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The equilibria $Ni(g) + {}^1/_2O_2(g) = NiO(g)$, $Cu(g) + {}^1/_2O_2(g) = CuO(g)$, $CuO(g) + Ni(g) = Cu(g) + NiO(g)$, and $Zn(g) + {}^1/_2O_2(g) = ZnO(g)$ were studied by high temperature mass spectrometry with a position-sensitive ion detection system. Except for ZnO(g), all gaseous species in these equilibria were observed. The $\Delta_f H^\circ_{298}$(II,III)[NiO(g)] and D°_0(II,III)[NiO(g)] determined reinforce literature values within experimental error. Values obtained for $\Delta_f H^\circ_{298}$[CuO(g)] and D°_0[CuO(g)] have a large uncertainty associated with them, perhaps due to lack of equilibrium. Moreover, second and third law heats are not in agreement. ZnO(g) was not observed; however, by evaluating the sensitivity of the instrument, a lower limit for the standard enthalpy of formation for ZnO(g) was determined: $\Delta_f H^\circ_{298}[ZnO(g)] \geq 151$ kJ/mol. From this value an upper limit for the dissociation energy of ZnO is determined: $D^\circ_0[ZnO(g)] \leq 226$ kJ/mol ($\leq$2.3 eV). This bond energy is 48 kJ/mol (0.5 eV) lower than the upper limit obtained from a previous thermochemical study but is in agreement with a more recent determination based on a study of threshold for an ion–neutral reaction.[7]

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High Temperature Mass Spectrometric Studies of the Bond Energies of Gas-Phase ZnO, NiO, and CuO

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The equilibria $Ni(g) + {}^1/_2O_2(g) \rightleftharpoons NiO(g)$, $Cu(g) + {}^1/_2O_2(g) \rightleftharpoons CuO(g)$, $CuO(g) + Ni(g) \rightleftharpoons Cu(g) + NiO(g)$, and $Zn(g) + {}^1/_2O_2(g) \rightleftharpoons ZnO(g)$ were studied by high temperature mass spectrometry with a position-sensitive ion detection system. Except for ZnO(g), all gaseous species in these equilibria were observed. The $\Delta_f H^\circ_{298}$(II,III)[NiO(g)] and D°_0(II,III)[NiO(g)] determined reinforce literature values within experimental error. Values obtained for $\Delta_f H^\circ_{298}$[CuO(g)] and D°_0[CuO(g)] have a large uncertainty associated with them, perhaps due to lack of equilibrium. Moreover, second and third law heats are not in agreement. ZnO(g) was not observed; however, by evaluating the sensitivity of the instrument, a lower limit for the standard enthalpy of formation for ZnO(g) was determined: $\Delta_f H^\circ_{298}[ZnO(g)] \geq 151$ kJ/mol. From this value an upper limit for the dissociation energy of ZnO is determined: $D^\circ_0[ZnO(g)] \leq 226$ kJ/mol ($\leq$2.3 eV). This bond energy is 48 kJ/mol (0.5 eV) lower than the upper limit obtained from a previous thermochemical study but is in agreement with a more recent determination based on a study of threshold for an ion–neutral reaction.[7]

