Equation of State of Liquid Carbon Dioxide [§]Liu Fusheng^{a,b}, Chen Xianmeng^a, Chen Panshen^b, Sun Yuc^a, Zhou Xuefeng^a, Zhang Qingfu^a, and Jing Fuqian^b*a. The Institute of Applied Physics, Sichuan Union University, Chengdu 610065, P.R. China**b. Lab. for Shock Wave and Detonation Physics Research, Southwest Institute of Fluid Physics, P.O.Box 523-61, Chengdu 610003, P.R. China*

In this paper, the Hugoniot equation of state of liquid carbon dioxide (CO₂) is studied by use of a two-stage light-gas gun. Six new data, ranged from 20 — 60 GPa, are obtained. When these data points, together with those of Schott, are plotted in $U_s - U_p$ plane, it is shown that the slope of the $U_s - U_p$ curve decreases at $U_p = 3.5$ km/s, which corresponds to a distinguishable volume softening above about 25 GPa on the $P - V$ curve. The statistical-mechanics theory including the chemical equilibrium is applied to explain this softening phenomena. [equation of state, liquid CO₂, molecular dissociation, shock wave, chemical equilibrium]

1. Introduction

Some scientists are especially interested in the equation of state of liquid CO₂ at high temperatures and high densities because CO₂ is an important component in the products of CHNO explosives. Schott[1] performed the Hugoniot measurements and theoretical consideration for determination of the parameters in the CO₂—CO₂ effective pair potential. Nellis et al.[2] complemented three points above 30 GPa, and observed an apparent softening phenomena on the $P - V$ curve, which was attributed to the molecular dissociation. When the molecular dissociation occurs, there will be several species (i.e. CO₂, CO, O, O₂, condensed carbon) in the system of liquid CO₂. The chemical equilibrium among these components probably affects the detonation properties of most CHON explosives. When the statistical chemical equilibrium theory is applied to describe the reactive system, it is found that its properties strongly depend on the complicate interactions between species. Undoubtedly, the accurate determination of interaction potentials between species of C-O system may improve the reliability of the statistical method in solving the detonation problem. The nowadays computation technique based on the first principle of quantum mechanics can not provide us available potentials which is satisfactorily accurate. So more Hugoniot data points in reactive region of the liquid CO₂ are still of importance. In this work, a cryogenic target system is established and a two-stage light-gas gun is used to obtain new Hugoniot data ranging from 20 — 60 GPa. The shock-induced dissociation of CO₂ and the molecular potentials between products are investigated on the basis of a liquid statistical chemical equilibrium theory.

2. Experiments

The cryogenic target system and the electronics measurement system in present work are similar to that of Nellis et al.[3, 4], except that a monitoring system is devised to determine the phase of the prepared sample, the height of liquid surface, and its boiling situation[5], because it is necessary for the measurement accuracy. In the cryogenic target system, the cold nitrogen gas is used as the coolant, which is produced by

evaporating liquid nitrogen. The pure CO₂ gas is condensed into liquid under the condition of (219.5K, 0.95MPa). So, the initial density of the sample in our experiments is 1.167g/cm³. The sample situations are judged according to its transparency. The monitoring system is made up of a fibre sensor, a light source, a photomultiplier (PM), and a recording meter. The fibre sensor composed of a couple of fibres is inserted into the sample cavity from the back, and its position depends on the needed surface height of the liquid sample. The light is conducted into the sample cavity by one fibre, and the giving out light is lead into the PM by the other one. So, the output of the PM, which is recorded by a recording meter, is correlated to the transparency of sample. When the liquid surface reaches to the fibre sensor, the output will obviously decrease, and go over to a even higher point when the surface goes higher above the sensor. After that, if there are some bubbles moving up in the sample, the output will oscillate randomly. If the solidation occurs, the light will be scattered, and the intensity of transparent light decreases to near zero.

Shock velocity, U_s , in the liquid CO₂ sample backed on the baseplate is measured by a kind of axially electric pins, while the particle velocity, U_p , and the shock pressure, P , behind the shock front are determined by shock impedance-matching technique. The oxygen free copper and pure aluminium is respectively chosen as the material for the flyer and the baseplate. In our experiments, the uncertainty of the time interval is within 2ns.

