

Uranium critical point problem

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Abstract

Significant uncertainty of uranium critical point parameters in present knowledge is considered. Paper is to reveal thermodynamic aspects of the problem through comparison of some available theoretical predictions for the uranium critical point parameters as well as to discuss in brief plausible versions to meet existing contradiction. New calculations of gas–liquid coexistence in uranium by modern thermodynamic code are included in the analysis.

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1. Introduction

Parameters of critical point (CP) of metallic uranium and uranium-bearing compounds ($\text{UO}_{2\pm x}$, UC, UN, UF_6 , etc.) are in urgent need, firstly, to develop perspective powerful devices (e.g. [1]), and, secondly, as an important ingredient for the analysis of nuclear safety in hypothetical severe reactor accidents at nuclear plants exploited recently (e.g. [2]). For most of metals including uranium both their critical temperature and pressure appear to be too high for precise experimental study (except heavy alkali and mercury). Thus, nowadays the CP parameters of uranium and uranium-bearing compounds are known mostly due to theoretical predictions. Various approaches have been used for this purpose (see reviews [3,4], etc.). As a rule, all the approaches give rather close results for most of substances. That is why it looks tempting to consider the deviation in results of various estimations as a measure of uncertainty in knowledge of critical point parameters. Hence, each case of violation of this empirical tendency is valuable in view of reliable understanding of the critical point problem.

This is just the case for uranium (and uranium dioxide) which represents remarkable exception from this empirical rule [5], i.e. outstanding *contradiction* between results of various approaches. Moreover, a similar contradiction proved to be valid [6] for the whole group of ‘bad’ metals (Co, W, Mo, etc.) with the precedent of uranium being the most prominent one. Despite of great applicative importance of uranium EOS, we are still not aware even approximately the parameters of high-temperature part of uranium gas–liquid coexistence including true parameters of its critical point. In search for the problem solving, it is essential (A) to disavow some results of one (or more) basic experiments on thermodynamic properties of liquid uranium or/and (B) to assume at least one (or more) significant anomaly in properties of gas–liquid phase transition in uranium. Present contribution is devoted to revealing of thermodynamic aspects of the problem, as well as to brief discussion of plausible variants for its possible resolutions.

2. EOS of uranium in applications

The high-temperature equation of state (EOS) of uranium, including its critical point, is of great importance

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for wide number of applications, in particular, design of non-traditional schemes for nuclear reactor. Such a perspective scheme has been developed recent decades [7,1]. In contrast to a nuclear reactor with solid fuel exploited presently, the basic feature of so-called *gas-core nuclear reactor* (GCNR) is a high-temperature dense plasma state of uranium fuel at its work cycle ($T_U \sim 10^4$ – 10^5 K, $p \sim 10$ – 10^2 GPa). The principal advantage of GCNR is its ability to heat working fluid up to the considerable temperature level of $T_{WF} \sim 10^3$ – 10^4 K. Such working fluid could be effectively used afterwards in rocket engine or in MHD energy converters, etc. [8].

High-temperature uranium EOS is also required for investigation of a nuclear safety problem to construct the global uranium–oxygen phase diagram [9,10,12,13] (see also [11,2]). It should be noted that EOS of pure uranium is often used as an explicit constituent of combined EOS of hypo-stoichiometric uranium–oxygen mixture, the latter being described as a binary solution of U and UO_2 [10] (Fig. 2 [12], Fig. 5 [13], etc.). It should be emphasized that serious uncertainty mentioned above on the presently known uranium EOS makes significant uncertainty of the whole hypo-stoichiometric part of total phase diagram for UO_{2-x} ($0 < x < 2$). The same is true for similar problem in uranium–carbon, uranium–nitrogen and other uranium-bearing systems.

3. Problem of theoretical estimation for critical point parameters. Uranium precedent

The critical data (temperature and pressure) for uranium are too high for precise experimental study. At the same time ab initio theoretical approaches are ineffective because of the rather complicated electron structure of uranium [14] and also the still existing problem of adequate theoretical description of strong Coulomb interaction in non-ideal uranium plasma [1,15]. The critical point parameters (CPP) for uranium are permanently estimated theoretically. Among theoretical approaches the dominating one is based on the assumption of strong correlation between CPP and low-temperature properties of condensed phase. There exist several versions of this approach which use either vaporization heat, or thermal expansion of liquid, or low-temperature vapor pressure as input quantity [3]. It should be stressed that whatever is used in frames of this approach does not matter – either any ‘primitive’ form of high-temperature extrapolation of thermodynamic properties of ‘cold’ condensed substance, such as Guldberg rule [3], or Kopp-Lang rule [16], or the law of ‘rectilinear diameter’ [17], etc. (see [3,4,18]), or a variant of ‘principle corresponding states’, or even any sophisticated forms of *modeling EOS* with free parameters. The point is which thermodynamic parameters of condense state to be preferably used in application of the principle corresponding

states or in ‘calibration’ of free parameters of modeling EOS.

To found this statement the special version of thermodynamic computer code, ‘SAHA-U’ has been developed in present work as a new implementation of SAHA code-line [19,1,20]. The gas–liquid phase coexistence in uranium has been calculated by SAHA-U in frames of so-called the quasi-chemical representation, i.e. a microscopic description of vapour and liquid uranium as equilibrium partially ionized non-ideal plasma (‘chemical picture’) [21]. This approach proved to be successful for joint self-consistent description of non-congruent evaporation in uranium dioxide [22,23,2]. Two variants of present calculation by SAHA-U code correspond to two competing variants of calibration of its free parameters fitting either caloric or thermal properties of liquid uranium. In the first variant (notation ‘SAHA-U(H)’) liquid density and handbook values of vaporization heat and Gibbs free energy (i.e. vapour pressure) of liquid uranium in melting point ($T = 1410$ K) were fitted. In the second variant (notation ‘SAHA-U(T)’) density and thermal expansion coefficient [29,30] of liquid uranium in melting point were fitted.

Among the approaches extrapolating low-temperature properties of condensed phase, the first and widely used version exploits the main *caloric quantity*, heat of vaporization as the basis for estimations of CPP. In accordance with the high value of uranium vaporization heat (~ 533 kJ/mol [24]), numerous attempts of such estimation predict relatively high values for the uranium critical temperature: $T_c \sim 11$ – 13×10^3 K ([25–27,4,28], etc.). As it has been expected, the high value of critical temperature $T_c \approx 12,800$ K is also obtained in calculations via SAHA-U code with caloric quantity used as the input calibration value (curve 4* at Fig. 1).

The second version of this approach is based on parameters of *thermal EOS*, i.e. it extrapolates to high temperature experimentally measured density vs. temperature of liquid uranium, $\rho_{\text{liquid}}(T)$ [29–32]. Good agreement should be emphasized for all four experiments in surprisingly high value of measured isobaric thermal expansion of liquid uranium (Fig. 1). Correspondingly in contrast to the ‘caloric’ way, the ‘thermal’ way results in the significantly lower values of predicted critical temperature and noticeably indefinite values of critical pressure $T_c \sim 5$ – 7 K; $p_c \sim 0.01$ – 0.5 GPa ([33,34,5]). The low value of critical temperature $T_c \approx 6840$ K is also obtained in calculations by SAHA-U code with *thermal* quantity being used as main input calibration value.

The third, an alternative approach, scarcely uses any empirical properties of condensed uranium in search of its critical point location. This approach is based on so-called ‘plasma hypothesis’ of nature of critical state in metals [35], it postulates strong correlation of critical point parameters with *ionization potential(s)* of metal and it predicts for uranium $T_c \sim 9400$ K [36,37].

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