, p 295.

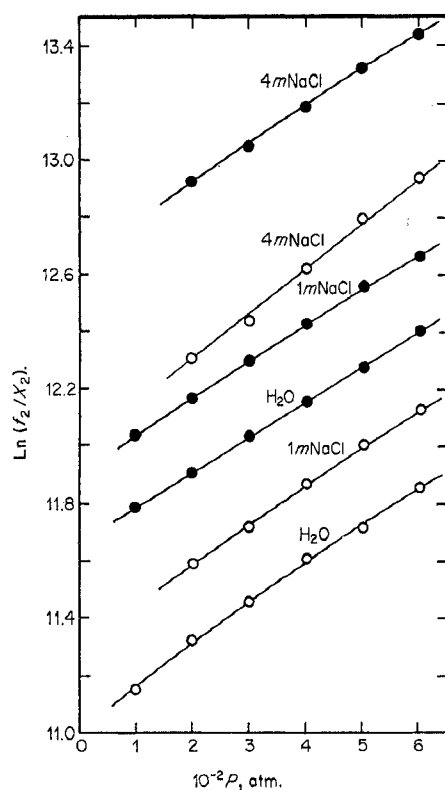


Figure 2. Solubility of N_2 and of CH_4 in H_2O , 1 m NaCl, and 4 m NaCl at 102.5° : \bullet , N_2 ; \circ , CH_4 .

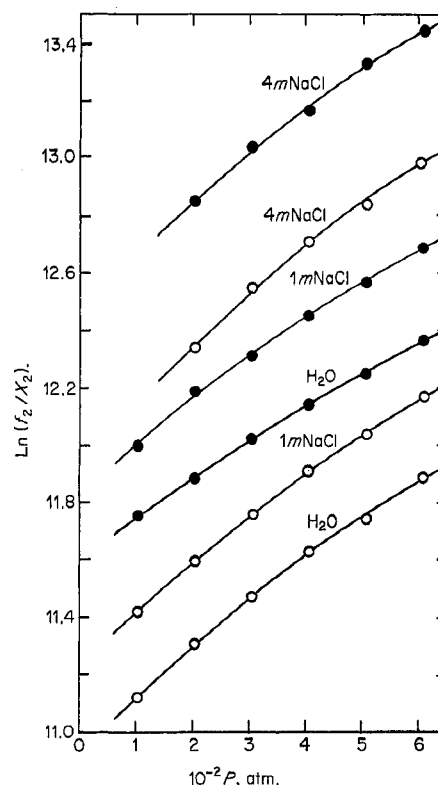


Figure 3. Solubility of N_2 and of CH_4 in H_2O , 1 m NaCl, and 4 m NaCl at 125.0° : \bullet , N_2 ; \circ , CH_4 .

these conditions is 99.1 atm, so f_{CH_4} is estimated to be $0.970(99.1) = 96.1$ atm, and $\ln(f_{CH_4}/X_{CH_4}) = 11.11$. The resulting graphs are shown in Figures 2 and 3 for 102.5° and 125.0° , respectively. It is evident that at these temperatures there is more scatter in the data, the increased difficulty of controlling the temperature of the large mass of the autoclave and the greater sensitivity of pressure to temperature being largely responsible. For this reason the location of the lines is uncertain, but it is clear that a curvature develops with rise in pressure, temperature, and, generally, salt concentration. This is the first time such curvature has been pointed out, although the data of Culberson and McKetta⁷ for methane in water at 102.5° (interpolated), for example, suggest it. It was apparently not considered by Kobayashi and Katz¹³ in their treatment of the same data.

