importance. In sea water, both sets of data show that over the temperature range 20° to 60° C. the solubility of gypsum is essentially independent of temperature. In the 6X brines, on the other hand, our data show a slightly steeper solubility-temperature slope than is indicated by Hara's work.

DISCUSSION

The increase in the solubility of gypsum with increasing temperature in strong brine seems to account for the formation of a calcium sulfate precipitate which does not foul heat transfer surfaces. However, our observations raise several problems. First, why does gypsum form? Even at 40° C. the data of Bock indicate that the stable form in strong brine should be anhydrite. Second, why is gypsum more soluble in sea water brine (this work) than in sodium chloride solutions (*9*)? It is our feeling that the answer to both of these questions may be connected with the presence of magnesium sulfate in the sea water brine.

A third problem which requires exploration is the rate at which gypsum converts to anhydrite in the temperature range 40° to 60° C. or a little above. This may be very important in terms of scale control in practical sea water conversion plants.

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Multiphase and Volumetric Equilibria of the Methane–*n*-Decane Binary System at Temperatures between −36° and 150° C.

JEAN M. BEAUDOIN[1] and JAMES P. KOHN
Department of Chemical Engineering, University of Notre Dame, Notre Dame, Ind.

Vapor-liquid equilibria are presented at seven temperatures between −25° and 150° C. at pressures up to 100 atm. The data are tabulated as vapor and liquid compositions, fugacity–mole fraction ratios, and liquid molar volumes as functions of temperature and pressure. The vapor-liquid data indicate that Henry's Law expressed as fugacity–mole fraction ratio holds as a reasonably accurate approximation at pressures below 30 atm. Data along the solid-liquid-vapor three-phase line are tabulated as pressure, liquid composition, and liquid molar volume as functions of temperature. The solid data lead to a value of the heat of fusion of *n*-decane in good agreement with the literature value.

THE STUDIES of Lavender, Sage, and Lacey (*7*) and of Reamer *et al.* (*10*) have furnished valuable vapor-liquid equilibrium behavior in the methane–*n*-decane system at temperatures higher than 21° C. and at elevated pressures. The present study presents additional vapor-liquid data in the lower methane concentration region, at temperatures down to −25° C. and presents three-phase vapor-liquid-solid information.

The volumetric behavior of methane has been reported in several studies (*2, 3, 6, 8, 9*). Matthews and Hurd (*8*) and Canjar (*2*) have evaluated the thermodynamic properties of methane from pressure, volume, temperature data. Data on the liquid density, vapor pressure, heat of fusion and other physical properties of *n*-decane have been reported by Rossini *et al.* (*11*).

EXPERIMENTAL

The equipment and experimental techniques have been adequately described and were identical to those used in other studies involving methane in binary systems (*1, 4, 5, 12, 13*). Briefly, the experimental technique involved accurate additions of methane gas to a 12-ml. internal volume borosilicate glass equilibrium cell which contained a known amount of *n*-decane. The equilibrium cell had an inside diameter of approximately 7.5 mm. and a working length of 230 mm. Temperatures were taken on a platinum resistance thermometer which was believed to be accurate to within 0.02° C. of the International Platinum Scale. Pressures were taken on bourdon tube gages which were accurate to ±0.07 atm. Each bourdon gage was checked at the start of an experimental run by use of an accurate dead weight gage. Liquid volumes were taken from calibra-

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[1] Present address: Minnesota Mining and Manufacturing Co., Minneapolis, Minn.

tion marks on the glass equilibrium cells and were accurate to ±0.01 ml.

The methane and *n*-decane were pure grade materials obtained from the Phillips Petroleum Co. Both components were stated to have 99% minimum purity. The methane was processed as described by Kohn (*4*) and the resulting gas was thought to have a purity in excess of 99.5%. The *n*-decane was deaerated before experimental use and used without further purification.

RESULTS

The vapor-liquid results are tabulated in Table I. At least two experimental runs were made at each temperature. The raw experimental data had an average deviation of ±0.0014 mole fraction, ±0.07° C. ±0.10 atm. and ±0.1 ml. per gram mole. The data were compared with those of Lavender, Sage, and Lacey (*7*) and Reamer *et al.* (*10*). The liquid phase compositions of Reamer *et al.* (*10*) are all higher in methane than those of this study. The difference averages about 0.0025 mole fraction at 10 atm., about 0.0065 mole fraction at 50 atm., and about 0.018 mole fraction at 100 atm. The liquid phase compositions of Lavender, Sage, and Lacey (*7*) seem to be randomly distributed around those of this study.

