Energy from the evaporation of water

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Some simple idealized engines that consume ambient heat and liquid water and produce work and vapor are described. The consideration of these engines gives (approximate) expressions for the available energy when water evaporates reversibly.

The process of evaporation in dry air permits one, in theory, to extract energy (from the water–dry-air system) in the form of useful work. While visions of driving across the desert in a car that is powered by evaporating water may seem to be in contradiction with the laws of physics, they are not! See Fig. 1.

In this paper we will describe some simple idealized engines that can permit water to evaporate (nearly) reversibly. (A process is reversible if it causes no increase in the entropy of the universe.) Hopefully, the consideration of these very simple engines will give insight into the energy of the water–air system that is available, for doing work, and insight into some natural processes, such as how water moves up tall trees.

Our title, of course, corresponds to common usage, e.g., we speak of the energy content of gasoline and consider air as free. By the "energy from the evaporation of water" we do not, of course, mean merely the latent heat of evaporation. Rather, we mean the thermal energy from the ambient environment that is available for doing work when water evaporates. In the constant pressure, constant temperature systems herein considered this energy is the difference between the Gibbs's free energy of the systems before and after the water evaporates. However, our "noncalculus" presentation does not presuppose any familiarity with the Gibbs's free energy. Rather, it will describe idealized engines that consume ambient heat and water and produce work and vapor.

The "pit machine" presented first is physically sound, though useless for anything but teaching since transfer rates are small. It illustrates how the available energy of the water–air system is related to the relative humidity.

PIT ENGINE

According to Dalton's law of partial pressures, each component of a mixture of ideal gases acts independently of the others. Thus insofar as we can consider water vapor as an ideal gas, its distribution in the pit will be independent of the other components (nitrogen, oxygen, etc.) of the air. (Also, we assume that adequate time is available in order to reach equilibrium.)

We do not need to know the pressure of the air in the pit. The relative humidity of the air adjacent to the surface of water at the bottom of the pit is, of course, 100%. Call the pressure of the water vapor there P_0. Now, by well-known altitude effect, pressure decreases exponentially with height in an isothermal atmosphere and, by the law of partial pressures, the water vapor component of the air can be considered separately. We assume that the walls of the pit can provide the necessary thermal energy for vaporization. Let P be the pressure of water vapor. If M is the molecular weight of water (18×10^{-3} kg/mol), R the gas constant (8.31 J/mol K), g the local gravitational field (9.8 N/kg), and T the ambient temperature, then the pressure of the water vapor will vary with height above the water surface according to the equation

$$P/P_0=\exp(-Mgh/RT)\,. \qquad (1)$$

The derivation of Eq. (1) follows trivially from the ideal gas law and Dalton's law. It is included in many introductory physics texts.

Imagine the pit illustrated in Fig. 2 to be so deep that the density of air (and water vapor) varies significantly from bottom to top. Choose the depth h of the pit such that if water vapor were in equilibrium with liquid water at depth h, then at height h (the desert floor) the vapor would be so thin [because of Eq. (1)] that it would have the same density as that of the desert air. Liquid water at the bottom of this pit would then be in equilibrium with the dry desert air. With infinitesimal work, liquid water at the bottom of the pit could be converted to vapor in the desert air (and vice versa).

If liquid water were removed from the pit the surface would, for a time, be lowered below h. Then more water would spontaneously condense until the water surface returned to its equilibrium level. Similarly, if water were added to the pit the surface would (slowly) return to the equilibrium level (because of evaporation).

The pit provides a convenient way to illustrate how much work can be done when water evaporates. Suppose a small mass m of water is poured into the pipe in Fig. 2 marked "liquid water." Let a mass m of water also pass through the "ideal water wheel." Here "ideal" means that there is no friction or leakage. The work W done on the

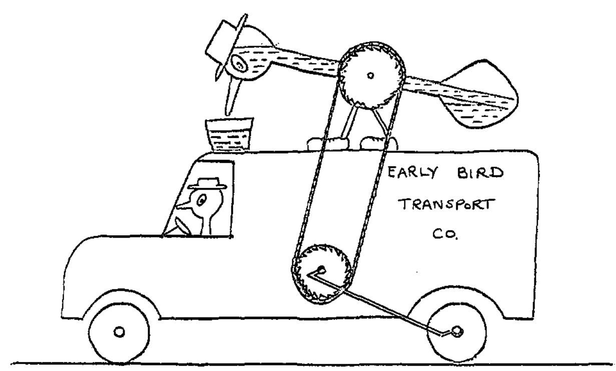

Fig. 1. Although this particular design for extracting work from the water–air system may be impractical, the theoretical limit (derived in this paper) for the work that can be extracted from the water–air system is impressive if the air is hot and dry. At 10% relative humidity and body temperature, the available energy per unit mass of water is about twice the available energy per unit mass of an automotive battery.