Curvature could conceivably be caused by one or more of the following: (1) inapplicability of Henry's law, (2) erroneous estimation of fugacities from faulty gas composition data and/or failure of the Lewis and Randall rule, (3) variation of \bar{V}_2 with P . Since, however, Henry's law is valid at 51.5° and would be expected to become more, rather than less, valid with rise in temperature, it seems reasonable to suppose that the curvature does not lie in (1). Validity of Henry's law means that \bar{V}_2 is independent of X_2 at fixed P . It is likewise possible to eliminate (2) since the lines are curved in the same direction even when no correction is

made to the fugacities for the presence of water vapor, and the corrections, even if known accurately, would reduce the uncorrected values of $\ln(f_2/X_2)$ more at the lower pressures than at the higher ones, thus making the curvature greater. It appears, therefore, that the curvature must be attributed to decrease of \bar{V}_2 with increase in P . Such a decrease in \bar{V}_2 is entirely to be expected. Furthermore, the increased curvature with rise in T requires that $[\partial(\bar{V}_2/RT)/\partial P]_T = (1/RT) \cdot (\partial\bar{V}_2/\partial P)_T$ become more negative with increase in T . This, in turn, requires that $(\partial\bar{V}_2/\partial P)_T$ become more negative—a reasonable possibility since $(\partial V/\partial P)_T$ does so for pure liquids. Thus the observed curvature can be accounted for qualitatively on the basis of the behavior of \bar{V}_2 .

In order to apply eq 3 to the results it would have been helpful to have low-pressure data to reduce the uncertainty of extrapolation to zero pressure. However, because of the paucity of such data at all temperatures and the inherent difficulty of fugacity measurements at higher temperatures, where the gas phase has an appreciable water content, only the data of the present study were used. The data for 51.5° were fitted to $\ln(f_2/X_2) = a + bP$ and those for 102.5° and 125.0° to $\ln(f_2/X_2) = a' + b'P + c'P^2$ (with the two exceptions indicated), giving the parameters shown in Table II. They generally reproduce the experimental values of $\ln(f_2/X_2)$ within 0.05, 0.06, and 0.07% at the three temperatures, respectively. Table III gives the

Table II: Parameters in $\ln (f_2/X_2) = a + bP$ and $\ln (f_2/X_2) = a' + b'P' + c'P^2$

Gas	Temp, °C	H ₂ O		1 m NaCl		4 m NaCl	
		<i>a</i>	10% <i>b</i>	<i>a</i>	10% <i>b</i>	<i>a</i>	10% <i>b</i>
N ₂	51.5	11.615	1.278	11.923	1.230	12.688	1.221
CH ₄	51.5	10.905	1.393	11.195	1.394	11.964	1.374

Gas	Temp, °C	H ₂ O			1 m NaCl			4 m NaCl		
		<i>a'</i>	10% <i>b'</i>	10% <i>c'</i>	<i>a'</i>	10% <i>b'</i>	10% <i>c'</i>	<i>a'</i>	10% <i>b'</i>	10% <i>c'</i>
N ₂	102.5	11.662 ^a	1.222 ^a		11.899	1.384	-1.93	12.644	1.389	-1.32
CH ₄	102.5	11.001	1.647	-3.94	11.286	1.507	-1.75	11.973 ^a	1.598 ^a	
N ₂	125.0	11.604	1.450	-3.25	11.826	1.807	-6.58	12.409	2.405	-12.2
CH ₄	125.0	10.943	1.905	-5.99	11.224	1.919	-6.09	11.888	2.473	-11.3

^a Parameters for $\ln (f_2/X_2) = a' + b'P$.**Table III:** Henry's Law Constants and Partial Molar Volumes of Dissolved Gas at 51.5°

	H ₂ O		1 m NaCl		4 m NaCl	
	N ₂	CH ₄	N ₂	CH ₄	N ₂	CH ₄
10% <i>k</i> ^a , atm	1.108	0.544	1.507	0.728	3.238	1.570
\bar{V}_2 , cm ³ mol ⁻¹	34.05	37.10	32.76	37.12	32.52	36.61

Table IV: Partial Molar Volumes of Dissolved Gas (cm³ mol⁻¹)

