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FREE ENERGY FUNCTIONS FOR SOME MO_2 OXIDES

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ABSTRACT

The free energy functions for nine transition metal dioxides have been estimated by considering them as linear symmetrical molecules.

Unlike the diatomic oxide case,[1,2] there are very few spectroscopic data available for the gaseous triatomic oxides of metals. Hence in calculating the thermodynamic functions for these dioxides, almost all of the necessary molecular constants have to be estimated. In the first instance, the free energy functions (fef) for nine transition metal oxides are calculated on the basis of a linear symmetrical molecular approximation.

(1) Electronic Free Energy Functions

Since the experimentally observed electronic states for any of these molecules are not known, an ionic model similar to one assumed in the calculating of fef for monoxides,[3] is assumed. Thus, the molecular electronic states are equated to the energy levels of M^{+4} ions as given by Moore.[4] Employing these energy levels of ions, the electronic free energy functions were calculated. However, no M^{+4} ion energy levels for Hf, Ta or W are available and the electronic free energy functions for them have been obtained by extrapolating the values of other molecules in the corresponding periodic groups.

(2) Rotational and Vibrational Free Energy Functions

In computing the rotational contribution to the fef, the interatomic distances of oxygen atom to central metal atom were approximated to the internuclear distance of the corresponding monoxides. This approximation implies that the bond order in the two classes of oxides are the same which may not

strictly be true. But the difference in the bond orders in these two classes introduces fairly small changes in the r_e values. However, this approximation of assuming the same bond distances in both dioxides and monoxides introduces a small correction in fef which is much smaller than the other uncertainties in calculating fef. Moreover, our knowledge of internuclear distances in the monoxides is not accurate to warrant any corrections. Walsh[5] has concluded that triatomic molecules with a total of 18 valence electrons would be bent as is observed for dioxides of the sulfur family. However, we have assumed that this would not be true with some of the electrons in d orbitals.

One of the biggest uncertainties introduced in calculating the fef for MO_2 oxides is in estimating the bending frequencies of vibration. These frequencies are generally small and are doubly degenerate. Hence the contribution of bending vibrational mode of molecule to fef is considerable and any estimation of this frequency introduces a large uncertainty.

In our calculation, we have assumed that the stretching force constants of dioxides are the same as the force constants of the corresponding monoxides. Bending force constants are thus calculated assuming a constant ratio for the bending force constant to stretching force constant and this ratio was considered the same for all molecules as for CO_2. Thus all the three fundamental frequencies of vibrations were evaluated using valence force method.

The total free energy functions and the estimated frequencies of vibration for gaseous TiO_2, VO_2, CrO_2, ZrO_2, NbO_2, MoO_2, HfO_2, TaO_2 and WO_2 are given in Table 1.

Table 1

Vibrational frequencies and $-\left(\frac{F^{o} - H_{o}^{o}}{T}\right)$ for MO_2 molecules

	$\omega_1 cm^{-1}$	$\omega_2 cm^{-1}$	$\omega_3 cm^{-1}$	298	1000	1500	2000	2500	3000
TiO_2	873	292	1125		60.5	65.5	69.3	72.3	74.9
VO_2	882	291	1125		64.2	69.4	73.0	76.4	79.0
CrO_2	785	259	996		66.0	71.4	75.4	78.6	81.2
ZrO_2	863	260	1000		62.4	67.5	71.2	74.3	76.8
NbO_2	870	262	1009		65.3	70.6	74.5	77.8	80.4
MoO_2	776	232	895		66.8	72.3	76.4	79.7	82.4
HfO_2*	860	244	935		64.3	69.4	73.2	76.2	78.8
TaO_2*	864	244	935		67.4	72.5	76.3	79.4	81.9
WO_2*	675	216	835		62.7	74.0	78.0	80.9	83.4

*electronic contributions are extrapolated values from values of other members of the same group.

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