The fourth column of Table I gives the fugacity of methane divided by the mole fraction of methane dissolved in the liquid phase. The leading value of fugacity-mole fraction ratio was obtained by extrapolating the data at finite methane mole fractions to zero mole fraction methane. The value represents the Henry's Law constant proper for the temperature indicated. The fugacity-mole fraction ratios at all seven temperatures in Table I increase with increasing composition of methane. However, at pressures below 30 atm., apparently Henry's Law is a reasonably accurate approximation. The fugacities of the methane were obtained from graphical integrations of the methane data of Keyes and Burks (*3*), Kvalnes and Gaddy (*6*), and Michels and Nederbragt (*9*) and are slightly higher than the corresponding fugacities reported by Matthews and

Table I. Properties of the Coexisting Vapor and Liquid Phases

	Liquid			
Pressure, Atm.	Mole fraction methane	Molar volume, ml./gram mole	Fugacity of methane, mole fraction atm.	Vapor, Mole Fraction Methane
		150° C.		
0.519[a]	...	227.28	283	...
10	0.0324	222.79	285	0.926
20	0.0664	217.44	288	0.964
30	0.0990	212.20	292	0.973
40	0.1311	207.02	294	0.978
50	0.1631	201.87	296	0.980
60	0.1935	196.98	298	0.982
70	0.2214	192.48	304	0.983
		100° C.		
0.094[a]	...	212.96	260	...
10	0.0372	207.30	264	0.988
20	0.0735	201.97	267	0.994
30	0.1080	196.79	271	0.996
40	0.1417	191.73	274	0.996
50	0.1730	187.03	278	0.997
60	0.2022	182.65	284	0.996
70	0.2298	178.50	290	0.996
80	0.2542	174.84	...	0.996
90	0.2766	171.48	...	0.996
100	0.2989	168.13	...	0.996
		75° C.		
0.0085[a]	...	206.83	239	...
10	0.0412	200.28	240	0.998
20	0.0789	194.61	248	0.998
30	0.1155	189.10	252	0.998
40	0.1498	183.94	257	0.998
50	0.1829	178.96	260	0.998
60	0.2153	174.09	264	0.998
70	0.2430	169.92	...	0.998
80	0.2679	166.17	...	0.998
90	0.2920	162.54	...	0.998
100	0.3152	159.05	...	0.998
		50° C.		
[a]	...	201.15	215	
10	0.0450	194.56	219	
20	0.0867	188.19	225	
30	0.1259	182.39	230	
40	0.1622	176.94	234	
50	0.1968	171.73	239	
60	0.2291	166.88	243	
		50° C. (*Continued*)		
70	0.2569	162.70	...	
80	0.2822	158.90	...	
90	0.3082	154.99	...	
100	0.3344	151.05	...	
		25° C.		
[a]	...	195.92	193	
10	0.0486	188.81	202	
20	0.0951	182.04	203	
30	0.1379	125.81	210	
40	0.1767	170.17	215	
50	0.2120	166.48	216	
60	0.2443	160.33	221	
70	0.2748	155.89	...	
80	0.3040	151.64	...	
90	0.3330	147.42	...	
100	0.3610	143.30	...	
		0° C.		
[a]	...	190.87	168	
10	0.0560	184.03	175	
20	0.1086	176.35	176	
30	0.1553	169.66	180	
40	0.1991	163.38	182	
50	0.2388	157.70	186	
60	0.2763	152.32	188	
70	0.3120	147.21	...	
80	0.3443	142.58	...	
90	0.3741	138.31	...	
100	0.4040	134.03	...	
		-25° C.		
[a]	...	186.08	138.0	
10	0.0702	176.70	138.0	
20	0.1330	167.95	140.7	
30	0.1901	159.86	142.8	
40	0.2408	152.68	145.0	
50	0.2850	146.42	148.3	
60	0.3256	140.66	...	
70	0.3635	135.30	...	
80	0.4000	130.13	...	
90	0.4350	125.17	...	
100	0.4708	120.10	...	

[a] At the vapor pressure of *n*-decane.

