資 料

*On the Thermochemical Properties of Uranium Carbides**

炭化ウランの熱化学的性質

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Although uranium carbides are becoming of considerable interest as nuclear fuel materials, few thermochemical data for these compounds are available and especially lack of specific heat data have made the assessment of these data unreliable. However, recently the authors made the measurement of specific heats on UC and UC₂ above room temperature, and the assessment of experimental data became possible in some accuracy.

In this paper, the specific heat functions for UC and UC₂ were derived as a function of temperature, from which the heats of formation, free energies of formation and entropies of formation of these carbides were also calculated as a function of temperature respectively. Then the assessment of these thermochemical data was carried out on the values so far reported.

In general, it was shown that the measurements at high temperatures by several authors gave a fairly good accordance with some scattering of data, which are not unreasonable in difficult experimental conditions. However, in order to make a more accurate estimation, especially for UC₂, it is considered necessary to obtain further data precisely.

INTRODUCTION

As the uranium carbides are becoming of considerable interest as high-temperature nuclear fuel materials, a knowledge of the thermochemical properties of these carbides is of great importance. In this respect, Huber and Holley⁽¹⁾ have reviewed the present state of knowledge about the heats, free energies, and entropies of the carbides of thorium, uranium and plutonium. As noticed in the paper, few measurements of thermochemical data for the U-C system have been made. However, at the Symposium on the Thermodynamics of Nuclear Materials held on 21 ~25 May 1962 in Vienna, several measured data on uranium carbides were appeared.

The present paper is an assessment of these thermochemical data obtained by several authors. At first, the specific heat functions of UC and UC₂ are estimated against temperature, then, the agreement of these thermochemical data is cross-checked at the same temperature.

The thermochemical properties of U₂C₃ will not be considered here, since the obtained data are not adequate to calculate them.

I. THERMOCHEMICAL PROPERTIES OF URANIUM CARBIDES

1. Specific heats

As the specific heats of uranium carbides, the following estimated values have been known,

$$Cp(UC) = 7.6 + 2.85 \times 10^{-3} T \quad (298^\circ \sim 2,400^\circ K)^{(2)} \quad (1)$$

$$Cp(UC_2) = 8.92 + 3.95 \times 10^{-3} T \quad (\text{No temperature range given})^{(3)}. \quad (2)$$

Boettcher and Schneider⁽⁴⁾ have reported the values of UC at 125° and 250°C as 0.048

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± 0.03 and 0.053 ± 0.003 cal/g°C respectively, from which the following equation was taken as the specific heat function of UC in the range of $298^\circ \sim 2,000^\circ\text{C}$ by Huber and Holley⁽⁴⁾.

$$C_p(\text{UC}) = 8.0 + 0.010T. \quad (3)$$

We have measured the specific heats of UC and UC_2 in the range of $100^\circ \sim 400^\circ\text{C}$ ⁽⁵⁾.

These data are shown in Fig. 1. It is seen from Fig. 1 that the estimated values by Eqs. (1) and (2) are too low, and the values by Eq. (3) are too high at high temperatures.

- ① $C_p(\text{UC})$ measured by Mukaibo, *et al.*
- ② $C_p(\text{UC})$ by Eq. (1)
- ③ $C_p(\text{UC})$ by Eq. (3)
- ④ $C_p(\text{UC})$ by Eq. (4)
- ⑤ $C_p(\text{UC}_2)$ measured by Mukaibo, *et al.*
- ⑥ $C_p(\text{UC}_2)$ by Eq. (5)
- ⑦ $C_p(\text{UC}_2)$ by Eq. (2)

Fig. 1 Specific heats of UC and UC_2

As the data measured are not sufficient to estimate the specific heats at high temperature, the following relation was assumed for estimating them,

$$\begin{aligned} C_p(\text{UC}) &= C_p(\gamma\text{-U or liq. U}) + C_p(\text{C}) \\ &= 13.30 + 1.02 \times 10^{-3}T - 2.1 \\ &\quad \times 10^5/T^2 \quad (298^\circ \sim 2,300^\circ\text{K}) \quad (4) \end{aligned}$$

$$\begin{aligned} C_p(\text{UC}_2) &= C_p(\gamma\text{-U or liq. U}) + 2C_p(\text{C}) \\ &= 17.40 + 2.04 \times 10^{-3}T - 4.2 \\ &\quad \times 10^5/T^2 \quad (298^\circ \sim 2,300^\circ\text{K}). \quad (5) \end{aligned}$$

The agreement of the estimated values by these equations with the measured data is satisfactory as seen in Fig. 1. It should be noticed that the assumption of Eqs. (4) and (5) is equivalent to assume $\Delta C_p = 0$ at temperatures higher than $1,045^\circ\text{K}$ in the formation of uranium carbides.

