

MELTING PHENOMENA IN SOLIDIFIED GASES

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ABSTRACT

Based on the Lindemann melting criterion and the Gruneisen equation of state, a melting law $\log(T_m/T_m^0) = 2(\gamma - 1/3) \log(v_0/v)$ is derived, which for small compressions gives a linear relation between T_m and $|\Delta v/v_0|$ as suggested recently by Kraut and Kennedy. The correlation between T_m and $|\Delta v/v_0|$ holds good very satisfactorily for the high pressure data on the following solidified gases: He^4 , He^4 , Ne, Ar, Kr, Xe, H_2 , D_2 , N_2 , O_2 , NH_3 , CO_2 , CH_4 , C_2H_4 , C_2H_6 and C_2H_2 . The Gruneisen constant γ calculated from the melting equation agrees well with the values calculated independently from thermal measurements, where they are available. In He^4 and H_2 , the decrease of γ at high compressions along the melting line is noticeable and agrees with the other thermal measurements. The present equation relates melting phenomena in a quantitative way with general solid state studies.

INTRODUCTION

The solidified gases have been studied for many years in detail because the interactions among the atoms and molecules are known and hence a critical comparison with the experimental data is used to refine the theoretical calculations. While this is satisfactory for many phenomena, as reviewed recently^{12, 25}, a problem of considerable difficulty was thrown up by Simon's investigation, in 1929, of the possible existence of a critical point for solid-fluid (gas or liquid) transition analogous to the liquid-gas a critical point. For instance helium, which has a liquid-gas critical point at $5.2^\circ K$ and 2.3 bar, can be solidified from gas even at $77^\circ K$ on the application of 14 kbar. Simon^{28, 29} found that the melting point T_m at a pressure P can be represented by the equation

$$P/a = (T_m/T_m^0)^c - 1 \quad [1]$$

where a and c are two arbitrary constants. These constants have been tabulated for a large number of materials² and Simon's equation shows that when P increases, T_m also increases indefinitely.

Recently some substances have been found to exhibit a maximum T_m after which T_m decreases with increase of P . A few other materials show a

decrease of T_m with P even from 1 bar. These examples are not adequately included in the simple Simon equation. Moreover it has not been possible to correlate a and c with other properties of the solid in a satisfactory manner because the various models of melting, based on an harmonic vibrations, order-disorder phenomena or vanishing of shear constants, all have their short-comings. In view of these limitations¹⁴ the recent suggestion of Kraut and Kennedy¹⁵ that T_m should be related to the volume compression $(v_0 - v)/v_0 = |\Delta v/v_0|$ at the same high pressure, in the form

$$T_m = T_m^0 [1 + A |\Delta v/v_0|] \quad [2]$$

has elicited considerable interest. It can be derived on the basis of rather simple theoretical considerations^{8, 18, 40} and the constant A can be expressed directly in terms of the thermal constants of the solid. A refinement of this equation thus offers the possibility of connecting melting phenomena with other thermodynamic properties of the solid.

A short account of the results for the inert gas solids (He, Ne, Ar, Kr and Xe) has been sent to CRYOGENICS for publication³⁹.

MELTING EQUATION AT HIGH PRESSURES

The melting at high pressures can be discussed on the basis of Lindemann's criterion

$$T_m = C.M. \theta^2 v^{2/3} \quad [3]$$

(C = a constant, M = mean atomic weight, θ = Debye temperature) and the Gruneisen relation

$$d\theta/dv = -\gamma \theta/v. \quad [4]$$

The range of validity of these relations are now well known. It suffices here to note that all the simple models of melting (in the general sense of transformation from solid to fluid, either liquid or gas) mentioned earlier lead to the Lindemann relation (3), but refinement of this simple relation has not been very profitable. The Gruneisen relation is also based on a simple model of a monatomic solid, but detailed lattice dynamic calculations have shown that is only a first approximation. Different vibrational modes have different γ 's and the average Gruneisen constant is a slowly varying function of T and v . Nevertheless equations (3) and (4) give a satisfactory account for a very wide range of materials.

