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Abstract

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PHYSICAL CHEMISTRY

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DEPENDENCE OF THE HEATS AND FREE ENERGIES OF FORMATION OF ZIRCONIUM NITRIDES ON COMPOSITION AND STRUCTURE

(Presented by Academician V. A. Kargin, 25 IV 1957)

In the literature it is customary to regard zirconium nitride as a phase of constant composition and to assign to it formulas with various integral coefficients ([1–10]). Accordingly, in thermochemical and thermodynamic studies of zirconium nitride, the data obtained were referred to the integral composition ZrN ([5,6,11–14,22]).

In the present work, using methods of precision X-ray and chemical analysis, we have shown that the composition ZrN is only a special case. In connection with this, it is important to investigate the dependence of the change in the heat of formation on the composition and structure of zirconium nitride.

Experimental Part

The starting materials were zirconium containing 1% hafnium (according to spectral-analysis data) and thoroughly purified nitrogen. The nitrides were synthesized in a furnace constructed by us with a tungsten heater ([15]), at an initial vacuum of 10^{-4} mm Hg and at temperatures up to 2500°K. The equilibrium of the compositions was attained by establishing the equilibrium pressure of nitrogen over the nitride phase. The preparations obtained were subjected to chemical and X-ray analysis. The heats of formation were determined by thermochemical combustion in a microbomb in an isothermal calorimeter. The thermal value (992.3 cal/degree) was established using standard benzoic acid with a heat of combustion of 6329 cal/g (Leningrad Institute of Metrology).

The best combustion of the nitrides occurred at an oxygen pressure of ~ 16 atm. At higher pressures, spraying of the products occurred. In order to exclude interaction of the burning sample with the quartz crucible (the nitride charge was of the order of 600 mg), a lining of calcined ZrO_2 was used. The initial and

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final combustion periods were 10 min each, the main period 8–10 min, and the temperature rise was $\sim 1.2^{\circ}$. Corrections were introduced: for the protruding mercury column of the Beckmann thermometer, for heat loss by the calorimeter to the surrounding medium, and for Joule heat liberated when electric current was passed through the platinum wire (during ignition of the preparation). The combustion products were also subjected to chemical and X-ray phase analysis. Corrections were introduced for the unburned nitride detected by analysis and for the carbon of the igniter—a thin cotton-paper fabric ([16]) (respectively 10–15 mg and 1–2 mg). Traces of nitric acid were found; the correction for it is beyond the limits of accuracy. Traces of CO and nitrogen oxide were not detected in the gas phase. The solid combustion products were identical with monoclinic ZrO_2.

Results of the Investigation

A series of zirconium nitrides was obtained, ranging in composition from $ZrN_{0.56}O_{0.02}$ to $ZrN_{1.0}O_{0.04}$. In this interval all compositions have a cubic face-centered lattice with an identity period of $4.586_6 \pm 0.001$ Å. This shows that the constancy of the lattice period cannot always serve as proof

phases of constant composition. The heats of formation of the nitrides (see Table 1) were calculated from the equation

$$ZrN_xO_y + \left(1 - \frac{Y}{2}\right) O_2 = ZrO_2 + \frac{x}{2} N_2. \quad (1)$$

The value of ΔH^0_{298} for ZrO_2 was taken as -261.5 ± 0.2 kcal/mole ([17]).

Table 1

Nitride formula	Lattice period, Å	Heat of formation, kcal/mole	Heat of formation, for oxygen-free, calculated, kcal/mole	Entropy change ΔS^0_{298} according to equation (2)	S^0_{298}	Free energy of formation ΔF^0_{298} for oxygen-free nitrides, ZrN_x kcal/mole	Partial molar free energy $F_1 = \left(\frac{\partial \Delta F^0_{298}}{\partial N_i}\right)_{N_2,P,T}$, kcal/mole	Partial molar free energy $F_2 = \left(\frac{\partial N_i F^0_{298}}{\partial N_i}\right)_{N_2,P,T}$, kcal/mole
$ZrN_1O_{0.04}$	4.587	90.7 ± 0.2	87.9	−22.9	9.3	−81.1	−81	
$ZrN_{0.89}O_{0.03}$	4.588	84.5 ± 0.5	82.4	−20.4	9.3	−76.3	−82	−30

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Fig. 1. Curves of dependence: $-\Delta H^0_{298} = f_1(x)$ for ZrN'_xO_y (I); $-\Delta H^0_{298} = f_2(x)$ for ZrN_x (II); $-\Delta F^0_{298} = f_3(x)$ for ZrN_x (III).

Figure 1: Fig. 1. Curves of dependence: $-\Delta H^0_{298} = f_1(x)$ for ZrN'_xO_y (I); $-\Delta H^0_{298} = f_2(x)$ for ZrN_x (II); $-\Delta F^0_{298} = f_3(x)$ for ZrN_x (III).

