

Supplementary Material for:  
**Non-stoichiometry effects and phase equilibria  
in the uranium–carbon–nitrogen ternary system<sup>1</sup>**

Artur A. Salamatin<sup>1,\*</sup>, Fei Peng<sup>1</sup>, Keith Rider<sup>2</sup>, Konstantin G. Kornev<sup>1</sup>

<sup>1</sup>*Dept. of Materials Science and Engineering, Clemson University, SC 29634, USA*

<sup>2</sup>*BWX Technologies, Inc., Lynchburg, VA 24504, USA*

*\*Corresponding author: asalama@clemson.edu*

## **1. Mapping the phase diagram**

### *1.1. Phase diagrams*

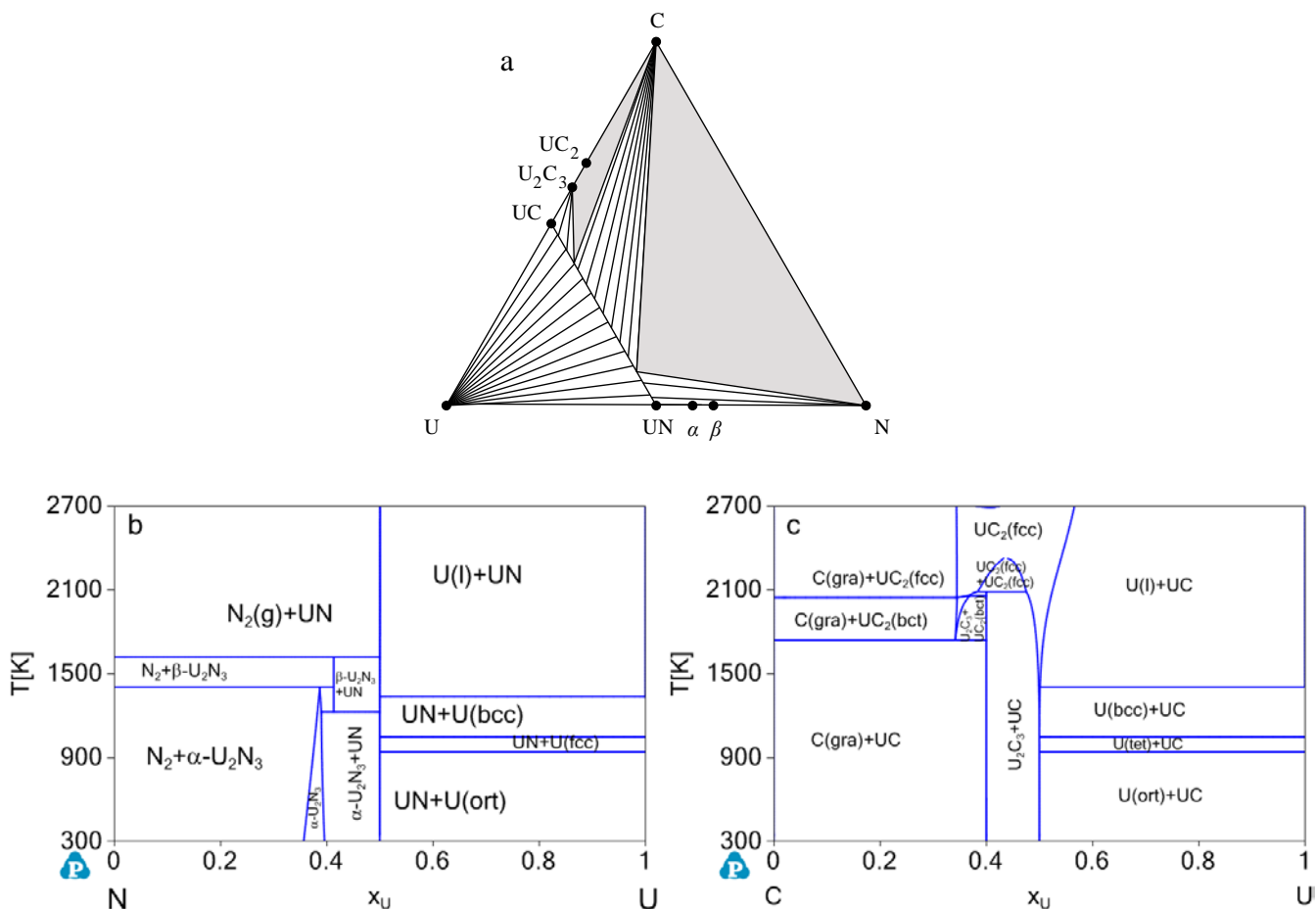
Phase diagrams show phases that co-exist in equilibrium at certain thermodynamic conditions that are fixed or considered as axes of the diagram. Thus, when the diagram is mapped, the enclosed regions show the conditions (given by the axes) when a corresponding set of phases is stable. Mapping the phase diagram means constructing the boundaries of domains and determining the set of (stable) phases that are in equilibrium when the axes-conditions are within the domain.

The typical examples of two-dimensional phase diagrams (with only two axes) are the so-called ternary plots<sup>[1]</sup> for the three component systems at fixed temperature and pressure, see Figure S1a. In these types of plots, the overall molar fractions of components are axes of the barycentric coordinate system. Other common examples are shown in Figure S1b and S1c. They are temperature-composition diagrams of the two-component U–N system at fixed pressure, 1 atm, and U–C system, respectively. The diagrams are obtained under the assumptions discussed in the main text and summarized in Sect. 3.3 of the current Supplementary Information: solubilities of C and N in liquid U

---

<sup>1</sup> This work was authored by employees of Clemson University and BWX Technologies, Inc. under Contract No. 80MSFC17C0006 with the National Aeronautics and Space Administration. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, or allow others to do so for United States Government purposes. All other rights are reserved by the copyright owner.

are neglected. The horizontal axis is the overall system composition, i.e., molar fraction of U, and the vertical one is the temperature.



**Figure S1.** Examples of phase diagrams with different thermodynamic variables as axes. (a) A ternary plot with the overall composition of the system as coordinates. The barycentric coordinate system is traditionally used to represent such diagrams. The grey triangles include overall compositions that correspond to ternary equilibria (phases are at the apexes of the triangle). Segments – tie lines that connect to phases in equilibrium. The line that connects UC and UN points in the diagram represents all compositions of the U(C, N) solid solution; (b) The temperature-composition diagram for the two-component U–N system at  $p = 1$  atm; (c) The temperature-composition diagram for the two-component U–C system. Solubility of C and N in liquid U is neglected for (b and c).

In general, the set of axes of phase diagrams does not necessarily include any characteristic related to the overall composition. This is found, for example, in single component  $P$ – $T$  diagrams showing the stability of certain phase (like liquid, solid modifications, or vapour for water) at corresponding values of axes variables. This type of “stability” diagrams we introduce in the main text in order to illustrate the stability conditions of U(C, N) compound exposed to the nitrogen gas.

## *1.2. Lower convex hull approach to map the ternary plot*

### *1.2.1. General idea*

The so-called lower convex hull approach is purely geometrical. It naturally occurs when one is mapping the ternary plots obtained at fixed intensive thermodynamic conditions,  $T$ ,  $p$  etc. Thus, the overall Gibbs energy of the system per mole of components,  $G(x_1, x_2, x_3)$ , is only a function of the overall composition and is convex when non-convex regions (resulting in phase separation) are substituted by common tangent lines. Hereinafter,  $x_1$ ,  $x_2$ , and  $x_3$  are the molar fractions of components 1, 2, and 3, respectively, and  $x_1 + x_2 + x_3 = 1$ .

In geometry, the convex hull is the smallest surface that wraps the set of points. Thus, the hull is always convex. For the particular application of the mapping of phase diagrams, the hull can be divided into two parts, i.e., lower and upper, where the lower part is the Gibbs energy surface, and the upper part has to be cut from the whole hull.

To apply the algorithm, one has to calculate the reference points of the hull, i.e. stencils. Thus, one has to fix the components of the system and then scale the formula unit for each phase to contain only one “average” component. A set of values of the molar Gibbs energy of phases (per mole of scaled formula units) is calculated. Generally, there is a single value for each stoichiometric phase and a continuous set of values for each solution. For geometrical considerations, the overall molar Gibbs energy of the system is the lower convex hull of this set of values.

There are three components in the present research: uranium, carbon, and nitrogen. Thus, disregarding the ordering in any phase, it can be viewed as a mixture of the three components with the formula unit  $U_{x_1}C_{x_2}N_{x_3}$ . Assuming that molar fractions of each component are constrained as  $x_1 + x_2 + x_3 = 1$ , one can say that there is a total of one “average” component in the formula unit. Thus, the formula unit is fixed as  $U_{2/5}C_{3/5}$  for the uranium sesquicarbide,  $U_{\frac{1}{2.42}}N_{\frac{1.42}{2.42}}$  for the high-temperature uranium sesquinitride, etc. The molar Gibbs energy of the phase is inversely proportional to the size of the formula unit.

