Solubility of carbon in high-pressure and high-temperature water

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Abstract
The solubility of carbon in water at the pressure of 7.7 GPa and at temperatures of 1000–2900 K is investigated by means of statistical mechanical theory, and it is found that the excess saturation concentration of carbon in hot water is very sensitive to the temperature. The peak of excess saturation concentration is located at 2450 K, according to calculations using the code CHEQ, where the driving force for graphite-to-diamond transformation reaches the maximum. The conclusions are consistent with those from recent diamond synthesis experiments.

1. Introduction

Studies of volatile inclusions in natural diamonds suggested that C–O–H fluids might play an important role in the formation of diamonds in the Earth [1–9], and the chemical equilibrium between solid carbon and C–O–H fluids at high pressure and high temperature (HPHT) was analysed [8–10] by means of the empirical equation of state (EOS) of the modified Redlich–Kwong (MRK) type model. Recently, some knowledge on diamond formation from the systems of graphite and supercritical fluids of H_2O has been obtained from a series of experiments [11–15]. It is of interest to perform a more precise chemical equilibrium calculation based on a more reliable EOS for the supercritical molecular fluids. The results are of great significance not only as regards understanding the genesis of natural diamond but also for optimizing the new methods of synthesis of diamond.

During the past two decades, modern statistical thermodynamics has been widely applied to describe the supercritical molecular fluids formed during the detonation of C–H–N–O explosives, and two EOS models (i.e., the Weeks–Chandler–Anderson (WCA) theory and the Mansoori–Canfield–Rasaiah–Srell–Ross (MCRSR) theory models) [16, 17] have become well established. Both models have been successfully applied to reproduce the detonation properties of a variety of C–H–N–O explosives, but our attention is focused on MCRSR theory, because it is more accurate and more extensively tested [18].

Table 1. Molecular interaction potential parameters.

Symbol	CHEQ [18, 19] model			CARTE [20] model		
	ε/k (K)	r^* (Å)	α	ε (K)	r^* (Å)	α
CO_2	245.6	4.28	13.0	173.0	4.48	12.9
CH_4	154.1	4.22	13.0	109.0	4.49	12.9
H_2	36.4	3.43	11.1	37.0	3.55	10.8
CO	108.3	4.12	13.0	75.8	4.36	12.9
k_{ij}	$k_{CO_2-N_2} = 1.035$			$k_{CO_2-N_2} = 1.00$		
	$k_{H_2O-N_2} = 1.045$			$k_{H_2O-N_2} = 1.03$		
	$k_{CO_2-H_2O} = 0.985$			$k_{CO_2-H_2O} = 0.94$		

It is noted that the (H_2O + carbon) system is actually a 'C–H–N–O' without a nitrogen element. So, the theoretical scheme developed well for describing the behaviours of the detonation products is in principle applicable for describing the compressed hot (H_2O + carbon) system. Although the temperature range of diamond synthesis experiments is relatively low compared to those for detonation events, the deviations are believed to be small, because the isentropic release properties of detonation products are also predicted reasonably well [20].

Recently, there have been two codes in extensive use, i.e., CHEQ and CARTE [19, 20]. Both of them were developed according to the variational perturbation MCRSR theory, which was proven to be the most precise and simple analytic method for obtaining the EOS of the molecular fluids and their mixtures. However, two different sets of molecular potential parameters are used in these two schemes. The uniqueness of the potential parameters can be simply attributed to the large numbers of empirical parameters, and discussing this problem is beyond the scope of this work. In this context, the discussions are mainly based on CHEQ calculations, together with CARTE potential parameters for comparison.

2. Methods

In the system of (H_2O + carbon) at high temperatures and high pressures (HTHP), some of the carbon will dissolve into the hot water via some chemical reactions, and the dominant products are supposed to be CO_2, CO, H_2, CH_4. Generally, the molecules of products will diffuse into hot water to form a conformal mixture of supercritical molecular fluid, and the thermodynamic properties of the mixture can be reasonably well described by statistical mechanical theories similar to those describing the behaviours of detonation products from C–H–N–O explosives, where the products were treated as a solid carbon phase and a supercritical molecular fluid phase. The main steps are simply outlined as follows [18, 19].

