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Thermodynamic modelling of the N–U system

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Abstract

Thermodynamic properties constitute part of our general knowledge about physical and chemical properties of nuclear materials, as the solid substance UN_{1-x}(fcc_B1). This is why the thermodynamic modelling of the N–U binary system is performed here from a critical assessment of most of the available experimental information, with one of the most commonly used optimization procedure. Optimized Gibbs energy parameters are given, and a comparison between the calculated and experimental equilibrium phase diagram or thermodynamic properties is presented. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The critical assessment of the N–U binary system is performed in this work by using the program of Lukas et al. [1]. We first describe the general principle of the thermodynamic modelling and assessment method. Then we present for the N–U binary system, the equilibrium phases, the complete analysis of the available experimental information, concerning both phase diagram and thermodynamic properties, and finally, the detailed optimization results. On the one hand, optimized Gibbs energy parameters of all condensed substance and solution phases are presented, and constitute a record in the specific nuclear part of the THERMALLOY solution database [2]; on the other hand, the optimized phase diagram and specific thermodynamic properties of the N–U binary system are calculated and compared to the experimental ones.

2. Thermodynamic modelling

2.1. Substances

In the classical substance databases, the fundamental thermodynamic properties stored for a substance are the enthalpy of formation $\Delta H^\circ f_{298.15\ \mathrm{K}}$, the entropy at room temperature $S^\circ_{298.15\ \mathrm{K}}$, the heat capacity C_p at constant pressure versus temperature T (K), according to the relation (1), and if necessary, the transition enthalpies L_{tr} if the substance shows structural transformations at temperatures T_{tr}.

$$C_p = C_k + D_k T + E_k T^2 + F_k T^{-2} + \cdots \\ (+ G_k T^3 + H_k T^4 + I_k T^6 + J_k T^{-10} + L_k T^{-3} + M_k T^{-4}) \\ \text{for } T_k < T < T_{k+1}. \quad (1)$$

In the format used for phase diagram calculations, the stored quantity is the Gibbs energy of the substance Φ, $G - H_{SER}$, referred to a given reference state. SER means 'stable element reference' and is defined by the use of $H_{298.15\ \mathrm{K}}$ and $S_{0\ \mathrm{K}}$ for the stable state of the pure elements at 298.15 K and 1 bar. It is possible to calculate directly this quantity from the fundamental thermodynamic values, and reciprocally.

$$G - H_{SER} = a_k + b_k T + c_k T \log T + d_k T^2 + e_k T^3 + f_k T^{-1} \\ + \cdots (+g_k T^4 + h_k T^5 + i_k T^7 + j_k T^{-9} \\ + k_k \log T + l_k T^{-2} + m_k T^{-3}) \\ \text{for } T_k < T < T_{k+1}. \quad (2)$$

In this expression, the coefficients $c, d, e, f, \ldots$ are connected to those of the heat capacity, while a and b are two integration constants depending on all the fundamental thermodynamic values. The points of suspension mean that extra terms may be added if necessary, and

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are often used for extrapolation outside the stable domain.

In some cases, the heat capacity is unknown, and is estimated by the Neuman–Koop rule. In this case, the Gibbs energy, referred to the pure elements with a given structure $(\mathrm{Ref}(1), \ldots, \mathrm{Ref}(i))$, varies linearly versus temperature according to the simple relation

$$\Delta G = G - \sum x_i G_i^{\circ(\mathrm{ref}(i))} = a + bT, \tag{3}$$

where a and b correspond directly to ΔH and $-\Delta S$ which are independent of temperature.

2.2. Solutions

In a general way, the Gibbs energy of a condensed solution phase is the sum of several terms: reference, ideal, excess and magnetism or ordering in some cases.

$$G = G^{\mathrm{Ref}} + G^{\mathrm{Id}} + G^{\mathrm{Ex}}(+G^{\mathrm{Mag}} + G^{\mathrm{Ord}}). \tag{4}$$

In this work, we have used for the solid and liquid solution phases the general multisublattice model described by Sundman and Agren [3].

$$G^{\mathrm{Ref}} = \sum_{\mathrm{r}} P_{\mathrm{r}}(Y)^{\circ}G_{\mathrm{r}}, \tag{5}$$

where ${}^{\circ}G_{\mathrm{r}}$ represents the Gibbs energy of all reference substances, obtained by making all the possible permutations on the different sublattices and by assuming successively that each sublattice is completely fulfilled by only one component. $P_{\mathrm{r}}(Y)$ is the corresponding product of site fractions from the Y matrix: $Y = (y_i^{\mathrm{sl}})$, atomic fractions of the component i (pure or associate species) on the sublattice sl.

$$G^{\mathrm{Id}} = RT\sum_{\mathrm{sl}} N_{\mathrm{s}}^{\mathrm{sl}} \sum y_i^{\mathrm{sl}} \log y_i^{\mathrm{sl}}, \tag{6}$$

where $N_{\mathrm{s}}^{\mathrm{sl}}$ is the number of sites of the sublattice sl and R is the perfect gas constant.

In the one- and two-sublattice model, the excess Gibbs energy for a multicomponent phase is equal to

$$G^{\mathrm{Ex}} = \sum G^{\mathrm{Ex}}\ (\mathrm{binary}) + G^{\mathrm{Ex}}\ (\mathrm{ternary}). \tag{7}$$

Expressions (8) and (9) are used for one lattice, (10) and (11) for two sublattices:

$$G^{\mathrm{Ex}}\ (\mathrm{binary}) = \sum_j \sum_k y_j y_k L_{j,k},$$

$$L_{j,k} = \sum_v L_{j,k}^{(v)} (y_j - y_k)^v, \tag{8}$$

Table 1
Experimental and calculated three-phase equilibria and congruent transformations in the N–U system

Reaction	Experimental				Calculated				
	T (K)	t (°C)	x (L)	P (atm)	Ref.	T (K)	t (°C)	x (L)	P (atm)
$L + G \Longleftrightarrow$ (UN)(fcc_B1)	3073	2800	0.55	1	[6]	3062	2789	0.575	1
	3078	2805	0.55	1	[7]	3098	2825	0.552	2.5
	3123	2850	0.50	>2.5	[13]	3134	2861	0.528	10
$G +$ (UN)(fcc_B1) $\Longleftrightarrow$ β-U_2N_3	1618	1345			[6]	1622	1349		
	1625	1352			[7]				
	1623	1350			[16]				
$G +$ β-U_2N_3 $\Longleftrightarrow$ α-U_2N_3	1523	1250			[6]	1408	1135		
	1405	1132			[7]				
β-U_2N_3 $\Longleftrightarrow$ α-U_2N_3 + (UN)(fcc_B1)	1393	1120			[6]	1228	955		
	1213	940			[7]				
$L \Longleftrightarrow \gamma$-U(bcc_A2)	1408	1135			[5]	1408	1135		
$L \Longleftrightarrow$ UN(fcc_B1) + γ-U(bcc_A2)	1403	1130	0.99983		[6]	1408	1135	0.99994	
	1403	1130			[14]				
	1403	1130			[15]				
	1405	1132			[7]				
γ-U(bcc_A2) $\Longleftrightarrow$ β-U(tet)	1049	776			[5]	1049	776		
β-U(tet) $\Longleftrightarrow$ α-U(ort_A20)	942	669			[5]	942	669		
β-U(tet) $\Longleftrightarrow$ α-U(ort_A20) + UN(fcc_B1)	938	665			[6]				
					[7]				

$$G^{\mathrm{Ex}}\ (\text{ternary}) = \sum_i \sum_j \sum_k y_i y_j y_k L_{i,j,k},$$

$$L_{i,j,k} = y_i L^1_{i,j,k} + y_j L^2_{i,j,k} + y_k L^3_{i,j,k}, \tag{9}$$

$$G^{\mathrm{Ex}}\ (\text{binary}) = \sum_l \sum_j \sum_k y_l y_j y_k L_{j,k:l},$$

$$L_{j,k:l} = \sum_v L^{(v)}_{j,k:l} (y_j - y_k)^v, \tag{10}$$

$$G^{\mathrm{Ex}}\ (\text{ternary}) = \sum_i \sum_j \sum_k \sum_l y_i y_j y_k y_l L_{i,j,k:l},$$

$$L_{i,j,k:l} = y_i L^1_{i,j,k:l} + y_j L^2_{i,j,k:l} + y_k L^3_{i,j,k:l}. \tag{11}$$

$L_{j,k}$ and $L_{i,j,k}$ or $L_{j,k:l}$ and $L_{i,j,k:l}$ represent the binary and ternary interaction parameters between the components i, j and k of one sublattice, the second sublattice (if existing) being supposed completely fulfilled by the component l. These parameters vary with temperature similar to relation (2). The binary interaction parameters are described by using a Redlich–Kister type polynomial expression [4].

