NONEQUILIBRIUM NONDISSIPATIVE THERMODYNAMICS IN CHEMICAL VAPOR DEPOSITION

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Classical thermodynamics has played an important role in chemical vapor deposition (CVD) for a long time. Especially, equilibrium phase diagrams provide powerful theoretical guide for designing and optimizing the CVD processes. However, in recent years, many new CVD processes or CVD processes for new materials have emerged, such as activated low pressure diamond synthesis, chemical vapor deposition of cubic boron nitride, preparation of carbon nitride, fullerenes, carbon nanotubes and so on. These processes do not take place under the conditions close to equilibrium. They may include a nonspontaneous reaction (i.e., a positive Gibbs free energy change reaction, if isothermal and isobaric conditions are concerned), so they are difficultly explained on the basis of classical thermodynamics. After about 12 years research on thermodynamics of low-pressure diamond synthesis, it is clear that there is a "bug" hidden in classical thermodynamics since its birth in the middle of the 19th century. That is, the equality of the second law of thermodynamics had been intuitively regarded for about 150 years as the necessary and sufficient condition for a system being in equilibrium. Such an intuitive point of view can still be used for simple systems without reaction coupling (uncoupling systems), but the classical thermodynamics should not be used for complex system including reaction coupling (coupling systems). The basic reaction inside the activated CVD diamond system may be a coupled reaction between a nonspontaneous transformation from graphite to diamond via gaseous hydrocarbons as intermediates (i.e., a positive Gibbs free energy change reaction at constant T and p) and a stronger spontaneous reaction of the association of superequilibrium atomic hydrogen (i.e., a bigger negative Gibbs free energy change reaction at constant T and p), so the CVD diamond system is a typical coupling system. Due to Gibbs free energy change of the whole reaction is still of a negative value, so CVD of diamond can occur under low pressures.

Based on the second law of thermodynamics, the criterion for reaction coupling at constant T and p is [$(\mathrm{d}G_1)_{T,p} > 0$, $(\mathrm{d}G_2)_{T,p} < 0$ & $(\mathrm{d}G)_{T,p} <= 0$]. Therefore, the complete systematization of modern thermodynamics at constant T and p may be written as shown in Table 1.

In general (i.e., for any systems, including isolaed, closed and open systems and under any conditions), the complete systematization of modern thermodynamics (in a generallized sense) may be written as shown in Table 2. All Gibbs free energy changes should be replaced by the corresponding entropy productions. $(\mathrm{d}G_1)_{T,p}$, $(\mathrm{d}G_2)_{T,p}$ and $(\mathrm{d}G)_{T,p}$ in the paper are Gibbs free energy changes of spontaneous reaction(s), spontaneous reactions and the whole system, respectively. That is similar for the corresponding entropy productions.

Reference

1. Ji-Tao Wang, Nonequilibrium nondissipative thermodynamics with application to low-pressure diamond synthesis, Springer, Berlin, 2002

Table 1 Systematization of Modern Thermodynamics [in a generalized sense for systems at constant T and p]

1. Classical Thermodynamics[$(\mathrm{d}G)_{T,P} <= 0$, no thermodynamic coupling]

1a. Classical Equilibrium Thermodynamics [$\mathrm{d}G)_{T,P}$=0] {Represented by classical equilibrium phase diagrams}

1b. Classical nonequilibrium Thermodynamics [$(\mathrm{d}G)_{T,P} < 0$] {Only as a criterion for nonequilibrium}

2. Modern Thermodynamics (in a specialized sense) [$(\mathrm{d}G_1)_{T,P} > 0$, $(\mathrm{d}G_2)_{T,P} < 0$ & $(\mathrm{d}G)_{T,P} <= 0$, with thermodynamic coupling]

2a. Nonequilibrium Nondissipative Thermodynamics [$(\mathrm{d}G_1)_{T,P} > 0$, $(\mathrm{d}G_2)_{T,P} < 0$ & $(\mathrm{d}G)_{T,P}$=0] {Represented by Wang's nonequilibrium phase diagrams}

2b. Modern Dissipative Thermodynamics [$(\mathrm{d}G_1)_{T,P} > 0$, $(\mathrm{d}G_2)_{T,P} < 0$ & $(\mathrm{d}G)_{T,P} < 0$]

2b(i). Linear Dissipative Thermodynamics [linear relation between J & X] {Represented by Onsager's reciprocity relation}

2b(ii). Nonlinear Dissipative Thermodynamics [nonlinear relation between J & X] {Represented by Prigogine's dissipative structures}

Table 2 Systematization of Modern Thermodynamics [in a generalized sense for any macroscopic system]

1. Classical Thermodynamics [$\mathrm{d}_iS >= 0$, no thermodynamic coupling]

1a. Classical Equilibrium Thermodynamics [d_iS=0] {Represented by classical equilibrium phase diagrams}

1b. Classical nonequilibrium Thermodynamics [$\mathrm{d}_iS > 0$] {Only as a criterion for nonequilibrium}

2. Modern Thermodynamics (in a specialized sense) [$\mathrm{d}_iS_1 < 0$, $\mathrm{d}_iS_2 > 0$ & $\mathrm{d}_iS >= 0$, with thermodynamic coupling]

2a. Nonequilibrium Nondissipative Thermodynamics [$\mathrm{d}_iS_1 < 0$, $\mathrm{d}_iS_2 > 0$ & d_iS=0] {Represented by Wang's nonequilibrium phase diagrams}

2b. Modern Dissipative Thermodynamics [$\mathrm{d}_iS_1 < 0$, $\mathrm{d}_iS_2 > 0$ & $\mathrm{d}_iS > 0$]

2b(i). Linear Dissipative Thermodynamics [linear relation between J & X] {Represented by Onsager's reciprocity relation}

2b(ii). Nonlinear Dissipative Thermodynamics [nonlinear relation between J & X] {Represented by Prigogine's dissipative structures}

Note: J : thermodynamic flux; X: thermodynamic force