3. Measurement results

Six Hugoniot data are obtained in our work. They are plotted respectively in the $U_s - U_p$ plane (Fig. 1) and in the $P - V$ plane (Fig. 2). The Schott data and those of Nellis et al. are also plotted in these two figures. The consistency among them is good in their overlap region. It is seen that the Schott data points are mainly gathered in the pressure region below 30 GPa, while our data are ranged between 20 GPa and 60 GPa. Although the data points of Nellis et al. reach to 70 GPa, they can not work out the accurate behavior in the mediate region of 20 — 50 GPa because the number of

Fig. 1. Shock velocity versus particle velocity for liquid CO_2 .

experimental data is too limited. In Fig. 1, straightline A and B respectively fits the present data points (U_p, U_s) and those of Schott[1] in $U_s - U_p$ plane, and the data points of Nellis et al. are at the lines except one. It is not difficult to see that the slope of the $U_s - U_p$ curve decreases above about $U_p = 3.5$ km/s, which corresponds to a volume softening in the $P - V$ plane above about 25 GPa, as seen in Fig. 2. Such volume softening implies that there exists a phase transition accompanied with an energy absorption in molecular liquid.

4. Theoretical consideration

Before discussing the molecular dissociation, we must determine the effective pair potential between CO_2 molecules. Then, we study the interactions between unlike-species, and their effects on the compositions of the system.

A. $\text{CO}_2 - \text{CO}_2$ potential. Under the condition of shock compression, the simple molecular liquid model[6] is considered to be true because of high temperatures, and the principle of corresponding state can be used to determine parameters (ϵ , r^* , α) in the EXP-6 type formula. It proves that this method can give a reasonable good description for the molecular liquids such as N_2 , O_2 , CO , CH_4 , etc.. However, this technique is not applicable for liquid CO_2 because the deduced parameters (245.6K, 4.17A, 13.0) can not reproduce the Schott low-pressure data below 25 GPa, and it predicts a too soft Hugoniot curve. A natural explanation for the deviation is due to the linear geometry of CO_2 molecule. But, which coefficient is most probably affected remains a question. Some authors changed the ϵ , others adjusted r^* , and the α was sometimes corrected too. We think that the linear geometry of CO_2 molecule may not change the position and depth of the minimum of the potential obviously, but affect the hardness in the short distance. Therefore we only adjust the repulsive parameter to reproduce the experimental data below about 25 GPa. The theoretical Hugoniot curve A in Fig. 2 fit them

considerable good, in which the parameter α values 14.02. It is seen that above 25 GPa experimental data points are obviously below Curve A. This volume softening on Hugoniot $P - V$ curve is considered to be caused by CO_2 molecular dissociation, and the chemical reaction in this region must be carefully considered in order to interpret such deviation.

B. Chemical equilibrium. We choose a liquid statistical theory with chemical equilibrium to describe the shock-compressed states of liquid CO_2 . The main points of this model are: (a) the important products of dissociation is supposed to be CO , O , O_2 and dense C; (b) the fluid mixture of CO_2 , CO , O and O_2 is described by van der Waals one-fluid model[7] and MCRSR theory[8]; (c) the carbon atoms separated from CO_2 exist in the condensed phase, which is described by a three phase model of Thiel and Ree[9]; (d) the composition of each component at a given (P , T) is determined by minimizing the Gibbs free energy of the system. The potentials between species in fluid are supposed to be of the well-known EXP-6 type. The EXP-6 parameters (ϵ_{ij} , r_{ij}^* , α_{ij}) for like species ($i=j$) are: O_2 (125.0K, 3.84A, 13.0)[6], CO (108.3K, 4.09A, 13.0)[6], and O (700K, 2.40A, 11.0)[10]. In this work, the potential parameters of $\text{CO}_2 - \text{CO}_2$ are chosen to be (245.6K, 4.17A, 14.02), which can satisfactorily reproduce Schott Hugoniot data in low-pressure region (curve A in Fig. 2). The corresponding parameters for unlike species ($i \neq j$) are evaluated by the extended Lorentz-Berthelot combination rule, i.e., $\epsilon_{ij} = I_j(\epsilon_{ii} \cdot \epsilon_{jj})^{1/2}$, $\alpha_{ij} = m_j(\alpha_{ii} \cdot \alpha_{jj})^{1/2}$, $r_{ij}^* = k_{ij}(r_{ii}^* + r_{jj}^*)/2$, where I_j , m_j , k_{ij} are correction coefficients which correlate the specific species. For the ideal mixtures, they equal 1. We perform a complete chemical equilibrium calculation for the discussed system. The result (Curve B in Fig. 2) is much different from the experimental data in higher pressure region. It implies that the ideal condition in the discussed system is not

