# Comments on the article "Persistent confusion of total entropy and chemical system entropy in chemical thermodynamics" [(1996) *Proc. Natl. Acad. Sci. USA* 93, 7452–7453]

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A comment is necessary on the article entitled "Persistent confusion of total entropy and chemical system entropy in chemical thermodynamics" by Gregorio Weber, which appeared in these PROCEEDINGS (1). The article purports to show that in all prior treatises and texts on thermodynamics the temperature variation of the Gibbs free energy of a single substance, and therefore also the van't Hoff equation for the temperature variation of the Gibbs free energy change of a reaction, have been misinterpreted.

Weber originally published his views in *J. Phys. Chem.* (2). His work there was criticized in refs. 3 and 4; he replied in ref. 5 but ignored most of the criticism. The purpose here is to point explicitly to Weber's errors in a simple way; the valid and pertinent arguments in refs. 3 and 4 are not repeated.

Consider a one-variable system. The Gibbs free energy is

$$G = H - TS; \qquad [1]$$

for differential changes we have

$$dG = Vdp - SdT. \qquad [2]$$

Symbols without subscripts refer to the system. For a process at constant pressure but not constant temperature

$$(\partial G/\partial T)_p = -S; \qquad [3]$$

in Eq. 3 $S$ is the entropy of the system, not the entropy of the system and the entropy of the surroundings, as Weber claims.

For a process at constant temperature and constant pressure

$$(dG)_{T,p} = 0, \qquad [4]$$

where we have added on $dG$ the notation that $T$ and $p$ are constant. Next we return to Eq. 1 and derive for a process at constant temperature

$$(dG)_T = dH - TdS. \qquad [5]$$

If in addition we hold the pressure constant, then

$$dH = đQ_p \qquad [6]$$

and the entropy change in the surroundings is given by

$$-dH = -đQ_p = T_{surr}dS_{surr}. \qquad [7]$$

Since both $T$ and $p$ are kept constant we may write

$$T = T_{surr} \qquad [8]$$

and

$$(dG)_{T,p} = -T[dS + dS_{surr}]. \qquad [9]$$

From Eq. 4 we see that Eq. 9 equals zero always. Another way of seeing that result comes from the fact that for a one-component system a process at constant $T$ and $p$ is reversible; hence

$$dS = -dS_{surr}, \qquad [10]$$

and Eq. 9 is zero. Eq. 9 is the same as equation 3 in ref. 1.

At this point Weber claims that Eq. 3, with $S$ interpreted by him to be the entropy of the system and the entropy of the surroundings (his equation 4), follows from Eq. 9 (his equation 3), but he gives no derivation. This is impossible, since the constraints on Eq. 9 are constant $T$ and $p$, but the constraints on Eq. 3 are constant $p$. Furthermore, Eq. 9 always equals zero, whereas Eq. 3 is not zero for any $T$ variation. $S$ in Eq. 3 is the entropy of the system, not the entropy of the system plus that of the surroundings, as Weber claims.

Weber failed to notice the different constraints on Eq. 9 (his equation 3) and on Eq. 3 (his equation 4); further, he failed to notice that Eq. 9 (his equation 3) is always zero. Hence all that follows in Weber's article is incorrect.

Another argument can be made against Weber's interpretation of Eq. 3.

Consider Weber's suggested relation for a one-variable system

$$\left(\frac{\partial G}{\partial T}\right)_p = -[S_{system} + S_{surr}],$$

which is equation 4 in Weber's article in the PROCEEDINGS. $G$ is the Gibbs free energy of the systems. For consistency we choose $G$ to be per mole of the system, $S_{system}$ to be the entropy per mole of the system, and $S_{surr}$ to be the entropy per mole of the surroundings. Suppose the surroundings are made of $N_2(g)$, which has a given value for its entropy per mole; if we change the surroundings to be water, then the entropy per mole of $H_2O$ has another value. Thus if we integrate the above equation at constant pressure

$$G(T_2, p) - G(T_1, p) = -\int_{T_1}^{T_2} [S_{system} + S_{surr}]dT,$$

then $G$ is no longer a state function—that is, a function dependent on the state of the system only. The integral depends on the specific material constituting the surroundings. Hence, given $G(T_1, p)$, the value of $G(T_2, p)$ depends not only on $T_2$, $p$ of the system but also on the specific material of the surroundings. This conclusion is absurd, and Weber's arguments cannot be correct.

1. Weber, G (1996) *Proc. Natl. Acad. Sci. USA* **93,** 7452–7453.
2. Weber, G. (1995) *J. Phys. Chem.* **99,** 1052–1059.
3. Holtzer, A. (1995) *J. Phys. Chem.* **99,** 13048–13049.
4. Ragone, R., Colonna, G. & Ambrosone, L. (1995) *J. Phys. Chem.* **99,** 13050.