Sometimes compounds themselves may act as components. This is true for the so-called pseudo-binary, ternary, and similar systems. Thus, Voskov et al<sup>[2]</sup> studied the quasi-ternary system  $AgNO_3$ – $LiNO_3$ – $NaNO_3$ . The system is electrically neutral, and a single  $NO_3^-$  group is associated with each cation. Hence, only the amount of each cation ( $Ag^+$ ,  $Li^+$ , and  $Na^+$ ) has to be specified to fix the system composition. The liquid ternary solution of the compounds, a quasi-binary solid solution  $(Ag, Na)NO_3$  demonstrating a miscibility gap, and one stoichiometric phase  $LiNO_3$  are distinguished in the system. A formula unit  $(Ag_{x_1}, Li_{x_2}, Na_{x_3})NO_3$  can be introduced that is common for each phase and contains one “average” cation.

The Gibbs energy of the phase at fixed composition can be represented as a point in the three-dimensional space. Barycentric coordinates  $(x_1, x_2, x_3)$  determine the projection of the point on the ternary plot, and the value of the molar energy is the height of the projection. All phases together determine a set of points. Multiple values may correspond to the same overall composition, due to allotropes, for example. Then, the phases with higher values of  $G$  cannot be stable. Therefore, the overall Gibbs energy of the system - the function  $G(x_1, x_2, x_3)$  of the overall composition - is the surface over  $(x_1, x_2, x_3)$  ternary plot, and geometrically it is a lower convex hull of the molar energies of all phases.

When there are only stoichiometric phases in the system, then the lower convex hull is exactly the overall Gibbs energy of the system at stable configurations. A special approach described below allows us account for the solution phases and to obtain a reasonable approximation of the Gibbs energy surface.

In any way, the hull for the three-component system is represented by a set of triangles oriented in space. Their projection onto the ternary plot defines the triangulation of the plot and is a very good approximation of the phase diagram at fixed  $T$  and  $p$ . The tie-lines and regions of ternary equilibrium could be distinguished after certain post-processing<sup>[2,3]</sup>.

To the best of our knowledge, this is the only algorithm that is robust in the case of phase separation and non-convex Gibbs energies of single phases. Thus, its modification is combined with the other popular approach that uses the notion of the zero phase fraction line<sup>[4–6]</sup> and implemented in the majority of commercially available software like ThermoCalc, MTDATA, PANDAT, FactSage, CatCalc<sup>[2]</sup>.

We explain the concept of the approach using the worked example in the next section assuming only stoichiometric phases in the system. In Sect. 1.2.3, how to generalize the algorithm to treat systems with solution and non-stoichiometric phases is explained.

### *1.2.2. Worked example for the system with only stoichiometric compounds*

Consider a simplified model for the ternary U–C–N system with only stoichiometric phases, each with the fixed composition  $\text{U}_{x_1}\text{C}_{x_2}\text{N}_{x_3}$ , where the numbers  $x_1$ ,  $x_2$ , and  $x_3$  show the number of corresponding atom in the formula unit of the phase. The formula unit of each phase is fixed so that  $x_1 + x_2 + x_3 = 1$ . Solution phases or phases with vacant sites on either sublattice (i.e., non-stoichiometric phases) are not introduced in the worked example.

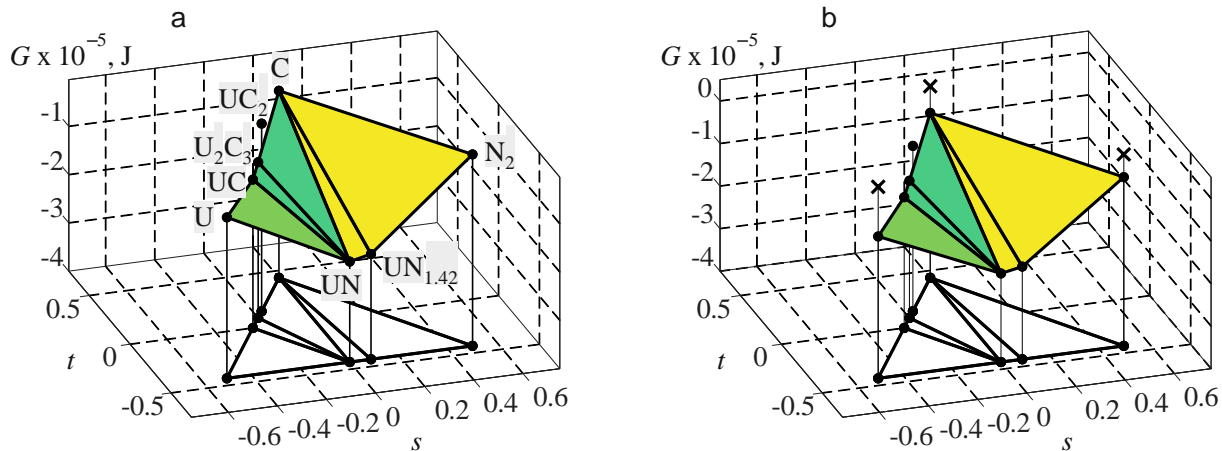
We consider pure uranium U (with  $x_1 = 1$ ;  $x_2 = 0$ ;  $x_3 = 0$ ), graphite C (0; 1; 0), nitrogen gas with the half molecule N (0; 0; 1) per formula unit, stoichiometric

compounds uranium carbide(1/2; 1/2; 0), and uranium nitride (1/2; 0; 1/2), as well as fcc uranium dicarbide (1/3; 0; 2/3), sesquicarbide (2/5; 3/5; 0), and high-temperature sesquinitride (1/2.42; 0; 1.42/2.42) as phases. Corresponding Gibbs energies per formula unit are calculated at  $T = 1000$  K and equal to  $g_{\text{U(tet)}}^0$ ,  $g_{\text{C}}^0$ ,  $0.5 g_{\text{N}_2}^0 + 100$  kJ,  $0.5 g_{\text{UC(fcc)}}^0$ ,  $0.5 g_{\text{UN(fcc)}}^0$ ,  $1/3 g_{\text{UC}_2(\text{fcc})}^0 + 50$  kJ,  $1/5 g_{\text{U}_2\text{C}_3}^0$ , and  $1/2.42 g_{\text{UN}_{1.42}}^0$ . See Sects.2 and 3 of Supplementary Information for the definition of these functions. The values of  $g_{\text{N}_2}^0$  and  $g_{\text{UC(fcc)}}^0$  are artificially increased in order to exaggerate some features of the diagram.

Each phase  $\gamma$  is represented by a single point in the ternary plot with the barycentric coordinates  $(x_1^{(\gamma)}, x_2^{(\gamma)}, x_3^{(\gamma)})$ , as shown in Figure S2. The relations that allow for the calculation of respective Cartesian coordinates  $(s, t)$  are

$$s = \frac{x_3 - x_1}{2}, \quad t = \frac{3^{1/2}}{2}(0.5 - x_3 - x_1), \quad x_1 + x_2 + x_3 = 1,$$

where  $x_1 = 1$  is pure U, i.e., left apex of the ternary plot,  $x_3 = 1$  is pure  $\text{N}_2$ , i.e. right apex of the plot, and the origin,  $s = 0, t = 0$  (equivalent to  $x_1 = x_3 = 0.25$ ), is in the center of the segment that connects the C ( $x_{\text{U}} = x_{\text{N}} = 0$ ) and UN ( $x_{\text{U}} = x_{\text{N}} = 0.5$ ) points of the Gibbs triangle.



**Figure S2.** Stencils for the lower convex hull of the overall molar Gibbs energy of the ternary system are shown in (a–b). The base of each stencil is the composition of the phase, and the height is determined by the value of the Gibbs energy of the phase for the

total number of moles of atoms in the phase. Axillary stencils are shown in (b) by crosses. Here, the energy 50 kJ is assigned to be larger than the energy of any real phase in the system. Observe that the UC<sub>2</sub> is above the lower convex hull but still below the cross-points. Thus, the phase is not stable at any overall composition of the system. Any triangle of the convex hull that contains at least one of the artificially introduced cross-points has to be excluded from the hull in order to obtain the lower convex hull, i.e., the Gibbs energy surface.

The point in space  $(s^{(\gamma)}, t^{(\gamma)}, G(x_U^{(\gamma)}, x_C^{(\gamma)}, x_N^{(\gamma)}))$  is obtained when one reconstructs the perpendicular to the ternary plot with the height equal to the value of the molar Gibbs energy of the corresponding phase  $\gamma$ . These spatial points are stencils for the convex hull constructed next, and its particular part of interest – the lower convex hull.

Once all stencils, each corresponding to a certain phase  $\gamma$ , are known, their convex hull is constructed. In MatLab, the built-in function `convhull` implements the so-called quickhull algorithm for the construction of the complete hull of the set of points, i.e., lower and upper parts. If one introduces axillary stencils at the corners of the ternary plot with values larger than the largest value of the energy among all phases, as shown in Figure S2b by the crosses, then one can easily manipulate the upper part of the hull and therefore distinguish between the lower and upper parts.

