

Decreasing the Energy of Evaporation Using Interfacial Water: Is This Useful for Solar Evaporation Efficiency?

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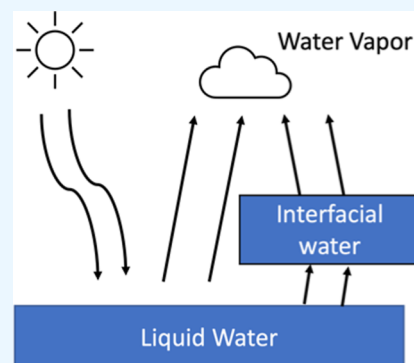
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ABSTRACT: Evaporation of water using solar power is an economical and environmentally friendly method for purification of aqueous solutions. It has been suggested that intermediate states can be used to lower the enthalpy of evaporation of water and therefore to increase the efficiency of evaporation that uses absorption of sunlight. However, the relevant quantity is the enthalpy of evaporation from bulk water to bulk vapor, which is fixed for a given temperature and pressure. The formation of an intermediate state does not alter the enthalpy of the overall process.



INTRODUCTION

Evaporation can be used for separating water from dissolved content and therefore for obtaining pure water or extracting valuable dissolved species, such as lithium salts. Solar-powered evaporation is advantageous for these applications because the CO₂ output is lower than when the combustion of fossil fuels is used to supply the heat, and this has stimulated recent research to optimize solar evaporation. Two fundamental directions of enquiry have been advanced: (1) methods for absorbing the maximum energy from the sun for use in evaporation (e.g., ref 1) and (2) methods for facilitating evaporation. Among the second category are methods where the energy of evaporation is reduced by evaporating interfacial water or other modified water.^{2–5} Several variants of this method have been discussed, and the purpose of this brief article is to discuss the potential of this idea from a thermodynamic perspective.

RESULTS AND DISCUSSION

Radiation from the sun heats the evaporation apparatus. At a constant external pressure, the heat, Q , required to evaporate bulk water is equal to the enthalpy of vaporization of bulk water

$$\Delta_{\text{vap}}H^{\text{BW}} = H^{\text{V}} - H^{\text{L}} \quad (1)$$

where H^{V} is the enthalpy of water vapor, and H^{L} is the enthalpy of the bulk liquid water. In this manuscript, all enthalpies refer to the molar enthalpy, and we note that the enthalpies depend on the pressure and the temperature. Here, we assume in all equations that we are discussing the same pressure (e.g., 1 atm) and a given temperature for the vapor and liquid.

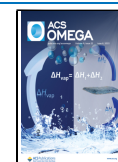
Current reported efforts to reduce the required enthalpy of vaporization are based on the idea of converting the bulk water into water in a different state and then evaporating that altered water. A variety of intermediate states of water have been considered, e.g., water in capillaries or droplets,⁴ water near polymers,^{5,6} and water near nanoparticles.² We will use the term interfacial support as a general term for the material used to hold the interfacial water in each of these cases. In general, the enthalpy of interfacial water, H^{I} , is not equal to the enthalpy of liquid water H^{L} so the enthalpy of vaporizing interfacial water, $\Delta_{\text{vap}}H^{\text{IW}}$, can be different from the enthalpy of vaporizing bulk water. The basic idea of using the intermediate of interfacial water is that if the enthalpy of intermediate water is greater than that of bulk water, then the enthalpy of vaporization is lower than for bulk water. This concept is illustrated in Figure 1.

However, prior to evaporation of the interfacial water, the interfacial water must be formed from bulk water, and the enthalpy for this process must be considered. Because enthalpy is a state function, the enthalpy of a process between given initial and final states is independent of the path taken by the process that occurs between the same initial and final states. Thus, the enthalpy for the process via the intermediate state is exactly the same as the direct process. The apparent enthalpy savings

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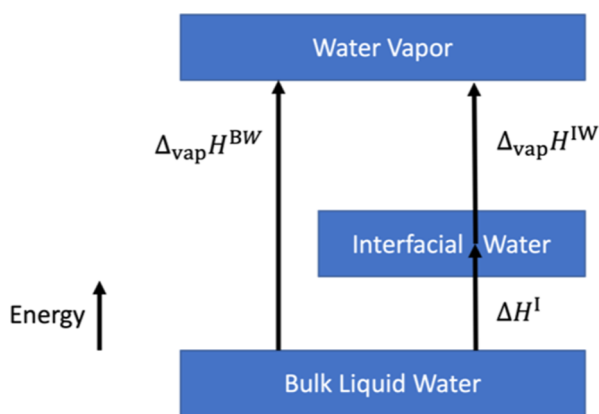


Figure 1. Schematic of the enthalpy of vaporization, illustrating different paths for evaporation. Although the enthalpy of vaporization of interfacial water may be less than that of bulk water, the enthalpy of vaporization of water from the bulk liquid state to the vapor state is independent of passage through intermediate states. This is a consequence of enthalpy being defined as a state function.