2.1. Minimization of the Gibbs function

At a given state (P, T), the Gibbs function formula can be expressed as

$$F_l = F_l^0(V_l(P_0, T), T, \{x_i\}) + \int_{V_0}^{V_l} P(V, T)\, dV \tag{1}$$

$$G = F_l + PV_l(P, T) + G_c(P, T, x_c). \tag{2}$$

The Helmholtz free energy (F_l^0) of supercritical fluid under normal pressure can be calculated directly from the data in table 1 of [16]. $V_l(P, T)$ is the EOS of the mixture fluid. The compositions of the HPHT system can be determined by minimizing its Gibbs function. In
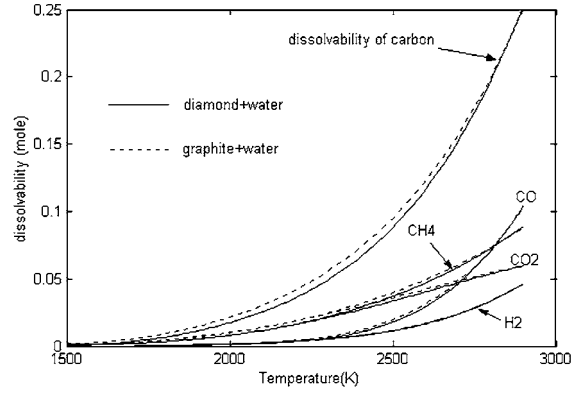
Figure 1. Concentrations of products of (carbon + water). The unit of concentration is 'mol', which is defined as the number of moles in a (1 mol carbon + 1 mol water) system.

our study, the system is composed of (1 mol H_2O + 1 mol carbon), and the solubility of the carbon in the compressed hot water is simply defined by

$$X = (x_{CO_2} + x_{CH_4} + x_{CO}) \times 100\%. \quad (3)$$

In order to discuss the driving force for the graphite-to-diamond transformation in this system, the solubility difference, or excess saturation concentration, of graphite and diamond in the hot compressed water at a given (P, T) is defined as

$$\Delta X = X_g - X_d. \quad (4)$$

2.2. MCRSR EOS theory

The excess Helmholtz free energy from the molecular interactions can be written as [17]

$$A = \frac{4\eta - 3\eta^2}{(1 - \eta)^2} NkT - \left(\frac{\eta^4}{2} + \eta^2 + \frac{\eta}{2}\right) NkT + \frac{\rho}{2} N \int_d^\infty \phi(r) g_{HS}(r) \, d\vec{r}. \quad (5)$$

Here, the value of d minimizes the A-function, $\eta = (1/6)\rho\pi d^3$ (packing fraction),

$$p = \frac{N}{V} kT + \rho^2 \, \partial A/\partial\rho,$$
$$E = \tfrac{3}{2} NkT + \partial(\beta A)/\partial\beta, \quad (6)$$
$$\beta = \frac{1}{kT}.$$

The molecular interaction potentials are chosen as the exp-6 form:

$$\phi(r) = \frac{\varepsilon}{\alpha - 6} \{6 \exp[\alpha(1 - r/r^*)] - \alpha(r^*/r)^6\} \quad (7)$$

in which three effective potential parameters $(\varepsilon, r^*, \alpha)$ should be determined. When the interactions between unlike species are considered, Lorentz–Bethelot combination rules [18] are used. When the mixture fluid is described, the van der Waals one-fluid (VdW–1f) model and mixing rules [18, 19] are needed. The values of the potential parameters are listed in table 1.
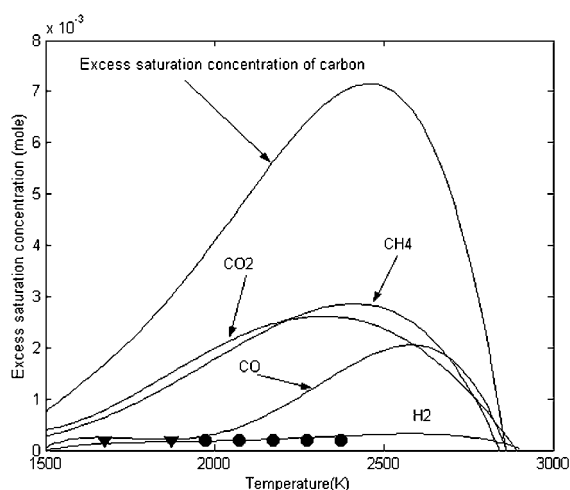
Figure 2. The excess saturation concentration of carbon in HTHP water and the concentrations of products. The unit of concentration is the mole dissolved in 1 mol of hot water. Black triangle symbols represent experiment temperatures from [14]; Black circles are for experiment temperatures from [12].

3. Results and discussion

When the calculations are done, the pressure is fixed at 7.7 GPa, because some experiments have been done under this condition. The solubilities (X_g and X_d) of graphite and diamond in HTHP water are determined by minimizing Gibbs functions of the (H_2O + carbon) chemical equilibrium system, and they are shown in figure 1, together with the concentrations of the product components (CO_2, CO, H_2, CH_4). It is seen from figure 1 that the graphite and diamond will begin to dissolve in hot water above 1500 K, and the solubility of graphite is a little higher than that of diamond; they reach the same value when the temperature is near the phase equilibrium value for graphite and diamond, at about 2850 K.

