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The Osmotic Pump

In principle, but probably not in practice, fresh water can be extracted from our oceans for no expenditure of energy.

Octave Levenspiel and Noel de Nevers

There have been occasional discussions in print and at university gatherings of the possibility of an "osmotic pump," which would produce fresh water from sea water at no expenditure of energy, and of its corollary, an "osmotic power plant," which would extract work from the ocean (*1*). Both employ semipermeable membranes. As far as we know, no analysis has been published of the scientific basis of these devices, or of their prospects as engineering devices. In this article we undertake those tasks.

The Pump, the Power Plant, and the Second Law of Thermodynamics

The osmotic pump and its workings are usually represented as follows. A pipe open at the top but capped at the bottom by a semipermeable membrane (permeable to water but not to dissolved salts) is lowered into the ocean as shown in Fig. 1. Because the osmotic pressure difference between fresh and salt water is about 23 atmospheres under ordinary conditions, the inside of the pipe will at first be free of water (Fig. 1a). When the pipe is lowered more than 231 meters the pressure difference across the membrane will exceed 23 atmospheres, and fresh water will flow into the pipe and rise to a level 231 meters below the ocean surface (Fig. 1b).

Now since salt water is about 3 percent denser than fresh water, if the pipe is lowered further the level of fresh water in the pipe will have to rise if the pressure difference at the membrane is to remain at 23 atm (Fig. 1c). Finally, if the pipe is lowered deep enough water in the pipe should rise above the surface (Fig. 1d).

Thus, in principle, if you grant an ideal membrane, we should be able to get a perpetual fountain of fresh water from the ocean without doing any work.

The osmotic power plant is a variation of the pump by which we would obtain power instead of fresh water from the oceans. A number of variations of such a device can be devised. Probably the simplest to visualize consists of two pipes lowered to different depths in the ocean (Fig. 2). Since fresh water will rise to different levels in these pipes we can allow water to flow from one to the other and thereby generate electricity.

The above arguments suggest that ideal semipermeable membrane devices can, in principle, effect a separation of salt and fresh water or extract useful work from the ocean. Is this not a flagrant violation of the second law of thermodynamics?

The answer to this question is certainly not clear-cut and unambiguous. We may or may not be able to extract fresh water from the ocean without doing work, depending on what we mean by the word "ocean." Do we have in mind a body of salt water at equilibrium, or uniform in composition, or something still different? Although the difference in these cases may seem to be small and unimportant, surprisingly they are large enough to give quite different answers to our original question—whether the osmotic pump will work.

Let us make an analysis of these various cases and see what results. We will treat in turn

1) the equilibrium ocean, where the salt concentration and density change with depth;

2) the uniform ocean, where the ratio of salt to water stays constant, but the density changes with depth;

3) the real ocean, which is neither at equilibrium nor uniform.

Preliminaries

The analysis of this problem rests on the following ideas and assumptions:

1) The fluids in the ocean and in the pipe are moving so slowly that they can be treated by the basic equation of fluid statics

$$\frac{dP}{dz} = \rho g \qquad (1)$$

where P is pressure; z is vertical distance, measured downward; ρ is density; and g is acceleration of gravity.

2) The ideal semipermeable membrane allows free passage for one component (water, in our case) but is completely impervious to the other component (salt). Thus, complete thermodynamic equilibrium for water is established across the membrane and in the language of thermodynamics we may express this condition by writing

$$\mu_{\text{water, one side}} = \mu_{\text{water, other side}} \qquad (2)$$

The authors are professors of chemical engineering, Dr. Levenspiel at Oregon State University, Corvallis 97314, and Dr. de Nevers at the University of Utah, Salt Lake City 84112.

where μ is the partial molal free energy, which J. Willard Gibbs gave the name "chemical potential"

$$\mu_i = \bar{g}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \qquad (3)$$

Here, i and j represent different components; $\bar{g}_i$ is the partial molal free energy of component i; G is free energy; n_i is the number of moles of component i; and the subscript T,P, n_j means that the temperature, pressure, and number of moles of component j are held constant. Most engineers are more accustomed to think in terms of the fugacity, f, a property invented by G. N. Lewis, which is defined by the equation

$$RT \, d\ln f_i = d\mu_i \qquad (4)$$

where R is the gas constant. From Eq. 4 it follows that for properly chosen reference conditions Eq. 2 is equivalent to

$$f_{\text{water, one side}} = f_{\text{water, other side}} \qquad (5)$$

However, Eq. 2 is the more fundamental relation and leads to simpler mathematics than Eq. 5 so we will proceed with it. Readers who feel uncomfortable with μ as a physical entity may mentally replace it, wherever it appears in this article, with $RT \ln f$).

