The fusion curves of xenon, krypton, and argon

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Abstract

The experimental results on the fusion of the heavier rare gases at very high pressures, obtained in the last 20 years, are examined and analysed in conjunction with the measurements made at lower pressures from 1940 onwards. The parameters in the Simon equation for the melting curves of Xe, Kr, and Ar are determined, and the coordinates of a possible high-pressure {s(fcc) + s(hcp) + f} triple-point are identified for each one of these three elements. The enthalpies of transition of the transformations involved are estimated as well as their respective values of the entropies of transition.

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1. Introduction

The scientific literature on the thermodynamic and physical properties of the rare gases is abundant but rather heterogeneous. While the bibliography on helium is extensive, including a significant number of specific monographs, the published data on the phase equilibrium of radon, which we examined recently [1], is much scarcer and old. For the other elements in the same group viz. neon, argon, krypton, and xenon, the situation is rather different. Most of the more accurate experimental results on the phase equilibrium curves, sublimation, vapourization, and fusion, were obtained during the years 1950s to 1970s. There are two relevant exceptions in this case. The first is that of argon on which Wagner and his co-workers [2–4] carried out rigorous measurements on the (vapour + liquid) equilibrium of the substance and analysed the whole set of experimental results (including pre-existing data) on sound physico mathematical criteria. On the contrary for xenon and krypton, it is necessary to go back four decades to find equations sufficiently detailed to describe the vapour pressure curves of both substances [5]. Neon (as helium) is, of course, a special case due to the well known quantum effects that led to modifications in the values of its (classical) critical properties whenever the macroscopic principle of corresponding states is used for describing the volumetric behaviour of the gas [6]. For such reasons, neon and helium will not be considered in the present work. The second exception is concerned with the fusion of the heavier rare gases, argon, krypton, and xenon, for which a number of new experimental results have been obtained more recently at much higher pressures than before [7–10], partly as a result of the advancement in laboratory techniques, namely the diamond-anvil cell (DAC), partly from the efforts of geologists to investigate the so-called “missing xenon problem” in the atmosphere of the earth [11,12], and also from the interest of many other scientists to attain and observe the metallic phase predicted by theory to exist for Xe above about (137 to 150) GPa [13,14].

In this paper, we examine the experimental information now available on the fusion equilibrium of the three elements to try and find equations to describe the solid–liquid curves of xenon, krypton, and argon. Data obtained prior to the adoption of the (first) international temperature scale (ITS-27) were not considered. Where relevant, at the relatively low temperatures registered for the original
experiments, the temperature scales used by the various authors have been converted into ITS-90 by recommended methods [15–17]. At the much higher fusion pressures measured in the last 20 years or so, where the corresponding equilibrium temperatures have been determined with reported uncertainties of the order of (1 to 10) K or even as high as \( T = 100 \text{ K} \) [9], there is no purpose in performing such temperature scale adjustments.

Tentative high-pressure \((p, T)\) phase diagrams are sketched for the three substances, and possible solid–solid–liquid triple-points under extreme conditions are suggested and localized. The respective estimated values of the enthalpies (and entropies) of transition are assessed and discussed.

### 2. Equations for the fusion curves

Not long ago, we showed [18] that by exactly integrating the Clapeyron equation the fusion curves of pure substances, whose volumes expand on melting as is the case for the low-pressure solid phases of the heavier rare gases, are of the form,

\[
p = p_0 + (A_t + D_t T + F_t T \ln T) / \{\Delta'_V(p_0, T_0)\},
\]

where \( p \) and \( T \) are, respectively, the natural variables pressure and temperature, the subscript \( 0 \) indicates a reference point on the fusion curve, \( V_m \) is the molar volume, \( \Delta'_V \) is the difference between the values of the molar property \( X_m \) for the liquid (\( l \)) and solid (\( s \)) phases, and \( A_t, D_t, \) and \( F_t \) are constants for each substance that can be calculated \textit{ab initio} from the molar heat capacities and enthalpies of the phases involved in the transition. At the high pressures, we examine in this work reliable information on such thermodynamic properties of the phases are unavailable at present. So, instead of equation (1), we decided to use the Simon equation [19],

