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Determination of the atomization energies of the gaseous molecules Nb_2O_4, Nb_2O_5, Nb_4O_9, and Nb_4O_{10}

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The complex gaseous niobium oxide molecules Nb_2O_4, Nb_2O_5, Nb_4O_9, and Nb_4O_{10} were identified for the first time in a Knudsen cell-mass spectrometric study of the vapors in equilibrium over a condensed phase resulting from extensive vaporization of lithium niobate with lithium depletion. These molecules were characterized thermochemically from the study of several all-gas equilibria. The resulting atomization energies are $\Delta H^0_{0,at}(Nb_2O_4) = 3322 \pm 45$ kJ mol^{-1}; $\Delta H^0_{0,at}(Nb_2O_5) = 3910 \pm 59$ kJ mol^{-1}; $\Delta H^0_{0,at}(Nb_4O_9) = 7958 \pm 82$ kJ mol^{-1}; $\Delta H^0_{0,at}(Nb_4O_{10}) = 8595 \pm 71$ kJ mol^{-1}. The corresponding standard heats of formation are $\Delta H^0_{f,298}(Nb_2O_4,g) = -909 \pm 45$ kJ mol^{-1}; $\Delta H^0_{f,298}(Nb_2O_5,g) = -1252 \pm 59$ kJ mol^{-1}; $\Delta H^0_{f,298}(Nb_4O_9,g) = -2889 \pm 82$ kJ mol^{-1}; $\Delta H^0_{f,298}(Nb_4O_{10},g) = -3281 \pm 71$ kJ mol^{-1}.

I. INTRODUCTION

Complex gaseous metal oxide molecules like Ti_2O_3, Ti_2O_4, and V_2O_4, which could not be positively identified in the equilibrium vaporization of the stable solid oxides phase of titanium and vanadium, have instead been rather easily observed when the vaporization of a ternary stoichiometric compound like $CoTiO_3$,[1] or a ternary system formed by oxides mixtures like ($CoO + TiO_2$) or ($Eu_2O_3 + V_2O_5 + V$),[2] was prolonged up to temperatures higher than those at which a more or less complete depletion of samples in cobalt and europium, respectively, had occurred. In both cases the vitreous look of the residues when powdered samples were vaporized indicate that, in the conditions in which the complex gaseous oxide species were observed, a liquid phase, or coexistent solid and liquid phases, were most likely evaporating; moreover, for the evaporating phase, an atomic oxygen-to-metal ratio somewhat different from that characterizing the known stable solid metal oxides may be hypothesized.

If these findings could be somewhat generalized, conditions favorable to the observation of unusual complex gaseous metal oxides should be obtained when a ternary M′–M″–O system or a M′ and M″ double oxide compound can be depleted in the M′ metal upon vaporization and the vaporization is prolonged up to higher temperatures.

A positive test of this possibility was obtained in the course of a mass-spectrometric investigation of the $LiNbO_3$ vaporization. After the samples were depleted in lithium, the species $Nb_2O_{4(g)}$, $Nb_2O_{5(g)}$, $Nb_4O_{9(g)}$, and $Nb_4O_{10(g)}$ have been identified and gaseous equilibria involving them have been studied to derive the atomization energy of the newly identified molecules. The results of these studies are presented here.

II. EXPERIMENTAL

A single focusing magnetic deflection mass spectrometer combined with a conventional Knudsen cell molecular source was used. Details of the instrument and of the experimental technique have been described previously.[3,4]

Commercial samples of $LiNbO_3$, 99.9% pure from A. D. Mackay Chemicals, were vaporized from a tungsten cell with a rhenium liner without lid inserted. The effusion cell orifice was knife edged, 1 mm in diameter. The cell was heated by radiation from a tungsten spiral resistance element and its temperature was measured with a disappearing filament optical pyrometer by sighting into a blackbody cavity in the bottom of the cell. Corrections were made for prism and window transmission. The vapors effusing from the cell were generally ionized with 70 eV electrons.

III. RESULTS AND DISCUSSION

A. Identification of ions

For each of the newly identified species, only the most abundant isotopic ion peak, corresponding to molecules involving ^{16}O atoms only, was detectable under the experimental conditions in which our mass spectra were recorded. Therefore, the identification was only based on the m/q ratios, the linearly extrapolated appearance potentials, (A.P.), and the shutter profiles.

