Phase Changes in the Atmospheric Hydrology Cycle

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Abstract. A natural distillation process as an atmospheric machine in producing fresh water from seawater is of importance to be relearned. This study aims to scrutinize a thermodynamic cycle involving evaporation on sea surface and condensation at a possible height to occur in lower temperature and pressure by comparing reversible and irreversible process. The main stratification of pressure and temperature are obtained from local radiosonde record. The result of this study will give an explanation about how the diabatic process restores the energy to maintain the system equilibrium.

1. Introduction

The global climate results from the interaction between the atmosphere and the ocean with warming from solar radiation, the gravitational force of the earth and the dynamics of the Coriolis force originating from the earth's rotation.[1]Heating occurs in annual and daily cycles, dependence on latitude, and increases by reflecting on the surface of the earth and clouds.[2]The formation of convective clouds in the tropics results in high rainfall in the Indonesian Maritime Continent.[3]These convective clouds in the upper troposphere can release latent heat, which will cause interference with the surrounding atmosphere.

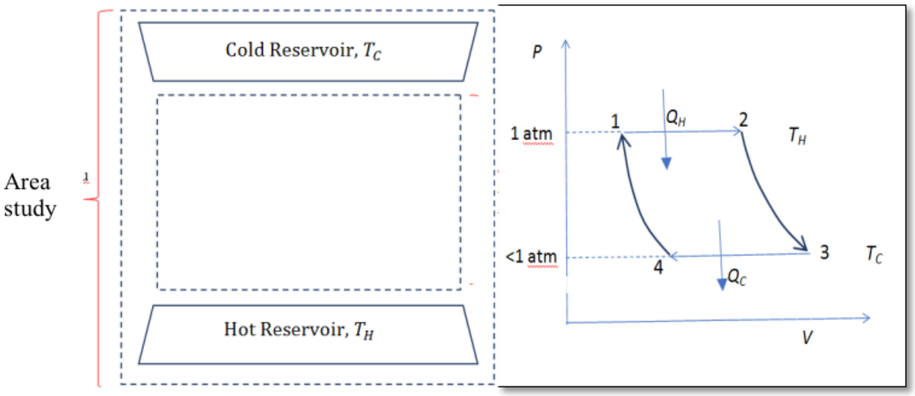
When the moist air rises and the value of the environmental lapse rate is in the range between the adiabatic lapse rate and saturated adiabatic lapse rate, will make the unstable condition of the atmosphere.[4]So the stability of the air is determined by the condition of humidity. Therefore, the amount of annual rainfall, intensity, duration, frequency and distribution of space and time varies greatly. [5]

In daily hydrologic cycles, several evaporation processes, the growth of atmospheric boundary layers, convection and precipitation can be viewed in a thermodynamic framework. [6]In the morning to the afternoon, the height of boundary layer has increased influencing stability on the atmosphere.[7]Several studies have also discussed atmospheric circulation by thermodynamic approaches.[8][9]This makes it possible to associate heat and humidity transport through atmospheric movements assuming maximum thermodynamic efficiency. [10]In addition, to analyze the classification of rain, a formulation of the thermodynamic parameters of the climate is needed.

In the condition of convective and stratiform condensation occurs, parameterization schemes have also been carried out which are used as modeling in predicting numerical fine mesh weather. [11]Parameterization of other atmospheric models has also been carried out in analyzing the properties of single cloud scattering and scaling of optical thickness under conditions of partial blurring.[12]The determination of rainfall also can be found by using ENSO and IOD parameters. [13]But the formulation of the thermodynamic physical parameters regarding the transformation of dry air and water vapor with its interaction with the condensation cells to form clouds is still not much discussed.[14]Therefore, it is necessary to conduct a study on the formulation of climate thermodynamic parameters in the process of rain formation to better understand the physical mechanism of the hydrologic cycle. So, the idealized hydrologic cycle described here is to scrutinize a thermodynamic cycle involving evaporation on the sea surface and condensation at a possible height to occur in lower temperature and pressure.

2. Hydrologic Cycle

A working engine system (ΔW) uses heat from the heat reservoir (ΔQ_{in}) and releases the heat to the cold reservoir (ΔQ_{out}). In 2012, Konings et al. [6]examined the hydrologic cycle between two hot and cold reservoirs. Hot reservoirs are at sea level with temperature $T_H$doing evaporation process, and cold reservoirs at a certain height with temperature T_C doing the condensation process.