Introduction

The thermochemical properties of gas-phase transition metal monoxides are of interest in materials research,[1] but are not well-known in some cases. We present in this report results from a study which was initiated to determine the dissociation energies of gaseous ZnO, CuO, and NiO using high temperature mass spectrometry. Pedley and Marshall[2] made a critical analysis of then-available data and derived $D^\circ_0(ZnO) \leq 267$ kJ/mol based on the measurements by Anthrop and Searcy,[3] who studied the vaporization of ZnO by Knudsen weight loss measurements, by mass spectrometric analysis, and by transpiration measurements in a stream of helium. They observed no evidence for the presence of gaseous ZnO in any of these studies, and the derived dissociation energy is based on the detection sensitivity. By contrast, Grade and Hirschwald[4] and Kazenas et al.,[5] also using Knudsen cell high temperature mass spectrometry, reported observing gaseous ZnO in thermal equilibrium. These latter studies yielded values of 284 ± 14 and 287 ± 4.2 kJ/mol, respectively, for $D^\circ_0(ZnO)$; the thermal functions given by Pedley and Marshall[2] were used to convert the $D^\circ_{298}(ZnO)$ results to $D^\circ_0(ZnO)$. In addition to these high temperature mass spectrometric studies discussed above, there have been two different kinetic studies which have yielded dissociation energies for ZnO. Wicke[6] studied the reaction of hyperthermal Zn atoms with nitrous oxide, where the zinc atoms were formed by laser vaporization of a thin film. Electronically-excited ZnO is formed by the collision of zinc atoms with nitrous oxide. By measuring the threshold kinetic energy value for chemiluminescence produced by ZnO(g) in the reaction, Wicke[6] deduced a bond energy of ≥270 ± 19 kJ/mol (≥2.8 ± 0.2 eV). An important cautionary note about this measurement is that the emission from ZnO* was quite weak, so that it was necessary to make broad-band measurements (i.e. the radiation was not dispersed spectroscopically); this could lead to confusion if there are emitting species other than ZnO* or if the emission is from an incorrectly-identified state of ZnO. More recently, Clemmer et al.[7] determined $D^\circ_0(ZnO) = 155 \pm 4$ kJ/mol (1.61 ± 0.04 eV) from a determination of threshold for the reaction $Zn^+ + NO_2 \rightarrow ZnO^+ + NO$. Clemmer et al.[7] concluded that the beam data may have been in error due to metastable contributions in the Zn atomic beam.

Recently, we equipped our high temperature mass spectrometer with a position-sensitive detector and have thereby increased the sensitivity by 2 orders of magnitude. In view of the large differences in reported values for the dissociation energy of ZnO(g) and the high sensitivity needed to detect ZnO(g) in the high temperature reaction

$$Zn(g) + {}^1/_2O_2(g) \rightleftharpoons ZnO(g) \qquad (1)$$

we have reinvestigated the zinc oxide thermochemistry using Knudsen cell high temperature mass spectroscopy. In addition to ZnO(g), the available data on CuO(g) are not conclusive or preliminary (Clemmer et al.[7]), and therefore equilibria involving this oxide are also included in this study. From the heat of reaction for

$$CuO(g) + Ni(g) \rightleftharpoons Cu(g) + NiO(g) \qquad (2)$$

Smoes et al.[8] determined D°_0(III)[CuO] to be 265.7 ± 21 kJ (as corrected by Pedley and Marshall[2]); we tried to use the same reaction as well as

$$Cu(g) + {}^1/_2O_2(g) \rightleftharpoons CuO(g) \qquad (3)$$

As will be discussed, our efforts at determining this dissociation energy have not been entirely successful.

The bond energy for NiO(g) had been previously determined by Grimley et al.;[9] however, a discrepancy between the second and third law values for the bond dissociation energy of NiO(g) is reported in that reference. We have therefore included a study of the reaction

$$Ni(g) + {}^1/_2O_2(g) \rightleftharpoons NiO(g) \qquad (4)$$

Experimental Section

The magnetic sector high temperature mass spectrometer (Nuclide Model 12-60) has been described in detail elsewhere[10,11] and is only briefly portrayed here. The apparatus is evacuated using 4- and 8-in.-diameter cryopumps (CTI Cryogenics) and one 4-in. ion pump (Varian). A Knudsen cell containing the sample is radiatively heated and can be optionally equipped with a gas-inlet tube. The temperature of the cell is determined by thermocouples or optical pyrometry. The neutral molecular beam effusing from the Knudsen cell orifice enters an electron-impact ion source through a moveable shutter. The ions are accelerated by a 4500-V potential drop into a 60°, 12-in.-radius magnetic mass filter where they are dispersed according to their mass-to-charge ratios. The dispersed ions in the mass-to-charge ratio

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range m/e to $1.2m/e$ are then detected by a position-sensitive detector system described below. The electron energy and the magnetic induction are controlled by a microcomputer.

