

Thermodynamics of the Hydrocratic Generator

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Background

The founders of Wader LLC have invented a device that allows energy to be extracted from the mixing of fresh water into a larger volume of salt water. They call this device a “hydrocratic generator.” While the device is new and quite novel, the principles of physical chemistry that describe the energy released by this mixing is old, dating to the pioneering work of the great thermodynamics expert, J. Willard Gibbs, in the nineteenth century.

The thermodynamics of mixing is described in standard texts. One such book is the classic text *Thermodynamics* by Lewis and Randall¹. Another is the widely used current textbook *Physical Chemistry* by P. W. Atkins² “,” by P. W. Atkins, (Fourth Edition, 1990, Section 7.2, pages 159ff), (Atkins).

In this short memorandum, I will outline the theory found in these books and others in hopes of helping the reader understand the behavior of the hydrocratic generator.

Comments on Thermodynamics

Thermodynamics is the study of energy, especially its generation, consumption and flow in chemical and physical processes. Since the middle of the 20th century, thermodynamic principles have been applied well beyond these areas, including cosmology and areas of economics. It is a heavily mathematical field, but is based securely in experimental observations. It is ultimately a reflection of everyday experience. Like any specialist field, it has its own vocabulary, including some familiar words that have well-defined usages within the field. One important term and concept is “free energy,” which describes the potential for physical and chemical changes to occur. (The adjective free should not be misconstrued as involving no cost.) Free energy for real systems may be calculated or measured in a variety of ways, and great effort has gone into making such calculations and measurements for many real systems.

For free energies describing systems held a constant pressure, we rely on what is called the Gibbs Free Energy, G. For changes in this value, we refer to ΔG . By convention, when a system undergoing change releases free energy into the surroundings, we say the free energy change for the system is negative, rather like a ball rolling downhill releases the energy provided by carrying it to the top of the hill. Thus, when any system adjusts itself to a more stable configuration, the Gibbs Free Energy for the system is negative.

As shown in Atkins on page 108, ΔG is described as the sum of an enthalpy term, ΔH , and an entropy term, $T\Delta S$:

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

In equation (1), T is the absolute temperature and ΔH and ΔS are the changes in enthalpy and entropy between the initial and final states. Because this description is so useful, enthalpy and entropy values for the chemical elements and an immense number of chemical compounds are

tabulated in widely used standard reference books. Examples are *The Handbook of Chemistry and Physics*³, and *Lange's Handbook of Chemistry*⁴ edited by J. A. Dean.

Thermodynamics of Mixing

Experience tells us that when two solutions with different compositions are brought into contact, there is a driving force for the solutions to mix and form a single solution. This takes place even in the absence of any mixing with a device such as a stirrer. This being the case, we can surmise that the Gibbs free energy change for such a mixture will be negative.

More than a century ago, equation (1) was solved for a system of fluids mixing at constant pressure:

$$\Delta G = nRT(X_A \ln X_A + X_B \ln X_B) \quad (2)$$

This equation can be found as equation 7 on page 159 of Atkins². In equation (2), n is the number of moles of molecules involved in the mixing, R is the gas constant in appropriate units, T is the absolute temperature, and X_A and X_B are the mole fractions of components A and B in the final mixture. Atkins states "Since mole fractions are never greater than 1, the logarithms in this equation are negative, and $\Delta G < 0$." This means that the driving force favors the mixed system in all cases. The most important application of the Gibbs Free Energy here is as a measure of osmotic potential.

In non-ideal systems, ΔG of mixing can have an enthalpy component. For miscible liquids and solutions, this component is typically negative, further driving the mixing. It is obvious that when the liquids being mixed are non-miscible, such as gasoline and water, the enthalpy component must be so large that it overwhelms the free energy described in equation 2, so that the calculated ΔG is positive.

The Free Energy released during mixing can be calculated using equation (2). Once mixed, the solution will not spontaneously separate into the starting solutions, and reversing the operation takes work. This too is consistent with everyday experience, where, for instance, salt water does not spontaneously separate into a layer of fresh water and a layer of denser salt water. In fact, to make such a separation we must resort to more aggressive methods such as distillation, where the solution is heated and some of the water is boiled off and collected by cooling.

Using equation (2), the amount of energy that can be derived from mixing fresh water with salt water can be calculated. Since the driving force is due to entropy, the amount of energy for a given amount of fresh water increases as the volume of salt water increases. The maximum energy is obtained by mixing the fresh water into an infinitely large volume of salt water. The final composition of the mixture would exactly equal the composition of the salt water. The change in free energy of the system is given by the term

$$\Delta G_{\max} = RT \ln X_{\text{H}_2\text{O}} \quad (3)$$

where $R = 8.314 \text{ J/Mole } ^\circ\text{K}$, the universal gas constant, $T = 293 \text{ } ^\circ\text{K}$ ($20 \text{ } ^\circ\text{C}$), and $X_{\text{H}_2\text{O}}$ is the mole fraction of water in the product. Sea water contains 3.50 wt% NaCl, meaning 100 grams of sea

water contains 3.5 grams of NaCl (0.0599 moles) and 96.5 grams of H₂O (5.36 moles). J stands for Joules, the unit of energy in the SI system.

The mole fraction X of water in sea water is

$$X_{\text{H}_2\text{O}} = 5.36/(5.36+0.0599) = 0.989 \quad (4)$$

Substituting the mole fraction into equation (3), we find that

$$\Delta G_{\text{max}} = 8.314 \times 293 \times \ln(0.989) = -8.314 \times 293 \times 1.11 \times 10^{-2} \text{ J/mole} = -27.1 \text{ J/mole}$$

Per gram of water, this is

$$\Delta G_{\text{max}} = -27.1/18 \text{ J/g} = -1.5 \text{ J/g} \quad (5)$$

The negative value for ΔG indicates that energy is released. This satisfying result tells us that the mixing will take place spontaneously, as we know from common experience. It also tells us that a device designed to recover the energy that drives this mixing can recover as much as 1.5 Joules for every gram of fresh water that is mixed into salt water.

Conclusions

While the principle described is very old, coming out of work done in the second half of the 19th century, a method for extracting some fraction of this energy is novel. Such a method is the one embodied in Wader's hydrocratic generator. The energy released in mixing a volume of fresh water with a much larger volume of salt water can be calculated using the methods of J. Willard Gibbs.

¹ Thermodynamics by G.N. Lewis and M. Randall ¹, as revised by K. S. Pitzer and L. Brewer (Second Edition, 1961); discussion of the thermodynamics of mixing begins on page 283.

² Physical Chemistry, by P. W. Atkins, Fourth Edition, 1990, New York, W. H. Freeman and Company; discussion of the thermodynamics of mixing is found in Section 7.2, beginning on page 159.

³ Handbook of Chemistry and Physics, edited by David R. Lide, published by the CRC Press, and updated annually.

⁴ Lange's Handbook of Chemistry, edited by John A. Dean, published by McGraw Hill Book Company, and updated regularly with new editions.