

Subject: Re: [Entropy] Manuscript ID: entropy-11532 - Submission Reject
From: Demetris Koutsoyiannis <dk@itia.ntua.gr>
Date: 12/10/2011 10:13
To: sarah.shao@mdpi.com
CC: Entropy Editorial Office / MDPI <entropy@mdpi.com>

Dear Ms Shao,

Thank you for your reply and your good wishes. Of course I understand that a journal cannot publish all papers it receives.

You can assure the anonymous editor--and anyone in the editorial board who may feel that they need to be protected--that they are not in any danger and do not need any protection from me. Furthermore, you can convey them my experience, because I am also an editor, that I never had any problem and never felt to need any protection, even though all my transactions as editor and associate editor, as well as a reviewer, are always eponymous and never anonymous.

Of course I would not make this comment if you explicitly stated in your Editors site (<http://www.mdpi.com/journal/entropy/editors/>) that the editors are anonymous.

Also, please convey the anonymous editor this: I cannot find in any of my messages any mention that I am frustrated. In this respect I cannot understand why s/he decided to interpret my feelings and to diagnose that I am frustrated.

I reciprocate your good wishes, wishing any success to your journal, which has such a beautiful title.

Kind regards,

Demetris

Demetris Koutsoyiannis
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Heroon Polytechniou 5, GR 157 80 Zographou, Greece
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On 12/10/2011 09:26, Sarah Shao/MDPI wrote:

Dear Dr. Koutsoyiannis,

Thank you for your email. Not revealing the editors' names are a means to protect the editors; it is not by any editor's request. Similar to the the half-way-blind method of peer review, it applies to all submissions.

The editor's original comments were:

I have looked over the response of the author. Some interesting points are made, but there remain many concerns by the reviewers. So I do not recommend a change in the decision. I understand the author's frustration, but in this case there are too many concerns to permit publication, in my view.

Please understand we receive more papers than we are able to publish and we wish you success with your research in future.

Kind regards,

Sarah Shao
Assistant Editor
Email: sarah.shao@mdpi.com

On 10/12/2011 12:41 PM, Demetris Koutsoyiannis wrote:

Dear Ms Shao,

Thanks for your reply. Please convey the anonymous editor my difficulty to see where he refers to my rebuttal in his comment (which could fit to any rebuttal referring to any paper). I also have a difficulty to see the ethical grounds of an editor being anonymous.

Sincerely,

Demetris Koutsoyiannis
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On 12/10/2011 05:51, Sarah Shao/MDPI wrote:

Dear Dr. Koutsoyiannis,

The Editor read your rebuttal. The following is the comment:

We think some interesting points are made, but there remain too many concerns by the reviewers to permit publication.

I am sorry to say we still cannot consider the publication of this paper in our journal.

Kind regards,

Sarah Shao
Assistant Editor
Email: sarah.shao@mdpi.com

On 10/11/2011 4:39 PM, Demetris Koutsoyiannis wrote:

Thanks very much. I look forward to hearing from the Editor.
Regards, Demetris

Dear Dr. Koutsoyiannis,

Thank you very much for your emails. The office was closed for a week and we are now sorting the emails. Sorry for the delayed reply.

I have consulted the Editor about your rebuttal and will reply to you as soon as possible.

Kind regards,

Sarah Shao
Assistant Editor
Email: sarah.shao@mdpi.com

On 10/11/2011 2:17 PM, Demetris Koutsoyiannis wrote:

Dear Ms Shao,

I wonder if my earlier email (sent 10 days ago and also copied below) reached you or not. Please let me know.

Kind regards,

Demetris

Demetris Koutsoyiannis
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On 29/09/2011 23:04, Demetris Koutsoyiannis wrote:

Dear Ms Shao,

I appreciate your consideration of my Note for publication in "Entropy" and I am grateful for the comments by five knowledgeable reviewers. Of course, rejections are common in life, but sometimes some further explanations may be helpful and constructive. I hope that you do not regard my reply too annoying.

I understand the comment by the editorial office:

We reject the paper, given that a large number of the reviews are strongly negative, for reasons that question the very foundations of the paper

However, from what I see, the "large number" of strongly negative reviews is 2 (#2 and #5)--and I am happy that an equally large number of reviewers (#1 and #4) recommend publication after minor revision.

