Heat of fusion of rhenium from first-principle simulations and the Richards–Tammann relation

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Abstract. We present quantum molecular dynamics calculations of thermophysical properties of expanded solid and liquid rhenium in the vicinity of melting. The dependence of specific enthalpy on temperature and the value of the heat of fusion is in good agreement with dynamic heating experimental data and do not confirm the high value of the enthalpy of fusion obtained using the Richards–Tammann relation.

1. Introduction
There is a well-known empirical systematic relation for the enthalpy of vaporization $\Delta H_v$ and the boiling temperature $T_b$ proposed by Trouton [1], known as Trouton’s rule. It provides a universal value of the entropy of vaporization as $\Delta S_v = \Delta H_v / T_b \approx 107 \text{ J mol}^{-1}\text{K}^{-1}$. A similar relation was suggested for the entropy of fusion of metals by Crompton, Richards and Tammann [2, 3]. The universal entropy of fusion was estimated as $\Delta S_f = \Delta H_m / T_m \approx 9.2 \text{ J mol}^{-1}\text{K}^{-1}$, where $\Delta H_m$ is the enthalpy of fusion and $T_m$ is the melting temperature. Later a detailed study was presented by Sawamura [4], who proposed classifying the entropy of fusion of metals into groups by the type of a crystal structure. According to that study the relation between the melting temperature and heat of fusion of fcc and hcp metals is the same in the region of high melting temperature. The author also suggested a quadratic polynomial relation between the melting temperature of elements and their heat of fusion. Further attempts of generalization of melting properties include taking into account the ratios of the heats and entropies of allotropic transitions [5, 6]. This modification of the Richards–Tammann’s rule introduced the concept of the cumulative entropy of fusion, defined as the sum of the entropy changes at all transformation temperatures up to the melting point, which is supposed to be constant for metals.

As a result the established picture was presented in the review by Kats and Chekhovskoi [12], which includes all known values of the entropy of fusion and some predictions for unknown cases including rhenium. The extrapolation for rhenium was made based on the entropy of fusion of fcc metals iridium, rhodium and platinum. It leads to the biggest enthalpy of fusion estimation among all simple metals of about 60 kJ/mol. It is the estimation that is presented in most of the reference books including IVTANTHERMO [7], SGTE data for pure elements [13] and CRC Handbook [14]. The current picture of reference values of the entropy of fusion of some metals is illustrated in figure 1.
Figure 1. Enthalpies of fusion for some hcp, fcc and bcc metals presented in IVTANTHERMO Handbook [7] versus their melting temperature. Experimental values of the heat of fusion for rhenium obtained in dynamic pulse heating experiments [8–11] are shown as colored hexagons.

Between the 80s and 90s, several papers on dynamic heating of rhenium wires appeared almost simultaneously [8–11]. The values of the heat of fusion presented in those works seriously contradict the existing estimation obtained using the Richards–Tammann relation. As can be seen from figure 1 the experimental values of the enthalpy of fusion of rhenium cannot be described by extrapolation of empirical data for refractory fcc metals. It is required to say that a detailed analysis of the time-resolved measurements do not reveal the existence of any type of polymorphic transition in the vicinity of the melting region. However, these data are still not considered as reliable enough to be treated as reference data for rhenium.

Lately, the first-principle method of quantum molecular dynamics (QMD) has been actively used for obtaining thermophysical information on properties of substances both at high compression [15–17] and rarefaction rate [18, 19] in case of lack of experimental data or contradictions between available experiments.

In this work we carry out QMD simulations of near-zero isobar for rhenium in the vicinity of melting and present our estimation of the heat of fusion.

