On the Concentration Potential

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Vaidhyanathan[1] is in great error in his 'Remarks on the composition potential' in regard to a quantity defined by us[2] recently. We defined a quantity C_p as the ratio of the mole fraction of the solute at any given molal concentration to that at saturation at the same temperature. Precisely we called this ratio C_p, the concentration potential and not the composition potential as he states in his remarks. What is most amusing is that Vaidhyanathan imagines that we have stated the above ratio as being a truly thermodynamic potential. We have not done so. A careful perusal of our paper (loc. cit.) shows that the wording is as follows:

"The concentration potential newly conceived herein is a truly thermodynamic *concept of concentration* dependent only on

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[1] V. S. Vaidhyanathan, This Bulletin, **32**, 99 (1959).

[2] C. V. Suryanarayana and V. K. Venkatesan, ibid. **31**, 442 (1958).

the initial and final states of stability of a solution and independent of any arbitrary scale of concentration or the nature of both the solvent and the solute". The *concept* is a thermodynamic one as explained by the rest of the above sentence but definitely it can never even imply that the ratio called by us 'concentration potential' is ever a thermodynamic potential at all.

We must point out incidentally that the definition of thermodynamic potentials given naively by Vaidhyanathan is in serious error. He states: "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". Excepting the last mentioned chemical potential which is the derivative of the Gibbs free energy with respect to the number of moles of the species at constant temperature and pressure all the other functions are extensive properties and are not called thermodynamic potentials merely by themselves. They have of course the properties of exact differentials. Thermodynamic potentials are always intensive[3] (expressed per mol.) especially for the chemist when dealing with solutions. Further what he states in the first part of his last para has either no purpose or contradicts the last part of his first para and hangs loosely.

What may be really a pertinent question is the reason why we have called the newly defined ratio a concentration potential. An answer to this is due to appear elsewhere (under publication), and is briefly as follows. When we picture what happens when a soluble solid solute is added to a solvent, we can imagine its dissolution at any instant giving in the vicinity of the solute a successive series of layers of solutions, the most concentrated one being nearest the solid and the least concentrated one the pure solvent itself. The most concentrated one is the saturation concentration and the lowest concentration is zero. In between, there is to be imagined a concentration gradient. It is so clear that the saturation concentration has a directive influence on the concentration gradient. Our main purpose in defining this new ratio is to indicate the soundness of comparing a physical property of solutions of two different solutes in a given solvent at identical gradients and not at identical arbitrary concentrations as is being done so far. In this context any arbitrary concentration between the saturation and zero values has been visualized as better represented by the ratio of mole fraction to that at saturation and called the concentration potential due to its relation to the above mentioned gradient. Any arbitrary concentration for a salt must occur in the concentration gradient given in the above picture of the dissolution of the same salt. The situation is similar to the well-known classical law of corresponding states. But it is too early to predict the usefulness of the newly defined ratio, especially whether equally important generalizations will accrue out of the use of C_p. Of course, C_p has the properties of an exact differential between the limits of zero concentration and saturation.

Again Vaidhyanathan states that apart from the fact that C_p is an intensive variable and is dimensionless, no other thermodynamic significance can be attributed to it. We should say that the above reasons are not enough to say that no other thermodynamic significance can be attributed to it. An understanding of the thermodynamic significance of the saturation state of a solution will be the final deciding factor in assessing the thermodynamic significance of the concentration potential defined by us. A perusal through Walden[4], van Laar[5], and Ricci and Davis[6] indicates enough thermodynamic importance of the saturated state.

In this back ground, though we should have no objection to call the concentration potential by any other name for any good reasons, we fail to see why it should not be called so as at present.

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[3] E. A. Guggenheim, "Thermodynamics", North Holland Publ. Co., Amsterdam, (1957).

[4] P. Walden, *Z. physik. Chem.*, **54**, 129, **55**, 683 (1906).

[5] J. J. van Laar, ibid., **58**, 567; **59**, 212 (1907).

[6] J. E. Ricci and J. W. Davis, *J. Am. Chem. Soc.*, **62**, 407 (1940).