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Note on the inconsistent definition assigned in the literature to the heat capacity of the so-called “equilibrium hydrogen” mixture.

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ABSTRACT

In classical chemical engineering thermodynamics, constant-pressure heat capacity has a rigorous – non-negotiable – definition. With this communication we aim to make researchers aware of a thermodynamically inconsistent definition assigned, in the literature, to the heat capacity of equilibrium gaseous mixtures of reacting ortho-hydrogen and para-hydrogen (the so-called “equilibrium-hydrogen mixtures”). Along this note we show that in order to define its heat capacity, the equilibrium reacting mixture is inconsistently assimilated to a pseudo pure component having the same enthalpy as the reacting mixture of p-H₂ and o-H₂ at chemical equilibrium. In so doing, the pseudo-component heat capacity aggregates not only sensible-heat effects but also thermal effects due to compositional changes.

Keywords: Equilibrium hydrogen, para-hydrogen, ortho-hydrogen, heat capacity.

1. INTRODUCTION

In nature, molecular hydrogen exists in the form of a mixture of two nuclear isomeric forms, ortho-hydrogen and para-hydrogen [1], in the proportions dictated by the temperature of the system, its dynamic variation and the kinetic characteristics of the (slow) reaction $o\text{-H}_2 \rightleftharpoons p\text{-H}_2$. More specifically, “equilibrium hydrogen” denotes, in the literature, the reactive system characterized by the proportion of ortho- and para-hydrogen dictated by the condition of thermodynamic equilibrium.

Since the 1930^s, many authors have been mentioning or treating the problem of computing the thermodynamic properties of equilibrium hydrogen under the assumption of perfect gas mixture.

In the context of a research project focused on the study of hydrogen liquefaction and storage, we came across the dissemination, in the literature, of an inconsistent presentation of the heat capacity of the equilibrium hydrogen mixture. Indeed, although modelled as perfect gas system, equilibrium hydrogen is surprisingly presented as a mixture whose specific heat capacity, at some temperatures, does not take an intermediate value between the ones of the two pure components that form the mixture, ortho-hydrogen and para-hydrogen [1–10]. Such a result is unquestionably in contradiction with well-established mathematical relationships that apply to perfect gas mixtures.

To our knowledge, only Pitzer [11] tried to explain the occurrence of such a behavior, by saying that the “heat capacity of the equilibrium mixture includes a term for the heat of conversion [...]”. According to such an explanation, the reason of the deviation from the expected trend of the specific heat capacity of equilibrium hydrogen has to be sought in the occurrence of the chemical reaction which characterizes hydrogen at thermodynamic equilibrium, $o\text{-H}_2 \rightleftharpoons p\text{-H}_2$. However, Pitzer’s statement clearly does not explain why a quantity, which does not verify the thermodynamic definition of the specific heat capacity of a mixture, is designated in the literature “specific heat capacity of equilibrium hydrogen”. It is, indeed, neither theoretically correct, nor of common practice to include the heat of reaction directly in

the specific heat capacity of a reactive system. In front of a hodgepodge of undigested thoughts available in the open literature, this note aims at clarifying how were defined the properties of “equilibrium hydrogen” and especially its heat capacity.

2. DISCUSSION

From classical chemical-engineering thermodynamics, the specific heat capacity of a mixture (of known mole-fraction vector \mathbf{z} , temperature T and pressure p) is defined as:

$$c_{p_{mix}}(T, p, \mathbf{z}) = \left[\frac{\partial h(T, p, \mathbf{z})}{\partial T} \right]_{p, \mathbf{z}} \quad (1)$$

(where h denotes the specific enthalpy of the mixture). In case of a nc -component perfect gas mixture, the constant pressure specific heat capacity results to be given by:

$$c_{p_{mix}}^{\bullet}(T, \mathbf{z}) = \left[\frac{\partial h^{\bullet}(T, \mathbf{z})}{\partial T} \right]_{\mathbf{z}} \quad (2)$$

as the enthalpy of a perfect gas mixture is pressure-independent. Note that symbol “ \bullet ” designates a perfect gas property. Analogously, by remembering that the heat-capacity change on mixing (c_p^M) is zero for a perfect gas mixture, one has:

$$c_{p_{mix}}^{\bullet}(T, \mathbf{z}) = \sum_{i=1}^{nc} z_i c_{p_{pure i}}^{\bullet}(T) \quad (3)$$

where:

$$c_{p_{pure i}}^{\bullet}(T) = \frac{dh_{pure i}^{\bullet}(T)}{dT} \quad (4)$$

is the specific heat capacity of pure perfect-gas i . According to Eq. (3), the specific heat capacity of any binary mixture takes an intermediate value between the specific heat capacity of the components which form that mixture. For completeness, the equilibrium composition of the system $o\text{-H}_2 \rightleftharpoons p\text{-H}_2$ – that can be determined by well-known theoretical considerations [1,12] – is a function of the temperature only. **Fig. 1** shows the graphical evolution of this function. An approximate correlation for this curve is reported by Wilhelmsen et al. [13].

