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Thermodynamically based melting-curve equation

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Abstract. An equation for the pressure dependence of the melting temperature based on thermodynamic principles has been developed, which generalizes the Simon–Glatzel equation and describes the rising and falling melting curves as well as curves with a maximum. The parameters appearing in the equation are identified in terms of the thermodynamic values. The equation accurately approximates the melting curves of different categories of substances over a large range of melting temperatures and pressures.

1. Introduction

The most well known and widely quoted relation for the pressure dependence of the melting temperature is the empirical equation proposed by Simon and Glatzel [1] in 1929. The equation can be written in the form

$$T_m = T_0(1 + \Delta P/a)^{1/c} \quad (1)$$

where $\Delta P = P - P_0$, T_m and P are the melting temperature and pressure, T_0 and P_0 are coordinates of the fixed (usually triple) point, and a and c are parameters.

The Simon–Glatzel equation is widely used for representation and extrapolation of the experimental T_m – P data [2]. It can be applied only to substances with rising (normal) melting curves. It describes well the melting behaviour of solids bonded by van der Waals forces, such as solid gases. For metals and ionic compounds with normal melting curves the Simon–Glatzel equation predicts melting temperatures significantly in excess of those found experimentally [3]. The Simon–Glatzel equation cannot be used for falling melting curves or curves with maxima.

The purpose of the present paper is to obtain an equation for different kinds of melting curve, which may be used for wide classes of substances.

2. Analysis

Melting is known to be a first-order phase transition. In accordance with the thermodynamic theory, the melting occurs when the Gibbs free energies of the liquid and solid are equal at a given temperature and pressure. The theory leads to the Clausius–Clapeyron equation, the fundamental equation governing the phase equilibrium:

$$d(\ln T_m)/dP = \delta V/L \quad (2)$$

where $\delta V = V_{\text{liq}} - V_{\text{sol}}$ is the volume discontinuity during melting and L is the latent heat of melting.

Expanding $y = \delta V/L$ in (2) at point $P = P_0$ up to the second order, one obtains

$$d(\ln T_m)/dP = y \simeq y_0 + y'_0 \Delta P + \frac{1}{2} y''_0 (\Delta P)^2 \quad (3)$$

where single and double primes denote the first- and second-order derivatives, respectively, with respect to pressure. Performing the Padé approximation to the right-hand side of (3), we obtain

$$\frac{d(\ln T_m)}{dP} = \frac{1 - \beta \Delta P}{\sigma(\alpha + \Delta P)} \quad (4)$$

where the parameters α , β and σ are given by

$$\begin{aligned} \sigma &= -y''_0/2y_0y'_0 \\ \alpha &= -2y'_0/y''_0 \\ \beta &= y''_0/2y'_0 - y'_0/y_0 \end{aligned} \quad (5)$$

There is a universal feature which all melting curves have in common, namely for all melting curves the concavity is towards the pressure or $y' < 0$, whether they rise or fall. Therefore, the pressure $P_{\text{extr}} = P_0 + 1/\beta$ corresponds to the melting-curve maximum (for the rising melting curve, $\beta \geq 0$ whereas, for the falling curve, $\beta < 0$ and the melting-curve maximum corresponds to a negative pressure).

By integrating (4) with respect to pressure, one obtains the equation for pressure dependence of melting temperatures in the form

$$T_m = T_0(1 + \Delta P/a_1)^{a_2} \exp(-a_3 \Delta P) \quad (6)$$

where $a_1 = \alpha$, $a_2 = (1 + \alpha\beta)/\sigma = y'_0\alpha^2$ and $a_3 = \beta/\sigma = -y'_0\alpha - y_0$. Note that the parameter a_2 is positive since $y'_0 < 0$. At $a_3 = 0$ (or at $\beta = 0$), equation (6) reduces to the Simon-Glatzel equation with σ (or $1/a_2$) equal to c .

The Simon-Glatzel equation corresponds to the differential equation

$$d[dP/d(\ln T_m)]/dP = c. \quad (7)$$

Using the Clausius-Clapeyron equation the Simon-Glatzel parameter c can be defined as

$$c = \Delta(L/\delta V)/\Delta P \quad (8)$$

where $\Delta(L/\delta V) = L/\delta V - (L/\delta V)_0$. Substituting $\alpha = (L/\delta V)_0/\sigma$ in (4), one finds that

$$\sigma = c - \beta \frac{L}{\delta V} \quad (9)$$

where c is defined by (8) and the parameter β is

$$\beta = \frac{\Delta c}{\Delta(L/\delta V)}. \quad (10)$$

Thus, the parameters α , β and σ (and hence the parameters a_1 , a_2 and a_3 of equation (6)) are identified in terms of the thermodynamic values.