2. Heats of formation

Uranium monocarbide, UC: The published

measurements of heats of formation of UC are $\Delta H^\circ_{298} = -20 \pm 5$ kcal/mole by Droege, *et al.*⁽⁶⁾ and $\Delta H^\circ_{298} = -21.0 \pm 1.0$ kcal/mole by Farr, *et al.*⁽⁷⁾ Both were obtained by measuring the heat of combustion of UC, and the agreement is good. Huber and Holley⁽⁴⁾ took the weighed average of both data, $\Delta H^\circ_{298} = -20.8 \pm 0.9$ kcal/mole as the heat of formation of UC.

Alcock and Grieseson⁽⁸⁾ have reported the following equation for the free energy of formation of UC by the activity measurement,

$$\Delta G^\circ_T = -25,200 + 3.6T \quad (1,723^\circ \sim 1,823^\circ\text{K}). \quad (7)$$

The heat of formation is calculated from Eq. (7) as $\Delta H^\circ_{1,723 \sim 1,823} = -25.2$ kcal/mole.

In order to check this value, we have calculated ΔH°_T using the value of $\Delta H^\circ_{298} = -20.8$ kcal/mole and Eq. (4). The results are shown in Fig. 2, and the details of the calculation are shown in the Appendix. As seen from Fig. 2, the calculated value of $\Delta H^\circ_{1,723 \sim 1,823}$ is -25.5 kcal/mole.

- ① ΔH°_T by Eq. (16)
- ② ΔH°_T by Huber & Holley

Fig. 2 Heats of formation of UC

Since the agreement of both measured values is quite satisfactory, the value of $\Delta H^\circ_{298} = -20.8$ kcal/mole seems to be more reliable than other estimated values of ΔH°_{298} such as -40 kcal/mole by Brewer, *et al.*⁽⁹⁾, -43 kcal/mole by Brewer, *et al.*⁽¹⁰⁾, and -28 ± 6 kcal/mole by Krikorian⁽¹¹⁾.

The Huber and Holley's estimation for ΔH°_T ⁽⁴⁾ is also shown in Fig. 2, which has higher values at high temperatures because of the higher values of specific heat of UC

taken.

Uranium dicarbide, UC_2 : Huber and Holley⁽¹⁾ have measured the heat of formation of $UC_{1.86}$ as $\Delta H^\circ_{298} = -18 \pm 4$ kcal/mole by measuring heat of combustion. The other measured values of ΔH° have been obtained by measuring the dissociation pressure of UC_2 at high temperatures. The following equations were calculated by combining the dissociation pressures of uranium dicarbide reported by respective authors with the value for the free energy of vaporization of uranium measured by Alcock and Grievson⁽¹²⁾.

$$\Delta G^\circ_r = -30,000 + 1.53T(2,450^\circ \sim 2,730^\circ K)$$

by Fujishiro⁽¹³⁾, (9)

$$\Delta G^\circ_r = -22,300 - 5.73T(1,930^\circ \sim 2,365^\circ K)$$

by Leitnaker & Witteman⁽¹⁴⁾, (10)

$$\Delta G^\circ_r = -19,900 - 5.80T(2,000^\circ \sim 2,900^\circ K)$$

by Lonsdale & Graves⁽¹⁵⁾, (11)

$$\Delta G^\circ_r = -32,600 + 3.6T(1,973^\circ \sim 2,073^\circ K)$$

by Alcock & Grievson⁽⁶⁾, (12)

$$\Delta G^\circ_r = -48,100 + 4.49T(2,060^\circ \sim 2,460^\circ K)$$

by Eick, *et al.*⁽¹⁶⁾ (13)

Fig. 3 shows the values of ΔH°_r obtained from these Eqs.(9)~(13) and Eq. (5). In this figure, ΔH°_r calculated from Huber and Holley's value of $\Delta H^\circ_{298} = -18$ kcal/mole is also shown. As a whole, the agreement of these values is not good with the exception

- ① ΔH°_r from the data by Fujishiro
- ② ΔH°_r from the data by Leitnaker & Witteman
- ③ ΔH°_r from the data by Lonsdale & Graves
- ④ ΔH°_r from the data by Alcock & Grievson
- ⑤ ΔH°_r from the data by Eick, *et al.*
- ⑥ ΔH°_r from the data by Huber & Holley

Fig. 3 Heats of formation of UC_2

that ΔH°_r by Leitnaker and Witteman is in good accordance with that by Huber and Holley.