2.3. Assessment method

The values used for the lattice-stabilities of the pure condensed elements have been taken from the Scientific Group Thermodata Europe (SGTE) database, published by Dinsdale [5], for the following stable or metastable structures: U_1(ort_A20, tet, bcc_A2, L), $N_1(L)$. The thermodynamic data for gaseous species are taken from the DATACOMP substance database [2], and reported in Table 9.

Table 2
Solubility of nitrogen in liquid uranium versus temperature from Bugl and Bauer [13]

T^{L} (K)	S (at.% N)	x^{L} (U) (atomic fraction)
1473	0.043	0.99957
1573	0.0998	0.99900
1673	0.209	0.99791
1773	0.405	0.99595
1873	0.728	0.99272
1973	1.23	0.9877
2073	1.99	0.9801
2173	3.07	0.9693
2273	4.56	0.9544
2373	6.55	0.9345
2473	9.13	0.9087
2573	12.41	0.8759
2673	16.48	0.8352
2773	21.45	0.7855
2873	27.41	0.7259
2973	34.44	0.6556
3073	42.65	0.5735
3123	48.16	0.5184

The critical assessment of the coefficients, $a_k, b_k, c_k, d_k, e_k, f_k, \ldots,$ for any other binary stoichiometric substances, and of the binary interaction parameters $L^{(v)}_{j,k}$ and $L^{(v)}_{j,k:l}$ for a binary or pseudo-binary solution, was performed for the binary N–U system by using the optimization program developed by Lukas et al. [1], which allows to take into account simultaneously all the available experimental information, equilibrium phase diagram and thermodynamic properties.

The optimized Gibbs energy parameters of lattice-stabilities and condensed substances are reported in Table 10 and the ones of solid solutions and liquid phase in Table 11. They constitute a part of the THERMALLOY solution thermodynamic database [2], devoted to nuclear applications.

3. Experimental information

3.1. Short presentation of the different phases

The phase diagram of the N–U binary system was successively reported in a compilation work by Shunk [6] and Okamoto [7]. The condensed solutions and stoichiometric substances, with the symbols currently used

Table 3
Experimental phase diagram information from Benz and Bowman[a] [15]

T (K)	$x^{\phi1}$ (U)	$x^{\phi2}$ (U)
UN liquidus: $L(\phi1) + N_{1-x}U_1(\text{fcc\_B1})(\phi2)$		
2273	0.960	(0.52)
2373	0.917	(0.53)
2823	0.660	(0.53)
2885	0.630	(0.54)
UN solidus: $N_{1-x}U_1(\text{fcc\_B1})(\phi1) + L(\phi2)$		
1773	0.51020	(0.99595)
1943	0.51813	(0.9894)
1960	0.51282	(0.98844)
2070	0.52083	(0.98036)
2070	0.52356	(0.98036)
2073	0.51813	(0.98009)
2085	0.52083	(0.97899)
2932	0.53476	(0.68579)
2992	0.53191	(0.64090)
2998	0.52910	(0.63618)
3024	0.51282	(0.61523)
3108	0.51282	(0.54188)
3109	0.51020	(0.54095)
3113	0.50505	(0.53724)
3126	0.50761	(0.52501)
3092	0.50761	(0.51000)
3093	0.50505	(0.51000)
3098	0.50761	(0.51000)
3103	0.50505	(0.51000)

[a] x = atomic fraction. Values between brackets are estimated.

Table 4
Experimental heat capacity and enthalpy of UN versus temperature from Counsell et al. [28], Westrum and Barber [29], Affortit [30,31], Cordfunke and Muis [32], and Takahashi et al. [42]

T (K)	C_p (J/(mol K) [28])	T (K)	C_p (J/(mol K) [30,31])	$H_T - H_{800}$ (J/mol)	T (K)	$H_T - H_{298}$ (J/(mol K) [32])	T (K)	C_p (J/(mol K) [42])	$H_T - H_{298}$ (J/mol)
298.15	47.086	800	56.902	0	386.8	2205	298.15	47.823	0
300	47.160	900	58.702	5782	397.8	2450	300	47.907	88
310	47.626	1000	60.459	11 736	433.2	3368	350	49.999	2540
320	48.080	1100	62.216	17 866	434.1	3377	400	51.547	5079
	[29]	1200	63.973	24 184	463.5	4102	450	52.760	7686
306.8	48.240	1300	65.731	30 669	485.4	4710	500	53.764	10 351
316.3	48.710	1400	67.488	37 321	508.6	5343	550	54.685	13 062
326.0	49.100	1500	69.245	44 141	513.0	5489	600	55.480	15 816
335.8	49.464	1600	71.002	51 170	531.1	6044	650	56.233	18 610
345.9	49.722	1700	72.760	58 367	546.4	6347	700	56.944	21 439
		1800	74.517	65 731	589.3	7621	750	57.614	24 301
		1900	76.274	73 262	617.5	8328	800	58.241	27 196
		2000	78.032	80 960	618.8	8344	850	58.869	30 125
		2100	79.789	88 868	638.1	8943	900	59.496	33 083
		2200	81.546	96 943	654.3	9328	950	60.082	36 075
		2300	83.262	105 186	658.5	9418	1000	60.668	39 091
					677.9	9922			
					701.3	10 615			

Table 5
Calculated thermal properties of UN versus temperature (this work) compared to assessed ones from Tagawa [16] and Matsui and Ohse [39]

T (K)	C_p (J/(mol K))			$H_T - H_{298}$ (J/mol)		
	[16]	[39]	Calc.	[16]	[39]	Calc.
298	47.572	47.82	47.356	0	0	0
300	47.656	47.91	47.468	88	88	88
400	51.505	51.55	51.540	5067	5079	5059
500	53.639	53.76	53.702	10 334	10 351	10 246
600	55.187	55.48	55.168	15 778	15 816	15 566
700	56.484	56.94	56.354	21 364	21 439	21 041
800	57.697	58.24	57.436	27 075	27 196	26 729
900	58.911	59.50	58.495	32 907	33 082	32 700
1000	60.124	60.67	59.576	38 857	39 091	38 980
1100	61.379	61.84	60.703	44 932	45 218	45 264
1200	62.718	63.01	61.891	51 137	51 461	51 513
1300	64.099	64.18	63.151	57 476	57 821	57 759
1400	65.563	65.31	64.487	63 957	64 295	64 037
1500	67.111	66.48	65.904	70 592	70 884	70 382
1600	68.743	67.61	67.405	77 383	77 586	76 828
1700	70.417	68.74	68.993	84 337	84 402	83 412
1800	72.216	69.87	70.668	91 471	91 330	90 171
1900	74.099	70.96	72.432	98 784	98 371	97 143
2000	76.023	72.09	74.285	106 286	105 525	104 365
2100	78.073	73.22	76.229	113 993	112 791	111 876
2200	80.207	74.34	78.263	121 905	120 168	119 713
2300	82.383	75.46	80.390	130 035	127 658	127 914
2400	84.684	76.58	82.607	138 386	135 260	136 519
2500	87.069	77.69	84.917	146 976	142 974	145 565
2600	89.538		87.318	155 804		155 092
2700	92.090		89.812	164 883		165 138
2800	94.726		92.397	174 226		175 741
2900	97.445		95.076	183 832		186 942
3000	100.29	83.27	97.847	193 719	183 216	198 779