By taking for the A.P. (NbO_2) the same value 9 ± 0.5 eV we obtained in the course of the experiments on the Eu–Nb–O[5] system, the A.P. values in eV, approximated to the nearest half-integer, were 10 ± 1, 9.5 ± 1, 11 ± 1, and 9.5 ± 1 for Nb_2O_4, Nb_2O_5, Nb_4O_9, and Nb_4O_{10} molecules, respectively.

The low partial pressures of these species and the noise levels at the high sensitivity scales used to record their ionization efficiency curves (IEC) prevented an analysis of the details in these curves. Therefore, the only information which could be inferred from the IEC about possible fragmentation processes was that, if they occurred, the extent of fragmentation for all the possible precursors should not have been particularly large with respect to the probability of simple ionization.

This information is supported by the significant variation with the temperature and pressure conditions of the intensity ratios measured at 70 eV for each possible ion couple.

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However the possibility of sufficient fragmentation to affect the equilibrium calculations involving the species of interest cannot be excluded.

Tests performed on the equilibria suggested that, whatever might have been the true fragmentation pattern, the overall effect could be attributed to a fragmentation of NbO_2 to NbO^+ and of Nb_4O_9 to $Nb_2O_4^+$ in the extent of 15.5% and 15%, respectively. With these assumed fragmentations the best results were obtained for all the reactions studied in terms of linear correlation of the second-law plots, consistency of second-law and third-law results, and absence of trends in the individual third-law values.

Therefore, the measured intensities were corrected accordingly before to be converted into pressures.

The necessary cross sections Q at the maximum of the IEC for NbO and NbO molecules were taken as 8.34 and 11.46, respectively, the same values we used in the work on the Eu–Nb–O[5] system. For the species Nb_2O_4, Nb_2O_5, Nb_4O_9, and Nb_4O_{10} the values 17.19, 17.54, 26.05, and 26.31, respectively, were obtained through the expressions

$$Q(Nb_2O_4) = 1.5\times Q(NbO_2);$$

$$Q(Nb_2O_5) = 0.75\times [Q(NbO_2 + Q(NbO_3)];$$

$$Q(Nb_4O_9) = 0.75\times [Q(Nb_2O_4) + Q(Nb_2O_5)];$$

$$Q(Nb_4O_{10}) = 1.5\times Q(Nb_2O_5).$$

The multiplier gains were taken inversely proportional to the square roots of the ionic masses.

Silver calibrations and, where possible, internal calibrations were used to obtain the necessary values of the instrumental constant in the various experiments performed.

The resulting values of the partial pressures for the species involved in the reactions studied are reported in Table I. The number of digits reported affords one the opportunity of minimizing numerical inconsistencies when the same pressure value is used in different reactions.

B. Gibbs energy and heat content functions

For use in second- and third-law evaluations of equilibrium data reported in the next section, the Gibbs energy functions and heat contents for $NbO_{(g)}$ and $NbO_{2(g)}$ were those reported in Ref. 5; for the newly identified species they were computed from estimated molecular parameters. In all the cases a single ground state was assumed, i.e., there was no electronic contribution to the thermodynamic functions.

1. $Nb_2O_{4(g)}$

A bridge bonded structure of D_{2h} symmetry was assumed for this molecule, by analogy with the assumed geometries for the $V_2O_4^2$ and $Ti_2O_4^1$ molecules. The molecular parameters and the normal frequencies for the selected structure were estimated by following the same criteria used to derive the corresponding quantities for $Ti_2O_{4(g)}$.[1]

Accordingly, and with the same notations, the adopted values were $r(Nb–O)_t = 0.1713$ nm; $r(Nb–O)_b = 0.192$ nm; $Nb–\hat{O}–Nb = 100°$. The normal frequencies in cm^{-1} were a_g: 970, 780, 370; b_{1u}: 400, 140; b_{1g}: 780, 400; b_{2u}: 780, 380; b_{2g}: 260; b_{3u}: 970, 780.

2. $Nb_2O_{5(g)}$

A planar structure of C_{2v} symmetry, with two NbO_2 terminal groups and a bridging bent Nb–O–Nb group, was assumed by analogy with $N_2O_{5(g)}$ and $P_2O_{5(g)}$.[6]

The Nb–O bond length in the NbO_2 terminal groups

TABLE I. Partial pressures (in atm)[a] measured in different vaporization experiments leading to the observation of the $Nb_2O_4(g)$, $Nb_2O_5(g)$, $Nb_4O_9(g)$, and $Nb_4O_{10}(g)$ molecules.