The estimated values of ΔH°_{298} are also known as -36 kcal/mole by Brewer, *et al.*⁽⁹⁾⁽¹⁰⁾, -42 kcal/mole by Rossini, *et al.*⁽¹⁷⁾, and -27 ± 8 kcal/mole by Krikorian⁽¹¹⁾.

The disagreement of these values leads to the conclusion that more careful measurement will be needed.

3. Free energies of formation

Uranium monocarbide, UC: The data by Alcock and Grievson⁽⁶⁾ shown in Eq.(7) represents the only measurement of the free energy of formation of uranium monocarbide. Then, as shown in the Appendix, we calculated ΔG°_r by using the value of $\Delta G^\circ_{1,800}$ from Eq.(7) and ΔH°_r functions obtained already.

The results are shown in Fig. 4. ΔG°_{298} is obtained as -20.5 kcal/mole.

Fig. 4 Free energies of formation of UC

In this figure, the estimated equations for ΔG°_r by Huber and Holley⁽¹⁾ and by Ward⁽²⁾ are also shown.

As the estimated value of ΔG°_{298} of UC, Brewer, *et al.*⁽⁹⁾ have reported -41 kcal/mole. It is necessary to have more experimental data in order to make the evaluation of values mentioned above.

Uranium dicarbide, UC_2 : The measured values of ΔG° of UC_2 are shown in Eqs. (9)~(13) which were all obtained by measuring the dissociation pressure of UC_2 at high temperatures.

ΔG°_r were calculated from Eqs.(9)~(13) and Eq.(5) as shown in the Appendix,

and the results are given in Fig. 5. In this figure, the curve ⑥ was obtained by using the value of $\Delta G^\circ_{2,023}$ from Alcock and Grievson's measurement and ΔH°_T function from Huber and Holley's measurement.

As seen from Fig. 5, the values of ΔG°_{298} are in the range of $-18 \sim -43$ kcal/mole.

The estimated equations for ΔG°_T by Huber and Holley⁽¹⁾ and by Ward⁽²⁾ are shown in Fig. 5.

- ① ΔG°_T from the data by Fujishiro
- ② ΔG°_T from the data by Leitnaker & Witterman
- ③ ΔG°_T from the data by Lonsdale & Graves
- ④ ΔG°_T from the data by Alcock & Grievson
- ⑤ ΔG°_T from the data by Eick, *et al.*
- ⑥ ΔG°_T from the data by Huber & Holley, and Alcock & Grievson
- ⑦ ΔG°_T by Huber & Holley
- ⑧ ΔG°_T by Ward

Fig. 5 Free energies of formation of UC_2

The estimated values of ΔG°_{298} of UC_2 are known as -38 kcal/mole by Brewer, *et al.*⁽⁹⁾, -42 kcal/mole by Rossini, *et al.*⁽¹⁷⁾

To evaluate these values, it is necessary to determine ΔG° at lower temperatures.

4. Entropies of formation

Uranium monocarbide, UC: There are no measurements of low temperature heat capacities from which the entropy of UC could be determined.

The estimated values of ΔS°_{298} of UC are known as $+2$ e.u. by Brewer, *et al.*⁽⁹⁾, -2 e.u. by Brewer, *et al.*⁽¹⁰⁾, -3.4 e.u. by Ward⁽²⁾, -1.5 ± 1.5 e.u. by Krikorian⁽¹¹⁾, and -2.1 e.u. by Huber and Holley⁽¹⁾, which are scattered around 0 e.u.

We have made the calculation of ΔS°_T by using ΔH°_T and ΔG°_T functions determined

above. The results are shown in Fig. 6. The value of ΔS°_{298} is derived to be -0.9 e.u., which gives the entropy of UC as $S^\circ_{298} = 12.5$ e.u.

Fig. 6 Entropy of formation of UC

Uranium dicarbide, UC_2 : No experimental data of low temperature heat capacities of UC_2 are available.

