Water Vapor and Mechanical Work: A Comparison of Carnot and Steam Cycles

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ABSTRACT

The impact of water vapor on the production of kinetic energy in the atmosphere is discussed here by comparing two idealized heat engines: the Carnot cycle and the steam cycle. A steam cycle transports water from a warm moist source to a colder dryer sink. It acts as a heat engine in which the energy source is the latent heat of evaporation. It is shown here that the amount of work produced by a steam cycle depends on relative humidity and is always less than that produced by the corresponding Carnot cycle.

The Carnot and steam cycles can be combined into a mixed cycle that is forced by both sensible and latent heating at the warm source. The work performed depends on four parameters: the total energy transport; the temperature difference between the energy source and sink; the Bowen ratio, which measures the partitioning between the sensible and latent heat transports; and the relative humidity of the atmosphere. The role of relative humidity on the work produced by a steam cycle is discussed in terms of the Gibbs free energy and in terms of the internal entropy production.

1. Introduction

The atmosphere acts as a heat engine that produces mechanical work by transporting energy from warm to cold regions. This work is used primarily to sustain atmospheric motions and to lift water substance, and it is lost when kinetic energy is dissipated either as an end result of a turbulent energy cascade or in the wake of falling hydrometeors (Pauluis et al. 2000). The amount of work produced by atmospheric flows depends on multiple factors, including the atmospheric temperature and humidity as well as the partitioning of the energy transport between sensible and latent heat. Previous studies (Pauluis and Held 2002a,b; Goody 2003) have shown that the presence of water vapor greatly reduces the ability of the atmosphere to convert internal energy into kinetic energy. This paper argues that the impact of water vapor on the production of kinetic energy can be captured by idealized thermodynamic cycles.

The Carnot cycle, named after Sadi Carnot, is the best known example of a heat engine. The Carnot cycle has been applied to discuss various atmospheric circulations such as moist convection (Rennó and Ingersoll 1996;

Emanuel and Bister 1996), tornadoes, dust devils (Rennó et al. 1998), and hurricanes (Emanuel 1986; Bister and Emanuel 1998; Emanuel 2003). It is argued here that, although many atmospheric phenomena can be viewed at least in part as heat engines, the analogy with a Carnot cycle often overestimates the conversion of internal energy into kinetic energy in the presence of water vapor. To better assess the role of water vapor, a novel thermodynamic cycle is introduced here: the steam cycle. A steam cycle transports water from a moist source to a dry sink; in doing so, it is able to produce mechanical work. The steam cycle is a heat engine that transports latent energy from a warm source associated with the evaporation of water to a colder energy sink.

Section 2 compares the Carnot and steam cycles. It is shown that the efficiency of the steam cycle, defined as the ratio of the work to the energy input, depends on relative humidity throughout the cycle. It is lowest for an unsaturated cycle and reaches the maximum Carnot efficiency for a fully saturated cycle. Section 3 discusses the work produced by a mixed Carnot–steam cycle in which the energy source is a combination of sensible and latent heating. This work depends on both relative humidity and Bowen ratio, and it is always less than or equal to the work done by a Carnot cycle. Section 4 offers two complementary explanations for the impact of relative humidity of the work done by a steam cycle. First, it is argued that the steam cycle acts to increase the

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free energy of water. From a thermodynamic viewpoint, such an increase in the free energy does not occur spontaneously but reduces the amount of work produced by the thermodynamic cycle. Second, the steam cycle can also be recast as an irreversible heat engine, in which entropy is internally produced when water vapor is exchanged between the cycle and its environment. Such an internal production of entropy is modulated by the relative humidity in the cycle and always results in a reduction in the mechanical output. The implications of these findings for atmospheric circulations are discussed in the conclusion.

2. Comparison between Carnot and steam cycles

a. Work and efficiency of a moist thermodynamic cycle

For a given thermodynamic cycle, the work produced per unit mass of dry air can be obtained by computing the integral

$$W = -\oint \alpha_d \, dp, \quad (1)$$

where α_d is the volume per unit mass of dry air and p is the total pressure. The integral can be rewritten by taking advantage of the thermodynamic relationship

$$dH - \alpha_d dp = T dS + g_v dr_v + g_l dr_l$$
$$= T dS + g_v dr_T + (g_l - g_v) dr_l. \quad (2)$$

Here, T is the temperature; H is the enthalpy per unit mass of dry air; S is the entropy per unit mass of dry air; g_l and g_v are the free energies per unit mass for liquid water and water vapor, respectively; and r_v, r_l, and $r_T = r_v + r_l$ are the mixing ratios for water vapor, liquid water, and total water. The expressions for these state variables are given in appendix A. The left-hand side of (2) is the amount of external heating required by a specific transformation of the fluid. For a single component fluid, (2) reduces to the expression for the entropy change as $dH - \alpha dp = T dS$. The two additional terms, $g_v dr_v$ and $g_l dr_l$ on the right-hand side of (2), are here necessary to properly account for change in composition of the mixture.

At saturation, the free energy of water vapor and liquid water are equal

$$g_v - g_l = 0. \quad (3)$$

Using (2), one can rewrite the integral in (1) as

$$W = \oint T \, dS + \oint g_v \, dr_T, \quad (4)$$

after taking advantage of the fact that the total change of enthalpy along a cycle vanishes and assuming that all phase transitions take place at saturation. The expression (4) makes it possible to compute the work based on the thermodynamic forcings alone: that is, on the changes in entropy dS and water content dr_T. The first integral on the right-hand side corresponds to the direct thermodynamic forcing associated with heating and cooling at different temperatures. The second integral depends on the Gibbs free energy of water vapor and accounts for the effects of adding and removing water substance. It vanishes for a closed thermodynamic cycle where no water is either added or removed but should not otherwise be neglected.

The external heating required with any transformation is given by

$$\delta Q = dH - \alpha_d dp = T dS + g_v dr_T. \quad (5)$$

The external heating includes both sensible and latent heating. The energy input is given by the integral

$$Q_{in} = \oint \delta Q^+, \quad (6)$$

where the energy source Q^+ is defined by

$$\delta Q^+ = \delta Q \quad \text{for} \quad \delta Q > 0$$
$$= 0 \quad \text{otherwise.}$$

The mechanical efficiency is defined as the ratio of the work to the net heating

$$\eta = \frac{W}{Q_{in}}. \quad (7)$$

b. Carnot cycle

A Carnot cycle transports heat from a warm source at a temperature T_{in} to a cold sink at temperature T_{out}. The cycle is described in Fig. 1 and is composed of four transformations:

- $1 \rightarrow 2$: isothermal expansion from p_1 to p_2 at temperature T_{in};
- $2 \rightarrow 3$: adiabatic expansion from p_2 to p_3 at constant entropy $S_2 = S_3$;
- $3 \rightarrow 4$: isothermal compression from p_3 to p_4 at constant temperature T_{out}; and
- $4 \rightarrow 1$: adiabatic compression from p_4 to p_1 at constant entropy $S_4 = S_1$.