(a) (b)

Figure 1. (a) Scoping of the study area. In hot reservoir, the evaporation process takes place with surface temperature T_H, while in the cold reservoir there is a process of condensation with upper temperature over T_C. This process will cause air circulation by involving a phase change from moist air to liquid air. (b)P-V diagram on the quasi-Carnot cycle following by 4 processes.Evaporation, adiabatic expansion, condensation, and compression. On P-V diagram above, the compression occurs diabatically. [15]

2.1. Evaporation

Underwater dome of the p-V diagram on **Figure 1,** transition from state1 to state 2 occurs at sea surface with temperature T_H as the process of isotherm-isobaric evaporation. A parcel of liquid water mass m_l is transformed into water vapor mass by keeping that $m_l = m_g$. This water vapor will joint with m'_g as a residual water vapor mass come downed from upper layer. The quality of mixing is expressed as:

$$x = m'_g/m_t \tag{01}$$

Where m_t is a total of liquid water and water vapor masses which is expressed by$m_t = m_l + m'_g$. Because ΔW=$m_t R T_H$, accordingly $m_l/m_t = m_g/m_t = 1 - x$.

In this process, we also assumed that the volume of liquid air is V_l evaporated to become V_{g2} and joining with residual vapor volume from diabatic process V'_{g1} to V'_{g2}, so the two processes can be written as $V_{t1} \rightarrow V_{t2}orV_{t1} = V_{l1} + V'_{g1} \rightarrow V_{t2} = V_{g2} + V'_{g2}$.

Change of volume due to isotherm isobaric process:

$$\Delta V_{12} = (V_{g2} - V_{l1}) + (V'_{g2} - V'_{g1}) \tag{02}$$

Because of: $V_{l1} \ll V_{g2}$ simply that:

$$\Delta V_{12} = V_{g2} + \left(V'_{g2} - V'_{g1}\right) \qquad (03)$$

By dividing equation (03) with m_t and considering the ongoing process will also isochoric, the specific volume of the process can be expressed,

$$\Delta v_{12} = (1 - x)v_{g2} \qquad (04)$$

Based on the process of phase change above, we found that specific work exerted by the system to the environment is,

$$\Delta w_{12} = (1 - x)RT_H \qquad (05)$$

Due to the isotherm process, the change of internal energy is$\Delta u_{12} = 0$. While the latent heat for evaporation is L_H, hence the heat required for evaporation is,

$$\Delta q_{12} = (1 - x)L_H \qquad (06)$$

2.2. Adiabatic Expansion

Transition from state-2 to state-3 is in the process of adiabatic expansion. A parcel of water vapor mass m_g is rising and joining with a residual vapor m'_g come downing from upper layer at the sea surface just after evaporation. Total water vapor mass is $m_t = m_g + m'_g$to the level where a process of condensation will be possible.The respective total volume will be$V_{t2} = V_{g2} + V'_{g2}$and $V_{t3} = V_{g3} + V'_{g3}$, the change of estimated volume is,

$$\Delta V_{23} = V_{t3} - V_{t2} \qquad (07)$$

By dividing equation (07) by m_t, we find the specific volume is,

$$\Delta v_{23} = (1 - x)\left(v_{g3} - v_{g2}\right) + x(v'_{g3} - v'_{g4}) \qquad (08)$$

In the right hand side of equation (08) is actually no need to distinguish, the phase is in vapor phase. Along the process which is occurred adiabatically, the specific work is,

$$\Delta w_{23} = -c_v(T_C - T_H) \qquad (09)$$

Based on the first law of thermodynamics $\Delta w_{23} = \Delta u_{23}$. Although this process occurs adiabatically, in reality there is still a heat needed by the system to change its potential thermodynamic ($\mu = T \ln \mathcal{H}$,$\mathcal{H}$ is the humidity) from the sea surface to the height of possible condensation. Therefore, this process is also referred as a pseudo-adiabatic process with heat input is added by potential thermodynamics in the last section,

$$\Delta q_{23} = R(T_H \ln \mathcal{H}_H - T_C \ln \mathcal{H}_C) \qquad (08)$$

2.3. Condensation

Transition from state-3 to state-4 occurs at the level of condensation with temperature T_C as the process of isotherm-isobaric condensation. A parcel of water vapor mass m_t is partly transformed into liquid water mass m_l, and partly remained as a residual water vapor mass m'_g,by keeping that the total water vapor remains as $m_t = m_l + m'_g$.

The volume $V_{t3} \to V_{t4}$, partly condensate, and is expressed as$V_{t3} = V_{g3} + V'_{g3} \to V_{t4} = V_{l4} + V'_{g4}$.

