Thermodynamics and Kinetics applied to the Stability of Polymorphs

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A great many of different physicochemical investigations must be applied to elucidate the thermodynamic or absolute stability relations as functions of temperature and pressure of two polymorphs of a chemical substance. In the presented consideration the pressure dependence shall be disregarded.
The research work afforded for stability studies, independent from the level of quality anticipated, may increase drastically with an increasing number of polymorphic forms found for a given chemical substance. The statement that the more research work is undertaken, the more polymorphs are found has a certain justification.
A fact is that any chemical substance incorporates in addition to the stability of their existing polymorphs also a basic chemical stability. Such instabilities of the anhydrate could be accentuated or diminished by the formation of new entities such as hydrates, hydrochlorides, solvates, salts.
The chemical stability of the molecule in the solid state is in addition more or less influenced by the thermodynamic stability expressed by the Gibbs free energy function for each of the polymorphs.
Anti-thermodynamic transitions of polymorphs would mean that a more stable polymorph is revealing a solid state transition into a less stable form. This whole subject is rather complex, because a discussion about an ideal crystal are coming into play as well as the discussion about the molecular changes of a solid state transition.
Some examples shall be discussed and the differentiation of the absolute or thermodynamic stability versus the qualitative stability outlined (1-5).

References

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