obtained by evaporating from the intermediate state must be “paid for” to reach the intermediate state. The enthalpy of formation of the intermediate state is exactly the enthalpy that was saved by “starting with” the interfacial water.

$$\Delta H^I = \Delta_{\text{vap}} H^{\text{BW}} - \Delta_{\text{vap}} H^{\text{IW}} \quad (2)$$

For a one-off process where one considers the intermediate water as the starting state, there is an enthalpy saving. In a continuous process, where interfacial water is continuously created from bulk water from the same interfacial support (e.g., polymer), one should consider the energy to replace the interfacial water once it has been evaporated. If the energy is in the form of heat, there is no thermodynamic benefit to using the intermediate of interfacial water. An analysis of the one-off process should consider the one-off cost of producing the polymer or other interfacial support and hydrating it.

It is possible that the conceptual basis for using an intermediate arises from thinking that the interfacial support is similar to a catalyst. That is, it provides a pathway of lower energy to a product. But a catalyst does not change the difference in energy between the reactant and product, which is a constant, as is $\Delta_{\text{vap}} H^{\text{BW}}$ here.

We now revisit the idea of treating the starting state as the interfacial water in the interfacial support. In this scenario, the water in the interfacial support could already be at a raised enthalpy, and therefore, the enthalpy of vaporization would be lower than for the evaporation of bulk water. The trouble with this thinking is that the interfacial support (possibly hydrated) is now a reactant in the process. That is, it is used up in the process, and the cost associated with its production must be considered. Again, if it is not a reactant, then to reuse it after the interfacial water has been evaporated, one must start with bulk water, so the process is again starting with bulk water. Because enthalpy is a state function, the enthalpy is the same as if the intermediate state were never employed.

Finally, we discuss another thermodynamic difficulty with some approaches to enhancing the evaporation of water. For clarity in the discussion, we use Gibbs energy, which is useful because it facilitates the description of spontaneous processes. Several evaporation enhancement strategies describe the use of hydrophilic intermediates. If the water spontaneously wets the

pores of a hydrophilic solid, the free energy of the combined water and interfacial support must decrease. After this wetting, the water must now climb further uphill than it would have from the original bulk water, i.e., $\Delta_{\text{vap}} G^{\text{IW}} > \Delta_{\text{vap}} G^{\text{BW}}$ (see Figure 2).

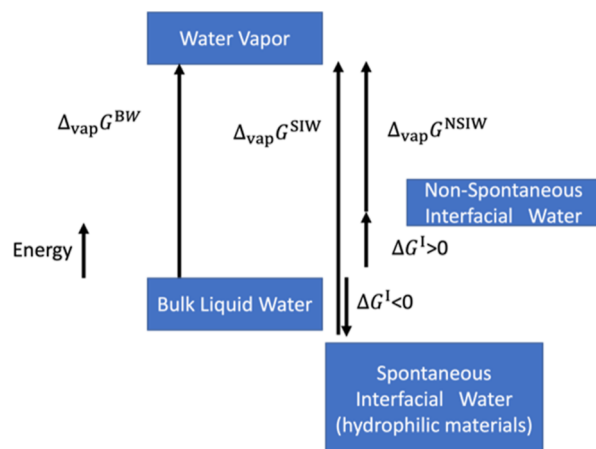


Figure 2. Schematic of Gibbs energy of vaporization. SIW = interfacial water formed spontaneously, NSIW = interfacial water formed nonspontaneously.

Even for a one-off process, evaporation is more difficult from this intermediate. Thus, water bound to hydrophilic solids is not, in general, useful even for lowering the energy for evaporation from the interfacial state. To decrease the Gibbs energy of vaporization, the Gibbs energy of the interfacial water must be greater than that of bulk water, e.g., by having fewer hydrogen bonds. Several authors have previously described such a scenario.^{2,5,6} However, formation of this nonspontaneous interfacial water requires work (or heat or both), and the overall enthalpy and free energy change to vaporize the water from bulk water is the same for this process that proceeds via the hydrophilic intermediate as it is without use of the intermediate state.

Before closing, it is important to note that the thermodynamic argument presented does not apply to all the proposed benefits of nanoscale water. It may still be useful to confine heat flows to smaller volumes of water near the points where solar radiation is absorbed, thereby enabling faster evaporation, to limit the conduction of heat away from heated water before the water evaporates.^{3,7} It may also be useful to increase the area of the liquid–vapor interface.⁸

CONCLUSIONS

In closing, we reiterate the main argument, which is that the enthalpy change of a process, being the difference between two state quantities, depends only on the initial and final states. If an intermediate state is utilized, the enthalpy of formation of that state from the initial state must be considered. This obviates any thermodynamic advantage of using an intermediate state in the solar evaporation of bulk water.

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Notes

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