Table 6
Experimental heat capacity and enthalpy of $UN_{1.54}$ versus temperature from Tagawa [16,18]

T (K)	C_p (J/(mol K))	$H_T - H_{800}$ (J/mol)
298.15	20.920	0
300	21.035	38
400	25.005	2362
500	27.245	4985
600	28.827	7791
700	30.062	10 737
800	31.149	13 799
900	32.121	16 962
1000	33.027	20 220
1100	33.900	23 567
1200	34.757	27 002
1300	35.580	30 519
1400	36.388	34 116
1500	37.195	37 796
1600	37.985	41 557
1700	38.776	45 395

in this work, are the following: liquid phase, L; UN intermediate solid solution, $N_{1-x}U_1$(fcc_B1); α-U_2N_3, N_3U_2(L_T), low-temperature form; β-U_2N_3, N_3U_2(H_T), high-temperature form; α-U, U(ort_A20); β-U, U(tet); γ-U, U(bcc_A2). Hansen and Anderko [8] also reported that no evidence of solution of nitrogen in uranium metal could be found (<100 ppm or 0.01 wt% over the entire range 823–1173 K). The gas phase is noted G.

The structures of the intermetallic compounds are given by Hansen and Anderko [8], Elliott [9] and Shunk [6].

The lattice parameter of UN, fcc_B1 type, isotypic with NaCl, was reported as $a = 4.890$ [8], $a = 4.890 \pm 0.001$, $a = 4.8899$ Å at 299.15 K [9], $a = 4.8895 \pm 0.0005$ Å [6]. Shunk [6] also reported $a = 4.8835 \pm 0.0005$ Å for $UN_{0.8}$, $a = 4.875 \pm 0.005$ Å for $UN_{1.04}$, $a = 4.893 \pm 0.005$ Å for $UN_{1.10}$. Two other values, $a = 4.8897 \pm 0.0004$ and $a = 4.8890 \pm 0.0004$ Å, were also given for UN. Muromura and Tagawa [10] showed the influence of the impurities O and C on the lattice parameter, and found that the value of 4.8892 Å

Table 7
Calculated thermodynamic functions of UN(fcc_B1) versus temperature (this work) compared to the assessed ones from Tagawa [16] and Matsui and Ohse [39]

T (K)	$\Delta H°f$(UN) (J/mol)			$\Delta S°f$(UN) (J/(mol K))		
	[16]	[39]	Calc.	[16]	[39]	Calc.
298	−295 809	−295 809	−294 353	−83.554	−83.53	−83.584
300	−295 809	−295 798	−294 353	−83.513	−83.50	−83.550
400	−295 056	−295 136	−293 697	−81.337	−81.61	−81.702
500	−294 261	−294 414	−293 061	−79.580	−79.98	−80.278
600	−293 675	−293 773	−292 566	−78.534	−78.79	−79.371
700	−293 382	−293 305	−292 247	−78.073	−78.08	−78.876
800	−293 298	−293 089	−292 101	−77.948	−77.79	−78.678
900	−293 382	−293 180	−292 108	−78.073	−77.88	−78.685
1000	−296 395	−296 050	−294 705	−81.253	−80.95	−81.450
1100	−300 830	−300 383	−298 882	−85.479	−84.86	−85.437
1200	−300 579	−299 644	−298 135	−85.270	−84.22	−84.787
1300	−300 244	−298 809	−297 414	−84.977	−83.55	−84.210
1400	−299 742	−297 881	−296 682	−84.642	−82.87	−83.667
1500	−306 562	−306 950	−305 997	−89.496	−89.31	−90.278
1600	−306 311	−306 863	−306 166	−89.328	−89.26	−90.388
1700	−305 892	−306 677	−306 211	−89.077	−89.14	−90.415
1800	−305 348	−304 734	−306 092	−88.743	−88.97	−90.347
1900	−304 595	−306 000	−305 771	−88.366	−88.76	−90.174
2000	−303 675	−305 507	−305 208	−87.906	−88.51	−89.886
2100	−302 587	−304 910	−304 366	−87.362	−88.22	−89.476
2200	−301 248	−304 211	−303 205	−86.734	−87.89	−88.937
2300	−299 742	−303 405	−301 686	−86.065	−87.53	−88.262
2400	−298 026	−302 491	−299 771	−85.312	−87.15	−87.447
2500	−296 060	−301 474	−297 418	−84.517	−86.73	−86.488
2600	−293 842		−294 591	−83.680		−85.379
2700	−291 374		−291 249	−82.718		−84.119
2800	−288 696		−287 353	−81.755		−82.703
2900	−285 725	−286 669	−282 864	−80.709		−81.128
3000	−282 462	−294 775	−277 743	−79.622	−84.30	−79.393

corresponded to 0.04 wt% carbon. They extrapolated a value of 4.8883 Å at zero carbon content. The oxygen content did not influence the lattice parameter in the range 0.011–0.094 wt%.

α-U_2N_3, bcc of the Mn_2O_3 (D53) type, forms solid solutions with N: it gradually changes to the Ca_1F_2 (C1) type with increasing N content. The parametric variation of the lattice parameter as a function of N is reported as follows: it decreases from $a = 10.688$ [6] or $a = 10.70$ Å [8] for $UN_{1.50}$, to $a = 10.636$ [6] or $a = 10.60$ Å [8] for $UN_{1.75}$. $UN_{2.00}$ can be prepared only at a high N_2 pressure (126 atm) and has the ideal Ca_1F_2 (C_1) structure ($a = 5.32$ Å) [8]. At higher N contents, the parameter for the fcc_C1 phase decreases from $a = 5.303$ Å at $UN_{1.80}$, to $a = 5.283$ Å at $UN_{1.86}$ [6].

The hexagonal structure reported by Hansen and Anderko [8] and Elliott [9] for U_2N_3 ($a = 3.69$ Å, $c = 5.83$ Å [8], $a = 3.70$ Å, $c = 5.80$ Å [9]) corresponds to the high-temperature form β-U_2N_3. [6] reported $a = 3.699 \pm 0.001$ Å, $c = 5.844 \pm 0.003$ Å at $UN_{1.48}$ and $a = 3.700$ Å, $c = 5.826$ Å at $UN_{1.50}$.

3.2. Phase diagram

In the following, T is the temperature in Kelvin, x(U) the atomic fraction of uranium in the N–U system, L the liquidus or the liquid, and S is the solidus.

The melting point of UN was determined as 2923 ± 100 K (2650°C) by Chiotti [11], 2753 ± 50 K (2480°C) by Newkirk and Bates [12], 3123 ± 30 K (2850°C) by Bugl and Bauer [13] for $P(N_2) > 2.5$ atm.

The invariant reactions and transition points reported in different compilation and experimental works from Dinsdale [5], Shunk [6], Okamoto [7], Storms [14], Benz and Bowman [15], and Tagawa [16] are reported in Table 1.

