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THE STABILITY OF GASEOUS SnO, ZnO, CdO, CuO, PbO, GeO, SiO and TiO

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1. Introduction.

In view of the instability of the gaseous alkali oxides[1], the gaseous alkaline earth oxides[2], FeO(g)[3], NiO(g)[4] and MnO(g)[5], an investigation has been made of the data in the literature relative to the observed volatility of other monoxides. In essentially all such studies, the stability of the gaseous diatomic oxide has been assumed, and where the accuracy and scope of the measurements permitted, the vapor-pressures and heats of sublimation have been calculated on the basis of this assumption. A rather simple method may be used to show whether or not the data actually indicate that the solid oxide is vaporizing by dissociation. This method involves the use of the heat of formation of solid oxide, which when combined with heat of sublimation of the metallic element concerned enables one to calculate the vapor-pressure of the metallic gas in equilibrium with the oxide. If such a calculation yields values which are in close agreement with those which have been measured experimentally, the dissociation of the oxide upon vaporization is shown to occur.

If the spectroscopic value for the heat of dissociation of the diatomic molecule is well established, one may combine this value with the heat of formation of the oxide to calculate the vapor-pressure of the gaseous oxide at the appropriate temperatures. If these values are much lower than those observed, further verification of dissociation is obtained. Actually the spectroscopic values are rarely of sufficient accuracy because of uncertainties in fixing the ground state of the molecule and the difficulties involved in

extrapolating observed vibrational levels to the true dissociation limit. In many cases it is the determination of the heat of dissociation by chemical methods which allows one to decide which of several possible spectroscopic values is correct.

In the following discussion, the methods of calculation applied to each diatomic oxide are presented. The sources of thermodynamic data used in these calculations are as follows: heats of formation of solid oxides, Brewer[2], National Bureau of Standards[6]; thermodynamic properties of the elements, Brewer[7]; entropies of inorganic compounds and elements at 298.1°K, Kelley[8]; $S_T - S_{298}$ and $H_T - H_{298}$ and heat capacity values for inorganic compounds and elements, Kelley[9]; dissociation energies of diatomic oxides, Gaydon[10] and Herzberg[11].

2. Thermodynamic Treatment.

A. SnO. The recent investigation of the stability and volatility of tin oxides carried out by Vesselovsky[12] essentially establishes the fact that SnO is a stable gaseous species. The volatility of a mixture of $SnO_2(s) + Sn(l)$ was studied in vacuum at temperatures where neither $SnO_2(s)$ nor Sn(l) have an appreciable volatility (721-893°C). The thirteen vapor-pressure measurements were combined with high temperature heat content and entropy data to yield the heat of formation of SnO(g):

$$Sn(s) + SnO_2(s) = SnO(g), \quad \Delta H_{298} = 136.9 \pm 0.7 \text{ kcal/mole}.$$

The heat of dissociation of the SnO molecule was calculated by use of the following thermochemical data:

$$Sn(s) + O_2(g) = SnO_2(s) \qquad \Delta H_{298} = -138.8 \text{ kcal/mole}$$

$$2Sn(g) = 2Sn(s) \qquad \Delta H_{298} = -140.0 \text{ kcal/mole}$$

$$2O(g) = O_2(g) \qquad \Delta H_{298} = -118.6 \text{ kcal/mole}$$

$$Sn(g) + O(g) = SnO(g) \qquad \Delta H_{298} = -130.2 \text{ kcal/mole}$$

$$\Delta C_p = -1.4 \text{ cal/mole/deg.}$$

$$\Delta H_o = -131.6 \text{ kcal/mole}$$

$$D_c(SnO) = 131.6 \text{ kcal/mole}$$

$$= 5.70 \text{ e.v./mole}$$

It is of interest that Herzberg[11] obtains the value 5.7 e.v. by a long linear extrapolation of lower vibrational levels and that Gaydon[10] reduces this value to 3.2 e.v. by empirical methods to correct for non-linearity of the vibrational levels. It appears that an uncorrected linear extrapolation of the vibrational levels gives the correct dissociation limit.

B. ZnO. Although the experimental techniques employed by Feiser[13] in the determination of the volatility of ZnO are not commensurate with high accuracy, the values so obtained are the only ones available. The volatility was measured by the rate of weight loss from an open sample heated in a static atmosphere. The vapor-pressure of metallic zinc was calculated from the heat of formation of ZnO and the heat of sublimation of Zn at the temperatures which Feiser reported. The calculated Zn partial pressures over ZnO are a factor of 2-3 greater than the ZnO pressures reported by Feiser and therefore the entire volatility can be accounted for by dissociation of the zinc oxide.