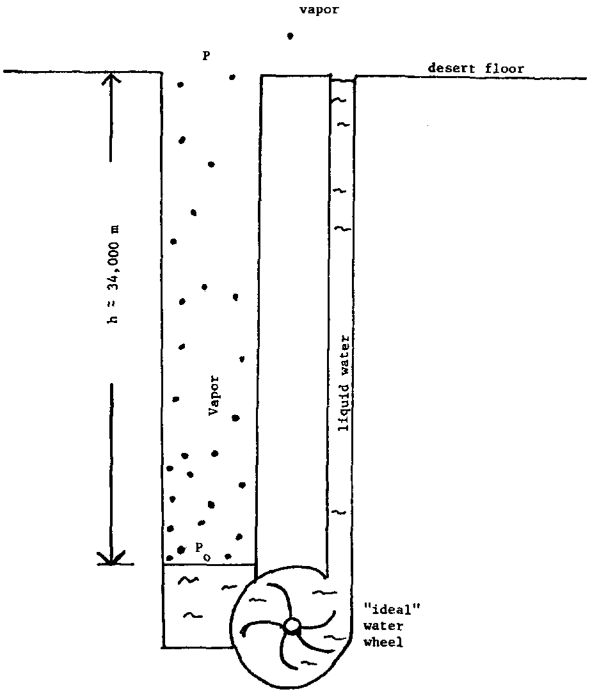

Fig. 2. Deep pit of depth h such that water at the bottom of the pit is energetically worthless. The vapor pressure at the surface of the water is saturated. This pressure decreases with height because of the altitude effect until at the desert floor the vapor pressure is that of the desert air. The liquid water at the bottom of the pit may be either increased or decreased with infinitesimal work by isothermally condensing vapor or evaporating water. The available energy of liquid water in the desert is that which could be extracted as it fell to the bottom of this pit. Conversely, the energy value of water in the desert would equal the energy necessary to raise water from the pit.

water wheel by the water is mgh. Solving Eq. (1) for h and using that expression in mgh gives

$$W = (mRT/M)\ln(P_0/P) . \tag{2}$$

Equation (2) gives the theoretical work that can be performed when a mass m of water evaporates. Note that at 100% relative humidity (when $P = P_0$) W is zero.

The pit engine could not actually provide useful amounts of energy because after pouring in a small mass m, a long time must pass before the water level in the pit will go back to equilibrium. Actually, an infinite time would be necessary to go back to equilibrium because evaporation rates would approach zero as equilibrium is approached. If only a finite time is allowed between successive additions of a small mass m of water, then the level of water in the pit will become higher than the equilibrium level h and less work will be obtained from the water than Eq. (2) indicates.

Solving Eq. (1) for h gives the surprisingly large value of 34 000 m for the "typical" desert parameters of 0.1 relative humidity (P/P_0) and 310 K temperature. This means that the energy theoretically available for doing work when water evaporates (at 310 K, 0.1 relative humidity) is as much as if the same amount of water went through a dam with a height (head) of 34 000 m! By comparison, all dams on the Columbia River have a combined head of about 430 m.

For an alternative comparison, the "head" of an automotive (lead–acid) battery is about 17 000 m. (Here head means the height that the battery could lift itself.)

The impracticality of this engine should not detract from its utility for illustrating thermodynamic relations. Let us now turn our attention to a machine that will extract work more rapidly.

IDEALIZED DRINKING DUCK ENGINE

Figure 3 shows a familiar engine energized by the evaporation of water. These clever devices work by having the bird's head wet and hence cooled by evaporation. Higher vapor pressure on the lower bulb (position A) forces fluid up the central stem to the head, making the bird top-heavy and causing it to tip to position B. A stop (not shown) prevents the bird from tipping too far, stopping the bird in position B, enabling the fluid to drain from the head, thus causing the bird to right itself and the cycle to repeat.