3. Numerical results

The right-hand side of (8) and (9) involves the thermodynamic values L and δV which may be measured on the melting curve by high-pressure experiments. The data are available for the solid gases Ar [4, 5], Ne [4], N_2 [6] and CH_4 [6] and for alkali metals [7–9]. The results of calculation of parameters from equations (8) and (9) and references are given in tables 1 and 2. In table 1 the values of the Simon–Glatzel parameter c at various pressures are shown for solid gases. It is seen that within the scatter of the data the parameter c is constant. Therefore, for solid gases the Simon–Glatzel equation is valid. Table 2 shows the values of the parameter σ for alkali metals at various pressures. For comparison in table 2 the values of the parameter c are also given. Table 2 shows that the parameter c , in contrast with σ , continuously varies with pressure and hence alkali metals do not conform to the Simon–Glatzel equation. Thus, it is shown that within experimental errors the parameters appearing in equations (4) and (6) are constants.

Table 1. Parameter c for various pressures P derived from experimental data [4–6] and equation (8).

| Ar [4] | | Ar [5] | | Ne [4] | | N ₂ [6] | | CH ₄ [6] | |
|-----------|------|-----------|------|-----------|------|--------------------|------|---------------------|------|
| P (GPa) | c | P (GPa) | c | P (GPa) | c | P (GPa) | c | P (GPa) | c |
| 0.11 | 1.65 | 0.61 | 1.44 | 0.04 | 1.69 | 0.22 | 1.81 | 0.01 | 1.93 |
| 0.21 | 1.60 | 0.78 | 1.50 | 0.08 | 1.68 | 0.43 | 1.76 | 0.02 | 1.72 |
| 0.50 | 1.57 | 0.95 | 1.51 | 0.12 | 1.65 | 0.55 | 1.75 | 0.32 | 1.65 |
| 0.76 | 1.54 | 1.14 | 1.52 | 0.17 | 1.65 | 0.70 | 1.78 | 0.68 | 1.63 |
| 0.90 | 1.54 | 1.33 | 1.53 | 0.22 | 1.62 | 0.84 | 1.82 | 0.87 | 1.78 |
| 1.04 | 1.53 | 1.54 | 1.53 | 0.33 | 1.61 | 1.02 | 1.77 | 1.05 | 1.81 |

Table 2. The parameters c and σ for various pressures P , derived from experimental data [7–9] and equations (8) and (9). The values of parameter β from (10) are 0.143 GPa^{-1} , 0.091 GPa^{-1} , 0.196 GPa^{-1} , 0.153 GPa^{-1} and 0.500 GPa^{-1} for Li, Na, K, Rb and Cs, respectively. Note that Cs has a melting temperature maximum at $P = 2.02 \text{ GPa}$.

| Li [7] | | | Na [8] | | | K [7] | | | Rb [7] | | | Cs [9] | | |
|-----------|------|----------|-----------|------|----------|-----------|------|----------|-----------|------|----------|-----------|--------|----------|
| P (GPa) | c | σ | P (GPa) | c | σ | P (GPa) | c | σ | P (GPa) | c | σ | P (GPa) | c | σ |
| 0.12 | 7.83 | 5.19 | 0.26 | 3.50 | 3.05 | 0.04 | 3.62 | 3.20 | 0.23 | 3.85 | 3.53 | 1.18 | 4.98 | 1.42 |
| 0.48 | 8.21 | 5.63 | 0.40 | 3.57 | 3.06 | 0.15 | 3.70 | 3.20 | 0.38 | 3.92 | 3.53 | 1.37 | 5.84 | 1.20 |
| 0.68 | 8.60 | 5.75 | 0.54 | 3.55 | 3.04 | 0.27 | 3.84 | 3.24 | 0.55 | 4.02 | 3.53 | 1.57 | 7.68 | 1.03 |
| 0.91 | 8.89 | 5.72 | 0.70 | 3.65 | 3.04 | 0.43 | 3.99 | 3.26 | 0.76 | 4.16 | 3.54 | 1.77 | 12.79 | 0.87 |
| 1.16 | 9.11 | 5.59 | 0.86 | 3.72 | 3.05 | 1.01 | 4.51 | 3.22 | 1.00 | 4.34 | 3.55 | 1.96 | 50.55 | 0.73 |
| 1.21 | 9.34 | 5.58 | 1.04 | 3.77 | 3.04 | 1.17 | 4.63 | 3.17 | 1.30 | 4.56 | 3.57 | 2.16 | -21.92 | 1.10 |

In figures 1 and 2 the least-square fits based on equation (6) for ten substances [10–19] are shown. In all cases the fits are as good as the experimental data. The fit parameters and references are listed in table 3.

