

Melting temperature of H₂, D₂, N₂ and CH₄ under high pressure

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MS received 6 May 2002; revised 20 June 2003; accepted 3 July 2003

Abstract. The melting temperatures of H₂, D₂, N₂ and CH₄ are analysed. The computed results are in very good agreement with the experimental data in each solid. Further, the analysis indicates the presence of the melting maximum in these solids.

Keywords. Melting temperature; high pressure; melting maximum; molecular solids.

PACS Nos 65.50.+m; 62.50.+p; 62.20.Dc

1. Introduction

In most solids, the melting temperature, T_m , is found to rise with increase in pressure, P_m . This rise in melting temperature with pressure in solids is not monotonous but the melting temperature passes through a maximum and is known as the melting maximum. This is exactly in accordance with the Tammann [1] hypothesis which states that the fusion temperature rises to a maximum and then falls. Thus, there is a particular pressure, $(P)_{max}$, at which the melting temperature is maximum. The experimental evidence of the melting maximum is available in the case of alkali metals [2].

Diatschenko *et al* [3] had reported the experimental data on melting temperature of H₂ and D₂ as a function of pressure. But Ross *et al* [4] had reported theoretical values of the melting temperature in case of hydrogen up to a pressure of 4800 kbar without a melting maximum. Therefore, the aim of the present paper is to show the validity and the success of the relation between melting temperature and pressure given by Dass and co-workers [2,5,6] in the case of H₂, D₂, N₂ and CH₄.

2. Theory

To analyse the melting temperatures of solids like H₂, D₂, N₂ and CH₄, we take the relation given by Dass and co-workers [2,5,6] because no other relation explains the melting maximum. The relation is expressed as

$$\ln\left(\frac{T_m}{T_0}\right) = -2\alpha P + \left[\left(C + \frac{2\alpha}{\beta}\right) \ln(1 + \beta P)\right], \quad (1)$$

where

$$P = P_m - P_0,$$

$$\alpha = \frac{\gamma'(P_0, T_0)}{B_T'(P_0, T_0)},$$

$$\beta = \frac{B_T'(P_0, T_0)}{B_T(P_0, T_0)},$$

and

$$C = 2 \times \frac{[\gamma(P_0, T_0) - \frac{1}{3}]}{B_T'(P_0, T_0)}.$$

In eq. (1), T_m and T_0 represent melting temperatures at pressure P_m and P_0 , respectively. $\gamma'(P_0, T_0)$ and $B_T'(P_0, T_0)$ are the first pressure derivatives of the Grüneison parameter, $\gamma(P, T_0)$, and bulk modulus, $B_T(P, T_0)$, at P_0 and T_0 , respectively.

One of the interesting result one gets from eq. (1) is that initially the melting temperature, T_m , will rise with the increase in pressure, reach to a maximum and then falls. Therefore, there is a particular pressure $(P)_{\max}$ at which T_m has the maximum value. As the pressure becomes larger than $(P)_{\max}$, T_m decreases. Hence, a melting maximum is obtained in T_m - P_m curve of the solid.

The pressure at which the T_m becomes maximum is given by

$$(P)_{\max} = \frac{[\gamma(P_0, T_0) - \frac{1}{3}]}{\gamma'(P_0, T_0)}. \quad (2)$$

The other important result of eq. (1) is that it can also be expressed in the form of Simon law provided α is neglected. Thus, eq. (1) can also be expressed as

$$\frac{T_m}{T_0} = [1 + \beta P]^C. \quad (3)$$

Table 1. Input data.

Molecular solids	H ₂	D ₂	N ₂	CH ₄
Pressure range (kbar)	0.48–77.1	12.8–53.4	0.0–10.195	0.0–10.487
Temperature range (K)	26.6–368.0	131.5–302.0	63.148–175.82	90.668–260.85
$B_T(P_0, T_0)$ (kbar)	3.8613	33.3752	13.707	19.942
$B_T'(P_0, T_0)$	4.798	2.0872	7.836	9.035
$\gamma(P_0, T_0)$	1.7183	1.0710	2.661	3.095
$\gamma'(P_0, T_0)$ ($\times 10^{-4}$ kbar)	2.4105	32.144	150.0	93.0
P_0 (kbar)	0.48	12.8	0.0	0.0
T_0 (K)	26.6	131.5	63.148	90.688
RMSD (in T_m)	1.1	0.68	0.15	0.17
$(P)_{\max}$ (in kbar)	5750.0	230.0	155.2	306.9

Equation (3) represents Simon law where the constants are identified in terms of the physical properties of the concerned solid.

The best fitted values of the parameters $B_T(P_0, T_0)$, $B'_T(P_0, T_0)$, $\gamma(P_0, T_0)$ and $\gamma'(P_0, T_0)$ are reported in table 1 along with some other relevant quantities to make the table self-explanatory.

