

NON-CONGRUENT PHASE EQUILIBRIUM IN HIGH-TEMPERATURE CHEMICALLY REACTING MEDIA

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Keywords: non-congruent phase balance, uranium dioxide, theoretical model, mixture parameters, calculation algorithm.

Abstract

On the basis of uniform theoretical concept («chemical model of plasma») the model of non-congruent phase equilibrium (evaporation) in high-temperature products of uranium dioxide heating has been worked out, taking into account multicomponent, partly ionized, strongly interacting mixture of atoms, molecules and nuclear and molecular ions. On the basis of theoretical model the efficient numerical algorithm, realized within the framework of a universal machine code "SAHA-IV", has been created to define the parameters of the mixture in the conditions simultaneous chemical, ionization and phase equilibrium. The approach chosen has for the first time allowed to reproduce correctly the general structure of phase boundary in the products of uranium dioxide heating, which, by a number of criteria, considerably differ from the similar structure of the phase boundary of evaporation of "usual" substances. The results obtained besides, being of scientific interest, have the important application value in view of safety problem of nuclear power engineering.

Introduction

Knowledge of the state equation (SE) of UO_2 heating products is needed for analyzing probable consequences of a major emergency on the existing and perspective types of nuclear reactors in which uranium dioxide is regular fuel. According to the existing scripts of such an emergency, the temperatures of many thousands degrees become really attainable in this process, which corresponds to estimations of steam pressure of hundreds of atmospheres. The basic feature of the process of uranium dioxide evaporation is in its non-congruent character, the latter being manifested in the ability of phases to coexist in spite of their different stehiometry. As a consequence there appears an opportunity of sharp oxygen enrichment of products of uranium dioxide evaporation, which is looked upon as an additional threat in the series of hypothetical consequences of nuclear emergencies.

Non-congruent character of evaporation is a distinctive feature of phase equilibrium in high-temperature chemically active non-ideal plasma [1,*]. Non-congruency substantially complicates the structure and properties of the high-temperature part of phase diagram for a wide class of chemical compounds. The problems coming from this circumstance, are especially urgent for thermal physics of phase equilibrium in many objects of nuclear power, such as uranium dioxide, UO_2 - for working reactors, in particular for breeder-reactors on fast neutrons [1*]. It is also important for development of many prospective nuclear energy installations, and, first of all, for a family of *gas-phase nuclear reactors* (so called "B" schemes [2-5]) in some of which the mixtures of uranium with different metals, hydrogen and other substances [3, 4] are used as operating environment. The specified non-congruency is of fundamental importance for gas-phase reactor schemes of uranium hexafluoride UF_6 [5, 6] as well. According to the mandatory practice accepted nowadays, both operation and modernization of working reactors, as well as designing new ones, besides design-theoretical and experimental research of regular modes, should be accompanied with obligatory design-theoretical (and whenever possible experimental) research of probable consequences of hypothetical emergency situations, including their extreme variants, so-called "beyond-cutoff" nuclear failures [1*].

Results and discussion

1. Thermodynamic model for calculating non-congruent phase equilibrium.

In the present work performed with the support of INTAC [7] thermodynamic model of highly heated liquid and gaseous uranium dioxide (UO_2) was developed. New state equation is intended for describing evaporation in uranium - oxygen mixture of both hypo- and hyper-stoichiometric structure [1]. The constructed model substantially differs from all other models offered earlier for describing thermodynamics of evaporation in high-temperature uranium dioxide (see for example [8, 9]). The present model for the first time gives correct consideration for the mentioned above non-congruency of evaporation in the whole range of temperatures, and as a consequence, it for the first time correctly reproduces the general structure of all phase boundary, including areas of the so-called backward condensation, points of extreme pressure and temperatures of phase boundary and, finally, the "true" critical point of non-congruent evaporation.