Hurd (*8*). At 100° and 150° C. the Lewis and Randall rule was applied also in obtaining the fugacity of the methane in solution. This procedure should be quite accurate since the vapor phase composition was never less than 0.926 mole fraction of methane. The Henry's Law constants at the seven temperatures were plotted as logarithm of Henry's constant *vs*. reciprocal absolute temperature. The graph was linear in the range from −25° to 100° C., and the slope of the line gave an enthalpy change of methane upon solution of

$$\Delta H = (H_{2\,(\text{gas})} - \bar{H}_2) = 895 \pm 36 \text{ cal./gram mole}$$

The linearity of the Henry's Law plot indicates that the following thermodynamic statements are accurate approximations for methane in the temperature range of −25° to 100° C. and up to 30 atm. pressure

$$\bar{H}_2^* = \bar{H}_2^V = H_2^V$$

$$\bar{H}_2^\circ = \bar{H}_2$$

$$\Delta C_p = C_{p2}^V - \bar{C}_{p2} = 0$$

Table II gives temperature, liquid phase compositions, and liquid phase molar volumes along the three-phase (solid-liquid-vapor) line. The gas phase is substantially pure methane while the solid phase is regarded to be pure *n*-decane. The three phase data were compared with those obtained by Stalkup (*14*) who used a chromatographic technique. The Stalkup data are about 0.65° C. lower than this study at pressures above 8 atm. The probable error in temperature in establishing the solid line in the present study is ±0.05° C. The freezing point of air saturated *n*-decane is within 0.01° C. of Rossini's value (*11*).

Table II. Solid-Liquid-Vapor Phase Behavior

Pressure, Atm.	Temperature, ° C.	Composition Liquid Phase, Mole Fraction of Methane	Molar Volume Liquid Phase, Ml./Gram Mole
1[a]	−29.67	...	184.95
5	−30.19	0.033	180.0
10	−30.72	0.065	175.2
15	−31.25	0.099	170.5
20	−31.77	0.132	166.2
25	−32.28	0.161	162.0
30	−32.79	0.190	157.7
35	−33.28	0.219	153.5
40	−33.78	0.250	149.1
45	−34.27	0.280	144.8
50	−34.76	0.307	140.8
60	−35.66	0.357	133.5
65	−36.05	0.381	130.2
70	−36.38	0.405	126.7

[a] Air saturated freezing point.

The lower pressure data of Table II were used to calculate the heat of fusion of *n*-decane by use of the Van't Hoff isochore and the triple point of *n*-decane reported by Rossini (*11*). The results of 6910 cal. per gram mole at 5 atm. and 7180 cal. per gram mole at 10 atm. are in good agreement with the value 6863 cal. per gram mole reported by Rossini *et al.* (*11*).

NOMENCLATURE

C_{p2}^V = molar heat capacity of pure methane in the gas phase at any temperature and pressure, cal./gram mole ×° K.
$\bar{C}_{p2}$ = partial molar heat capacity of methane in a liquid solution of any dilution, cal./gram mole ×° K.
H_2^V = molar enthalpy of pure methane in the gas phase at any pressure and temperature, cal./gram mole
$\bar{H}_2^V$ = partial molar enthalpy of methane in a gaseous solution of any dilution, cal./gram mole
$\bar{H}_2^\circ$ = Partial molar enthalpy of methane in an infinitely dilute liquid solution, cal./gram mole

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Three Phase Equilibria in the Binary Systems Ethane–*n*-Docosane and Ethane–*n*-Octacosane

ALLAN B. RODRIGUES and JAMES P. KOHN
Department of Chemical Engineering, University of Notre Dame, Notre Dame, Ind.

EXPERIMENTAL determination of volumetric and phase data on hydrocarbon mixtures continue to be of importance owing to the lack of sound theoretical predictive relationships. The phenomenon of partial miscibility in certain hydrocarbon mixtures has been of considerable interest recently.

Partial miscibility is a fairly common occurrence in binary liquid mixtures where one of the components is polar. However, studies have shown that certain binary paraffin mixtures exhibit a three phase (L_1 - L_2 - V) region over a short temperature range bounded below by the L.C.S.T. (Lower Critical Solution Temperature at which the two liquid phases are in critical equilibrium) and above by the Type *K* point (at which the lighter liquid phase is in critical equilibrium with the vapor phase). Rowlinson and coworkers have reported the occurrence of this phenomenon in several binary mixtures involving methane and ethane (*1, 9, 10*) with higher paraffins. Kohn (*3*) has reported partial miscibility in the system methane–*n*-heptane. Kim (*2, 5*) found that the systems ethane–*n*-