Estimation of the critical temperatures of alkaline metals on the basis of specified data on surface tension polytherms

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Abstract. The critical temperatures of alkali metals are calculated on the basis of refined data on temperature dependences of surface tension of alkali metals approximated with linear equations. It is shown that the calculated values of the critical temperatures of alkali metals are in satisfactory agreement with the experimental results and theoretical calculations available in the literature.

The study of the temperature dependence of surface tension (ST) allowed D I Mendeleev to predict in 1860 the existence of the critical point \( (T_c) \), which he termed the absolute boiling point, and to establish that the extent of the liquid phase is finite \[1, 2\]. The fact that surface tension becomes zero at the critical point can be used to estimate the \( T_c \). We assume linear dependence of surface tension \( \sigma(T) \) on temperature in the entire range of liquid phase of alkali metals. We note that for alkali metals the data on surface tension \( \sigma(T) \) are available in the widest temperature intervals, including those in the relative proximity to the critical temperatures \[3–8\]. It should also be noted that alkali metals are good model objects and meet the criteria of thermodynamic equivalence.

In \[2\], experimental data on temperature dependence of surface tension \( \sigma(T) \) obtained in high vacuum \[5\] were used to estimate the critical temperatures \( T_c \) of alkali metals, as well \( T_c \) calculated using the following equation from \[9\]:

\[
\sigma = \frac{kT}{2} \ln \frac{\rho'}{\rho''} \frac{1}{\omega},
\]

in which \( \sigma \) is the surface tension, \( T \) is the absolute temperature, \( k \) is the Boltzmann constant, \( \rho' \) and \( \rho'' \) are the density of the liquid and vapor, respectively, and \( \omega \) is the effective molar area of the surface layer.

In this work we present, in table 1, the results of \( T_c \) calculations based on experimental \( \sigma(T) \) data obtained in \[4, 5, 10\], approximated using linear functions of the critical temperature

\[
\sigma(T) = \sigma_m - \frac{\partial \sigma}{\partial T} (T_c - T_m),
\]

where \( T_m \) is the melting temperature, \( \sigma_m \) is the ST at \( T_m \).
Table 1. The results of theoretical calculations and experimental measurements of $T_c$ (K).

| Me  | Li     | Na     | K     | Rb     | Cs     | Fr     |
|-----|--------|--------|-------|--------|--------|--------|
| [11] | 3293   | —      | —     | —      | —      | —      |
| [12] | —      | 2800   | 2440  | 2190   | 2150   | —      |
| [13] | —      | 2880   | 2440  | —      | —      | —      |
| [14] | 3223 ± 600 | 2573 ± 350 | 2223 ± 600 | 2093 ± 25 | 2057 ± 40 | —      |
| [15] | 2938   | —      | —     | —      | —      | —      |
| [16] | 3286   | 2573 ± 60 | 2173 ± 50 | —      | —      | —      |
| [5]  | —      | 2136   | 1790  | —      | —      | —      |
| [17] | —      | —      | —     | —      | —      | 1550   |
| [18] | 3831   | 2635   | 2185  | 2061   | 1942   | —      |
| [19] | 3223   | 2573   | 2223  | 2093   | 2057 ± 40 | 1810   |
| [20] | —      | 2504   | 2281 ± 5 | 2106   | 2048 ± 4 | —      |
| [2]  | —      | 2326   | 1924  | —      | —      | —      |
| [21, 22] | 3680 ± 300 | 2503 ± 50 | 2281 | 2106 ± 15 | 2043 ± 15 | 1980 ± 50 |
| [23] | —      | 2504 ± 50 | 2240 ± 40 | 2097 ± 10 | 2043 ± 6 | —      |
| [24] | —      | —      | 2280  | 2090   | 2010   | —      |
| [25] | —      | —      | —     | —      | 1924   | —      |
| [26] | 3503 ± 10 | 2497 ± 18 | 2239 ± 49 | 2100 ± 15 | 2035 ± 23 | —      |
| [26] | 3344 ± 42 | —      | —     | —      | —      | —      |
| [27] | 3741   | 2429   | 2195  | 1995   | 2018   | —      |
| [28] | 3474   | 2590   | 2195  | —      | —      | —      |
| [7]  | 3407   | —      | 2050  | —      | —      | —      |
| [8]  | 3232   | —      | —     | —      | —      | —      |
| [29] | —      | —      | —     | —      | 1938 ± 10 | —      |
| [30] | —      | 2485   | 2280  | 2017   | 1924   | —      |
| [4]  | 3285   | 2421   | 2106  | 1796   | 1736   | —      |
| [31] | 3214   | 2908   | 2152  | 1912   | 1770   | —      |
| [32] | 3350   | 2263   | 2111  | 1946   | 1884   | —      |
| [6]  | 3225   | —      | —     | —      | —      | —      |
| [33, 34] | 3503 ± 10 | 2497 ± 18 | 2239 | —      | 2035 ± 23 | —      |
| [35] | 3210   | 2480   | 2230  | 2120   | 2020   | —      |
| [36] | —      | —      | —     | —      | 1400   | —      |
| [37] | —      | —      | 1987  | 1822   | —      | —      |
| [38] | 3940   | 2489   | —     | —      | —      | —      |
| [39] | —      | —      | —     | —      | 1690   | —      |
| [40] | 2797   | 2180   | 2233  | 1836   | 1786   | —      |
| This work | 3190   | 2420   | 2106  | 1930   | 1830   | 1690   |