The new state equation of 'uranium - oxygen' system describes the known properties of liquid uranium dioxide near its melting temperature and is further used for extrapolating thermodynamic description of UO_{2+x} properties to the high temperature area, including the parameters of "gas - liquid" transition in the area of its critical point. Major characteristic and fundamental distinction of the present model from the previous ones [8, 9] is in designing thermodynamic description of both phases and in performing the appropriate calculations of parameters of high-temperature equilibrium in uranium dioxide within the framework of the *uniform theoretical approach* - quasi-chemical representation ("mixture method" [SeSh75]) - for neutral and chemically reacting systems, as well as so called "Chemical model of plasma"- for partially ionized plasma (see for example [3])). Both coexisting phases, liquid and gas-plasma, are described in uniform presentation, as multicomponent, strongly interacting ("non-ideal") mixture of chemically reacting atoms, molecules, nuclear and molecular ions and electrons.

2. Thermodynamic model of non-congruent evaporation in "uranium - oxygen" system.

In direct calculations of thermodynamically equilibrium system "uranium - oxygen" the following set of components was used:
 $\text{U}, \text{U}^+, \text{U}^{++}, \text{UO}, \text{UO}_2, \text{UO}_3, \{\text{U}_2\text{O}_n\} (n = 0, 1, 2, 3, 4, 5, 6), \text{O}, \text{O}^-, \text{O}_2, \text{UO}^+, \text{UO}_2^+, \text{UO}_2^-, \text{UO}_3^-.$ (1)

On calculating chemical and ionization equilibrium we used thermochemical constants and statistical sums of excitation of all atom-molecular and ion-molecular components of the system "uranium – oxygen" in accordance with the data of IVTAN-TERMO database current version reviewed by the department of thermodynamics at ITEC RAS under supervision of V.C. Jungman, L.N. Gorohov, et al.[10, 1, 1*]. It is known that the indicated individual thermodynamic functions of the components from the base IVTAN-TERMO are intended only for calculating chemical and ionization equilibrium in ideal-gas conditions. The basic moment of the approach suggested in the present work was in the fact that the use of the same ideal - gas individual thermodynamic functions of "uranium – oxygen" system components was extrapolated to calculation of chemical and ionic equilibrium in strongly non-ideal system "uranium – oxygen" corresponding to liquid uranium dioxide. In real calculations of phase equilibrium the above-mentioned ideal-gas characteristics were supplemented by the whole complex of so-called "non-ideality corrections", self-consistently allowing for the effects of all spectrum of intensive interparticle interactions in the system [3]. Numerous and practically unknown beforehand parameters of interparticle interactions of all charged and neutral components of the system were originally estimated theoretically [1, 1*] and then were finally corrected ("were calibrated") with the aim of reproducing a set of known thermodynamic properties of liquid uranium dioxide (density, steam pressure, etc.) at the melting point ($T = 3120\text{K}$).

3. Numerical algorithm and computing code.

For efficient search for parameters of coexisting phases in the conditions of actively proceeding chemical reactions, ionization and intensive interparticle interaction we have worked out a special algorithm, realized as a universal code "SAHA-VI" [1,1*]. As a basis for its construction there has been used the modernization of the technique of thermodynamic calculation of the appropriate series of "SAHA" codes [11, 3], which has been developed by the authors for many years, the latter being designed for calculating multiphase, multicomponent, non-ideal, chemically reacting plasma [GrIoFo00].

4. Co-conditions for chemical, ionization and phase equilibrium.

A fundamental peculiarity of non-congruent phase equilibrium discussed in the present work is impossibility to find the parameters of coexisting phases using the standard variant of the so called "double tangent" rule (or Maxwell's rule of "equal areas"). With the equality of temperatures and total pressures of coexisting phases, the true phase equilibrium in present work was found directly from conditions of equality of *chemical potentials* for all neutral component of both phases (atoms and molecules). For the charged particles (ions and electrons) to phase equilibrium there corresponds equality of *electrochemical potentials* (e.g. [12]). Still chemical potentials of the charged components are *not equal* in coexisting phases. The direct consequence of this is the presence of stationary difference of electrostatic potentials between coexisting phases [IoDFi]. The real expressions for all specified chemical and electrochemical potentials, as well as for other thermodynamic functions of both phases, contained the appropriate "non-ideality corrections", self-consistently taking into account the effects of all kinds of interparticle interactions, including intensive repulsion of all particles at close distances ("intrinsic volume"), "residual" (extrachemical) short-range attraction responsible for presence of phase transition, as well as Coulomb interaction of charged particles.