Throughout this article we will be discussing the chemical potential of water, either in sea water or in fresh water; we will never be discussing the chemical potential of the salt in the sea water. Thus we will drop the subscript i on the μ and it will be understood that whenever μ appears we are referring to the chemical potential of water, not of salt.

3) The chemical potential of water in pure water or in solution is a function of pressure, temperature, and composition

$$\mu = \mu(P,T,x_s) \qquad (6)$$

where x_s is the mole fraction of water in the salt water solution. By straightforward differentiation

$$d\mu = \left(\frac{\partial \mu}{\partial T}\right) dT + \left(\frac{\partial \mu}{\partial P}\right) dP + \left(\frac{\partial \mu}{\partial x_s}\right) dx_s \qquad (7)$$

4) We will not need the value of $(\partial\mu/\partial T)$ because in all that follows we will not be concerned with temperature changes. From any thermodynamics text (*2*) we can find that

$$(\partial\mu/\partial P)_{T,x_s} = \bar{v}_s \qquad (8)$$

where $\bar{v}_s$ is the partial molal volume of water in solution (for fresh water $\bar{v}_s$ is equal to v, the molar volume), and the subscript on the left side indicates that T and x_s are held constant. For dilute solutions of salt in water we may safely assume ideal solution behavior, for which we may write

$$\left(\frac{\partial \mu}{\partial x_s}\right)_{T,P} = \frac{RT}{x_s} \qquad (9)$$

(Note that we are here assuming ideal solution behavior for the solvent, not for the solute. Because the solute concentrations are always relatively small—up to 7 percent by weight—the solute can deviate considerably from ideal solution behavior without a significant deviation from ideal solution on the part of the solvent.)

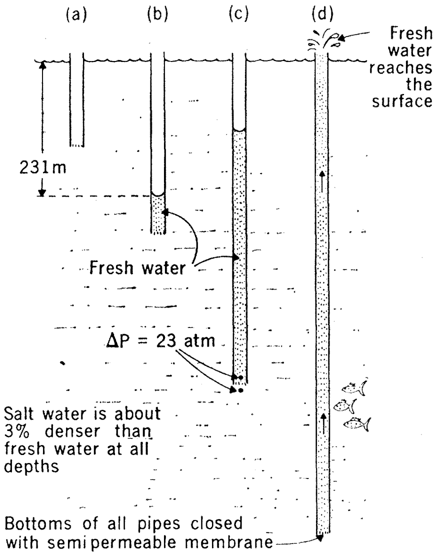

Fig. 1. The osmotic pump. The pressure difference across the membrane is ΔP.

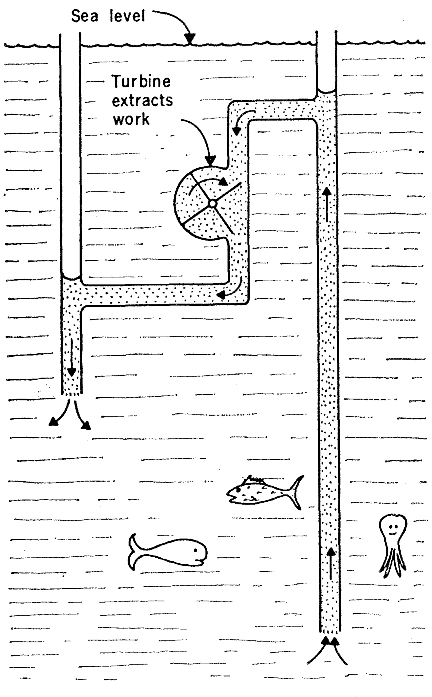

Fig. 2. The osmotic power plant.

5) Making these substitutions into Eq. 7, setting dT equal to zero, and dividing by dz so that we can use Eq. 1 to eliminate dP/dz, we find

$$\frac{d\mu}{dz} = \bar{v}_s \rho_s g + \frac{RT}{x_s}\frac{dx_s}{dz} \qquad (10)$$

This expression tells us how the chemical potential of water changes with depth and composition in an isothermal, ideal-solution ocean. We are now ready to proceed to our osmotic pump in various "oceans."

Equilibrium Ocean

An equilibrium ocean is one in which the temperature, pressure, and salt concentration are in thermodynamic equilibrium throughout. For thermal equilibrium the temperature must be uniform, so that an equilibrium ocean is isothermal. The basic equation of hydrostatics, Eq. 1, is the expression of pressure equilibrium in a zero-velocity ocean, so that thermodynamic equilibrium with respect to pressure exists when Eq. 1 is satisfied.