Fig. 2. Hugoniot of liquid CO_2 . The symbolled points are experimental data, and the (A, B, C, D) are theoretical curves.

true, and that the unlike-species potential must be carefully investigated.

C. CO_2 — O and CO — O inter-potential. Because the theoretical curve B is high above the measurements in the reactive region, some unknown softening mechanism must function. We do not exclude the possibility of the existence of a new dense phase of C:O alloy which may be more stable than diamond at such high temperatures and pressures, but we consider in this work the potential softening between unlike species to be the main mechanism. The absorption trend between CO_2 —O and CO—O may be interpreted to be the co-valent bond action because of the open shell electronic structure of oxygen atom. We can describe this mechanism by optimizing the correction coefficient k_{ij} . Our calculation confirm that the decrease of $k_{\text{CO}_2 \cdot \text{O}}$ can improve the agreement between theoretical and experimental results. When it is adjusted to reproduce the measurement data between 30—40 GPa, it is found that the result (Curve C) can not explain the points above 40 GPa unless the $k_{\text{CO} \cdot \text{O}}$ is changed. As shown in Fig. 2, the theoretical Curve D fits experimental data reasonable well with $k_{\text{CO}_2 \cdot \text{O}}=0.895$, and $k_{\text{CO} \cdot \text{O}}=0.8$.

D. Compositions. The compositions of all components along Hugoniot curves are plotted in Fig. 3 with the O_2 omitted because of its little amount. It is found that the decrease of $k_{\text{CO}_2 \cdot \text{O}}$ value will increase the dissociation of the CO_2 like $\text{CO}_2 \rightarrow \text{CO} + \text{O}$, which is the main process for the contraction below 40 GPa, and it will also cause the dissociation of CO like $\text{CO} \rightarrow \text{C}(\text{dense}) + \text{O}$, which is the main process for the contraction above 40 GPa. Otherwise, the decrease of $k_{\text{CO} \cdot \text{O}}$ will slow down the dissociation of CO. The considerable amount of CO and O at 25 GPa, seen from Fig. 3, indicates that the volume softening in Fig. 2 is caused by the shock-induced deoxidation of CO_2 (i.e., $\text{CO}_2 \rightarrow \text{CO} + \text{O}$). Although some carbon atoms in diamond phase or liquid phase separate from CO_2 above 40

GPa, where two carbon atoms are removed from one CO_2 molecule (i.e., $\text{CO}_2 \rightarrow \text{C} + 2\text{O}$), it does not change the slope of $U_S - U_P$ line apparently, it does not cause obvious softening on the $P - V$ curve, either.

We remark that the composition change of CO along the Hugoniot curve is sensitive to the correction coefficient $k_{\text{CO} \cdot \text{O}}$. So, if the concentration change trend of CO could be measured by other techniques (e.g., spectroscopy), strong constraints may be given to the value of $k_{\text{CO} \cdot \text{O}}$ independently. Moreover, the inter-potentials of molecule—molecule, especially molecule—atom, should be studied theoretically as well as experimentally in the future.

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Fig. 3. Compositions versus pressure along the Hugoniot curve of liquid CO_2 . The curves of O_2 are not shown because of small amounts.