5. Description of effects of interparticle interaction.

The description of effects short-range repulsion and attraction in the model is based on thermodynamic perturbation theory advanced in [13], and modified in view of the features of multicomponent chemically reacting systems [14, 15, 1]. "Coulomb" non-ideality is described within the framework of special modification of "mean spherical approximation" (Mean Spherical Approximation - MSA) advanced for ionic liquids, modified for the case of multicomponent mixture [16]. The parameters of interaction for various components of the mixture were previously estimated theoretically [1], and then they "were calibrated" [1, 15] on the known properties of liquid uranium dioxide UO_2 in the melting point ($T \approx 3120\text{K}$). The derived uniform SE of liquid and gaseous uranium dioxide is further used for calculating the parameters of gas-liquid equilibrium in the whole range of parameters, including the prospective critical point area ($T \leq 10\text{--}20 \cdot 10^3\text{K}$, $P \leq 1\text{--}2\text{ GPa}$).

6. Model validation.

Owing to the above-stated "calibration" procedure the thermodynamic model of liquid and gas-plasma state of uranium dioxide $\text{UO}_{2.0}$ reproduced a limited set of properties of liquid UO_2 in the melting point ($T = 3120\text{K}$). Further extrapolation of the model into the area of high temperatures and stehiometries of the mixture, different from $\text{O/U} = 2.00$, reflected already the properties of the model, internally inherent in it, and thus, the comparison of results of such extrapolations with the known properties of liquid and gas-plasma uranium dioxide, not used within the framework of calibration procedure, serves for checking up its extrapolation properties ("validation" of model). Such comparison of calculation results of equilibrium steam pressure in the range $T \leq 5500\text{K}$ with the most reliable experimentally measured data [17] confirms adequacy of the derived SE for uranium dioxide. Much more rigid test for the theory is the comparison of calculation results of isobaric thermal capacity $C_P(T)$ of liquid uranium dioxide with the measurements data in the range $T \leq 8000\text{K}$ [18]. It should be emphasized that the UO_2 state equation, derived in the present work, is now the only one which is capable to reproduce correctly the non-monotonous character of the experimentally measured temperature dependence $C_P(T)$ [18] (fig. 1).

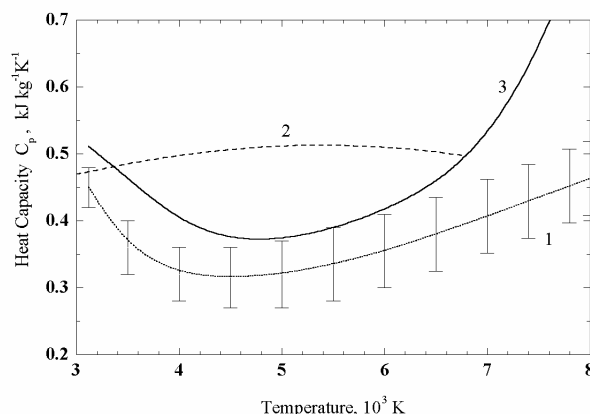


Fig. 1. Isobaric thermal capacity of liquid uranium dioxide ($\text{UO}_{2.0}$). Comparison of calculated results with experimental data; 1 – measurement data of Ronchi *et al.* [18]; 2 – results of model calculation [9] (E.Fischer-1989); 3 – calculated results of the present work (EOS INTAS-99) [1, 15].