Let us idealize this engine to be as efficient as the laws of thermodynamics permit. Let the bird be as efficient as a Carnot engine operating between the ambient temperature T_1 and the dew point T_2. (The dew point is the theoretical limit to which evaporation could chill the fabric in the duck's bill.) Heat flows from the ambient air to the working fluid (a freon) in the lower bulb. The working fluid deposits waste heat in the head where it is used to evaporate water in the fabric. Heat that flows directly from the air to the bird's head, thereby bypassing the lower bulb, represents a short circuit and must be eliminated in our idealized bird by using a barrier that transmits vapor but not heat. (If the heat barrier were not present, evaporation could only chill the fabric to the wet-bulb temperature, which is higher than the dew-point temperature.)

The heat exhausted Q_2 is related approximately to the mass m of the water consumed by the equation

$$Q_2 = Lm , \tag{3}$$

where L is the latent heat of evaporation (about 2.4 MJ/K). Not included in Eq. (3) is the heat extracted when the water chills to the dew point, nor the heat added when the vapor

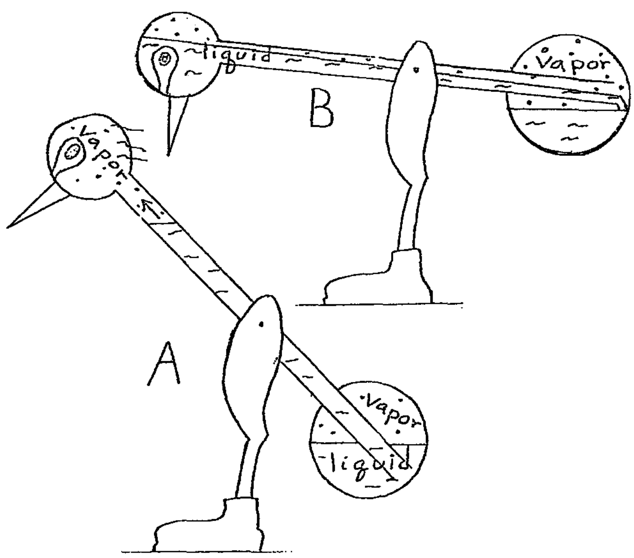

Fig. 3. Familiar heat engine that operates on the temperature difference between the ambient temperature and the dew-point temperature. When the "bird" is in the vertical position A and the head is wet, vapor in the warmer lower bulb forces fluid up to the cool head through a tube. As the head gets full, the bird gets top-heavy and topples into position B. In position B, the lower end of the aforementioned tube comes out of the liquid, permitting the head to drain and hence the bird to right itself and repeat the cycle.

Table I. The relative humidity of air at 40°C as a function of the dew point temperature T_2. Values for the relative humidity obtained from Eq. (6) agree closely (but not exactly) with measured values found in a handbook. The disparity (due to the assumptions) becomes greater as the relative humidity decreases. Equation (6) was obtained by equating the work of the idealized machine shown in Fig. 2 with an idealized version of the machine shown in Fig. 3. We used $R = 8.3144$ J/C° mole, $M = 18.0153$ g/mole, $L = 2402.2$ J/g, and $T_1 = 313.15$ K (40°C).

Dew point T_2 (°C)	Relative humidity from handbook	Relative humidity from Eq. (5)
40	1.0000	1.0000
30	0.5752	0.5779
20	0.3170	0.3218
10	0.1665	0.1719
0	0.0828	0.0877

warms to the ambient or the fact that L varies slightly with temperature.

For a Carnot engine,

$$Q_1/T_1 = Q_2/T_2 \text{ (conservation of entropy).} \tag{4}$$

The work output W is then

$$W = Q_1 - Q_2 = Lm(T_1 - T_2)/T_2 . \tag{5}$$

Equation (5) seems superficially unrelated to Eq. (2) and provides another expression for the available energy when water evaporates.