The work done by the Carnot cycle can be computed analytically for an ideal gas using (1). For moist air, computing the integral (1) requires obtaining the specific
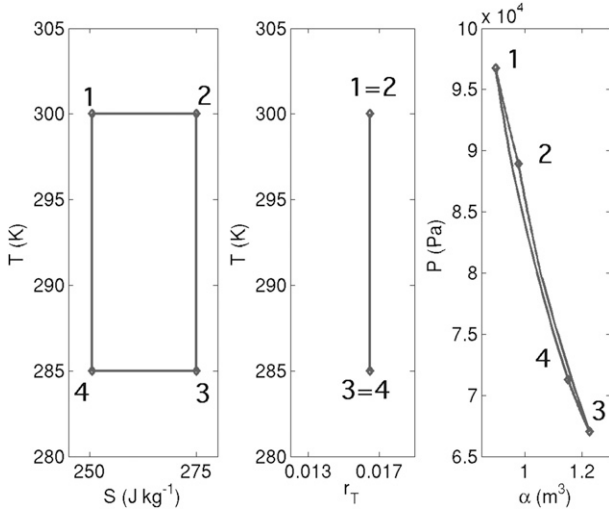
FIG. 1. Idealized representation of the Carnot cycle: (left) temperature T and entropy S through the cycle; (middle) mixing ratio for total water r_T and temperature T; and (right) specific volume α and pressure p. The numbers 1–4 indicate the different stages of the cycle. See text for details.

FIG. 2. As in Fig. 1, but for the steam cycle.

volume α_d as a function of the entropy, total mixing ratio, and pressure. This is commonly done in numerical models but requires a cumbersome inversion of the equation of state. A much easier approach is to use (4) to obtain the mechanical output from the changes in entropy and water content.

The total water content is constant during the entire Carnot cycle, even though its partitioning between water vapor and liquid water might vary. Hence, the second integral on the right-hand side of (4) vanishes. Furthermore, the entropy is constant through the adiabatic expansion (second transformation; $2 \rightarrow 3$) and compression (fourth transformation; $4 \rightarrow 1$). The total work by the Carnot cycle is thus given by

$$W = \oint T\,dS = \int_1^2 T\,dS + \int_3^4 T\,dS$$
$$= T_{\text{in}}(S_2 - S_1) + T_{\text{out}}(S_4 - S_1) = (T_{\text{in}} - T_{\text{out}})\Delta S, \quad (8)$$

with $\Delta S = (S_2 - S_1) = (S_3 - S_4)$, the entropy difference between the two adiabatic transformations. Only the first transformation $(1 \rightarrow 2)$ is associated with a net heating, and the energy input is

$$Q_{\text{in}} = \int_1^2 T\,dS = T_{\text{in}}\Delta S. \quad (9)$$

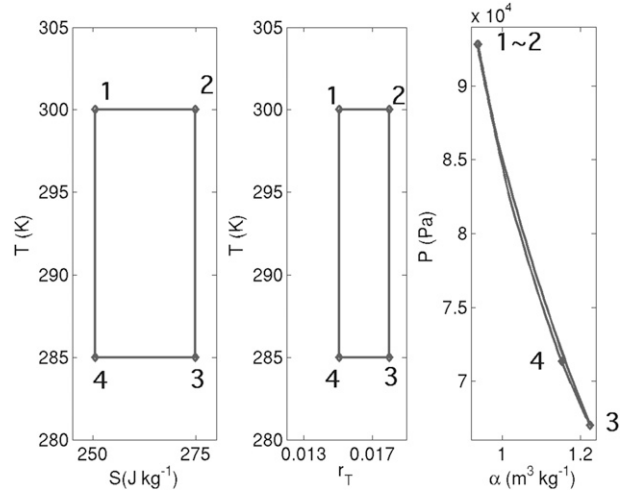Dividing the work by the energy input yields the classic Carnot efficiency,

$$\eta_C = \frac{W}{Q_{\text{in}}} = \frac{T_{\text{in}} - T_{\text{out}}}{T_{\text{in}}}. \quad (10)$$

c. Steam cycle

A steam cycle transports water vapor from a warm moist source to a colder, dryer sink. As such, it can be viewed as a Carnot cycle in which the energy source and sink are associated with the addition and removal of water vapor and thus of latent heat. The thermodynamic diagrams associated with this cycle are presented in Fig. 2. The four steps of the steam cycle are as follows:

- $1 \rightarrow 2$: isothermal expansion and moistening by adding water vapor at constant temperature T_{in} (this step is done without any addition of sensible heat);
- $2 \rightarrow 3$: adiabatic expansion from p_2 to p_3 at constant entropy $S_2 = S_3$ and total water content $r_{T2} = r_{T3}$;
- $3 \rightarrow 4$: isothermal drying and compression at constant temperature T_{out}; and
- $4 \rightarrow 1$: adiabatic compression from p_4 to p_1 at constant entropy $S_4 = S_1$ and total water content $r_{T4} = r_{T1}$.

A key difference between the steam cycle and the Carnot cycle is that the former is an open cycle in which mass is added and removed. When computing the work of a steam cycle, one must include the second term on the right-hand side of (3). It depends on the free energy of water vapor which is given by (A6) in appendix A,

$$g_v = C_l\left(T - T_0 - T\ln\frac{T}{T_0}\right) + R_v T\,\ln\mathcal{H} = 0. $$

The work performed by the cycle is obtained through (4),

$$W = \oint T \, dS + \oint g_v \, dr_T$$
$$= (T_{in} - T_{out})\Delta S + (\overline{g}_{v,in} - \overline{g}_{v,out})\Delta r_T. \quad (11)$$

The averaged chemical potentials $\overline{g}_{v,in}$ and $(T_{in} - T_{out})\Delta S \geq 0$, during the moistening and drying stages are defined as

$$\overline{g}_{v,in} = \frac{1}{\Delta r_T} \int_1^2 g_v \, dr_T \quad \text{and} \quad (12a)$$

$$\overline{g}_{v,out} = -\frac{1}{\Delta r_T} \int_3^4 g_v \, dr_T. \quad (12b)$$

Similarly, the surface heating is given by

$$Q_{in} = \int_1^2 T \, dS + \int_1^2 g_v \, dr_T = T_{in}\Delta S + \overline{g}_{v,in}\Delta r_T = L_v \Delta r_T. \quad (13)$$