An alumina-lined molybdenum Knudsen cell with an 0.5-mm effusion hole is used. For equilibrium 1, the solid phase is either ZnO(s) or a mixture of ZnO(s) and NiO(s), while, for equilibria 2–4, the solid phase is a mixture of CuO(s) and NiO(s). Ion intensities are measured 3 eV above the appearance potential of each species. The electron energy is calibrated using the known ionization potentials of nickel (7.635 eV),[12] copper (7.726 eV),[12] or oxygen (12.063 eV).[13] Ionization efficiency curves were used to determine the appearance potentials (ionization energies) by the vanishing current method. Ni(g) and Cu(g) are detected simultaneously, as are NiO(g) and CuO(g). O_2 ion count rates are measured concurrently. The intensities of all five species are measured as a function of temperature over the range 1470–1620 K. Unlike the study by Smoes et al.,[7] who used a mixture of NiO(s) and Cu(s), we have chosen NiO(s) and CuO(s) in order to reduce the activity of Cu. At 1700 K, Cu has a vapor pressure that approaches the molecular flow limit.

The position-sensitive detector and associated electronics are described in detail elsewhere[11] and will be described here only briefly. The detector (Galileo Electro-Optics Corp.) consists of two stacked microchannel plates (Chevron assembly) backed by a resistive anode encoder (RAE). Upon ion impact, the microchannel-plate assembly produces a secondary-electron pulse with a gain of 10^8. This pulse strikes the RAE resulting in a signal which is monitored at both ends of the RAE. The widths of the pulses are dependent on the RC characteristics of the RAE and are related to the position where the ion originally strikes the upper microchannel plate, and therefore to the mass-to-charge ratio of the ion. Output pulses from each end of the RAE are processed in parallel by preamplifiers and spectroscopy amplifiers. Two constant fraction single channel analyzers convert the two different pulse widths into a time difference between the transistor–transistor logic (TTL) output pulses. The two TTL pulses are used as the "start" and "stop" signals of a time-to-amplitude converter single channel analyzer (TAC SCA). The TAC output pulses are input into a microcomputer-based multichannel analyzer in a pulse-height-analysis mode. The position-sensitive detection system permits the observation and isotopic identification of species with densities in the Knudsen cell that result in less than 1 count/s. This detection limit of the counting system corresponds to a pressure of $\sim 1.6 \times 10^{-10}$ atm for silver; by comparing the electron impact ionization cross sections of silver and zinc, we derive a detection limit of 2×10^{-10} atm for ZnO.

Results and Discussion

Partial pressures are calculated from the ion intensities for each species by calibration with silver. Species are identified by isotope ratios (as shown in Figure 1) and ionization potentials. Examples of ionization efficiency curves for Ni and NiO, Cu, and CuO are shown in Figures 2–4, respectively. The appearance potentials for CuO and NiO, determined by the vanishing current method, are 9.1 ± 0.5 and 8.8 ± 0.3 eV, respectively. The ionization energy scale is calibrated through ionization efficiency curves of Ni and Cu and their known ionization potentials.[12] These appearance potentials, which we equate with the adiabatic ionization potentials, are in close agreement with those given by Fisher et al.;[14] namely, IP(CuO) = 8.86 ± 0.27 eV and IP(NiO) = 8.77 ± 0.18 eV. The electron impact ionization cross sections used in the equilibrium calculations are given in Table III of the Appendix. The metal oxides are estimated to have ionization cross sections similar to those of the corresponding metals. Auxiliary thermodynamic data necessary for second and third law calculations and for the determination of the heats of formation and bond energies are given in the Appendix and are taken from the JANAF Thermochemical Tables[15] or from Pedley and Marshall.[2]

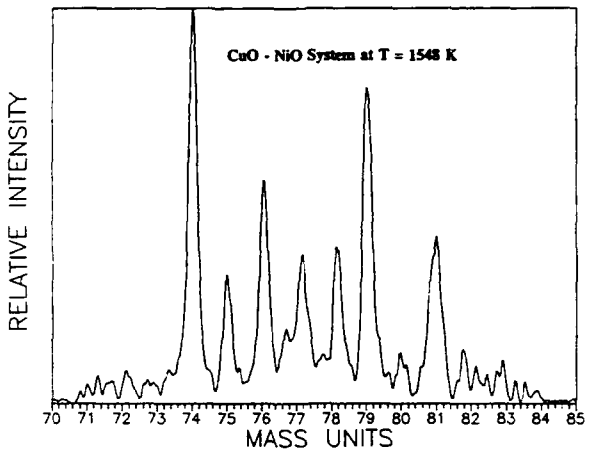

Figure 1. Mass spectrum of reaction 2 NiO and CuO constituents obtained with the position-sensitive detection system.