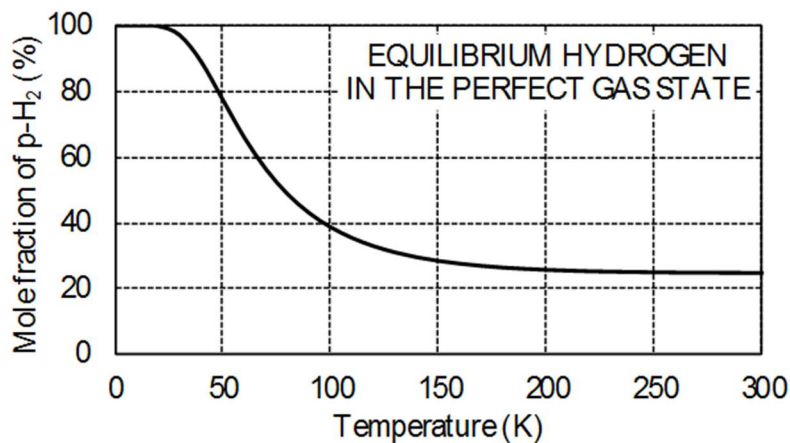


Figure 1. Mole fraction of para-hydrogen in perfect gas equilibrium hydrogen.

Published values for specific heat capacities of equilibrium hydrogen follow the curve named “Literature equilibrium hydrogen” in **Fig. 2**. Consistently with Eq. (1) (i.e., the rigorous definition of a heat capacity, coincident with Eq. (4) for a pure fluid), it is possible to show from the quantic theory [11] that the specific heat capacities of pure para-hydrogen and ortho-hydrogen follow the dashed curves represented in **Fig. 1**. Moreover, **Fig. 1** shows the specific heat capacity of the equilibrium hydrogen mixture calculated accordingly to the uncontested Eq. (3) (namely, “Actual equilibrium hydrogen”), considering the determined composition of the equilibrium

mixture (**Fig. 1**) and the specific heat capacities of pure ortho-hydrogen and para-hydrogen. Being equilibrium hydrogen a binary mixture of ortho-hydrogen and para-hydrogen, its specific heat capacity should be, by definition, between that of these two pure components and should coincide with the curve labeled “Actual equil. hydrogen” in **Fig. 2**.

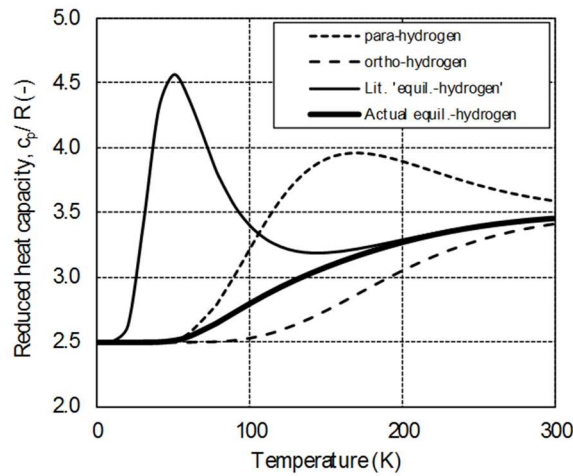


Figure 2. Reduced specific heat capacity of para-hydrogen, ortho-hydrogen, literature ‘equilibrium-hydrogen’ and actual equilibrium hydrogen.

From the above, it is possible to conclude that the specific heat capacity of “literature equilibrium hydrogen” totally disagrees with the theory. To clarify this discrepancy, we need to go back to the definition of “Literature equilibrium hydrogen” specific heat capacity.

The heat capacity of “Literature equilibrium-hydrogen” is calculated, under the assumption of perfect gas, as:

$$c_{p_{mix}}^{\bullet}(T) = \frac{dh_{equilibrium}^{\bullet}[T, z_{equ.}(T)]}{dT} \quad (5)$$

Differently from the rigorous definition given in Eq. (2), Eq. (5) is unquestionably a derivative of the enthalpy of the mixture with respect to temperature but evaluated along the equilibrium path, i.e., at variable (rather than constant) composition. Indeed, as previously discussed (see **Fig. 1**), composition of the equilibrium mixture is temperature-dependent.

We can conclude that Eq. (5) is thus not the correct – thermodynamically consistent – definition of the specific heat capacity of the mixture $o\text{-H}_2 \rightleftharpoons p\text{-H}_2$. **What is titled, in the literature, “equilibrium hydrogen heat capacity” is, in fact, the heat capacity of a fictive pure component having the same enthalpy as a reacting mixture of para-hydrogen and ortho-hydrogen at chemical equilibrium.** In other words, the term represented by Eq. (5) is actually a pure-component quantity aggregating the sensible-heat and reaction thermal effects of an equilibrium hydrogen mixture:

$$c_{p_{mix}, Eq. (5)}(T) = c_{p, \text{fictive pure fluid}}(T) \quad (6)$$

*having the same
enthalpy as the
reactive mixture
o-H₂ ⇌ p-H₂*

In support to such a conclusion, we observe that the molar thermal power, Q/n , exchanged by the equilibrium hydrogen mixture along its isobaric cooling from inlet temperature, T_{in} , to the outlet temperature, T_{out} , can be **equivalently** calculated either treating such a system as a fictive pure component characterized by the specific heat capacity curve named in **Fig. 2** “Lit. equilibrium hydrogen”:

$$\frac{Q}{n} = \int_{T_{in}}^{T_{out}} c_{p, \text{fictive pure fluid}}(T) \cdot dT \quad (7)$$

