The Second Law in Modern Thermodynamics

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For complex multiprocess system nonspontaneous process(es), which entropy production is negative, is(are) possible to take place simultaneously in the same system together with spontaneous process(es), which entropy production is positive, if the sum of entropy production of all process(es) is still positive or equal to zero. That is the general mathematic expression of the second law in modern thermodynamics, and it can also be called thermodynamic coupling.

Under isothermal isobaric conditions entropy productions can be substituted by the corresponding Gibbs free energy changes, if the sign of Gibbs free energy changes of all process(es) is reversed, because Gibbs free energy change equals minus entropy production times temperature. However, the standard Gibbs free energy changes had often been incorrectly used instead of the practical Gibbs free energy changes in the literature. That made the concept of thermodynamic coupling bogged down in the last seventy years.

The achievement of activated low-pressure synthetic diamonds, including the recent carat-size single-crystal synthetic diamonds [1], puzzled classical thermodynamics since the 1970s. The new diamond technology also puzzled the recent so-called nanothermodynamics, because carat-size single-crystal synthetic diamonds have no so-called nanometer size limitation. Our thermodynamic coupling model of modern thermodynamics provides predictions and quantitative explanations for world-wide reliable experimental data of activated low-pressure diamond synthesis, including the carat-size single-crystal synthetic diamonds, by nonequilibrium phase diagrams, which belong to a new field of nonequilibrium nondissipative thermodynamics in modern thermodynamics. In this way a view of whole thermodynamics has been drastically changed. Thermodynamic coupling plays an important role of watershed between classical thermodynamics and modern thermodynamics.

[1] C.-S. Yan et al., *PNAS* **99**, 12523 (2002), *Phys. Stat. Sol.* **201**, R25 (2004); R.J. Hemley et al., *Elements* **105** (2005).
[2] J.-T. Wang, Nonequilibrium Nondissipative Thermodynamics, Springer, Heidelberg (2002); J.-T. Wang, Modern Thermodynamics, Fudan University Press, Shanghai (2005).