Taking Feiser's values as upper limits to the vapor-pressure of ZnO(g) the calculated value for the heat of dissociation of ZnO(g) to the gaseous atoms is $\Delta H_0 \leq 92$ kcal/mole.

C. CdO. Uyeno[14] has reported the results of measurements of the vapor-pressure of CdO which were made by the effusion method. Since his experimental techniques were of an accurate nature and he gives a comprehensive report of the data taken, a more extensive treatment of his results has been made.

In Table I column 2 the vapor-pressures of CdO(g) reported by Uyeno are given. Column 3 gives the vapor-pressures of Cd(g) as calculated from thermochemical data. The calculated values for P_{Cd} are in very good agreement with those for P_{CdO} and shown conclusively that CdO vaporizes by the reaction $CdO(s) = Cd(g) + \frac{1}{2} O_2(g)$.

From the weight loss of the effusion cell per unit time which Uyeno reports, the standard heat of formation of CdO may be calculated. In order to do this it is necessary to have some knowledge of the ratio of escaping $O_2(g)$ molecules to Cd(g) atoms in order to apply the reported weight losses to such a calculation. During the vapor-pressure measurement the composition of the solid necessarily falls within the CdO solid solution range because at the Cd - CdO edge the vapor-pressure of Cd is about 0.9 atm. and $P_{O_2} = 3.0 \times 10^{-5}$ atm. and at the CdO - O edge, $P_{Cd} = 7.3 \times 10^{-9}$ atm and $P_{O_2} = 1$ atm at 1000°K. If the solid solution range were sufficiently narrow an equilibrium vapor-pressure measurement such as the saturation of an inert gas stream would be done under conditions wherein the composition of the solid CdO would have the same atom ratio as the gas phase, namely $Cd:\frac{1}{2}O_2$. In an effusion measurement the situation is slightly

Table I

T°K	P_{CdO} (atm)	P_{Cd} (atm)	$-\Delta H_{298}$
1003	1.27×10^{-6}	1.45×10^{-6}	66.03
1013	1.68×10^{-6}	2.00×10^{-6}	66.08
1023	1.27×10^{-6}	2.46×10^{-6}	65.90
1033	3.00×10^{-6}	3.17×10^{-6}	65.89
1043	4.16×10^{-6}	4.27×10^{-6}	65.80
1053	5.30×10^{-6}	5.76×10^{-6}	65.95

different than that which obtains in the inert gas measurement. However, if the solid solution range is sufficiently narrow, the Cd atoms and O_2 molecules must escape in the ratio $Cd:\frac{1}{2}O_2$. It is assumed that the composition change in the solid is so small that its composition is essentially stoichiometric CdO. Since the Cd atoms and O_2 molecules are escaping in the ratio $Cd:\frac{1}{2}O_2$, the square root dependence of the rate of escape will not give pressures of Cd(g) and O_2(g) of this same ratio. This effect has been taken into account in the calculations. The equilibrium constants obtained in this manner have been combined with available free energy functions to give the standard heat of formation for the reaction $Cd(s) + \frac{1}{2}O_2(g) = CdO(s)$. The value for each experimental temperature is given in column 4 Table I, the average value being $\Delta H_{298} = -65.9 \pm 0.1$ kcal/mole. Bichowsky and Rossini[15] give for the same reaction $\Delta H_{298} = -65.2$ kcal/mole, whereas the Bureau of Standards Tables[6] give $\Delta H_{298} = -60.86$ kcal/mole. In view of the apparent accuracy of Uyeno's experimental results one is led to conclude that the Bureau of Standards' value should be corrected in favor of the value $\Delta H_{298} = -65.9$ kcal/mole.

If one takes the vapor-pressures given by Uyeno as a generous upper limit to P_{CdO} at the reported temperatures, the calculated upper limit to the heat of dissociation of the gaseous CdO molecule to gaseous atoms is $\Delta H_{298} \leq 88$ kcal/mole.

D. CuO. The stability of gaseous CuO is indicated by the measurement of the vapor-pressure of solid CuO by Mark, Osterhof and Krauer.[16] Although their experimental methods are subject to large error, the vapor-pressures of Cu(s) which they determined in conjunction with those of CuO(s) agree reasonably with those given

by Kelley[17], and therefore it is assumed that the values given for CuO are reasonably accurate. The values given by Mack, et al, for the vapor-pressures of CuO(g) between 873° and 1223°K are a factor of 10^6 - 10^8 higher than the vapor-pressure of Cu(g) in equilibrium with CuO(s) as calculated from the heat of formation of CuO(s). Since these experiments were conducted in 1 atm O_2, it must be concluded that the principle gaseous species is CuO(g).

Since this stability is out of line with that of FeO(g) and NiO(g) it is possible that polymerization to Cu_2O_2(g) is contributing to the observed stability. Effusion measurements of the vapor-pressure of CuO would help determine if this were the case.