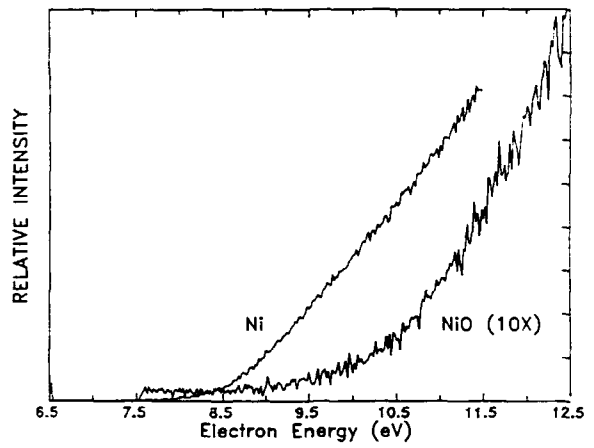

Figure 2. Ionization efficiency curve of Ni and NiO.

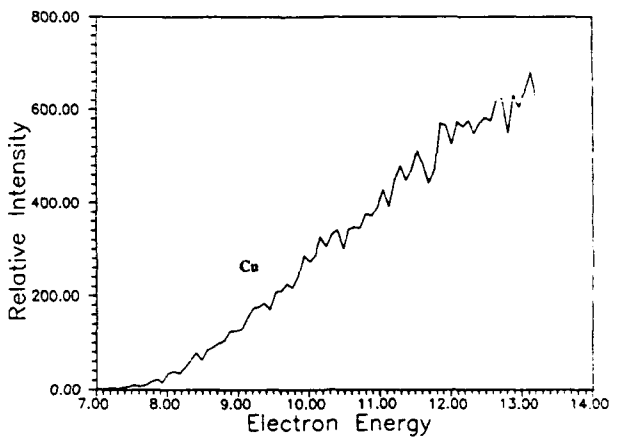

Figure 3. Ionization efficiency curve of Cu.

D°_0(ZnO): ZnO(g) is not observed when ZnO(s), a mixture of ZnO(s) and Ni(s), or either of these with an additional O_2(g) flow (to force the equilibrium in favor of ZnO(g)) is heated in the Knudsen cell up to 1700 K. As discussed in the previous section, the detection limit of the instrument for ZnO(g) is 2×10^{-10} atm; from this we calculate an upper limit for the standard third law heat of reaction for equilibrium 1, $\Delta_r H^\circ_{298}(\mathrm{III})_a \leq 20.3$ kJ/mol. This results in $\Delta_f H^\circ_{298}[\mathrm{ZnO(g)}] \geq 151$ kJ/mol and $D^\circ_0(\mathrm{ZnO}) \leq 226$ kJ/mol ($\leq$2.3 eV). This upper limit for the bond energy is 48 kJ/mol (0.5 eV) lower than the upper limit reported by Anthrop and Searcy[3] and supports the lower bond energy of 155 ± 4 kJ/mol determined by Clemmer et al.[7] The high values obtained by Grade and Hirshwald[4] and Kazenas et al.[5] suggest a higher partial pressure of ZnO than is derived either from our results or from the measurements by Clemmer et al.[7]

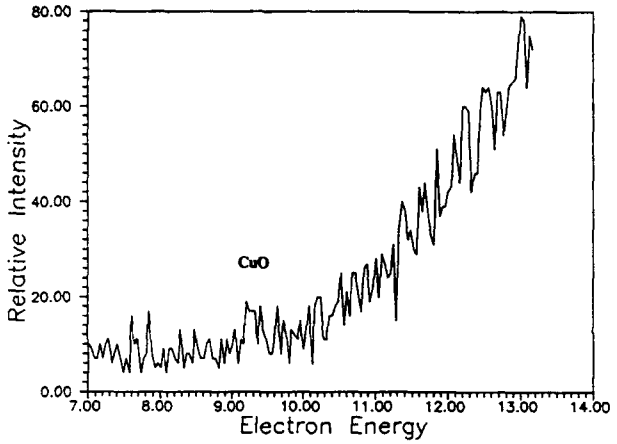

Figure 4. Ionization efficiency curve of CuO.

