

Correction for Comment on “Equilibrium Constants and Rate Constants for Adsorbates: 2D Ideal Gas, 2D Ideal Lattice Gas, and Ideal Hindered Translator Models”

Aditya Savara^{1*}

1. Chemical Sciences Division, Oak Ridge National Lab, 1 Bethel Valley Road, Oak Ridge, TN 37830

* To whom correspondence should be addressed. E-mail: savaraa@ornl.gov 865-576-6311

There was an error in the original Comment.¹ The entropy term arising from $1/N!$ should be free from dimensional dependence, but also negative. In the original Comment, the nN_A arising from $1/N!$ was inadvertently moved into the dimensional dependent term of Eqs. 2 and 3. To avoid confusion and to keep the same numbering as before, the equations should be as follows. There are changes in Equations 2-4, with no change in Equation 1.

$$S_{\text{Sackur-Tetrode}(D)} = nR \ln \left(\left(\frac{\sqrt{2\pi mkT}}{h} \right)^D \frac{L^D}{nN_A} \right) + nR \left(\frac{D}{2} + 1 \right) \quad (1)$$

Equation 1 includes the nN_A in the first term, as the Sackur-Tetrode equation is often presented this way. If one derives the equation while keeping the portion of the entropy with no dimensional dependence as a separate term, the equation can be written as:

$$S_{\text{Sackur-Tetrode}(D)} = nR \ln \left(e^{D/2} \left(\frac{\sqrt{2\pi mkT}}{h} \right)^D \frac{L^D}{1} \right) + nR \ln \left(\frac{e^1}{nN_A} \right) \quad (2)$$

As in the original Comment, the second term of Equation 2 has no dimensional dependence, but is now negative (as it should be).

Due to this error, there was an erroneous statement that appeared later in the Comment, regarding Equations 3 and 4. A possible source of confusion will be clarified, regarding Equations 3 and 4, and then the correct statement provided. Once a standard state has been defined, the value of L becomes fixed (or becomes a function of that standard state's definition), and subscripts will be used here to indicate which standard state a particular value of L corresponds to. When the standard state is associated with a concentration, the corresponding value of “ L ” can be regarded as being fixed as being equal to the side-length of an equilateral box with the corresponding volume/area. For example, the IUPAC 3D gas standard state has a molar volume associated with it, which we will call the standard molar volume, $V_{(m,3D-I)}^\circ$. We can then define the standard molar length as the one associated with an equilateral box (i.e., cube) containing a mole of gas molecules at that standard state: $(L_{(m,3D-I)}^\circ)^3 = V_{(m,3D-I)}^\circ$. We can then also define the standard box-length *per particle* as that associated with an equilateral box of the volume associated with each particle (each molecule): $(L_{(p,3D-I)}^\circ)^3 = (L_{(m,3D-I)}^\circ)^3 / N_A$. Similarly, for the 2D gas standard state recommended by Savara,² the standard molar area can be found from:

$A_{(m,2D-S)}^\circ / N_A = (V_{(m,3D-I)}^\circ / N_A)^{2/3}$, leading to $(L_{(m,2D-S)}^\circ)^2 = A_{(m,2D-S)}^\circ$ and correspondingly $(L_{(p,2D-S)}^\circ)^2 = (L_{(m,2D-S)}^\circ)^2 / N_A$. The 2D gas standard state recommended by Savara is based precisely

on these relations: the standard state recommended by Savara was based on setting the box-length per particle as the same between the 3D gas and 2D gas standard states, $(L_{(p,2D-S)}^\circ) = (L_{(p,3D-I)}^\circ)$, since Savara viewed this as removal of one translation per particle. For the 2D gas standard state recommended by Campbell,³ which was based on a similar idea that will be noted below, the standard molar area can be found from: $A_{(m,2D-C)}^\circ/N_A = (V_{(m,3D-I)}^\circ/N_A)^{2/3}e^{-1/3}$, leading to $(L_{(m,2D-C)}^\circ)^2 = A_{(m,2D-C)}^\circ$. In Campbell's recommendation for the 2D gas standard state, algebra shows that $(L_{(p,2D-S)}^\circ) \neq (L_{(p,3D-I)}^\circ)$. The factor of Avogadro's number appears in some of these equations due to the entropy being related to the number of particles in a box. However, since we are interested in molar entropies, our equations usually use molar quantities. From the above conversions, the length to be used in the Sackur-Tetrode equation is then dependent on the standard state being used as well as the dimensionality: for both Savara's recommendation and Campbell's recommendation, $L_{(m,2D)}^\circ \neq L_{(m,3D)}^\circ$. Two additional conversion factors will be used below, and were obtained by algebra: $(L_{(m,2D-S)}^\circ)^2 = (L_{(m,3D-I)}^\circ)^2 N_A^{1/3}$ and $(L_{(m,2D-C)}^\circ)^2 = (L_{(m,3D-I)}^\circ)^2 N_A^{1/3} e^{-1/3}$.

