

## Comment on “Equilibrium Constants and Rate Constants for Adsorbates: Two-Dimensional (2D) Ideal Gas, 2D Ideal Lattice Gas, and Ideal Hindered Translator Models”

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The work by Campbell et al.<sup>1</sup> was recently brought to my attention. This comment is written to provide greater clarity to the community to prevent misconceptions regarding the entropies being discussed in that work and to clarify the differences between the adsorbate standard states suggested by Campbell and by Savara. For distinguishable independent molecules, the canonical partition function is  $Q_{\text{dist}} = q^N$ , where  $N$  is the number of molecules and  $q$  is the molecular partition function given by  $q = q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vib}} \cdot q_{\text{electronic}}$ . For indistinguishable independent molecules (such as a gas), the canonical partition function is  $Q_{\text{indist}} = q^N/N!$ , and the denominator can be considered a type of quantum configurational term (this quantum configurational term is used for indistinguishable particles when the number of available molecular quantum states is much greater than the number of particles—which is generally true except in the cases of extreme densities<sup>2</sup>). For mathematical convenience, when dealing with gases, the terms are typically evaluated as follows:  $Q_{\text{indist}} = (q_{\text{trans}})^N/N! \times (q_{\text{rot}} \cdot q_{\text{vib}} \cdot q_{\text{int}})^N$ . Note that for mathematical convenience the translational term has been grouped with  $N!$  to yield the combined term  $(q_{\text{trans}})^N/N!$ . When evaluated, this term illustrates that the entropy can be treated as a function of the gas-phase density (and subsequently gas-phase pressure) giving rise to the Sackur–Tetrode equation. For a gas with  $D$  translational dimensions, the Sackur–Tetrode equation is given by

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

where  $n$  is the number of moles;  $N_A$  is Avogadro's number;  $R$  is the ideal gas constant;  $L$  is the length of the box;  $m$  is the molar mass;  $k$  is the Boltzmann constant;  $h$  is Planck's constant; and  $T$  is the temperature in Kelvin. In this equation,  $nN_A/L^D$  is a density. The Sackur–Tetrode equation can also be written as

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

which emphasizes that the latter term in eq 2 has no dimensional dependence and originates from the indistinguishability of the particles (i.e., the  $N!$  term associated with quantum configurations). For the remainder of this comment, we will refer to eq 2 when discussing the Sackur–Tetrode

equation. Note that not only does the first term depend on the number of dimensions, it is in fact linear with the number of dimensions—such that  $D = 2$  has twice the entropy as  $D = 1$  for the same box length,  $L$ , while  $D = 2$  has 2/3 of the entropy associated with  $D = 3$  for the same box length,  $L$ . For most real-world 3D gas-phase densities, eq 2 is dominated by the first term. The linearity of this first term with the number of dimensions, and its dominance, is the reason that Campbell,<sup>1</sup> Savara,<sup>3</sup> and de Boer<sup>4</sup> each suggested that the 2D gas standard state be defined as a state with one-third less translational entropy relative to the 3D gas standard state. Unfortunately, eq 3 of Campbell et al.<sup>1</sup> removes the factor of one-third from the entire Sackur–Tetrode equation (the entire eq 2), rather than just the term related to the dimensional contributions. In effect, Campbell et al.'s procedure artificially lowers the 2D gas standard state entropy's quantum configurational term—the second term in eq 2—as though scaling that term to reflect a smaller number of molecules. This ultimately leads to an artificial coefficient of 1.40 in eq 7A of reference 1 (and also leads to a choice for the 2D gas standard state pressure/concentration that differs from that put forth by Savara and by de Boer).

