

Interactive comment on “Where do winds come from? A new theory on how water vapor condensation influences atmospheric pressure and dynamics” by A. M. Makarieva et al.

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Reply to the eight questions of Dr. Nick Stokes: What independent physics is contained in Eq. 34

We thank Dr. Nick Stokes for his continued interest in our work. Here we answer his eight questions concerning Eq. 34 and its derivation in our previous comment¹ (hereafter M10-C1). By doing so we also attend to the first out of the four issues outlined

¹‘Condensation rate and hydrostatic equilibrium of moist air’, <http://www.atmos-chem-phys-discuss.net/10/C10922/2010/>

by Dr. Judith Curry in her review²: the need to clarify the meaning and derivation of Eq. 34. Here we abbreviate the questions and re-arrange their order and encourage readers to refer directly to Dr. Stokes comment³ regarding his precise wordings.

1. What is N_v ?

Eq. (34), see also Eq. (8) in M10-C1 and below, is based on the premise that the deviation k_v of the vertical distribution of water vapor (or indeed any other condensable component) from equilibrium is due to condensation alone. (This premise is empirically testable: where condensation is absent, the vertical water vapor distribution should have the same scale height as the non-condensable gases and moist air as a whole.) This relaxes the need to consider N_v as the saturated vapor concentration and ensures that Eq. (34) is generally applicable. When $k_v = 0$, the condensation rate is zero independent of whether water vapor is saturated or not. When $k_v \neq 0$, N_v is saturated water vapor by formulation.

5, 8. Linearity of S over N_v

The assumption of linearity is based on consideration of condensation as a first-order reaction over saturated molar density N_v of the condensing gas⁴. The rate of first-order reactions is directly proportional to the molar density of the reagent, with the proportionality constant having the dimension of inverse time: $S = CN_v$, where C (dimension s^{-1}) is in the general case independent of N_v .

This linearity is a natural theoretical assumption justified by the particular physical nature and stoichiometry of condensation, with gas turning to liquid. Note, for example, that the reverse process (evaporation) should be a zero-order reaction over N_v . Experimental validation of the linearity of condensation rate over N_v can be made by

²<http://www.atmos-chem-phys-discuss.net/10/C11235/2010/>

³<http://www.atmos-chem-phys-discuss.net/10/C11071/2010/>

⁴This was discussed in our response to the first comment of Dr. Stokes that was published prior to the eight questions of Dr. Stokes, see <http://www.atmos-chem-phys-discuss.net/10/C11046/2010/> p. C11049.

considering condensation of water with different isotopic composition⁵.

1, 6. The limit $N_v \rightarrow 0$

Coefficient C in chemical kinetics depends on temperature and the molecular properties of the reagent as follows from the law of mass action. Since the saturated concentration N_v of condensable gas depends on temperature as dictated by the Clausius-Clapeyron law, we can ask what the proportionality coefficient C physically means in this case. Different substances have different partial pressures of saturated vapor at any given temperature – this is controlled by the vaporization constant L and the molecular properties of the substance. Note too that for any given substance (like water) the saturated concentration depends on various additional parameters including the curvature of the the liquid surface and availability of condensation nuclei. Therefore, a range of saturated concentrations is possible at any given temperature. This allows one to consider C and N_v as independent variables in the space of all possible combinations of C and N_v , see also the discussion below.

7. The limit behaviour $\partial N_d / \partial x \rightarrow 0$

Putting $S = CN_v$ into Eq. (7) of M10-C1 we have

$$\frac{\partial N_d}{\partial x} = -wk_v \frac{N_d}{u} \left(1 + \frac{N_v}{N_d} + \frac{C}{wk_v} \right). \quad (1)$$

We require that $\partial N_d / \partial x \rightarrow 0$ at $N_v \rightarrow 0$ (no horizontal density gradients in the absence of condensable substance). This condition follows from considering that, except condensation, there are no processes in the atmospheric column that would make the air distribution deviate from the static equilibrium. This limit is general and should apply to all conditions, including cases where all other variables in (1) are independent of

⁵E.g., Fluckiger B., Rossi M.J. 'Common Precursor Mechanism for the Heterogeneous Reaction of D2O, HCl, HBr, and HOBr with Water Ice in the Range 170-230 K: Mass Accommodation Coefficients on Ice', J. Phys. Chem. 107 (2003) 4103, see also here: http://www.iupac-kinetic.ch.cam.ac.uk/datasheets/pdf/H2O+ice_V.A1.6.pdf

N_v . From this condition we obtain $C = -wk_v$ and $S = -wk_vN_v$ (Eq. 34 of M10). An experiment to test this relationship would be to consider a circulation with given vertical and horizontal velocities w and u , set k_v and N_d and change the saturated molar density N_v by either changing the condensable gas or the amount of condensation nuclei in the atmosphere or temperature (see below) or both. One will observe that as the condensable gas disappears from the atmosphere, the horizontal pressure gradients vanish.