7. Peculiarities of non-congruent evaporation of high-temperature system "uranium-oxygen".

The most important result obtained within the framework of the present work is unusual structure of the predicted phase boundary of the process of uranium dioxide evaporation. The calculation results demonstrate the basic distinction of this structure from the known analogues of high-temperature phase boundary in "elementary" substances, for example in metals.

This distinction is a direct consequence of the above-mentioned non-congruent character of evaporation in non-ideal chemically reacting plasma, and in particular, in plasma of uranium dioxide. The major distinctive feature of this evaporation is the sharp dependence of its parameters, such as steam pressure, and degree of their oxygen enrichment on *evaporation rate* [19]. In the language of thermodynamics this is equivalent to splitting a former uniform dependence of pressure of saturated steam on temperature, $P_{st}(T)$, into two differing borders: - *boiling curve* (boiling curve - BC) and *saturation curve* (saturation curve - SC) (fig. 2). The first boundary ("BC") corresponds to equilibrium (chemical, ionization and phase) of liquid uranium dioxide stoichiometric structure, $UO_{2.0}$, with non-stoichiometric (oxygen-enriched) steam phase, UO_{2+x} ($x \geq 0$). Dynamically it corresponds to the mode of slow, thermodynamically completely balanced evaporation $UO_{2.0}$, which is closest to the mode, and can be actually realized during the hypothetical failure on nuclear reactor. The second border ("SC"), on the contrary, corresponds to the balance of steam phase stoichiometric structure, $UO_{2.0}$, with non-stoichiometric (vitiated) liquid UO_{2+x} ($x \leq 0$). Dynamically it corresponds to the mode superfast *forced congruent* mode with only partial equilibrium of evaporation, at which stoichiometry of steam does not have time to change at evaporation ("Forced Congruent Mode" - FCM) [19].

Direct consequence of non-congruent character of evaporation in uranium dioxide is remarkably high level of maximal steam pressure, theoretically predicted on the boiling curve ($P_{max} \sim 1$ GPa) (fig. 2). The other important consequence predicted by the present theory is extremely high degree of maximal oxygen enrichment of the steam phase which is taking place in equilibrium with boiling uranium dioxide of stoichiometric structure, $UO_{2.0}$. $\{\max(O/U)_{BC} \sim 7 \text{ at } T \sim 8000K\}$ (fig. 3).

One more important consequence, predicted by the present theory, is the unusual form of the phase diagram of non-congruent evaporation in enthalpy-temperature coordinates, again, quite distinct from the analogous $H-T$ diagram of evaporation of "common" substances (fig. 4).

The brightest feature here is sharply non-monotonous dependence on temperature for the analogue of evaporation heat, $Q_{vap} \equiv H(T)_{vap} - H(T)_{liquid}$ liquid. All listed above features are extremely important for the applications connected with the problem of nuclear safety.

8. Critical point parameters of non-congruent evaporation of uranium dioxide.

Advantage of theoretical approach used in present work is the possibility to give a uniform and self-coordinated description of SE of strongly interacting system "uranium – oxygen" in the area of the true critical point of non-congruent phase transition.

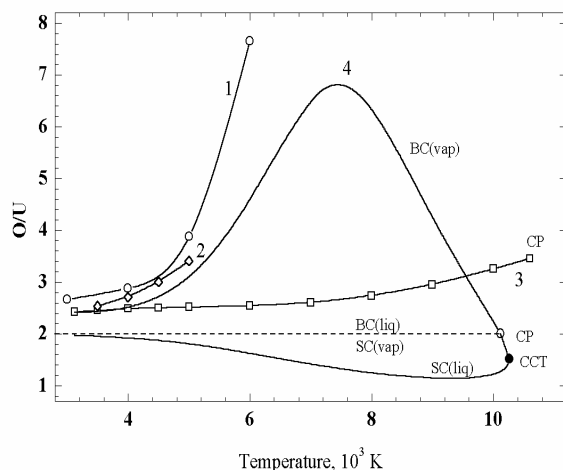


Fig. 3. O/U ratio of coexisted phases in process of noncongruent evaporation of uranium dioxide ($UO_{2.0}$)

