

**MODERN THERMODYNAMICS FOR  
LOW-PRESSURE DIAMOND AND CUBIC BORON  
NITRIDE SYNTHESSES**

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Since the success of the activated low-pressure diamond synthesis, about 30 years has past. The question why diamond can grow under low-pressure had been regarded as “thermodynamic paradox” for a long time. A thermodynamic coupling model was proposed at the beginning of 1990s and a series of nonequilibrium phase diagrams for the low-pressure diamond synthesis have been quantitatively calculated since the middle of 1990s. Theoretical nonequilibrium phase diagrams agree excellently with a lot of worldwide reported experimental data. In recent years nonequilibrium phase diagrams for low-pressure cubic boron nitride have also been calculated, and agree very well with experimental observations. The model and these nonequilibrium phase diagrams have been cited by more and more scientists (1, 2). However, it was still difficult to be accepted on the basis of classical thermodynamics what is the meaning of nonequilibrium phase diagram. Finally, it was found that there was a “bug” hidden in the classical thermodynamics for about 150 years, because the equality of the second law of thermodynamics was treated as a necessary and sufficient condition for a system being in equilibrium without demonstration.

Due to the achievement of low-pressure diamond synthesis, thermodynamic coupling [i.e.,  $(dG_1)_{T,p} > 0$ ,  $(dG_2)_{T,p} < 0$  &  $(dG)_{T,p} \leq 0$ ] has been quantitatively verified (3). That is, the nonspontaneous transformation from graphite to diamond [ $(dG_1)_{T,p} > 0$ ] is coupled with a spontaneous association of superequilibrium atomic hydrogen [ $(dG_2)_{T,p} < 0$ ]. Based on the second law of thermodynamics low-pressure diamond synthesis is possible, if  $(dG)_{T,p} \leq 0$  for the whole system. However, the situation of [i.e.,  $(dG_1)_{T,p} > 0$ ,  $(dG_2)_{T,p} < 0$  &  $(dG)_{T,p} = 0$ ] for coupling systems was out of consideration in classical thermodynamics, and is a new field in modern thermodynamics as well. The complete systematization of modern thermodynamics has to be drastically changed as shown in Table. 1 for isothermal isobaric system. In this paper  $(dG_1)_{T,p}$ ,  $(dG_2)_{T,p}$  and  $(dG)_{T,p}$  are isothermal and isobaric Gibbs free energy changes of nonspontaneous reaction(s), spontaneous reaction(s) and the whole system, respectively. In general, the corresponding entropy production [i.e.,  $d_i S$ ] should be used for any macroscopic system as shown in Table 2, instead of Gibbs free energy changes in Table 1. If  $(dG_1)_{T,p} < 0$  or  $d_i S_1 > 0$ , it means no nonspontaneous reaction in the system.

This paper is a new progress after the publication of Wang’s English book (3) by Springer in 2002.

Reference

1. Yury Gogotsi, Sascha Welz, Daniel A. Ersoy, and Michael J. McNallan, Nature, 411, 283(2001)  
2. Burkhard Heimann, Vadim Raiko and Voler Buck, International Journal of Refractory Metals & Hard Materials, 19, 169(2001)  
3. Ji-Tao Wang, Nonequilibrium nondissipative thermody-

namics with application to low-pressure diamond synthesis, Springer, Berlin, 2002

Table 1 A Complete Systematization of Modern Thermodynamics [for any macroscopic system at constant  $T$  and  $p$ ]

- 1. Nondissipative Thermodynamics [ $(dG)_{T,p} = 0$ ]
  - 1a. Classical Equilibrium Thermodynamics [for uncoupling system  $(dG_1)_{T,p} = 0$ ,  $(dG_2)_{T,p} = 0$  &  $(dG)_{T,p} = 0$ ] {Represented by classical equilibrium phase diagrams}
  - 1b. Nonequilibrium Nondissipative Thermodynamics [for coupling system  $(dG_1)_{T,p} > 0$ ,  $(dG_2)_{T,p} < 0$  &  $(dG)_{T,p} = 0$ ] {Represented by Wang’s nonequilibrium phase diagrams}
- 2. Dissipative Thermodynamics [ $(dG)_{T,p} < 0$ ]
  - 2a. Classical Nonequilibrium Thermodynamics [for uncoupling system  $(dG_1)_{T,p} < 0$ ,  $(dG_2)_{T,p} < 0$  &  $(dG)_{T,p} < 0$ ] {Only as a criterion for nonequilibrium}
  - 2b. Dissipative Thermodynamics [for coupling system  $(dG_1)_{T,p} > 0$ ,  $(dG_2)_{T,p} < 0$  &  $(dG)_{T,p} < 0$ ]
    - 2b(i). Linear Dissipative Thermodynamics [for coupling system  $(dG_1)_{T,p} > 0$ ,  $(dG_2)_{T,p} < 0$  &  $(dG)_{T,p} < 0$ ] {Represented by Onsager’s reciprocity relation}
    - 2b(ii). Nonlinear Dissipative Thermodynamics [for coupling system  $(dG_1)_{T,p} > 0$ ,  $(dG_2)_{T,p} < 0$  &  $(dG)_{T,p} < 0$ ] {Represented by Prigogine’s dissipative structures}

Table 2 A Complete Systematization of Modern Thermodynamics [for any macroscopic system]

- 1. Nondissipative Thermodynamics [ $d_i S = 0$ ]
  - 1a. Classical Equilibrium Thermodynamics [for uncoupling system  $d_i S_1 = 0$ ,  $d_i S_2 = 0$  &  $d_i S = 0$ ] {Represented by classical equilibrium phase diagrams}
  - 1b. Nonequilibrium Nondissipative Thermodynamics [for coupling system  $d_i S_1 < 0$ ,  $d_i S_2 > 0$  &  $d_i S = 0$ ] {Represented by Wang’s nonequilibrium phase diagrams}
- 2. Dissipative Thermodynamics [ $d_i S < 0$ ]
  - 2a. Classical Nonequilibrium Thermodynamics [for uncoupling system  $d_i S_1 > 0$ ,  $d_i S_2 > 0$  &  $d_i S > 0$ ] {Only as a criterion for nonequilibrium}
  - 2b. Dissipative Thermodynamics [for coupling system  $d_i S_1 < 0$ ,  $d_i S_2 > 0$  &  $d_i S > 0$ ]
    - 2b(i). Linear Dissipative Thermodynamics [for coupling system  $d_i S_1 < 0$ ,  $d_i S_2 > 0$  &  $d_i S > 0$ ] {Represented by Onsager’s reciprocity relation}
    - 2b(ii). Nonlinear Dissipative Thermodynamics [for coupling system  $d_i S_1 < 0$ ,  $d_i S_2 > 0$  &  $d_i S > 0$ ] {Represented by Prigogine’s dissipative structures}