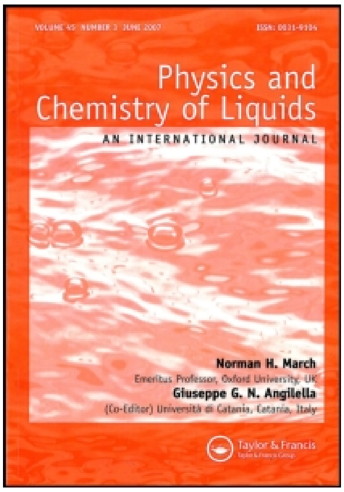

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CRITICAL DATA OF METALS–ESTIMATIONS FOR TUNGSTEN

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Earlier estimations of the critical temperature of tungsten supply two groups of values different from one another by a factor of about 2. By calculating the critical values from a van der Waals-like equation of state modified for metals using Coulomb interaction in the attractive part, the lower temperature (about 12,000 K) has been supported. Besides the other critical parameters, the number of free electrona per atom has been obtained ($z_c = 3.14$). A scaling of the critical temperature with the plasmon energy also fits numerically, although there is a different dependence upon the electron density.

KEY WORDS: Critical temperature, plasmon energy.

INTRODUCTION

Critical data of metals are of basic interest and of importance for high-temperature technical applications. The material in the environment of the critical point is in the thermodynamic state of a strongly coupled plasma, and it is therefore a suitable subject for styding this state. There exist different methods for estimating critical data; an experimental verification, however, has until now been given only for the heavier alkalis caesium, rubidium, and potassium and for mercury. This was done in static experiments. Higher melting or refractory metals typically have critical values in the order of 10,000 K and 10,000 bar, therefore static experiments are no longer possible.

Few groups have tried to tackle the problem of critical data for higher melting metals by pulse experiments[1,2,3,4]. These experiments as a rule were not accompanied by relevant theoretical studies. In preparing experiments on critical data especially of refractory metals using wire explosions, considerations for the estimation of such data should be presented here in the light of more recent theoretical attempts. As an example tungsten has been chosen as the element with the highest boiling point[5] and the highest vaporization enthalpy[5], which should presumably lead also to the highest critical temperature.

There are some simple rules for estimating the critical temperature of a metal starting from thermophysical data at atmospheric pressure. The Guldberg rule[6] relates the critical temperature to the normal boiling temperature[10].

$$T_c^{\mathrm{Gu}} = (2.07 \pm 0.04)\, T_b. \tag{1}$$

The factor has been obtained using the critical temperatures for potassium[7], rubidium[8] and caesium[9] which are given with other alkali data in Table 1.

Assuming validity for all metals and especially for tungsten, its critical temperature will then be $(T_b = 5931\,K)^{10}$:

$$T_c^{\mathrm{Gu}}(W) = (12{,}227 \pm 237)\,K.$$

The Kopp–Lang rule[6] relates the critical temperature to the vaporization enthalpy[5,10,11] at atmospheric pressure:

$$T_c^{\mathrm{KL}} = (28.0 \pm 0.5)\Delta H_v\,\mathrm{kJ}^{-1}\,\mathrm{mol\ K}. \tag{2}$$

As for Eq. (1), the factor was obtained using the alkali data (Tab. 1[10]). For tungsten, the critical temperature after Kopp–Lang $(\Delta H_v = 806.78\ \mathrm{kJ\ mol}^{-1})^{10}$ is then

$$T_c^{\mathrm{KL}}(W) = (22{,}590 \pm 403)\,K$$

where the error using different values for the vaporization enthalpy given in literature is larger than that given by Eq. (2). There is an apparent difference between both of these estimations which has a certain parallel in the deviation of the vaporization entropy of tungsten ($\Delta S_v = 136\,\mathrm{J\,mol}^{-1}\,\mathrm{K}^{-1}$) from the corresponding value of Trouton's rule[6] ($74.8\ \mathrm{J\ mol}^{-1}\ \mathrm{K}^{-1}$), both at atmospheric pressure.