<i>P</i> , atm	H ₂ O		1 m NaCl		4 m NaCl	
	N ₂	CH ₄	N ₂	CH ₄	N ₂	CH ₄
			102.5°			
200	37.7	45.9	40.3	44.3	41.2	49.3
400	37.7	41.1	37.9	42.1	39.6	49.3
600	37.7	36.2	35.5	40.0	38.0	49.3
			125.0°			
200	43.1	54.4	50.5	54.7	62.7	66.1
400	38.9	46.6	41.9	46.8	46.7	51.3
600	34.6	38.7	33.2	38.8	30.8	36.5

limiting Henry's law constants and partial molar volumes (pressure and composition independent) at 51.5° determined from the parameters. At the higher temperatures, where extrapolation was deemed too uncertain, and where curvature indicated a pressure dependence of \bar{V}_2 , only the latter was calculated, and this for rounded pressures, not infinite dilution (Table IV).

The Henry's law constant of Table III for nitrogen in water at 51.5° may be compared with the following obtained by interpolation of the results of low-pressure solubility measurements: 1.109 (ref 20) and 1.117×10^5 atm (ref 10), and that in 1 *m* NaCl with 1.441×10^5 (ref 20). Those for methane in water may, similarly, be compared with 0.580 (ref 20), 0.585 (ref 10), and 0.581×10^5 (ref 21), and in 1 *m* NaCl with 0.763×10^5 (ref 20). The high-pressure data of Wiebe, *et al.*,² for nitrogen yield 1.103×10^5 and those of Culberson and McKetta⁷ for methane 0.541×10^5 (both in water) at this temperature—in support of the present values

rather than of some of the data of low-pressure studies. One wonders whether lower temperature Henry's law constants, determined by linear extrapolation of good high-pressure data, are not actually the more reliable. Similar doubt of the validity of certain commonly used techniques for determining gas solubilities at low pressures has been expressed by Horiuti.²²

It is possible to estimate, from the data of Table I, that 1 ft³ of sedimentary rock, of 20% porosity, saturated with brine (50,000 ppm NaCl), can accommodate about 1 mol of methane in solution when in equilibrium with that gas at the pressure and temperature existing at a depth of 10,000 ft.

Nearly all of the previously published partial molar volumes at temperatures of 50° and higher have been obtained by extrapolation of high-pressure data. The values in Table III are in excellent agreement with those obtained by others^{12,13} using the same method. Direct experimental measurements of \bar{V}_2^0 at these temperatures have been attempted by Krichevski and Il'nskaya,²³ who claimed that the experimental values did not agree with those obtained by the use of eq 2. They attributed this to the failure of the isobaric Henry's law and consequent invalidity of eq 2 as a means of finding \bar{V}_2^0 . This seems unlikely, however, in view of the arguments presented above. Glew²⁴ suggests that the values of \bar{V}_2^0 measured directly²³ are in error as a result of ignoring the difference between apparent and partial molar volumes, even in such dilute solutions. At the higher temperatures only partial molar volumes obtained by extrapolation of high-pressure data are available: $36.2^{12,13}$ cm³ mol⁻¹ for nitrogen in water at 100° (using the same data²), and 40.6^{13} and 40.2^{24} for methane at 102° (using the same data⁷).

(20) T. J. Morrison and F. Billet, *J. Chem. Soc.*, 3819 (1952).(21) S. K. Shoor, R. D. Walker, Jr., and K. E. Gubbins, *J. Phys. Chem.*, **73**, 312 (1969).(22) J. Horiuti, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, **17**, 125 (1931).(23) I. R. Krichevski and A. Il'nskaya, *Acta Physicochim. URSS*, **20**, 327 (1945).(24) D. N. Glew, *J. Phys. Chem.*, **66**, 606 (1962).