Nitride formula	Lattice period, Å	Heat of formation, kcal/mole	Heat of formation, for oxygen-free, calculated, kcal/mole	Entropy change ΔS^0_{298} according to equation (2)	S^0_{298} ZrN_x	Free energy of formation ΔF^0_{298} for oxygen-free nitrides, kcal/mole	Partial molar free energy $F_1 = \left(\frac{\partial \Delta F^0_{298}}{\partial N_i}\right)_{N_2,P,T}$, kcal/mole	Partial molar free energy $F_2 = \left(\frac{\partial N_i F^0_{298}}{\partial N_i}\right)_{N_2,P,T}$, kcal/mole
$ZrN_{0.74}O_{0.00}$	4.586	72.2 ± 0.9	72.2	−16.5	9.7	−67.3	−84	−18
$ZrN_{0.69}O_{0.00}$	4.587	68.7 ± 1.8	68.7	−15.4	9.7	−64.1	−88	−10
$ZrN_{0.56}O_{0.02}$	4.585	57.5 ± 0.7	56.1	−12.7	9.4	−52.3	−95	−2

In Table 1, for each composition the mean value from three determinations is given. As is seen from the table, the heats of formation vary by a considerable amount: from 57,500 to 90,700 cal/mole, i.e., by 33,000 cal/mole when x changes from 0.56 to 1. This effect is much larger (( )2 times) than in the case of carbide systems ([16,20]). It follows from this that use of the value ΔQ^0_{298} for "ZrN," cited in the literature (+82 200 cal/mole ([5]), 87,300 cal/mole ([19])), may lead to serious errors (up to 30,000 cal/mole).

According to the chemical-analysis data, Y reached 0.04 g-atoms of oxygen. According to literature data, for TiN $Q^0_{298} = 80.4 \pm 0.27$ kcal/mole ([21]), for TiO_2 $Q^0_{298} = 224.89 \pm 0.06$ kcal/mole; Q^0_{298}/x—the mean heat of dissolution of oxygen in the lattice—changes from $TiO_{0.871}$ to $TiO_{1.009}$ by an amount from 60.18 to 62.88 kcal/g-atom ([24]); for $ZrNO_{0.04}$ $Q^0_{298} = 90.7 \pm 0.24$ kcal/mole (our data), and for ZrO_2 $Q^0_{298} = 261.5$ kcal/mole ([17]). Applying Kireev' s rule, which is well satisfied in this case, we obtain the mean heat of dissolution of oxygen in the cubic lattice equal to 70 kcal/g-atom O.

Fig. 1. Curves of dependence: $-\Delta H^0_{298} = f_1(x)$ for ZrN'_xO_y (I); $-\Delta H^0_{298} = f_2(x)$ for ZrN_x (II); $-\Delta F^0_{298} = f_3(x)$ for ZrN_x (III).

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In the graph of Fig. 1 are shown the curves of the dependence of the heats of formation of zirconium nitrides on composition for the preparations obtained, and the calculated curve for oxygen-free nitrides. To construct the latter, the value calculated above for the heat of dissolution of zirconium in the cubic-

···in the nitride lattice. In calculating the heats of formation, a content of 1% Hf was taken into account. The correction should have been introduced according to the equation:

$$Q_{p\,(\mathrm{Zr+Hf})\mathrm{N}_x} \cong Q_{p\,\mathrm{ZrN}x} + \left[Q_p(\mathrm{HfN}) - Q_p(\mathrm{ZrN})\right] \cdot \frac{1}{100}.$$

The value of the heat of formation of hafnium nitride was taken as 88.34 kcal/mole ([18]). It follows from this that $Q_{p\,(\mathrm{ZrN}x)} \cong Q_{p\,(\mathrm{Zr+Hf})\mathrm{N}_x}$ within the limits of experimental error. Therefore, the content of 1% Hf may be disregarded in the investigation of heats of formation.

In the works cited above, the content of oxygen and hafnium impurities was not determined, and the data on heats of formation are given without corrections. From the data on Q^0_{298} in Table 1 for pure nitrides (after subtracting the heat contributed by oxygen), obtained from the graph in Fig. 1, and from literature data for the standard entropies: $S^0_{298\mathrm{N2}} = 45.767$ e.u. ([28]), $S^0_{298} = 9.28 \pm 0.08$ e.u., $S^0_{298} = 9.29 \pm 0.05$ e.u. ([22]), we calculated the standard free energies of nitrides as a function of nitrogen content, using the equation:

$$\mathrm{Zr} + \frac{x}{2}\mathrm{N}_2 = \mathrm{ZrN}_x. \tag{2}$$

As can be seen, the entropies of the solid phases differ only by 0.01 e.u. and, in the calculation, mutually compensate; the value ΔS^0_{298} is determined by the large value of the entropy of nitrogen and by the coefficient x in equation (2).