\[
(p - p_0)/a = \{ (T/T_0)^c - 1 \},
\]

where the reference point (subscript \( 0 \)) originally indicates the \((s + \ell + g)\) triple-point, with the parameters \( a \) and \( c \) being statistically adjustable to experiment. In some studies, the coordinates of the normal melting point have also been taken for \((p_0, T_0)\). A modified version of the Simon equation has been in use, adapted to describe fusion curves exhibiting a maximum temperature [20], but it is not relevant for the substances that interest us here. Although equation (2) is empirical, it has proved to be most effective in describing the melting curve of many substances [21]. Voronel [22] suggested that equation (2) can be obtained from the Clapeyron equation,

\[
\frac{dp}{dT} = \Delta'_H / (T \cdot \Delta'_V),
\]

that governs all first-order transitions between phases (s and \( \ell \) in this case) of pure substances, by admitting that the quotient of the molar enthalpy to the molar volume in the \( s \rightarrow \ell \) transition is a linear function of the fusion pressure [23];

\[
(\Delta'_H / \Delta'_V) = c(p + a).
\]

Recent measurements on the fusion of the heavier rare gases showed that for each of these substances at room temperature a solid hexagonal close packed (hcp) phase exists at much higher pressures instead of the face centred cubic (fcc) solid phase dominant at the relatively lower pressures measured in earlier studies [9, 10]. The transition from the fcc-solid to the hcp-structure is not yet well characterized being referred in some studies as “kinetically hindered” [11], “sluggish” [24, 25], or “martensitic” in nature [24, 26, 27]. Moreover, according to Cynn et al. [26] the “observations demonstrate a profound hysteresis of the fcc/hcp transition”. The pressures above which the solid exists solely as hcp-phase, and below which only the fcc-solid phase is stable have been determined at or near room temperature. For xenon, a recent theoretical study [27] admitting the existence of a face centred orthorhombic (fco) solid phase at intermediate pressures does not match the conclusions of previous work [25]. In any case, the experimental evidence [9] shows that the slope \((dp/dT)\) of the melting curve of xenon increases sharply at high temperature and pressure. The same seems to happen, though less notably, for krypton and even less clearly for argon. This change of slope means that the fusion of the two solid phases (fcc and hcp) should not be described by the same equation for each one of the three heavier rare gas elements. Furthermore, this observation leaves room to envision that a triple-point \((s(fcc) + s(hcp) + \ell)\) may exist at high temperature and pressure, where the fusion curves (of different slope) of the two solid phases cross each other.

In this study, we consider that the Simon equation also applies to the fusion curve of the high-pressure hcp-solid form of the rare gases since the reference (subscript \( 0 \)) in equation (2) can be taken as the crossing point of the two fusion curves, whose \((p, T)\) coordinates should provide an estimate of those of one possible \((s(fcc) + s(hcp) + \ell)\) triple-point, which has not yet been reported as so, although Ross et al. [28] suggested the existence of a triple-point of a different nature in the same region, involving an icosahedral short-range ordered (ISRO) structure [29]. Also, Belonoshko et al. [30] mention that (in their opinion) the position of the “triple fcc–bcc–liquid point” has an uncertainty of 2.5 GPa.

In this section, we find the parameters of Simon equation for argon, krypton, and xenon from the experimental data available in the literature, and report on the procedures used to achieve the values of such parameters.

For the \((s(fcc) + \ell + g)\) triple-point pressure where it is necessary to establish the lower pressure forms of equation (2), we have taken the values analysed by the criteria and selected by Staveley et al. [31].