The phase relations in the system uranium–nitrogen were determined by Bugl and Bauer [13]. Cast specimens of UN were heated in a controlled nitrogen-pressure apparatus in order to study the decomposition behaviour: at pressures of nitrogen below 2.5 atm, UN decomposed at temperatures below 3123 K (2850°C), while at pressures greater than 2.5 atm, it melted congruently at 3123 K (2850°C). The equilibrium phase boundary between liquid (uranium-rich phase) and UN was determined by heating uranium in a UN crucible and then quenching and analysing the equilibrated phase. The calculated values of the solubility of nitrogen are reported in Table 2 ($S = 2.45 \times 10^4 \exp(19\,525/T)$, expressed in atomic percent and for temperature in K). The formation of a series of continuous solid solutions between the structurally dissimilar compounds N_2U_1 (formed at high pressures and low temperatures) and N_3U_2 was shown from experiments performed with a Sievert apparatus. UN decomposed at 3073 K (2800°C) and N_3U_2 at 1618 K (1345°C) at $P(N_2) = 1$ atm.

The U–N partial phase diagram was determined by Benz and Bowman [15] by using X-ray, metallographic, chemical and thermal analyses of phases equilibrated

Table 8
Comparison of calculated and experimental thermodynamic functions of formation of compounds $N_{0.500}U_{0.500}$(fcc_B1), $N_{1.5–1.75}U_1$ (α-N_3U_2) and $N_{0.587}U_{0.413}$(β-N_3U_2)

$N_{0.500}U_{0.500}$(fcc_B1)		$N_{1.5–1.75}U_1$ (α-N_3U_2)		$N_{0.587}U_{0.413}$ (β-N_3U_2)	
$\Delta H°f_{298.15\ K}$ (J/g at)	Source	$\Delta H°f_{298.15\ K}$ (J/g at)	Source	$\Delta H°f_{298.15\ K}$ (J/g at)	Source
−143 302*	[34]	−150 190 ($UN_{1.51}$)	[37]	−147 161 ($UN_{1.466}$)	[38]
−145 603	[35]	−146 362 ($UN_{1.69}$)	[37]		
−147 068	[35]	−148 210 ($UN_{1.60}$)	[37]		
−146 649	[35]	−146 410 ($UN_{1.674}$)	[38]		
−148 428	[36]	−146 662 ($UN_{1.606}$)	[38]		
−148 433 ($UN_{0.9957}$)	[33]				
−145368 ($UN_{0.997}$)	[38]				
−147 904	[16,39]				
−147 176	Calc.	−141 016 (mean)	Calc.	−140 272 ($UN_{1.42}$)	Calc.
$\Delta S°f_{298.15\ K}$ (J/(g at. K))	Source				
−41.793	[16]				
−41.793	[39]				
−41.792	Calc.				
$S°_{298.15\ K}$ (J/(g at. K))	Source	$S°_{298.15\ K}$ (J/(g at. K))	Source		
31.213	[16]				
31.108	[28]	25.104 ($UN_{1.59}$)	[28]		
31.317	[29]	24.123 ($UN_{1.73}$)	[28]		
31.213	[40]	24.337 ($UN_{1.59}$)	Calc.		
31.210	Calc.	25.000 ($UN_{1.73}$)	Calc.		

Table 9
Gibbs energy parameters of pure gaseous species in the N–U binary system, stored in DATACOMP [2]

$G(\mathrm{Sub}) - G(\mathrm{Ref}) = a_k + b_k T + c_k T \log(T) + d_k T^2 + e_k T^3 + f_k T^{-1}$ for $T_k < T < T_{k+1}$

T_k					
a_k	b_k	c_k	d_k	e_k	f_k
$G(\mathrm{N_1}(G)) - H_{\mathrm{SER}}$ = 298.15					
+4.6646852160E+05	−1.4043771609E+01	−2.0794084898E+01	+2.2542189921E−05	−3.8832427557E−09	0
2700.00					
+4.6433455071E+05	+3.5050010837E+00	−2.3181084295E+01	+9.6263901363E−04	−6.6145675285E−08	+1.2332984354E+05
5100.00					
+5.8098701922E+05	−3.0232501406E+02	+1.2875036338E+01	−4.0401611730E−03	+6.5071330824E−08	−7.1472897705E+07
9400.00					
+1.1710925656E+05	+3.7925440880E+02	−6.1732606449E+01	+1.3467192742E−03	−8.5528220648E−09	+4.7489547519E+08
20 000.00					
+1.0000000000E+06	0	0	0	0	0
$G(\mathrm{N_2}(G)) - H_{\mathrm{SER}}$ = 298.15					
−8.3813869009E+03	−7.0709454305E−01	−2.8554404245E+01	+6.9736551083E−04	−1.0549986152E−06	−1.8789410840E+04
700.00					
−7.5266242005E+03	−2.5478635371E+01	−2.4420991924E+01	−5.4409059692E−03	+4.3597971057E−07	0
1700.00					
−1.9879734861E+04	+6.1143084893E+01	−3.6214645214E+01	−3.0059390056E−04	+8.0030387261E−09	+2.5109876935E+06
4100.00					
−6.8125887672E+04	+1.9379573420E+02	−5.1954122735E+01	+2.0101453323E−03	−5.6768614057E−08	+3.0451600692E+07
7400.00					
−5.8980273939E+04	+2.1852189752E+02	−5.5341421331E+01	+2.8254888499E−03	−7.9801245428E−08	0
10 500.00					
+2.3833313259E+06	−2.9945309064E+03	+2.9152283156E+02	−1.9150310573E−02	+1.8222855139E−07	−3.2361228051E+09
16 000.00					
−4.9437049202E+06	+3.6937509567E+03	−3.9995639136E+02	+9.9271651301E−03	−4.7605507842E−08	+1.1359091965E+10

20 000.00					
+1.0000000000E + 06	0	0	0	0	0
$G(\mathrm{N}_3(G)) - H_{\mathrm{SER}} = 298.15$					
+4.0307563647E + 05	−1.4324522775E + 01	−2.9559541516E + 01	−2.4131220209E − 02	+3.6156035861E − 06	+5.5714144000E + 04
800.00					
+3.8893720702E + 05	+1.5880927573E + 02	−5.5404528000E + 01	−2.6570491791E − 03	+1.9365644070E − 07	+1.5364484800E + 06
2000.00					
+3.8089800489E + 05	+2.1020746780E + 02	−6.2295576418E + 01	+6.5726455791E − 06	−7.8680120000E − 10	+3.3369492000E + 06
6000.00					
+1.0000000000E + 06	0	0	0	0	0
$G(\mathrm{U}_1(G)) - H_{\mathrm{SER}} = 298.15$					
+5.1859170123E + 05	+1.3908624797E + 01	−3.2542315284E + 01	+1.1279854842E − 02	−2.4286028070E − 06	+1.5190430400E + 05
1000.00					
+5.4014082978E + 05	−2.0181340371E + 02	−1.4447352000E + 00	−9.0591968628E − 03	+1.1778657403E − 07	−2.6970064000E + 06
2200.00					
+5.7537873757E + 05	−4.1603165833E + 02	+2.6972156000E + 01	−1.9057492358E − 02	+7.6790346667E − 07	−1.0691375200E + 07
3800.00					
+2.3772000934E + 05	+6.9331218572E + 02	−1.0784929398E + 02	+5.0126412000E − 03	−4.2475270527E − 08	+1.4886253600E + 08
4100.00					
+1.9452121614E + 05	+8.0155056149E + 02	−1.2051405094E + 02	+6.6447359409E − 03	−8.1749084000E − 08	+1.7611773960E + 08
6000.00					
+1.0000000000E + 06	0	0	0	0	0

Table 10

Gibbs energy parameters of condensed pure elements (lattice-stabilities) and stoichiometric compounds in the N–U binary system, stored in THERMALLOY [2]

$G(\mathrm{Sub}) - G(\mathrm{Ref}) = a_k + b_kT + c_kT\log(T) + d_kT^2 + e_kT^3 + f_kT^{-1}$ for $T_k < T < T_{k+1}$ in J/g at.