If equation (4) is used to eliminate $(d\theta/dv)$ in (dT_m/dv) from equation (3), it follows easily that

$$-(dT_m/dv) = 2(\gamma - \frac{1}{3}) T_m/v, \quad [5]$$

If γ were strictly a constant, on integrating equation (5) from T_m^i and v_i one has

$$\log (T_m/T_m^i) = 2(\gamma - \frac{1}{3}) \log (v_i/v). \quad [6]$$

Usually T_m^i and v_i are the values T_m^0 and v_0 at 1 atmosphere pressure, but equation (6) may also start from any solid state phase transition when γ , of course, refers to the new phase. If the compression $|\Delta v/v_0|$ is small equation (2)

$$T_m = T_m^0 [1 + 2(\gamma - \frac{1}{3}) |\Delta v/v_0|] \quad [7]$$

follows from equation (6) involving the Gruneisen constant γ of the solid.

Normally $T_m \gg \theta$ and γ varies little at these "high" temperatures. At high compressions, however, it is known that the effective γ decreases slightly so that $\log (T_m/T_m^0)$ plotted as a function of $\log (v_0/v)$ begins to flatten out slightly. Thus the experiments may be fitted in such cases by an equation of the form

$$T_m = T_m^0 [1 + A |\Delta v/v_0| - B |\Delta v/v_0|^2 + \dots] \quad [8]$$

where B is related to γ and its derivative with respect to volume. For most substances experimental data are available up to small compressions only and in such cases equation (7) gives a good account of the experimental observations^{15, 39, 40}.

DATA FOR SOLIDIFIED GASES

The freezing of gases under high pressures has been studied for many years mainly to evaluate Simon's problem. The measurement of (isothermal) compressions of solids, which is required in addition for a test of equation (6), has been done in recent years. The data are best discussed in three groups. The first group is the set of monatomic inert gases helium, neon, argon, krypton and xenon. The second group consists of diatomic "permanent" gases hydrogen, deuterium, nitrogen and oxygen. The third set contains polyatomic gases, ammonia, carbondioxide, methane, ethane, ethylene, propane and propylene.

The melting data of neon, argon, krypton and xenon have been taken from the review of Pollack²⁵. The compression data for neon (at 4.2°K), argon (at 77°K) and krypton (at 77°K) are taken from Stewart³¹ and for xenon (at 160°K) from Packard and Swenson²⁴. In the case of helium-4, Stewart³⁴ has given the compression data from 2 kbar (20°K) only. At these pressures helium behaves nearly like a classical solid and so the quantum complications are not present. The melting data for helium are from Grilly and Mills⁹ up to 10 kbar and the point at liquid nitrogen temperature

and 14 kbar is from the work of Langer¹⁷. The plots of $\log(T_m/T_m^\circ)$ against $\log(v_0/v)$ for these cases are given in figures I and II. Additional data on the compression of argon at 65°K³¹ and xenon at 80°K and 40°K²⁴ are also used for testing equation (6). For helium-3 rather meager data are available in the β -phase above 1 kbar³⁴ and melting data from Grilly and Mills⁹ are used to find out γ . It appears that the different crystallographic phases of solid He³ and He⁴ have same melting line.