Let us equate the work output given by Eq. (5) to that given by Eq. (2). (Here T is the same as T_1.) This situation would correspond to a "bird" being able to pump just enough water from the pit to "live." (This condition is rate independent; if the bird pumps faster it needs proportionately more water.) If the resultant equation is then solved for the relative humidity P/P_0, we obtain

$$P/P_0 = \exp[LM(T_2 - T_1)/RT_1T_2] . \tag{6}$$

Equation (6) is an expression relating the relative humidity to the ambient temperature and the dew point. The seemingly different expressions for the available energy from water obtained by considering Figs. 2 and 3 are thus related. Equation (6) is not exact because of the approximations made in deriving Eqs. (2) and (5). It is obtained conventionally by integrating the Clausius–Clapeyron equation.

We can determine how good Eq. (6) is by comparing the relative humidity calculated from it (for given ambient and dew point temperatures) with actual relative humidities (see Table I). The close agreement suggests that the idealizations and assumptions made did not depart far from "reality."

The column in Table I labeled "Relative humidity from handbook" was obtained by dividing the measured vapor pressure of water at the dew point temperatures by the measured vapor pressure of water at 40 °C. This explanation is given since, to a very small extent, the dew point depends on the absolute pressure of the air. Columns 2 and 3 both neglect any effect due to the nonwater components of air.

VAPOR ENGINE

Another, superficially different way of obtaining work from the evaporation of water is the vapor engine (Fig. 4).

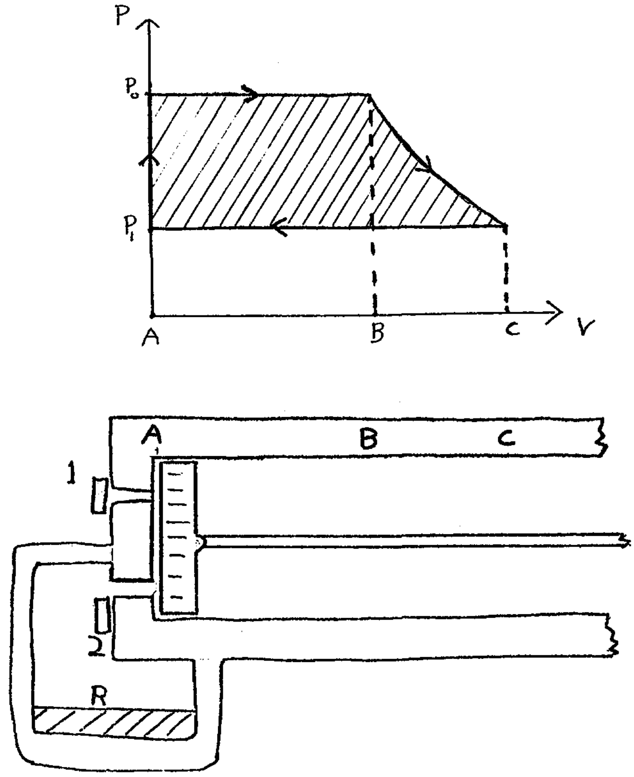

Fig. 4. Vapor engine with PV diagram. The idealized piston transmits air freely but not water vapor molecules. Initially, the piston is at position A and valve 1 is closed, valve 2 is open. Heat conducts freely across all boundaries and all processes are slow and isothermal. The piston moves to position B while water from the reservoir R evaporates and the vapor exerts a constant pressure P_0 on the piston. While at position B, valve 2 is closed, then the piston is permitted to move (while the pressure drops) until (at position C) the pressure on the two sides of the piston is P_1; the ambient vapor pressure of water. Valve 1 is then opened and the piston is returned to initial position A, where valve 1 is closed and valve 2 is opened in preparation for another cycle. The net work performed by the vapor on the piston is represented by the shaded area on the PV diagram. It agrees with the work obtained by the pit engine [Eq. (2)]. Of course, either engine can also run in reverse and use energy to extract water.

This imaginary idealized engine has a piston that has the property of being impervious to water vapor molecules but air molecules can go through it without resistance. All parts of the engine freely transmit heat. The engine's cycle is described in the caption of Fig. 4.

The work performed, when the engine completes a cycle, is illustrated by the shaded area of the PV diagram shown in Fig. 4.

The work performed in going around a cycle is the same as would be obtained if the same amount of water fell into the pit engine (Fig. 2). The reader may wish to verify this fact by calculating the shaded area of the PV diagram in Fig. 4 and noting that the result is the same as Eq. (2).