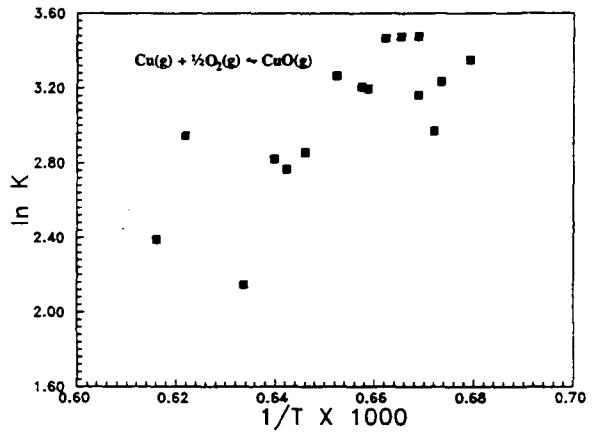

Figure 5. Plot of ln $k_{eq}(2)$ vs $1/T$.

Such a condition would occur if there were impurities in the sample or if the pressure in the Knudsen cell were high enough that the effusion was no longer molecular. The reported temperatures[4] seem to indicate that the second hypothesis is not the cause of the discrepancy. Thus the most likely explanation is that an impurity was mistakenly identified as ZnO. Due to the very low signal levels, isotopic identification may have been infeasible. Interestingly, the limit obtained here for the dissociation energy of ZnO, $D^\circ_0(\mathrm{ZnO}) < 2.3$ eV, is consistent not only with the recent measurements reported by Clemmer et al.[7] but also with the theoretical calculations of Bauschlicher and Langhoff[16] who report a value of 1.2 eV for the dissociation of ZnO into ground-state products. These theoretical calculations are based on an ionic model, Zn^+, O^-, which predicts a ground state in the configuration $^1\Sigma^+$, with a $^3\Pi$ state lying 54 cm^{-1} above the ground state.

D°_0(NiO): Gas-phase equilibria 2–4 were studied simultaneously over a solid-phase mixture of NiO(s) and CuO(s), which yielded reproducible results. The results obtained when O_2 gas passed through the Knudsen cell were inconsistent, and therefore it was assumed that the systems were not in equilibrium, a condition we have observed before when a gas-phase reactant was used.[17] The standard heats for equilibria 2–4 were determined by both the second and third law methods. For equilibrium 4, $\Delta_f H^\circ_{298}(\mathrm{III})[\mathrm{NiO}] = 301 \pm 3$ kJ/mol and $\Delta_f H^\circ_{298}(\mathrm{II})[\mathrm{NiO}] = 309 \pm 30$ kJ/mol were obtained. These yielded $D^\circ_0(\mathrm{III})[\mathrm{NiO}] = 373 \pm 3$ kJ/mol and $D^\circ_0(\mathrm{II})[\mathrm{NiO}] = 366 \pm 30$ kJ/mol. The second and third law values are consistent within the experimental errors (1 standard deviation). In addition, the third law values, shown in Table I, show no trend in temperature, indicating that equilibrium was established for this reaction. The NiO(g) bond dissociation energies are in agreement with the value, $D^\circ_0(\mathrm{III})[\mathrm{NiO}] = 362 \pm 21$ kJ/mol, reported by Grimley et al.,[9] who noted that their second and third law determinations were not in agreement but who had more confidence in the third law value. The good agreement between the second and third law values of this work and the temperature independence of the latter eliminate doubts raised by the second law data of Grimley et al.[9] Our results are further corroborated by values derived from metathetical reactions of 377 ± 17 kJ/mol given in ref 8.