1 – stoichiometry of gas phase with model [20]; 2 – the same by results of calculation of equilibrium composition in work [21]; 3 – the same according to calculations by the theory of "significant structures" (SST) [9]; 4 – boundary of biphasic area of noncongruent evaporation, calculated in the present work (EOS INTAS-99) [1, 15]. Marked are stoichiometry of coexisted steam and liquid in mode of boiling (BC) and saturation (SC), as well as true critical point (CP) and point of temperature maximum on saturation curve (CCT).

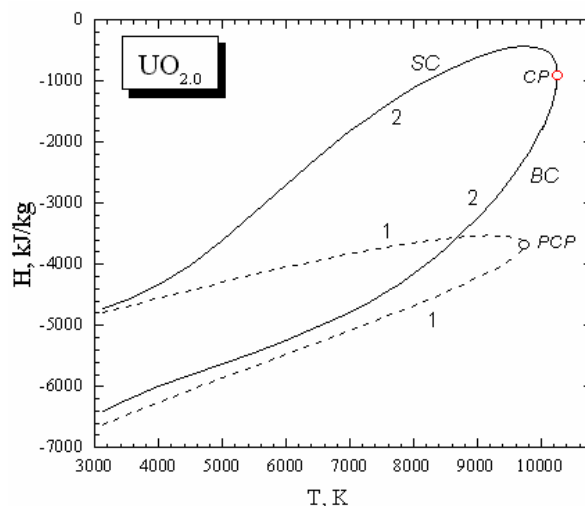


Fig. 4. Phase diagram enthalpy - temperature for noncongruent evaporation of uranium dioxide ($UO_{2.0}$)

1 – boundary of biphasic area of uranium dioxide described in representation of monomolecular system of interacting molecules UO_2 (standard type of phase diagram with pseudo-critical point (PCP)); 2 – true boundary of biphasic area of noncongruent evaporation with boiling curve (BC), saturation curve (SC) and true critical point (CP) by results of the present work (EOS INTAS-99) [1, 15];

The properties of this critical point, as well as the whole phase transition, substantially differ from the properties of the critical point of "common" phase transition "gas – liquid", to which there corresponds the performance of the standard relations: $[(\partial P/\partial V)_T = (\partial^2 P/\partial V^2)_T = 0; (\partial^3 P/\partial V^3)_T < 0]$. In particular, isothermal compressibility of the system in the critical point of non-congruent phase transition does not tend to infinity, but turns out to be close to ideal - gas value, $(\partial \ln P/\partial \ln V)_T \sim 1 \neq 0$. Still the defining feature of the critical point of non-congruent phase transition is the loss of positive definiteness by the matrix $\|\partial \mu_i/\partial n_j\|$ (μ_i and n_i - chem. potential and concentration of i - grade of particles). The present model predicts the following parameters of this critical point: $T_{kp} \approx 10120K$,

$P_{kp} \approx 965$ MPa, $\rho_{kp} \approx 2.61$ g/cm³, $S_{kp} \approx 1.84$ kJ/kg·K, $C_p \approx 1.8$ kJ/kg·K, $\beta_T \equiv \rho^{-1}(\partial\rho/\partial P)_T \approx 1.03 \times 10^{-4}$ [1/bar], $\alpha_P \equiv \rho^{-1}(\partial\rho/\partial P)_T \approx 5.15 \times 10^{-4}$ [1/K], $G_D \equiv e^2/kT R_D \approx 1.2$.