The relation (2) is used often along with various methods for estimating $T_c$ [21, 39]. However, as justly noted in the works of L Fokin et al [21, 22], it depends on reliable data on $\sigma(T)$. We note that a number of input parameters that were used in these methods became obsolete and have since been revised [31, 41].

The studies [21, 22], in which estimates of $T_c$ for alkali metals obtained using relation (2) were presented, were published decades ago. Since then the experimental methods have improved and precision techniques were developed for determining the ST and density of alkali metals. The
application of these techniques with samples of improved purity in ultrahigh vacuum conditions provided new data which allowed to substantially refine the previous data [6, 25, 29, 42–45].

Table 1 shows the experimental data [4,6–8,16,21,22,31,40,46,47] for determining the critical temperature and, for comparison, the main results of $T_c$ calculations by different authors.

The values of $T_c$ for lithium obtained in this study are 10% lower than the experimental and theoretical results available in the literature. This difference can be explained by several factors. The approximate nature of the majority of theoretical studies of $T_c$ of lithium. The errors of the experimental measurements of $T_c$ are still large, and amount to about 10% [21,22]. With the exception of francium, the temperature dependence of the surface tension of lithium is still the least studied among alkali metals. This, in our opinion, is due to the methodological peculiarities (its unusually large capillary constant) and the resulting significant difficulties in the experimental study of physicochemical properties of lithium. Unlike the other alkali metals, high-purity samples of lithium are still in short supply. Lithium samples presently used in the experiments contain no more than 99.9% of the main element. Furthermore, the impurities present in these samples (sodium, potassium, and oxygen, etc. [48,49]) are surface-active relative to lithium, which can affect and distort significantly the results of measurements of its physical and chemical properties.

The comparison of the calculated and experimental values of $T_c$ presented in table 1 indicates that the $T_c$ estimates obtained using our $\sigma(T)$ data for lithium, sodium, potassium and cesium [4, 19, 23, 29, 41, 46] are in satisfactory agreement with data from direct $T_c$ measurements by P. Achener et al. [16], within the error margins of the latter.

The somewhat lower values of $T_c$ for sodium and cesium calculated by the authors of [2] using experimental data for $\sigma(T)$ from [5] suggest, in our opinion, that the temperature dependences of ST of sodium and cesium obtained in [10] are more reliable than the results of $\sigma(T)$ measurements obtained in [5].

Thus the critical temperatures for lithium, sodium, potassium, rubidium and cesium were calculated based on refined data on the temperature dependences of surface tension of alkali metals. It is shown that the calculated values for the critical temperatures of these metals are in satisfactory agreement with the results of experimental studies.

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