Having provided the above clarification and conversion factors, several versions of Equations 3 and 4 from the original Comment are provided below. These equations allow visual comparison of the 2D gas standard state entropies that are associated with Savara's recommendation and Campbell's recommendation. The equations also enable readers to calculate the 2D gas standard state entropy either explicitly or in reference to the 3D gas standard state entropy (different readers may have different applications). In these equations, $S_{(Int-I)}^\circ$ represents the entropy associated with the internal modes of the molecule (e.g., rotations and vibrations) at the IUPAC 3D gas standard state. The entropy associated with the IUPAC 3D gas standard state, $S_{(3D-I)}^\circ$, then implicitly includes the entropy from $S_{(Int-I)}^\circ$. For an ideal gas, Equations 3a-3d each give the same value as each other (these equations are related to Campbell's 2D gas standard state).

$$S_{(2D-C)}^\circ = S_{(3D-I)}^\circ - \frac{1}{3} * \left[nR \ln \left(e^{3/2} \left(\frac{\sqrt{2\pi mkT}}{h} \right)^3 (L_{(m,3D-I)}^\circ)^3 \right) + nR \ln \left(\frac{e^1}{nN_A} \right) \right] \quad (3a)$$

$$S_{(2D-C)}^\circ = S_{(3D-I)}^\circ - \frac{1}{3} * \left[nR \ln \left(e^{3/2} \left(\frac{\sqrt{2\pi mkT}}{h} \right)^3 (L_{(m,2D-C)}^\circ)^3 e^{1/2} N_A^{-1/2} \right) + nR \ln \left(\frac{e^1}{nN_A} \right) \right] \quad (3b)$$

$$S_{(2D-C)}^\circ = \left[nR \ln \left(e^{2/2} \left(\frac{\sqrt{2\pi mkT}}{h} \right)^2 (L_{(m,2D-C)}^\circ)^2 \right) + nR \ln \left(\frac{e^1}{nN_A} \right) \right] + S_{(Int-I)}^\circ \quad (3c)$$

$$S_{(2D-C)}^\circ = \left[nR \ln \left(e^{2/2} \left(\frac{\sqrt{2\pi mkT}}{h} \right)^2 (L_{(m,3D-I)}^\circ)^2 N_A^{1/3} e^{-1/3} \right) + nR \ln \left(\frac{e^1}{nN_A} \right) \right] + S_{(Int-I)}^\circ \quad (3d)$$

For an ideal gas, Equations 4a-4d each give the same value as each other (these equations are related to Savara's 2D gas standard state). Equation 4a was derived from Equation 4d using the Sackur-Tetrode equation and algebra, during which the factor of $nR \ln \left(\frac{e^1}{nN_A} \right)$ cancelled.

$$S_{(2D-S)}^\circ = S_{(3D-I)}^\circ - \frac{1}{3} * \left[nR \ln \left(e^{3/2} \left(\frac{\sqrt{2\pi mkT}}{h} \right)^3 (L_{(m,3D-I)}^\circ)^3 N_A^{-1} \right) \right] \quad (4a)$$

$$S_{(2D-S)}^\circ = S_{(3D-I)}^\circ - \frac{1}{3} * \left[nR \ln \left(e^{3/2} \left(\frac{\sqrt{2\pi mkT}}{h} \right)^3 (L_{(m,2D-S)}^\circ)^3 N_A^{-3/2} \right) \right] \quad (4b)$$

$$S_{(2D-S)}^\circ = \left[nR \ln \left(e^{2/2} \left(\frac{\sqrt{2\pi mkT}}{h} \right)^2 (L_{(m,2D-S)}^\circ)^2 \right) + nR \ln \left(\frac{e^1}{nN_A} \right) \right] + S_{(Int-I)}^\circ \quad (4c)$$

$$S_{(2D-S)}^\circ = \left[nR \ln \left(e^{2/2} \left(\frac{\sqrt{2\pi mkT}}{h} \right)^2 (L_{(m,3D-I)}^\circ)^2 N_A^{1/3} \right) + nR \ln \left(\frac{e^1}{nN_A} \right) \right] + S_{(Int-I)}^\circ \quad (4d)$$