The estimated values of ΔS°_{298} of UC_2 are known as $+4$ e.u. by Brewer, *et al.*⁽⁹⁾, -0.8 e.u. (or $S^\circ_{298}(UC_2) = 14$ e.u.) by Rossini, *et al.*⁽¹⁷⁾, -5 e.u. by Brewer, *et al.*⁽¹⁰⁾, $+2.8 \pm 3.0$ e.u. by Krikorian⁽¹¹⁾, and $+4.1$ e.u. (or $S^\circ_{298}(UC_2) = 18.88$ e.u.) by Leitnaker and Witterman⁽¹³⁾.

Fig. 7 shows the results of our calculation of ΔS°_T . The values of ΔS°_{298} are in the

- ① ΔS°_T from the data by Fujishiro
- ② ΔS°_T from the data by Leitnaker & Witterman
- ③ ΔS°_T from the data by Lonsdale & Graves
- ④ ΔS°_T from the data by Alcock & Grievson
- ⑤ ΔS°_T from the data by Eick, *et al.*
- ⑥ ΔS°_T from the data by Huber & Holley, and Alcock & Grievson

Fig. 7 Entropies of formation of UC_2

range of $-1.3 \sim +8.7$ e.u., which give the value of the entropy of UC_2 in the range of $13.5 \sim 23.5$ e.u.

II. CONCLUSION

The assessment of such thermochemical data of UC and UC_2 as heat capacity, heat of formation and free energy of formation was carried out on the values so far reported.

In general, it was recognized that the measurements at high temperatures by several authors gave a fairly good accordance with some scattering of data, which are not unreasonable in difficult experimental conditions.

However, in order to make a more accurate estimation, especially for UC_2 , it is considered to be necessary to obtain further data on such items as the heat of combustion at lower temperatures with samples of the accurately known assay, or a measurement of free energy of formation by some direct method, such as e.m.f. measurements using UC or UC_2 as an electrode.

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[Appendix]

Specific heats

The specific heats of UC and UC_2 were obtained assuming that

$$Cp(UC) = Cp(\gamma\text{-U or liq. U}) + Cp(C) \quad (4)'$$

$$Cp(UC_2) = Cp(\gamma\text{-U or liq. U}) + 2Cp(C) \quad (5)'$$

Taking⁽¹⁸⁾

$$Cp(\gamma\text{-U}) = Cp(\text{liq. U}) = 9.2 \quad (\text{above } 1,045^\circ\text{K})$$

$$Cp(\text{graphite}) = 4.10 + 1.02 \times 10^{-3}T - 2.1 \times 10^5/T^2 \quad (298^\circ \sim 2,300^\circ\text{K})$$

we have

$$Cp(UC) = 13.30 + 1.02 \times 10^{-3}T - 2.1 \times 10^5/T^2 \quad (298^\circ \sim 2,300^\circ\text{K}) \quad (4)$$

$$Cp(UC_2) = 17.40 + 2.04 \times 10^{-3}T - 4.2 \times 10^5/T^2 \quad (298^\circ \sim 2,300^\circ\text{K}). \quad (5)$$

Heats of formation

Uranium monocarbide: We calculate the heat of formation for U (α -, β -, γ -, liq.) + C(s) $\rightarrow$ UC(s).

Taking⁽¹⁸⁾⁽¹⁹⁾

$$\left. \begin{aligned} Cp(\alpha\text{-U}) &= 3.3 + 8.02 \times 10^{-3}T + 0.7 \times 10^5/T^2 \quad (298^\circ \sim 935^\circ\text{K}) \\ Cp(\beta\text{-U}) &= 10.2 \quad (935^\circ \sim 1,045^\circ\text{K}) \\ Cp(\gamma\text{-U}) &= 9.2 \quad (1,045^\circ \sim 1,405^\circ\text{K}) \\ Cp(\text{liq. U}) &= 9.2 \quad (1,405^\circ \sim 3,000^\circ\text{K}) \\ \alpha\text{-U} \rightarrow \beta\text{-U} &: \Delta H = 674 \text{ cal} \quad (935^\circ\text{K}) \\ \beta\text{-U} \rightarrow \gamma\text{-U} &: \Delta H = 1,085 \text{ cal} \quad (1,045^\circ\text{K}) \\ \gamma\text{-U} \rightarrow \text{liq. U} &: \Delta H = 3,200 \text{ cal} \quad (1,405^\circ\text{K}) \\ Cp(\text{graphite}) &= 4.10 + 1.02 \times 10^{-3}T - 2.1 \times 10^5/T^2 \quad (298^\circ \sim 2,300^\circ\text{K}). \end{aligned} \right\} \quad (14)$$

we have

$$\left. \begin{aligned} \Delta Cp &= 5.9 - 8.02 \times 10^{-3}T - 0.7 \times 10^5/T^2 \quad (298^\circ \sim 935^\circ\text{K}) \\ \Delta Cp &= -1.0 \quad (935^\circ \sim 1,045^\circ\text{K}) \\ \Delta Cp &= 0 \quad (\text{above } 1,045^\circ\text{K}). \end{aligned} \right\} \quad (15)$$

