Table II. Composition of Sea Water Concentrates

Density at 20 °C., G./Cc.	Composition, % by Weight					
	Cl	SO_4	Na	K	Ca	Mg
1.024[a]	1.94	0.267	1.01	0.037	0.038	0.133
1.203[b]	14.7	1.41	7.95	0.29	0.058	0.96
1.219[c]	15.9	1.64	7.95	0.35	0.064	1.14
1.226	...	...	7.20	0.37	...	...
1.249	...	...	5.25	0.83	...	...
1.254	15.7	4.6	4.84	1.05	0.165	3.38
1.293	16.2	5.7	1.69	1.84	0.083	5.40

[a] Original sea water.

[b] Concentrate before sodium chloride crystallization.

[c] Concentrate after sodium chloride crystallization.

The composition of the original sea water is close to that expected from Barnes' comprehensive tables for the ionic composition of sea water (*2*). Calculations on the ratio of ions present in the concentrates show that the initial precipitation of calcium sulfate occurs at a density below 1.203 grams per cc.

After sodium chloride crystallizes out, the sodium concentration decreases, and magnesium, potassium, and sulfate concentrations increase. Madgin and Swales (*9*) have studied the calcium sulfate-sodium chloride-water system at 25 °C. and the same system with the addition of sodium sulfate. A very complete study of the sodium chloride-sodium sulfate-magnesium chloride-magnesium sulfate system has been made by Yanatieva (*20*); the concentrations recorded in Table II vary in a manner similar to that found by these authors.

Previous authors have analyzed concentrated sea waters. Thus Oka and Inagaki (*10*) examined bitterns up to density 1.29 grams per cc., while Valyashko (*19*) analyzed concentrated Black Sea water at the points where gypsum, halite, epsomite, sylvite, and carnallite begin to crystallize out. The results in both papers are expressed as compounds present in the solution, while Table II gives ionic concentrations. In each case the same trend in change of composition is shown. Valyashko (*19*) also gives the volume changes with density in the density region 1.30 to 1.36 grams per cc., where potassium salts begin to crystallize out.

Vapor Pressure. Robinson (*13*) found that the vapor pressure of natural sea water is higher than that of a sodium chloride solution of equal density, and the present results demonstrate that this also applies for concentrated sea water. This increase in vapor pressure over that of sodium chloride might be expected from the fact that solutions of sodium chloride contain more potential ions in a given volume than do equal density solutions of magnesium chloride, sodium sulfate, magnesium sulfate, and calcium chloride. Moreover, at 25 °C. the activity coefficient of magnesium chloride (*17*) in solutions up to slightly over 1 molal (approximately 10%) is lower than that of sodium chloride (*14*), as are also the activity coefficients of potassium chloride (*14*) and magnesium sulfate (*15*). However, this is to some extent offset by the fact that, in solutions more concentrated than 1 molal, the activity coefficient of magnesium chloride increases rapidly (*17*) and exceeds that of sodium chloride. The high ionic strength of the concentrated sea water solutions must further increase the activity coefficient of the magnesium chloride.

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Volumetric Behavior of the Methane-Ethane System

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The volumetric behavior of the methane-ethane system in the gaseous region was investigated experimentally at temperatures from 70° to 460° F. (*2*) and these data were resmoothed in connection with the preparation of a monograph pertaining to the thermodynamic properties of the lighter hydrocarbons (*3*). More recently, the volumetric behavior of mixtures of methane and ethane was measured by Bloomer, Gami, and Parent (*1*) from −50° to 90° F. The agreement between the two sets of measurements at 70° F., which was the only temperature at which a direct comparison was possible, was not particularly satisfactory.

The two sets of experimental data at 70° F. are compared in Figure 1. The agreement at mole fractions of methane greater than 0.5 is acceptable. However, at the

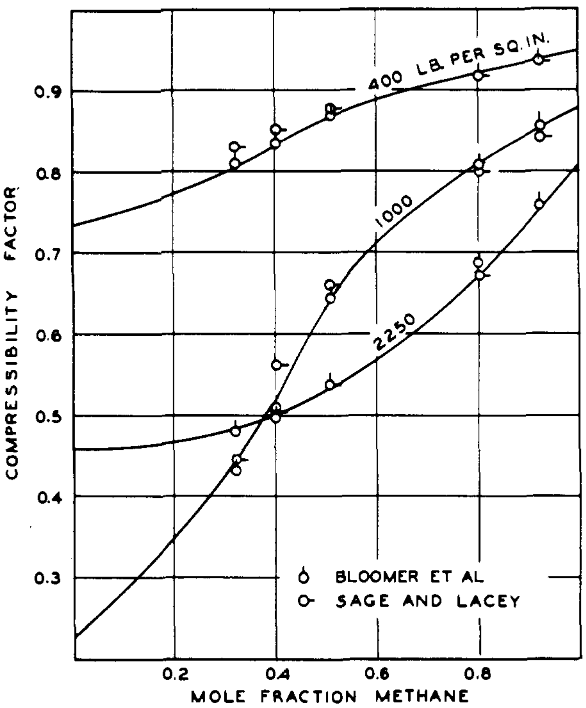

Figure 1. Compressibility factor for methane-ethane system at 70° F.