In any equilibrium liquid solution the chemical composition changes with depth because the molal densities of the various species are not the same. In normal engineering and laboratory practice where the elevation changes are a few feet or less the changes in chemical composition are negligibly small. However, in the oceans the depths are large enough for the changes in chemical composition to be significant. The principal application of these changes in composition with depth is in ultracentrifuges, which are used in analytical work to separate substances of different molecular weight. In these, at very high centrifugal accelerations, the equilibrium concentrations of high molecular weight materials are much larger at the outside than the inside. Similarly, the gas centrifuge can apparently be used to separate isotopes of uranium, by creating an equilibrium difference in concentration from outside to inside. The kind of effects produced in a few inches at very high centrifugal forces can be produced in thousands of feet by the weak gravity forces in the ocean.

The theory of composition changes

due to centrifugal or gravity fields has mostly been worked out for the centrifuges described above. Without bothering with the derivations we can borrow the result (*2*, p. 492) that for any component of a mixture which is at equilibrium in a gravity field

$$\frac{d\mu}{dz} = Mg \qquad (11)$$

where M is the molecular weight of the substance (water in this case).

This equation shows that μ changes with depth in the same way for fresh water as for salt water. So if $\Delta\mu = 0$ across the membrane when it is at a depth of 231 m (Fig. 3a), then when the pipe is lowered but the water level is kept unchanged in the pipe, $\Delta\mu$ will still be zero across the membrane at any other level (Fig. 3b). From this argument we see that the water rises to the same level in the pipe no matter how deep the pipe is lowered in an equilibrium ocean.

One consequence of this finding is that the equilibrium ΔP across the membrane rises as the pipe is lowered. This can be understood if we realize that at equilibrium the salt concentration also rises with depth (*3*). To find how the salt concentration changes with depth, combine Eqs. 10 and 11 to obtain

$$Mg = \bar{v}_s \rho_s g + \frac{RT}{x_s}\frac{dx_s}{dz} \qquad (12)$$

or

$$\frac{d\ln x_s}{dz} = \frac{g}{RT}\,(M - \bar{v}_s\rho_s) \qquad (13)$$

To find the depth at which the salt concentration is double the surface value, we must integrate Eq. 13, taking into account that as the salt concentration increases the density of the salt water increases, so that the right side of Eq. 13 increases. If we use typical values for the properties of salt solutions we can linearize the equation and integrate, finding that the salt concentration is double the surface value at a depth of about 7,000 m or 23,000 feet. If this is the depth in Fig. 3b, the concentration of salt in the ocean outside the membrane will be twice that at the surface, and (according to our ideal solution simplification) the required pressure difference to bring about osmotic equilibrium is 46 atm. Thus, the pressure across the membrane is 46 atm. The difference in density between the fresh water in the pipe and the salt water outside is adequate to produce a difference in pressure of 23 atm, so that the water level in the pipe must stand at the level in the ocean where the gauge pressure is 23 atm—that is, 231 m, the same elevation shown in Fig. 3a. By similar arguments we can show that the osmotic power plant would produce zero net work in an equilibrium ocean. One of the many ways of stating the second law of thermodynamics is, "one cannot extract any work from a system at equilibrium." These computations show that for an equilibrium ocean the osmotic pump and the osmotic power plant do not violate the second law; they cannot extract any work from a system at equilibrium.

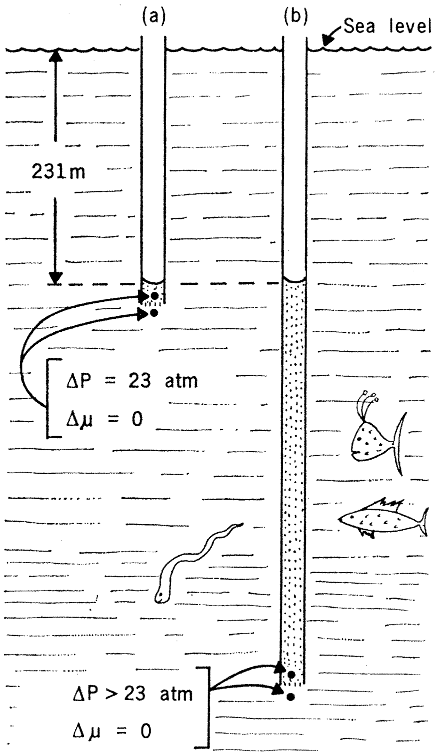

Fig. 3. Pressure (P) and chemical potential (μ) relations for an equilibrium ocean.