We then get the following equations

$$\left. \begin{aligned} \Delta H^\circ_r &= \Delta H^\circ_{298} + \int_{298}^T Cp dT \\ &= -20,800 + \int_{298}^T Cp dT \\ \Delta H^\circ_r &= -22,440 + 5.9T - 4.01 \times 10^{-3}T^2 + 0.7 \times 10^5/T \quad (298^\circ \sim 935^\circ\text{K}) \\ \Delta H^\circ_r &= -20,120 - 1.0T \quad (935^\circ \sim 1,045^\circ\text{K}) \\ \Delta H^\circ_r &= 22,250 \quad (1,045^\circ \sim 1,405^\circ\text{K}) \\ \Delta H^\circ_r &= -25,450 \quad (\text{above } 1,405^\circ\text{K}). \end{aligned} \right\} \quad (16)$$

Uranium dicarbide: Using the values of respective specific heats shown above, ΔCp for U (α -, β -, γ -, liq.) + 2C(s) $\rightarrow UC_2$ (s) are calculated as follows

$$\left. \begin{aligned} \Delta Cp &= 5.9 - 8.02 \times 10^{-3}T - 0.7 \times 10^5/T^2 \quad (298^\circ \sim 935^\circ\text{K}) \\ \Delta Cp &= -1.0 \quad (935^\circ \sim 1,045^\circ\text{K}) \\ \Delta Cp &= 0 \quad (\text{above } 1,045^\circ\text{K}). \end{aligned} \right\} \quad (17)$$

Then, the heat of formation is obtained by taking Huber and Holley's value⁽¹⁾, $\Delta H^\circ_{298} = -18,000$ cal/mole,

$$\left. \begin{aligned} \Delta H^\circ_r &= -19,640 + 5.9T - 4.01 \\ &\quad \times 10^{-3}T^2 + 0.7 \times 10^5/T \\ &\quad (298^\circ \sim 935^\circ\text{K}) \\ \Delta H^\circ_r &= -17,320 - 1.0T \\ &\quad (935^\circ \sim 1,045^\circ\text{K}) \\ \Delta H^\circ_r &= -19,450 (1,045^\circ \sim 1,405^\circ\text{K}) \\ \Delta H^\circ_r &= -22,650 \text{ (above } 1,405^\circ\text{K).} \end{aligned} \right\} (18)$$

On the other hand, the following measured data of dissociation pressure of UC_2 at high temperatures are reported

$$\log P = \alpha/T + \beta \quad (20)$$

where,

α	β	Temperature range ($^\circ\text{K}$)	Reference
-30,600	6.36	2,450~2,730	Fujishiro ⁽¹²⁾
-28,930	4.77	1,930~2,365	Leitnaker & Witteman ⁽¹³⁾
-28,400	4.76	2,000~2,900	Lonsdale & Graves ⁽¹⁴⁾
-31,170	6.81	1,973~2,073	Alcock & Grievesson ⁽⁶⁾
-34,586	7.01	2,060~2,460	Eick, <i>et al.</i> ⁽¹⁵⁾

The pressure equations are converted to the free energy of formation equations using the relation

$$\Delta G^\circ = -RT \ln P \quad (21)$$

$$\left. \begin{aligned} \Delta G^\circ_r &= +140,000 - 29.10T \\ &\quad \text{by Fujishiro} \\ \Delta G^\circ_r &= +132,320 - 21.82T \\ &\quad \text{by Leitnaker & Witteman} \\ \Delta G^\circ_r &= +129,900 - 21.77T \\ &\quad \text{by Lonsdale & Graves} \\ \Delta G^\circ_r &= +142,600 - 31.17T \\ &\quad \text{by Alcock & Grievesson} \\ \Delta G^\circ_r &= +158,100 - 32.06T \\ &\quad \text{by Eick, *et al.*} \end{aligned} \right\} (22)$$