Equation (13) results from the fact that the heating during the first transformation ($1 \rightarrow 2$) is due solely to latent heat of vaporization. The entropy change can be written as

$$\Delta S = \frac{L_v - \overline{g}_{v,in}}{T_{in}} \Delta r_T.$$

Used in (11), this yields

$$W = \frac{T_{in} - T_{out}}{T_{in}}(L_v - \overline{g}_{v,in})\Delta r_T + (\overline{g}_{v,in} - \overline{g}_{v,out})\Delta r_T$$
$$= \frac{T_{in} - T_{out}}{T_{in}} L_v \Delta r_T + \left(\frac{T_{out}}{T_{in}}\overline{g}_{v,in} - \overline{g}_{v,out}\right)\Delta r_T. \quad (14)$$

The efficiency of the steam cycle can be obtained by dividing (14) by (13),

$$\eta_S = \frac{W}{Q_{in}} = \frac{T_{in} - T_{out}}{T_{in}} + \frac{\dfrac{T_{out}}{T_{in}}\overline{g}_{v,in} - \overline{g}_{v,out}}{L_v}. \quad (15)$$

The first term on the right-hand side corresponds to the Carnot efficiency, whereas the second term is related to the Gibbs free energy of water vapor.

Expression (15) can be further simplified if one neglects the heat capacity of liquid water $C_1 \cong 0$ and of water vapor $C_{pv} \cong 0$. In this case, the free energy of liquid water vanishes $g_1 \cong 0$, and the free energy of water vapor is $g_v \cong R_v T \ln H$. For simplicity, the approximation $C_1 \cong 0$ will be used for explicit computation in this paper and will be indicated by use of the approximately equal to sign ($\cong$). Note that taking simultaneously $C_1 \cong 0$ and $C_{pv} \cong 0$ implies that the latent heat of vaporization L_v is

independent of temperature. The analysis of the steam cycle for $C_1 \neq 0$ is discussed in appendix B and does not differ significantly. Under the assumption $C_1 \cong 0$, the Gibbs free energy can be written as

$$\overline{g}_{v,in} \cong R_v T_{in} \ln\overline{\mathcal{H}}_{in} \quad \text{and} \quad (16)$$

$$\overline{g}_{v,out} \cong R_v T_{out} \ln\overline{\mathcal{H}}_{out}, \quad (17)$$

with $\overline{\mathcal{H}}_{in}$ and $\overline{\mathcal{H}}_{out}$ the average relative humidity during the moistening and drying stages. The efficiency (15) is given by

$$\eta_S \cong \frac{T_{in} - T_{out}}{T_{in}} + \frac{R_v T_{out}}{L_v} \ln\frac{\overline{\mathcal{H}}_{in}}{\overline{\mathcal{H}}_{out}}. \quad (18)$$

In the case of a saturated cycle, we have $\overline{\mathcal{H}}_{in} = \overline{\mathcal{H}}_{out} = 1$. It follows that a saturated steam cycle has the same efficiency as a Carnot cycle,

$$\eta_{S,sat} \cong \frac{T_{in} - T_{out}}{T_{in}} = \eta_C.$$

For an unsaturated steam cycle however, the efficiency depends on the ratio $\overline{\mathcal{H}}_{in}/\overline{\mathcal{H}}_{out}$. The relative humidity of moist air increases as it expands adiabatically, $(\partial\mathcal{H}/\partial p)_{S,r_T} \leq 0$ [for a proof, see Emanuel (1994)]. In a heat engine, the energy source is not only warmer than the sink, $T_{in} > T_{out}$, but also at a higher pressure. Therefore, the relative humidity at the source is always lower or equal to the relative humidity at the sink, $\overline{\mathcal{H}}_{in} \leq \overline{\mathcal{H}}_{out}$. The second term on the right-hand side of (18) is always negative: the efficiency of a steam cycle is lower than or equal to the Carnot efficiency,

$$\eta_S \leq \eta_C = \frac{T_{in} - T_{out}}{T_{in}}.$$

The equality only occurs in the case of a steam cycle working at saturation (i.e., for $\overline{\mathcal{H}}_{in} = \overline{\mathcal{H}}_{out} = 1$).[1]

The efficiency of a steam cycle depends on relative humidity: two different steam cycles transporting the same amount of water across the same temperature difference can produce different amounts of work depending on the relative humidities $\overline{\mathcal{H}}_{in}$ and $\overline{\mathcal{H}}_{out}$ at which they are operating. Figure 3 shows the efficiency of a steam cycle working between a warm source at $T_{in} = 300$ K and a cold sink at $T_{out} = 285$ K as function of r_T during the moistening step. The pressure during the moistening

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[1] It is possible to obtain $n_s > n_c$ when the heat capacity of liquid water is included, as discussed in appendix B.
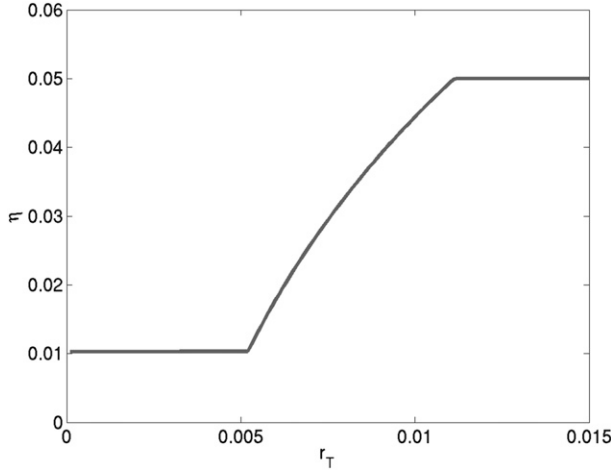
FIG. 3. Efficiency of a steam cycle as function of $\bar{r}_{T,\text{in}}$ during the moistening stage, assuming $T_{\text{in}} = 300$ K, $T_{\text{out}} = 285$ K, and $P_{\text{in}} = 1000$ mb.

stage is set at 1000 mb. The pressure during the drying stage depends on the amount of water vapor in the cycle. For these calculations, the change in mixing ratio is assumed to be small in comparison to the water content $\Delta r_T \ll r_T$ so that the relative humidity can be assumed to be constant during the moistening and drying stages. In Fig. 3, it is possible to distinguish between three regimes: an unsaturated regime at low value of the mixing ratio ($\overline{\mathcal{H}}_{\text{in}} < \overline{\mathcal{H}}_{\text{out}} < 1$); a partially saturated regime, in which the drying stage becomes saturated ($\overline{\mathcal{H}}_{\text{out}} = 1$) but the moistening stage is not ($\overline{\mathcal{H}}_{\text{in}} < 1$); and a saturated regime, when both the moistening and drying stages are saturated ($\overline{\mathcal{H}}_{\text{in}} = \overline{\mathcal{H}}_{\text{out}} = 1$). In the unsaturated regime, the efficiency is the lowest and almost constant. Once the drying stage becomes saturated, the efficiency rapidly increases with the amount of water in the cycle. Finally, once the cycle is fully saturated, the efficiency remains constant and is equal to the Carnot efficiency.