9. Comparison with the results of experimental pressure measurements at ITEC RAS.

In most recent time at ITEC RAS important results have been obtained by A. Basharin and his co-workers on measurement of steam pressure of non-congruent evaporation of uranium dioxide. The details of experimental engineering techniques and special ways used for carrying out the correct measurements and obtaining significant experimental results are discussed in the work of A. Basharin et al. [Bash.02]. Theoretical analysis of the data obtained by Brykin M. (private communication) and authors of the present work have led to the conclusion that in view of substantial non-congruency of uranium dioxide evaporation, steam pressure measured by A. Basharin in experiment, corresponds not to the conditions of complete equilibrium (quasi-stationary) mode of boiling, but, on the contrary, to the mode of fast "forced congruent" evaporation, which in terms of thermodynamic modes of non-congruent evaporation corresponds to the mode of saturation, i.e. to the equilibrium of vitiated liquid with uranium dioxide steam of strictly stoichiometric structure (O/U = 2.00) (see fig. 3). The comparison of A. Basharin's experiment results with the results of calculations on the described above theoretical model (carried out long before obtaining the discussed experimental data) confirms this conclusion and serves an additional reason for the benefit of adequacy of the constructed theoretical state equation of high-temperature system "uranium-oxygen" (uranium dioxide). This comparison is given in fig. 5.

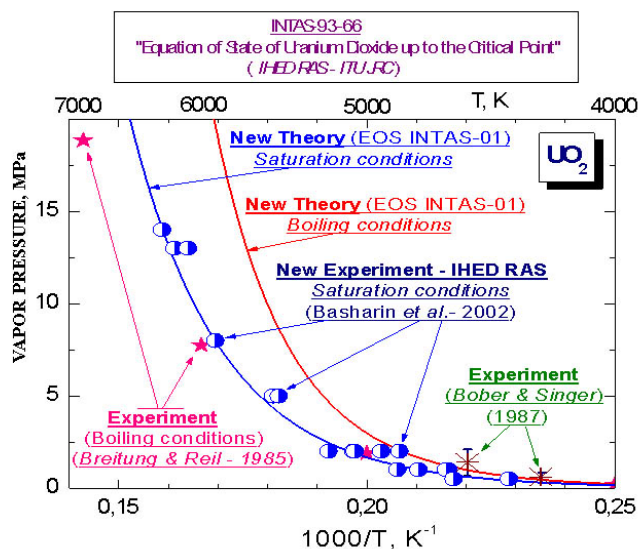


Fig. 5. Phase P - T diagram of uranium dioxide evaporation (UO_2). Comparison of predictions of the theory with measurement results.

Calculation results:

- 1 – boiling curve (BC); 2 – saturation curve (SC);
- 3 – Experiments of A. Basharin and coworkers (ITEC RAS) (theoretically are considered appropriate to a mode of saturation);
- 4 – results of "ampul" ("in-pile") experiment *Breitung and Reil, KfK (theoretically are considered to be corresponding to boiling mode);
- 5 – results of pulse laser heating (Bober and Singer, 1987).

Conclusions

On the basis of uniform theoretical presentation ("chemical model of plasma") the model of non-congruent phase equilibrium (evaporation) in high-temperature products of heating of uranium dioxide as in multicomponent, partially ionized, strongly interacting mixture of atoms, molecules as well as nuclear and molecular ions has been constructed. On the basis of theoretical model the efficient numerical algorithm realized within the framework of universal machine code "SAHA-IV", allowing to find parameters of a mixture in conditions of simultaneous chemical, ionizing and phase balance. The chosen approach has allowed for the first time to obtain the correct general structure of phase border in products of heating of uranium dioxide, which in many ways considerably differ from similar structures of phase border of evaporation of "common" substances. The obtained results besides the overall physical interest have the important practical application in view of safety problems of nuclear power engineering.

Aknowledgements

The authors express deep gratitude to V.C. Jungman, L.H. Gorochov and other workers of the Department of thermodynamics ITEC IVTAN, critically modified within the framework of the Project INTAS-93-66 with the whole set of thermochemical constants and ideal - gas properties (so called "Individual" thermodynamic functions [10]) for the whole set of atoms, molecules and ions of the considered "uranium – oxygen" system.

The work is sponsored by the Grant INTAS-93-66 and Program of RAS "Physics and chemistry of extreme states of substances".

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