From the ionic-polymeric syntax for acid-base and redox exchanges in silicate melts, to the modeling of volcanic degassing

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This contribution aims at shedding light on the use of the ionic-polymeric models to model melt properties and chemical reactions involving silicate melts. If on one side ionic-polymeric approaches have been criticized essentially because of the appearance of the so-called free-oxygens (nearly undetectable in high-SiO_2 compositions, such as natural ones), on the other hand it must be remarked that they only can provide the reference frame to write chemical exchange in aluminosilicate melts. These are in fact a special category of fused salts (oxides, in our case), in which the silicate structure is such that cations and anions have actual charges lower than formal ones, and the residual charge distribution from bonding of bridging oxygen to silicon allows oxygen bonding with other cations. This characteristics makes the relative contribution of nonbridging and bridging oxygens to the oxygen coordination of the other cations poorly known, avoiding to readily distinguish solute and solvent like in aqueous solutions and consequently the complexes needed to define acid-base reactions. Therefore, the distinction between solute and solvent becomes blurred in systems such as silicate melts, because speciation is not only complex, but it changes with the marked depolymerization of the silicate framework that obtains from pure SiO_2 to metal-oxide rich compositions. However, these may not be serious limits to account correctly for the acid-base reactions that take place in every kind of magmatic setting, provided a 'syntax' describing the effective interactions among significative cationic and anionic entities. So-called ionic-polymeric models highlight the mutual correspondence between polymerization and acid-base properties of dissolved oxides through the Lux-Flood formalism for molten oxides. They thus provide the syntax to write chemical exchanges, but have no pretension to structural description. The unique validity of ionic-polymeric approaches is shown for iron redox equilibria in which no shift of activity coefficient can explain observations. We also show the case of biphasic gas-melt equilibria involving water, halogens, sulfur. The latter, particularly, is used to show that the ionic-polymeric syntax can take simultaneously into account joint patterns of redox equilibria and $^{34}S/^{32}S$ measured in volcanic systems.