	NbO		NbO_2		Nb_2O_4		Nb_2O_5		Nb_4O_9	Nb_4O_{10}
T(K)	$P\times10^x$	x	$P\times10^x$	x	$P\times10^x$	x	$P\times10^x$	x	$P\times10^9$	$P\times10^9$
2016	1.14_5	7	2.08	6	3.42_5	9	4.91	9	···	···
2147	1.06	6	1.09	5	1.69	8	1.66	8	···	···
2225	2.63	6	2.12_5	5	2.15_5	8	1.91	8	1.32	0.526
2288	5.15_5	6	3.96_5	5	3.70_5	8	3.36	8	1.52_5	0.579
2157	1.73_5	6	2.03	5	5.70_5	8	6.64_5	8	···	···
2194	3.11_5	6	3.34_5	5	8.57_5	8	9.82	8	···	···
2252	6.02	6	5.76_5	5	1.06	7	1.12_5	7	···	···
1877	1.13_5	8	2.79_5	7	4.93	10	7.67	10	1.32	1.54
1969	···	···	9.66_5	7	1.65	9	2.49_5	9	1.80_5	1.79_5
1990	8.94	8	1.65	6	3.52	9	5.08_5	9	3.89	3.41
2095	4.71	7	6.25	6	1.23	8	1.50	8	5.99	3.81_5
1948	3.42_5	8	7.15_5	7	9.45_5	10	1.43	9	1.05	1.04_5
1979	···	···	···	···	1.32_5	9	1.97	9	1.11_5	1.01_5
2029	1.26	7	2.18_5	6	2.76	9	3.94_5	9	1.34_5	1.09
2060	2.52	7	3.69_5	6	5.64	9	7.33	9	2.12_5	1.47_5
2168	4.09	7	4.81_5	6	2.34	9	2.77_5	9	···	···
2157	···	···	···	···	1.16	8	1.41	8	1.81_5	1.06
2016	···	···	1.89_5	6	3.15_5	9	4.29_5	9	1.99_5	1.60_5
2089	3.42	7	5.12	6	8.49	9	1.12	8	3.87_5	2.74_5
2157	···	···	1.47	5	2.39	8	2.83_5	8	6.44_5	3.64_5

[a] 1 atm = 101 325 Pa.

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was taken equal to the $r(\text{Nb–O})_t$ distance in $Nb_2O_{4(g)}$ and a value of 0.187 nm was estimated for the Nb–O distance in the bridge, by assuming the same $r(\text{Nb–O})_b/r(\text{Nb–O})_t$ ratio as in $P_2O_{5(g)}$.[6]

The 15 normal vibration frequencies were estimated as follows: The symmetrical and asymmetrical stretchings of the $-NbO_2$ groups were assigned the same values of the corresponding stretching in $NbO_{2(g)}$[7]; a common value of 500 cm^{-1}, very close to the bending frequency in $NbO_{2(g)}$,[7] was assigned to all the bendings of the NbO_2 groups in $Nb_2O_{5(g)}$; from the literature range of bridge stretching frequencies values reported for $Re_2O_{7(g)}$[8] and for several metal oxides solid phases,[8,9] values of 800 and 500 cm^{-1} were, respectively, selected for the symmetrical and asymmetrical stretching of the bridge in $Nb_2O_{5(g)}$; a value of 350 cm^{-1} for the bending of the bridge was scaled from the value adopted for the NbO_2 terminal groups bending, through the geometrical mean of the adjacent bonds; the same value 350 cm^{-1} was adopted for all the out-of-plane vibration modes of Nb_2O_5, while a value of 50 cm^{-1} was assigned to the torsional mode. In summary, the frequencies adopted were a_1: 1010, 850, 500, 500, 500, 350; b_1: 1010, 850, 800, 500, 500: a_2: 50, 350; b_2: 350, 350. All values are in cm^{-1}.