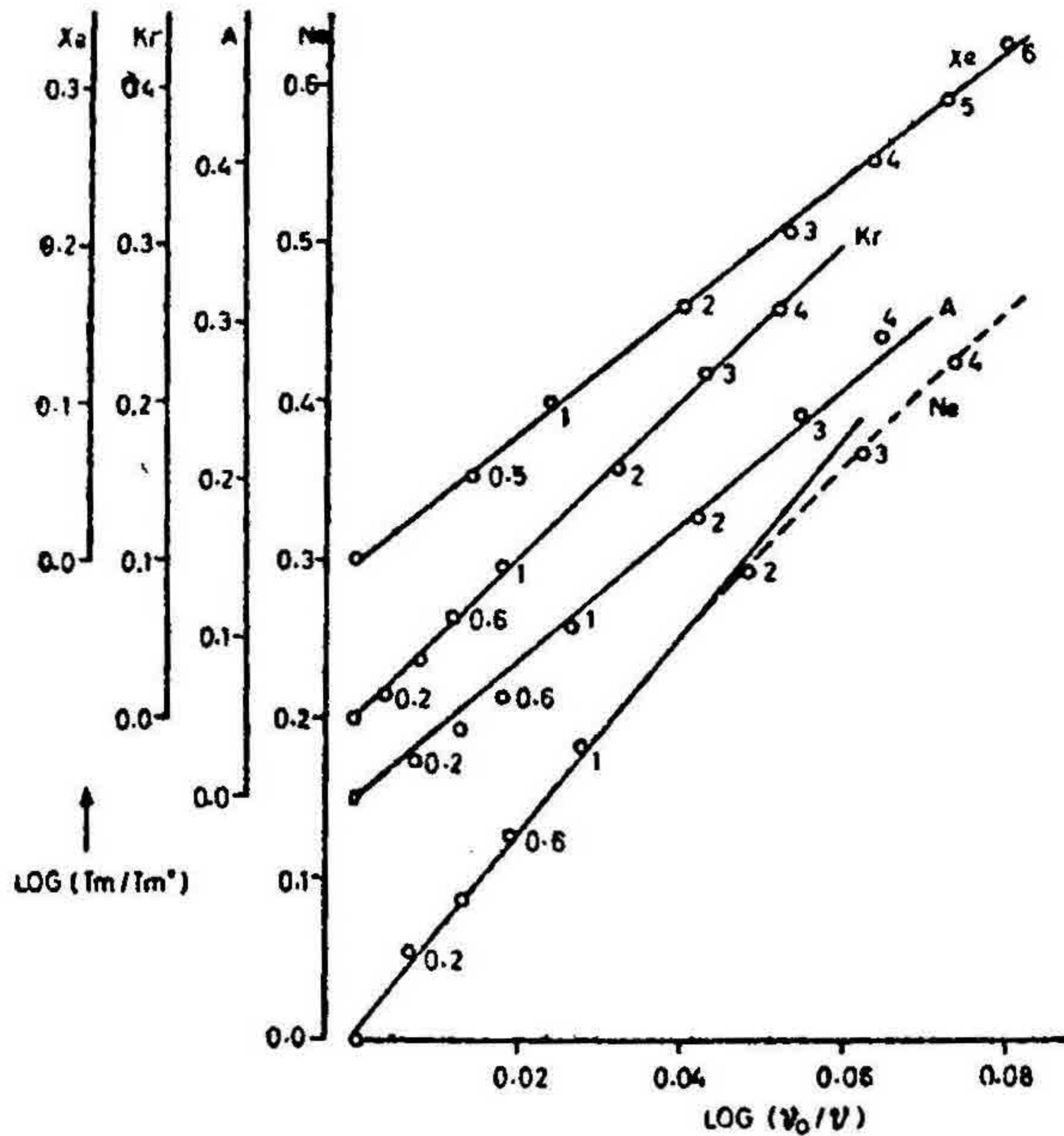


FIG. 1

Plot of $\log(T_m/T_m^\circ)$ against $\log(v_0/v)$ for solid neon, argon, krypton and xenon. Numbers near the experimental points are the pressures in kbar. Note the off-set ordinates for the four solids.

In the case of hydrogen, deuterium, nitrogen and oxygen, the melting data are taken from Mills and Grilly²³ (H₂ and D₂), Robinson²⁷ (N₂) and Mills and Grilly²² (O₂), while the compression data are taken from Stewart and Swenson³⁶ (H₂ and D₂ at 42°K), Swenson³⁸ (N₂ at 53°K) and Stevenson³⁰ (O₂ at 52°K). Nitrogen shows a $\beta \rightleftharpoons \gamma$ phase transition at 7.3 kbar and 53°K and the present data refers to the β phase below 7.3 kbar. Oxygen has a similar $\alpha \rightleftharpoons \beta$ phase change at 1.5 kbar and 52°K. The data for the high pressure β phase is used. The $\log(T_m/T_m^\circ)$ vs $\log(v_0/v)$ plots are linear and similar to figure 1. So they are not reproduced except the curve for hydrogen (figure II) which has some unusual features to be discussed below.