From the vapor-pressures given by Mack, et al, one calculates the heat of dissociation of CuO(g) to gaseous atoms to be ΔH_0 = 113 kcal/mole.

E. PbO. Feiser[13] also reports measurements of the volatility of PbO by the same method used to determine the vapor-pressure of ZnO described above. The values given for temperatures between 1023° and 1323°K are at least a factor of 10^2 higher than those which one calculates for the vapor-pressure of Pb(g) in equilibrium with PbO(s) at those temperatures. Thus one is led to conclude that PbO(g) is a stable gaseous species under these conditions. From the vapor-pressures given by Feiser one calculates the heat of dissociation of PbO(g) to gaseous atoms to be ΔH_0 = 98 kcal/mole. Herzberg[11] gives for this value, D_0(PbO) = 99 kcal/mole from a linear Birge-Sponer extrapolation and Gaydon[10] gives D_0(PbO) = 76 kcal/mole by correction of the extrapolated value for non-linearity by empirical methods. As in the case of SnO, it appears that the linear extrapolation gives the better agreement with the chemical value.

F. GeO. No experimentally determined values for the vapor-pressures of GeO are available. However Herzberg[11] gives D_0(GeO) = 139 kcal/mole by a linear extrapolation and Gaydon[10] gives D_0(GeO) = 127 kcal/mole. Although the results for PbO and SnO indicate that the linear extrapolation given by Herzberg is probably a better value than that given by Gaydon, the latter is taken as a lower limit to the stability of the GeO(g) molecule. If the standard heat of formation of GeO(s) is taken as ΔH_{298} = -64 kcal/mole, one then may calculate that at 1000°K the vapor-pressures of GeO(g) and Ge_2O_2 in equilibrium with GeO(s) are respectively 6.2 x 10^{-6} atm and 3.1 x 10^{-14} atm. If the values given by Herzberg and Gaydon are for the ground state of GeO molecule dissociating to unexcited atoms, then the stability of gaseous GeO at 1000°K is strongly indicated by these calculations.

G. SiO. The vapor-pressure of SiO(g) over the mixture Si(s) + SiO_2(s) has been studied by Geld and Kochmer[18] who measured the rate of weight loss from a quartz effusion cell in which the mixture was heated in vacuum. The existence of SiO(g) as a stable gaseous species has been established by the observed volatility under conditions where neither Si(s) nor SiO_2(s) have appreciable vapor-pressures. Their observed entropy of vaporization 35 e.u., indicates that at the temperatures 900-1155°C the Si and SiO_2 solid phases may react to form a SiO(s) phase, since the expected entropy of sublimation SiO(s) = SiO(g) should be about 34 e.u., whereas for the reaction $\frac{1}{2}$Si(s) + $\frac{1}{2}$$SiO_2$(s) = SiO(g) the entropy is about 41 e.u.

Because of the uncertainty of the actual reaction occurring under their experimental conditions, it is not possible to make a

conclusive calculation of the heat of dissociation of the SiO molecule. Assuming only the SiO(s) phase present during volatilization one calculates $D_0(SiO) = 170$ kcal/mole; and assuming the phases Si(s) + SiO_2(s) present, one calculates $D_0(SiO) = 160$ kcal/mole. From a linear Birge-Sponer extrapolation of the ground $^1\Sigma$ state of SiO Herzberg obtains $D_0(SiO) = 7.4$ e.v. and Gaydon gives $D_0(SiO) = 7.8$ e.v. (correcting for slight positive curvature) assuming unexcited atomic products. Linear extrapolation of the $^1\Pi$ state of SiO yields $D_0(SiO) = 8.9$ e.v. for the ground $^1\Sigma$ state if the $^1\Pi$ state goes to unexcited atoms as Gaydon suggests. However $D_0(SiO)$ may assume lower values if the $^1\Pi$ state goes to excited atoms. Gaydon chose 8 $\pm$ 1 e.v. but indicated it as very uncertain. The chemical values of 7.0 to 7.4 e.v. would indicate that the linear extrapolation of the $^1\Sigma$ state gives a reasonably correct value. However, because of the uncertainty in the ground state of SiO, in the accuracy of the extrapolated values and in the states of Si and O atoms as well as the uncertainty in the chemical values, a definitive value for the $D_0(SiO)$ cannot be given on the basis of the available data.

Gold and Kochnev state that the constancy of the measured vapor-pressure during experiments in which 25% of the solid mixture vaporized was evidence that the solid was the single phase SiO and not the mixture Si and SiO_2. Unfortunately this observation cannot be used in support of the direct sublimation they propose since it is actually the two phase system and not the single phase system which is invarient during such an experiment.

