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Response by the author

GREGORIO WEBER

University of Illinois School of Chemical Sciences, 600 South Mathews Avenue, Urbana, IL 61801

Contributed by Gregorio Weber, September 11, 1996

It would be too easy to talk past each other by reference to equations that are nothing more than an expression of the concepts that one holds as valid before writing any equations. It seems more profitable to refer to these concepts directly and fix attention on the differences between our respective beliefs.

In my view the point at issue is as follows: Must one distinguish from the start between the changes in entropy of system and surroundings (total entropy) and the change in entropy within the chemical system (intrinsic entropy), or is this distinction unnecessary? As I say in my note, Planck distinguished between them, and I have followed his views. Gibbs considered only the total entropy increase and for that purpose assumed that "the reagents are enclosed in a rigid and fixed envelope which is impermeable to and unalterable by any of the substances enclosed, and *perfectly non conducting to heat*" (ref. 1; my italics). Thus, the change in entropy that Gibbs defined is the one that obtains under *adiabatic* conditions. If the adiabatic condition is relaxed so that the chemical system within the Gibbs envelope equalizes temperature with surroundings of large enough heat capacity, what remains inside is the isothermal heat of the chemical system (determined by its intrinsic entropy), while the entropy of the surroundings changes as demanded by the changes in both intrinsic entropy and enthalpy upon reaction, *not the enthalpy change alone* (more extensively discussed in ref. 2), as in equation **7** of the comment by Dr. Ross. Experimentally we cannot separate the changes in enthalpy and entropy by measuring independently either quantity, but "significant discrepancies between van't Hoff and calorimetric enthalpies" have been documented recently in these PROCEEDINGS (3). Such discrepancies arise because when temperature is changed each reagent undergoes internal chemical reactions and the changes in intrinsic entropy and enthalpy in these internal reactions are *independent* just as in any other chemical reaction. This is the situation that, in my opinion, leads to the failure of the van't Hoff equation and necessitates the application of specific thermodynamic models that make explicit the relations of the changes of enthalpy and intrinsic entropy with temperature for each reagent.

1. Gibbs, J. W. (1993) *The Scientific Papers of J. Willard Gibbs, I. Thermodynamics* (Ox Bow, Woodbridge, CT), p. 62.
2. Weber, G. (1995) *J. Phys. Chem.* **99,** 13051.
3. Naghibi, H., Tamura, A. & Sturtevant, J. M. (1995) *Proc. Natl. Acad. Sci. USA* **92,** 5597–5599.