3. $Nb_4O_{9(g)}$

The structure adopted was C_{3v} symmetry by analogy with one of the structures proposed for $P_4O_{9(g)}$ in Ref. 10. The Nb–O terminal bond length, $r(\text{Nb–O})_t = 0.165$ nm value was obtained from the value in $Nb_4O_{10(g)}$ by scaling through the ratio of the corresponding distances in $P_4O_{9(g)}$ and $P_4O_{10(g)}$.[10] The remaining Nb–O distances were all derived from the $r(\text{Nb–O})_t$ value by assuming as a scale factor the ratio of the corresponding P–O distances in $P_4O_{9(g)}$.[10] If for marking the atoms in $Nb_4O_{9(g)}$ the same notation is adopted as for those of $P_4O_{9(g)}$,[10] the resulting bond lengths, in nm, were $r(\text{Nb}_a\text{–O}_a) = 0.193$; $r(\text{Nb}_b\text{–O}_a) = 0.187$; $r(\text{Nb}_b\text{–O}_b) = 0.185$. All the Nb–$\hat{O}$–Nb and O–$\widehat{Nb}$–O bond angles were taken equal to the corresponding P–$\hat{O}$–P and O–$\hat{P}$–O angles in $P_4O_{9(g)}$. In lack of even indirect information on the $Nb_4O_{9(g)}$ normal frequencies, the vibrational contribution was derived from those calculated for $Nb_4O_{6(g)}$ and $Nb_4O_{10(g)}$. To this end the normal frequencies of $Nb_4O_{6(g)}$ were obtained from those reported for $P_4O_{6(g)}$[11] with the same procedure adopted to obtain the $Nb_4O_{10(g)}$ frequencies from those of $P_4O_{10(g)}$ (see below). Finally, the $Nb_4O_{9(g)}$ vibrational contribution $c_v(Nb_4O_9)$ was obtained from the relation $c_v(Nb_4O_9) = c_v(Nb_4O_6) + 0.75[c_v(Nb_4O_{10}) - c_v(Nb_4O_6)]$.

4. $Nb_4O_{10(g)}$

The assumed structure was of T_d symmetry, the same reported for $P_4O_{10(g)}$.[10] The $r(\text{Nb–O})_t = 0.166$ nm value was taken equal to the tetrahedral Nb–O distance in the α–Nb_2O_5 solid phase[12] and hence the value $r(\text{Nb–O}) = 0.186$ nm was derived for the remaining Nb–O bond lengths in $Nb_4O_{10(g)}$, by assuming the same ratio as for the corresponding P–O bond distances in $Nb_4O_{10(g)}$.[10] All the Nb–$\hat{O}$–Nb and O–$\widehat{Nb}$–O bond angles were taken equal to the corresponding P–$\hat{O}$–P and O–$\hat{P}$–O angles in $P_4O_{10(g)}$.[10]

The normal frequencies were estimated as follows. First the frequencies reported by Chapman[11] for $P_4O_{10(g)}$ were used for obtaining those of $V_4O_{10(g)}$ through the two experimentally known[13] frequencies of $V_4O_{10(g)}$; then, the $V_4O_{10(g)}$ frequencies were scaled through the geometrical mean of the frequencies in $NbO_{2(g)}$[7] and in $VO_2(g)$[2] to obtain the $Nb_4O_{10(g)}$ frequencies. The resulting values in cm^{-1} were a_1: 990, 560, 430; f_1: 740, 300, 240; f_2: 970, 780, 590, 440, 330, 210; e: 600, 290, 180.

The Gibbs energy and heat-content functions calculated with the above assumptions for the molecular parameters are reported in Table II. The number of the digits has the same significance as for the data in Table I and do not infer six-digit accuracy. Absolute accuracy can be better inferred from the effects on the calculated thermodynamic functions induced by reasonable changes in the assumptions made.

To this end, it is useful to compare the results of preliminary computations we made for $Nb_2O_{5(g)}$ with different assumptions for the bridge bond angle (130° instead of 100°), for the Nb–O bridge bond length [0.192 nm instead of 0.187 nm, by analogy with the $r(\text{Nb–O})_b$ value in $Nb_2O_{4(g)}$], for

TABLE II. Thermodynamic functions of $Nb_2O_4(g)$, $Nb_2O_5(g)$, $Nb_4O_9(g)$, $Nb_4O_{10}(g)$, $-(G_T^0 - H_0^0)/T$ in $JK^{-1}\,mol^{-1}$, $(H_T^0 - H_0^0)$ in $kJ\,mol^{-1}$.[a]

