

***Interactive comment on* “On the validity of representing hurricanes as Carnot heat engine” by A. M. Makarieva et al.**

A. M. Makarieva et al.

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We thank Dr. Nefiodov (Nefiodov 2008 ACPD 8: S8164) and Dr. Sherman (Sherman 2008 ACPD 8: S8318) for their comments, where, although from different sides, the nature of potential energy associated with water vapor condensation (see Discussion paper, p. 17434) is discussed. Here we would like to further comment on the notion of latent work, as it clarifies the origin of this potential energy, which is converted to kinetic energy in the atmosphere as well as in the drinking bird toy considered by Dr. Sherman. In the previous comment (Makarieva 2008 ACPD 8: S7609) latent work was estimated for atmospheric air with a realistically small amount of water vapor ($\gamma \ll 1$). Here we first explore the nature of latent work for pure water vapor, then discuss the relevance of latent work for the origin of atmospheric circulation (convection).

Latent heat L can be measured in a cylinder with piston that is placed within a calorime-

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ter. The lower part of the cylinder is filled with water. Initially the piston rests on the water surface. Then the piston is gradually lifted within the cylinder and heat is added to the calorimeter to compensate energy expenditures on evaporation and to maintain constant temperature T within the cylinder. A constant pressure p_v of saturated water vapor sets in that is independent of the changing volume under the lifting piston. This pressure is related to molar volume v_v of water vapor by the equation of state $p_v v_v = RT$. As the piston is being lifted, evaporation continues, the volume occupied by water vapor and the number of mols of water vapor in the cylinder grow, heat is absorbed from the heat source. Per each mol of water vapor added to the cylinder via evaporation, work $p_v v_v = RT$ is performed and an equal amount of potential energy stored within the cylinder. The process of heat absorption from the heat source as gas expands and exerts work over the piston and the reverse process of heat disposal to the heat sink when gas is compressed and work is exerted on the gas occur at constant pressure and temperature, i.e. they are isobaric-isothermal. It is for this reason that the associated quantities of heat and work can be termed as 'latent'.

The amount of latent heat L associated with evaporation of one mol of saturated water vapor consists of energy L_v that has to be spent to overcome the attraction of molecules of liquid water and energy needed to perform work A during the expansion of water vapor at constant pressure p_v to molar volume v_v , $A = p_v v_v = RT$, i.e. $L = L_v + RT$. Thus, measuring the total amount of heat absorbed during evaporation allows one to determine the value of L , while the simultaneous measurement of pressure p_v and molar volume v_v (or temperature T) makes it possible to determine the bond dissociation energy L_v for molecules of liquid water. Namely L_v directly describes the process of phase transition.

We will now pursue the question of whether L_v or L enters the Clausius-Clapeyron equation. This equation, which relates increment dp_v of saturate pressure of water vapor to temperature increment dT , can be obtained from the condition of phase equilibrium at constant p_v and T . The thermodynamic potential (Gibbs function) defined as

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$g = U + pv - Ts$ depends on T and p only, as molar internal energy U obeys the first law of thermodynamics $dU = Tds - pdv$, so $dg = vdp - sdT$ and $g = g(T, p)$. The total system of gas and liquid containing N mols of substance, n mols of gas and $N - n$ mols of liquid is characterized by total thermodynamic potential $G = ng_v + (N - n)g_l$, where g_v and g_l are molar thermodynamic potentials of the gas and liquid, respectively. In thermodynamic equilibrium function G has an extreme. Minimum of G function indicates that the equilibrium is stable. In the point of minimum we have $dG = 0$. At constant N we have $(g_l - g_v)dn = 0$ for any dn , which gives $g_l(T, p) = g_v(T, p)$. The latter equality means that pressure p is a function of temperature T . Differentiating this equality and using $dg = vdp - sdT$ we obtain $(v_v - v_l)dp = (s_v - s_l)dT$. Taking into account that $v_l \ll v_v = RT/p_v$, where $p_v = p$ is pressure of saturated water vapor, the latter equality can be written as

$$v_v dp_v = L \frac{dT}{T}, \quad \text{or} \quad \frac{dp_v}{p_v} = \frac{L}{RT} \frac{dT}{T}, \quad L \equiv (s_v - s_l)T. \quad (1)$$

As is clear from Eq. (1), which is Clausius-Clapeyron equation, the value of L represents the total amount of energy accompanying the transition of one mol of liquid to one mol of gas originally taken at pressure $p = p_v$ and temperature T as the temperature changes by dT (and pressure by dp_v). Thus, parameter L in Clausius-Clapeyron equation (1) includes latent work.

