



Soviet-era science, translated into English

CHEMISTRY

S. A. SHUKAREV, G. A. SEMENOV, and K. E. FRANTSEVA

1962

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196201.45094>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

CHEMISTRY

S. A. SHUKAREV, G. A. SEMENOV, and K. E. FRANTSEVA

DETERMINATION OF THE SATURATED VAPOR PRESSURE OF NIOBIUM DIOXIDE

(Presented by Academician A. N. Terenin, March 2, 1962)

Only one paper has been devoted to measuring the vapor pressure of niobium dioxide (¹); its authors, using Knudsen's effusion method, obtained a series of vapor-pressure values in the temperature interval 1489–1905° K. In other works (^{2,3}) it is stated only that NbO₂ has appreciable volatility at 1650–1700°, and that at 1850–1900° the rate of evaporation of this oxide is quite high. We previously reported (⁴) on a study of the evaporation of NbO₂ by the mass-spectrometric method. In that case the composition of the vapor over niobium dioxide during evaporation from its open surface was established, and it was shown that NbO₂ evaporates without dissociating. Having measured the temperature dependence of the ion currents, we calculated, for the temperature interval 1500–1880°K, the heat of sublimation of NbO₂, equal to 142 ± 3 kcal/mole.

In the present work we measured the vapor pressure of niobium dioxide by Knudsen's effusion method, using a differential variant of the method similar, for example, to that described in works (^{5,6}). The cylindrical effusion chamber was made of forged molybdenum (Fig. 1). It consists of a body (1) and a lid (2) with an effusion orifice, whose diameter is 0.308 mm. The ratio of the area of the evaporating substance to the area of the effusion orifice is 500 : 1. In the lower part of the chamber body there is an opening in which a thermocouple (3), made of tungsten-rhenium alloys containing 5 and 20% rhenium (⁷), is fastened by a screw (4). The thermocouple was calibrated against the readings of a first-class optical pyrometer in the High-Temperature Laboratory of the D. I. Mendeleev All-Union Scientific Research Institute of Metrology. The temperature is also measured with a pyrometer, which was focused on the thermocouple junction through a narrow channel drilled in the lower part of the chamber body and which was checked in the laboratory of the same institute against a second-class temperature lamp. The effusion chamber is heated by electron bombardment. Stabilization of the cathode emission current and of the high voltage made it possible to ensure sufficient stability of the chamber temperature (2°). The effusion chamber is surrounded by tantalum radiation shields and a water jacket. The sublimate condenses on targets cooled with liquid nitrogen and replaced by means of a magnetic pusher. The all-metal effusion apparatus makes it possible to obtain a vacuum of the order of $1 \cdot 10^{-5}$ mm Hg at a working chamber temperature of 2100°K.

Fig. 1. Effusion chamber: 1 –body, 2 –lid, 3 –thermocouple, 4 – thermocouple fastening screw

Figure 1: Fig. 1. Effusion chamber: 1 –body, 2 –lid, 3 –thermocouple, 4 – thermocouple fastening screw

Fig. 1. Effusion chamber: 1 –body, 2 –lid, 3 –thermocouple, 4 –thermocouple fastening screw

The starting material for obtaining niobium dioxide was pentoxide labeled with the radioactive isotope Nb^{95} . According to spectral-analysis data, it contained 0.24% impurities. Niobium pentoxide was reduced to NbO_2 with hydrogen at a temperature of 1000° for three hours. The composition of the product obtained was $\text{NbO}_2.008$, as determined from the weight increase

during calcination. The X-ray diffraction pattern of the sample corresponded to the literature data (⁸).

Having first measured the vapor pressure of silver and obtained results differing from those known in the literature (⁹) by no more than 10%, we then measured the vapor pressure of NbO_2 . The results obtained are presented graphically as the straight line 1 (Fig. 2), described by the equation:

$$\lg P = -\frac{30300}{T} + 12.42 \text{ mm.}$$

Fig. 2. Vapor pressure of niobium dioxide:
1–experimental data, 2–data of Golubtsov et al. (¹)

The heat of sublimation of NbO_2 , calculated from the slope of straight line 1, is 138 ∓ 2 kcal/mole. Straight line 2 represents the data of work (¹). The heat of sublimation calculated by us from the slope of this straight line is only 37.5 kcal/mole. The latter value is evidently erroneous. Table 1 gives the data needed to calculate the sublimation enthalpy $\Delta H_0^0[\text{NbO}_2]$.

For calculating the change in the reduced isobaric-isothermal potential $\Delta\Phi^*$ upon sublimation of NbO_2 , we used published data on the temperature dependence of the functions $-\frac{F_T^0 - H_{298}^0}{T}$ and the differences in heat contents $H_{298}^0 - H_0^0$ for condensed (¹⁰, ¹¹) and gaseous (¹²) NbO_2 . Knowing $\Delta\Phi^*$, from the equation

$$\Delta H_0^0 = -RT \ln P - \Delta\Phi^*T$$

we obtained the value of the heat of sublimation $\Delta H_0^0 = 141 \mp 0.4$ kcal/mole.