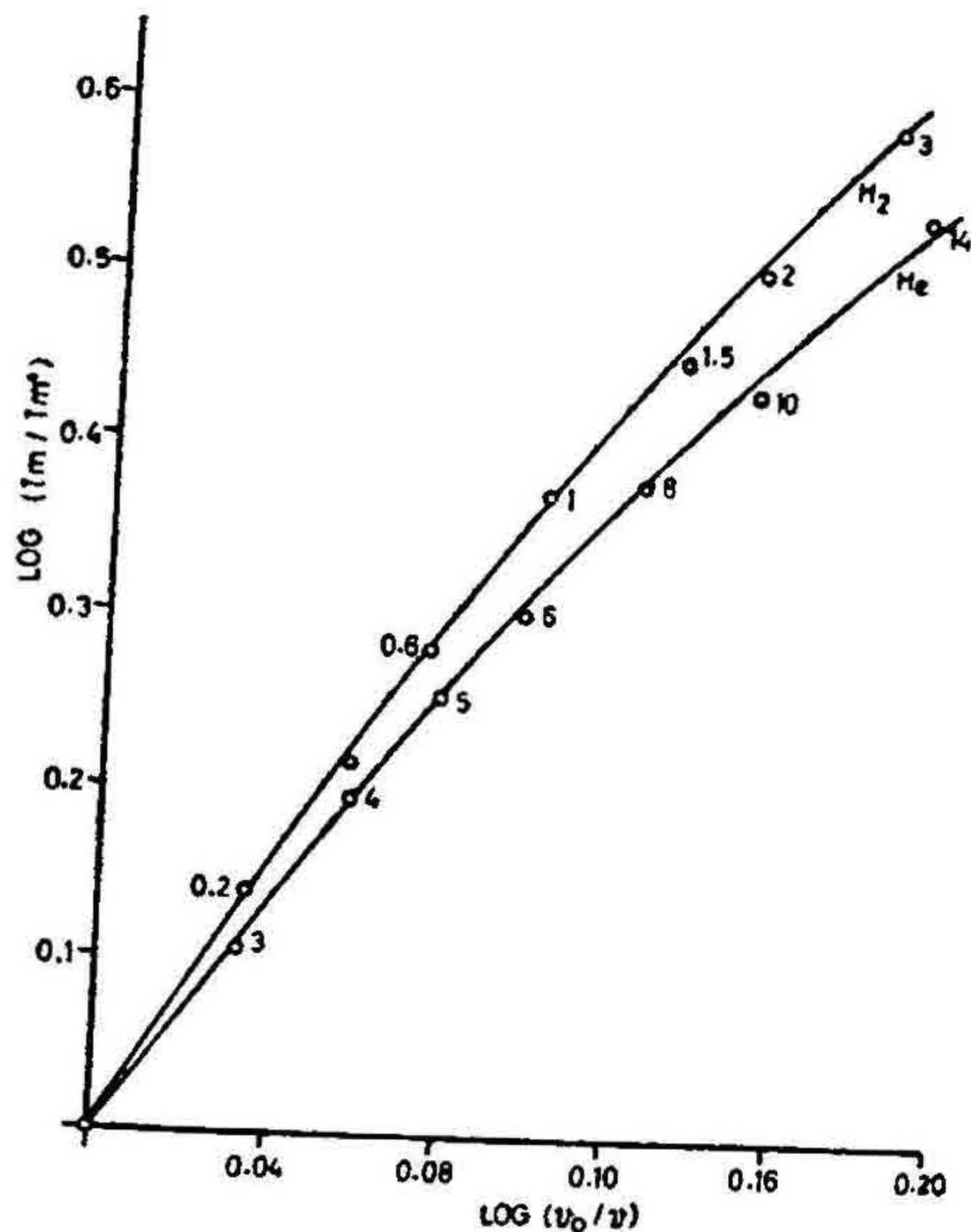


FIG. II

Melting curves of helium⁴ and hydrogen. For helium⁴, v_0 is the volume at 2 kbar. Pressures in kbar are also given near the experimental points.

A number of other gases have also been studied in the solid state. Melting data have been taken for ammonia from Vereschagin and Voronov⁴² carbon dioxide from Bridgman⁵, methane from Stryland, Crawford and Mastoor³⁷ and for ethylene, propane and propylene from Reeves, Scott and Babb²⁶. Compression data are from Stewart^{33, 35} (CH_4 at 77° and NH_3 at 155°K), Stevenson³⁰ (CO_2 at 185°K , 145°K and 77°K) and from Stewart and La Rock³⁵ (C_2H_4 , C_3H_8 and C_3H_6 at 77°K). The $\log(T_m/T_m^0)$ vs. $\log(v_0/v)$ plots for these substances are also linear and are not reproduced.