An alternative expression for the efficiency (18) can be obtained that emphasizes changes in the partial pressure of water vapor. First, one can take advantage of the Clausius–Clapeyron relationship to rewrite

$$\ln\frac{\overline{\mathcal{H}}_{\text{in}}}{\overline{\mathcal{H}}_{\text{out}}} = \ln\frac{\bar{e}_{\text{in}}}{\bar{e}_{\text{out}}} - \ln\frac{e_s(T_{\text{in}})}{e_s(T_{\text{out}})}$$
$$= \ln\frac{\bar{e}_{\text{in}}}{\bar{e}_{\text{out}}} + \frac{L_v}{R_v}\left(\frac{1}{T_{\text{in}}} - \frac{1}{T_{\text{out}}}\right).$$

Here, $\bar{e}_{\text{in}}$ and $\bar{e}_{\text{out}}$ are the average partial pressures of water vapor during the moistening and drying stages. Introducing this into (18), the efficiency becomes

$$\eta_S \cong \frac{R_v T_{\text{out}}}{L_v} \ln\frac{\bar{e}_{\text{in}}}{\bar{e}_{\text{out}}}. \tag{19}$$

The amount of work performed by a steam cycle is thus given by

$$W \cong R_v T_{\text{out}} \ln\frac{\bar{e}_{\text{in}}}{\bar{e}_{\text{out}}} \Delta r_T. \tag{20}$$

This is the work that would be produced by expanding a mass Δr_T of water vapor from a pressure $\bar{e}_{\text{in}}$ to a pressure $\bar{e}_{\text{out}}$ at constant temperature T_{out}. However, this does not imply that the work performed by a steam cycle is done solely by the water vapor. Rather, this reflects the fact that the same thermodynamic forcing—the injection of water vapor at high partial pressure and its removal at a lower partial pressure—would result in the same mechanical output.

The logarithm in (19) can be written as

$$\ln\frac{\bar{e}_{\text{in}}}{\bar{e}_{\text{out}}} = \ln\frac{\bar{p}_{d,\text{in}}}{\bar{p}_{d,\text{out}}} + \ln\frac{\bar{r}_{\text{in}}}{\bar{r}_{\text{out}}}, \tag{21}$$

with $\bar{r}_{\text{in}}$ and $\bar{r}_{\text{out}}$ being the averaged mixing ratios (for water vapor not total water) during the moistening and drying stages and $\bar{p}_{d,\text{in}}$ and $p_{d,\text{out}}$ being the mean partial pressure for dry air during the moistening and drying stages. In an unsaturated steam cycle, the mixing ratio is equal to the total water mixing ratio, which implies that $\bar{r}_{\text{in}} = \bar{r}_{\text{out}}$. The efficiency η_S can then be approximated by

$$\eta_{S,\text{unsat}} \cong \frac{R_v T_{\text{out}}}{L_v} \ln\frac{\bar{p}_{d,\text{in}}}{\bar{p}_{d,\text{out}}} \approx \frac{R_v C_{pd} T_{\text{in}}}{R_d L_v} \ln\frac{T_{\text{in}}}{T_{\text{out}}}$$
$$\approx \frac{T_{\text{in}}}{1540\,\text{K}} \frac{T_{\text{in}} - T_{\text{out}}}{T_{\text{in}}} + O\left[\left(\frac{T_{\text{in}} - T_{\text{out}}}{T_{\text{in}}}\right)^2\right] \tag{22}$$

after using the relationship between the pressure and temperature $C_{pd} \ln T = R_d \ln p$ for a dry adiabat and the Taylor expansion for the logarithm. For Earth-like conditions, the efficiency of a fully unsaturated steam cycle lies between one-sixth and one-fifth of the Carnot efficiency.

3. Mechanical work in a mixed steam–Carnot cycle

Here, we construct a mixed steam–Carnot cycle to account for the fact that the atmosphere is heated up through a combination of sensible and latent heat fluxes. This cycle is illustrated on Fig. 4 and is composed of the following four steps:

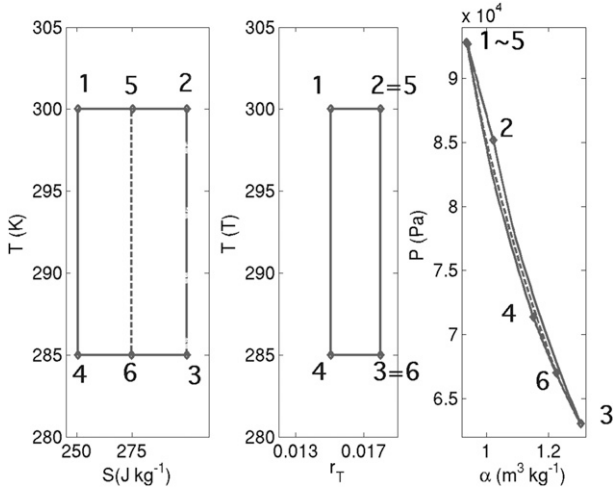• $1 \rightarrow 2$: isothermal moistening and expansion at constant temperature T_{in};

FIG. 4. As in Fig. 1, but for the mixed steam–Carnot cycle. The numbers 1–6 indicate the different stages of the cycle. See text for details.

- $2 \rightarrow 3$: adiabatic expansion from p_2 to p_3 at constant entropy $S_2 = S_3$ and water content $r_{T2} = r_{T3}$;
- $3 \rightarrow 4$: isothermal drying and compression at constant temperature $T_{out} = T_3 = T_4$; and
- $4 \rightarrow 1$: adiabatic compression from p_4 to p_1 at constant entropy $S_4 = S_1$ and water content $r_{T4} = r_{T1}$.