Table 1

Vapor pressure and thermodynamic functions of niobium dioxide

No.	$T_{\text{avg.}}, ^\circ\text{K}$	P, mm	Solid,	Solid,	Solid,	Gaseous,	Gaseous,	Gaseous,	ΔH_0^0 subl., kcal/mole	
			kcal/mole	kcal/mole	kcal/mole	kcal/mole	kcal/mole	kcal/mole		
			deg:	deg:	deg:	deg:	deg:	deg:	$\Delta\Phi^*$	
			$F_T^0 - H_{298}^0$	$- H_{6T}^0$	$- H_{6T}^0$	$- H_{298}^0$	$- H_{6T}^0$	$- H_{6T}^0$		
			T	T	T	T	T	T		
1	1938	6.02· 10 ⁻⁴	30.25	1.19	29.06	75.45	1.41	74.04	44.98	141.3
2	1948	8.27· 10 ⁻⁴	30.31	1.18	29.13	75.53	1.40	74.13	45.00	140.7
3	1978	1.22· 10 ⁻³	30.48	1.16	29.32	75.76	1.38	74.38	45.06	140.5
4	1978	1.17· 10 ⁻³	30.48	1.16	29.32	75.76	1.38	74.38	45.06	141.7
5	1992	1.51· 10 ⁻³	30.56	1.16	29.40	75.84	1.37	74.47	45.07	141.7
6	2005	2.16· 10 ⁻³	30.63	1.15	29.48	75.93	1.36	74.57	45.09	141.2
7	2031	3.19· 10 ⁻³	30.77	1.13	29.64	76.07	1.34	74.73	45.09	141.5
8	2037	3.22· 10 ⁻³	30.81	1.13	29.68	76.11	1.34	74.77	45.09	141.9
9	2081	7.55· 10 ⁻³	31.05	1.11	29.94	76.35	1.31	75.04	45.10	141.4
10	2122	1.12· 10 ⁻²	31.33	1.08	30.25	76.58	1.29	75.29	45.04	142.5

Taking from the literature sources the following quantities: the heat of formation $\Delta H_{298}^0 = -191.7$ kcal/mole (¹³) and the difference in heat contents $H_{298}^0 - H_0^0 \simeq 2300$ cal/mole (¹⁰) for condensed NbO_2 , as well as the sublimation heat of metallic Nb $\Delta H_0^0 = 171.8$ kcal/g-at. (¹⁴) and the heat of

atomization of oxygen, $\Delta H_0^0 = 118.0$ kcal/mole (¹⁵), we calculated the dissociation energy of the gaseous molecule NbO_2 , which proved to be equal to 14.9 ∓ 0.1 eV.

Leningrad State University
named after A. A. Zhdanov

Received
27 II 1962

REFERENCES

1. I. V. Golybtsov, A. A. Lapitskii, V. K. Shiryaev, *Izv. vyssh. uch. zav. SSSR, khim. i khim. tekhnol.*, **3**, 571 (1960).

2. O. P. Kolchin, V. N. Sumarokova, N. P. Chuveleva, *Atomic Energy*, **3**, 575 (1957).
3. N. P. Sazhin, O. P. Kolchin, N. V. Sumarokova, *Izv. AN SSSR, Metallurgy and Fuel*, no. 6, 8 (1961).
4. S. A. Shchukarev, G. A. Semenov, K. E. Frantsen, *ZhNKh*, **4**, 2638 (1959).
5. T. E. Phipps, G. W. Sears, O. C. Simpson, *Manhattan Project, Div. IV, 14b, The Transuranium Elements*, N. Y., 1949, p. 704.
6. An. N. Nesmeyanov, *Atomic Energy*, **3**, 227 (1957).
7. S. K. Danishevsky, *Zav. lab.*, **21**, 1470 (1958).
8. S. N. Alyamovskii, G. P. Shveikin, P. V. Gel' d, *ZhNKh*, **3**, 2437 (1958).
9. An. N. Nesmeyanov, L. A. Smakhtin, V. I. Lebedev, *DAN*, **112**, 700 (1957).
10. J. L. Margrave, *Proc. of the Symposium on High Temperature—a Tool for the Future*, Berkeley, California, 1956.
11. *Physicochemical Measurements at High Temperatures*, ed. Bockris, White, Mackenzie, Butterworths Sci. Publ., 1959.
12. L. Brewer, G. M. Rosenblatt, *Chem. Rev.*, **61**, 3, 257 (1961).
13. F. G. Kusenko, P. V. Gel' d, *Izv. Sib. fil. AN SSSR*, no. 2, 46 (1960).
14. R. Speiser, P. Blackburn, H. L. Johnston, *J. Electrochem. Soc.*, **106**, 52 (1959).
15. P. Brix, G. Herzberg, *J. Chem. Phys.*, **21**, 2240 (1953).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.