CAPILLARY ACTION ENGINE: HOW TREES MOVE WATER

Trees transfer large amounts of water from the roots to the leaves. In the main, this movement of water is energized by the evaporation of water at the leaves. Most trees often have the water in their sapwood (xylem) under tension. The tension is caused by capillarity in the pores of the leaves. (Plants that move water by means of positive root pressure, caused by osmotic pressure across the root membranes

would also be subject to similar thermodynamic relations as will be seen in the next section when we discuss osmotic pressure engines.)

Here, since we are not concerned with rates, we can consider a simple capillary tube as a model of the water conducting system of a tree. Such a constant diameter capillary tube would have far too much resistance to the movement of water in a real tree. Real trees have water conducting systems involving compartments connected to one another with tubes of capillary dimensions. The effective resistance to the movement of water through the larger compartments is much less than that through a small capillary tube, and the interconnecting capillary tubes provide safety stops. (If an air bubble breaks into one compartment, it cannot spread to adjacent compartments because the capillary forces would be too large.) I refer the reader to Refs. 1–3 for a thorough description of the morphology of plants and how water passes from the soil to the leaves.

With these qualifications, consider Fig. 5(a) as a model of a tree with the meniscus in a leaf and the bulk water in the

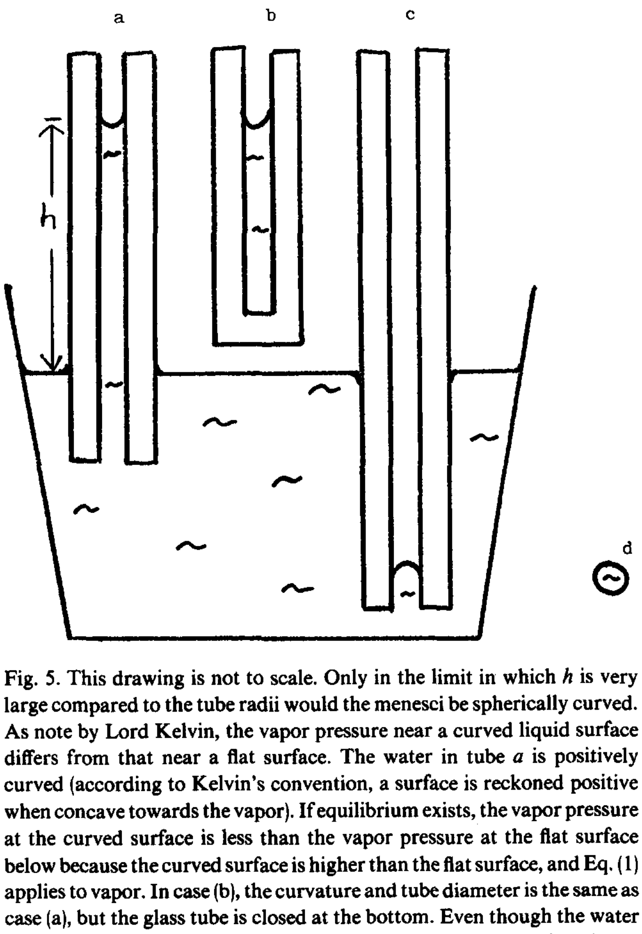

Fig. 5. This drawing is not to scale. Only in the limit in which h is very large compared to the tube radii would the menesci be spherically curved. As note by Lord Kelvin, the vapor pressure near a curved liquid surface differs from that near a flat surface. The water in tube a is positively curved (according to Kelvin's convention, a surface is reckoned positive when concave towards the vapor). If equilibrium exists, the vapor pressure at the curved surface is less than the vapor pressure at the flat surface below because the curved surface is higher than the flat surface, and Eq. (1) applies to vapor. In case (b), the curvature and tube diameter is the same as case (a), but the glass tube is closed at the bottom. Even though the water in the tube is not connected to the bulk flat water, the level in tube (b) under equilibrium conditions will be the same as that in tube (a), according to Kelvin, who obtained a formula relating curvature to vapor pressure. Tube (c) is made of a material that water does not wet, say wax, and the sign of the curvature differs from case (a). In case (c) the vapor pressure is greater than that of flat water because the equilibrium level is below that of flat water. In case (d) we have a spherical droplet with the same curvature as case (c), so it too would be in equilibrium with vapor at greater than 100% relative humidity. In this case, the equilibrium is unstable since evaporation makes droplets smaller, i.e., they have higher vapor pressure and evaporate more rapidly.

soil. Here I wish to consider water standing in a capillary tube very near equilibrium as being a slight variation of the pit engine. Suppose, for argument, that the vapor pressure adjacent to the curved surface of the water in Fig. 5(a) is infinitesimally less that the equilibrium vapor pressure P. Suppose then, that a small amount of water m would evaporate from the top of the curved surface. The surface tension would then do work mgh moving other water up since the level of the meniscus is maintained.