Reviewer #5, who recommends rejection, is right in his major concern, that is,

While the author tries to work terms like "entropy maximization" into the article, this is just old-fashioned chemical thermodynamics where entropy concepts are part of the fabric but do not play a central role, so the connection to "entropy" is tenuous at best.

I had a similar concern myself about this, so I worked the issue further and made a better derivation, really based on entropy maximization and free from the notion of chemical potential. Even more than this, I located an additional problem, not reported in the original version of the Note, in those derivations based on the chemical potential and found in almost all textbooks .

I am attaching a revised version, which contains the new derivation in the new section 4 (the new stuff is marked in red). I will appreciate it if the Editorial Office and Reviewer 5 could have a quick look on it to see if the decision could, in principle, change after this. Of

course, the reviewers provided also other comments which I have to address if, in principle, my Note could be reconsidered. In any case, please do not regard the attachment as an uninvited resubmission.

I wish also to provide a clarification for Reviewer #2, who also recommends rejection, based on the major concern that:

However, unfortunately the results of these more precise derivation is already known:

<http://www.chem.arizona.edu/~salzmanr/480a/480ants/clapeyro/clapeyro.html>

I do not think he/she is right. For I do not say in the paper that my result is new. On the contrary, I clarify it from the beginning and I give a couple of more formal references (8 and 9) about it. Specifically, in lines 47-50 of my Note I state:

A theoretically consistent closed solution exists [8, p. 203; see also below] and is not much more complex than (1), but it is rarely mentioned (e.g. none of the above referenced books contain it). Even when it is mentioned, it is still presented along with (1), which may again be characterized as the best known approximation to calculate the liquid-vapour equilibrium pressure [9].

What is new is that I try to show that the more common result (eqn. 1) is inconsistent. Interestingly, the link the reviewer provides, presents it as a consistent approximation (see my second attachment, where I marked the relevant point in yellow) while it presents the consistent result as "fancier" (again marked in yellow).

Please feel free to share the email message and attachments with editors and reviewers. I will appreciate their reaction.

Kind regards,

Demetris Koutsoyiannis
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On 29/09/2011 12:42, Sarah Shao wrote:

Dear Dr. Koutsoyiannis,

It is with regret we must inform you that your manuscript has been rejected for publication:

Manuscript ID: entropy-11532

Type of manuscript: Short Note

Title: A note on the Clausius-Clapeyron equation and the saturation

vapour
pressure
Authors: Demetris Koutsoyiannis *
Received: 07 September 2011
[E-mails:dk@itia.ntua.gr](mailto:dk@itia.ntua.gr)

This decision was based on the comments of external experts who carefully peer-reviewed your paper. For your consideration you can find their review reports by clicking this link:

<http://susy.mdpi.com/user/manuscripts/resubmit/c5fb305efb40b28d81e939c20dcf44c5>

The following comments are from the Editorial Office:

We reject the paper, given that a large number of the reviews are strongly negative, for reasons that question the very foundations of the paper. It is well written, but the author seems to be not fully aware of the relevant thermodynamics - based on what many of the reviewers indicated.

You are welcome to incorporate the reviewers' suggestions into your manuscript should you wish to submit it elsewhere for publication.

We would like to thank you for having considered Entropy as a venue for your work and wish you every success in the future.

If you have any questions, please never hesitate to contact us.

Kind regards,

Sarah Shao
Assistant Editor
[Email:sarah.shao@mdpi.com](mailto:sarah.shao@mdpi.com)

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Journal Entropy (ISSN 1099-4300)
<http://www.mdpi.com/journal/entropy/index>

Manuscript ID entropy-11532
 Type Short Note
 Title A note on the Clausius-Clapeyron equation and the saturation vapour pressure
 Number of Pages 7
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 Authors Demetris Koutsoyiannis
 Received 07 September 2011

Review Report Form

High Average Low No Answer

* Originality / Novelty () (x) () ()
 * Significance of Content (x) () () ()
 * Quality of Presentation (x) () () ()
 * Scientific Soundness (x) () () ()
 * Interest to the readers () (x) () ()
 * Overall Merit (x) () () ()

* **Overall Recommendation** () Accept in present form
 (x) Accept after minor revision, I do not need to see the revised version
 () Reconsider after major revision, I want to see the revised version
 () Reject

* **English Language and Style** (x) English language and style are fine
 () Minor spell check required
 () Extensive editing of English language and style required

Comments and Suggestions for Authors

* **Comments and Suggestions for Authors** This is a nice paper, and a good reminder about the shortcomings of the integrated Clausius-Clapeyron equation that is given in textbooks.

