Melting Curves of Hydrogen, H₂O, Helium and Argon at High Pressure

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Experiments were carried out to determine the melting curves of H₂, H₂O (ice VII), ⁴He and Ar. A resistive heating technique in a diamond anvil cell was used. The use of an *in-situ* method to measure pressure and temperature provides accurate data. The large number of melting points and their good precision very well constrain the melting curves of these elements in the studied range. Simon equations were found to well reproduce the present measurements. [melting curve, simple systems, resistive heating, diamond anvil cell]

1 Introduction

Knowledge of the properties of H₂, ⁴He, Ar and H₂O at high density is both of fundamental interest and of astrophysical, geophysical or technological relevance. The study of the solid-fluid transition may provide useful informations on the effects of elevated pressures and temperatures on these systems. Further, because these systems are relatively simple, they play a reference role for testing theoretical models of melting.

In H₂, it is expected that the rate of molecular dissociation increases in the fluid phase with pressure and temperature. That should be reflected in the evolution of its melting curve. In a similar way, going up in pressure and temperature changes the relative abundance of ionized molecules in water, leading to a partially or fully ionized state which should be characterized by a change in the melting properties. The study of ⁴He is not only motivated by the density related properties of this element, but also because its properties may be extrapolated, from the law of corresponding state, to the other rare gases in *P* – *T* regions which remain difficult to access by experiment. Ar is known to be a very good model for the study of simple classical fluids or solids. Its melting curve was measured to 6 GPa and is very well reproduced by theoretical calculations based on lattice dynamics and liquid perturbation theory.¹ It was used as a test system in the present work.

We present here the results of our experimental determinations of the melting curves of these elements up to about 750 K. A resistive heating method in a diamond anvil cell was used. The large number and good accuracy of our measurements very well constrain the melting line of these elements in the studied range.

2 Experimental method

The present experiments were conducted with a membrane DAC² which was designed to allow the generation of high temperatures with a heating gasket.³ Rhenium or composite rhenium-gold gaskets were used to confine the samples. High purity gases were loaded at room temperature using high pressure loading techniques. Pressure and temperature were measured *in situ* by means of two optical pressure sensors, SrB₄O₇:Sm²⁺ and ruby, using the metrology described

Fig. 1. Micro-photograph of the H₂O sample at melting around 400 K, showing the three compartments in the gold ring inserted in the rhenium gasket: (1) large water sample with one ruby ball; (2) SrB₄O₇:Sm²⁺ sample in water; the large relative amount of borate powder with respect to water prevented from the total dissolution of the pressure sensor; (3) one ruby ball in water; one can see that melting occurs simultaneously in the three holes, which supports the fact that identical conditions of *P* and *T* are sustained.

in a recent paper.⁴ The accuracy of our measurements is estimated to be better than ±5 K and 0.2 GPa in the *P* – *T* range covered by these experiments.

Melting could be usually detected by visual observation of the sample: by rising temperature at constant load, we observed the appearance of crystal grain boundaries, and by further increase of temperature, of (a) small crystal(s) in equilibrium with the fluid. *P* – *T* measurements were realized at points where this equilibrium was reached. Pressure and temperature were then slowly increased so that this topology was conserved. This procedure could not be used in helium because the difference in the indexes of the two phases is too small. Hence, quasi-isochoric scans near the melting line were performed: starting from the solid phase, temperature was increased at constant load by steps of 2 K. At melting, the pressure rises due to the volume difference between the two phases, up to the point where the solid totally disappears. The mid-point of the isochore so obtained was taken as a melting point.

Figure 1 shows a micro-photograph of a H₂O sample at melting near 400 K. In this experiment, a gold liner was used to isolate the sample from the rhenium gasket. Inert materials like Au are actually required for H₂O and H₂ be-

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Fig. 2. Melting curve of argon. $\circ$: this work (exp. data); ∇ : Hardy *et al.* [5]; Δ : Zha *et al.* [1]; solid line: Simon law determined in this work.

cause of the high chemical reactivity of these elements at elevated pressures and temperatures. H_2O also reacted with the $\text{SrB}_4\text{O}_7\text{:Sm}^{2+}$ sample used as the pressure gauge, resulting in the total disappearance of the optical sensor above 650 K. This was resolved by drilling three separate holes as shown in Fig. 1: a large one for observation of the water sample, a second smaller one with a $\text{SrB}_4\text{O}_7\text{:Sm}^{2+}$ sample in large relative amount, and a third one with a ruby ball.