Combining the equations with the values for the free energy of vaporization of uranium measured by Alcock and Grievesson⁽¹⁶⁾, the following free energy of formation equations of UC_2 from liquid uranium and solid carbon are obtained

$$\Delta G^\circ_r = -30,000 + 1.53T \quad \text{by Fujishiro (9)}$$

$$\Delta G^\circ_r = -22,320 - 5.73T \quad \text{by Leitnaker & Witteman (10)}$$

$$\Delta G^\circ_r = -19,900 - 5.80T \quad \text{by Lonsdale & Graves (11)}$$

$$\Delta G^\circ_r = -32,600 + 3.6T \quad \text{by Alcock & Grievesson (12)}$$

$$\Delta G^\circ_r = -48,100 + 4.49T \quad \text{by Eick, *et al.* (13)}$$

ΔH° at each temperature region are obtained according to the relation

$$\Delta H = -[\partial(\Delta G/T)/\partial T]T^2 \quad (23)$$

$$\left. \begin{aligned} \Delta H^\circ (2,450^\circ \sim 2,730^\circ\text{K}) &= -30,000 \\ &\quad \text{by Fujishiro} \\ \Delta H^\circ (1,930^\circ \sim 2,365^\circ\text{K}) &= -22,320 \\ &\quad \text{by Leitnaker & Witteman} \\ \Delta H^\circ (2,000^\circ \sim 2,900^\circ\text{K}) &= -19,900 \\ &\quad \text{by Lonsdale & Graves} \\ \Delta H^\circ (1,973^\circ \sim 2,073^\circ\text{K}) &= -32,600 \\ &\quad \text{by Alcock & Grievesson} \\ \Delta H^\circ (2,060^\circ \sim 2,460^\circ\text{K}) &= -48,100 \\ &\quad \text{by Eick, *et al.*} \end{aligned} \right\} (24)$$

Then, the heat of formation equations of UC_2 are derived according to the relation

$$\Delta H^\circ_r = \int \Delta C_p dT + I \quad (25)$$

where, the constant, I , above $1,405^\circ\text{K}$ is evaluated from the value of ΔH° obtained above.

Then

$$\left. \begin{aligned} \Delta H^\circ_r &= a_1 + 5.9T - 4.01 \times 10^{-3}T^2 \\ &\quad + 0.7 \times 10^5/T \text{ (} 298^\circ \sim 935^\circ\text{K)} \\ \Delta H^\circ_r &= a_2 - 1.0T \text{ (} 935^\circ \sim 1,045^\circ\text{K)} \\ \Delta H^\circ_r &= a_3 \text{ (} 1,045^\circ \sim 1,405^\circ\text{K)} \\ \Delta H^\circ_r &= a_4 \text{ (above } 1,405^\circ\text{K)} \end{aligned} \right\} (26)$$

here,

$$\left. \begin{array}{cccc} a_1 & a_2 & a_3 & a_4 \\ -26,990 & -24,670 & -26,800 & -30,000 \\ & & & \text{by Fujishiro} \\ -19,340 & -16,990 & -19,120 & -22,320 \\ & & & \text{by Leitnaker & Witteman} \\ -16,890 & -14,570 & -16,700 & -19,900 \\ & & & \text{by Lonsdale & Graves} \\ -29,590 & -27,200 & -29,400 & -32,600 \\ & & & \text{by Alcock & Grievesson} \\ -45,090 & -42,770 & -44,900 & -48,100 \\ & & & \text{by Eick, *et al.*} \end{array} \right\} (26)'$$

The values of ΔH°_{298} thus calculated are shown below.

$$\left. \begin{array}{ccc} \text{Reference} & \text{Fujishiro} & \text{Leitnaker,} \\ & & \text{Witteman} \\ \Delta H^\circ_{298} & -25.3 & -17.7 \\ (\text{kcal/mole}) & & \\ \text{Lonsdale,} & \text{Alcock,} & \text{Eick,} \\ \text{Graves} & \text{Grievesson} & \text{et al.} \\ -15.3 & -28.0 & -43.4 \end{array} \right\} (27)$$

Free energies of formation

Uranium monocarbide: The free energies of formation for $\text{U}(\alpha-, \beta-, \gamma-, \text{liq.}) + \text{C}(s)$

→UC(s) are derived according to the relation

$$\Delta G^\circ_r/T = -\int (\Delta H^\circ_r/T^2) dT + I \quad (28)$$

where, H°_r have been obtained as shown in Eq.(16), and the constant, I , above 1,405°K is evaluated from the following experimental value by Alcock and Grieverson⁽⁸⁾

$$\Delta G^\circ_r = -25,200 + 3.6T \quad (1,723^\circ \sim 1,823^\circ K) \quad (7)$$