#### 2.1. Xenon

Of the three rare gases that interest us here, xenon is the most extensively measured where high-pressure fusion
is concerned. Table 1 systematizes the experimental data in the literature from 1940 onwards. The results from references [32–35] were used to determine a first approximation to the values of parameters \( a \) and \( c \) in the Simon equation for the fusion of the fcc-phase which is, no doubt, the stable solid form under relatively lower temperatures and pressures. The extrapolation to higher temperatures and pressures of the first form of the equation so obtained showed that it also fits the two experimental points due to Jephcoat and Besedin [8] and those measured by Boehler et al. [9] at temperatures up to about 2800 K. This observation led us to include the 16 points at the lower temperatures reported in reference [9] and the two points mentioned in reference [8] to obtain a second, better, approach to the fusion curve equation of the fcc-solid phase of xenon. In the resulting Simon equation (2), for the fcc-solid phase fusion curve, where \( p_0 = 81.675 \) kPa, \( T_0 = 161.404 \) K are the coordinates of the low-pressure \( \{s(fcc) + \ell + g\} \) triple-point [31], the parameters are \( a = (259.351 \pm 2.059) \) MPa, \( c = (1.4905 \pm 0.0029) \). The correlation coefficient \( (r) \) of this fitting is 0.997, and the average absolute deviation (AAD) for the 70 experimental points used in this fitting is less than 8\%.

For the melting of the high-pressure (hcp) form of the solid, the calculations are more involved since the coordinates of the reference point are still to be determined at the beginning. To start the necessary iterations, we considered that such coordinates can be taken as those of the point with the highest temperature used in establishing the parameters in equation (2) for the fusion of the fcc-solid. Tentative values of the parameters \( a \) and \( c \) were then found, which led to better values of \((p_0, T_0)\), and so on until convergence is obtained. Using this procedure and the 13 experimental values for the melting of the hcp-solid at the higher pressures measured by Boehler et al. [9], at the end of the iteration we arrived at \( a = (6506 \pm 384) \) MPa, \( c = (7.6194 \pm 0.2472) \), with \( T_0 = (2670 \pm 15) \) K, and \( p_0 = (16 \) 750 \pm 850) \) MPa. These are the coordinates of the possible high-pressure \( \{s(fcc) + s(hcp) + \ell\} \) triple-point of xenon, i.e., the crossing point of the fusion curves of the two solid forms. The correlation coefficient of the high-pressure fitting is \( r = 0.919 \), with AAD less than 9\%, which are acceptable values in view of the uncertainties attached to the experimental determinations (cf. footnote c to table 1). The two calculated fusion curves are shown in figure 1. For clarity only part of the 70 experimental points for the fcc-fusion curve are represented in this figure.

### 2.2. Krypton

For the fusion of fcc-solid krypton, we used the experimental data collected in table 2, excluding the high-pressure measurements by Boehler et al. [9]. Using the

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**TABLE 1**

Experimental data on the fusion of xenon used in this work

<table>
<thead>
<tr>
<th>Year</th>
<th>No. of points</th>
<th>Range ((T \text{ and } p))</th>
<th>Original (T)-scale</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1940</td>
<td>11</td>
<td>((161.36 \text{ to } 164.34) ) K ((0.7 \text{ to } 7.7) ) MPa</td>
<td>( T^A \phantom{0} )</td>
<td>[32]</td>
</tr>
<tr>
<td>1960</td>
<td>18</td>
<td>((165.2 \text{ to } 261.2) ) K ((12.8 \text{ to } 302.0) ) MPa</td>
<td>IPTS-48 ( \phantom{0} )</td>
<td>[33]</td>
</tr>
<tr>
<td>1962</td>
<td>14</td>
<td>((161.55 \text{ to } 215.3) ) K ((0.6 \text{ to } 151.4) ) MPa</td>
<td>( T^A \phantom{0} )</td>
<td>[34]</td>
</tr>
<tr>
<td>1962</td>
<td>9</td>
<td>((234 \text{ to } 363) ) K ((194.6 \text{ to } 653.5) ) MPa</td>
<td>\phantom{0} \phantom{0}</td>
<td>[35]</td>
</tr>
<tr>
<td>1997</td>
<td>2(^a)</td>
<td>((1783; 2083) ) K ((7.33; 11.78) ) GPa</td>
<td>\phantom{0} \phantom{0}</td>
<td>[8]</td>
</tr>
<tr>
<td>2001</td>
<td>28(^b)</td>
<td>((1700 \text{ to } 3270) ) K ((8.41 \text{ to } 42.73) ) GPa</td>
<td>\phantom{0} \phantom{0}</td>
<td>[9]</td>
</tr>
</tbody>
</table>

