

Modern Thermodynamics for CVD Diamond
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Since the success of activated CVD (chemical vapor deposition) diamond process in about 1970, more than 30 years has past. Scientists in activated CVD diamond forum often ask about the thermodynamic reason why we can growth diamond under low pressure, even sometime from graphite as a unique carbon source. The diamond growth together with simultaneous graphite etching under low pressure had been regarded by some scientists as “thermodynamic paradox” maybe “violating the second law of thermodynamics” for a long time.

However, up to now and even further more nobody can design the second kind of perpetual machine on the basis of the activated CVD diamond process. It means that the activated low-pressure diamond process agrees with and subordinates to the second law of thermodynamics. The concept of thermodynamic coupling between the nonspontaneous transformation from graphite to diamond (reaction 1) and the spontaneous association of superequilibrium atomic hydrogen (reaction 2) for the activated CVD diamond process was proposed by the first author Wang together with Carlsson in 1990[1]. As pointed out by Y. Gogosti et al., in *Nature* that “Theoretical aspect of hydrogen assisted diamond growth at low pressures and the thermodynamic coupling model that can be used to explain the formation of diamond in reaction (1) and (2) have been well developed[2].”[3]

On the basis of the coupling model, a series of nonequilibrium phase diagrams for the activated CVD diamond process have been calculated. These phase diagrams agree excellently with a lot of worldwide reported data, and, especially, agree quantitatively with Marinelli’s critical experimental data. In this way, it was demonstrated that thermodynamics for the activated CVD diamond process is really out of the framework of the applicability of classical thermodynamics, because the concept of nonequilibrium phase diagram is unacceptable in the basic concepts of classical thermodynamics. The key point may be that the activated CVD diamond synthesis should be treated by modern thermodynamics, and the watershed between classical thermodynamics and modern thermodynamics may just be thermodynamic coupling, so the complete systematization of thermodynamics has to be drastically changed.[4, 5]

It has been found that there was a “bug” hidden in thermodynamics for about 150 years. That is, the equality of the second law was practically regarded as a criterion (necessary and sufficient condition) of equilibrium system, but everybody in thermodynamics forum knows that the real criterion (necessary and sufficient condition) of equilibrium system should be an extremum of its corresponding state function (not only its first-order derivative equals zero, but also its second-order derivative is bigger than zero for a minimum, or smaller than zero for a maximum) like that as shown in Figs. 1a or 1b in the concerned range. However, for coupling (or multi-irreversible-process) systems, such as the activated CVD diamond system, their corresponding state function may be without an extremum in the concerned range like that as shown in Fig. 2. In this way, a new field of modern

thermodynamics – nonequilibrium nondissipative thermodynamics [$d_i S_1 < 0$, $d_i S_2 > 0$ & $d_i S = 0$] or [$(dG_1)_{T,p} > 0$, $(dG_2)_{T,p} < 0$ & $(dG)_{T,p} = 0$] has been found. Nonequilibrium nondissipative thermodynamics provides a firm thermodynamic theoretical base of nonequilibrium phase diagrams not only for the activated CVD diamond process but also for other activated CVD cubic-BN or CN_x processes.

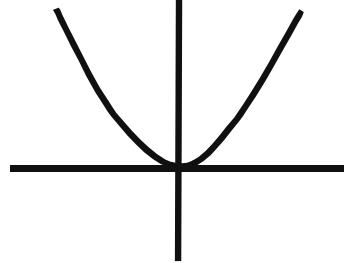


Fig. 1a A mathematic function with a minimum at $x = 0$.
 $y = x^2$, $y' = 2x$, and $y'' = 2 > 0$

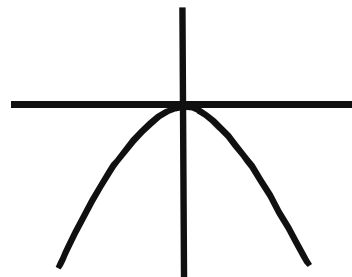


Fig. 1b A mathematic function with a maximum at $x = 0$.
 $y = -x^2$, $y' = -2x$, and $y'' = -2 < 0$

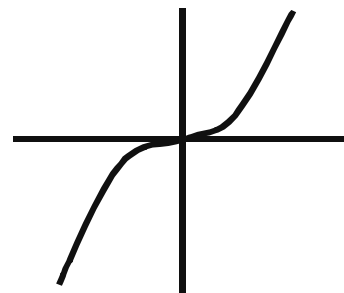


Fig. 2 A mathematic function without an extremum at $x = 0$.
 $y = x^3$, $y' = 3x^2$, and $y'' = 6x$

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