3. Discussions and conclusion

For the present analysis, we have taken the melting temperatures for H_2 and D_2 from Diatschenko *et al* [3] and that for N_2 and CH_4 from Cheng *et al* [7]. It is clearly evident from table 1 as well as from figures 1–4 that there is a very good agreement between the calculated values and the experimental data of the melting temperature in all the solids studied here.

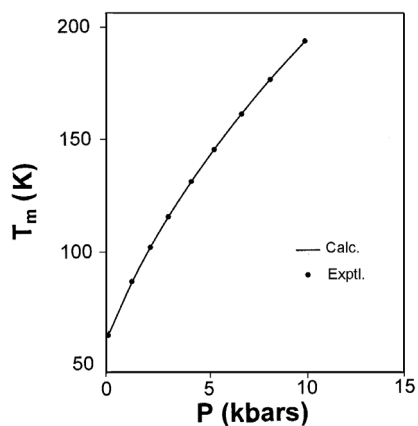


Figure 1. Melting temperature of N_2 .

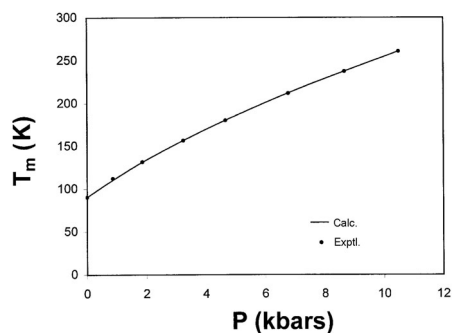


Figure 2. Melting temperature of CH_4 .

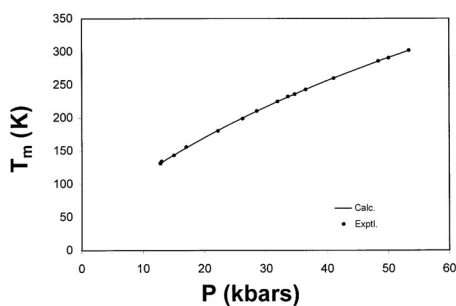


Figure 3. Melting temperature of D_2 .

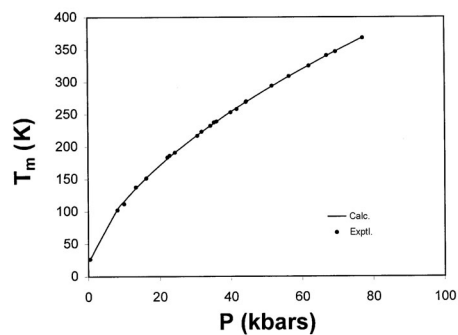


Figure 4. Melting temperature of H_2 .

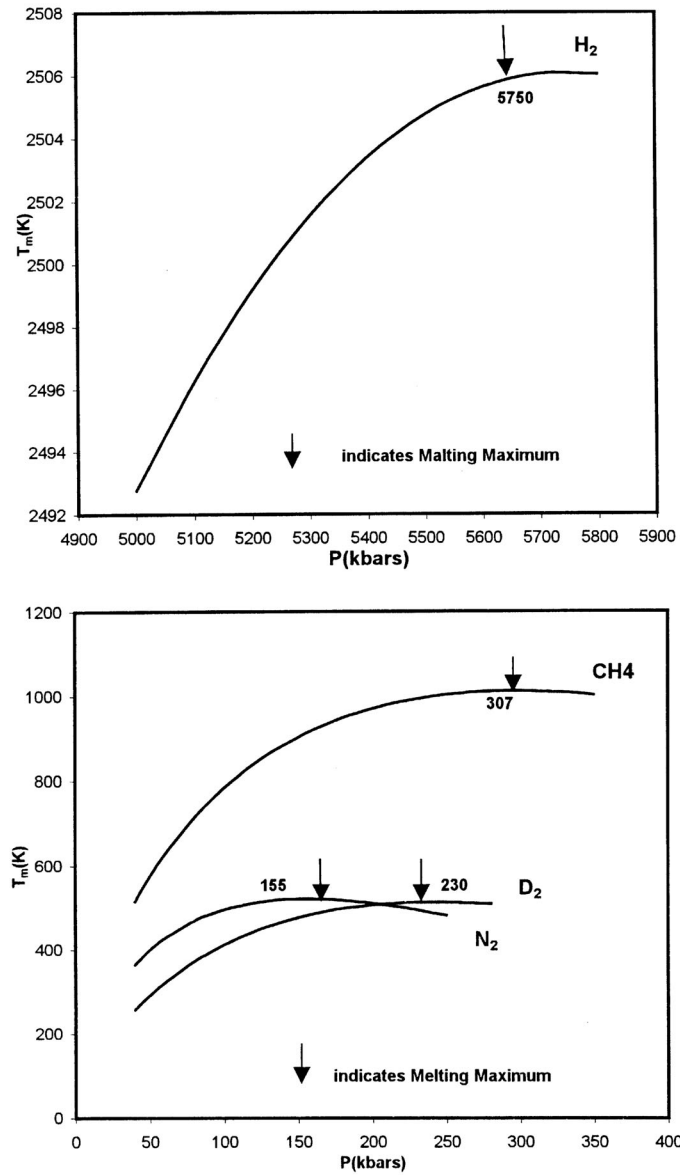


Figure 5. Melting temperature vs. pressure showing melting maximum in H_2 , CH_4 , N_2 and D_2 .