In the absence of solution phases, the lower convex hull is exactly the molar Gibbs energy of the system. Only ternary regions are present in case of equilibrium between stoichiometric phases. The phase diagram is mapped once the hull (triangles that construct it) is projected onto the horizontal plane. As discussed below, the lower convex hull approach can also deal with the thermodynamic systems with solution and non-stoichiometric phases.

### 1.2.3. Set of discrete compounds to approximate solutions

As opposed to the stoichiometric phases, the solution phases have the internal degrees of freedom, i.e., the composition of the phase is not fixed. In disordered systems, like liquids and gases with a single sublattice, each molar fraction of a species is a single internal degree of freedom of the phase. The total number of degrees of freedom is reduced by one since the sum of all fractions within the sublattice must be unity. In ordered systems with multiple sublattices, the total number of degrees of freedom is the sum of numbers of site occupancies introduced for each sublattice that is reduced by the number of sublattices (single constraint per sublattice). Thus, the U(C, N) and  $\alpha$ -U<sub>2</sub>N<sub>3</sub> phases described in the main text have only one degree of freedom (three occupancies and two sublattices), and there are two degrees of freedom in each modification of the uranium dicarbide phase (four occupancies and only two sublattices).

The lower-convex-hull approach addresses this case by introducing a set of discrete stoichiometric phases with fixed composition instead of each “continuous” solution phase. A worked example is demonstrated in Figure S3 for a regular solution phase, A<sub>x</sub>B<sub>1-x</sub>, with a single lattice and the interaction parameter  $\Omega = 2.3$ . There is one degree of freedom, molar fraction  $x$  of component A in the phase, and the Gibbs energy, normalized by  $RT$ , reads as

$$\frac{G}{RT} = xg_A^0 + (1-x)g_B^0 + x \log x + (1-x) \log(1-x) + \Omega x(1-x), \quad (\text{S1})$$

$$g_A^0 = 0, \quad g_B^0 = 0.1, \quad \Omega = 2.3.$$

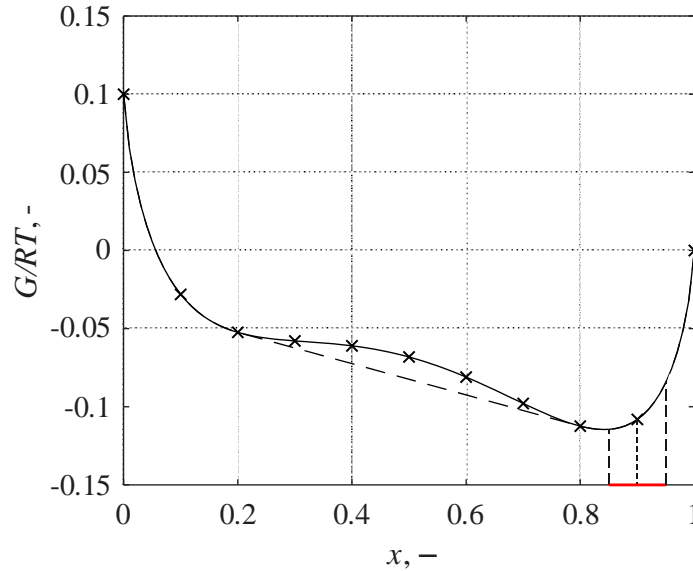
The fraction  $x$  varies from zero to one, and a uniform mesh is introduced as follows:

$$x_j = hj \in [0;1], \quad j = 0..m, \quad h = 1/m.$$

A stoichiometric phase, A <sub>$x_j$</sub> B<sub>1- $x_j$</sub> , with the composition  $x_j$  is associated with the  $j$ -th mesh point. The Gibbs energy is equal to the one of the solution at the composition of the stoichiometric phase. There is a continuous set of compositions,  $x_j - h/2 < x < x_j + h/2$ ,



that are close to the single mesh point,  $x_j$ . These solutions are indistinguishable within the approach and are all represented by the mesh point solution  $A_{x_j} B_{1-x_j}$ .



**Figure S3.** A set of discrete solutions ( $m = 10$ ) that represent the original continuous solution with the phase separation, i.e. miscibility gap at approximately  $0.2 < x < 0.8$ . The solid curve is the non-convex molar Gibbs energy Eq. (S1) of the continuous solution as a function of composition  $x$ ; markers show the Gibbs energy of introduced discrete stoichiometric compounds; and the dashed curve is the lower convex hull of the molar energy that indicates the phase separation. The red segment represents continuous solutions that are indistinguishable from the mesh point  $x_9 = 0.9$ .

The multidimensional mesh is introduced for the solutions with multiple degrees of freedom. Importantly, there might be multiple realizations of the same solution with the same overall composition but a different constitution. Consider, for example, the high-temperature uranium dicarbide. Its lattice occupancies are given by the formula unit  $U(C_{y_1}, (C_2)_{y_2}, Va_{y_3})$  and corresponding overall composition is  $UC_{y_1+2y_2}$ . Any two carbon atoms in this phase may choose to form a  $C_2$ -dumbbell or remain separate without changing the overall composition. Thus, all solutions with  $y_1 + 2y_2 = const$  are characterized by the same overall composition but different Gibbs energies. In order to

account for this situation, one has to introduce the multidimensional mesh for each solution in the space of occupancy variables ( $y_1, y_2, y_3\dots$ ) but not in the space of the overall composition variables ( $x_1, x_2, x_3$ ).

When the solution phases are present in the system, the accuracy of the approximation of the overall Gibbs energy increases with the decrease of the mesh step. Once each “continuous” solution phase is substituted by a discrete set of stoichiometric compounds, one can apply the approach described in the previous section.

#### *1.2.4. Post-processing*

In the case of three components, the lower convex hull is a set of triangular faces that approximates the true overall molar Gibbs energy. Thus, in the projection triangles correspond to single-phase, two-phase, and three-phase equilibria.

Simple geometrical rules allow one to distinguish between various types of triangles. These are thoroughly discussed by Voskov et al<sup>[2]</sup>. Briefly, they state the following; There are two necessary criteria to distinguish triangles that correspond to the one-phase equilibrium. First, all three apexes of triangles have to correspond to the same solution phase; otherwise, the triangle does not represent a single phase. Second, the lengths of all three sides are on the order of the mesh step  $h$ . Therefore, the triangle shrinks into a point with  $h \rightarrow 0$ . Otherwise, the phase demonstrates a binary or ternary miscibility gap. The two-phase equilibria are represented by triangles that have a pair of apexes corresponding to the same phase, and the third apex may correspond to another phase. The distance between the first pair of apexes should be on the order of  $h$ . The triangle shrinks into a tie-line with  $h \rightarrow 0$ . Real ternary equilibria are approximated by relatively large triangles. Their dimensions are not significantly affected by  $h$ , and various phases may correspond to the apexes.

### 1.3. *Assembly of isoplethal sections*

The temperature-composition diagrams discussed in Sect. 1.1 of Supplementary Information or, more generally, the isoplethal cross sections introduced in Sect. 4 of the main text and discussed in Sect. 3 of Supplementary Information are assembled following the ideas introduced by Voronin et al<sup>[7,8]</sup> and developed by Voskov et al<sup>[2]</sup>. First, we introduce a mesh with a fixed step along the temperature axis of the triangular temperature-composition prism. Then, the ternary plot is constructed for each node of the temperature mesh, and triangles that represent the true ternary equilibria are distinguished. We were only interested in those triangles that have the U(C, N) phase as one of the apexes since these apexes engrave the boundary curves of the isoplethal diagram. The composition  $x$  of the  $UC_xN_{1-x}$  solution, temperature  $T$  of the ternary plot, and the indices of the two phases that are in equilibrium with the solution are associated with each triangle of interest. This data is used then to map the isoplethal cross section constrained by the condition  $x_U = 0.5$ .

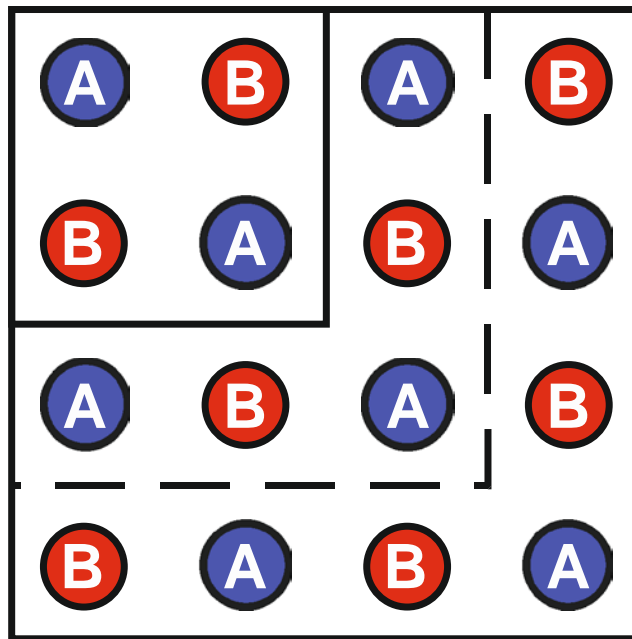
## 2. Model formulation

### 2.1. *Definition of formula unit and end-member*

Any compound is viewed as a number of interpenetrating sublattices. There is a single lattice for pure compounds (uranium, graphite, nitrogen gas) and two sublattices, for stoichiometric binary compounds (UC, UN,  $U_2C_3$  etc.) as well as solid solutions. Species – chemical elements (U, C, N) or molecules ( $C_2$  or  $N_2$ ) – occupy the lattice sites of their own sublattice. The pseudo chemical element, Va (vacancy), is introduced to distinguish vacant sites on either sublattice.