Using the value, $\Delta G^\circ_{1,800} = -18,720$ cal/mole, we get the following free energy equations

$$\left. \begin{aligned} \Delta G^\circ_r &= -22,440 + 38.37T - 13.59T \log T \\ &\quad + 0.35 \times 10^5/T + 4.01 \times 10^{-3}T^2 \\ &\quad (298^\circ \sim 935^\circ K) \\ \Delta G^\circ_r &= -20,120 - 7.530T + 2.303T \log T \\ &\quad (935^\circ \sim 1,045^\circ K) \\ \Delta G^\circ_r &= -22,250 + 1.461T \\ &\quad (1,045^\circ \sim 1,405^\circ K) \\ \Delta G^\circ_r &= -25,450 + 3.739T \\ &\quad (\text{above } 1,405^\circ K). \end{aligned} \right\} \quad (29)$$

From these equations we find

$$\Delta G^\circ_{298} = -20.5 \text{ kcal/mole.} \quad (30)$$

Uranium dicarbide: The experimental data of ΔG°_r for the reaction, $U(l) + 2C(s) \rightarrow UC_2(s)$, are shown in Eqs. (9)~(13). Then, ΔG°_r at each temperature range are derived by using Eqs.(28) and (26) as following

$$\left. \begin{aligned} \Delta G^\circ_r &= a_1 + b_1T - 13.59T \log T + 0.35 \\ &\quad \times 10^5/T + 4.01 \times 10^{-3}T^2 \\ &\quad (298^\circ \sim 935^\circ K) \\ \Delta G^\circ_r &= a_2 + b_2T + 2.303T \log T \\ &\quad (935^\circ \sim 1,045^\circ K) \\ \Delta G^\circ_r &= a_3 + b_3T \quad (1,045^\circ \sim 1,405^\circ K) \\ \Delta G^\circ_r &= a_4 + b_4T \quad (\text{above } 1,405^\circ K) \end{aligned} \right\} \quad (31)$$

where, the values of a_1 – a_4 are shown in Eq. (26)', and b_1 – b_4 are

$$\left. \begin{array}{cccc} b_1 & b_2 & b_3 & b_4 \\ +36.2 & -9.72 & -0.744 & +1.533 \\ & & & \text{by Fujishiro} \\ +28.94 & -17.00 & -8.011 & -5.733 \\ & & & \text{by Leitnaker \& Witteman} \\ +28.84 & -17.06 & -8.078 & -5.80 \\ & & & \text{by Lonsdale \& Graves} \\ +38.21 & -7.690 & +1.332 & +3.6 \\ & & & \text{by Alcock \& Grieverson} \\ +39.2 & -6.76 & +2.21 & +4.49 \\ & & & \text{by Eick, et al.} \end{array} \right\} \quad (31)'$$

We then get the values of ΔG°_{298} as follows.

Reference	Fujishiro	Leitnaker, Witteman
ΔG°_{298} (kcal/mole)	-25.7	-20.3
Lonsdale, Graves	Alcock, Grieverson	Eick, et al.
-17.8	-27.7	-43.0

(32)

As ΔH°_r , we derived another equation from the value obtained by Huber and Holley⁽¹¹⁾ as shown in Eq.(18). From this equation, we can also calculate ΔG°_r according to Eq.(28).

However, the constant, I , should be evaluated from the value of ΔG° at given temperature. If we take $\Delta G^\circ_{2,023} = -25,320$ cal/mole, from the measurement by Alcock and Grieverson⁽¹²⁾ shown in Eq.(12), for example, we get the following equation of ΔG°_r

$$\left. \begin{aligned} \Delta G^\circ_r &= -19,640 + 33.25T - 13.59T \log T \\ &\quad + 4.01 \times 10^{-3}T^2 + 0.35 \times 10^5/T \\ &\quad (298^\circ \sim 935^\circ K) \\ \Delta G^\circ_r &= -17,320 - 11,940T + 2.303T \log T \\ &\quad (935^\circ \sim 1,045^\circ K) \\ \Delta G^\circ_r &= -19,450 - 3.646T \\ &\quad (1,045^\circ \sim 1,405^\circ K) \\ \Delta G^\circ_r &= -22,650 - 1.362T \\ &\quad (\text{above } 1,405^\circ K). \end{aligned} \right\} \quad (33)$$

Similar calculation can be made with any value from Eqs.(9)~(13).

