Activity and activity coefficients IV: brines and $\gamma > 1$

In our previous consideration of activity and activity coefficients, we viewed activity as inevitably less than concentration. That was because we considered interactions in the solution to inevitably lessen the availability of specific ions for chemical reaction (and thus the activity coefficient would always be less than 1.0). All this hinged on the assumption that a suite of ions all hydrated, but not further complexed or coordinated, was a suite of ions maximally available for chemical reaction.

That assumption breaks down in a very concentrated solution. In such a solution, the proportion of water molecules involved in hydration of ions may become so large that there are insufficient water molecules for the hydration of all those ions. In that case, at least some individuals of our ion of interest may be less hydrated than is their normal condition. The sketch at right tries to portray that situation. It has the same number of water molecules as the sketch in Part I of this series, but it has more individuals of our blue ion of interest. With water molecules now scarce, some of those ions are less fully hydrated.

Because dehydration is a barrier to chemical reaction, the less-hydrated ions are now more chemically reactive: the probability of their dehydration, and possible participation in a chemical reaction, is greater. Thus their activity is now greater than in the dilute condition, where γ was 1.0, and so γ is now greater than 1.0.