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\( ^a \) Values extracted as precisely as possible from the graphics in figure 2 of reference [9].

\( ^b \) Temperatures as given in the original papers; pressures were converted into SI units.

\( ^c \) \( T^A \) are temperature scales used by the original authors, transformed by us into ITS-90 for the calculations. Both Clusius [32] and Michels [34] give numerical values for some particular (fixed) points in the scales they used. Clusius used a somewhat peculiar lead thermometer. In reference [35] the temperatures are given at integer figures. Boehler et al. [9] mention that the precision of their temperature measurements is \( \pm 10 \) K, with an uncertainty of the order of \( 100 \) K at the highest temperature.
TABLE 2

Experimental data on the fusion of krypton used in this work

<table>
<thead>
<tr>
<th>Year</th>
<th>No. of points</th>
<th>Range (T and p)</th>
<th>Original T-scale</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1940</td>
<td>12</td>
<td>(115.95 to 119.34) K (0.9 to 11.0) MPa</td>
<td>T^A</td>
<td>[32];</td>
</tr>
<tr>
<td>1960</td>
<td>16</td>
<td>(120.3 to 192.6) K (18.6 to 302.1) MPa</td>
<td>IPTS-48</td>
<td>[33];</td>
</tr>
<tr>
<td>1962</td>
<td>15</td>
<td>(115.89 to 157.03) K (0.6 to 151.6) MPa</td>
<td>T^A</td>
<td>[34];</td>
</tr>
<tr>
<td>1962</td>
<td>7</td>
<td>(169 to 362) K (219 to 1177) MPa</td>
<td></td>
<td>[35];</td>
</tr>
<tr>
<td>1971</td>
<td>23</td>
<td>(115.77 to 291.70) K (78.8 to 800.9) MPa</td>
<td>IPTS-68</td>
<td>[36];</td>
</tr>
<tr>
<td>1997</td>
<td>1</td>
<td>2300 K</td>
<td>23 GPa</td>
<td>[8]; cf. [9];</td>
</tr>
<tr>
<td>2001</td>
<td>6'</td>
<td>(2400 to 3000) K (25.5 to 60.5) GPa</td>
<td></td>
<td>[9];</td>
</tr>
</tbody>
</table>

^a Values extracted as precisely as possible from the graphics in figure 2 of reference [9].

^b Temperatures as given in the original papers; pressures were converted into SI units.

^c T^A are temperature scales used by the original authors, transformed by us into ITS-90 for the calculations. Both Clusius [32] and Michels [34] give numerical values for some particular (fixed) points in the scales they used. Clusius used a somewhat peculiar lead thermometer. In reference [35] the temperatures are given at integer figures. Boehler et al. [9] mention that the precision of their temperature measurements is ±10 K, with an uncertainty of the order of 100 K at the highest temperature.