*having the same
enthalpy as the
reactive mixture
o-H₂ ⇌ p-H₂*

or according to the rigorous method:

$$\begin{aligned} \frac{Q}{n} = & z_{p-H_2}^{eq}(T_{in}) \int_{T_{in}}^{T_{out}} \dot{c}_{p,pure\ p-H_2}(T) dT + \\ & + z_{o-H_2}^{eq}(T_{in}) \int_{T_{in}}^{T_{out}} \dot{c}_{p,pure\ o-H_2}(T) dT + \\ & + \frac{\xi}{n} \Delta_R H^\circ(T_{out}) \end{aligned} \quad (8)$$

where ξ/n is the extent of reaction specific to the molar flow, which can be determined by the knowledge of the equilibrium composition [13], and $\Delta_R H^\circ(T_{out})$ the enthalpy of reaction at the outlet temperature:

$$\begin{aligned} \Delta_R H^\circ(T_{out}) = & \left(\Delta_f H_{p-H_2}^\circ(T_{ref}) + \int_{T_{ref}}^{T_{out}} \dot{c}_{p,pure\ p-H_2}(T) dT \right) \\ & - \left(\Delta_f H_{o-H_2}^\circ(T_{ref}) + \int_{T_{ref}}^{T_{out}} \dot{c}_{p,pure\ o-H_2}(T) dT \right) \end{aligned} \quad (9)$$

being $\Delta_f H_i^\circ(T_{ref})$ the standard enthalpies of formation of ortho-hydrogen and para-hydrogen, at the reference temperature.

Furthermore, we would like to highlight that the design of the heat capacity of a fictive pure fluid being thermally equivalent to a reactive mixture at thermodynamic equilibrium is possible only when the mixture behaves as a perfect gas and if the reaction does not involve a variation of the number of moles of the reactive system, i.e., if:

$$\sum_i^{NR} |v_i| = \sum_i^{NP} |v_i|, \text{ that is: } \sum_i^{NC} v_i = 0 \quad (10)$$

where NR and NP denote the number of reactants and products, respectively, and v_i is the stoichiometric coefficient of each i -th species involved in the reaction.

Indeed, for these types of reactive systems, the composition, \mathbf{z} , at chemical equilibrium and thus the corresponding enthalpy $\left[h_{\text{equilibrium}}^\circ = \sum_{i=1}^{NC} z_i \cdot h_{\text{pure } i}^\circ(T) \right]$ is only function of temperature.

Proof can be obtained by writing the condition of thermodynamic equilibrium (see Eq. (11) in which the mathematical expression of the temperature-dependent equilibrium constant only depends on the equilibrium composition):

$$\begin{aligned} K(T) &= \prod_i^{NC} \left(\frac{f_i}{p^\circ} \right)^{v_i} \\ &= \left(\frac{p}{p^\circ} \right)^{\sum_i^{NC} v_i} \prod_i^{NC} z_i^{v_i} \\ &= \prod_i^{NC} z_i^{v_i} \end{aligned} \quad (11)$$

f_i is the fugacity of the i -th pure component and p° is standard-state pressure.

The composition at chemical equilibrium and the corresponding enthalpy $\left[h_{\text{equilibrium}}^{\circ} = \sum_{i=1}^{nc} z_i \cdot h_{\text{pure } i}^{\circ}(T) \right]$ depending only on temperature, application of Eq. (5) makes it

possible to design the heat capacity of a fictive pure perfect gas thermally equivalent to the reactive mixture. For different types of reactive systems, the variation of the equilibrium composition with pressure would entail the necessity of defining the heat capacity of a fictive pure perfect gas for each pressure level. Such an approach would thus lose its peculiar simplification feature, which is the reason at the basis of its application.

Finally, to insist on the physical difference between the constant-pressure calorimetric quantities treated in this work, we would like to stress that calorimetric measurements performed on reactive fluids characterized by non-negligible reaction rates would lead to measure the calorimetric quantity represented by Eq. (5), which contains the contribution of the heat of reaction. In particular, in the ideal case of a perfectly catalyzed reaction between o-H₂ and p-H₂, such calorimetric measurement would lead to obtain the curve labeled “Lit. equil.-hydrogen” in **Fig. 2**. On the other side, in the absence of a catalyzer, the reaction between o-H₂ and p-H₂ is so slow that the effect of the reaction is negligible in the characteristic time of these experimental measurements. As a consequence, calorimetric measurements at constant-pressure on such a system would lead to measured quantities which respond to Eq. (3): the actual specific heat capacity of mixtures composed by o-H₂ and p-H₂, in their time-invariant proportion fixed by the initial composition of the system under analysis.

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GRAPHICAL ABSTRACT