More recently, Likalter[12] proposed an equation of state for metals on the basis of the percolation theory. For the critical values one obtains

$$\begin{aligned} kT_c &= (4.29 \pm 0.04) \times 10^{-2} z_c I, \\ p_c &= (0.409 \pm 0.008) z_c^2 I^4\ \mathrm{bar}/(\mathrm{eV})^4, \\ n_{i,c} &= (10 \pm 1) p_c/(z_c + 1) kT_c. \end{aligned} \tag{3}$$

I is the ionization energy of the undisturbed atom. The factors are again from a fit to the alkali values (Tab. 1). The quantity z_c is the number of free electrons per atom at the critical point, a value which is usually not known. Eliminating z_c from Eq. (3), a relation between p and T is obtained which should be valid for the real couple p_c and T_c.

$$p_c = (1.65 \pm 0.05) \times 10^{-6}\, T_c^2 I^2\ \mathrm{bar}/K^2(\mathrm{eV})^2. \tag{4}$$

Table 1 Data of alkali metals for calibration purposes.

	T_b/K	$\Delta H_v/kJmol^{-1}$	T_c/K	p_c/bar	$\rho/g\ cm^{-3}$	n_c/cm^{-3}
K	1039.54	79.556	2178	148	0.180	2.76 + 21*
Rb	970.385	72.220	2017	124.5	0.292	2.04 + 21
Cs	947.967	67.659	1924	92.5	0.379	1.71 + 21

*read: 2.76×10^{21}

To get the actual values p_c, T_c, Eq. (4) has simultaneously to be solved with the vapour pressure equation[13] which in the case of tungsten is given by

$$\log(p_v/\mathrm{bar}) = 7.21754 - 4.44353 \times 10^4/(T/K) + 1.36632 \times 10^{-1} \log(T/K). \qquad (5)$$

Eq. (5) is a fit to the numerical data of Hultgren *et al.*,[14]. From Eqs. (4) and (5) follows ($I^W = 7.98\,\mathrm{eV}$)

$$T_c(W) = (12{,}466 \pm 116)\,K; \quad p_c(W) = (16{,}317 \pm 319)\,\mathrm{bar}.$$

(The errors given here are obtained not taking into account the errors in the vapour pressure equation which could be considerable.) Inserting this in Eq. (3) yields

$$z_c(W) = 3.14; \quad n_{i,c}(W) = (2.29 \pm 0.23) \times 10^{22}\,\mathrm{cm}^{-3}; \quad \rho_c(W) = 6.99\,\mathrm{g\ cm}^{-3}.$$

Comparing the critical densities given by Fortov[18] with the solid state density at standard conditions, an expansion by a factor of 3 to 5 up to the critical point can be obtained (cf. also Young[24]). The factor got here is 2.76 (19.3 compared with 6.99 g cm^{-3}). The number of free electrons in *solid* tungsten is given by Pauling[15] as $z_S = 6$. It seems reasonable that during an expansion by a factor of about 3 (from the solid state up to the critical point) the number of free electrons per atom will be reduced. The critical density of free electrons will then be

$$n_{e,c}(W) = z_c n_{i,c} = 7.19 \times 10^{22}\mathrm{cm}^{-3}.$$

Chapman and March[23] emphasized the importance of Coulomb forces for the behaviour of the alkali metals ($z_c = 1$). They found for the exponent k of an empirical relation

$$T_c \sim n_{i,c}^k \qquad (6)$$

the value 0.28 which compares with 1/3 which can be obtained by using Coulomb forces in the attractive part of the equation of state. Eq. (6) with $k = 1/3$ also immediately follows from Eq. (3) which is no surprise because of the Coulomb-like forces Likalter[12] used in deriving them. Again calibrated with the alkali data (Tab. 1), the corresponding equation (now also for $z_c > 1$) reads:

$$T_c = (1.28 \pm 0.03) \times 10^{-4}(z_c + 1)^{1/3}\, z_c^{2/3}\, n_{i,c}^{1/3}\ K\,\mathrm{cm}. \qquad (7)$$

With the values for z_c and $n_{i,c}$ derived earlier the critical temperature of tungsten comes to just that value which follows from Eqs. (3), (4) and (5) ($T_c \approx 12{,}470\,\mathrm{K}$).

