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Comment on "Concepts against mathematics: self-inconsistency in thermodynamic evaluations, V. A. Drebushchak, Journal of Thermal Analysis and Calorimetry (2011) 103:753–759"

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In 2011, Drebushchak published his paper [1]. Swendsen already published a Comment on it [2]. However, his Comment has a disadvantage: he commented on the main body of Drebushchak's paper but did not comment on the paradox that Drebushchak had proposed in the Appendix of his paper.

I would like to Comment on this paradox (I insert the letter "D" into Drebushchak's equation numbers).

In Appendix of [1], a paradox was presented. It goes as follows. A conventional result for the ideal gas was taken:

$$C_P = C_V + R, \tag{D38}$$

where R is the gas constant. Both sides of this equation were multiplied by dT:

$$C_P \mathrm{d}T = C_V \mathrm{d}T + R\mathrm{d}T, \tag{D39}$$

and taking into account that $R\mathrm{d}T = \mathrm{d}RT = \mathrm{d}(PV)$, Eq. D39 was transformed into

$$C_P \mathrm{d}T = C_V \mathrm{d}T + \mathrm{d}(PV). \tag{D42}$$

Then, if one divided Eq. D42 by dT, one obtained the paradox:

$$C_P = C_V + V\frac{\mathrm{d}P}{\mathrm{d}T} + P\frac{\mathrm{d}V}{\mathrm{d}T} = C_V + 2R. \tag{D43}$$

Now let us repeat this procedure. Multiply left - hand side and right - hand side of Eq. D43 by dT:

$$C_P \mathrm{d}T = C_V \mathrm{d}T + 2R\mathrm{d}T = C_V \mathrm{d}T + 2\mathrm{d}(PV). \tag{1}$$

Dividing Eq. 1 by dT, one obtains:

$$C_P = C_V + 2V\frac{\mathrm{d}P}{\mathrm{d}T} + 2P\frac{\mathrm{d}V}{\mathrm{d}T} = C_V + 4R. \tag{2}$$

If one iterates this calculation n times, one obtains

$$C_P = C_V + 2^n R. \tag{3}$$

Now let us take the gas constant R, and multiplying it by dT, one obtains

$$R\mathrm{d}T = \mathrm{d}(PV). \tag{4}$$

Dividing this equation by dT, one again obtains:

$$R = V\frac{\mathrm{d}P}{\mathrm{d}T} + P\frac{\mathrm{d}V}{\mathrm{d}T} = 2R. \tag{5}$$

Iterating n times, one obtains

$$R = 2^n R. \tag{6}$$

It is obvious that Drebushchak's paradox does not have connection to the heat capacities but results from inappropriate use of the differential equation. Its explanation is, of course, the following one. In the left part of Eq. D42, there is the value C_PdT. This means that we have a system with a constant pressure and want to calculate C_PdT for it, which is unknown to us. In the right part of this equation, there is a value C_VdT which is known to us. To obtain C_PdT, we have to add to C_VdT a term d(PV) which characterizes our system with a constant pressure. Therefore, in this term, P is constant.

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