Consider the following example: if we take the tabulated gas-phase standard entropy of methanol<sup>5</sup> as  $(239.81 \text{ J mol}^{-1} \text{ K}^{-1})$  and multiply it by two-thirds, the result is  $159.87 \text{ J mol}^{-1} \text{ K}^{-1}$ . That calculation would be considered an inappropriate way to remove the effects of one translational mode from the entropy because that procedure would also have reduced the entropy associated with the molecular vibrations and rotations by one-third. While less easily appreciated, the value of  $159.87 \text{ J mol}^{-1} \text{ K}^{-1}$  also reflects having artificially reduced the quantum configurational contribution by one-third. Similar to this example, Campbell et al.'s<sup>1</sup> eq 3 inadvertently reduces the quantum configurational entropy contribution by one-third when attempting to calculate a 2D gas standard state entropy in relation to a 3D gas standard entropy.

Let us take a closer look at what happens with the example of methanol when applying the suggestion given by Campbell<sup>1</sup> versus that given by Savara.<sup>3</sup> Both authors have written that the intent is to subtract one-third of the translational entropy of a 3D gas standard state.<sup>1,3,6</sup> Campbell recommends subtracting one-third of the entropy provided by the Sackur–Tetrode

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equation for the 3D gas standard state, based on the idea that this is sufficiently intuitive and accessible to experimentalists. In this case

$$S_{\text{methanol}}^{\circ}(\text{2D-gas}) = S_{\text{methanol}}^{\circ}(\text{3D-gas}) - \frac{1}{3} \left[ nR \ln \left( e^{3/2} \left( \frac{\sqrt{2\pi mkT}}{h} \right)^3 \frac{L^3}{nN_A} \right) + nR \ln(e^1) \right] \quad (3)$$

While Savara suggests to only remove one-third of the first term, which is the term that has a dimensional dependence

$$S_{\text{methanol}}^{\circ}(\text{2D-gas}) = S_{\text{methanol}}^{\circ}(\text{3D-gas}) - \frac{1}{3} \left[ nR \ln \left( e^{3/2} \left( \frac{\sqrt{2\pi mkT}}{h} \right)^3 \frac{L^3}{nN_A} \right) \right] \quad (4)$$

The entropy difference between Campbell's suggestion and Savara's suggestion is on the order of 10% for a typical 2D gas standard state.<sup>3</sup> So if one of the equations was dramatically simpler, that simplicity could justify use of a less correct equation. However, we see that Campbell's suggestion is not only less correct since it subtracts one-third of the quantum configurational term but also additionally marginally less simple of an equation than Savara's suggestion. There seems to be no benefit in either accuracy or effort to subtract one-third of the entire 3D Sackur–Tetrode entropy rather than just reducing solely the term associated with the number of translational dimensions.

An additional issue is the choice of the standard state for a 2D lattice confined adsorbate (i.e., for Langmuir adsorption). Campbell suggests setting a standard state density for 2D lattice confined adsorbates to have the same density as the 2D gas standard state. In my view, intentionally matching the 2D gas standard state density is inappropriate. To shed light on this issue conceptually, consider the following question: Do we set the density of the standard state of a 3D solid equal to that of a 3D gas? No, of course not: We merely accept that when comparing the 3D gas standard state to the 3D gas solid standard state that there is compression, which is reflected in the entropy. Similarly, when comparing a 2D gas adsorbate state and a 2D lattice confined adsorbate state (the latter being like a 2D crystalline solid with vacancies), we must recognize that they are different types of phases. There is no reason to believe that going from a 2D gas standard state to a 2D lattice confined standard state would be a comparison without compression.