I have a couple of questions for the author to consider that are related to the temperature range used to demonstrate the new equations (i.e., -40 C to 50 C). Is there a particular reason for limiting the temperature range in this way (it seems somewhat arbitrary)? How well do the new equations work outside of this temperature range? Does the relative error increase? If so, can the author provide an explanation for such behavior? On a related note, I was surprised to see the equation work so well below the freezing temperature of water since liquid water is always assumed in the derivation. Can the author comment on this?

Date & Signature

Date of manuscript submission 07 September 2011 5:27:36

Date of this review 27 September 2011 20:24:19

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 (x) Reject

* **English Language and Style** (x) English language and style are fine
 () Minor spell check required
 () Extensive editing of English language and style required

Comments and Suggestions for Authors

* Comments and Suggestions for Authors

Dear Author,
 I enjoyed reviewing your paper which is well presented and clearly written. The paper presents a discussion on the derivation of the clausius-clapeyron equation and its validity. Two alternative derivations have been presented and describes a more precise derivation.

However, unfortunately the results of these more precise derivation is already known:
<http://www.chem.arizona.edu/~salzmanr/480a/480ants/clapeyro/clapeyro.html>

The limited validity of setting the latent heat as a constant is known and many approaches exists to improve the description. Additionally the results presented show that the deviation in the region -50 to 50 °C is quite low. Figure 1 clearly indicates the small deviation.

Date & Signature

Date of manuscript submission 07 September 2011 5:27:36
 Date of this review 26 September 2011 9:29:49

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* **English Language and Style** (x) English language and style are fine
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 () Extensive editing of English language and style required

Comments and Suggestions for Authors

- * **Comments and Suggestions for Authors**
- The heat of vaporization does not really vary linearly with temperature. Its a good approximation over certain temperature ranges, but it is not really true. Its perhaps a better approximation than assuming the heat of vaporization is constant, but its still an approximation.
 - Unless I'm misunderstanding something, the heat capacity/specific heat (c_P and c_L) appears in the equations as a constant. Heat capacity depends on temperature. If you're making a big argument that the dependence of the heat of vaporization on temperature is not constant, it doesn't seem right to completely ignore the fact that heat capacity is also temperature-dependent.
 - I don't see what new information this provides. The McQuarrie&Simon physical chemistry textbook in the section on the Clausius-Clapeyron equation (page 942) states that we can recognize that the heat of vaporization varies with temperature by writing

$$\Delta H_{\text{vap}} = A + BT + CT^2 + \dots$$
 where A, B, and C, etc. are constants. The integration then yields

$$\ln p = -A/RT + (B/R) \ln T + (C/R)T + \text{constant} + \dots$$
 ignoring the (C/R)T term, we can re-write this as

$$p = \text{constant} \cdot \exp\{-A/RT\} \cdot T^{B/R}$$
 which looks the same as the equation in the paper, except in the paper $B = c_P - c_L$
 - In the example for water, the author states c_P and c_L values. Apart from the issue of assuming they are constant, there is no reference for where these numbers come from. I tried looking them up and found different values. Different values for c_P and c_L will obviously change the results, so perhaps the 'new' equation isn't really as good as his results seem to indicate.

