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DELIQUESCENCE OF NANOPARTICLES: ACTIVATION OR NUCLEATION?

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ABSTRACT

Deliquescence, the uptake of water by a dry solute to form a saturated solution, occurs when the relative humidity RH is increased to a value RH_D at which the free energy barrier to water uptake vanishes; this is deliquescence by activation. For large particles this phase transition is abrupt and occurs at the bulk deliquescence value $RH_{D,bulk}$. For sufficiently small particles RH_D typically differs from $RH_{D,bulk}$ by an amount that depends on properties of the solute and is, to lowest order, inversely proportional to the first power of the dry particle diameter; RH_D may be greater than or less than $RH_{D,bulk}$. For RH less than RH_D, the possibility arises that fluctuations can drive the system (consisting of the dry solute plus water vapor) over the barrier to attain a state of lower free energy and thus that the particle will continue to uptake water until a saturated solution drop is formed; this is deliquescence by nucleation. An analytic expression for the barrier height is presented in terms of the dry particle size, RH, and RH_D. This height depends on properties of the solute and is, to lowest order, directly proportional to the fourth power of the dry particle diameter and to the square of the difference between RH_D and RH. Thus, large particles must attain RH very nearly equal to $RH_{D,bulk}$ before the barrier height is sufficiently low that there is any appreciable chance that deliquescence by nucleation can occur. However, for sufficiently small particles, those with diameters of several nanometers, there is a wider range of values below RH_D for which there is an appreciable chance of crossing the barrier (i.e., nucleating) to form a solution drop. This range of values may result in apparent non-abrupt deliquescence of a population of particles.