Substance	Ref.	T_k	a_k	b_k	c_k	d_k	e_k	f_k
$N_1(L)$	$N_2(G)$	298.15	+29 550.0	+59.02				
$N_3(\alpha\text{-}N_3U_2)$	$N_2(G)$	298.15	+150 000					
U_1(ort_A20)	SER	298.15	−8407.734	+130.95515	−26.9182	+1.25156E − 3	−4.42605E − 6	+38 568
		955	−22 521.8	+292.121093	−48.66			
U_1(tet)	SER	298.15	−5156.136	+106.976316	−22.841	−1.084475E − 2	+2.7889E − 8	+81 944
		941.5	−14 327.309	+244.16802	−42.9278			
U_1(bcc_A2)	SER	298.15	−752.767	+131.5381	−27.5152	−8.35595E − 3	+9.67907E − 7	+204 611
		1049	−4698.365	+202.685635	−38.2836			
$U_1(L)$	SER	298.15	+3947.766	+120.631251	−26.9182	+1.25156E − 3	−4.42605E − 6	+38 568
		955	−10 166.3	+281.797193	−48.66			
U_1(fcc_B1)	U_1(ort_A20)	298.15	+50 000					
$U_1(L)$	U_1(ort_A20)	298.15	+12 355.5	−10.3239				
$N_{0.600}U_{0.400}(S)$ $(\alpha\text{-}N_3U_2)$	$N_2(G)$ U_1(bcc_A2)	298.15	−152 126.72	+126.53137	−9.890359	+1.977238E − 3	−0.63222E − 6	+345 388
$N_{0.587}U_{0.413}(S)$ $(\beta\text{-}N_3U_2)$	SER	298.15	−151 899.72	+172.94947	−29.278101	−0.828498E − 3	−0.45202E − 6	+417 539
$N_{0.500}U_{0.500}(S)$ N_{1-x}U(fcc_B1)	SER	298.15	−156 765.70	+157.03712	−27.765544	−0.037916E − 3	−0.38839E − 6	+191 878
$N_{0.500}U_{0.500}(S)$ N_{1-x}U(fcc_B1)	$N_2(G)$ U_1(ort_A20)	298.15	−152 392.43	+139.43570	−15.215831	+12.737587E − 3	−1.63922E − 6	+257 141
$N_{0.500}U_{0.500}(L)$	$N_1(L)$ $U_1(L)$	298.15	−72 096.465	+83.31969	−15.215831	+12.737587E − 3	−1.63922E − 6	+257 141

Table 11
Gibbs energy parameters of condensed solutions in the N–U binary system, stored in THERMALLOY [2]

$$L_{j,k:l} = \sum_v L^{(v)}_{j,k:l}(y_i - y_k)^{(v)}\, {}^{(v)}L^{(v)}_{j,k:l} = a_{j,k:l} + b^{(v)}_{j,k:l}T$$

Phase	Formula	Excess interaction parameters		
		Name	$a^{(v)}_{j,k:l}$	$b^{(v)}_{j,k:l}$
Liquid	$[N_1, N_1U_1, U_1]_1\langle L\rangle$	$L^0[N_1, N_1U_1]_1\langle L\rangle$	0	0
		$L^0[N_1, U_1]_1\langle L\rangle$	0	0
		$L^0[N_1U_1, U_1]_1\langle L\rangle$	0	0
Fcc_B1	$[N_1, Va]_1[U_1]_1\langle \text{fcc\_B1}\rangle$	$L^0[N_1, Va]_1[U_1]_1\langle \text{fcc\_B1}\rangle$	+26878.59	0
α-N_3U_2	$[N_1]_3[U_1, Va]_2\langle \alpha\text{-}N_3U_2\rangle$	$L^0[N_1]_3[U_1, Va]_2\langle \alpha\text{-}N_3U_2\rangle$	−52537.90	+87.72937
		$L^1[N_1]_3[U_1, Va]_2\langle \alpha\text{-}N_3U_2\rangle$	+128136.72	0

Table 12
Fundamental thermodynamic properties of UN(fcc_B1), stored in DATACOMP [2]

$C_p = 55.531088 + 0.151664E - 3T + 4.66068E - 6T^2$
$-767512T^{-2}$ J/mol, $298.15 < T < 3000$
$\Delta H^\circ f_{298.15\ K} = -294354$ J/mol
$S^\circ_{298.15\ K} = 62.42$ J/(mol K)

with N_2 (up to 5 atm), at temperatures up to 3123 K (2850°C). The uranium-rich side is of eutectic type (composition near pure U). The phase boundaries (N/U, x(U), T) of the UN solid solution were measured as: U-rich – 0.96 ± 0.02, 0.510 ± 0.005, 1773 K (1500°C); 0.92 ± 0.02, 0.521 ± 0.005, 2073 K (1800°C). N-rich – 1.04 ± 0.02, 0.490 ± 0.005, 1873 K (1600°C). UN congruent melting point: 0.96 ± 0.03, 0.510 ± 0.007, 3108 ± 30 K (2835°C). The α-U_2N_3(bcc) $\Longleftrightarrow$ β-U_2N_3 (hexagonal) transition temperature of the sesquinitride was found to be 1393 K (1120°C), but may depend on composition. The composition of the hexagonal phase is $UN_{1.47} \pm 0.02$ at 1588 K (1315°C), near the decomposition pressure. Experimental phase diagram information is reported in Table 3.

More recently, Benz and Hutchinson [17] studied reaction layers formed on uranium at temperatures varying up to 2673 K (2400°C) in nitrogen (0.003–2.0 atm). Uranium-saturated UN phase boundaries (N/U, x(U), T) range from 0.991, 0.498, 1973 K (1700°C) to 0.997 ± 0.006, 0.499 ± 0.002, 3073 ± 30 K (2800°C), respectively. From a detailed argumentation, these authors concluded that the lower N/U values previously reported by Benz and Bowman [15] are in error. The N/U ratios of the UN phase in equilibrium with nitrogen at pressures up to 2 atm are concluded to be very near the value of 1.00 at temperatures between 1773 K (1500°C) and 2373 K (2100°C).

The phase relations of the N–U system were reported by Tagawa [16]. Emphasis was placed on the non-stoichiometry of uranium sesquinitride. According to [16], the non-stoichiometry range of β-U_2N_3 is $UN_{1.45–1.50}$ ($0.4 < x(U) < 0.408$) and reported from various authors as $UN_{1.34–1.46}$ ($0.407 < x(U) < 0.427$), $UN_{1.48}$, $UN_{1.51}$ ($x(U) = 0.398, 0.403$). The sesquinitride decomposes between UN and nitrogen at 1623 K (1350°C) at 1 atm. The mean value of N content for β-U_2N_3 is 1.425, i.e., $x(U) = 0.412$. The non-stoichiometry range of α-U_2N_3 is $UN_{1.54–1.75}$ ($0.3636 < x(U) < 0.3937$). The mean value of N content for α-U_2N_3 is 1.645, i.e., $x(U) = 0.378$.

The non-stoichiometry range of α-U_2N_3 was experimentally studied by Bugl and Bauer [13], Tagawa [18], Lapat and Holden [19], Naoumidis and Stocker [20], Katsura et al. [21], Urabe et al. [22], Serizawa et al. [23], Nishimaki et al. [24] and Nagawa et al. [25].

Bugl and Bauer [13] studied the region U_2N_3–UN_2 using a Sievert type apparatus and determined the equilibrium compositions as a function of pressure and temperature.

Tagawa [18] measured equilibrium nitrogen pressures over the two-phase region $UN + U_2N_3$ between 1023 and 1323 K. The U-rich phase boundary was obtained as $N/U = 1.542$.

Lapat and Holden [19] measured equilibrium decomposition pressures of U_2N_3 from 873 to 1373 K and $1.6 < N/U < 1.7$ by using a continuous vacuum balance technique and located some of the phase boundaries of the nitrides.

Naoumidis and Stocker [20] measured equilibrium pressures at different temperatures and thermodynamic data for $1.5 < N/U < 1.75$. An isothermal pressure dependence of composition in the U_2N_3–UN_2 region was constructed.