Date & Signature

Date of manuscript submission 07 September 2011 5:27:36
 Date of this review 20 September 2011 20:55:52

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 * Overall Merit () (x) () ()

* **Overall Recommendation** () Accept in present form
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 () Reject

* **English Language and Style** () English language and style are fine
 (x) Minor spell check required
 () Extensive editing of English language and style required

Comments and Suggestions for Authors

* **Comments and Suggestions for Authors** In this work, it is shown that a solution of the Clausius Clapeyron equation, derived without the assumption of constant latent heat of vaporization, might be a convenient simple formula for calculating rather accurate values of saturation vapor pressures.
 Although the solution is known (Ref. 8), its application in meteorology has not been tested yet and might be relevant. For this reason I would suggest to calculate and explicitly state the relative error of the proposed optimized equation (Eq. 26 of the manuscript) against observations. Moreover it would be interesting if the Author could provide an estimate of the deviations of the proposed equation from the Magnus-type equation outside the investigated temperature range.

Date & Signature

Date of manuscript submission 07 September 2011 5:27:36

Date of this review 26 September 2011 19:06:39

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 * Overall Merit () () (x) ()

* **Overall Recommendation** () Accept in present form
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 () Reconsider after major revision, I want to see the revised version
 (x) Reject

* **English Language and Style** () English language and style are fine
 (x) Minor spell check required
 () Extensive editing of English language and style required

Comments and Suggestions for Authors

* Comments and Suggestions for Authors See attached PDF
[review-report.v1.pdf](#)

Date & Signature

Date of manuscript submission 07 September 2011 5:27:36
 Date of this review 20 September 2011 17:27:10

* denotes required fields.

Review for Entropy

Koutsoyiannis, "A note of the Clausius-Clapeyron equation and the saturation vapor pressure"

I do not believe that this paper should be published, especially not in this journal.

The work really does not fall under the Subject Areas listed on the journal website. While the author tries to work terms like "entropy maximization" into the article, this is just old-fashioned chemical thermodynamics where entropy concepts are part of the fabric but do not play a central role, so the connection to "entropy" is tenuous at best. More appropriate journals might be the Journal of Chemical Thermodynamics or the Journal of Thermodynamics. My recommendation is not based on that, however; ultimately the Editor must decide if it is in the journal scope.

My recommendation for rejection is due to the lack of any significant scientific contribution. While there is not much in the paper that is wrong, there is also nothing novel or useful. One of the main points is that the enthalpy of vaporization is not constant and that therefore Eq. (1) is not a good vapor-pressure equation over a significant range of temperature. But this point is obvious and is known to anybody with a minimal knowledge of chemical thermodynamics. No knowledgeable person would use Eq. (1) as a wide-ranging vapor-pressure equation, which is why Antoine or Magnus forms are so widely used. Then the author goes through some manipulations to produce a different functional form with one more parameter, which becomes an empirical fitting function – but it is fitted not to any real data or physical constraints, but to a previous work's Magnus equation, just the form they are saying is inferior!

If the ultimate goal of the work is to provide a "better" vapor-pressure equation for water, there are additional problems. First, I see no recognition of the fact that, below 273.16 K, the equilibrium condensed phase is ice, not liquid water. Presumably the author is trying to correlate the vapor pressure of metastable liquid water in this region (a relevant quantity for atmospheric science), for which there are few if any data, but the author seems ignorant of the fact that he is trying to cover two different regions. Second, as mentioned above, a "best" equation should be fitted to the best information, including experimental data, not some equation developed by others. For water's vapor pressure (excluding metastable states), the best information is cited by Wagner & Pruss, *J. Phys. Chem. Data* **31**, 387 (2002) (see Sec. 2.3 and references therein). Third, some of the cited pure-water values (Sec. 4) are not the best. I have access to a database that calculates properties from the international standard for thermodynamic properties of water adopted by the International Association for the Properties of Water and Steam. For the 273.15 point, the IAPWS vapor pressure is 6.1121 hPa (a better choice for anchoring a correlation would be 273.16 K, where there is a very accurate datum of 611.657 Pa at the triple point). The given latent heat is fine, and the liquid C_p is not far off (IAPWS gives 4220), but the vapor C_p number is significantly wrong (IAPWS gives 1884, and the uncertainty on that should be small because one is near the ideal gas at this low pressure).

More minor points: Fig. 1 is worthless because the lines are indistinguishable. Something like Fig. 2 gives more useful information. And if the author is worrying about fine points of thermodynamics, it does not make sense to use the approximate ideal-gas law in a derivation.