In multilattice phases, the ratio of number of sites of different sublattices is important. It represents the crystal order. For example, UC and UN, as well as U(C, N) have the ratio 1:1, and the prescribed stoichiometry of  $\beta$ - $U_2N_3$  is 1:1.42 as discussed in Sect. 2.2 of the main text.

The sites from different sublattices could be grouped according to stoichiometry, and the following notion of formula units is introduced<sup>[9-11]</sup>. Let A and B stand for the sites of the first and second sublattices, respectively. Then, a group of  $a$  sites of A and  $b$  sites of B is designated as the  $A_aB_b$ . It contains  $a + b$  sites total, with the ratio  $a:b$ . The size  $a + b$  of the formula unit can be varied arbitrarily, while the ratio  $a:b$  is the characteristic of the phase, as illustrated in Figure S4. For example, the unit cell of uranium carbide contains  $4 + 4$  atoms, while the common formula unit is UC that contains  $1 + 1$  atom; the arbitrary formula unit  $U_kC_k$  stands for the stoichiometric uranium monocarbide at any positive  $k$ .



**Figure S4.** Two-dimensional compound AB with two sublattices (red and blue). Formula units  $A_kB_k$  containing  $k = 2$  and 8 sites of sublattices A and B are circumscribed by solid squares. The energy of one mole of the formula units at  $k = 8$  is four times larger than the one at  $k = 2$ . The dashed square circumscribes a group  $5A + 4B$  that is not a formula unit for the compound.

Molar Gibbs energy  $g_i$  of any alloy or ceramic is conventionally given per mole of formula unit<sup>[10]</sup>

$$G^{(i)} = n_i g_i, \quad (\text{S2})$$

where  $G^{(i)}$  is the Gibbs energy of the phase  $i$  with  $n_i$  moles of specified formula units. Importantly, the Gibbs energy of the phase is invariant with respect to the size of the formula unit.

Molar energy only depends on  $T$  and  $p$  when the chemical composition of the compound is fixed, e.g., when there is only one species per sublattice, like  $\text{N}_2$ ,  $\text{C}$ ,  $\text{U}_2\text{C}_3$  etc. Otherwise, the energy also depends on the composition of the phase or formula unit. In this situation, multiple species occupy the same sublattice. For example, uranium carbonitride is designated as  $\text{U}(\text{C}, \text{N})$ ,  $\alpha$ - and  $\beta$ - $\text{UC}_2$  – as  $\text{U}(\text{C}, \text{C}_2, \text{Va})$ , and  $\alpha$ - $\text{U}_2\text{N}_3$  – as  $(\text{U}, \text{Va})_2\text{N}_3$  where the parenthesis embrace species from the same lattice and subscripts determine the ratio of sites on the two lattices (index one is omitted). In the limits, there will be only one species on each sublattice, and stoichiometric compounds are thus defined as “end-members of the solution phase.” End-members have the same lattice structure as their solution, and different solutions may have the same end-members. The total number of different end-members of the phase is equal to the product of the numbers of species in each sublattice. Thus, the end-members of  $\beta$ - $\text{UC}_2$  are  $\text{UC}$ ,  $\text{UC}_2$ , and  $\text{UVa}$ . The latter is the so-called fictive structure, since it is never observed in the experiment. It has a fully vacant non-metal sublattice.

For each alloy, one can view the formula unit as a mixture of stoichiometric end-members. The following equations relate the composition of the formula unit with the end-members fraction in the lattice, where subscripts specify the occupancy of each lattice by certain species:

$$\text{U}(\text{C}, \text{N}): \quad \text{U}(\text{C}_x \text{N}_{1-x}) = x\text{UC} + (1-x)\text{UN}, \quad (\text{S3})$$

$$\alpha - \text{U}_2\text{N}_3: \quad (\text{U}_y \text{Va}_{1-y})_2\text{N}_3 = y\text{U}_2\text{N}_3 + (1-y)\text{Va}_2\text{N}_3, \quad 0 < y < 1, \quad (\text{S4})$$

$$\alpha, \beta - \text{UC}_2: \quad \text{U}(\text{C}_{y_1} (\text{C}_2)_{y_2} \text{Va}_{1-y_1-y_2}) = y_1\text{UC} + y_2\text{UC}_2 + (1-y_1-y_2)\text{UVa}, \quad 0 \leq y_i \leq 1, \quad i = 1, 2. \quad (\text{S5})$$

The corresponding molar Gibbs energy per mole of formula units includes the energies of formation of end-members, and the energy of their mixing. The composition of the formula unit is determined by lattice occupancies, i.e.,  $x$ ;  $y$ ; and  $y_1, y_2$ . Measurement details and the definition of molar Gibbs energy of end-members and their solid solutions are given below. Conventionally, the molar energy of the pure end-member,  $g_i^0$ , is distinguished from the energy of the same compound,  $g_i$ , as a component of the solution by the addition of the superscript 0.

## 2.2. Overall Gibbs energy of the system

The analytical expression for the overall Gibbs energy  $G = \sum_{i=1}^s G^{(i)}$  is given as a sum of energies  $G^{(i)}$  of all phases that can form in the system at any conditions, where index  $i = 1..s$  spans over all  $s$  phases. We distinguish  $s = 9$  phases that could be formed in the system. Numbers 1 to 9 are hereinafter assigned to U, C, N<sub>2</sub>, U(C, N),  $\alpha$ -UC<sub>2</sub>,  $\beta$ -UC<sub>2</sub>, U<sub>2</sub>C<sub>3</sub>,  $\alpha$ -U<sub>2</sub>N<sub>3</sub>, and  $\beta$ -U<sub>2</sub>N<sub>3</sub> phases, respectively. Since uranium can only exist in a single state at a given temperature, the same index, 1, is assigned to all states of pure uranium (solid  $\alpha$ -,  $\beta$ -, and  $\gamma$ -U modifications, and liquid U), and the molar Gibbs energy is calculated as the minimum of respective increment energies of every phase required to shift from a certain common reference temperature (designated in what follows as  $T_{\text{SER}}$ ) to  $T$

$$g_{\text{U}}^0 = \min \left\{ g_{\text{U(ort)}}^0, g_{\text{U(tet)}}^0, g_{\text{U(bcc)}}^0, g_{\text{U(liq)}}^0 \right\}. \quad (\text{S6})$$

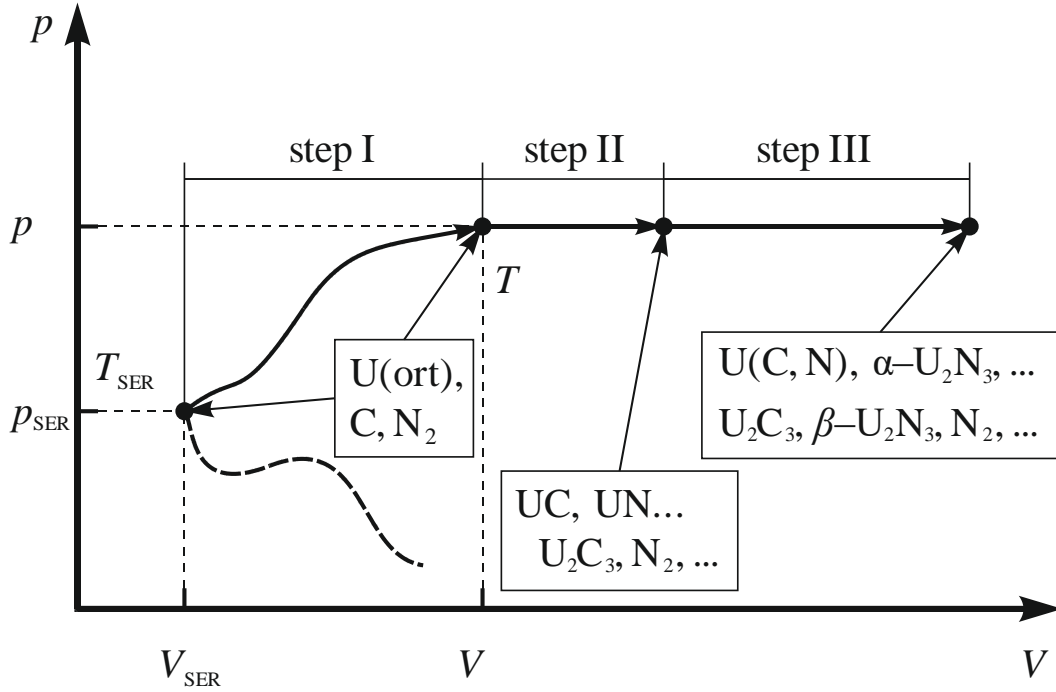
Each function in the right hand side of Eq. (S6) is a function of temperature only and defined in Sect. 3 of SI.