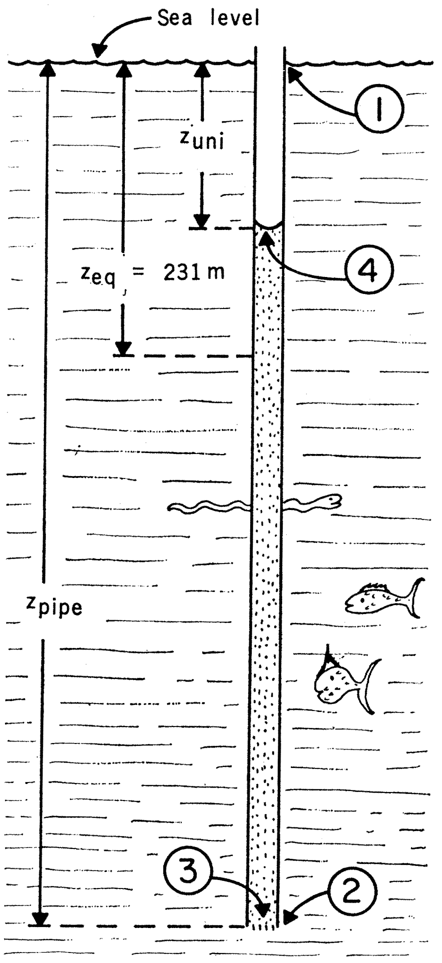

Fig. 4. Pressure relations for a uniform ocean. Abbreviations: z, depth; uni, uniform ocean; eq, equilibrium ocean.

Uniform Ocean (Uniform Temperature and Salinity)

Since this is not an ocean at equilibrium, the deeper we thrust the pipe the more we can take advantage of the deviation from equilibrium; hence the higher the water level should rise in the pipe, as shown in Fig. 1. How much does this come to? Is it high enough to bring water to the surface? Let us see.

Since $dT/dz = 0$ and $dx_s/dz = 0$, the general expression, Eq. 10, reduces to

$$\frac{d\mu}{dz} = \bar{v}_s\rho g \qquad (14)$$

Now consider a pipe of length z_{pipe} thrust in a uniform ocean as shown in Fig. 4, and let us find how the chemical potential changes as we go from 1 to 2 to 3 to 4. If we go from 1 to 2 on the ocean side, integration of Eq. 14 gives

$$\mu_2 - \mu_1 = g\int_0^{z_{\text{pipe}}} \rho_s\bar{v}_s dz \qquad (15)$$

Across the membrane, Eq. 2 gives

$$\mu_3 = \mu_2 \qquad (16)$$

Going from 3 to 4 in the fresh water of the pipe

$$\mu_4 - \mu_3 = g\int_{z_{\text{pipe}}}^{z_{\text{uni}}} \rho_f v_f dz \qquad (17)$$

where z_{uni} is the height to which fluid will rise in a uniform composition ocean, and the subscript f denotes fresh water. Adding the above three expressions gives

$$\left(\frac{\mu_4 - \mu_1}{g}\right) = \int_0^{z_{\text{pipe}}} \rho_s\bar{v}_s dz + \int_{z_{\text{pipe}}}^{z_{\text{uni}}} \rho_f v_f dz \qquad (18)$$

If we take $\bar{v}_s = v_f$ (a good approximation), if we use average densities of fresh and salt water ρ_f and ρ_s, and if we note that $\rho_f v_f = M$, we obtain

$$\left(\frac{\mu_4 - \mu_1}{gM}\right) = \frac{\bar{\rho}_s}{\bar{\rho}_f} z_{pipe} + z_{uni} - z_{pipe} \qquad (19)$$

but from the osmotic pressure of sea water we may compute that $(\mu_4 - \mu_1)/gM = 231$ m, so

$$z_{uni} = 231 \text{ m} - \left(\frac{\rho_s}{\rho_f} - 1\right) z_{pipe} \qquad (20)$$

This is the useful expression for finding the water level in a pipe inserted to a depth z_{pipe} in a uniform ocean.

As an example of its use, if we plunge a pipe 10,000 m into a 3.5 percent salt ocean at 0°C (just as deep as we can go), Eq. 20 gives

$$z_{uni} = 231 - \left(\frac{1.050}{1.023} - 1\right) 10{,}000 = 231 - 264 = -\ 33 \text{ m} \qquad (21)$$

Hence water will rise 33 m above the ocean surface (note that z is measured downward).