It is interesting to note the following. Given that the spatial distribution of N_v is exponential, $N_v(z) = N_0 \exp(-z/h_N)$, the local condition $N_v \rightarrow 0$ corresponds to complete disappearance of the condensable component from the atmosphere and restoration of equilibrium in the horizontal plane. In comparison, the local condition $k_v \rightarrow 0$ does not presume that condensation is absent everywhere else in the atmosphere (it is plausible that k_v changes stepwise at the point where condensation commences).

Let us now explore the physical meaning of k_v by attending to the remaining questions of Dr. Stokes.

2. What is equilibrium?

The notion of equilibrium and deviation from it is key to determining the rate of any reaction. For example, in the case of evaporation the deviation from equilibrium is measured by the water vapor deficit: the deviation of relative humidity from unity. Atmospheric condensation is peculiar in being physically associated with air movement in a particular direction – water vapor condenses as the air moves vertically towards the lower temperature.

Here by equilibrium we understand the vertical distribution that the water vapor would locally take in the absence of condensation, all other conditions being equal. Let us denote the inverse scale height of such an equilibrium distribution for k_E . Since in equilibrium there is no condensation, we now assume that the condensation rate S is proportional to the first order deviation k_v of the *observed* vertical distribution of water

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vapor from the equilibrium:

$$k_v = -\frac{1}{N_v} \frac{\partial N_v}{\partial z} - k_E. \quad (2)$$

The physics of Eq. (2) consists in the fact that the character of equilibrium distribution is not affected by condensation. For example, for the case of *hydrostatic equilibrium* any gas having molar mass M , temperature T and finding itself on a planet with acceleration of gravity g in the presence of a temperature gradient $\partial T/\partial z$ will have a distribution of its molar density following $-\partial N/\partial z = k_E N$, where $k_E = Mg/RT + (1/T)\partial T/\partial z$.

3.4. What are k , k_v , and k_d ?

As follows from Eq. (2), the expression for condensation rate depends on the nature of the equilibrium under consideration. The case considered in M10 corresponds to the case when it is *moist air as a whole* that is in equilibrium. This means that $k_E = -(1/N)\partial N/\partial z \equiv k$. Then k_v is obtained from Eq. (2) with $k_E = k$ and $k_d \equiv -(1/N_d)\partial N_d/\partial z - k$ is obtained from the relationship $N = N_v + N_d$.

From consideration of the Clausius-Clapeyron law and hydrostatic equilibrium (see also Eqs. (20), (24) and (25) in our paper, pp. 24024, 24026) one can see that

$$k_v = \frac{L\Gamma}{RT^2} - \frac{Mg}{RT}, \quad (3)$$

where L is molar vaporization constant, $\Gamma \equiv -\partial T/\partial z$ is temperature lapse rate, and M is molar mass of air.

The value of k_v is controlled by temperature lapse rate Γ – keeping all other variables constant, changing Γ it is possible for k_v to take any value, $-\infty < k_v < \infty$. This validates our assumption that k_v can be kept independent of N_v when investigating the limit behavior $N_v \rightarrow 0$ in Eq. (1): for any N_v (e.g., set by ambient temperature) any value of k_v can be prescribed by changing Γ .

The independent physics of Eq. 34

The answer to the last (unnumbered) question of Dr. Stokes, *what extra physics makes Eq. 34 independent of Eqs. 32 and 33*, is as follows (note that it is also given on p. 24034 in M10).

Eqs. 32 and 33, taken together, contain the information that it is water vapor and not dry air that undergoes condensation. Eq. 34 contains information about the magnitude of deviation from equilibrium that causes condensation. Jointly considered, these facts are sufficient to determine the horizontal pressure gradient produced by condensation.

We emphasize the point we made in our paper, p. 24033, and M10-C1: if it is dry air that is in equilibrium, i.e. $k_E = -(1/N_d)\partial N_d/\partial z$, the same consideration of the same equations gives $\partial N_d/\partial x = 0$ instead of $\partial N_d/\partial x = S/u$ as in the case when it is moist air that is in equilibrium. This profound impact of the nature of equilibrium on the dynamics associated with condensation has never been expored in meteorological theory.

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