The change of volume due to condensation, $\Delta V_{34} = V_{t4} - V_{t3}$

$$\Delta V_{34} = \left(V_{l4} - V_{g3}\right) + \left(V'_{g4} - V'_{g3}\right) \qquad (09)$$

Because of $V_{l4} \ll V_{g3}$, and vapor component is undergoing in isochoric process, simply the equation (09) will be,

$$\Delta V_{34} = -V_{g3} \tag{10}$$

The work performed on the system is given by:

$$\Delta w_{34} = -(1-x)RT_C \tag{11}$$

Due to the isotherm change, the internal energy $\Delta u_{34} = 0$, and the latent heat for condensation is L_C, the heat deliberated during condensation is,

$$\Delta q_{34} = -(1-x)L_C \tag{12}$$

2.4. Diabatic compression

Transition from state-4 to state-1 is in the process of diabatic compression. There are two parcels water masses come down to the sea surface. The first is liquid water mass m_l as a precipitation, and the second is water vapor mass m'_g experiencing diabatic compression. The compression of volume is $V_{t4} \rightarrow V_{t1}$, where $V_{t4} = V_{l4} + V'_{g4}$ and $V_{t1} = V_{l1} + V'_{g1}$. Due to the incompressibility of liquid water, $V_{l4} = V_{l1}$, and the change of volume due to diabatic compression will be:

$$\Delta V_{41} = V_{t4} - V_{t1}$$
$$\Delta V_{41} = (V_{l1} - V_{l4}) + \left(V'_{g1} - V'_{g4}\right) \tag{13}$$

Simply it is rewritten as:

$$\Delta V_{41} = \left(V'_{g1} - V'_{g4}\right) \tag{14}$$

Change of specific volume due to diabatic compression will be:

$$\Delta v_{41} = x\left(v'_{g1} - v'_{g4}\right) \tag{15}$$

Following Konings et al. (2015) the specific work that is done to the system and is related to the change in internal energy,

$$\Delta w_{41} = x\left(L_H \ln\left(\frac{T_H}{T_C}\right) - R(T_H - T_C)\right) \tag{16}$$

Because the change of internal energyis$\Delta u_{41} = -c_v(T_C - T_H)$the specific heat will be,

$$\Delta q_{41} = -c_v(T_C - T_H) + x\left(L_H \ln\left(\frac{T_H}{T_C}\right) - R(T_H - T_C)\right) - xR(T_H \ln \mathcal{H}_H - T_C \ln \mathcal{H}_C) \tag{17}$$

The third term in the right hand side of equation (17) is due to the change in potential thermodynamics.

3. Irreversible System of Thermodynamic Processes

Following standard book of thermodynamics,[15] a sum of change of the system and reservoir entropy expresses the change of universe entropy,

$$dS_{\text{system}} + dS_{\text{reservoir}} > 0 \tag{18}$$

There is a flow of heat $\text{đ}Q$ from the reservoir:

$$dS_{\text{reservoir}} = -\frac{\text{đ}Q}{T} = -\frac{L_e + L_H}{T} \tag{19}$$

Substitute (19) to (18), we have:

$$dS_{\text{system}} - \frac{dQ}{T} > 0 \quad \text{or} \quad \text{đ}Q - TdS_{\text{system}} < 0 \tag{20}$$

Using the first law of thermodynamics$\text{đ}Q = dU + \text{đ}W = dU + pdV$, equation (18) becomes:

$$dU + pdV - TdS < 0 \text{or} d(U + pV - TS) < 0 \text{ or } dG < 0 \tag{21}$$

$$TdS > d(U + pV) \tag{22}$$

$$\text{đ}Q > d(U + pV) \tag{23}$$

Equation (21) explains that Gibbs function during the irreversible process at temperature and pressure constant will remain to decrease until a final equilibrium condition is achieved. Equation (22) and (23) informs that latent heat absorbed and deliberated by the system is larger than its enthalpy $H = U + pV$.If the thermodynamic potential of liquid water μ_l and thermodynamic potential of gas is μ_g, the general expression for Gibbs function will be,

$$dG = -SdT + Vdp + \mu_l dm_l + \mu_g dm_g \tag{24}$$

In the isotherm-isobaric process, Gibbs function will be,

$$dG = \mu_l dm_l + \mu_g dm_g \tag{25}$$

Specific Gibbs function,

$$dg = \frac{dG}{m_t} = \mu_l d\left(\frac{m_l}{m_t}\right) + \mu_g d\left(\frac{m_g}{m_t}\right) = -\mu_l dx + \mu_g dx = (\mu_g - \mu_l)dx \tag{26}$$