Entropies of formation

Uranium monocarbide: The entropies of formation for $U(\alpha, \beta, \gamma, \text{liq.}) + C(s) \rightarrow UC(s)$ are derived according to the relation

$$\Delta S = (\Delta H - \Delta G)/T \quad (34)$$

From Eqs.(16), (29) and (34), we get

$$\left. \begin{aligned} \Delta S^\circ_r &= -32.470 + 13.59 \log T - 8.02 \\ &\quad \times 10^{-3}T + 0.35 \times 10^5/T^2 \\ &\quad (298^\circ \sim 935^\circ K) \\ \Delta S^\circ_r &= 6.530 - 2.303 \log T \\ &\quad (935^\circ \sim 1,045^\circ K) \\ \Delta S^\circ_r &= -1.46 \quad (1,045^\circ \sim 1,405^\circ K) \\ \Delta S^\circ_r &= -3.74 \quad (\text{above } 1,405^\circ K). \end{aligned} \right\} \quad (35)$$

Then

$$\Delta S^\circ_{298} = -0.9 \text{ e.u.} \quad (36)$$

Uranium dicarbide: From Eqs.(26), (31) and (34), we have the following equations

$$\left. \begin{aligned} \Delta S^\circ_r &= -(b_1 - 5.9) + 13.59 \log T - 8.02 \\ &\quad \times 10^{-3} T + 0.35 \times 10^3 / T^2 \\ &\quad (298^\circ \sim 935^\circ \text{K}) \\ \Delta S^\circ_r &= -(b_2 + 1.0) - 2.303 \log T \\ &\quad (935^\circ \sim 1,045^\circ \text{K}) \\ \Delta S^\circ_r &= -b_3 \quad (1,045^\circ \sim 1,405^\circ \text{K}) \\ \Delta S^\circ_r &= -b_4 \quad (\text{above } 1,405^\circ \text{K}) \end{aligned} \right\} (37)$$

where, the values of b_1 – b_4 are shown in Eq. (31)'.

The values of ΔS°_{298} thus calculated are shown below.

$$\left. \begin{array}{ccc} \text{Reference} & \text{Fujishiro} & \text{Leitnaker,} \\ & & \text{Witteman} \\ \Delta S^\circ_{298} (\text{e.u.}) & +1.3 & +8.7 \\ \text{Lonsdale,} & \text{Alcock} & \text{Eick,} \\ \text{Graves} & \text{Grieverson} & \text{et al.} \\ & +8.7 & -0.7 & -1.3 \end{array} \right\} (38)$$

From Eqs. (18), (33) and (34),

$$\left. \begin{aligned} \Delta S^\circ_r &= -27.35 + 13.59 \log T - 8.02 \\ &\quad \times 10^{-3} T + 0.35 \times 10^3 / T^2 \\ &\quad (298^\circ \sim 935^\circ \text{K}) \\ \Delta S^\circ_r &= 10.94 - 2.303 \log T \\ &\quad (935^\circ \sim 1,045^\circ \text{K}) \\ \Delta S^\circ_r &= -3.65 \quad (1,045^\circ \sim 1,405^\circ \text{K}) \\ \Delta S^\circ_r &= -1.36 \quad (\text{above } 1,405^\circ \text{K}) \end{aligned} \right\} (39)$$

$$\text{Then } \Delta S^\circ_{298} = +4.2 \text{ e.u.} \quad (40)$$

These results obtained are summarized in Table 1.

Table 1 Thermochemical functions for the formation of uranium carbides

Compound	ΔH°_{298} (kcal/ mole)	ΔG°_{298} (kcal/ mole)	ΔS°_{298} (e.u.)	S°_{298} (e.u.)	Reference
UC	-20.8 ± 0.9	-20.5	-0.9	12.5	Huber & Holley ⁽¹⁾ , and Alcock & Grieverson ⁽⁸⁾
UC ₂	-18.0 ± 4				Huber & Holley ⁽¹⁾
	-25.3	-25.7	+1.3	16.1	Fujishiro ⁽¹³⁾
	-17.7	-20.3	+8.7	23.5	Leitnaker & Witteman ⁽¹⁴⁾
	-15.3	-17.8	+8.7	23.5	Lonsdale & Graves ⁽¹⁵⁾
	-28.0	-27.7	-0.7	14.1	Alcock & Grieverson ⁽⁸⁾
	-43.4	-43.0	-1.3	13.5	Eick, et al. ⁽⁶¹⁾
	-18.0	-19.2	+4.2	19.0	Huber & Holley ⁽¹⁾ , and Alcock & Grieverson ⁽⁸⁾

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