Katsura et al. [21] obtained the composition of U_2N_{3+x} in equilibrium with N_2 at 873 K by reacting uranium with nitrogen.

Urabe et al. [22] determined N_2 pressure-composition isotherms at 673, 873 and 1073 K for $1.6 < N/U < 1.8$, but at insufficient pressure to reach the phase boundaries at 1atm.

Serizawa et al. [23] studied the dissolution of nitrogen in nitrogen-rich α-U_2N_{3+x}, prepared by the reaction of UH_3 and an $NH_3 + H_2$ gas stream.

Nishimaki et al. [24] analysed the thermodynamics of nitrogen-rich uranium sesquinitride formation by reaction of uranium monocarbide with ammonia.

Nagawa et al. [25] performed equilibrium measurements and obtained the N_2 pressure-composition isotherms in the temperature range 673–1173 K for the single phase α-U_2N_{3+x} ($1.63 < N/U < 1.76$).

Fujino and Tagawa [26] proposed a statistical model for analyzing experimental thermodynamic properties of non-stoichiometric uranium sesquinitride.

The U–N phase diagram reported by Okamoto [7] modifies the liquidus on the uranium side to concur with the thermodynamic calculation reported by Ogawa [27], who claimed that the calculated boundary agrees well with selected experimental data, but the data source is unknown.

3.3. Thermodynamic properties

The heat capacities of UN, $UN_{1.59}$ and $UN_{1.73}$ were measured from 11 to 320 K by Counsell et al. [28]. The entropy at room temperature was reported as $S^\circ_{298.15\ K} =$ 30.953, 25.104, 24.123 J/(g at. K), respectively.

Westrum and Barber [29] determined the low-temperature heat capacity of UN by adiabatic calorimetry and $S^\circ_{298.15\ K} = 31.317$ J/(g at. K).

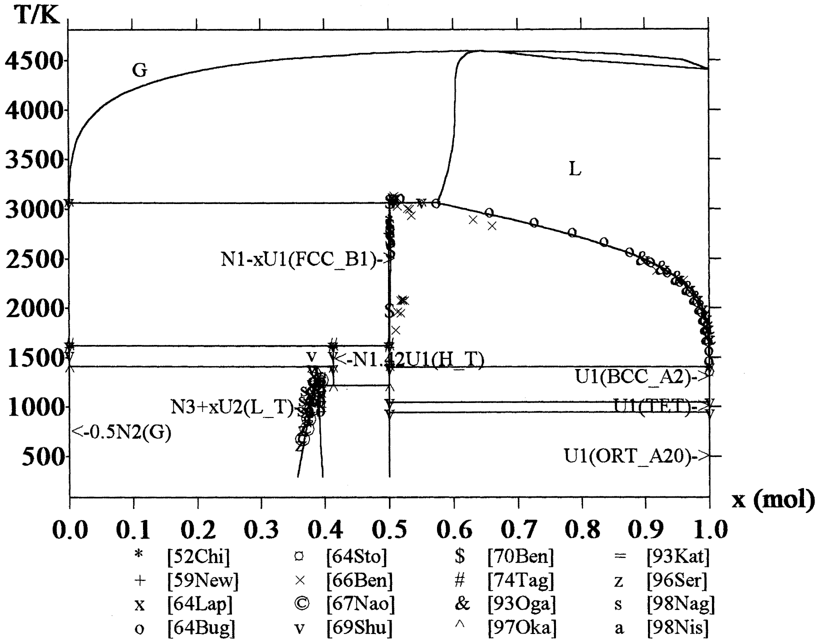
The heat capacity at constant pressure and the enthalpy of UN were determined by Affortit [30,31]. Results between 800 and 2300 K are reported in Table 4. The heat capacity of UN is represented by a linear variation versus temperature between 1000 and 2000 K:

$$C_p(\mathrm{UN}) = 42.6768 + 17.5728 \times 10^{-3} T\ \mathrm{J/(mol\ K)}. \quad (12)$$

The heat capacity at constant pressure and the enthalpy of UN were also measured by Cordfunke and Muis [32] between 380 and 702 K (Table 4).

The experimental values measured by Oetting and Leitnaker [33] from 298 to 1700 K can be expressed by the following equations:

$$\begin{aligned} H^\circ(T) - H^\circ(298.15\ \mathrm{K}) = {} & 48.873304T \\ & + 5.560954\mathrm{e}^{-3} T^2 \\ & + 41.0534 \times 10^4 T^{-1} \\ & - 16443.12\ \mathrm{J/mol}, \end{aligned} \quad (13)$$



THREE-PHASE REACTIONS

942.02	1.000	1.000	0.500
1049.00	1.000	1.000	0.500
1407.90	1.000	1.000	0.500
3062.00	0.575	0.502	0.000
1622.10	0.413	0.500	0.000
1408.00	0.379	0.413	0.000
1228.20	0.379	0.413	0.500

TRANSITIONS

942.00	1.000
1049.00	1.000
1408.00	1.000
4409.00	1.000

Fig. 1. Calculated N–U equilibrium phase diagram (this work) compared to the experimental information.

$$C_p(\mathrm{UN}) = 48.873304 + 11.1219088 \times 10^{-3}T - 41.0534 \times 10^{4}T^{-2}\ \mathrm{J/(mol\ K)}. \quad (14)$$

The thermodynamic properties of the compounds were studied by Tagawa [16,18]. The thermal functions of UN are reported in Table 5, the ones of $UN_{1.54}$ (U_2N_3) in Table 6, while the thermodynamic functions for the formation of UN are given in Table 7. By using values of heat capacity from various sources, Tagawa [16] proposed the following equation between 800 and 1700 K, and the average entropy $S^{\circ}_{298.15}(\mathrm{UN}) = 62.42528$ J/(mol K).

$$C_p(\mathrm{UN}) = 54.149328 + 22.8065656 \times 10^{-4}T + 4.37228 \times 10^{-6}T^2 - 6.81251432 \times 10^{5}T^{-2}\ \mathrm{J/(mol\ K)}. \quad (15)$$

The heat of formation, $\Delta H^{\circ}f_{298.15\ \mathrm{K}}$ (UN), in J/mol, was measured as −286 604 ± 8368 by Neumann et al. [34] with very impure uranium, −291 206 ± 1674 by Gross et al. [35] who preferred the more negative values −294 135, −293 298 due to the formation of small amounts of sesquinitride, −296 855 by Hubbard [36], −299 156 ± 4603 for $UN_{0.965}$ by O'Hare et al. [37], −296 227 for $UN_{0.9957}$ recalculated by Oetting and Leitnaker [33], −290 300 ± 2200 by Johnson and Cordfunke [38] for $UN_{0.997}$, and assessed as −295 809 J/mol by Tagawa [16] and Matsui and Ohse [39].