In the process of evaporation and condensation (isotherm-isobaric), specific Gibbs function which is previously written as $G = H - TS = U + pV - TS$, its change during the process is,

$$dg = pdV - Tds \tag{27}$$

Substitute (25) into (26) will be found that,

$$Tds = pdv - (\mu_g - \mu_l)dx \tag{28}$$

During evaporation at the sea surface, the mass of liquid water phase m_l is transformed into a mass of vapor water phasem_g, hence $m_t = m'_g + m_g$. Following Pauluis(2010), if $\mathcal{H}_H$ and $\mathcal{H}_C$ is humidity in the surface and upper air, Gibbs function at the sea surface where evaporation takes place:

$$G_H = \mu_l m_l = m_l RT_H \ln \mathcal{H}_H ;\mu_l = \mu_H = RT_H \ln \mathcal{H}_H \tag{29}$$

Specific Gibbs function at the sea surface:

$$g_H = (1 - x)\mu_l = (1 - x)RT_H \ln \mathcal{H}_H \tag{30}$$

Gibbs function at the height where condensation takes place, but the vapor mass (m_t) is partly (m_l) condensed attemperature $T_C$and constant pressure $p(T_C)$ with the remaining mass of water vapor of the amountm_g:

$$G_C = \mu_g m_l = m_l RT_C \ln \mathcal{H}_C;\ \mu_g = \mu_C = RT_C \ln \mathcal{H}_C \tag{31}$$

Specific Gibbs function at the condensation level:

$$g_C = (1-x)\mu_g = (1-x)RT_C \ln \mathcal{H}_C \tag{32}$$

All processes of the quasi-Carnot cycle are listed following the first law of thermodynamics as depicted in **Table 1**.

Table 1. Thermodynamic Process of Evaporation and Condensation

Trans	Δu	Δw	$\Delta\mu$	Δq
1 → 2	0	$(1-x)RT_H$	0	$(1-x)L_H$
2 → 3	$C_v^g(T_C - T_H)$	$-C_v^g(T_C - T_H)$	$-R(T_C \ln \mathcal{H}_C - T_H \ln \mathcal{H}_H)$	$R(T_H \ln \mathcal{H}_H - T_C \ln \mathcal{H}_C)$
3 → 4	0	$-(1-x)RT_C$	0	$\Delta q_{34} = -(1-x)L_C$
4 → 1	$C_v^g(T_H - T_C)$	$\Delta w_{41} = x\left(L_H \ln\left(\frac{T_H}{T_C}\right) - R(T_H - T_C)\right)$	$-xR(T_H \ln \mathcal{H}_H - T_C \ln \mathcal{H}_C)$	$C_v^g(T_H - T_C) + x\left(L_H \ln\left(\frac{T_H}{T_C}\right) - R(T_H - T_C)\right) - xR(T_H \ln \mathcal{H}_H - T_C \ln \mathcal{H}_C)$
TOTAL	$\oint du = 0$ Where: $C_v^g \approx C_v^l$	$\oint \text{đ}w = C_p^g(T_H - T_C) + x\left(L_H \ln\left(\frac{T_H}{T_C}\right) - 2R(T_H - T_C)\right)$ Where: $C_p^g = R + C_v^g$	$\oint d\mu = (1-x)R(T_H \ln \mathcal{H}_H - T_C \ln \mathcal{H}_C) = (1-x)R\Delta\mathcal{H}$	$\oint \text{đ}q = (1-x)(L_H - L_C) + C_v^g(T_H - T_C) + x\left(L_H \ln\left(\frac{T_H}{T_C}\right) - R(T_H - T_C)\right)(1-x)R(T_H \ln \mathcal{H}_H - T_C \ln \mathcal{H}_C)$

If we assumed that $\Delta T = T_H - T_C$, and $\Delta q_{in}$is total heat inputted by the system for $q > 0$in each process. By using formulas in **Table 1**, the efficiency of the Carnot cycle will be as follows:

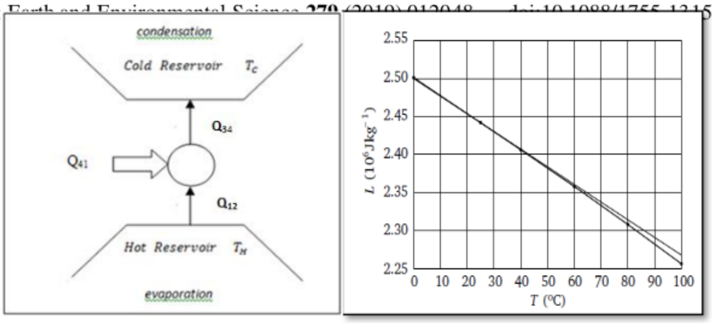
$$\eta = \frac{\oint \text{đ}w}{\Delta q_{in}} \tag{33}$$

