

## The Generalized Setchenov Constant Near Critical Conditions

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In the vicinity of the binary critical end-point, the solubility of solids in supercritical solvents shows strong variations with pressure and temperature, a consequence of the diverging osmotic susceptibility of the binary system.[1] Similarly, the addition of a third component (co- or anti-solvent) at constant pressure and temperature, has a great impact on near-critical solubilities. Far from critical conditions, the effect of a third component in the solubility of solids is traditionally described in terms of the Setchenov's law constant  $K_S$ , originally employed for describing the effect of ionic third components, but that can be generalized to include non-ionic compounds as well. We have recently analyzed the validity of the Setchenov equation and evaluated the behavior of the Setchenov constant  $K_S$  as the critical end-point is approached. [2] The problem is isomorphic with that of a dilute solute near the solvent's critical point; that is,  $K_S$  diverges at critical end-point in a similar way the solute's partial molar volume at infinite dilution  $V_2^\infty$  does at the solvent's critical point. The signs of the divergence of  $K_S$  and  $V_2^\infty$  are related to the initial slopes of the critical end-line of the ternary system and of the critical line of the binary dilute mixture, respectively. Here we summarize the main aspects of the problem and analyze the limiting values of the solid's solubility at the critical end-point, which becomes path-dependent.

[1] Levelt Sengers, J. M. H. In *Supercritical Fluid Technology*; Bruno, T. J., Ely, J. F., Eds.; CRC Press: Boca Raton, FL, 1991; pp 1-56.

[2] K.I. Gutkowski, R. Fernández-Prini and M.L. Japas, *J. Phys. Chem. B* 2008, 112, 5671-5679.