Discussion of the issue of adsorbate standard states is complicated by the fact that—for a fixed area—the total chemical entropy of a 2D gas scales linearly with the number of molecules,  $N$ , while the total chemical entropy for an immobile adsorbate is not directly proportional to the number of molecules,  $N$ . As pointed out in the Supporting Information of reference 3 the implication of this is that the differential molar entropy of a 2D gas is equal to the integral molar entropy of a 2D gas (i.e., in the absence of internal molecular modes, both are equal to eq 2). In contrast, for an immobile adsorbate the differential and integral molar entropies are not equal to each other and must be defined by separate equations (see Supporting Information of ref 3). The differential molar entropy is the one that is relevant for defining chemical thermodynamic equilibria: the chemical potential is given by a differential molar free energies—such as  $\left(\frac{\partial G}{\partial n}\right)_{T,P,n}$  or

$\left(\frac{\partial A}{\partial n}\right)_{T,V,n}$ —which must be set to 0 for the condition of chemical thermodynamic equilibrium. The standard states should thus be chosen independently for a 2D lattice confined adsorbate and a 2D gas adsorbate. Savara<sup>3</sup> argued that for a 2D lattice confined adsorbate using a relative coverage of  $\theta^{\circ} = 0.5$  for the standard state allows the most direct incorporation into tabulations of thermodynamic values and direct comparison between systems (see ref 3 for more details). Note that using  $\theta^{\circ} = 0.5$  for the 2D lattice confined standard state leads to the following relation for the standard entropy relative to that of a 2D gas

$$S_{\text{2D-gas}}^{\circ} \approx S_{\text{2D-Lattice-Confined}}^{\circ} + S_{\text{Sackur-Tetrode(2D-gas)}} \quad (5)$$

This is in line with the idea that when comparing the entropies and free energies of the standard states the differences should be reflective of the changes in molecular degrees of freedom between the different phases (or states) being compared. In contrast, Campbell et al.<sup>1</sup> argued that a specified relative coverage (or absolute coverage) should be used for the 2D lattice confined adsorbate, based on the idea that such a choice will cause some terms to cancel out when comparing entropies of the 2D gas standard state and the 2D lattice confined standard state. The relative coverage specified by Campbell et al.<sup>1</sup> is  $\theta^{\circ} = 0.012$ . There are two shortcomings associated with Campbell's method for specifying the 2D lattice confined standard state: (1) The coverage of  $\theta^{\circ} = 0.012$  was chosen by Campbell et al. "arbitrarily" based on using a value of  $10^{15}$  sites  $\text{cm}^{-2}$ —so the 0.012 coverage does not enable appropriate general comparison for the same adsorbate on different surfaces nor different adsorbates on the same surface since the saturation densities will not generally be  $10^{15}$  sites  $\text{cm}^{-2}$ . (2) Such a choice confuses the issue because Campbell is trying to cancel part of the *translational* entropy of the 2D gas term with a *spatial configurational entropy* of the immobile adsorbate. Although both of the terms are density dependent, the statistical mechanical origins of their density dependences are categorically different. Trying to cancel those terms only obfuscates molecular entropy comparisons rather than illuminating them. (For an ideal 2D gas, the translational entropy is density dependent, while the quantum configurational entropy is not. In contrast, for a 2D lattice confined adsorbate, the particles are distinguishable, and there is a spatial configurational entropy term which is density dependent.) In contrast, the standard state suggestions put forth in ref 3 were chosen for enabling molecular knowledge to be gained by comparison to tabulated standard entropies—in line with existing practice.

Finally, by definition, the standard chemical potential is given by the chemical potential at the standard state of that phase,<sup>7</sup>  $\mu^{\circ}(T) = \mu(T, P^{\circ})$  or  $\mu^{\circ}(T) = \mu(T, \pi^{\circ})$ , where  $P^{\circ}$  is the 3D standard state pressure and  $\pi^{\circ}$  is the standard state 2D pressure. In this context, making an appropriate choice for the standard states not only enables molecular information to be gained but also enables equilibria to be calculated using chemical potentials relative to that of the standard state. For this reason, standard states should be chosen based on the equations associated with differential molar entropies, and in a way that enables useful molecular information to be gained by comparing standard state thermodynamic quantities (entropy, enthalpy, free energies). I agree with the spirit of the ideas published by Campbell et al.<sup>1</sup> and hope that the community finds this

comment to provide additional understanding of the details and to be helpful at preventing misconceptions.

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### Notes

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