Again, the length of pipe needed to just bring water to the surface ($z_{uni} = 0$) is

$$z_{pipe} = 8750 \text{ m}$$

By similar and quite straightforward arguments we can show that the work (per gram of water passing through) which can be extracted by the osmotic power plant is given by

$$\text{Work} = g\Delta z[(\bar{v}_s \rho_s / v_f \rho_f) - 1] \qquad (22)$$

For the well-mixed ocean this is about 3 percent of the work for an equivalent mass of water passing through an ordinary hydroelectric plant with the same elevation change.

The Real Ocean

Looking through oceanography books (*4*), we find that except for a shallow zone rather close to the surface (compared to the maximum depth) the real ocean is practically uniform in properties, with the temperature between 1° and 3°C; the salinity between 3.47 and 3.49 percent by weight; and the density, corrected to surface pressure, about 1.0278 g/cm^3. Consequently the real ocean is somewhere between the equilibrium ocean and the uniform ocean, but very much closer to the latter. So, if a pipe with ideal membrane was thrust into the deepest point in the ocean, fresh water would rise out of the top.

The fact that the real ocean is closer to the uniform ocean than to the equilibrium ocean should not surprise us. Diffusion tends to bring the oceans to equilibrium, while the currents in the ocean tend to mix waters and make it uniform. These currents are driven by the equivalent of a giant heat engine, in which the high temperature source is the sun's energy in the tropics, and the low temperature sink is the radiation of heat to outer space near the poles. This engine overwhelms the diffusive tendency toward equilibrium. Thus the osmotic pump and the osmotic power plant, which appear to get "something for nothing," do not violate the laws of thermodynamics; they merely harvest some of the sun's energy, as do windmills and hydroelectric plants.

Since ocean waters do vary from place to place, we would need detailed data on the variation of temperature and salinity with depth at the particular location we had in mind if we wished to determine the precise level to which the water would rise in the osmotic pump, or precisely how much power could be extracted from the osmotic power plant.

Practical Applications of the Osmotic Pump

The practical applications of the osmotic pump and the osmotic power plant face the same difficulties as reverse osmosis desalination of sea water (*5*). (One may think of the osmotic pump as merely a special case of the reverse osmosis of sea water in which the pressure gradient is supplied by gravity and the difference in densities.) One can readily show that the power costs for such reverse osmosis desalination are quite low in the ideal case. However, in order to get a high throughput one needs a large membrane area, which means a high capital cost. The membranes must have good physical properties, good lifetimes, and so on. If a membrane system could be developed which was practical for the osmotic pump or osmotic power plant, then it would likely also be satisfactory for reverse osmosis, with pumps to drive the water through the membrane, rather than using gravity. The later arrangement would likely be more convenient to users, and lower in overall cost.

In principle, at locations where the oceans are deepest the osmotic pump should be able to bring fresh water to the surface of the real ocean and the osmotic power plant should be able to generate significant electric power. However, these devices are not likely to be economically feasible at the present time. If membranes far superior to those now available are developed and if the ratio of the cost of power to charges on fixed capital greatly increases, then these devices might merit further consideration for practical application.

One may think of this as a way of harvesting some of the sun's free energy which is stored in the nonequilibrium state of the ocean. So far, mankind has harvested such solar energy where it is more concentrated—through photosynthesis, fossil fuels, hydroelectric power, winds, and tides. There are other untapped sources of solar energy and possibilities which may be more economically attractive than this one, such as the steep temperature gradients in the tropical oceans and photovoltaic conversion. For the near future this osmotic approach seems less likely to be commercialized than others, although as we have shown here it is thermodynamically feasible.

References and Notes

1. R. C. Reid informs us that E. R. Gilliland of the Massachusetts Institute of Technology brought up the question of the osmotic pump in discussions and talks some time in the early 1960's. In the literature see: O. Levenspiel, T. J. Fitzgerald, R. E. Peck, *Chem. Eng. Educ.* **2**, 46 (1968); I. Parker, *New Sci.* **41**, 575 and 686 (1968). See also *ibid.* **42**, 192 and 363 (1969); *ibid.* **43**, 38 and 311 (1969); C. L. Strong, *Sci. Am.* **225** (No. 6), 100 (1971); *ibid.* **226** (No. 4), 110 (1972).
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5. V. Merten, Ed., *Desalinization by Reverse Osmosis* (MIT Press, Cambridge, Mass., 1966).
6. We thank R. C. Reid for useful discussion on this problem.