Because there is a thermodynamic potential effect on the process that takes place, so the calculation of efficiency can also be done using a comparison between the total heat in each process and the heat entering the system. In other hand, efficiency can be written as follows,

$$\eta = \frac{\oint q_{net}}{\Delta q_{in}} \tag{34}$$

4. Role of Diabatic Process

In equation (24) we defined that during the irreversible process, latent heat absorbed and deliberated by the system $\text{đ}Q$ is larger than its enthalpy $H = U + pV$. If assumed that Q_{in} in the heat flux input from evaporation and diabatic compression process, then Q_{out} is heat flux output from the condensation process, it's shown from Table 4 that estimations of Q_{out} is always larger than Q_{in} because the latent heat of evaporation is always lower than the latent heat of condensation.



(a) **(b)**

Figure 2(a) shows a representation of the irreversible process on evaporation and condensation. The process occurs between the hot reservoir at sea level and cold reservoir in the atmospheric boundary layer. (b) The variations of Latent heat through the atmosphere temperature. [16]

In order to bring the condition to the initial process, it is need to restore work from diabatic process. To recognize this condition, the condensation process in the hydrological cycle is examined as part of the diabatic process rather than the adiabatic process.

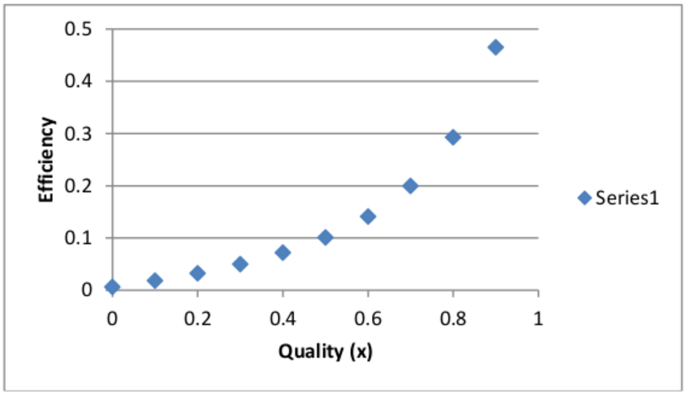


Figure 3. Efficiency of the system through the quality (x) assumed that temperature of sea surface and lifting condensation level were 300 K and 273 K. The C_v^g, C_v^g, R are assuming constant.

The efficiency through the quality system *(x)* is ranged between 1 <*x*<0. This situation fulfills the process of rain formation which can be viewed in the quasi-Carnot cycle which is not all the mass of air that has been condensed falls in the form as rain m_l. There is always residual vapor remaining at m_g. When the *x* = 0, then all mass of m_g that has been condensed to m_l falls in the form of rain. As for *x* = 1, there is no rain because the entire air parcel that has been condensed has re-evaporated as m_g. The higher the efficiency, the smaller the amount of water vapor converted to precipitation. On the contrary, the lower the efficiency, the higher water vapor converted to precipitation. So, the efficiency and quality of the system that shows the potential for rain to occur are inversely proportional.

Table 2. The energy estimations due to reversible processes, assumed that temperature of sea surface and lifting condensation level were $\mathcal{H}_H = 0.9$ and $\mathcal{H}_C = 1$. The c_v^g, c_v^g, R are assumed to be constant.

X	Qin	Qnet	Efficiency
0	16846.74	-74034.8	-0.02976

0.1	42065.21	-42935.6	-0.01894
0.2	67283.69	-11836.4	-0.00579
0.3	92502.16	19262.78	0.010557
0.4	117720.6	50361.98	0.031408
0.5	142939.1	81461.18	0.058929
0.6	168157.6	112560.4	0.09693
0.7	193376.1	143659.6	0.152807
0.8	218594.5	174758.8	0.24305
0.9	243813	205858	0.413442
1	269031.5	236957.2	0.85606

In the **Table 2**, the energy flux enters the system and the amount of energy produced continues to increase as the value of quality increases. In one complete cycle, not all air masses are transformed into liquid in the form of precipitation. But there is a vapor phase of the overall air mass undergoes evaporation before reaching the surface.

5. Conclusion

This paper analyzed the evaporation and condensation in the hydrologic cycle by using irreversible process. Due to the irreversible process, latent heat absorbed and deliberated by the system $đQ$ is larger than its enthalpy $H = U + pV$. In order to bring the condition to the initial process, it is need to restore work from diabatic process. To recognize this condition, the condensation process in the hydrological cycle is examined as part of the diabatic process rather than the adiabatic process. The efficiency of the system is proportional to the quality. The higher the efficiency, the smaller the amount of water vapor converted to precipitation

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