3 Accurate determinations of melting curves

3.1 Argon

The melting curve of argon was determined between 295 and 740 K, corresponding to melting pressures ranging from 1.3 to 6.3 GPa. Above 3.6 GPa, melting could still be visually observed contrary to what Zha *et al.*¹ reported. The results of four experiments are shown in Fig. 2. As one can see, a large number of melting points have been recorded which show a very good reproducibility between the different experiments. The small dispersion of the experimental data testifies to the good accuracy of our measurements. Figure 2 also shows the precise data obtained by Hardy *et al.*⁵ in a piston-cylinder up to 1.14 GPa and the only experimental data available in the same range as that investigated here obtained by Zha *et al.*¹ in a diamond anvil cell. Near room temperature, the present determination lies very well in the extrapolation of the measurement of Hardy *et al.*⁵ The observed evolution of the melting curve at higher pressures is slightly below the determination of Zha *et al.*¹ but this discrepancy might be ascribed to their larger experimental errors.

Fig. 3. Melting curve of ice VII. $\circ$: this work (exp. data); dashed line: Pistorius *et al.* [6]; ∇ : Mishima and Endo [7]; Δ : Fei *et al.* [8]; solid line: Simon law fitted to this work.

3.2 Ice VII

Ice VII is the stable form of ice at room temperature and pressures in excess of 2.2 GPa. Its melting curve has already been the subject of several studies⁶⁻⁹ but surprisingly, the different determinations very poorly agree for temperatures above 550 K. In the present work, the melting curve of ice VII was determined up to 750 K and 13 GPa. As described previously, a special care was given to the experimental conditions because of the high chemical reactivity of water. Here again, a very large number of melting points have been measured, from five different samples, showing very good reproducibility. These are gathered in Fig. 3 and compared to previous determinations. As one can see, the melting line presently determined lies well below the previous measurements. A better agreement is found with the most recent results of Fei *et al.*,⁸ however a difference of 4 GPa separates the two melting curves at 700 K. The reasons of this discrepancy are not clear. Pistorius *et al.*⁶ report that their pressure measurement is "somewhat uncertain" above 8 GPa. This emphasizes the need of *in-situ* methods for measurements at high P and T , such as that used in this study.

An interesting point in water is the important rise of electrical conductivity observed in shock wave experiments at shock pressures above 10 GPa, corresponding to temperatures around 700 K.¹⁰ This is thought to be due to the relative increase of ionic species such as OH^- and H_3O^+ or more complex hydrates. The possible effects of this partial ionization on the melting curve was one motivation of this study. However, the melting line presently determined shows a monotonic increase with temperature and no obvi-

Table 1. Parameters of the Simon equation. P is expressed in GPa and T in K.

	A	B	c	P_0	T_0	Eq.
Ar	-0.21	2.172×10^{-4}	1.556			(1)
$^4\text{He}^{(a)}$	0	1.607×10^{-4}	1.565			(1)
H_2	0	1.63×10^{-4}	1.824			(1)
$\text{H}_2\text{O}^{(b)}$		1.253	3.0	2.17	354.8	(2)

(a) After Ref. 11

(b) Ice VII

ous signs of changes which might be related to the change in electrical behaviour can be observed in the studied range.

4 Parameters of the Simon equation

The present measurements of the melting lines have been fitted to Simon-type equations, using either one of the two forms:

$$P = A + BT^c \quad (1)$$

or

$$P - P_0 = B[(T/T_0)^c - 1] \quad (2)$$

where P_0 and T_0 are fixed experimental values. The results are given in table 1. In H_2 , measurements of the melting curve were limited to 15 GPa and 530 K due to strong diffusion of the sample into the gasket, even when gold was used – many other gasket materials were tested, such as NaCl which is known to be a hydrogen leakant, with no more success. In helium, only one experiment has been yet performed which was prematurely interrupted by the failure of the membrane used to generate the force on the piston. The observed evolution up to 450 K is in good agreement with the measurements of Vos *et al.*¹¹ The Simon equation is found to well reproduce our data on argon and H_2O , as illustrated in Fig. 2 and 3.

It is generally found that the extrapolation of a melting law like the Simon equation cannot be used confidently outside the range in which it has been determined.¹² In Fig. 4, we compare the extrapolation of the argon Simon curve as presently determined to the recent results obtained by Jephcoat *et al.*¹³ in laser heating experiments up to 47 GPa. The agreement is good, taking into account the large uncertainty of the laser heating results, and tends to show that the present Simon law can be confidently extrapolated at least in this $P - T$ range.

5 Conclusion

In this paper, we have shown that accurate measurements of melting curves in the temperature range of a thousand K can be conducted in a diamond anvil cell. The use of a method which provides in-situ measurements of pressure and temperature is most important. The results of our experiments were presented, which showed improved accuracy with respect to previous determinations. This provides more severe constraints for the predictions of theoretical melting models.

Fig. 4. Melting curve of argon. $\square$: laser heating exp. data from Jephcoat *et al.* [13]; solid line: Simon law determined in this work.

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