To estimate the change in entropy on going from the literature value $S^0_{298\mathrm{ZrN}}$ to $S^0_{298\mathrm{ZrN}x}$, we take the entropy increment of nitrogen for a series of nitrides, equal to 2.7-2.9 e.u. ([27]); we obtain the increment S^0_{298} for zirconium: $9.28 - 2.8 = 6.5$ e.u. Assuming, as a first approximation, that the entropy contributed by each subsequent nitrogen atom is the same, we obtain, approximately:

$$S^0_{298\mathrm{ZrN}x} = 6.5 + 2.8x + S^{0k},$$

where S^{0k} is the configurational part of the entropy, which appears when $x < 1$. The latter is calculated from the equation: $S^{0k} = k \ln W$. For the cubic face-centered lattice of ZrN_x, a formula is obtained as for the entropy of mixing of a binary ideal solution ([23]), since, when the octahedral interstices are occupied by nitrogen, $N_i = x$, $N_h = 1 - x$, and $N_i + N_h = 1$.

$$S^{0k} = -R[x \ln x + (1 - x) \ln(1 - x)]^*.$$

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By a known graphical method ([23]), the values of the partial molar free energies of ZrN_x were calculated as a function of the fraction of sites occupied and unoccupied by nitrogen, N_i and N_h**. Since the number of Zr atoms in the lattice does not change, or changes only insignificantly in comparison with N_i and N_h, $\Delta\bar{F}^0_{298}$ depends only on N_i and N_h; the values of $\Delta\bar{F}^0_{298}$ are given in Table 1.

Conclusions

1. The dependence of the heats and free energies of formation of zirconium nitrides on composition has been investigated. In contrast to literature data, it has been established that zirconium nitride is a phase of variable composition with a wide–

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* The entropy of mixing in the case of a body-centered lattice was calculated in ([26]).

** The consideration of lattice defects as independent variables in thermodynamic calculations was first introduced by Schottky and Wagner in their well-known work ([25]).

a wide homogeneity range. We have obtained specimens in the interval from $ZrN_{1.0}O_{0.04}$ to $ZrN_{0.56}O_{0.02}$, whose heats and free energies of formation vary, respectively, from 90.7 to 57.5 kcal/mole and from −81.1 to −52.3 kcal/mole.

2. Despite the wide variation in the compositions of the nitrides and in the heats and free energies of formation, the lattice period remains practically constant.

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CITED LITERATURE

1. A. E. Arkel, *Physica*, **4**, 286 (1924).
2. E. Friederich, L. Sittig, *Zs. anorg. allgem. Chem.*, **143**, 293 (1925).
3. R. Lorenz, J. Wootcock, *Zs. anorg. Chem.*, **176**, 289 (1928).
4. G. Agte, K. Moers, *Zs. anorg. Chem.*, **198**, 233 (1931).
5. B. Neumann, C. Kröger, H. Kunz, *Zs. anorg. Chem.*, **218**, 379 (1934).

SovietRxiv

6. M. Hoch, D. Dingledy, L. Johnston, *J. Am. Chem. Soc.*, **77**, 304 (1955).

7. G. Hägg, *Zs. Phys. Chem.*, **6**, 221 (1929).

8. G. V. Samsonov, *DAN*, **86**, 329 (1952).

9. Matthews, *J. Am. Chem. Soc.*, **20**, 843 (1898).

10. E. Wedekind, *Lieb. Ann.*, **395**, 177 (1913).

11. L. Brewer, H. Haraldsen, *J. Electr. Soc.*, **102**, 399 (1955).

12. K. K. Kelly, *US Bur. Mines Bull.*, **8**, 407 (1937).

13. *Selected Values of Chemical Thermodynamic Properties Circular of the National Bureau of Standards*, 500 (1952).

14. *National Nuclear Energy Series Manhattan Project Technical Section*, Div. IV, **1913** (1950).

15. E. I. Smagina, V. S. Kutsev, B. F. Ormont, *Zav. lab.*, No. 10, 1249 (1956).

16. V. I. Smirnova, B. F. Ormont, *ZhFKh*, **30**, 1327 (1956).

17. G. L. Humphrey, *J. Am. Chem. Soc.*, No. 4, **76**, 978 (1954).

18. G. L. Humphrey, *J. Am. Chem. Soc.*, No. 6, 2806 (1953).

19. A. D. Mah, N. L. Gellert, *J. Am. Chem. Soc.*, **78**, 3261 (1956).

20. V. I. Smirnova, B. F. Ormont, *DAN*, **100**, 127 (1955).

21. G. L. Humphrey, *J. Am. Chem. Soc.*, **73**, 2261 (1951).

22. S. S. Todd, *Bur. Mines*, **11**, No. 477 (1950).

23. V. A. Kirillin, A. E. Sheindlin, *Thermodynamics of Solutions*, Moscow, 1956.

24. M. P. Morozova, E. V. Lyubimova, S. M. Aria, *Vestn. LGU*, No. 22, issue 4 (1956).

25. C. Wagner, W. Schottky, *Zs. phys. Chem.*, **11**, 163 (1931).

26. M. I. Temkin, L. A. Shvartsman, *ZhFKh*, **23**, 755 (1949).

SovietRxiv

27. W. M. Latimer, *J. Am. Chem. Soc.*, **73**, 1480 (1951).

28. *Brief Handbook of Physicochemical Quantities*, Moscow, 1955.

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