The γ values obtained from these plots are collected together in Table I (rare gas solids) and Table II (other solidified gases).

DISCUSSION OF THE GRUNEISEN CONSTANTS OF SOLIDIFIED GASES

The linearity of the $\log(T_m/T_m^0)$ vs. $\log(v_0/v)$ plots is very good in all cases (except for helium and hydrogen at high compressions which will be discussed below). The Kennedy equation gives a similar linear fit in the case of many other materials also^{15, 39, 40, 41}. A quantitative test of equation can

TABLE I
Gruneisen Constants of inert gas solids

Solid	Melting Law		Thermal Data	
	$ \Delta v/v $ at	$\gamma(\text{melting})$	Temp.	$\gamma(\text{thermal})$
He ³	4.2° K	1.97	1° K	2.24 (a)
He ⁴ (b)	4.2°	1.95 (21.6° K)	20.8 (b)	1.96 (c)
	„	1.64 (52.8° K)	53.9 (b)	1.74 (c)
Ne	4.2	3.36	10	2.85 (d)
			20	2.68 (d)
A	65	2.78	60	2.83 (d)
	77	2.47	80	2.4 (e)
Kr	77	2.70	80	2.33 (d)
Xe	40	3.09	40	2.91 (d)
	77	2.88	89	2.88 (d)
	160	2.30	150	2.1 (f)

(a) From Heltemes and Swenson¹⁰.

(b) Along the melting line.

(c) From Dugdale⁷.

(d) From Pollack²⁰.

(e) From Dobbs *et. al.*⁸.

(f) From Packard and Swenson²⁴.

be made by comparing the values of the Gruneisen constant calculated from these melting plots with the thermal values obtained from the relation $\gamma = v\beta/K_T C_v$ (β = coefficient of cubical expansion, K_T isothermal compressibility). These values, are given in Table I and II along with the sources for γ (thermal). For He⁴ and H₂, γ (thermal) values are based on a direct evaluation of $\gamma = -d \log \theta / d \log v$ (eq. 4).

On the whole there is reasonable agreement between γ (melting) and γ (thermal) in Table 1 and 2, especially in view of the scatter in the γ (thermal) values. Considering the rather wide differences in the properties of the various gases, such an overall agreement should be taken as very satisfactory. It is noticed that in a few cases the present values of γ are in the nature of predicted estimates which may be used with reasonable confidence in discussing their thermal behaviour.

TABLE II
Gruneisen Constants of solidified gases

Solid	Melting Law		Thermal Data	
	$ \Delta v/v_0 $ at	γ (melting)	Temp.	γ (thermal)
H ₂ (a)	4.2 °K	2.66 (14 °K)	14 °K	2.58 (b)
	„	1.73 (47 °K)		
D ₂	4.2	2.04	1.81 (c)
N ₂	53	2.36
O ₂	51.6	2.13
NH ₃	155	1.39	155	1.22 (d)
CO ₂	185	2.06	185	2.89 (e)
	145	2.37	145	2.28 (e)
	77	3.31	77	2.26 (e)
CH ₄	77	2.43	80	1.68 (f)
C ₂ H ₄	77	2.45
C ₃ H ₈	77	3.03
C ₃ H ₆	77	1.69 (g)
		2.43 (h)

(a) Along the melting line.

(b) From Ahlers¹.

(c) Estimated by Megaw²¹.

(d) Calculated from the data of Manzhelii and Tolkachev¹⁹ (V and β), Itterbeek¹² (p 208, kT) and Landolt-Bornstein⁸ (1961, C_p). Manzhelii and Tolkachev¹⁹ have calculated $\gamma=1.11$ at 150 °K from their new experiments.

(e) Calculated from the data of Mass and Barnes²⁰ (V and β), Keesom and Kochler¹⁸ (V and β), Stevenson²⁰ (kT) and Landolt-Bornstein¹⁰ (C_p).