The equation for the calculation of each  $G^{(i)}$ , or, equivalently, the energy  $g_i$  per mole of corresponding formula unit, has to be introduced. Provided that the solid solutions are modelled as mixtures of corresponding end-members, there is a standard way of introducing the parametric description for each phase starting from the

stoichiometric phases, e.g., U, C, N<sub>2</sub>,  $\beta$ -U<sub>2</sub>N<sub>3</sub> etc., continuing with end-members, e.g., UC, UN, Va<sub>2</sub>N<sub>3</sub>, and finishing with the solution phases, e.g., U(C, N),  $\alpha$ -U<sub>2</sub>N<sub>3</sub>, and  $\alpha$ -,  $\beta$ -UC<sub>2</sub>. It is based on the thermodynamic path considered below.

The overall Gibbs energy  $G(T, p)$  of the heterogeneous system is the increment of the state function between the two equilibrium states of the system: the so-called Standard Element Reference (SER) state and the final one corresponding to desired thermodynamic conditions. As conventionally accepted, the SER is the stable state of the element at temperature  $T_{\text{SER}} = 25^\circ\text{C}$  and pressure  $p_{\text{SER}} = 1 \text{ atm}^{[12]}$ . Below, we describe one possible thermodynamic path that connects two equilibrium states and explains the structure and physical meaning of state functions referred to the SER state. Particular expressions obtained<sup>[13,14]</sup> for the system that also account for the mixing of end-members are given in Sect. 3 of SI and briefly summarized in Sect. 3 of the main text.

Consider  $x_{\text{U}}$ ,  $x_{\text{C}}$ , and  $x_{\text{N}}/2$  moles of formula units U, C, and N<sub>2</sub> of the three single-lattice SER phases:  $\alpha$ -U, graphite, and N<sub>2</sub> gas. The corresponding absolute molar Gibbs energies  $\tilde{g}_{\text{U}}^{\text{SER}}$ ,  $\tilde{g}_{\text{C}}^{\text{SER}}$ , and  $\tilde{g}_{\text{N}_2}^{\text{SER}}$  per the mole of formula unit at  $T_{\text{SER}}$ ,  $p_{\text{SER}}$  are introduced. By slowly changing thermodynamic conditions, one can measure the molar increment of the Gibbs energy for each compound, i.e., energies  $g_{\text{U}}^0(T)$ ,  $g_{\text{C}}^0(T)$ , and  $g_{\text{N}_2}^0(T, p)$  per mole of corresponding formula units. This is the step I shown in Figure S5 by the solid curve.



**Figure S5.** Thermodynamic path from the SER state to the final one corresponding to desired thermodynamic conditions. The path starts at  $T_{\text{SER}} = 25^\circ\text{C}$ , and  $p_{\text{SER}} = 1 \text{ atm}$ , and  $\alpha$ -U, graphite, and  $\text{N}_2$  gas are placed into separate sections of the chamber. As the first step, thermodynamic conditions are raised to desired values of  $T$  and  $p$ . For the next step, pure phases are allowed to react and form only stoichiometric compounds with a single species per sublattice. Finally, stoichiometric compounds are used as the end-members for the multicomponent alloys. Composition of alloys and their amounts are determined by the thermodynamic conditions and the overall system composition. The dashed segment shows the preliminary step of the proposed thermodynamic path. It is considered if the initial state is not the SER one, and initial reagents are introduced into the reaction chamber as UC, UN, and C powders,  $\text{N}_2$  gas, etc. Energy balance along the dashed segment can be measured in the same way as for the main path. In the diagram, it is arbitrarily assumed that the system expands along the path.

Step I ends when the desired thermodynamic conditions are established in the furnace. From now on,  $T$  and  $p$  are fixed and certain reactions are allowed; we only manipulate with the distribution of atoms between phases. As indicated by step II in



Figure S5, stoichiometric compounds and future end-members of solid solutions – i.e., the formula units with only one species per lattice - are formed first from the SER phases. This is described by chemical reactions of formation, e.g., one face-centered cubic formula unit UN for the end-member of the U(C, N) phase is obtained upon reaction of one formula unit U of the  $\alpha$ -U phase with the half of N<sub>2</sub> molecule



Some energy  $e_{\text{UN}}(T, p)$  (per mole of UN formula unit) is associated with the reaction (S7). The absolute molar energy of UN phase  $\tilde{g}_{\text{UN}}(T)$  is independent of pressure  $p$ . The molar increment  $g_{\text{UN}}^0(T)$  is a molar Gibbs energy required to form 1 mole of UN formula units at temperature  $T$  starting from U and N<sub>2</sub> at the SER conditions. All three functions are related as follows:

$$g_{\text{UN}}^0(T) = \tilde{g}_{\text{UN}}(T) - \left( \tilde{g}_{\text{U}}^{\text{SER}} + 0.5 \tilde{g}_{\text{N}_2}^{\text{SER}} \right) = \left( g_{\text{U}}^0(T) + 0.5 g_{\text{N}_2}^0(T, p) \right) + e_{\text{UN}}(T, p).$$

Accordingly, Eq. (S2) for the uranium nitride stoichiometric phase becomes  $G^{\text{UN}} = n_{\text{UN}} g_{\text{UN}}^0(T)$ . According to the formula unit approach the energy of one mole of N atoms that constitute 0.5 mol of N<sub>2</sub> molecules of the gas phase is  $g_{(\text{N}_2)_{0.5}}^0 = 0.5 g_{\text{N}_2}^0$ . The notion (N<sub>2</sub>)<sub>0.5</sub> stands for the one atom of the N<sub>2</sub> gas molecule that should not be confused with the one-atomic nitrogen gas N<sub>1</sub> that can form at large temperatures<sup>[13]</sup>.

In the same manner, the molar increment  $g_{\text{A}_a\text{B}_b}^0(T)$  of any stoichiometric compound with the formula unit A<sub>a</sub>B<sub>b</sub> is simply the sum of increments per each atom in the compound plus the associated energy  $e_{\text{A}_a\text{B}_b}$  of formation

$$g_{\text{A}_a\text{B}_b}^0 = \tilde{g}_{\text{A}_a\text{B}_b} - \left( a \tilde{g}_{\text{A}}^{\text{SER}} + b \tilde{g}_{\text{B}}^{\text{SER}} \right) = \left( a g_{\text{A}}^0 + b g_{\text{B}}^0 \right) + e_{\text{A}_a\text{B}_b},$$

and  $G^{\text{A}_a\text{B}_b} = n_{\text{A}_a\text{B}_b} g_{\text{A}_a\text{B}_b}^0(T)$ .

The structures with the vacant sublattices like Va<sub>2</sub>N<sub>3</sub> and UVa are unstable and never observed in the experiment. Thus, the corresponding energy  $e$  cannot be measured, and typically a constant value, independent of temperature and pressure, is assigned

(arbitrarily)<sup>[13,14]</sup>. Simultaneously, molar energy of vacant sites  $g_{\text{Va}}^0$  is zero at equilibrium<sup>[9–11]</sup>. Hence,

$$g_{\text{UVa}}^0(T) = \tilde{g}_{\text{UVa}}(T) - \tilde{g}_{\text{U}}^{\text{SER}} = g_{\text{U}(\text{bcc})}^0(T) + e_{\text{UVa}}, \quad e_{\text{UVa}} = 20 \text{ kJ/mol}.$$

Here,  $g_{\text{U}(\text{bcc})}^0$  is the molar Gibbs energy of the U formula unit of the  $\gamma$ -U phase at temperature  $T$ .

At the final step of the thermodynamic path, the stoichiometric structures, real and fictive ones - i.e., end-members - are mixed to form the solid solutions. Consider equations –. The corresponding energy of mixing  $e^{\text{mix}}$  per mole of formula units of the product on the left-hand side is the composition and temperature dependent, e.g.  $e_{\text{U}(\text{C,N})}^{\text{mix}}(x, T)$  for U(C, N),  $e_{\alpha\text{-U}_2\text{N}_3}^{\text{mix}}(y, T)$  for  $\alpha$ -U<sub>2</sub>N<sub>3</sub>, and  $e_{\alpha, \beta\text{-UC}_2}^{\text{mix}}(y_1, y_2, T)$  for  $\alpha$ -,  $\beta$ -UC<sub>2</sub>.