remaining 74 data points in this table and the \( \{s(fcc) + \ell + g\} \) triple-point selected by Staveley et al. [31] \((i.e., \ p_0 = 72.999 \text{ kPa}, \ T_0 = 115.772 \text{ K})\) we obtain as parameters in the Simon equation (2), for the fusion of the lower pressure fcc-solid, \( a = (266.627 \pm 0.061) \text{ MPa} \) and \( c = (1.4951 \pm 0.0001) \), with a correlation coefficient exceeding 0.9999, and AAD less than three per cent. By applying the same procedure as that described above for xenon and using the experimental information provided by Jephcoat and Besedin [8] and by Boehler et al. [9], we arrived at the values of the parameters in equation (2) for the hcp-solid form: \( a = (7947 \pm 331) \text{ MPa} \), \( c = (6.4594 \pm 0.1374) \), with \( T_0 = (2310 \pm 10) \text{ K} \), and \( p_0 = (23130 \pm 840) \text{ MPa} \) as coordinates of the plausible \( \{s(fcc) + s(hcp) + \ell\} \) triple-point of krypton. The correlation coefficient for the hcp-solid/liquid calculated melting curve is \( r = 0.987 \), and AAD is less than 4%. Both fusion curves are represented in figure 2 where, for clarity, only a portion part of the 74 experimental points for the fcc-solid melting has been plotted.

2.3. Argon

In the case of argon, the measurements made by Boehler et al. [9] do not indicate a change in the \( (dp/dT) \) slope of the fusion curve to be as sharp as that for xenon (and to a lesser extent for krypton). Therefore, it is only to be expected that the coordinates of a (possible) high-pressure \( \{s(fcc) + s(hcp) + \ell\} \) triple-point of Ar are to be determined with a much larger uncertainty than those encountered for Xe and Kr assuming, of course, that the same procedures can be used for the same purpose. The experimental values registered in the literature and included in table 3 have been used in the calculations. By using the \( \{s(fcc) + \ell + g\} \) triple-point pressure given in reference [31], \( p_0 = 68.898 \text{ kPa} \), and the corresponding value of temperature \( (T_0 = 83.8058 \text{ K}) \) which is a fixed point in ITS-90) we obtain the parameters for the fcc-solid phase fusion curve: \( a = (224.471 \pm 3.191) \text{ MPa} \) and \( c = (1.5354 \pm 0.0044) \), with AAD of 2% and a correlation coefficient above 0.999, for the 269 experimental points involved in the adjustment. Due to the fuzzy nature of the intersection of the fcc and hcp-fusion curves, as shown in figure 2 of reference [9], only the eight measurements made by Boehler et al. [9] and the two points from Jephcoat and Besedin [8] at the higher pressures of their measurements were considered to estimate the parameters in the argon hcp-fusion curve. In this way we obtained: \( a = (29534 \pm 1617) \text{ MPa} \), \( c = (3.0344 \pm 0.1223) \); and the coordinates of the crossing high-pressure (possible) triple-point: \( T_0 = (2395 \pm 20) \text{ K} \), and \( p_0 = (38340 \pm 1340) \text{ MPa} \). For the hcp-curvature fitting \( r = 0.955 \), and AAD is 6%. Shown in figure 3 is the plot of the two calculated fusion curves of argon and of a portion of the 269 experimental points used in this study.
from which the molar enthalpy of fusion $\Delta'_m$ can be derived, provided the change in the molar volume for the same transition $\Delta'_V$ has been measured as a function of temperature up to about 400 K for the three rare gases we are examining here [7,35,39,41,46]. Theoretical calculations for argon carried out by Zha et al. [7] up to $T = 3000$ K agree quite comfortably with the earlier experimental measurements at lower temperatures (figure 4). The following equation [47],

$$\Delta'_V = A/(T - B)^C,$$  

(6)

where $A$, $B$, and $C$ are adjustable parameters, represents within a good approximation both the experimental and the theoretical results for argon. As far as we are aware, no values for the change in the molar volumes $\Delta'_V$ with temperature have been measured for krypton and xenon above $T = 400$ K. However, on the basis of the observations with argon, one can admit that for Kr and Xe the change in the quantity $\Delta'_V$ with temperature can also be represented by equation (6). With this assumption, the

