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# Vapor Pressure of Sea Water Concentrates

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In the planning stage of a plant for the manufacture of salt by atmospheric evaporation of sea water, it was desired to calculate the rate of evaporation of bitterns at various densities. It was therefore necessary to know the vapor pressure of sea water at different stages of concentration. Values up to the crystallization point of sodium chloride are available in the literature (*1,8*), but data past this point, when the other constituents of sea salt begin to concentrate in the solution, are of special interest. Analyses by Dittmar (*5*) have shown that apart from variations in salinity, sea water from the major oceans of the world has a practically constant composition. It was therefore considered that correlation of vapor pressure with density would adequately express the data.

Sea water was obtained from about 10 miles off the coast in Cook Strait, New Zealand. The natural flow of ocean currents is sufficient to ensure that this water is substantially open-ocean water, uncontaminated by rivers and sewage. This water was concentrated in the laboratory. Once the crystallizing point was reached, the temperatures of the solution were not permitted to rise above the temperatures of measurement, thus ensuring that the various salts crystallized in the same sequence as they would in an evaporating pond. This was achieved by evaporating in a stream of cold air under an infrared lamp.

## ISOPIESTIC METHOD

The isopiestic method of Robinson and Sinclair (*16*) was used in a simplified form for the vapor pressure measurements at 20° and 25°C. A solution of concentrated sea water, two widely differing solutions of sodium chloride, and a solution of sulfuric acid were put into small silica crucibles in a vacuum desiccator, and the whole was evacuated on a Geissler pump. The desiccator (suitably weighted with lead) was put in the thermostatic bath and left for 2 weeks, without any internal stirring or rocking as is normally employed to hasten equilibrium in the isopiestic method.

After 2 weeks, the densities of the four solutions were determined in a specific gravity bottle at 20°C.; the two sodium chloride solutions always were identical to 1 part in 1000. By using sulfuric acid as a reference material [Collins (*3*) for values at 20°C. and Stokes and Robinson (*18*) for 25°C.] the vapor pressure of the concentrated sea water could be ascertained. Values for the sodium chloride solutions showed good agreement with those of Olynyk and Gordon (*11*).

For the higher concentrations of sea water, with vapor pressures below that of saturated sodium chloride, an even simpler apparatus was employed. A 600-ml. lipless beaker was quarter filled with lead shot and bitumen, and a Petri dish with a glass division cemented across the middle was placed on the bitumen surface. Concentrated sea water was placed on one side of the division, and sulfuric acid on the other, a rubber bung and glass tap being used to seal the beaker. The evacuated beakers (with rubber caps over the tap ends) were again left in the water bath for 2 weeks, and the density of the solutions was then determined at 20°C. The sulfuric acid was always checked for the absence of chlorides at the conclusion of each experiment.

The results by the isopiestic method are estimated to be accurate to ± 0.1 mm.

## STATIC METHOD

A static method of vapor pressure determination (*12*) was also used at 20°, 25°, and 30° (all thermostat temperatures to ±0.05°C.). The values obtained are estimated to be accurate to ±0.1 mm. at 30°C. but only ±0.3 mm. at 20°C.; the tendency is to obtain slightly high results, undoubtedly due to incomplete outgassing of the solutions, especially at the lower temperatures. The apparatus was checked with distilled water and solutions of sodium chloride (analytical reagent grade); for the latter the values for vapor pressure were those obtained by Olynyk and Gordon (*11*), who employed an elaborate static method, taking extreme precautions to out-gas their solutions.

While satisfactory agreement with the more accurate isopiestic values was obtained at 20° and 25°C., only the isopiestic results are quoted at these temperatures; at 30°C., where the static method is equally accurate, values obtained by this method are given.

## ANALYTICAL DATA

Past the sodium chloride crystallization point chloride was determined by Mohr's method, sulfate by direct titration (*6*), calcium and magnesium by a modification of the Versenate titration (*4*), and sodium and potassium by flame photometry. For other metals a spectrographic arc method was used.

The volumes of the filtered concentrates from 10 liters of sea water were determined at a number of different densities.

## RESULTS

**Vapor Pressure.** The values determined by the isopiestic method at 20° and 25°C., including those of sodium chloride solutions up to saturation, and results obtained by the static method at 30°C., are shown in Table I.

In Figure 1 these values are plotted to enable comparison with data of previous authors. Up to the crystallization point of sea water results are calculated from Arons and Kientzler's paper (*1*), by using chlorinity-density data of Higashi (*8*) and of Hampel (*7*), and for sodium chloride solutions calculated from Olynyk and Gordon's (*11*) work.

As a first approximation the product of the increase in density of solution over water and the lowering of vapor pressure should be constant, or $(d-1)\ (p_0-p)=c$. In Figure 2 $(d-1)$ is plotted against $(p_0-p)$ at 25°C. on a logarithmic scale and is approximately linear over the whole range.

**Volume.** Ten thousand milliliters of sea water were evaporated to various volumes, $V$, and $V(d-1)$ should be approximately constant up to sodium chloride saturation. In Figure 2, therefore, $(d-1)$ is plotted against $V$ on a logarithmic scale, giving a straight line up to the crystallization point and then showing a sharp break, after which density changes only slowly with volume.

**Composition.** A number of concentrates were analyzed (Table II). The most concentrated solution of density 1.293 grams per cc. was examined spectrographically; no other metal was present in excess of 0.01%.