(f) Calculated from the data of Manzhelii and Tolkachev¹⁹ (V and β) Bezuglyi, Burma and Minyafaev⁴ (k_s) and Landolt-Bornstein¹⁰ (C_p).

(g) Low pressure phase.

(h) High pressure phase.

It is known that γ depends to some extent on temperature and so more realistic comparison should involve $|\Delta v/v_0|$ and γ (thermal) at the same temperature. This is possible for argon and xenon and the trend in the

thermal values is clearly reproduced in γ (melting) also. It may be mentioned that in the case of a number of alkali halides (which melt at high temperatures but for which compressions are available at room temperatures) a similar temperature correction substantially improves the agreement between γ (melting) and γ (thermal)⁴¹.

The slight curvature of the $\log(T_m/T_m^0)$ Vs $\log(v_0/v)$ curve of helium⁴ and hydrogen at high compressions was mentioned earlier. If one takes the slopes as a measure of the effective γ at the appropriate T and v , one gets for helium⁴ the values 1.95 at 22°K (molar volume 10.7 cm³) and 1.64 at 53°K (molar volume 8cm³). These values compare favourably with the trend of thermal γ , namely 1.96 at 21°K and 1.74 at 54°K, along the melting line of He-4⁷. For solid hydrogen along the melting curve, γ equals 2.66 at 14°K (molar volume 22.6 cm³) and 1.73 at 47°K (16 cm³). The thermal value at 14°K is 2.58, averaged over the volume range of 22.6 and 19.8 c-c¹. No value is available along the melting line, but the present estimate is in reasonable agreement with the results of Ahlers¹ if they are extrapolated to 47°K and 16 cm³. It may be added that other substances should also show a similar flattening at high compressions if data at sufficiently high pressures are obtained. For neon the tendency is just perceptible in Figure I.

The change in γ along the melting line arises from a decrease in γ with increasing pressure and (in these cases of solidified gases where $T_m \approx \theta$) to a change of γ with temperature. Quasi-harmonic theories of the solid state predict that γ (at zero pressure) should be independent of temperature¹¹ for $T > \theta/2$ but in many rare gas solids, where data are available, γ shows a slight decrease in this range²⁵. The behaviour is similar to that of the Debye θ wherein the decrease for $T \gtrsim \theta/2$ is attributed to the anharmonicity of vibrations and the consequent breakdown of the quasiharmonic theory. At present there is no quantitative theoretical estimate of this effect in rare gas solids.

The dependence of γ upon volume can be calculated from the theoretical equations of state of the solid. For instance Packard and Swenson²⁴ have made such calculations for xenon. It is seen that a 10% decrease in volume causes roughly a 10% decrease in γ . Beecroft and Swenson³ have calculated the change in γ with volume for sodium and find the effect to be very much smaller. Perhaps this is associated with the differences in the nature of the interatomic forces, namely Van der Waals type in inert gas solids and Coulomb forces in metals. Slater's method of calculating γ as a function of v from the compressions at high pressures gives the same trend for xenon as the results based on the equation of state, but the values are $\sim 20\%$ higher. Further in sodium the method appears to give larger γ at higher pressure in contradiction with the results based on the equation of state. It is desirable to investigate this further.

The suggestion by Kennedy, of relating T_m to v thus appears to have great promise in relating melting phenomena to general solid state studies. But one should also mention some limitations of the melting equation (6). They stem from the shortcomings of the original Lindemann and Gruneisen theories. As mentioned earlier, the data at high compressions require a power series in $|\Delta v/v_0|$ for adequate representation (eq. 8). Though the parameter B of equation (8) may be related to the volume and temperature derivations of γ , the simplicity of the original Kennedy suggestion is lost. Secondly it is found that some materials have a negative value of (dT_m/dP) at $P = 1$ atm. According to equation (7) this requires $\gamma < \frac{1}{3}$, which is not the case if one calculates the thermal values of γ . As Klement and Jayaraman¹⁴ have pointed out, nearly all such substances show phase transitions even at moderately high pressures. This might be connected in some, as yet unknown, manner with the discrepancy between γ (melting) and γ (thermal). However even these complicated melting curves are well represented by equation (8) if $A, B \dots$ are taken as empirical parameters.

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