2. Methods and parameters of calculations
We carry out first-principles simulations using the Vienna ab initio simulation package (VASP) [20,21] based on density functional theory (DFT). The electron exchange and correlation effects are treated within the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof form [22, 23]. 7 valence electrons are taken into account for rhenium and the ionic cores are represented by the projector augmented wave potentials [24, 25]. The applicability of the chosen pseudopotential for a given range of thermodynamic parameters have been checked through the comparison of results of calculations with more accurate pseudopotentials as described in [16, 26, 27]. The Brillouin zone was represented by the Baldereschi mean-value point [28]. The cutoff energy is equal to 400 eV. We use 54 atoms in a supercell for all simulations in the canonical ensemble (NVT) with the Nosé–Hoover [29] thermostat. The time step is 2 fs and the simulations run for no less than 15000 time steps. All simulations for the solid state
are carried out for hcp lattice. Thermodynamic quantities are taken as time averages of the molecular dynamics runs after equilibration.

3. Results
For comparison with pulse-heating experimental data, we have calculated more than dozen points along the near-zero isobar of rhenium in the solid and liquid state in the range of 1500–6000 K. The volume is adjusted as the temperature varied to provide an average pressure between 0 and 10 kbar. Figure 2 demonstrates the dependence of the QMD-calculated enthalpy on temperature as well as available experimental data and approximation given in the IVTANTHERMO handbook. Due to isobaric conditions the enthalpy variation in a dynamic heating experiment is equal to the amount of heat \( Q \) supplied to the system. Thus, it can be expressed by the integral of electrical power over time. This quantities can be measured with good accuracy in pulse-heating experiments, so enthalpy measurements of different authors are usually quite well harmonized. On the other hand, temperature measurements remain one of the main difficulties of rapid experiments. The fast heating and high temperatures require non-contact measurements such as optical pyrometry. The unknown emissivity of liquid metals and the very large variation of the optical intensities due to the wide temperature range aggravate the calibration procedure of the high-speed pyrometry devices that may become a potential source of errors [30].

As can be seen from the figure, our points agree very well with all sets of data in the solid phase. There is a discrepancy in enthalpy versus temperature measurements for liquid rhenium between Hixson [10] and other authors. Our calculations do not confirm such behavior of specific enthalpy. The best agreement of the QMD results is observed for data by Pottlacher et al. The linear approximation of the calculated enthalpy–temperature dependences up to the melting temperature \( T_m = 3458 \) K for the solid and down to \( T_m \) for the liquid phase provides our estimation of enthalpy of fusion as about 25 kJ/mol. This value agrees with estimates presented

![Figure 2. Specific enthalpy versus temperature for rhenium. Red stars are QMD data. Experimental data by Pottlacher et al [8], Hixson and Winkler [10], Thevenin et al [11] are shown as symbols. Dependence presented in IVTANTHERMO Handbook is dashed line, ITS-90 dependence is shown as dotted line [31].](image-url)
Figure 3. Density versus temperature for rhenium. Star symbols are QMD data. Experimental data of Pottlacher et al [8], Hixson and Winkler [10], Thevenin et al [11] are shown as solid symbols. Liquid density by electrostatic levitation technique [32] is green solid line. Density of molten rhenium by pendant drop method [33] is open green triangle.

by Pottlacher et al [8] 27.93 kJ/mol, Hixson and Winkler [10] 28.49 kJ/mol and Thevenin et al [11] 29.42 kJ/mol. It is quite higher than predicted by Dolomanov et al [9] 33.5 and Lin and Frohberg [34] 34.1 kJ/mol.

Figure 3 presents density as a function of temperature. As can be seen, significant discrepancy between measurements of different authors is observed, that is why ab initio data on density–temperature dependence are of a great importance, because they can be treated as independent reference data. Despite good agreement with QMD data in the enthalpy–temperature plane, the density measurements by Pottlacher et al are significantly controversial, especially in the liquid phase. Our calculations of density of liquid rhenium are close to the data of Thevenin et al [11] and Vinet et al [33]. We should mention here that additional calculations may be required to refine QMD data in the solid phase as the sampling of the Brillouin zone with only one k-point is quite rough for an ordered system.

4. Conclusion
In this paper we have demonstrated that resistive-pulse-heating experimental data can be successfully described theoretically using first-principle simulations. We use this fact to independently confirm a low value of the enthalpy of fusion of rhenium observed in dynamic experiments. In our opinion, the empirical Richards–Tammann relation strongly overestimates the heat of fusion for rhenium.