The excess saturation concentration of carbon in hot water, which is closely related to the driving force for the graphite-to-diamond transformation, is defined as the solubility difference ($X_g - X_d$) at a given (P, T), which is shown in figure 2. To facilitate discussion of the mechanism of the transformation from graphite to diamond in hot water, the concentration differences of the molecular products are also plotted in figure 2.

It is found that the excess saturation concentration of carbon is very sensitive to the temperature. There are three particular features:

(1) There seems to be a lower temperature limit, only beyond which will there be enough driving force for the graphite-to-diamond transformation. This can be understood in that the necessary condition for the graphite-to-diamond transformation is the dissolution of the graphite into the hot water at a given temperature. So, diamond formation would be impossible if the temperatures was below the lower limit. However, the lower limit seems to be very sensitive to both the potential parameters and the accuracy of the calculation; the determination of the onset temperature for the graphite-to-diamond transformation is difficult not only in experiment but also theoretically.

(2) There is also an upper temperature limit for forming diamond, which is about 2850 K according to both models. This can be attributed to the phase transition from diamond to graphite at higher temperatures.

(3) Between the two temperature limits, there is a peak, which is considered to represent the optimizing driving force condition for graphite-to-diamond transformation. The CHEQ model gives the peak at 2450 K, while the CARTE model gives the peak at 1900 K, which is not shown in figure 2.

Synthesis experiments do indeed imply the existence of such a peak in driving force for graphite-to-diamond transformation. The diamond formation temperatures are shown in figure 2. The points (black circles) above 1973 K indicate that diamond could be formed from graphite after 2 h [12], and spontaneous nucleation could occur rapidly above 2373 K. The peak of the driving force was thought to be near 2450 K, if the effect of temperature on the reaction rate is considered. For the points (black triangles) below 1973 K, the diamond transformation could occur, but needs a longer time, 24 h [14]. This means that the transformation rate decreases to a low value. In other words, the driving force for the graphite-to-diamond transformation becomes weaker. From the obvious tendency towards decrease of the driving force, we conclude that the CHEQ calculation seems reasonable.

From the trends of change of the concentration difference of CO_2, CH_4, and CO in graphite and the diamond plus water system, in figure 2, the formation mechanisms of diamond may be: (1) below 2000 K, $C(g) + H_2O \rightarrow CO_2 + CH_4 \rightarrow C(d) + H_2O$; (2) above 2000 K, including another mechanism: $C(g) + H_2O \rightarrow CO + CH_4 \rightarrow C(d) + H_2O$. It is seen that H_2 has no effect on the formation process because there is no concentration change of H_2 in the graphite system and in the diamond system.

Acknowledgment

References

[1] Melton C E and Giardini A A 1974 *Am. Mineral.* **59** 775
    Melton C E and Giardini A A 1975 *Am. Mineral.* **60** 413
[2] Haggerty S E 1986 *Nature* **30** 34
[3] Navon O, Hutcheon I D, Rossman G R and Wasserburg G J 1988 *Nature* **335** 784
[4] Navon O 1991 *Nature* **353** 746
[5] Schrauder M and Navon O 1993 *Nature* **365** 4
    Schrauder M and Navon O 1994 *Geochim. Cosmochim. Acta* **58** 761
[6] Boyd S R, Pineau F and Javoy M 1994 *Chem. Geol.* **116** 29
[7] Corte D, Cartigny P, Shatsky V S, Sobolev N V and Javoy M 1998 *Geochim. Cosmochim. Acta* **62** 3765
[8] Deines P 1980 *Geochim. Cosmochim. Acta* **44** 943
[9] Taylor W R 1990 *Stable Isotopes and Fluid Processes in Mineralization (University of Western Australia Publication No 23)* ed H K Herbert and S E Ho p 333
[10] Frost B R 1979 *Am. J. Sci.* **279** 1033
[11] Yamaoka S, Akaishi M, Kanda H and Osawa T 1992 *J. Cryst. Growth* **125** 375
[12] Hong S M, Akaishi M and Yamaoka S 1999 *J. Cryst. Growth* **200** 326
[13] Shaji Kumar M D, Akaishi M and Yamaoka S 2000 *J. Cryst. Growth* **213** 203
[14] Yamaoka S, Shaji Kumar M D, Akaishi M and Kanda H 2000 *Diam. Relat. Mater.* **9** 1480
[15] Akaishi M, Shaji Kumar M D, Kanda H and Yamaoka S 2000 *Diam. Relat. Mater.* **9** 1945
[16] Ree F 1976 *J. Chem. Phys.* **64** 4601
[17] Ross M 1979 *J. Chem. Phys.* **71** 1567
[18] Ree F 1984 *J. Chem. Phys.* **81** 1251
[19] Van Thiel M, Ree F H and Haselman L C 1995 *Lawrence Livermore National Laboratory Report (UCRL-ID-120096)*
[20] Charlet F, Turkel M L and Danel Kazandjian J F 1998 *J. Appl. Phys.* **84** 4227