In tables 2 and 3, we compare our calculated results of T_m with the data provided by various other workers in H_2 and D_2 [3]. Here again the agreement in general is very good indicating the usefulness and success of eq. (1) and particularly in case of H_2 where the pressure used is up to 4800 kbar. It is evident from table 2 that the melting maximum in H_2 does not exist at least up to 4800 kbar.

Table 2. Melting temperature of H₂.

<i>P</i> (kbar)	<i>T_m</i> (K)		<i>P</i> (kbar)	<i>T_m</i> (K)		<i>P</i> (kbar)	<i>T_m</i> (K)	
	(Calc.)	Others		(Calc.)	Others		(Calc.)	Others
0.4	25.0	25.0	6.9	94.3	90.6	22.93	185.0	182.0
0.49	26.7	25.5	7.4	98.0	100.0	26.30	200.0	140.0
1.03	35.9	35.3	7.76	100.7	100.8	26.90	202.5	200.0
1.5	42.6	42.0	8.0	102.4	99.0	39.80	253.1	250.0
1.63	44.3	43.8	8.09	103.0	102.3	54.20	301.6	298.0
1.8	46.5	50.0	9.78	114.5	115.5	55.0	304.2	298.0
2.09	50.1	49.5	9.80	114.6	112.0	57.0	310.4	298.0
2.99	60.2	58.9	10.2	117.2	117.0	59.60	318.4	300.0
4.02	70.3	67.4	11.77	127.0	125.8	108.6	447.4	400.0
4.73	76.8	75.0	12.53	131.5	133.6	159.8	555.9	500.0
4.76	77.0	75.4	13.41	136.6	135.4	169.0	573.6	580.0
4.80	77.4	70.0	14.63	143.5	143.8	647.0	1186.0	1000.0 ^a
5.0	79.1	77.4	15.90	150.4	150.0	1686.0	1857.0	1500.0 ^a
5.2	80.8	77.4	16.44	153.2	152.6	3096.0	2289.0	2000.0 ^a
6.2	88.9	84.0	16.77	155.0	154.0	4808.0	2484.0	2500.0 ^a
6.38	90.4	88.8	18.71	164.9	163.9	–	–	–

^aData are taken from ref. [4]. All other data are taken from ref. [3].

Table 3. Melting temperature of D₂.

<i>P</i> (kbar)	<i>T_m</i> (K)		<i>P</i> (kbar)	<i>T_m</i> (K)		<i>P</i> (kbar)	<i>T_m</i> (K)	
	(Calc.)	Others		(Calc.)	Others		(Calc.)	Others
0.2	42.3	25.0	7.963	101.6	102.1	23.00	185.0	192.0
0.57	47.7	30.0	8.6	105.8	100.0	29.70	214.5	200.0
1.25	51.7	40.0	10.021	114.8	115.5	35.80	240.3	244.0
2.00	58.1	50.0	12.11	127.5	128.4	37.20	245.8	248.0
2.08	58.7	50.0	13.47	135.4	136.3	43.10	267.6	250.0
3.04	66.4	60.0	14.77	142.7	145.3	46.60	279.7	282.0
4.68	78.9	75.0	15.38	146.1	147.8	50.50	292.6	298.0
4.70	79.0	75.2	16.97	154.7	155.7	51.60	296.1	300.0
5.647	85.8	85.0	17.47	157.3	159.0	57.20	313.2	295.0
7.01	95.3	94.7	17.80	159.1	150.0	61.10	324.5	333.0
7.044	95.5	95.1	22.65	183.4	185.0	78.0	367.5	372.5

It is clear from table 1 that the melting maximum occurs at pressures 5750, 230.0, 155.2 and 307 kbar in H₂, D₂, N₂ and CH₄, respectively. Thus, the melting maximum is not confined only to hydrogen. Further, it is clearly evident from figure 5 that melting maximum does exist in solids as studied in the present paper.

In conclusion, it may be said that the melting temperatures of H₂, D₂, N₂ and CH₄ are successfully analysed. The analysis clearly indicates the presence of the melting maximum in each solid.

Acknowledgements

One of the authors (KK) is thankful to the Director, College of Engineering Roorkee, Roorkee for financial and technical help.

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