**Table I. Vapor Pressure of Sea Water Concentrates**

| Temp., °C. | Density at 20°C., Sodium Chloride Solutions | Density at 20°C., Sea Water Concentrates | Vapor Pressure, Mm. Hg | Lowering of V.P. $(p_0-p)$, Mm. Hg |
|---|---|---|---|---|
| | | Isopiestic Method | | |
| 20 | 1.087 | 1.093 | 16.1 | 1.4 |
| | 1.135 | 1.152 | 15.1 | 2.4 |
| | ... | 1.214 | 13.2 | 4.3 |
| | ... | 1.248 | 12.3 | 5.2 |
| | ... | 1.298 | 11.1 | 6.4 |
| 25 | 1.076 | 1.084 | 22.1 | 1.7 |
| | 1.119 | 1.131 | 20.9 | 2.9 |
| | 1.182 | 1.193 | 18.7 | 5.1 |
| | ... | 1.217 | 17.8 | 6.0 |
| | ... | 1.240 | 17.0 | 6.8 |
| | ... | 1.258 | 16.4 | 7.4 |
| | ... | 1.272 | 15.7 | 8.1 |
| | ... | 1.297 | 15.0 | 8.8 |
| | | Static Method | | |
| 30 | ... | 1.111 | 29.0 | 2.8 |
| | ... | 1.157 | 27.4 | 4.4 |
| | ... | 1.170 | 26.5 | 5.3 |
| | ... | 1.187 | 25.4 | 6.4 |
| | ... | 1.206 | 24.4 | 7.4 |
| | ... | 1.246 | 22.4 | 9.4 |
| | ... | 1.270 | 21.0 | 10.8 |
| | ... | 1.298 | 19.8 | 12.0 |

## DISCUSSION OF RESULTS

**Composition.** Table II shows that once the crystallization point is reached, the chloride content of the solutions stays approximately constant. The usual practice in oceanographic literature of expressing all results in chlorinities (parts per thousand by weight of halogen, expressed as equivalent chloride) is therefore not applicable to this paper and all results obtained are, instead, correlated with the density of the solutions.

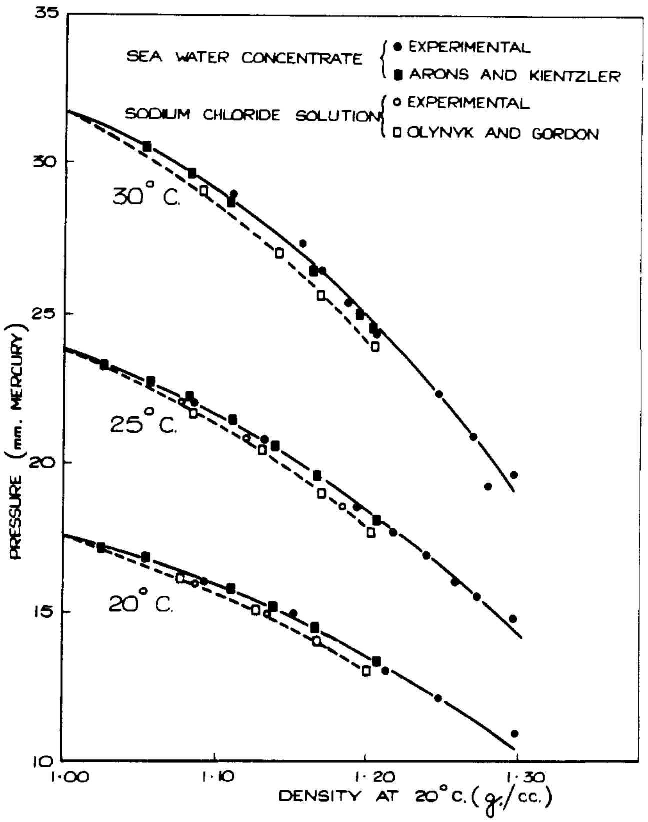

Figure 1. Vapor pressure of sea water concentrates and sodium chloride solutions

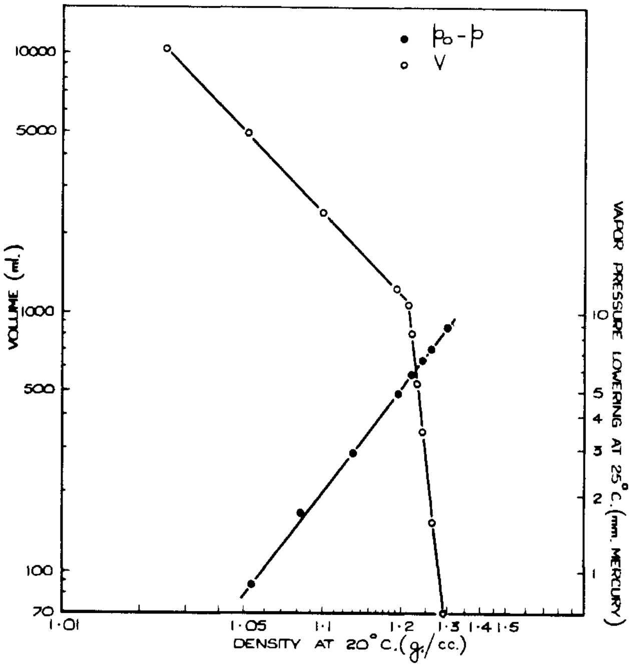

Figure 2. Relation of volume and vapor pressure lowering of sea water concentrates to density of solution

**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