Thus, for the energy  $g_{\text{U}(\text{C,N})}$  of formation of the U(C<sub>*x*</sub>N<sub>*1-x*</sub>) formula unit, one writes

$$\begin{aligned} g_{\text{U}(\text{C,N})}(T, x) &= \tilde{g}_{\text{U}(\text{C,N})} - \left( \tilde{g}_{\text{U}}^{\text{SER}} + x\tilde{g}_{\text{C}}^{\text{SER}} + (1-x)\tilde{g}_{\text{N}}^{\text{SER}} \right) = \\ &= xg_{\text{UC}}^0(T) + (1-x)g_{\text{UN}}^0(T) + e_{\text{U}(\text{C,N})}^{\text{mix}}(T, x). \end{aligned}$$

By multiplying this equation by the number  $n_{\text{U}(\text{C,N})}$  of moles of the U(C, N) formula units of uranium carbonitride phase, one obtains the corresponding total Gibbs energy  $G^{\text{U}(\text{C,N})}$  of the phase,  $G^{\text{U}(\text{C,N})} = n_{\text{U}(\text{C,N})}g_{\text{U}(\text{C,N})}$ , according to the definition (S2).

Further details on the parametric approximation of energy of mixing  $e^{\text{mix}}$  as well as molar energies  $g_{\text{A}_a\text{B}_b}$  of stoichiometric compounds and end-members are given in Sect. 3 of SI.

Assuming that the SER conditions are common for each constituting element, the minimum value of the overall Gibbs energy changes by a constant value with the shift of SER values of  $T$  and  $p$ , while the point of minimum – i.e., the set of stable phases and their compositions- remains unchanged. Thus, the constants  $\tilde{g}_{\text{U}}^{\text{SER}}$ ,  $\tilde{g}_{\text{C}}^{\text{SER}}$ , and  $\tilde{g}_{\text{N}_2}^{\text{SER}}$  are not important, and the absolute value  $\tilde{G}(T, p)$  of the overall Gibbs energy of the system with total of 1 mole of components is related to the increment  $G$  between the two states as

$$G(T, p) = \tilde{G}(T, p) - \tilde{G}^{\text{SER}},$$

$$\tilde{G}^{\text{SER}} = x_{\text{U}} \tilde{g}_{\text{U}}^{\text{SER}} + x_{\text{C}} \tilde{g}_{\text{C}}^{\text{SER}} + x_{\text{N}} 0.5 \tilde{g}_{\text{N}_2}^{\text{SER}}.$$

According to the first law of thermodynamics, the final equilibrium state does not depend on the thermodynamic path provided that it passes through infinitesimally close equilibrium states. The preliminary step could be added to the path in order to include the state when the starting reagents, such as UC, UN, and C powders, and N<sub>2</sub> gas, are introduced into the furnace, see the dashed segment in Figure S5. Therefore, all available experimental protocols could be described by the proposed model.

### 3. Molar energies of phases

#### 3.1. Molar Gibbs energy for stoichiometric compounds

The molar Gibbs energy of the stoichiometric compound,  $g_{f.u.}^0(T)$ , with the formula unit *f.u.* only depends on temperature (and pressure for the nitrogen gas) and is not known in advance. It is deduced from the available experimental data, i.e., the heat capacity and enthalpy measurements as well as phase equilibria data, using the least square approach. Thus, the function is approximated by a series with respect to the temperature. Typically, the overall temperature interval is divided into a couple of subintervals, and unique expansion coefficients are determined for each subinterval  $[T_k; T_{k+1}]$

$$T_k < T < T_{k+1} : \quad g_{f.u.}^0(T) = a_k + b_k T + c_k T \ln T + d_k T^2 + e_k T^3 \\ + f_k T^{-1} + g_k T^{-2} + h_k T^{-3} (+RT \ln p), \quad (\text{S8})$$

where  $T$  is in K, and  $p$  is in atm. The term in parentheses is introduced for the gas phase. Temperature intervals of interest for the present research and corresponding polynomial coefficients for each stoichiometric compound are given in Table AI of the Appendix to the main text. The formula unit *f.u.* is specified in the first column.

### 3.2. Molar Gibbs energy of solution phases

Following Chevalier et al<sup>[13,14]</sup>, we only consider three contributions to the Gibbs energy of the phase per mole of the formula units. Thus, for each phase with the formula unit  $f.u.$  one can write

$$g_{f.u.} = g_{f.u.}^{\text{ref}} + g_{f.u.}^{\text{id}} + g_{f.u.}^{\text{ex}}, \quad e_{f.u.}^{\text{mix}} = g_{f.u.}^{\text{id}} + g_{f.u.}^{\text{ex}}. \quad (\text{S9})$$

These terms are the total energy  $g_{f.u.}^{\text{ref}}$  of all end-members that constitute the phase. As it is explained in Sect. 2 of SI, this term does not consider any interactions between the end-members. The second term,  $g_{f.u.}^{\text{id}}$ , accounts for the combinatorial entropy of mixing various species within each sublattice. The third term,  $g_{f.u.}^{\text{ex}}$ , accounts for specific interactions between atoms and describes the deviation of the phase from the ideal behavior given by  $g_{f.u.}^{\text{ref}} + g_{f.u.}^{\text{id}}$  terms.

Particular expressions of each term in Eq. (S9) depend on the number of sublattices, the number of species occupying a certain sublattice, and their interaction within the sublattice influenced by the presence of species on other sublattices.

#### 3.2.1. Contribution from end-members

Assume that there is only one sublattice in the solution that is shared by  $n > 1$  species. Their site occupancies are  $y_1, y_2, \dots, y_n$ , and  $y_1 + y_2 + \dots + y_n = 1$ . Then, there are exactly  $n$  end-members, and  $g_{f.u.}^{\text{ref}}$  is simply

$$g_{f.u.}^{\text{ref}} = \sum_{i=1}^n y_i g_{f.u.,i}^0, \quad (\text{S10})$$

where  $g_{f.u.,i}^0$  is the molar energy of the end-member  $i = 1..n$  obtained when the sublattice is only occupied by the species  $i$ . Thus, for the solution phases  $\text{U}(\text{C}, \text{N})$  and low-temperature  $\text{U}_2\text{N}_3$  one obtains:

$$\text{U}(\text{C}_{y_1} \text{N}_{y_2}): \quad g_{\text{U}(\text{C},\text{N})}^0 = y_1 g_{\text{UC}}^0 + y_2 g_{\text{UN}}^0,$$

$$(U_{y_1} Va_{y_2})_2 N_3 : \quad g_{(U,Va)_2 N_3}^0 = y_1 g_{U_2 N_3}^0 + y_2 g_{Va_2 N_3}^0 .$$

Both modifications of uranium dicarbide, according to Chevalier et al<sup>[13,14]</sup>, have the same lattice structure. Metal sublattice is only occupied by U, and non-metal sublattice is shared by C, C<sub>2</sub>, and Va species. Thus, while the Eq. (S10) assumes the same form

$$U(C_{y_1} (C_2)_{y_2} Va_{y_3}) : \quad g_{U(C,C_2,Va)}^0 = y_1 g_{UC}^0 + y_2 g_{UC_2}^0 + y_3 g_{UVa}^0 ,$$

particular expressions for end-member energies are different, as indicated in Tables AII and AIII of the Appendix to the main text.

Particular approximations of some end-members energies are referred to the molar energies of pure substances that react to produce the end-member. Thus, for the end-members UVa of both uranium dicarbide modifications (fcc and tetragonal, tet),

$$g_{UVa(fcc,tet)}^0 - g_{U(bcc)}^0 = e_{UVa} = 20 \text{ kJ/mol} .$$

The molar energy of UC end-member of the low-temperature modification of uranium dicarbide is referred to the energy of the same end-member of the high-temperature modification as follows

$$g_{UC(tet)}^0 - g_{UC(fcc)}^0 = e_{UC(tet)} = 500 \text{ J/mol} .$$

The molar energy of the Va<sub>2</sub>N<sub>3</sub> end-member of the low temperature uranium sesquinitride is referred to the atomic state of nitrogen, N<sub>1</sub> (do not confuse with the molecular N<sub>2</sub> gas which is a different species), as follows

$$g_{Va_2 N_3}^0 - 3g_{N_1}^0 = e_{Va_2 N_3} = 150 \text{ kJ/mol} .$$

The definition of  $g_{N_1}^0$  is given in Table AI (last three lines for different temperature intervals). An analogous expression holds for the U<sub>2</sub>N<sub>3</sub> end-member

$$g_{U_2 N_3}^0 - 3g_{N_1}^0 - 2g_{U(bcc)}^0 = e_{U_2 N_3} . \quad (S10)$$

Expansion (S8) holds for the energy  $e_{U_2 N_3}$ , and other end-members  $g_{UN(fcc)}^0$ ,  $g_{UC(fcc)}^0$ ,  $g_{UC_2(fcc)}^0$ , and  $g_{UC_2(tet)}^0$ . Corresponding coefficients are given in Table AII, first line for  $e_{U_2 N_3}$ .