H. TiO. From Ehrlich's[19] observation that about 1% of a sample of TiO volatilized in 15 min. at 1600°C and the dimensions of the containing vessel one can calculate an approximate vapor-pressure of

TiO at 1873°K: $P_{TiO} = 1.1 \times 10^{-5}$ atm. The heat of formation of TiO(s) is known but if one accepts the value $\Delta H_{298} = -127$ kcal/mole[2] which makes TiO just barely stable towards disproportionation at room temperature it can be shown that the saturation titanium pressure over the TiO solid solution range at 1873°K will be $P_{Ti} = 2.5 \times 10^{-8}$ atm and that of oxygen will be $P_{O_2} = 1.2 \times 10^{-20}$ atm. Thus the solid TiO must lose Ti at this temperature and the composition must change towards an oxide of higher Ti content. Therefore there is no invariant vaporizing composition within the TiO solid solution range and TiO(g) cannot be an important vaporizing species. Even if TiO(s) is more stable than shown by the assumed heat of formation, the difference in order of magnitude between the titanium and oxygen pressure is great enough to allow this conclusion. The factor of four between the P_{TiO} calculated from Ehrlich's observation and P_{Ti} over the TiO solid solution must be attributed to the very crudeness of the observational data.

An upper limit to the heat of dissociation of TiO(g) to gaseous atoms is $\Delta H_0 \leq 184$ kcal/mole, calculated by assuming $P_{TiO} = 1.1 \times 10^{-5}$ atm as a generous upper limit. That the actual partial pressure of TiO(g) must be much smaller is shown by comparison of the value $\Delta H_0 \leq 184$ kcal/mole with the spectroscopic values $D_0(TiO) = 159$ and 127 kcal/mole given respectively by Herzberg by a linear Birge-Sponer extrapolation and by Gaydon who corrects the extrapolation for non-linearity.

3. Summary.

The results of the above investigation are summarized in Table II. The first column gives the diatomic oxide; the second column, the temperature or temperature range for which the vapor-pressure has been measured or calculated; the third the predominate gaseous

Table II

Oxide	Temp Range, °K	Gaseous Species	D_o (kcal/mole)	Spectroscopic D_o (kcal/mole) LB	LBC
SnO	994 - 1166	SnO	132	131	74 ± 23
ZnO	1673 - 1748	Zn, O_2	≤ 92	—	—
CdO	1003 - 1053	Cd, O_2	≤ 88	—	—
CuO	873 - 1223	CuO	113	—	104 ± 35
PbO	1023 - 1323	PbO	98	99	76 ± 9
GeO	1000	GeO	—	159	127 ± 23
SiO	1173 - 1428	SiO	160, 170	170	184 ± 23
TiO	1873	Ti, O_2	≤ 184	159	127 ± 23

species in equilibrium with the oxide at the indicated temperature; the fourth, the calculated upper limit to or the value for the heat of dissociation as determined by chemical means; the sixth, the values given by Herzberg[11] (LB) and Gaydon[10] (LBC) in which the former has used a linear Birge-Sponer extrapolation of vibrational levels and the latter corrected the linear extrapolation by empirical methods.

It is evident that a large uncertainty is inherent in the spectroscopic values for D_0 for two reasons: (1) when only a few lower vibrational levels are available for extrapolation to the dissociation limit one cannot be certain of the linearity of the change in energy between successive levels, and (2) in many cases it is not known whether or not the particular set of vibrational levels is for the ground state molecule dissociating to unexcited atoms. Chemical determination of the D_0 are necessary in many cases to establish the ground state dissociation energy.

Such is the case for PbO; Table I gives D_0 = 99 kcal/mole in which Herzberg chose the $^1\Sigma$ state as the ground state, and applied a linear extrapolation to the seven available levels. On the other hand, Gaydon assumed the $^1\Sigma$ state probably goes to the Pb ($^3P_2$) atom which would give D_0 = 78 kcal/mole which he lowered to 76 kcal/mole by empirical methods. It is evident that if the chemical evidence is correct the linear extrapolation of the $^1\Sigma$ state to unexcited Pb and O atoms is the proper interpretation. Vago and Barrow[20] give the heat of dissociation of PbO which is in agreement with the value given by Herzberg and give the reasoning by which they conclude PbO dissociates to the unexcited atoms.

Another conclusion which may be drawn from Table II is that for the oxides of the fourth group elements the linear extrapolation

appears to be correct rather than applying an empirical corrective factor to the extrapolation as Gaydon does. This is shown particularly by the chemical D_0 values for SnO and PbO, and less conclusively by SiO. While not discussed in this paper, it is of interest to note that the D_0 for CO obtained by a linear extrapolation is in good agreement with thermochemical values obtained from a recent determination[21] of the heat of sublimation of graphite.

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