Thermodynamic properties (vapour pressure, heat capacity and enthalpy of formation) of UN were critically evaluated by Matsui and Ohse [39]. From the assessed values of the heat capacity (16, 17) and $S^{\circ}_{298.15\ \mathrm{K}} = 62.43$ J/(mol K), the thermal functions were calculated and reported in Table 5, while the thermodynamic functions for the formation of UN were also

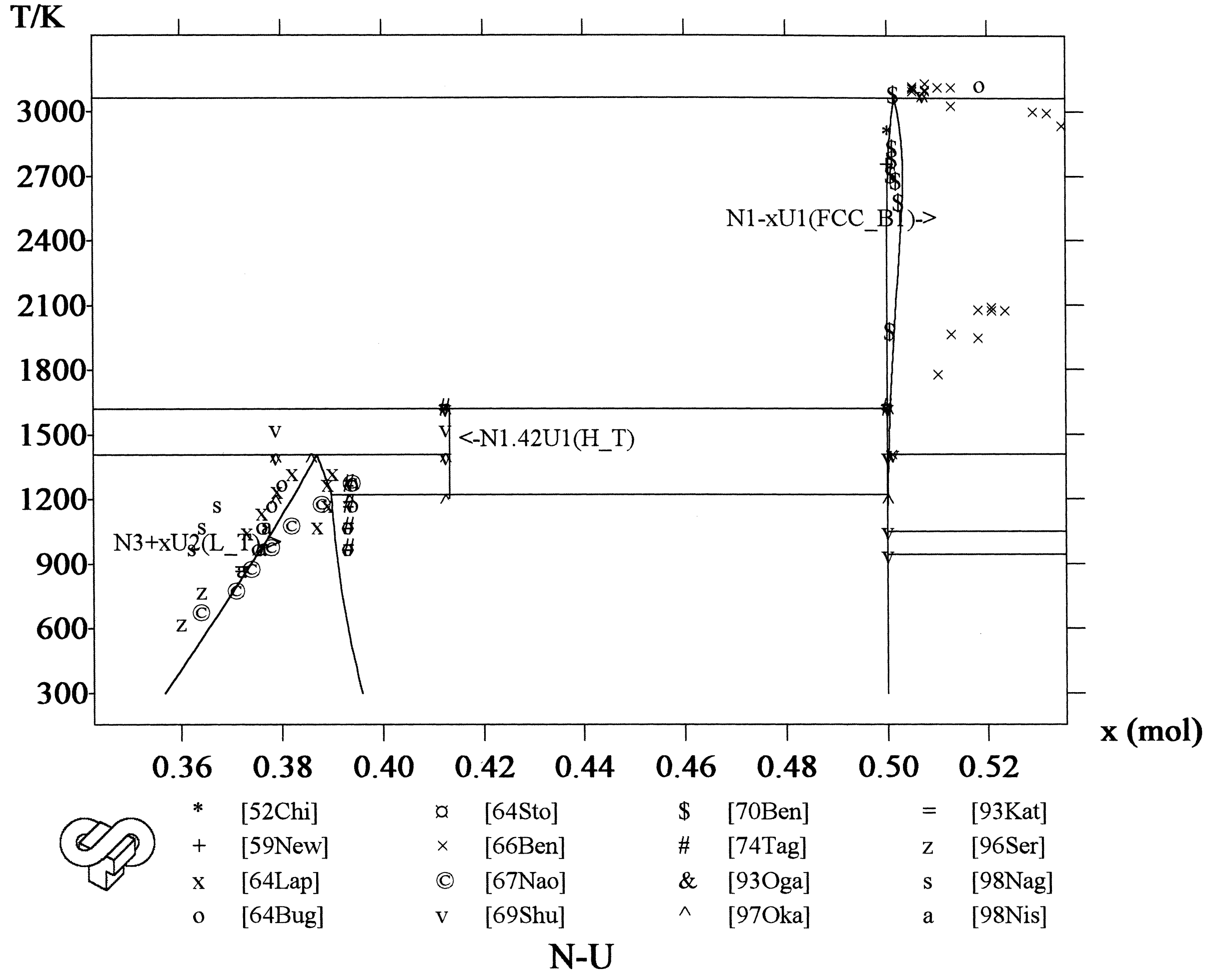


Fig. 2. Enlargement of the non-stoichiometric compounds domain of the N–U equilibrium phase diagram (this work) compared to the experimental information.

obtained from the assessed values of the thermal functions and $\Delta H°f_{298.15\,\mathrm{K}} = -295\,809$ J/mol.

$$C_p(\mathrm{UN}) = 50.54 + 1.066 \times 10^{-2}T - 5.238 \times 10^{5}T^{-2}\ \mathrm{J/(mol\,K)}, \quad (298.15 < T < 1000\ \mathrm{K}), \tag{16}$$

$$C_p(\mathrm{UN}) = 49.96 + 1.112 \times 10^{-2}T - 4.105 \times 10^{5}T^{-2}\ \mathrm{J/(mol\,K)}, \quad (T > 1000\ \mathrm{K}). \tag{17}$$

In a more recent work, Hayes et al. [40] reviewed and collected the experimental thermodynamic data (specific heat, enthalpy, entropy, Gibbs free energy, free energy function, nitrogen and uranium vapour pressures, melting point) of uranium mononitride and developed empirical correlations for these properties versus temperature or nitrogen pressures. This compilation reported the high-temperature calorimetric data of Conway and Flagella [41] for the enthalpy of UN versus temperature, which allowed to extrapolate the heat capacity above 1700 K. Other experimental works of Takahashi et al. [42] and Fulkerson et al. [43] were also taken into account in the UN heat capacity assessment.

The heat of formation, $\Delta H°f_{298.15\,\mathrm{K}}$ (α-U_2N_3), was measured by different authors: Gross et al. [35] obtained $-121\,964$ J for the reaction $2\mathrm{UN} + 0.5\mathrm{N_2} \Longleftrightarrow \mathrm{U_2N_3}$. O'Hare et al. [37] calculated the enthalpy of formation of $\mathrm{UN_{1.51}}$ and $\mathrm{UN_{1.69}}$ to be $-376\,978$ and $-393\,714$ J/mol, respectively ($-385\,346$ for $\mathrm{UN_{1.6}}$). Tagawa [16,18] recalculated $-69\,873$ J/mol for $\mathrm{UN_{1.54}}$. This value is in total disagreement with the others and the more recent ones of Johnson and Cordfunke [38], which gives $-391\,500 \pm 2300$ (α-$\mathrm{UN_{1.674}}$), $-382\,200 \pm 2300$ (α-$\mathrm{UN_{1.606}}$), and $-362\,900 \pm 2300$ (β-$\mathrm{UN_{1.466}}$).

On a modelling aspect, the thermodynamics of gas dissolution in liquid metals with extensive solubility was studied by Wang and Olander [44] who derived the pressure–composition–temperature relationships by using thermodynamic constraints and a modified Sievert's law.