The energy input Q_{in} can be subdivided into a latent energy input,

$$Q_{lat} = L_v \Delta r_T,$$

and a sensible energy input,

$$Q_{sen} = \int_1^2 T\, dS + \int_1^2 (g_v - L_v)\, dr_T.$$

The Bowen ratio B is defined as the ratio of the sensible energy input to the latent energy input,

$$B = \frac{Q_{sen}}{Q_{lat}}. \tag{23}$$

This cycle can be decomposed into two subcycles by introducing two intermediary states 5 and 6. State 5 is obtained by an isothermal moistening of state 1 by adding an amount Δr_T of water vapor, and state 6 is obtained by a similar isothermal moistening of state 4. The cycle 1–5–6–4 is a steam cycle with energy input Q_{lat}, and the cycle 5–2–3–6 corresponds to a Carnot cycle with energy input Q_{sen}. The work done by the whole cycle is thus

$$W = \eta_S Q_{lat} + \eta_C Q_{sen}. \tag{24}$$
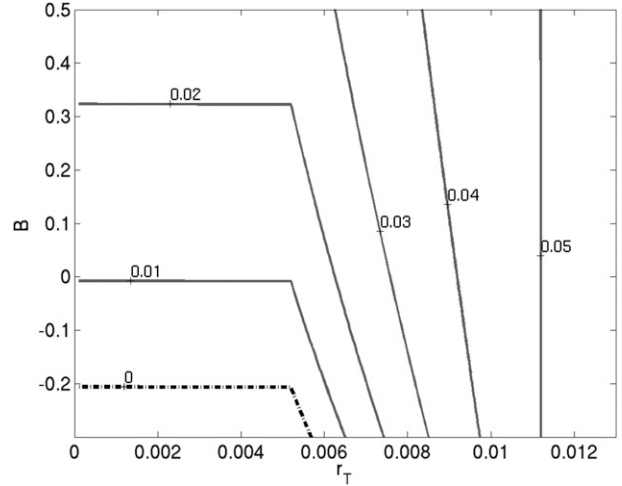

FIG. 5. Efficiency of a mixed steam–Carnot cycle as function of $\bar{r}_{T,in}$ and B, assuming $T_{in} = 300$ K, $T_{out} = 285$ K, and $P_{in} = 1000$ mb.

The efficiency is obtained by dividing (24) by $Q_{in} = Q_{lat} + Q_{sen}$, which yields

$$\eta_{mix} = \frac{1}{1+B}\eta_S + \frac{B}{1+B}\eta_C$$
$$\cong \frac{T_{in} - T_{out}}{T_{in}} - \frac{1}{1+B}\frac{R_v T_{out}}{L_v}\ln\frac{\overline{\mathcal{H}}_{in}}{\overline{\mathcal{H}}_{out}}. \tag{25}$$

This efficiency depends on the temperatures T_{in} and T_{out}, B, and $\overline{\mathcal{H}}_{in}$ and $\overline{\mathcal{H}}_{out}$.

Figure 5 shows the efficiency of a mixed cycle operating between $T_{in} = 300$ K and $T_{out} = 285$ K as a function of the Bowen ratio and r_T. When the cycle is saturated, the efficiency is equal to the Carnot efficiency. Otherwise, efficiency increases with both Bowen ratio and humidity. A mixed cycle can still produce mechanical work for a negative Bowen ratio. In such case, the cycle transports sensible energy from cold to warm, although the total energy (sensible plus latent) transport is still from warm to cold. This configuration can be viewed as a steam cycle that drives a reverse Carnot cycle. The minimal value of the Bowen ratio at which the efficiency of the mixed cycle remains positive is

$$B_{min} = -\frac{\eta_C}{\eta_S}.$$

The work done by the mixed steam–Carnot cycle is given by

$$\eta_{mix}(Q_{sen} + Q_{lat})$$
$$\cong \left(\frac{T_{out} - T_{in}}{T_{out}} + \frac{1}{1+B}\frac{R_v T_{out}}{L_v}\ln\frac{\overline{\mathcal{H}}_{in}}{\overline{\mathcal{H}}_{out}}\right)Q_{in}. \tag{26}$$

Expression (26) offers a quantitative assessment of the factors that determine the work done in a moist atmosphere, measured in terms of its production of mechanical energy. The factors that control the work are as follows:

- the energy flux Q_{in};
- the depth of convection measured in terms of the temperature difference and the corresponding Carnot efficiency $\eta_C = (T_{in} - T_{out})/T_{in}$;
- the ratio of sensible to latent heating, that is, the Bowen ratio B; and
- the degree of saturation, quantified through $\overline{\mathcal{H}}_{in}/\overline{\mathcal{H}}_{out}$.

The first two controlling factors, total energy flux and depth of convection, are the same as what would be expected for a Carnot cycle and imply that more mechanical work is produced by deeper convection and larger energy transport.

4. Efficiency, free energy, and irreversible entropy production

The work done by a steam cycle depends on relative humidity. In a steam cycle, condensation in the steam cycle occurs during the adiabatic expansion, whereas reevaporation occurs during both the drying and adiabatic compression so that the latent heat release by condensation occurs on average at a warmer temperature than its consumption by reevaporation. Such distribution of latent heat release is compensated for by an enhanced transport of sensible heat from warm to cold, which explains the enhanced mechanical work in a saturated cycle.

Although this explanation offers a good qualitative intuition, it has several limitations. First, from a conceptual point of view, latent heat release is not an external energy source but corresponds to an internal energy conversion. One must address the question of how an internal process can affect the mechanical work produced by a thermodynamic system. Second, this intuition does not necessarily provide the correct quantitative answer. For instance, it does not explain why an unsaturated steam cycle generates mechanical work. Third, although exact computations of the work based on the distribution of latent heat release are feasible, they require nontrivial calculations for the condensation and evaporation rates, which is akin to computing the work based on (1).

This section offers two complementary explanations for why relative humidity affects the mechanical efficiency of a steam cycle. The first interpretation focuses on the increase in the Gibbs free energy of water as it is transported from the moist source to the dry sink. The second interpretation views the steam cycle as an irreversible heat engine, in which the irreversibility is associated with the exchange of water vapor between the cycle and the moisture source and sink. These two explanations are tied together because of the close relationship between internal entropy production and Gibbs free energy.

a. Thermodynamic forcing and Gibbs free energy

The steam cycle is an open system that exchanges water with its environment. The thermodynamic forcing depends on the properties of water when it is added or removed. Equation (11) provides a general expression for the mechanical work by an idealized thermodynamic cycle,

$$W = (T_{in} - T_{out})\Delta S + (\overline{g}_{v,in} - \overline{g}_{v,out})\Delta r_T. \qquad (27)$$

The first term on the right-hand side is the work done by a Carnot cycle. The second term accounts for the change in the free energy of the water vapor as it is transported by the cycle.

For an isothermal system, with $T_{in} = T_{out}$, the work is equal to the change in free energy, $W = (\overline{g}_{v,in} - \overline{g}_{v,out})\Delta r_T$. The free energy can be interpreted as the amount of enthalpy that can freely be converted into mechanical energy in an isothermal transformation. A direct application of this is the work associated with the isothermal expansion of mass Δr_T of water vapor. The free energy formula yields

$$W = (\overline{g}_{v,in} - \overline{g}_{v,out})\Delta r_T = R_v T_{out}(\ln\overline{\mathcal{H}}_{in} - \ln\overline{\mathcal{H}}_{out})\Delta r_T$$
$$= R_v T_{out} \ln\frac{e_{in}}{e_{out}}\Delta r_T,$$

which corresponds to the expression for work done by the isothermal expansion of an ideal gas.

