Remarks on the Composition Potential

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Suryanarayana and Venkatesan[1] have defined a quantity, which they call the composition potential, viz., the ratio of the mole fraction of a solute (electrolyte) in a solution at an arbitrary concentration to the mole fraction at the saturation point. The authors have stated that this ratio, denoted by C_p, to be a truly thermodynamic potential. This is not in accordance with the accepted definition of thermodynamic potentials. The thermodynamic potentials have and must have the following fundamental property[2]. "If we know one of the thermodynamic potentials as a function of its variables, to which it corresponds, we can express all the other thermodynamic variables as a function of this potential and its derivatives". The potentials that can be defined as "thermodynamic potentials" and which conform to this statement are the Gibbs and Helmholtz functions, energy, enthalpy, entropy and the chemical potential and they alone. From a more general point of view, the potential can be defined as one whose gradient yields the force in a direction. To neither of these definitions does the definition of the composition potential agree.

The number of moles is an extensive variable and the ratio of two extensive variables yields an intensive variable[3]. The mole-fractions are intensive. We know that the ratio of two intensive quantities to be intensive, and that any combinations of them to be still intensive. The derivative of an extensive variable with respect to another extensive is intensive. The composition potential defined by the said authors, is an intensive variable and is dimensionless. Apart from this, no other thermodynamic significance can be attributed to 'C_p'. It is a property of the solution and a variable in the thermodynamic sense. The mere fact that a particular property (e. g. the sum of the mole fractions) has a constant specified value does not merit being called thermodynamic potential.

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1) C. V. Suryanarayana and V. K. Venkatesan, This Bulletin, **31**, 442 (1958).
2) I. Prigogine, "The Molecular Theories of Solutions", North Holland Publ. Co., Amsterdam (1957).
3) E. A. Guggenheim, "Thermodynamics", North Holland Publ. Co., Amsterdam (1952).