Recently Goldstein[16] proposed a scaling between the critical temperature of metals and the plasmon energy at the critical point. This leads to

$$T_c = (4.42 \pm 0.25) \times 10^{-8} \sqrt{n_{e,c}\,\mathrm{cm}^3}\ K. \qquad (8)$$

Again the factor is from the alkalis (Table 1, $n_{e,c} = n_c$, $z_c = 1$). Applying Eq. (8) to tungsten using $n_{e,c}$ determined otherwise leads to

$$T_c(W) = (11{,}852 \pm 670)\,K.$$

Earlier estimations of critical data for tungsten can easily be divided into two groups. The first group shows critical temperatures above 20,000 K; the values are given in Table 2. These estimations are based on the vaporization enthalpy at the normal boiling point. The second group is characterized by significantly lower temperatures around 12,000 K based on the boiling temperature at atmospheric pressure or on dynamic experiments using exploding wires (Table 3).

In Table 4, the results of the present work has been given. Remarkably, three completely different approaches lead to practically the same value for the critical temperature around 12,000 K confirming so the low-T_c group estimations from Table 3.

The first value is derived from the boiling temperature at atmospheric pressure (Guldberg rule). From the beginning, it is not quite clear why the boiling temperature seems to be better suitable to describe the critical temperature of tungsten than the corresponding vaporization enthalpy because of the good agreement of both methods in the case of the alkalis. Possibly it is connected with the increase of vaporization entropy with increasing standard boiling temperature, i.e. with a deviation from Trouton's rule that metals should all have the same vaporization entropy. In this case, the additional energy must be raised for bridging larger structural differences at vaporization (e.g., a high structural complexity of tungsten

Table 2 Critical data estimations for tungsten; high T_c group.

T_c *in K*	p_c *in bar*	ρ_c *in g cm*$^{-3}$	*Reference*
23,000	> 10,000	–	Grosse[17]
21,010	15,830	5.87	Fortov[18]
22,590	–	–	Eq. (2)

Table 3 Critical data estimations for tungsten; low T_c group.

T_c *in K*	p_c *in bar*	ρ_c *in g cm*$^{-3}$	*Reference*
11,500	425	0.297	Gates[19]
12,000	–	–	Fokeev[20]
11,880	6,126	–	Martynyuk[21]
13,400	3,370	4.275	Seydel *et al.*[22]

Table 4 Critical data estimations for tungsten; this work.

T_c *in K*	p_c *in bar*	ρ_c *in g cm*$^{-3}$	*Reference*
12,277	–	–	Eq. (1)
12,466	16,317	6.99	Eqs. (3), (4), (5)
11,852	–	–	Eq. (8)

which follows from a high percentage of d-character bond-hybrids[25] and which is – to a certain part – retained in the liquid and/or a transition to monomers in the case of tungsten compared with dimers in the case of the alkalis), and it therefore cannot be used for thermal effects. Or in other words, the increase of the vaporization entropy with increasing standard boiling temperature is due to the increasing structural part of the vaporization enthalpy, and this is the reason for failing in calculating the critical temperatures of higher melting materials from the vaporization enthalpy.

A similar behaviour is known for the *melting* of tungsten where the higher value of the entropy of fusion compared with Richard's rule is considered to be due to large differences in the vibrational and bounding characteristics between the solid state and the melt[25].

The second group of values from Table 4 results from a van der Waals-like equation of state modified for metals and combined with a vapour pressure equation. As in the case of the Guldberg and Kopp–Lang rules, the fit of the critical properties of the three best known metals by the Likalter theory appears quite remarkable. Concerning the vapour pressure equation and especially its extrapolation to higher pressure, here the largest error is expected, and an experimental support is an urgent need[26].

The third value for the critical temperature in Table 4 stems from the plasmon energy at the critical point (Eq. (8)) using the electron density derived from Eqs. (3), (4) and (5). Of course, there is an inconsistency in the temperature-density relations of Likalter and March/Chapman ($T_c \sim (z_c + 1)^{1/3} z_c^{1/3} n_{e,c}^{1/3}$ on the one side and of Goldstein ($T_c \sim n_{e,c}^{1/3}$) on the other. As has been shown, however, for the alkalis and tungsten which are far apart with respect to their thermophysical properties, both relations supply similar results. The reason is in the use of the valence in the first relation which nearly compensates its weaker dependence upon $n_{e,c}$ over the two relevant orders of magnitude in the electron density. A discrimination in favour of the one or the other relation should therefore be possible only by theoretical arguments.

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