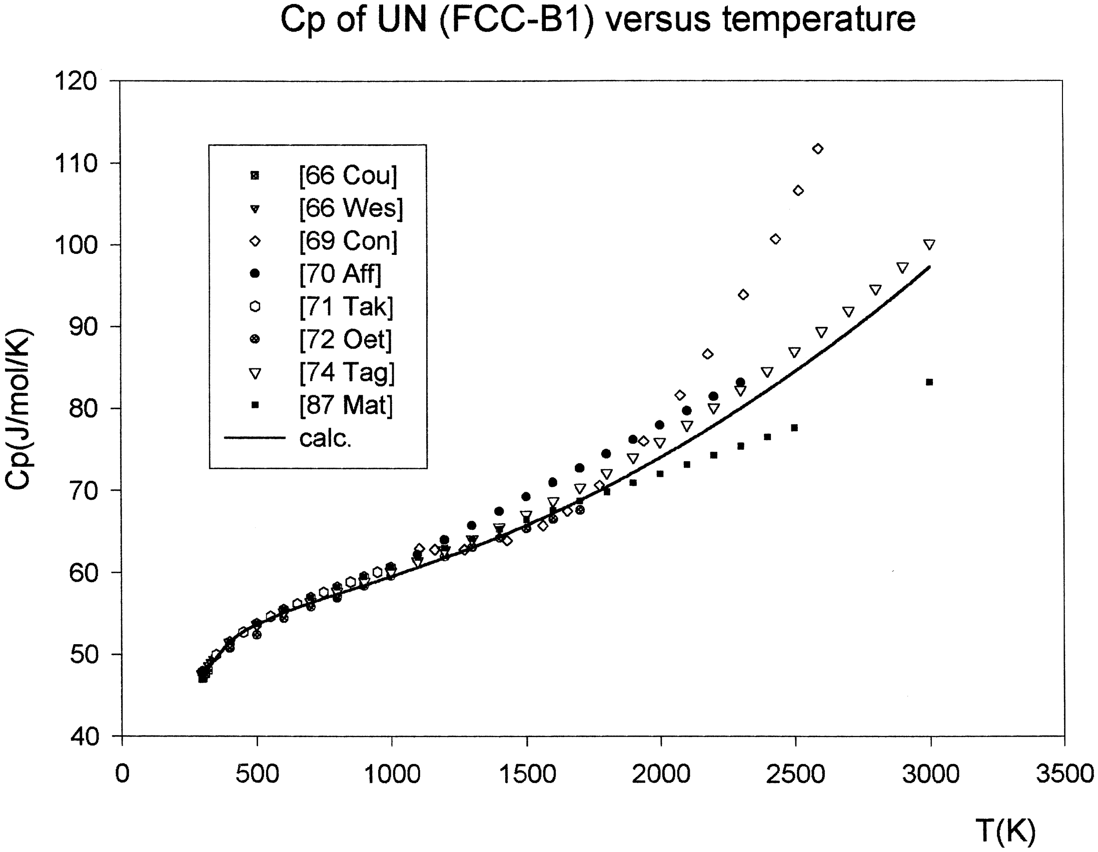


Fig. 3. Calculated specific heat (J/(mol K)) of the uranium mononitride UN(fcc_B1) versus temperature (this work) compared to the experimental or assessed information.

4. Optimization results

4.1. Gibbs energy parameters

All experimental values (phase diagram and thermodynamic properties) have been taken into account in the optimization process, except the two low melting points of UN from Chiotti [11] and Newkirk and Bates [12], and the estimated thermodynamic functions of formation of $UN_{1.54}$ (α-U_2N_3) from Tagawa [16] based on an enthalpy of formation different from the other experimental ones. The optimized Gibbs energy parameters are given in J/mol for solution phases and J/g at. for stoichiometric compounds ($x(\mathrm{N}) + x(\mathrm{U}) = 1$).

The liquid phase was described by an ideal associate model with one lattice, occupied by pure species $N_1(L)$ and $U_1(L)$, and associate species $N_1U_1(L)$. It corresponds to the following formula: $[N_1, N_1U_1, U_1]_1\langle L\rangle$.

The Gibbs energy of the associate species $N_1U_1(L)$ was optimized from the whole experimental information.

$$\Delta G(N_1U_1(L)) = G(N_{0.500}U_{0.500}(L)) - 0.500G(N_1(L)) - 0.500G(U_1(L)).$$

The interaction terms $L[N_1, N_1U_1]_1\langle L\rangle$, $L[N_1, U_1]_1\langle L\rangle$, $L[N_1U_1, U_1]_1\langle L\rangle$ were set to zero.

The non-stoichiometric UN solid solution was described by a two-sublattice model, by assuming the presence of vacancies on the nitrogen sublattice. It corresponds to the following formula: $[N_1, \mathrm{Va}]_1[U_1]_1\langle \mathrm{fcc\_B1}\rangle$.

The Gibbs energy of the nitrogen-rich side of the fcc_B1 solid solution, N_1U_1(fcc_B1), was described by a six-term function versus temperature, and referred either to $N_2(G)$ and U_1(ort_A20) or to the standard element reference (SER) state:

$$\Delta^{(a)}G(N_1U_1(\mathrm{fcc\_B1})) = G(N_{0.500}U_{0.500}(\mathrm{fcc\_B1})) - 0.500G(0.5N_2(G)) - 0.500G(U_1(\mathrm{ort\_A20}))$$

or

$$\Delta^{(b)}G(N_1U_1(\mathrm{fcc\_B1})) = G(N_{0.500}U_{0.500}(\mathrm{fcc\_B1})) - H_{\mathrm{SER}}.$$

The 'lattice-stability' of the fictive fcc_B1 structure for pure uranium, $G(U_1(\mathrm{fcc\_}B1)) - G(U_1(\mathrm{ort\_A20}))$, was arbitrarily fixed to 50 000 J, to be unstable.

The interaction parameter $L[N_1, \mathrm{Va}]_1[U_1]_1\langle \mathrm{fcc\_B_1}\rangle$ was optimized from the selected experimental limit of solubility.

The sesquinitride phase N_3U_2 presents a low-temperature form, α-N_3U_2, and a high-temperature form, β-N_3U_2.

The high-temperature form β-N_3U_2 was considered as a stoichiometric compound, corresponding to the formula $N_{1.42}U_1(H\_T)$.

The low-temperature form α-N_3U_2 was considered as a solid solution with a non-stoichiometry range corresponding to the formula $N_{1.54\text{–}1.75}U_1(L\_T)$. The non-stoichiometric α-N_3U_2 solid solution was also described by a two-sublattice model, by assuming the presence of vacancies on the uranium sublattice. It corresponds to the following formula: $[N_1]_3[\mathrm{Va}, U_1]_2\langle \alpha\text{-}N_3U_2\rangle$.

The Gibbs energy of the stoichiometric compounds $N_{1.42}U_1(H\_T)$ and $N_3U_2(L\_T)$ was described by a six-term function versus temperature, and referred to the standard element reference (SER) state for the first one and to $N_2(G)$ and U_1(bcc_A2) for the second one. The heat capacity of the low- and high-temperature forms was calculated from the estimated one of Tagawa [16,18] and the experimental data of Counsell et al. [28].

The lattice-stability of the fictive $N_3(\alpha\text{-}N_3U_2)$ structure, $G(N_3(\alpha\text{-}N_3U_2)) - G(0.5N_2(G))$, was arbitrarily fixed to 150 000 J, to be unstable.

The interaction parameter $L\_[N_1]_3[\mathrm{Va}, U_1]_2\langle \alpha\text{-}N_3U_2\rangle$ was optimized from the selected experimental limits of solubility.

The gas phase was treated as an ideal mixture of pure species, $N_1(G)$, $N_2(G)$, $N_3(G)$, $U_1(G)$. Thermodynamic data of pure gaseous species are taken from the DATACOMP substance database [2] and reported in Table 9.

All Gibbs energy parameters of condensed solution phases and stoichiometric compounds are stored in a special record of the THERMALLOY solution database [2], devoted to nuclear applications, and reported in Tables 10 and 11. The assessed fundamental thermodynamic properties of N_1U_1(fcc_B1) are reported in Table 12 and stored in DATACOMP substance database [2].

4.2. Comparison of calculated and experimental properties

The calculated phase diagram compared to the available experimental information is presented in Fig. 1. The overall agreement is quite satisfactory. An enlargment of the non-stoichiometric compounds domain is shown in Fig. 2.

The calculated invariant reactions are compared to the experimental ones from Shunk [6], Okamoto [7], Storms [14], Benz and Bowman [15], and Tagawa [16] in Table 1. The temperature of decomposition of UN(fcc_B1) is reported as a function of the total pressure.

The calculated thermal properties (C_p in J/(mol K), $H_T - H_{298}$ in J/mol) of the stoichiometric compound UN are reported in comparison with the experimental values in Table 5 and Fig. 3.

The thermodynamic functions of formation (ΔH_f° in J/mol, ΔS_f° in J/(mol K)) of the stoichiometric compound UN are reported in comparison with the experimental values in Table 7 versus temperature, and in Table 8 at room temperature.

5. Conclusion

The N–U binary system was assessed thermodynamically in this work from the criticism of the available experimental data on both phase diagram and thermodynamic properties.

The liquid phase was described by an ideal associate model, the mononitride and the low-temperature form of the sesquinitride solid solutions by a non-ideal two-sublattices model; the high-temperature form of the sesquinitride was considered as a stoichiometric compound.

A consistent set of Gibbs energy parameters for the various phases was obtained. The agreement between experimental and calculated phase diagram or thermodynamic properties is quite satisfactory. These parameters may be integrated in a solution thermodynamic database for complex calculations in multicomponent systems.

Appendix A

See Tables 9–12.

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