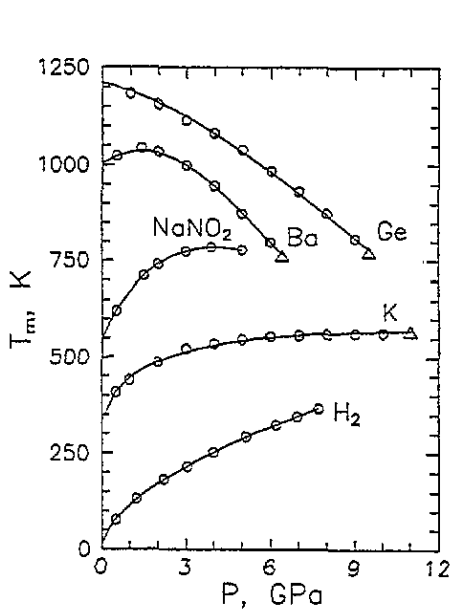


Figure 1. Melting curves for Ge, Ba, NaNO_2 , K and H_2 : —, (---, curve for KH_2AsO_4 in the metastable region) fits based on equation (6); O, experimental data; Δ , high-pressure triple points.

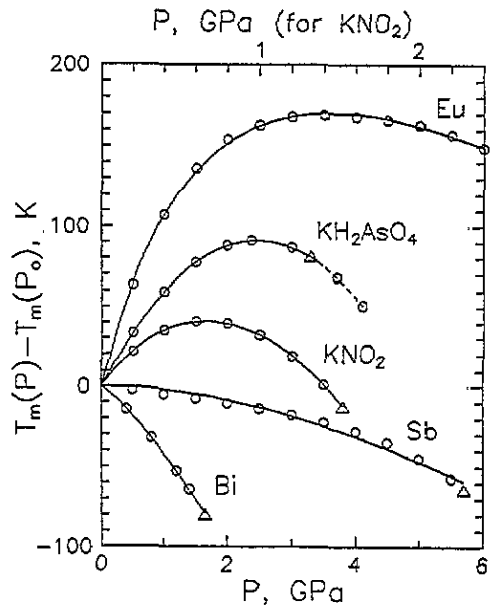


Figure 2. Melting curves for Eu, KH_2AsO_4 , KNO_2 , Sb and Bi: —, (---, curve for KH_2AsO_4 in the metastable region) fits based on equation (6); O, experimental data; Δ , high-pressure triple points.

Table 3. The least-squares fit parameters of equation (6).

| | α_1 GPa | α_2 | α_3 GPa^{-1} | Reference |
|---------------------------|-------------------|------------|---------------------------------|-----------|
| H_2 | 0.0261 | 0.5781 | 0.0024 | [10] |
| K | 0.2440 | 0.1824 | 0.0154 | [11] |
| Eu | 0.9273 | 0.1862 | 0.0415 | [12] |
| Ba | 5.0857 | 1.3402 | 0.2116 | [13] |
| NaNO_2 | 1.8353 | 0.7215 | 0.1234 | [14] |
| KNO_2 | 3.2466 | 3.4998 | 0.8950 | [15] |
| KH_2AsO_4 | 8.9317 | 5.7108 | 0.5043 | [16] |
| Bi | 5.0141 | 1.3120 | 0.3207 | [17] |
| Sb | 22.3757 | 2.4394 | 0.1018 | [18] |
| Ge | 20.8504 | 4.0370 | 0.2054 | [19] |

4. Discussion

The proposed equation predicts the melting-curve maxima. The hypotheses that all substances have a maximum on the melting curve was first suggested by Tammann [20] in 1903. This phenomenon was discovered in a number of elements and compounds [21] and it could not be considered as an anomaly. Kawai and Inokuty [22] reintroduced Tammann's idea and postulated that the melting-curve maximum could be at positive or negative pressure and the rising and decreasing melting curves could be treated on the same basis. The behaviour of the melting curve of the given solid phase can be masked by phase transformation into the next high-pressure phase. At extreme high pressures the 'last' solid

phase, in accordance with the Lindemann melting law, would be destroyed by quantum vibrations and melted at the absolute zero of temperature [23]. Therefore, at extreme high pressures the liquid state is more stable than the solid. The calculation of the ground-state energy for a system of interacting electrons and positive ions confirms a result favouring a liquid state at extreme high pressures [24].

5. Summary

The results obtained in this paper are summarized as follows.

(1) An equation for the pressure dependence of melting temperature based on thermodynamic principles has been developed. It generalizes the Simon-Glatzel equation and describes rising and falling melting curves as well as curves with maximum.

(2) The parameters appearing in the equation are identified in terms of the thermodynamic values.

(3) Comparison with high-pressure experimental data shows that within the scatter of the data the parameters are indeed constants.

(4) The equation accurately approximates, as good as experimental data, the melting curves of different categories of substances over a large range of melting temperatures and pressures.

(5) The analysis of the present equation and experimental melting-curve data supports Tammann's hypothesis that all materials have a maximum melting temperature at high (or negative) pressures.

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