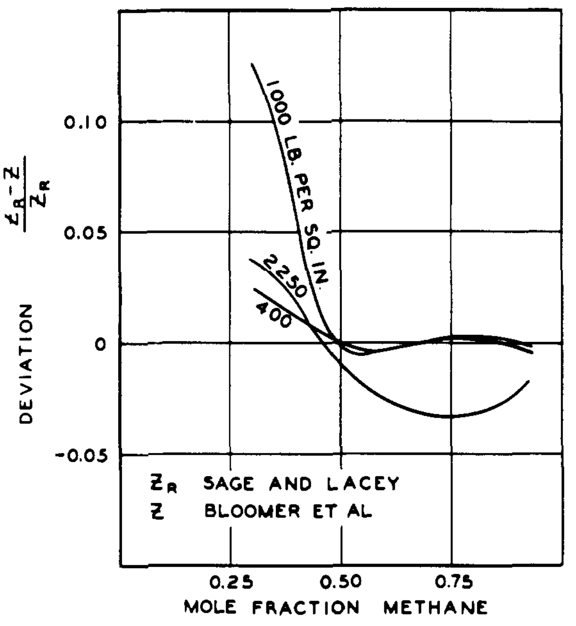

Figure 2. Comparison of data from two investigations at 70° F.

lower mole fractions of methane, the data for all pressures included in Figure 1 yield markedly lower compressibility factors from the measurements of Bloomer (*1*) than were reported earlier (*3*). The greatest discrepancy is at 1000 pounds per square inch, where the smoothing of the data for the monograph (*3*) ignored measurements corresponding to 0.3191 mole fraction methane, because data were not obtained at this composition for pressures above 1250 pounds per square inch. Some uncertainty was attached to the experimental information at the lower pressures for this mixture.

With the confirmatory measurements of Bloomer it appears that the data in the monograph should be revised at 70°F. for mixtures containing less than 0.4 mole fraction methane. These revised values are submitted in Table I. At 90° F. the data of Bloomer and coworkers (*1*) are in good agreement with the interpolation of the earlier measurements (*2*), and no revision of the data (*2*) for the higher temperatures appears to be required. The primary cause of the discrepancy at 70° F. resulted from the lack of data prior to the work of Bloomer at low mole fractions of methane for pressures above 1250 pounds per square inch.

The deviation of Bloomer's data from the earlier tabulations (*3*) and the data of Table I are submitted in Figure 2. The original study of mixtures of methane and ethane (*2*) was made with equipment that would not give as high accuracy as more recently constructed apparatus.

It is believed that the information submitted in Table I is a reasonable description of the volumetric behavior of mixtures of methane and ethane in the single-phase region at 70° F. The work of Bloomer and his associates has contributed materially to the knowledge of the behavior in this low-temperature region.

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Table I. Corrected Volumetric Properties of Methane-Ethane System at 70° F.

Pressure, Lb./Sq.Inch Absolute	Compressibility Factor	Residual Vol., Cu.Ft./Lb. Mole	Compressibility Factor	Residual Vol., Cu.Ft./Lb. Mole	Compressibility Factor	Residual Vol., Cu.Ft./Lb. Mole	Compressibility Factor	Residual Vol., Cu.Ft./Lb. Mole
	Mole Fraction Methane							
	0.1		0.2		0.3		0.4	
200	0.8843	3.288	0.8910	3.098	0.9025	2.771	0.9189	2.305
400	0.7555	3.475	0.7780	3.155	0.8045	2.778	0.8379	2.304
600	0.4635	5.083	0.6130	3.666	0.7009	2.834	0.7589	2.284
800	0.3357	4.720	0.4563	3.863	0.5798	2.986	0.6651	2.380
1000	0.2980	3.990	0.3519	3.684	0.4145	3.328	0.5241	2.705
1250	0.2894	3.232	0.3127	3.126	0.3530	2.942	0.4446	2.526
1500	0.3380	2.509	0.3490	2.467	0.3781	2.357	0.4305	2.158
1750	0.3749	2.030	0.3870	1.991	0.4085	1.921	0.4495	1.788
2000	0.4185	1.653	0.4261	1.631	0.4409	1.589	0.4740	1.495
2250	0.4651	1.351	0.4669	1.347	0.4760	1.324	0.5026	1.257
2500	0.5035	1.129	0.5050	1.126	0.5121	1.109	0.5357	1.056
2750	0.5480	0.934	0.5480	0.934	0.5525	0.925	0.5700	0.889
3000	0.5840	0.788	0.5911	0.775	0.5955	0.766	0.6080	0.743