Table V: Salting-out Coefficients (k_{NaCl})

Temp, °C	<i>m</i>	Approx <i>P</i> , atm					
		100	200	300	400	500	600
Nitrogen							
51.5	1	0.129	0.131	0.129	0.126	0.120	0.122
51.5	4	...	0.116	0.115	0.113	0.113	0.113
102.5	1	0.110	0.114	0.115	0.118	0.121	0.113
102.5	4	...	0.111	0.110	0.112	0.113	0.112
125.0	1	0.107	0.132	0.126	0.135	0.137	0.139
125.0	4	...	0.105	0.110	0.111	0.117	0.114
Methane							
51.5	1	0.122	0.128	0.128	0.126	0.127	0.125
51.5	4	...	0.111	0.115	0.115	0.114	0.113
102.5	1	...	0.115	0.111	0.114	0.125	0.117
102.5	4	...	0.103	0.106	0.110	0.116	0.107
125.0	1	0.132	0.122	0.124	0.120	0.129	0.122
125.0	4	...	0.112	0.117	0.117	0.119	0.119

For methane in water at 125° one finds 41.4¹³ and 40.0²⁴ in treatments of the same data⁷ by different authors. Clearly, much depends on how the extrapolation is made. If one recognizes the curvature shown in Figures 2 and 3 the four last-quoted values are probably all low (*cf.* Table IV). If, due to intermolecular forces, the activity coefficient of the permanent gas in the gas-water vapor phase were seriously different from unity at the higher temperatures both k^* and \bar{V}_2^0 , obtained by extrapolation, would require further correction.

Examination of Tables III and IV shows that, for both gases, \bar{V}_2 (1) increases appreciably with temperature in water and salt solution, (2) decreases slightly with salt concentration at 51.5°, and (3) generally increases markedly with salt concentration at 102.5 and 125.0°—if one accepts the argument given above that \bar{V}_2 is independent of concentration at a given pressure and temperature. The large temperature coefficient of \bar{V}_2 corresponds to the general belief that water becomes a more "normal" liquid as the temperature is raised. The larger partial molar volume of a dissolved gas in a solvent more normal than water is well documented.²⁵ Apparently the presence of salt in water enhances the return to normalcy in this respect.

The effect of change of salt concentration at a given temperature may be accounted for as follows. At lower temperatures the salt ions are surrounded by a shell of oriented water molecules which induce an icelike, and therefore open, structure in the water adjacent to the periphery of the shell—even more open than in the bulk liquid—thus slightly reducing \bar{V}_2 . At the higher temperature, however, where the bulk hydrogen-bonded network has largely disintegrated, and the water structure collapsed, addition of salt tightens the structure even more, and solution of gas therein produces considerable expansion and large values of \bar{V}_2 . At 600 atm, however, especially for nitrogen, the pressure is high enough to counteract this effect.

Table VI: Solubility of CH₄ in H₂O, 1.000 *m* NaCl, and 4.00 *m* NaCl at a Partial Pressure of Methane of 200 Atm (Mole Fraction of Dissolved Gas × 10⁴)

Temp, °C	<i>P</i> , atm	X_{CH_4}		
		H ₂ O	1 <i>m</i> NaCl	4 <i>m</i> NaCl
51.5	200.0	22.79	16.95	8.05
60.0	200.0	...	16.57	7.92
65.0	200.0	21.51	...	7.96
70.0	200.3	21.44	16.25	7.91
75.0	200.3	21.36	16.30	7.97
80.0	200.3	21.33	16.40	8.03
85.0	200.7	21.48
90.0	200.7	21.72	16.74	8.08
102.5	201.0	22.05	16.93	8.26
115.0	202.7	22.76	17.47	8.22
125.0	204.0	23.21	17.52	8.25