	Nb_2O_4		Nb_2O_5		Nb_4O_9		Nb_4O_{10}	
$T(K)$	$-(G_T^0 - H_0^0)/T$	$H_T^0 - H_0^0$	$-(G_T^0 - H_0^0)/T$	$H_T^0 - H_0^0$	$-(G_T^0 - H_0^0)/T$	$H_T^0 - H_0^0$	$-(G_T^0 - H_0^0)/T$	$H_T^0 - H_0^0$
298.15	268.535	17.348	287.476	19.577	339.031	35.100	331.020	37.241
1500	405.328	162.298	447.268	191.851	645.836	374.111	659.265	402.335
1600	412.356	175.310	455.577	207.307	662.039	404.298	676.693	434.936
1700	419.036	188.355	463.477	222.802	677.448	434.511	693.272	467.614
1800	425.401	201.429	471.007	238.331	692.134	464.860	709.078	500.354
1900	431.478	214.525	478.199	253.886	706.163	495.216	724.179	533.148
2000	437.293	227.643	485.082	269.466	719.588	525.612	738.634	565.986
2100	442.867	240.777	491.680	285.060	732.459	556.043	752.495	598.864
2200	448.219	253.927	498.017	300.684	744.818	586.503	765.808	631.777
2300	453.365	267.089	504.111	316.317	756.707	616.989	778.614	664.720
2400	458.322	280.264	509.982	331.964	768.156	647.499	790.951	697.688
2500	463.101	293.448	515.643	347.622	779.199	678.028	802.850	730.679

[a] Based on assumed molecular geometries and estimated molecular parameters.

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TABLE III. Equilibrium data and heats of the pressure-independent reactions (2), (5), and (6) in kJ mol^{-1}.

T(K)	$\ln K_{p(2)}$	$-\Delta H^0_{0(2)}$	$-\ln K_{p(5)}$	$-\Delta H^0_{0(5)}$	$-\ln K_{p(6)}$	$-\Delta H^0_{0(6)}$
2016	2.54	43.4	...	...	...	...
2147	2.35	43.5	...	...	...	...
2225	2.21	42.9	3.01	6.4	0.80	49.3
2288	2.14	43.1	3.01	6.3	0.87	49.4
2157	2.31	43.1	3.01	...	...	...
2194	2.24	42.7	...	...	...	...
2252	2.20	43.4	...	...	...	...
1877	2.76	43.2	3.05	6.1	0.29	49.3
1990	2.55	42.9	3.04_5	6.1	0.50	48.9
1969	...	...	...	...	0.42	49.7
2095	2.38_5	42.8	3.03_5	6.1	0.65	48.9
1948	2.62_5	43.0	3.04_5	6.1	0.42	49.1
1979	...	...	...	...	0.49	48.8
2029	2.49_5	43.0	3.06_5	5.7	0.57	48.7
2060	2.42_5	42.6	3.05	5.9	0.62_5	48.5
2157	...	...	...	...	0.75_5	48.5
2168	2.29_5	43.1	...	...	...	...
2016	...	...	...	...	0.52_5	49.2
2089	2.43	43.4	3.05	5.9	0.62	49.3
2157	...	...	...	...	0.74	48.8
Avg. third-law: ΔH^0_0:		-43.1 ± 0.3			-6.1 ± 0.2	-49.0 ± 0.4
Avg. temperature: T:		2096			2060	2057
Second-law: ΔH^0_T:		-53.4 ± 1.3			-9.0 ± 1.2	-51.2 ± 1.8
Second-law: ΔH^0_0:		-42.7 ± 1.3			-5.0 ± 1.2	-49.7 ± 1.8
Proposed ΔH^0_0:		-43 ± 30			-6 ± 30	-49 ± 30
Derived $\Delta H^0_{0,\mathrm{at}}$ (Nb_2O_5) = 3910 ± 59			$\Delta H^0_{0,\mathrm{at}}$ (Nb_4O_{10}) = 8595 ± 90		$\Delta H^0_{0,\mathrm{at}}$ (Nb_4O_{10}) = 8595 ± 115	

the molecular symmetry (D_{2h} instead of C_{2v}) and for the normal frequencies scaled from those of $P_2O_{5(g)}$ through the geometrical mean of the frequencies in $NbO_{2(g)}$ and $PO_{2(g)}$.