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References
[1] Trouton F 1884 Philos. Mag. (1798-1977) 18 54–57
[2] Kubaschewski O, Evans A L and Alcock C B 1967 Metallurgical Thermochemistry (Oxford: Pergamon Press)
[3] Tammann G 1913 Z. Phys. Chem. (Muenchen, Ger.) 85 273–296
[4] Sawamura H 1972 Trans. Jpn. Inst. Met. 13 225–230
[5] Cho S A 1974 J. Solid State Chem. 11 234–238
[6] Tiwari G 1978 Met. Sci. 12 317–320
[7] Gurvich L V, Veits I V and Medvedev V A 1982 Thermodynamic Properties of Individual Substances. Volume 4 [in Russian] (Nauka, Moscow)
[8] Pottlacher G, Neger T and Jäger H 1986 Int. J. Thermophys. 7 149–159
[9] Dolomanov L A, Kovalyev K S, Lebedev S V and Savvatimskii A I 1988 High Temp. 26 359–366
[10] Hixson R and Winkler M 1992 Int. J. Thermophys. 13 477–487
[11] Thevenin T, Arles L, Boivineau M and Vermeulen J M 1993 Int. J. Thermophys. 14 441–448
[12] Kats S and Chekhovskoi V Y 1979 High Temp. – High Pressures 11 629–634
[13] Dinsdale A T 1991 CALPHAD: Comput. Coupling Phase Diagrams Thermochem. 15 317–425
[14] Lide D R (ed) 2005 CRC Handbook of Chemistry and Physics, Internet Version 2005 (CRC Press, Boca Raton, FL)
[15] Minakov D V, Levashov P R, Khishchenko K V and Fortov V E 2014 J. Appl. Phys. (Melville, NY, U. S.) 115 223512
[16] Minakov D V and Levashov P R 2016 Comput. Mater. Sci. 114 128–134
[17] Paramonov M A, Minakov D V and Levashov P R 2018 J. Phys.: Conf. Ser. 946 012089
[18] Minakov D V, Paramonov M A and Levashov P R 2018 Phys. Rev. B 97 024205
[19] Miljacic L, Demers S, Hong Q J and van de Walle A 2015 CALPHAD: Comput. Coupling Phase Diagrams Thermochem. 51 133–143
[20] Kresse G and Hafner J 1993 Phys. Rev. B 47 558
[21] Kresse G and Hafner J 1994 Phys. Rev. B 49 14251
[22] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[23] Perdew J P, Burke K and Ernzerhof M 1997 Phys. Rev. Lett. 78 1396
[24] Perdew J, Chevary J, Vosko S, Jackson K, Pederson M, Singh D and Fiolhais C 1992 Phys. Rev. B 46 6671
[25] Kresse G and Joubert D 1999 Phys. Rev. B 59 1758
[26] Levashov P R, Sin’ko G V, Smirnov N A, Minakov D V, Shemyakin O P and Khishchenko K V 2010 J. Phys.: Condens. Matter 22 505501
[27] Sin’ko G V, Smirnov N A, Ovechkin A A, Levashov P R and Khishchenko K V 2013 High Energy Density Phys. 9 300–314
[28] Baldereschi A 1973 Phys. Rev. B 7 5212–5215
[29] Nosé S 1984 J. Chem. Phys. 81 511–519
[30] Boivineau M and Pottlacher G 2006 International Journal of Materials and Product Technology 26 217–246
[31] Arblaster J W 1996 CALPHAD: Comput. Coupling Phase Diagrams Thermochem. 20 343–352
[32] Ishikawa T, Paradis P F, Irimi T and Yoda S 2005 Meas. Sci. Technol. 16 443
[33] Vinet B, Garandet J and Cortella L 1993 J. Appl. Phys. (Melville, NY, U. S.) 73 3830–3834
[34] Lin R and Frohberg M 1992 High Temp. – High Pressures 24 537–542