### 3.2.2. Combinatorial entropy of mixing

The combinatorial term,  $g_{f.u.}^{id}$ , is proportional to the number of sites of the lattice per formula unit where multiple species are present. Thus, for the U(C, N), low-temperature U<sub>2</sub>N<sub>3</sub>,  $\alpha$ -, and  $\beta$ -UC<sub>2</sub> phases one can write

$$\begin{aligned} \text{U}(\text{C}_{y_1} \text{N}_{y_2}): \quad & g_{\text{U(C,N)}}^{id} = RT(y_1 \ln y_1 + y_2 \ln y_2), \\ (\text{U}_{y_1} \text{Va}_{y_2})_2 \text{N}_3: \quad & g_{(\text{U,Va})_2 \text{N}_3}^{id} = 2RT(y_1 \ln y_1 + y_2 \ln y_2), \\ \text{U}(\text{C}_{y_1} (\text{C}_2)_{y_2} \text{Va}_{y_3}): \quad & g_{\text{U(C,C}_2\text{,Va)}}^{id} = RT(y_1 \ln y_1 + y_2 \ln y_2 + y_3 \ln y_3). \end{aligned}$$

Observe the coefficient 2 in the line for the (U<sub>y<sub>1</sub></sub> Va<sub>y<sub>2</sub></sub>)<sub>2</sub>N<sub>3</sub> phase with the sites ratio 2:3 in the formula unit.

### 3.2.3. Excess terms

The excess terms,  $g_{f.u.}^{ex}$ , depend on composition, and can also depend on temperature. The so-called Redlich–Kister type polynomial expressions<sup>[15]</sup> are used by Chevalier et al<sup>[13,14]</sup> and other research groups<sup>[12]</sup> to account for the composition dependence. The linear dependence of expansion coefficients, i.e., interaction parameters, on temperature is typically introduced.

The U(C, N) phase is conventionally modelled as an ideal solid solution. It means that the corresponding  $g_{\text{U(C,N)}}^{ex}$  is taken to be zero.

The excess term for the low temperature uranium sesquinitride per mole of (U, Va)<sub>2</sub>N<sub>3</sub> formula unit is introduced by Chevalier et al<sup>[13,14]</sup> as follows

$$\begin{aligned} (\text{U}_{y_1} \text{Va}_{y_2})_2 \text{N}_3: \quad & g_{(\text{U,Va})_2 \text{N}_3}^{ex} = y_1 y_2 \left( L_{\text{U:Va}}^{(0)}(T) + L_{\text{U:Va}}^{(1)}(y_1 - y_2) \right), \\ & L_{\text{U:Va}}^{(0)} = -157613.7 + 263.18811T, \quad L_{\text{U:Va}}^{(1)} = 384410.16, \end{aligned}$$

where  $T$  is in K.

The excess term of both uranium dicarbide modifications per mole of U(C, C<sub>2</sub>, Va) formula unit takes the same form

$$U(C_{y_1}(C_2)_{y_2}Va_{y_3}): \quad g_{U(C,C_2,Va)}^{\text{ex}} = y_1y_3L_{C:Va}^{(0)} + y_1y_2\left(L_{C:C_2}^{(0)} + L_{C:C_2}^{(1)}(y_1 - y_2) + L_{C:C_2}^{(2)}(y_1 - y_2)^2\right),$$

where interaction parameters,  $L$ , related to certain phase are specified by subscript fcc and tet

$$L_{C:Va(\text{fcc})}^{(0)} = L_{C:Va(\text{tet})}^{(0)} = 87340.5 - 32.77837T,$$

$$L_{C:C_2(\text{fcc})}^{(0)} = 40264.38, \quad L_{C:C_2(\text{fcc})}^{(1)} = 5013.7,$$

$$L_{C:C_2(\text{tet})}^{(0)} = 38923.11, \quad L_{C:C_2(\text{tet})}^{(1)} = 4222.04,$$

$$L_{C:C_2(\text{fcc})}^{(2)} = L_{C:C_2(\text{tet})}^{(2)} = 6965.85.$$

### 3.3. Ideal vs. non-ideal non-stoichiometric models

The two thermodynamic models of the ternary U–C–N system, i.e., ideal stoichiometric one, introduced by Besmann et al<sup>[16]</sup>, and its extension, introduced in the present work, are compared in this section. First, we describe what is common for both models, and then highlight the differences. See Table S1 for the brief summary.

Table S1. Observed phases in the ternary system, and their thermodynamic model assumed within two different approaches. First column – phase designation; columns number two and three show whether the phase is introduced in either approach.

observed phases	present research	Besmann et al	Comments
U(liq)	+	+	solubility of C and N is neglected in both approaches
C(graphite)	+	+	single-component phase
U <sub>2</sub> C <sub>3</sub>	+	+	stoichiometric compound with the ratio 2:3
β-U <sub>2</sub> N <sub>3</sub>	+	+	stoichiometric compound with the ratio 1:1.42
U(C, N)	+	+	ideal stoichiometric solid solution of UC and UN end-

			members in both approaches
gas	N <sub>2</sub>	N <sub>2</sub> + U	two species in the gas phase according to Besmann et al
U(tet, ort, bcc)	+	–	all three modifications are not introduced by Besmann et al
$\alpha$ -U <sub>2</sub> N <sub>3</sub>	+	–	here, it is a non-stoichiometric solid solution
$\alpha$ -UC <sub>2</sub>	+	–	here, it is a non-stoichiometric solid solution
$\beta$ -UC <sub>2</sub>	+, as a solid solution	+, as a UC <sub>2</sub> end-member	here, it is a non-stoichiometric solid solution

Both models take into account the liquid state, U(liq), of uranium. Solubility of C and N in the phase is neglected. The solid state of carbon is graphite. Following Chevalier et al<sup>[13,14]</sup>, both high-temperature uranium sesquinitride and uranium sesquicarbide are considered as stoichiometric compounds with the ratio of numbers of chemical elements 1:1.42 and 2:3 respectively. The U(C, N) solid solution is considered as an ideal solution of stoichiometric UC and UN end-members with  $g_{U(C,N)}^{\text{ex}} = 0$  in Eq. (S9).

The two approaches are distinguished by the models of the other observed phases. Thus, Besmann et al introduced uranium atoms in the gas phase in addition to N<sub>2</sub> species. They also do not consider the solid modifications of uranium, though they are not stable in the temperature range studied by these authors. Low temperature uranium sesquinitride and dicarbide are not considered either. The assumed thermodynamic model of the high-temperature uranium dicarbide is simply the UC<sub>2</sub>(fcc) end-member. In the present research, all three phases,  $\alpha$ -U<sub>2</sub>N<sub>3</sub>,  $\beta$ -UC<sub>2</sub>, and  $\alpha$ -UC<sub>2</sub> are considered as solid solutions following original expressions deduced by Chevalier et al<sup>[13,14]</sup>.

#### 4. Datasets of phase equilibria in ternary U–C–N system

##### 4.1. Data from Austin and Gerd<sup>[17]</sup>

T, K	Lattice constant, Å	Phases in equilibrium with U(C, N)
2073	4.9415	–
2073	4.9068	–
2073	4.9565	UC <sub>2</sub>



2073	4.9495	UC <sub>2</sub>
2073	4.9487	UC <sub>2</sub>
2073	4.9482	–
2073	4.948	UC <sub>2</sub>
2073	4.9474	UC <sub>2</sub>
2073	4.9454	–
2073	4.9417	UC <sub>2</sub> , C
2073	4.9393	C
2073	4.9096	–
2073	4.9088	–
2273	4.9416	UC <sub>2</sub> , C

#### 4.2. Data from Leitnaker<sup>[18]</sup>

T, K	p, atm	Lattice constant, Å	Mole fraction of UN	Phases in equilibrium with U(C,N)
1773	0.1302	4.90497	0.7779	C
1773	0.1286	4.90525	0.774	C
1773	0.0628	4.9099	0.7085	C
1773	0.1975	4.90268	0.8102	C
1773	0.1642	4.90395	0.7923	C
1773	0.7864	4.89692	0.8913	C
1773	0.0974	4.9068	0.7521	C
1773	0.9188	4.89663	0.8954	C
1773	0.1964	4.90284	0.8079	C
1773	0.0658	4.90962	0.7124	C
1773	0.13	4.90498	0.7778	C
1773	0.1297	4.90521	0.7745	C
1773	0.0653	4.91007	0.7061	C
1773	0.1955	4.90295	0.8063	C
1773	0.2618	4.90134	0.829	C
1773	0.2624	4.90151	0.8266	C
1773	0.2635	4.90124	0.8304	C
1773	0.2662	4.9016	0.8254	C
1773	0.5245	4.89851	0.8689	C
1773	0.7858	4.89694	0.891	C
1773	0.2619	4.90122	0.8307	C
1773	0.5211	4.90904	0.8708	C
1873	0.8556	4.90268	0.8102	C
1873	0.7868	4.90388	0.7932	C
1873	0.8506	4.90246	0.8132	C
1873	0.3274	4.90801	0.7351	C
1873	0.5248	4.90516	0.7752	C
1873	0.7925	4.90257	0.8117	C