At a temperature of 2100 K, close to the average temperature in our ranges of measurements (see Tables III and IV), the Gibbs energy functions values in J K^{-1} mol^{-1} obtained with the different aforementioned assumptions were in the following order: 493.863, 492.054, 490.869, and 521.586. The corresponding heat-content values, in kJ mol^{-1}, were 285.066, 286.066, 285.066, and 286.389.

The comparison of these data with those reported in Table II shows that the main uncertainties arise from the

TABLE IV. Equilibrium data and heats of pressure-dependent reactions (1), (3), and (4) in kJ mol^{-1}.

T(K)	$-\ln kp_{(1)}$	$\Delta H^0_{0(1)}$	$-\ln kp_{(3)}$	$\Delta H^0_{0(3)}$	$-\ln kp_{(4)}$	$\Delta H^0_{0(4)}$
2016	6.67_5	512.8	...	...	...	...
2147	4.96	514.0	...	...	...	...
2225	3.86_5	511.7	14.98	725.0	14.18	774.4
2288	3.16	512.1	14.02	726.3	13.15	775.7
2157	4.93	515.9	...	...	...	...
2194	4.34	513.5	...	...	...	...
2252	3.46_5	510.0	...	...	...	...
1877	8.75	511.1	21.97_5	725.2	21.68_5	774.5
1969	7.47_5	514.5	19.90	725.4	19.48	775.2
1990	7.16_5	514.5	19.19_5	721.3	18.69_5	770.2
2095	5.75	515.9	17.29_5	721.5	16.64_5	773.4
1948	7.52	509.9	20.47	727.3	20.05	776.4
1979	...	...	19.87_5	728.8	19.38	777.6
2029	6.36	510.7	18.63_5	725.4	18.06_5	774.1
2060	6.02_5	512.5	17.75_5	721.2	17.13	769.7
2157	...	...	16.245	726.5	15.49	775.1
2168	4.61_5	512.6	...	...	...	...
2016	6.78_5	514.6	18.80_5	723.8	18.28	773.0
2089	5.78	515.1	17.52_5	726.7	16.90	776.0
2157	4.70_5	511.9	16.07	723.4	15.32_5	772.2
Avg. third-law ΔH^0_0:		513.0 ± 1.9		725.1 ± 2.2		774.1 ± 2.3
Avg. temperature T:		2087		2057		2057
Second-law ΔH^0_T:		489.8 ± 8.6		697.3 ± 11.2		748.5 ± 12.1
Second-law ΔH^0_0:		511.9 ± 8.6		726.8 ± 11.2		776.6 ± 12.1
Proposed ΔH^0_0:		512 ± 35		726 ± 35		775 ± 35
Derived $\Delta H^0_{0,\mathrm{at}}$ (Nb_2O_4) = 3322 ± 45			$\Delta H^0_{0,\mathrm{at}}$ (Nb_4O_9) = 7958 ± 82		$\Delta H^0_{0,\mathrm{at}}$ (Nb_4O_{10}) = 8595 ± 123	

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estimated frequencies and that possible errors in the estimates which can heavily affect the Gibbs energy functions produce only minor effects on the heat-content functions. This implies that the heat content values reported in Table II can be used for deriving second-law heats of reactions from experimental data measured at high temperatures with much greater confidence than the corresponding Gibbs energy functions can be used for deriving third-law heat of reactions from the same data. Indeed, by taking $Nb_2O_{5(g)}$ as an example, if the last of the assumptions considered had been chosen for this molecule, the use of the Gibbs energy functions in Table II in third-law calculations made at an average temperature of 2100 K would result in a possible error of $n \times 51.5$ kJ mol^{-1} on the ΔH_0^0 value of a reaction involving $Nb_2O_{5(g)}$ with stoichiometric coefficient n. For the same reaction and the same conditions, however, the use of the heat-content functions in Table II in second-law calculations would produce a possible error in the ΔH_0^0 of reaction not larger than $n \times 1.4$ kJ mol^{-1}.