Clausius-Clapeyron equation can also be derived by considering Carnot cycle. During the isobaric-isothermal process occurring at temperature $T_s = T + dT$ of the heat source and pressure $p + dp$, heat is absorbed from the heat source in amounts $Q_s = L_v + (p_v + dp_v)v_v = L + dp_v v_v$ per each mol of evaporated water vapor and gas performs work $(p_v + dp_v)v_v$. During the isobaric-isothermal process at temperature $T_0 = T$ of heat sink and pressure p_v heat is lost to the heat sink in amounts $Q_0 = L_v + p_v v_v = L$, work is exerted over gas in the amount of $p_v v_v$. These two isobars-isotherms are connected via two infinitely narrow adiabates to close the cycle; the contribution of these adiabates to the cycle's energetics is negligibly small. The resulting work dA of

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the cycle is equal to the difference of works performed along the two isotherms $dA = (p_v + dp_v)v_v - p_v v_v = dp_v v_v$. Entropy conservation within the cycle $Q_s/T_s - Q_0/T_0 = 0$ takes the form

$$\frac{L + dp_v v_v}{T + dT} - \frac{L}{T} = 0. \quad (2)$$

Considering that $1/(T + dT) = (1/T)[1 - dT/T + o(dT)^2]$ and discarding the second-order terms proportional to $(dT)^2$ and $dp_v dT$, we obtain Eq. (1) from Eq. (2) above. Thus, the first equality in Eq. (1) can be written as $dA = \varepsilon Q_s$, where $\varepsilon = (T_s - T_0)/T_s = dT/T$ is the efficiency of obtaining useful work in Carnot cycle.

As shown above, $L = L_v + RT$, where L_v describes energy of intramolecular attraction of water molecules. Formula (1) can be thus written as

$$\frac{dp_v}{p_v} = \xi \frac{dT}{T}, \quad \xi \equiv \frac{L}{RT}, \quad \xi = \xi_v + 1, \quad \xi_v \equiv \frac{L_v}{RT}. \quad (3)$$

Since it is L_v that describes the energy of dissociation of molecules in the liquid, namely this quantity should have perhaps been more properly termed the heat of vaporization. As one can see from the above consideration, the conventionally defined heat of vaporization (vaporization constant) L in meteorology implicitly includes latent work RT together with the bond dissociation energy L_v . This is a correction to an earlier statement (Makarieva 2008 ACPD 8: S7609) that latent work has not been accounted for altogether. Latent work has not been accounted for theoretically and its physical meaning not discussed, eventhough it can be, as shown above, calculated explicitly from the equilibrium thermodynamics. According to measurements, $L \approx 44 \text{ kJ mol}^{-1}$ at $T = 15^\circ \text{ C}$, latent work at the same temperature is $RT = 2.4 \text{ kJ mol}^{-1}$. This gives $\xi = L/RT = 18$, $\xi_v = 17$, i.e. latent work, RT , makes up 6% of latent heat L .

Accordingly, we would like to make three amendments to the previous comment on latent work (Makarieva 2008 ACPD 8: S7609):

In formula (1) on p. S7610 L_v should be replaced by L ;

In formulae (9) on p. S7611 and (10) on p. S7612 ($\xi + 1$) should be replaced by ξ , while $\xi(\xi + 1)$ should be replaced by ξ^2 .

Phrases "This formula differs from the one listed in meteorological textbooks and glossaries, where $(\xi + 1)$ in (10) is replaced by ξ . This indicates that latent work has not so far been taken into account in meteorology." on p. S7612 should be replaced by "This formula is identical to the ones listed in meteorological textbooks and glossaries, indicating that latent work has been implicitly included into the empirically determined value of L , so that the magnitude of latent work was not explicitly estimated and its physical meaning not discussed."

Consideration of latent work clarifies the origin of kinetic energy that forms during condensation of water vapor.

We note that gas pressure (dimension J m^{-3}) **always** represents a store of potential energy. The appearance of a pressure gradient leads, in accordance to Bernoulli's equation, to the appearance of forces that accelerate air masses and transform the accumulated potential energy into kinetic energy. However, since the atmosphere is stable, the potential energy of air should be in its minimum. For this reason, the major so far recognized way of extracting potential energy from air and converting it to kinetic energy has been at the expense of the differential heating of the atmosphere.

In the meantime, the continuous cycle of water observed in the atmosphere, when water evaporates, water vapor condenses and the associated dynamic air motions develop at the expense of the released potential energy p_v (it is equal to molar latent work $p_v v_v$ per unit molar volume v_v), represents a non-trivial phenomenon demanding a theoretical explanation. It was shown (Makarieva and Gorshkov 2007 HESS 11: 1013) that atmospheric water vapor cannot be in aerostatic equilibrium if the vertical lapse rate of air temperature exceeds the critical value of 1.2 K km^{-1} . The observed mean tropospheric lapse rate is about six times larger. Namely this fact makes the observed vertical distribution of water vapor in the atmosphere a non-equilibrium one.

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Potential energy corresponding to partial pressure of atmospheric water vapor is not in its minimum in the atmosphere and can be continuously (as long as there is input of water vapor to the atmosphere from the hydrosphere) converted to the kinetic energy of air motion. Therefore, partial pressure of water vapor represents a (previously unaccounted) store of potential energy in the order $\sim 10^3 \text{ J (kg air)}^{-1}$ (convective potential energy) that is available for formation and maintenance of atmospheric circulation (horizontal and vertical air velocities) irrespective of the presence/absence of differential heating.

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