The unsmoothed results for the salt solutions given in Table I are restated as salting-out coefficients (k_{NaCl}) in Table V where $k_{\text{NaCl}} = \log (S^0/S)/m$, S^0 and S being the gas solubilities in water and salt solution of molality *m*. (Apart from the work of Morrison and Billet,²⁰ there is no previous study with which to compare these results. For 1 *m* NaCl at 50° interpolation of their data gives $k_{\text{NaCl}} = 0.11$ for both gases from low-pressure data.) The following general conclusions can be drawn. NaCl has approximately the same coefficient for both N₂ and CH₄ over a considerable range of temperature and pressure, and for both gases it is practically independent of pressure, seems to pass through a minimum with rise in temperature, and shows an appreciable decrease with increase in salt concentration. The variation of the coefficient with salt concentration is not surprising since several other gases, even at lower pressures, also show poor constancy.²⁶ The

(25) See, for example, K. W. Miller and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **90**, 3001 (1968).

low-pressure data of Braun²⁷ for nitrogen in the same salt up to 2 *M* at 25° show an even greater variation. Expressing the data of Table V in terms of molarity instead of molality makes no significant improvement in the constancy. Although McDevit and Long²⁸ found k_{NaCl} to be independent of salt concentration up to 4 *M* when the solute is benzene, it appears that this is not in general true for small molecules like nitrogen and methane.

Table VI gives the results of the isobaric runs for methane. The total pressures used and quoted were estimated as giving an approximately constant partial pressure of methane of 200 atm. The data reveal that, at this pressure, its solubility passes through a minimum with rise in temperature at 79 ± 2 , 72 ± 3 , and $69 \pm 5^\circ$ for H_2O , 1 *m* NaCl, and 4 *m* NaCl, respectively. The location of the minimum for H_2O agrees excellently with ref 7. (Michels, *et al.*,⁸ found no minimum for water or salt solutions.) The decrease, with rise in temperature, of the solubility of slightly soluble gases

in water as contrasted with the increase in more normal solvents is well known.²⁹ In water, as well as in salt solutions, more normal behavior may be expected as the temperature is raised. Thus the existence of the minimum in solubility may be explained. The small decrease in the temperature of the minimum with increasing salt concentration seems to be outside the limits of experimental error and suggests that the addition of salt confers some "normalcy" on the water, in agreement with the observation made earlier.

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Hydration of the Alkali Ions in the Gas Phase. Enthalpies and

Entropies of Reactions $\text{M}^+(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} = \text{M}^+(\text{H}_2\text{O})_n$

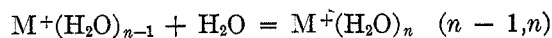
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The equilibrium constants $K_{n-1,n}$ for the gas-phase reactions $\text{M}^+(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} = \text{M}^+(\text{H}_2\text{O})_n$ were determined at different temperatures and water pressures in the Torr range for all alkali ions. Values for the enthalpies and entropies $\Delta H_{n-1,n}$, $\Delta S_{n-1,n}$ were obtained for n up to about 6. The measurements were done with a mass spectrometer incorporating a high-pressure ion source. The enthalpies are compared with potential energies of the clusters $\text{M}^+(\text{H}_2\text{O})_n$ calculated on the basis of an electrostatic model. Comparison of the absolute values does not prove very meaningful; however, comparison of the relative values indicates that some covalent bonding is present in the $\text{Li}^+(\text{H}_2\text{O})$ and $\text{Na}^+(\text{H}_2\text{O})$. The electrostatic calculations also indicate the approximate n at which the water molecules become nonequivalent, *i.e.*, the point where a transition to a new structure occurs. Calculated entropies $\Delta S_{0,1}$ based on statistical mechanics equations and parameters of the electrostatic calculations are found in good agreement with the experimental values. The experimental $-\Delta S_{n-1,n}$ are found to increase with increase of n for all alkali ions. This is taken as evidence for loss of freedom in the complex due to crowding.

Introduction

In a series of papers published over the past few years¹⁻⁶ we have tried to show that important information on the solvation of ions can be obtained by measurement of reaction equilibria involving gaseous ions and molecules of a given "solvent" vapor. An example of such an equilibrium is the clustering of water molecules around an alkali ion M^+ . The method relies on



mass spectrometric determination of the intensities of the reactant ions escaping through a small leak from a

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