Having provided these equations with the appropriate subscript, we can now correct the erroneous statement from the original comment. The original Comment¹ stated that Savara's 4a equation corresponded to removal of 1/3 of the first term in the Sackur-Tetrode Equation (the dimensionally dependent term of Equation 2). As can be seen by comparing the corrected version of Equation 2 (above) with Equation 4a, that statement was erroneous: Equation 4a has factor of N_A^{-1} inside the term with a 1/3 coefficient, while the corrected version of Equation 2 (above) does not have the same N_A^{-1} factor. The $1/N_A$ factor in Equations 4a and Equation 2 come from different sources, as during the derivation of Equation 4a the $nR \ln \left(\frac{e^1}{nN_A} \right)$ was removed by cancellation. To better understand equation 4a, the sources of these equations should be considered. Savara's 2D gas standard state is intended to correspond to the loss of one dimension per particle between the 3D gas standard state and the 2D gas standard state. With this idea in mind,² Savara first defined $A_{(m,2D-S)}^\circ/N_A = (V_{(m,3D-I)}^\circ/N_A)^{2/3}$ as a starting point from which Equation 4d then follows, and Equation 4a was then produced by algebra. In contrast, with a similar idea in mind,³ Campbell first defined a 2D gas standard entropy using Equation 3a (a loss of 1/3 of the 3D gas Sackur-Tetrode entropy) from which $A_{(m,2D-C)}^\circ/N_A = (V_{(m,3D-I)}^\circ/N_A)^{2/3} e^{-1/3}$ then follows, and equation 3d was produced here by algebra. Note the near reversal of which equation would be the "starting point" to produce the set of four equations: Savara's order would be $A_{(m,2D-S)}^\circ \rightarrow 4d \rightarrow 4a$, while Campbell's order would be $3a \rightarrow A_{(m,2D-C)}^\circ \rightarrow 3d$. A Supporting Information is provided for this Correction, which uses an excel file example for Ag(g) with the entropy contribution from the internal modes assumed to be 0 J mol⁻¹ K⁻¹. The example in the Supporting Information shows that Equations 3a-3d each produce the same value as each other, and that Equations 4a-4d each produce the same value as each other. The difference in recommendations for the 2D gas standard state by Savara and Campbell corresponds to standard-state concentrations that differ only by a factor of $e^{1/3}$,³ which leads to 2D gas standard state entropies that typically differ by only ~10%.¹ The similarity of the entropies associated with these two 2D gas standard state choices is interesting, given that Equation 4a does not correspond to removal of 1/3 of the first term in Equation 2. Savara's recommendation for the 2D gas standard state is based upon setting the "box-length per particle" at the same value between the 3D gas and 2D gas standard states, $(L_{(p,2D-S)}^\circ) = (L_{(p,3D-I)}^\circ)$. Savara's recommendation implies a 2D gas standard-state concentration (in molecules per area) that is equal to the 3D gas standard-state concentration (in molecules per volume) to the power of 2/3. Campbell's recommendation for the 2D gas standard state is based upon removing 1/3 of the entropy from the Sackur-Tetrode equation (relative to the 3D gas standard state). There are additional subtleties regarding temperature dependence (beyond the scope of the original Comment); thus, authors should state during any analysis whether the density of the standard state used has any temperature dependence, or not. The main conceptual content of the original Comment remains unchanged.

Supporting Information

The supporting information includes an excel spreadsheet with example calculations for Equations 3a-3d and 4a-4d.

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References:

1. Savara, A. Comment on "Equilibrium Constants and Rate Constants for Adsorbates: Two-Dimensional (2d) Ideal Gas, 2d Ideal Lattice Gas, and Ideal Hindered Translator Models". *The Journal of Physical Chemistry C* **2016**, *120*, 20478-20480.
2. Savara, A. Standard States for Adsorption on Solid Surfaces: 2d Gases, Surface Liquids, and Langmuir Adsorbates. *J Phys Chem C* **2013**, *117*, 15710-15715.
3. Campbell, C. T.; Sprowl, L. H.; Arnadottir, L. Equilibrium Constants and Rate Constants for Adsorbates: Two-Dimensional (2d) Ideal Gas, 2d Ideal Lattice Gas, and Ideal Hindered Translator Models. *J Phys Chem C* **2016**, *120*, 10283-10297.