The relative humidity at the moist source is always lower or equal to the relative humidity at the dry sink, $\overline{\mathcal{H}}_{in} \leq \overline{\mathcal{H}}_{out}$. As a result, the free energy of water vapor is lower when it is injected than when it is removed,

$$\overline{g}_{v,in} - \overline{g}_{v,out} \leq 0. \qquad (28)$$

The steam cycle acts to increase the free energy of water vapor. However, as implied by (11), this requires a positive thermodynamic forcing associated with the entropy transport, $(T_{in} - T_{out})\Delta S \geq 0$, and reduces the work produced by the system. As the degree of saturation of the steam cycle increases, the free energy of the water vapor injected at the moist source increases; the penalty for raising this free energy from its surface value $\overline{g}_{v,in}$ to its value at the dry sink $\overline{g}_{v,out}$ is reduced, and the work produced by the cycle increases accordingly.
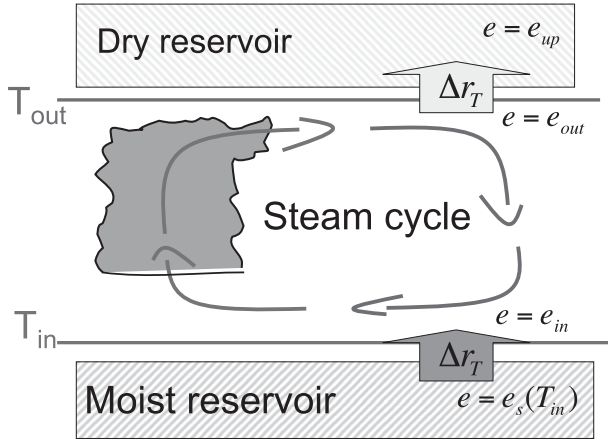
FIG. 6. Schematic representation of the thermodynamic system discussed in section 4b. A given amount of water vapor Δr_T is transferred from a moist reservoir to a steam cycle at warm temperature T_{in}. The cycle then carries this water vapor to a lower temperature T_{out}, where it is diffused into a dry reservoir. See text for details.

b. The steam cycle as an irreversible heat engine

In an isothermal transformation, the change in the free energy provides an upper bound in the amount of mechanical energy that can be extracted. There is, however, no guarantee that a given system will be able to convert any of this free energy into mechanical energy. To illustrate this, one can contrast isothermal expansion with diffusion. The expansion of Δr_T produces $W = (g_1 - g_2)\Delta r_T$: all the free energy is indeed converted into mechanical work. In contrast, if water vapor is diffused rather than allowed to expand, no mechanical work is produced. In this case, the reduction in free energy does not result in a mechanical output but is associated with irreversible entropy production in agreement with the second law of thermodynamics.

Consider a thermodynamic system described in Fig. 6. This system is composed of the steam cycle and two reservoirs that act as the warm source and cold sink for the cycle. Explicitly including the warm and moist reservoirs allows us to treat the exchange of water vapor as internal processes and to take into account the internal entropy production by diffusion. The warm reservoir contains liquid water at T_{in}, and the cold reservoir contains air at T_{out} and partial pressure of water vapor e_{up}. A mass of water vapor Δr_T evaporates adiabatically in the warm reservoir and then is injected during the moistening stage of the steam cycle. The cycle adiabatically expands moist air to T_{out}, and the water vapor is then diffused from the cycle to the cold reservoir. The two reservoirs are assumed to be large enough so that T_{in}, T_{out}, and e_{up} remain constant.

These transformations result into two effects: water vapor is transported from the warm source to the cold sink, and work is produced on an external environment. Furthermore, evaporation is treated as an adiabatic process, with the energy taken from the warm reservoir. This implies that, although total mass and energy are exchanged between the different subsystems, the total energy is constant (neglecting the variations of latent heat with temperature). Because the cycle is producing W, the system requires an external energy source Q, with

$$Q = W. \tag{29}$$

In the construction of the humidifier cycle, it is assumed in (13) that the surface heating is due solely to the latent heat flux, without any addition of sensible heat. It ensues that the additional Q takes place during the drying stage of the steam cycle: that is, at T_{out}.

The second law of thermodynamics applied to this system can be written as

$$\Delta S_{\mathrm{tot}} = \frac{Q}{T_{\mathrm{out}}} + \Delta S_{\mathrm{irr}}. \tag{30}$$

Here, ΔS_{tot} is the total change of entropy in the system and ΔS_{irr} is the irreversible entropy production. The entropy change associated with the external energy source is given by Q divided by the temperature at which it occurs: T_{out} here. Using (29), the entropy budget can be rewritten as

$$W = T_{\mathrm{out}}\Delta S_{\mathrm{tot}} - T_{\mathrm{out}}\Delta S_{\mathrm{irr}}. \tag{31}$$

The first term on the right-hand side of (31) is the maximum work that would be performed by a reversible system. The second term is the reduction of the mechanical output associated with the internal irreversibilities in the system.

We can obtain ΔS_{tot} by computing the change in each of the subsystems. Because the steam cycle functions in a cycle, its entropy does not change. The entropy changes of the lower and upper reservoir are given by the mass of the water vapor added or removed multiplied by its specific entropy. The total entropy change is

$$\Delta S_{\mathrm{tot}} \cong -\frac{L_v}{T_{\mathrm{in}}}\Delta r_T + \left[\frac{L_v}{T_{\mathrm{out}}} - R_v \ln\frac{e_{\mathrm{up}}}{e_s(T_{\mathrm{out}})}\right]\Delta r_T$$
$$\cong -R_v \ln\frac{e_{\mathrm{up}}}{e_s(T_{\mathrm{in}})}\Delta r_T, \tag{32}$$

after using the Clausius–Clapeyron relationship under the approximation $C_l \cong 0$. The total change of entropy in

the system corresponds to the entropy increase resulting from transforming Δr_T at T_{in} and partial pressure $e_s(T_{in})$ into water vapor at T_{out} and e_{up}.