Equation (1) would be the relationship between the maximum theoretical equilibrium height h of a tree and the ratio P/P_0, where P_0 would be the vapor pressure of the water in the soil and P would be the vapor pressure at the leaves.

Under equilibrium conditions, water would move to the tree leaves at an infinitesimal rate.

If the vapor pressure of the leaves was less than that of the air, water would condense in the leaves and flow out the roots.

Figure 5(b) emphasizes that the equilibrium height of the water in a capillary tube depends on the curvature of the water surface, and not on the fact that the water in the capillary is connected (by other than vapor) to the bulk water. If, for example, water in Fig. 5(b) were higher (or lower) than water in Fig. 5(a), water in Fig. 5(b) would evaporate (or condense) until the level in Fig. 5(b) was the same as that of Fig. 5(a). This process of approaching equilibrium would be very slow.

William Thomson (Lord Kelvin)[4] used a drawing similar to Fig. 5(b) in the derivation of the "Kelvin formula," which relates the vapor pressure of water to its (Laplacian) curvature. The Kelvin formula is an approximation, good when the change in vapor pressure is small compared to the total vapor pressure. William Thomson suggested that the moisture in wheat flour biscuits, oatmeal, or cotton cloth at temperatures far above the dew point of the surrounding atmosphere is a manifestation of the phenomena illustrated in Fig. 5(b).

Figures 5(c) and 5(d) are included for completeness. Figure 5(d) can be easily generalized (not shown) to the case of an electrically charged, dirty smog droplet. If such a drop were to evaporate an infinitesimal amount, work would have to be done: (i) against surface tension to change the area of the drop; (ii) against osmotic pressure; and (iii) against electrical forces (since the charge on the drop remains constant but the radius changes). Equating this total work to that available when water evaporates [Eq. (2)] gives the Thomson equation[5] for the vapor pressure of a drop. This equation is named after J. J. Thomson, the discoverer of the electron.

OSMOTIC PRESSURE ENGINES

Osmotic pressure provides numerous opportunities for doing work. When rivers run into the sea, the mixing of fresh and salt water represents a lost opportunity to do work. If instead, the river water entered the sea by reversible thermodynamic processes, as much work could be performed as if the water were lowered about 240 m (as will be shown). One can use Fig. 6, a variation of the pit machine, to illustrate how river water might enter the ocean reversibly. Energy can be extracted (by a mechanism not illustrated) when water is lowered to the bottom of the pit (Fig. 6). Osmotic pressure would then transport water across the membrane to the brine sea. Water would evaporate reversibly from the brine sea since the vapor pressure of the brine

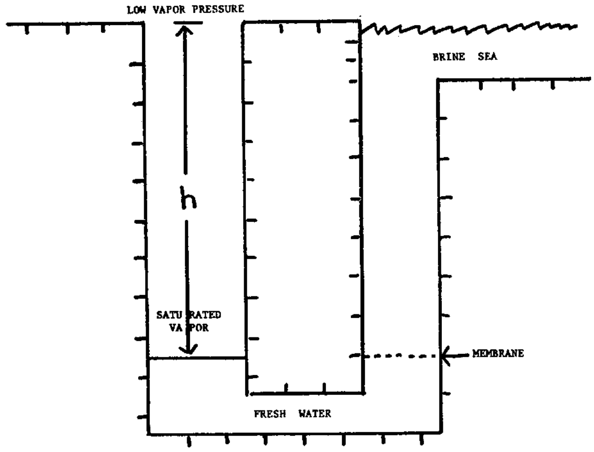

Fig. 6. "Equivalent pit." Water in the brine sea is in equilibrium with fresh water at the bottom of the equivalent pit. Water from the bottom of the pit can be transferred reversibly to the brine sea either through the idealized membrane (which transmits solvent but not solute) or by vapor path (evaporating and recondensing). For the vapor path, the equilibrium height h is determined by the vapor pressure of the brine, the vapor pressure of water, and Eq. (1). For the path across the membrane, h is determined by the osmotic pressure. For equilibrium, these two methods of determining h must agree with each other. Consequently, osmotic pressure is simply related to vapor pressure.

is the same as that in the adjacent air. Eq. (1) applies to the vapor (assumed to be in equilibrium).