D°_0(CuO): Equilibrium 3 data lead to $\Delta_f H^\circ_{298}(\mathrm{III})[\mathrm{CuO}] = +329 \pm 5$ kJ/mol, $\Delta_f H^\circ_{298}(\mathrm{II})[\mathrm{CuO}] = +433 \pm 33$ kJ/mol. The discrepancy between third and second law values and curvature in a plot of ln $K_{eq}(3)$ vs $1/T$, which is shown in Figure 5, indicate that equilibrium involving Cu(g) and CuO(g) was not established in the Knudsen cell. An indication of lack of equilibrium is that the heat of vaporization of Cu derived from

$$\mathrm{Cu(c)} \rightarrow \mathrm{Cu(g)} \tag{5}$$

is incorrect. Likewise, for the equilibrium

$$\mathrm{CuO(c)} \rightarrow \mathrm{CuO(g)} \tag{6}$$

a plot of ln k_{eq} vs $1/T$ shows much scatter and, perhaps, some curvature. These observations suggest that both Cu(c) and CuO(c) are not at unit activity; hence it is not possible to derive thermodynamic data from these measurements. If we assume that Cu–CuO equilibrium is not established except at the six low temperatures marked in Table II, then we can obtain a reasonable heat of vaporization of Cu (≈318 kJ/mol). The implication is that equilibrium is maintained only over a narrow temperature interval of 50°. These equilibria then lead to a third law dissociation energy of CuO = 259 kJ/mol; the uncertainty is estimated to be about 30 kJ/mol, due to cummulative errors.

In view of the uncertainty in the thermochemical measurements, the best value for $D^\circ_0(\mathrm{CuO})$ is probably the preliminary result

TABLE I: Equilibrium Constants and Third Law Results for the Reaction Ni + $^1/_2O_2$ ⇌ NiO

temp (K)	P(Ni) ($\times 10^{-8}$ atm)	$P(O_2)$ ($\times 10^{-7}$ atm)	P(NiO) ($\times 10^{-10}$ atm)	equilib const (K)	$\Delta_f H^\circ_{298}$(III) (kJ mol^{-1})	D°_0(III) (kJ mol^{-1})
1472	1.42	2.35	1.97	28.5	302.5	372.4
1485	2.06	2.95	2.84	25.4	302.9	372.0
1488	2.20	3.58	2.57	19.5	305.8	369.0
1495	2.49	3.77	5.24	32.3	299.2	375.7
1495	3.54	4.25	5.13	23.6	302.9	372.0
1503	2.47	5.85	6.10	32.3	298.3	376.6
1510	3.30	6.43	8.47	32.0	297.9	377.0
1518	2.81	8.56	8.62	24.4	300.4	374.5
1521	4.70	8.24	10.6	24.7	300.0	374.9
1533	5.24	8.98	13.0	26.2	298.3	376.6
1548	8.23	11.6	15.4	17.4	302.5	372.4
1557	10.6	15.7	21.1	15.9	302.4	372.0
1563	13.0	14.1	25.9	16.8	301.7	373.2
1578	4.25	180	15.5	8.55	309.2	365.7
1608	7.87	79.5	42.2	19.0	295.8	378.7
1623	9.42	66.9	26.5	10.9	302.5	372.4
					av: 301.2	av: 373.2

TABLE II: Equilibrium Constants and Third Law Results for the Reaction $Cu + {}^1/_2O_2 \rightleftharpoons CuO$