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3. Discussion

Having established plausible equations for the fusion curves of the three heavier rare gases it is possible, at least in principle, to assess their respective enthalpies of transition either as functions of temperature or at reasonably assigned triple-points. In fact, by combining equations (2) and (3), one obtains

$$\Delta'_H = \Delta'_V \cdot (a \cdot c) \cdot (T/T_0)^\gamma,$$  

(5)
enthalpies of transition are easily estimated. The results are registered in table 4. (Calculations for Ar have not been considered here due to the uncertainties involved in determining the slopes of its fusion curves). From the values of $\Delta'_m$ in this table (where $s \equiv fcc$ or $s \equiv hcp$), one can derive the molar enthalpy of transition between the two solid phases $\Delta^{m}_{hcp}$ for each of the substances considered since a simple thermodynamic cycle shows that at the (possible) high-pressure triple-point:

$$\Delta^{m}_{hcp} = \Delta^{m}_{fcc} - \Delta^{m}_{hcp}.$$  

Hence, for Xe one obtains $\Delta^{m}_{hcp}(Xe) = 4400 \text{ J} \cdot \text{mol}^{-1}$, and $\Delta^{m}_{hcp}(Kr) = 3740 \text{ J} \cdot \text{mol}^{-1}$ for Kr as illustrated in figure 5. Each of these seems to be reasonable values for the molar enthalpy of transition between two solid phases of the same substance. Since for any first-order transition between phases $\alpha$ and $\beta$ at the temperature $T_{\alpha\beta}$, the corresponding change in the entropy of transition is $\Delta^{\alpha\beta}_{S_m} = \Delta^{m}_{H_m} / T_{\alpha\beta}$ one easily obtains at the high-pressure (possible) triple-point: $\Delta^{\alpha\beta}_{S_m}(Xe) = 1.61 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for Xe, and $1.62 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for the same quantity of Kr. These values are virtually the same, as expected, since at the high pressures involved the transformation of an hexagonal close packed structure into a face centred cubic one should not be much different for molecular monatomic solids as Xe and Kr really are.

References


![FIGURE 4. Molar volume change in fusion $\Delta'_V_m$ as function of temperature. Legend: the solid line (−) is for Ar; the dashed line (−−−) is for Kr; the dash-dotted line (−−) is for Xe. These curves are calculated from equation (6). The symbols are, for Ar: ×, reference [35]; Δ, reference [36]; +, reference [41]; ●, reference [7], calculated. For Kr: ○, reference [35]; □, reference [46]. For Xe: ▲, reference [35]; ■, reference [46].](image1)

![FIGURE 5. Molar enthalpies of fusion $\Delta'_H_m$ of Kr and Xe as functions of temperature $T$. The solid lines are for the fusion of the fcc-solid phases; the dash-dotted lines are for the melting of the hcp-solid phases; the arrows indicate the enthalpy change in the transition between the fcc and hcp solid phases $\Delta^{m}_{hcp}$ of the two substances at the $\{s(fcc) + s(hcp) + \ell\}$ plausible triple-point. The circles indicate the $\{s(fcc) + \ell + g\}$ triple-point.](image2)

**TABLE 4**

Molar enthalpies of fusion $\Delta'_m$ of Xe and Kr (estimated)

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T$/K</th>
<th>Transition</th>
<th>$\Delta'_m$ (J mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe</td>
<td>161.404</td>
<td>s(fcc) $\rightarrow$ $\ell$</td>
<td>2190</td>
</tr>
<tr>
<td></td>
<td>2 672</td>
<td>s(fcc) $\rightarrow$ $\ell$</td>
<td>4602</td>
</tr>
<tr>
<td></td>
<td>2 672</td>
<td>s(hcp) $\rightarrow$ $\ell$</td>
<td>8998</td>
</tr>
<tr>
<td>Kr</td>
<td>115.772</td>
<td>s(fcc) $\rightarrow$ $\ell$</td>
<td>1783</td>
</tr>
<tr>
<td></td>
<td>2 308</td>
<td>s(fcc) $\rightarrow$ $\ell$</td>
<td>7983</td>
</tr>
<tr>
<td></td>
<td>2 308</td>
<td>s(hcp) $\rightarrow$ $\ell$</td>
<td>11721</td>
</tr>
</tbody>
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