Solving Eq. (1) for h gives 240 m if T is 300 K and P/P_0 is 0.95 (the approximate measured value for sea water). Since Fig. 6 represents an equilibrium configuration, the osmotic pressure of sea water must also be (about) 240 m.

ELECTRICAL ENGINES

Another variation of the pit engine illustrates that the energy necessary for electrolysis varies with pressure of the gases. Since the details of the "idealized water wheel" in Fig. 1 are not important, it should not matter if the device works by disassociating the water to hydrogen and oxygen and reassociating the hydrogen and oxygen to water at the bottom of the pit. This process is illustrated in Fig. 7. Since energy is conserved, the energy obtained by the reverse electrolysis at the bottom of the pit must equal precisely the energy needed for electrolysis at the top, plus the loss in potential energy, mgh, of the water. The pressures of the gases at the bottom of the pit exceeds the pressures of the gases at the top according to the altitude effect.

We can combine the lesson in Fig. 6 with the lesson in Fig. 7 and obtain Fig. 8. In the ideal, reversible limit more energy must be obtained by reverse electrolysis in the brine solution than was used for electrolysis in the water because the brine solution is, in the sense of Fig. 6, energetically equivalent to water at the bottom of a pit. Some of the output work of Fig. 8 could supply the work input, leaving some net work surplus. Liquid water and ambient heat are consumed in Fig. 8 to produce water vapor and electrical work.

DISCUSSION

I trust some of my figures indicate that they are not to be taken with complete seriousness. The reason, of course, why these devices will not solve our "energy crisis" is that

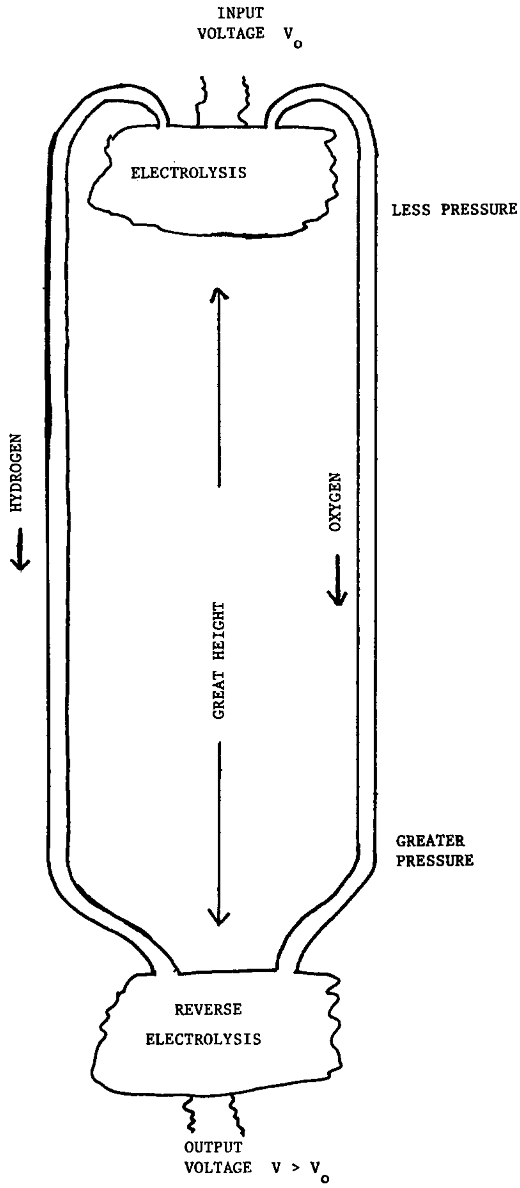

Fig. 7. This variation of the pit machine shows that the voltage for electrolysis varies with the pressure of the gases. Water is electrolyzed to H_2 and O_2 at the top. The H_2 and O_2 are recombined at the bottom in a fuel cell. If all processes are reversible, the voltage at the bottom must be greater than that at the top. The energy generated at the bottom must equal the energy consumed at the top plus the energy needed to lift the transferred water back to the top.

