

Corrigendum on “Clausius-Clapeyron equation and saturation vapour pressure: simple theory reconciled with practice”

Demetris Koutsoyiannis

Department of Water Resources and Environmental Engineering, School of Civil Engineering, National Technical University of Athens, Greece

E-mail: dk@itia.ntua.gr; URL: <http://itia.ntua.gr/dk>

Abstract An error related to a partial derivative, which affected some statements in the original paper but not the final results or their derivation, is corrected.

At the end of Section 4, entitled “Alternative derivation in a statistical mechanical framework”, of my paper [1], an analysis of chemical potentials of the liquid and gaseous phase has been included. This analysis starts with equation (36) which provides the definition of chemical potential in terms of the partial derivative of entropy with respect to the number of particles. While the equation is correct as shown, the partial derivative should be meant for constant internal energy U rather than constant thermal energy E as used in the paper. The two are identical for the gaseous phase but differ for the liquid phase as $E_L = U_L + N_L\zeta$. Consequently, the partial derivatives, $\partial S_L(U_L, N_L)/\partial N_L$ and $\partial S_L(E_L, N_L)/\partial N_L$, will differ too, as implied by the chain rule:

$$\frac{\partial S_L(U_L, N_L)}{\partial N_L} = \frac{\partial S_L(E_L, N_L)}{\partial N_L} + \frac{\partial S_L(E_L, N_L)}{\partial E_L} \frac{\partial E_L(U_L, N_L)}{\partial N_L} = \frac{\partial S_L(E_L, N_L)}{\partial N_L} + \frac{1}{T} \zeta \quad (1)$$

where equation (30) was also used to evaluate the last term. Therefore, the term ζ/T should be added in the second part of (37) referring to the chemical potential of the liquid phase. In turn, the term $-\zeta/T$ should be added to the right-hand side of (38) and the term $-\zeta$ should be added to the right-hand side of (39). This makes the difference of the chemical potentials of the two phases equal to zero, rather than ζ , as the original derivation had it. In turn, both equations (3) and (4) hold true.

Several statements in the original paper [1] were based on the mistaken version of (39), such as the statement in the abstract “*There is an additional erroneous assumption for the derivation of the Clausius-Clapeyron equation, related to the equality of chemical potentials of the two phases, which does not affect the final result but puts into question the logical coherence of the equation’s derivation.*” It seems fair that this could be now flipped so that questioning the logical coherence of the equation’s derivation refers to my paper. Fortunately, however, the affected equations (36)-(39) are not part of my derivation and were included for completeness. For the affected equations and the invalid statements about non equality of chemical potentials I apologize.

Nonetheless, the derivation of the Clausius-Clapeyron equation in section 4, based on merely the entropy maximization, holds and this derivation does not need additional assumptions (like equality of temperatures, chemical potentials or differentials thereof, all of which are consequences of the principle of maximum entropy). In this respect, the statement that the quantification of the phase change relies on maximization of uncertainty, i.e. entropy, is valid. Also, all results but (36)-(39) hold, including the final relationships plotted in Figures 1-3. After all, these are compared with real world data, which offer the ultimate judgment of models and theories. Models can be wrong and sometimes mathematics may delude some of us, but real world data are usually irrefutable.

Acknowledgement Pekka Pirilä’s critical discussion of the paper in Judith Curry’s blog (<http://judithcurry.com/2012/02/20/god-and-the-arrogant-species>), his persistence that chemical potentials should be equal and his continual (albeit ineffective) effort to locate errors prompted me to revisit the derivations and spot the error I report here. I also wish to thankfully acknowledge the anonymous (nicknamed) bloggers who contributed to this blog discussion.

References

[1] Koutsoyiannis D 2012 Clausius-Clapeyron equation and saturation vapour pressure: simple theory reconciled with practice, *European Journal of Physics*, 33 (2), 295–305.