temp (K)	P(Cu) ($\times 10^{-6}$ atm)	$P(O_2)$ ($\times 10^{-7}$ atm)	P(CuO) ($\times 10^{-10}$ atm)	equilib const (K)	$\Delta_f H^\circ_{298}$(III) (kJ mol^{-1})	D°_0(III) (kJ mol^{-1})
1472[a]	4.91	2.35	1.95	0.082	333.0	256.9
1485[a]	6.39	2.95	3.19	0.092	331.8	258.6
1488	5.92	3.58	2.87	0.081	333.5	256.9
1495[a]	7.42	3.77	5.72	0.126	328.0	262.3
1495[a]	7.14	4.25	3.00	0.065	336.0	254.0
1503	7.41	5.85	6.54	0.115	328.9	261.5
1510[a]	9.33	6.43	7.26	0.097	331.0	259.4
1518	7.77	8.56	9.34	0.130	327.2	263.2
1521[a]	10.6	8.24	9.86	0.103	330.1	260.2
1533	12.0	8.98	25.8	0.227	320.1	270.3
1548	14.2	11.6	15.7	0.103	330.1	260.2
1557	14.5	15.7	16.3	0.090	331.8	258.6
1563	15.8	14.1	21.3	0.114	328.9	261.5
1578	12.6	180	76.2	0.143	325.5	264.4
1608	16.3	79.5	108	0.236	318.8	271.5
1623	17.4	66.9	63.3	0.140	325.5	264.8
					av: 328.9	av: 261.5

[a] Measurement at these temperatures yields a heat of vaporization for Cu which agrees with published data.

TABLE III: Electron Impact Ionization Cross Sections

atom or molecule	electron energy (eV)	ionization cross section (cm^2)
Zn	12.4	8.9×10^{-17} [20]
Cu	10.6	4.7×10^{-17} [22]
Ni	10.6	5.2×10^{-17} [21]
O_2	15.1	0.69×10^{-17} [22]
Ag	10.5	7.0×10^{-17} [23]

TABLE IV: Free Energy Functions[8,24]

temp (K)	$(-(G^\circ_T - H^\circ_{298})/T$ (J mol^{-1} K^{-1}))						
	CuO(g)	Cu(g)	NiO(g)	Ni(g)	ZnO(g)	Zn(g)	O_2
1400	262.422	182.186	257.062	200.643	251.263	176.778	229.158
1500	264.469	183.325	259.026	201.987	253.244	177.917	231.002
1600	266.420	184.409	260.901	203.263	255.133	179.000	232.768
1700	268.281	185.443	262.693	204.477	256.935	180.032	234.462
1800	270.061	186.430	264.408	205.634	258.659	181.018	236.089

TABLE V: Enthalpy Functions[8,24]

temp (K)	$(H^\circ_T - H^\circ_{298}$ (kJ mol^{-1}))						
	CuO(g)	Cu(g)	NiO(g)	Ni(g)	ZnO(g)	Zn(g)	O_2
1400	41.132	22.907	39.430	27.051	39.784	22.903	36.957
1500	44.938	24.991	43.157	29.461	43.494	24.982	40.599
1600	48.753	27.079	46.892	31.854	47.208	27.060	44.266
1700	52.576	29.174	50.636	34.230	50.924	29.139	47.958
1800	56.408	31.277	54.386	36.590	54.644	31.217	51.673

of 207 ± 14 kJ/mol (2.85 ± 0.15 eV) reported by Clemmer et al.[7] using ion–molecule reaction threshold information. This dissociation energy of CuO agrees well with theoretical calculations: (1) using semi-empirical pseudopotentials, Igel et al.[18] calculated D_e(CuO) = 2.53–2.80 eV; (2) *ab initio* SCF and CI calculations by Mahadevan and Newton[19] yield D_e(CuO) = 2.1–2.57 eV. In both cases the bonding in CuO is considered to be ionic, Cu^+, O^-.

Summary and Conclusions

With regard to the bond energy of ZnO(g), our results ($D^\circ_0 \leq 226$ kJ/mol) are consistent with the findings of Clemmer et al.[7] but are inconsistent with those of Anthrop and Searcy,[3] Grade and Hirschwald,[4] Kazenas et al.,[5] and Wicke.[6] The previously reported bond energy of NiO(g) has been confirmed, and a disparity between second and third law values has been eliminated. The discrepancy between second and third law values for the CuO(g) bond energy precluded a determination of its thermochemical properties.

Acknowledgment. We thank AFOSR for supporting this work under Task 2303G201. We also wish to thank one of the reviewers for calling our attention to the ionization potential measurements by Fisher et al.[14]

Appendix

The auxiliary thermochemical data given in Tables III–V were used to determine the quantities given in the main body of the paper.

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