Although the transformations associated with the steam cycle are reversible, exchanging water vapor between the cycle and the two reservoirs is not. The irreversible entropy production associated with the diffusion at constant temperature of a mass Δr_T from a partial pressure e_1 to a partial pressure e_2 is given by $R_v \Delta r_T \ln(e_1/e_2)$. The irreversible entropy productions $\Delta S_{irr,low}$ and $\Delta S_{irr,up}$ due to diffusion of water vapor between the lower reservoir and the steam cycle and between the steam cycle and the upper reservoir are given by

$$\Delta S_{irr,low} = -\Delta r_T R_v \ln\frac{\overline{e}_{in}}{e_s(T_{in})} \quad \text{and} \quad (33a)$$

$$\Delta S_{irr,up} = \Delta r_T R_v \ln\frac{\overline{e}_{out}}{e_{up}}. \quad (33b)$$

The total work can then be obtained by using (32), (33a), and (33b) in (31),

$$W = T_{out}(\Delta S_{tot} - \Delta S_{irr,low} - \Delta S_{irr,up})$$
$$= \Delta r_T R_v T_{out}\left[\ln\frac{e_s(T_{in})}{e_{up}} - \ln\frac{e_s(T_{in})}{\overline{e}_{in}} - \ln\frac{\overline{e}_{out}}{e_{up}}\right]$$
$$= \Delta r_T R_v T_{out} \ln\frac{\overline{e}_{in}}{\overline{e}_{out}}. \quad (34)$$

This is equal to the work of a steam cycle, (19).

The impact of saturation on the efficiency can be discussed through its impacts on internal entropy production. The total entropy production due to diffusion is given by summing (33a) and (33b),

$$\Delta S_{irr} = \Delta r_T R_v \ln\frac{e_s(T_{in})}{e_{up}} - \Delta r_T R_v \ln\frac{\overline{e}_{in}}{\overline{e}_{out}}$$
$$= \Delta S_{tot} - \Delta r_T R_v \ln\frac{\overline{e}_{in}}{\overline{e}_{out}}. \quad (35)$$

The first term is the total change of entropy in the system, and it depends only on the state of the water source and sink. It is also equal to the total entropy production that would occur if water vapor were to directly diffuse from its source to its sink without the intervention of the steam cycle. The second term is the reduction in irreversible entropy production due to the presence of the steam cycle. As implied by the irreversible heat engine framework (31), such a reduction of the internal entropy production also translates into an increase in W. The ability of the steam cycle to reduce the internal entropy

production is tied to the fact that the partial pressure of water vapor in the cycle is smaller during the moistening stage than during the drying stage: that is, $\overline{e}_{out}/\overline{e}_{in} < 1$. In particular, because the partial pressure of water pressure decreases more rapidly for a saturated adiabat than for an unsaturated adiabat, it ensues that a saturated cycle corresponds to a larger reduction in entropy production than an unsaturated cycle and hence can produce more mechanical work.[2]

The two discussions of the work of the steam cycle presented in this section—in terms of free energy and in terms of internal entropy production—are closely related. In isothermal diffusion, the irreversible entropy production δS_{irr} per unit of mass of water vapor diffused is equal to the difference in free energy between the initial and final states divided by the temperature,

$$\delta S_{irr} = \frac{g_i - g_f}{T} = R_v \ln\frac{e_i}{e_f},$$

where g_i and g_f are the free energy of the water vapor in its initial and final states and e_i and e_f are its partial pressure. Because the steam cycle transports water vapor from warm to cold, it also increases its free energy at the expense of the mechanical output. In theory, this additional free energy could potentially be used to recover the mechanical work, for example by expanding the water vapor. However, when water vapor is diffused into the environment, any free energy that the water gained in the steam cycle is wasted, resulting in a larger internal entropy production. By increasing the relative humidity in the steam cycle, it is possible to reduce the amount of waste and thus to increase the mechanical output of the cycle.

5. Conclusions

In many phenomena, such as convection, hurricanes, or the global circulation, the atmosphere acts as a heat engine that generates kinetic energy by transporting energy from a warm source to a cold sink. However, the work produced by such flows depends critically on the

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[2] It should also be noted that expression for the internal entropy production (35) only include the entropy production because of the exchange between the steam cycle and its environment, consistently with the assumption that the idealized steam cycle is fully reversible. However, if one were to include irreversible processes within the cycle (e.g., associated with diffusion of water vapor between updraft and downdraft), this would lead to an additional production of entropy and thus a decrease in the mechanical work in the system. The reader can refer to Pauluis and Held (2002a) for a more complete discussion of the impacts of internal entropy production on moist convection.

presence of water vapor in the atmosphere. Previous studies (Pauluis and Held 2002a,b; Goody 2003) have shown that the work produced by moist convection is significantly less than what would be expected in dry convection. This paper introduces a novel thermodynamic cycle, the steam cycle, to assess the impacts of water vapor on mechanical work. A steam cycle generates mechanical work by transporting water vapor from a warm moist source to a dry cold sink. The amount of work produced by a steam cycle depends on the relative humidity; it is the lowest for an unsaturated cycle and gradually increases to reach that of a Carnot cycle when all transformations occur at saturation.

The steam and Carnot cycles can be combined into a mixed cycle that is driven by a combination of latent and sensible heating. The work produced by a mixed cycle given by (26) depends on four key factors: the surface energy flux Q_{in}; the depth of convection measured by the temperature difference across the convective layer $T_{in} - T_{out}$; the Bowen ratio B; and the degree of saturation of the cycle, quantified through the ratio $\overline{\mathcal{H}}_{in}/\overline{\mathcal{H}}_{out}$. The first two controlling factors, energy flux and temperature difference, are the same factors that control the work of a Carnot cycle. All other things being equal, the deeper the convection and the larger the energy transport, the more work and kinetic energy will be produced. The last two controlling factors, the Bowen ratio and saturation, reflect the fact that a steam cycle is less efficient than a Carnot cycle working between the same energy source and sink.

A particular insight from the expression (26) for the total work done by convection lies in the impacts of the atmospheric humidity and its implications for extreme weather. For instance, the potential intensity theory for hurricanes (Emanuel 1986) is consistent with a mechanical efficiency on the order of $\frac{1}{3}$ for surface heating in the eyewall. To achieve such a high efficiency, the circulation must transport energy to a very low temperature $T_{out} \approx$ 200 K typical of the tropical tropopause. In addition, because the Bowen ratio in a hurricane is small, relative humidity must be close to unity to prevent any reduction of the work done in an unsaturated cycle. The efficiency implied by the potential intensity theory (Emanuel 1986) thus requires the eyewall to be fully saturated, with no entrainment of unsaturated air. More generally, the behavior of the mixed Carnot–steam cycle indicates that convective activity should be favored in regions where the relative humidity of the troposphere is high.