1873	0.7939	4.90254	0.8121	C
1873	0.7912	4.90275	0.8092	C
1873	0.6554	4.90383	0.794	C
1873	0.3957	4.90644	0.7572	C
1973	0.7888	4.90905	0.7204	C
1973	0.7881	4.91008	0.7059	C
1973	0.2599	4.91746	0.602	C
1973	0.6574	4.91135	0.688	C
1973	0.2623	4.91861	0.5858	C
1973	0.8546	4.90936	0.7161	C
1973	0.7211	4.90993	0.708	C
1973	0.3922	4.9137	0.6549	C
1973	0.3917	4.91414	0.6487	C
1973	0.5236	4.91187	0.6807	C
1973	0.3925	4.91419	0.648	C
1973	0.2582	4.91768	0.5989	C
1973	0.7865	4.9097	0.7113	C
1973	0.7854	4.90904	0.7206	C
1973	0.5233	4.91154	0.6854	C
1973	0.7859	4.90907	0.7202	C
2073	0.394	4.92349	0.517	C
2073	0.7218	4.91792	0.5955	C
2073	0.8561	4.9166	0.6141	C
2073	0.5246	4.92	0.5662	C
2073	0.2645	4.92906	0.4386	C
2173	0.2635	4.9366	0.3324	C
1973	0.5316	4.91108	0.6918	C
1973	0.2639	4.91477	0.6398	C
1973	0.7917	4.90839	0.7297	C
1773	0.2637	4.89985	0.85	C
1773	0.5263	4.89746	0.8837	C
1773	0.7928	4.89603	0.9038	C
1773	0.1312	4.90319	0.803	C
1773	0.3979	4.89807	0.8751	C

### 4.3. Data from Henry and Blickensderfer<sup>[19]</sup>

T, K	Lattice constant, Å	Phases in equilibrium with U(C, N)
1973	4.96	U <sub>2</sub> C <sub>3</sub>
1973	4.961	U <sub>2</sub> C <sub>3</sub>
1973	4.942	UC <sub>2</sub>
1973	4.945	UC <sub>2</sub>
1973	4.949	UC <sub>2</sub>

1973	4.953	UC <sub>2</sub>
1973	4.956	UC <sub>2</sub>
1973	4.958	UC <sub>2</sub>
1973	4.924	C
1973	4.94	C
1973	4.929	C
1973	4.909	C
1973	4.908	C
1973	4.903	C
1973	4.893	C, U <sub>2</sub> N <sub>3</sub>
1973	4.889	U <sub>2</sub> N <sub>3</sub>
1973	4.89	U <sub>2</sub> N <sub>3</sub>

#### 4.4. Data from Cordfunke and Ouweltjes<sup>[20]</sup>

T, K	p, atm	Lattice constant, Å	Composition, N/(N + C + O)	Phases in equilibrium with U(C,N)
1873	0.0128	4.9305	0.495	C
1873	0.0973	4.914	0.694	C
1873	0.488	4.9043	0.81	C
1873	1.004	4.9018	0.84	C
1968	0.0013	4.951	0.193	UC <sub>2</sub>
1968	0.0111	4.9398	0.372	C
1968	0.0111	4.9403	0.365	C, UC <sub>2</sub>
1968	0.0324	4.9335	0.457	C
1968	0.11	4.9226	0.591	C
1968	0.253	4.9164	0.665	C
1968	0.525	4.9118	0.72	C
1968	0.994	4.9082	0.763	C
2053	0.0011	4.9513	0.188	UC <sub>2</sub>
2053	0.0103	4.9447	0.3	UC <sub>2</sub>
2053	0.0328	4.9397	0.374	C, UC <sub>2</sub>
2053	0.106	4.931	0.489	C
2053	0.245	4.9245	0.568	C
2053	0.52	4.9188	0.637	C
2053	0.972	4.9152	0.679	C
2153	0.001	4.9509	0.195	UC <sub>2</sub>
2153	0.0106	4.9482	0.243	UC <sub>2</sub>
2153	0.0307	4.9443	0.306	UC <sub>2</sub>
2153	0.107	4.9383	0.393	C, UC <sub>2</sub>
2153	0.255	4.9335	0.457	C
2153	0.525	4.9298	0.504	C
2196	0.001	4.9543	0.13	UC <sub>2</sub>
2196	0.0105	4.9482	0.243	UC <sub>2</sub>

2196	0.0336	4.9459	0.281	UC <sub>2</sub>
2196	0.11	4.9393	0.379	UC <sub>2</sub>
2196	0.25	4.9369	0.412	UC <sub>2</sub>
2196	0.526	4.9333	0.459	UC <sub>2</sub>
2196	0.999	4.9244	0.57	C

#### 4.5. *Data from Naoumidis and Stöcker*<sup>[21]</sup>

<i>T, K</i>	<i>p, atm</i>	<i>Carbon content x, –</i>
2023	0.000396	0.921081
2023	0.006239	0.824169
2023	0.028916	0.727905
2023	0.156153	0.627797
2023	0.419694	0.545944
2023	0.962172	0.486096
1923	0.000123	0.898448
1923	0.000565	0.844644
1923	0.014356	0.691791
1923	0.116529	0.555845
1923	0.959011	0.354582
1823	0.0004	0.812953
1823	0.009235	0.614603
1823	0.041474	0.50192
1823	0.048924	0.488919
1823	0.110115	0.434191
1823	0.95636	0.221919
1733	0.000787	0.665011
1733	0.013211	0.466299
1733	0.26756	0.174339
1733	0.942368	0.014115
1653	0.001312	0.52012
1653	0.001748	0.512905
1653	0.004181	0.456724
1653	0.026032	0.229543
1653	0.162286	0.011038
1503	0.002622	0.14741

## References in Supplementary Information

- 1 V.E. Alvarez-Montaño, M.H. Farías, F. Brown, I.C. Muñoz-Palma, F. Cubillas, and F.F. Castellón-Barraza: *J. Chem. Educ.*, 2017, vol. 94, pp. 1247–54.
- 2 A.L. Voskov, A. V Dzuban, and A.I. Maksimov: *Fluid Phase Equilib.*, 2015, vol. 388, pp. 50–8.
- 3 A.L. Voskov and G.F. Voronin: *Russ. J. Phys. Chem. A*, 2010, vol. 84, pp. 525–33.
- 4 H. Gupta, J.E. Morral, and H. Nowotny: *Scr. Metall.*, 1986, vol. 20, pp. 889–94.
- 5 Y.-B. Kang and P. Chartrand: *Calphad*, 2016, vol. 55, pp. 69–75.
- 6 R. Schmid-Fetzer: DOI:10.1007/s11669-014-0343-5.
- 7 G.F. Voronin: *Russ. J. Phys. Chem. A*, 2005, vol. 79, pp. 1890–902.
- 8 G.F. Voronin: *Russ. J. Phys. Chem. A*, 2003, vol. 77, pp. 1685–94.
- 9 B. Sundman and J. Ågren: *J. Phys. Chem. Solids*, 1981, vol. 42, pp. 297–301.
- 10 B. Sundman, X.-G. Lu, and H. Ohtani: *Comput. Mater. Sci.*, 2015, vol. 101, pp. 127–37.
- 11 M. Hillert: *J. Alloys Compd.*, 2001, vol. 320, pp. 161–76.
- 12 C. Guéneau, N. Dupin, B. Sundman, C. Martial, J.-C. Dumas, S. Gossé, S. Chatain, F. De Bruycker, D. Manara, and R.J.M. Konings: *J. Nucl. Mater.*, 2011, vol. 419, pp. 145–67.
- 13 P.-Y. Chevalier, E. Fischer, and B. Cheynet: *J. Nucl. Mater.*, 2000, vol. 280, pp. 136–50.
- 14 P.-Y. Chevalier and E. Fischer: *J. Nucl. Mater.*, 2001, vol. 288, pp. 100–29.
- 15 O. Redlich and A.T. Kister: *Ind. Eng. Chem.*, 1948, vol. 40, pp. 345–8.
- 16 T.M. Besmann, D. Shin, and T.B. Lindemer: *J. Nucl. Mater.*, 2012, vol. 427, pp. 162–8.
- 17 A.E. Austin and A.F. Gerds: *The Uranium-Nitrogen-Carbon System. BMI-1272*, 1958.

- 18 J.M. Leitnaker: in *Thermodynamics of nuclear materials*, International Atomic Energy Agency, Vienna, 1968, pp. 317–30.
- 19 J.L. Henry and R. Blikensderfer: *J. Am. Ceram. Soc.*, 1969, vol. 52, pp. 534–9.
- 20 E.H.P. Cordfunke and W. Ouweltjes: *J. Nucl. Mater.*, 1979, vol. 79, pp. 271–6.
- 21 A. Naoumidis and H.J. Stöcker: in *Thermodynamics of nuclear materials*, International Atomic Energy Agency, Vienna, 1968, pp. 287–300.