C. Heats of reactions and atomization energies

The following gaseous equilibria were studied:

$$Nb_2O_4(g) = 2NbO_2(g)\,, \quad (1)$$

$$Nb_2O_5(g) + NbO(g) = Nb_2O_4(g) + NbO_2(g)\,, \quad (2)$$

$$Nb_4O_9(g) = Nb_2O_5(g) + Nb_2O_4(g)\,, \quad (3)$$

$$Nb_4O_{10}(g) = 2Nb_2O_5(g)\,, \quad (4)$$

$$Nb_4O_9(g) + NbO_2(g) = Nb_4O_{10}(g) + NbO(g)\,, \quad (5)$$

$$Nb_4O_9(g) + Nb_2O_5(g) = Nb_4O_{10}(g) + Nb_2O_4(g)\,. \quad (6)$$

Although, in principle, only four of the reported equilibria are independent, the set of points available for a direct study of the equilibrium (5) is rather different from those available for the reaction which yield indirect data on this same equilibrium. Since different systematic errors might have been different at different temperatures and/or might have played different roles in the thermodynamic treatment of the different sets of points, particularly in the second-law treatment of the data, equilibrium (5) may be considered as an independent one. This was not the situation with equilibrium (6) which was studied only to ascertain whether or not it could provide a more reliable value for the atomization energy of $Nb_4O_{10(g)}$ than that derivable from the study of equilibrium (4).

The equilibrium constants and third-law data for the pressure-independent reactions (2), (5), and (6) and for pressure-dependent reactions (1), (3), and (4) are reported in Tables III an IV, respectively. Also reported in the same tables are the second-law heats obtained through the usual least-squares treatment of $\ln K_p$ vs $1/T$ data points from these reactions. The errors quoted on the average third- and second-law heats of reactions are standard deviations on the individual points and slopes.

Within these errors there is a good agreement between second- and third-law results but this agreement, as well as the absence of temperature trends in the individual third-law data and the good linear correlation of the $\ln K_p$ vs $1/T$ dependences, cannot definitely exclude the presence of significant systematic errors. In fact, many of the quantities required in the third- and second-law evaluations of the experimental data had to be estimated and possible errors in the estimates, as well as systematic errors in the measured quantities might have compensated.

Better information on the true reliability of the results reported in Tables III and IV can be obtained by inquiring into the limits in which an accidental compensation of errors from different sources was really effective. To this end, the effects of reasonable changes in the choice of the estimated quantities on the calculated heats of reactions were compared with those of the systematic errors in temperature, fragmentation evaluation, and ion intensity readings assumed as large as suggested by the actual performance of the experimental apparatus.

In summary, we were able to conclude that in spite of the relative importance of the associated standard deviations there are no reasons to prefer the third-law to the second-law heats of reactions, and vice versa. Therefore, their averages were selected and reported as "proposed values" for ΔH_0^0 of reactions. These proposed values should be considered reliable within three times their associated errors which represent estimated standard deviations accounting for the distribution, assumed as normal, of the effects of all the various uncertainties connected with data acquisition and evaluation.

The atomization energy values reported in Tables III and IV for the new niobium oxide molecules were derived by combining the proposed values for the heats of the various reactions with the values $\Delta H_{0,at}^0(NbO_2) = 1405 \pm 14$ kJ mol^{-1} and $D_0^0(NbO) = 774 \pm 18$ kJ mol^{-1} selected in our study of the Eu–Nb–O system,[5] and assuming the errors in the ancillary data have the same significance as those associated with our proposed heats of reactions.

As shown in the same tables, there is numerical coincidence of the $Nb_4O_{10(g)}$ atomization energy values derived from reactions (4), (5), and (6) but, at least in the case of reaction (5), it is to be considered as completely accidental. Therefore the $\Delta H_{0,at}^0(Nb_4O_{10})$ values from reaction (5) and either reaction (4) or (6) can be combined to give a more reliable value coincident. Thus, by taking the value with the lower associated uncertainty, i.e., from reaction (6), the resulting mean value was $\Delta H_0^0(Nb_4O_{10}) = 8595 \pm 71$ kJ mol^{-1}.

The standard heats of formation $\Delta H_{f,298}^0$ for the newly identified molecules were obtained from their atomization energies and standard heat content values reported here along with the standard heats of formation of $Nb_{(g)}$[12] and $O_{(g)}$.[13] The resulting values for $Nb_2O_{4(g)}$, $Nb_2O_{5(g)}$, $Nb_4O_{9(g)}$, and $Nb_4O_{10(g)}$, in kJ mol^{-1}, were -909 ± 45, -1252 ± 59, -2889 ± 82, and -3281 ± 71, respectively.

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