These results should be put in the broader context of the role of moist processes in the entropy balance of the atmosphere. Pauluis and Held (2002a,b) argue that moist convection acts both as a heat engine that produces mechanical work by transporting energy from

warm to cold and as a dehumidifier that continuously removes water vapor through condensation and precipitation. These two aspects are in competition with each other, in the sense that the amount of work generated by convection is limited by how much it behaves as a dehumidifier, which can be quantified by the internal entropy production due to diffusion of water vapor and irreversible evaporation. The steam cycle illustrates this fundamental aspect of moist atmospheres. Indeed, in section 4, it is shown how the ability of a steam cycle to produce more mechanical work at high relative humidity is tied to its ability to reduce the internal production of entropy due to diffusion. On a global level, this finding also shows how nonprecipitating convection can modulate the amount of entropy produced by diffusion of water vapor and, in doing so, allows for the atmosphere to sustain stronger circulations than if the moistening of dry air was solely done through diffusion from the ocean surface. This also unambiguously confirms that the hydrologic cycle plays a central role in determining the amount of work that is generated and dissipated in a moist atmosphere.

APPENDIX A

Thermodynamic Properties of Moist Air

Moist air is treated as an ideal mixture of dry air, water vapor, and condensed water. Dry air and water vapor behave as perfect gases, whereas the volume of liquid water is neglected. Under these conditions, the specific enthalpies of dry air h_d, water vapor h_v, and liquid water h_l are given by

$$h_d = C_{pd}(T - T_0), \tag{A1a}$$

$$h_l = C_l(T - T_0), \quad \text{and} \tag{A1b}$$

$$h_v = C_l(T - T_0) + L_v. \tag{A1c}$$

Here, T is the temperature; T_0 is an arbitrary reference temperature; C_{pd} and C_l are the specific heat at constant pressure of dry air and liquid water, respectively; and L_v

is the latent heat of vaporization. The latent heat of vaporization itself is function of temperature, with $L_v = L_{v_0} + (C_{pv} - C_l)(T - T_0)$, where C_{pv} is the specific heat of water vapor at constant pressure. The specific entropies of dry air s_d, water vapor s_v and liquid water s_l are given by

$$s_d = C_{pd} \ln\frac{T}{T_0} - R_d \ln\frac{p_d}{p_0}, \qquad \text{(A2a)}$$

$$s_l = C_l \ln\frac{T}{T_0}, \quad \text{and} \qquad \text{(A2b)}$$

$$s_v = C_l \ln\frac{T}{T_0} + \frac{L_v}{T} - R_v \ln\mathcal{H}. \qquad \text{(A2c)}$$

Here, p_d is the partial pressure of dry air, p_0 is arbitrary reference pressure, R_d and R_v are the ideal gas constant for dry air and water vapor. The relative humidity $\mathcal{H} = e/e_s$ is the ratio of the partial pressure of water vapor e to the saturation vapor pressure e_s. The enthalpy H and entropy S per unit mass of dry air are given by

$$H = h_d + rh_v + r_l h_l$$
$$= (C_{pd} + r_T C_l)(T - T_0) + rL_v \quad \text{and} \qquad \text{(A3)}$$

$$S = s_d + rs_v + r_l s_l$$
$$= (C_{pd} + r_T C_l) \ln\frac{T}{T_0} - R_d \ln\frac{p_d}{p_0} + r\frac{L_v}{T} - rR_v \ln\mathcal{H}, \qquad \text{(A4)}$$

where r, r_l, and $r_T = r + r_l$ are the mixing ratios for water vapor, liquid water, and total water, defined as the ratio of the mass of water vapor, liquid water, or total water to the mass of dry air.

The Gibbs free energy of water vapor g_v and g_l depends on the integration constants in the definition of the specific enthalpy and entropy. For the choices made in (A1b), (A1c), (A2b), and (A2c), we have

$$g_l = h_l - Ts_l = C_l\left(T - T_0 - T\ln\frac{T}{T_0}\right) \quad \text{and} \qquad \text{(A5)}$$

$$g_v = h_v - Ts_v = C_l\left(T - T_0 - T\ln\frac{T}{T_0}\right) + R_v T \ln\mathcal{H}. \qquad \text{(A6)}$$

APPENDIX B

Impacts of the Specific Heat on the Efficiency

The calculations in section 2 assume that the specific heat of liquid water is negligible: $C_l \cong 0$. Here, the efficiency of the steam cycle is determined for constant C_l. The Gibbs free energy of the water vapor now includes a term proportional to C_l,

$$g_v = C_l\left(T - T_0 - T\ln\frac{T}{T_0}\right) + R_v T \ln\mathcal{H}. \qquad \text{(B1)}$$

For simplicity, the reference temperature T_0 is taken to be the temperature of the heat source, $T_0 = T_{\text{in}}$. The work performed by the steam cycle is given by (14). The inclusion of the specific heat term in this expression results in an additional term δW,

$$\delta W = -C_l\left(T_{\text{out}} - T_{\text{in}} + T_{\text{out}}\ln\frac{T_{\text{in}}}{T_{\text{out}}}\right)\Delta r_T. \qquad \text{(B2)}$$

Using the Taylor expansion of ln yields

$$\delta W \approx \frac{1}{2}C_l\frac{(T_{\text{in}} - T_{\text{out}})^2}{T_{\text{out}}}\Delta rT. \qquad \text{(B3)}$$

For $C_l > 0$, the enthalpy transport associated with a constant water flux increases as the temperature decreases. The quantity $(1/2)C_l(T_{\text{in}} - T_{\text{out}})\Delta r_T$ is the mean value of this additional heat transport when the water is transported from T_{in} to T_{out}. The additional work δW can be interpreted as the additional work that would be performed by transporting this additional energy between the energy source at T_{in} and the energy sink at T_{out}.

When this additional work is accounted for, the efficiency for a saturated cycle can be slightly larger than that of the Carnot cycle. This is not a violation of the second law: the Carnot efficiency is an upper bound on the efficiency of a closed cycle, whereas the steam cycle is an open cycle. That the efficiency of the steam cycle obtained when assuming $C_l = 0$ is bound by the Carnot efficiency is however not accidental. Indeed, one can consider a modification to the steam cycle to make it work as a closed cycle. During the drying stage, water vapor, rather than being removed, is transferred to a separate reservoir, where it is forced to condense at constant temperature. This liquid water in this reservoir is then separately brought back to the warm reservoir. During the moistening stage, the liquid water is then evaporated and transferred to the cycle. The work performed by this modified steam cycle is given by

$$W = \oint T\,dS + \oint (g_v - g_l)\,dr, \qquad \text{(B4)}$$

where dr is the change in the mixing ratio for water vapor. The difference between these two Gibbs free energies is

$$g_v - g_l = R_v T \ln \mathcal{H}. \qquad (B5)$$

It is zero when evaporation and condensation occur at saturation but negative during the reevaporation of water at the warm source. Expression (B4) is identical to the work obtained when neglecting the contribution from C_l in the steam cycle, and the efficiency of this modified cycle is given by η_S in (18). This modified cycle is closed, and its efficiency is indeed less or equal to the Carnot efficiency.

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