diffusion is a slow process. Readers interested in a quantitative answer as to why the "pit engine" will not work may wish to solve a random walk problem that would model the diffusion of water vapor molecules in the pit. I find that the time required for water molecules in air to have a "root mean square" displacement of 34 000 m is on the order of a million years at ordinary temperatures and pressures. Since the lower part of the pit would contain air at more than 1 atm pressure, the time constant for water molecules at the bottom to diffuse to the top would be far longer that a million years. Great patience would be required to obtain a small amount of energy.

The vapor engine also will not work because it relies on a nonexistant material, viz., the membrane that efficiently transmits air molecules but not vapor molecules.

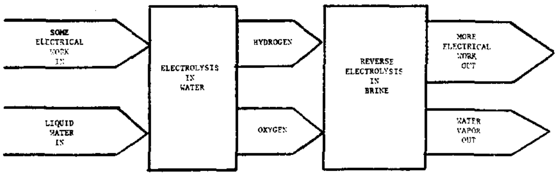

Fig. 8. Electrical work from the evaporation of water. Liquid H_2O of low salinity is electrolized to H_2 and O_2. The H_2 and O_2 are then used as fuel in a fuel cell (reverse electrolysis). The salinity of the brine is determined by the relative humidity of the desert air. Since water from the brine can be transferred to an "equivalent pit" with zero work, the difference between the energy generated by the fuel cell and that used by electrolysis must be equal to the energy needed to lift the water from the equivalent pit. The depth of the equivalent pit is determined by the relative humidity of the desert air as illustrated in Fig. 6. All processes are isothermal and reversible. Work is not conserved and heat is exchanged with the ambient.

The electrical engines that work on electrolysis and reverse electrolysis sound less promising when it is realized that the 34 000 m head corresponds to only 0.06 eV/mol. Since two electrons are transferred for each molecule electrolyzed, this 0.06 eV corresponds to a reduction in electrolysis voltage of only 0.03 V.

Osmotic pressure engines are occasionally discussed in the literature and may hold some promise, but diffusion across membranes is slow, and membranes can get clogged by impurities in the water. Still, perhaps these engines may some day be useful.

The tree engine is, of course, a working success (in nature). Much water is pumped by the capillary forces in the leaves in the world's trees.

A variation of the drinking duck engine was proposed in a study[6] by the Rand Corporation for pumping water in the Egyptian desert. Skepticism seems merited. A Carnot type heat engine that would work for the temperature difference between the ambient and dew-point temperatures is not feasible because the surface area of the condensor and heat absorber would have to be too large.

Of course, some value from water evaporation can be obtained in composite systems. The mere fact that the dew point, rather than the ambient temperature, is the lower temperature being approached would permit a power plant that used evaporative cooling to deliver more work than it could without evaporation.

None of the engines considered in this paper will solve the energy crisis, nor will they lead to previously unknown thermodynamic relations, but the engines do illustrate the concept of water evaporating reversibly in concrete, and possibly humorous, ways.

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[6]R. Morrow, Saturday Rev. 51, (3 June 1967). See also Introduction by John Lear, p. 49, same issue.

SOLUTION TO THE PROBLEM ON PAGE 225

The potential is symmetrical. Hence,

$$nh = 4\int_0^{x_m} p\,dx = 4\int_0^{x_m} (2mE - 2max^q)^{1/2}\,dx$$
$$= \text{const}\,E^{(q+2)/2q}.$$

Thus $E(n)/E(1) = n^{2q/(q+2)}$. For $q = 1$, $E \sim n^{2/3}$ (quantum bouncer); for $q = 2$, $E \sim n$ (oscillator); etc. For $q \to \infty$, $E \sim n^2$. This result was obtained by Nieto and Simmons [Am. J. Phys. **47**, 634 (1979)] using the WKB method in which n is replaced by $n + 1/2$. The dependence of the energy levels on the quantum number n has also been discussed recently by Fernandez and Castro [Am. J. Phys. **50**, 921 (1982)] using a variational method.

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