A Note on Brønstedian Energetics

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Sir: I enjoyed the interesting article by Gaggioli and Petit, "Use the Second Law First" (CHEMTECH, August 1977, p 496). It might interest readers to know that the stimulating approach to the second law used by these authors was originally formulated by J. N. Brønsted in the late 1930s and early 1940s. Brønsted called his version of thermodynamics "energetics" (not to be confused with the earlier version of energetics advocated by Mach, Ostwald, and Helm near the turn of the century) in order to emphasize that it dealt with generalized energy transformations and not just with those involving idealized thermal phenomena.

Brønsted's alternative, but equivalent, formulation of thermodynamics is process rather than system oriented and is based on a distinction between idealized reversible processes and naturally-occurring irreversible processes.

In reversible processes, all energy redistributions (i.e., work) can be represented as the transport of some capacity factor between two different intensities or potentials:

$$\delta A_r = (P_1 - P_2)\delta K_r \qquad [1]$$

where P_1 and P_2 represent the two initial potentials and δK_r represents the conjugate capacity factor for the type of work, δA_r, involved. Exemplary capacity factors would be gravitational mass, moles of chemical substance, electrical charge, volume, etc.; the corresponding potentials would be gravitational potential, chemical potential, voltage, and negative pressure.

Brønsted pointed out that reversible thermal interactions are completely analogous to reversible work interactions and can also be represented by means of equation 1, where the absolute temperature functions as the potential and the transferred entropy increment as the capacity factor. In reversible processes, entropy, like most other capacity factors, is conserved.

Reversible changes generally involve the coupling of two or more work processes, and mechanics teaches us that, in an isolated system, the net work change resulting from such couplings among its constituent subsystems is always zero (i.e., work, not just energy, is conserved):

$$\Sigma_r \delta A_r = \Sigma_r (P_1 - P_2)\delta K_r = 0 \qquad [2]$$

Brønsted called this the "work principle."

Irreversible processes, however, represent an entirely different situation. Here equation 2 no longer applies and experience teaches us that, in an isolated system, there is always a net decrease in the available work and a corresponding isothermal generation of entropy:

$$\Sigma_r \delta A_r + T\delta S_{irr} = 0 \qquad [3]$$

This process is unidirectional because entropy at a constant temperature (or indeed, any equipotential energy) cannot be converted back into work. Brønsted called this the "equivalence principle," and it may be combined with equation 2 to give the general relation:

$$-\Sigma_r \delta A_r = T\delta S_{irr} \geq 0 \qquad [4]$$

where the equal sign refers to the reversible case and the inequality to the irreversible case.

In that none of the fundamental work of Brønsted is referenced by Gaggioli and Petit, I take the liberty of attaching a selected bibliography of papers in English which deal with Brønsted's approach. Of particular interest is the 1949 paper by LaMer et al. and the 1976 paper by Sørensen, both of which prove the equivalence between equation 4 and the conventional forms of the first and second laws.

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