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THERMODYNAMIC PROPERTIES OF PROPELLANT COMBUSTION PRODUCTS

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Newport Beach, California

Introduction

The objective of this program is to provide thermodynamic data for species which are potentially important combustion products of advanced chemical rockets and for related species. Enthalpy and entropy data are obtained from equilibrium measurements made by torsion-free evaporation and torsion-effusion techniques and by high temperature mass spectrometry.

Heat of Vaporization of Aluminum

The torsion-effusion measurements of the vapor pressure of aluminum in which [illegible]llia cells were used have been completed.[1] There is no apparent affect of cell parameters on the vaporization rate, however, it was noted that a granular sample had a lower vaporization rate than a sample cut from a rod. Furthermore, the vaporization rate of the rod sample usually dropped off sharply (ca. 10%) after it was allowed to freeze. In either case, the vaporization rate could be increased by cleaning the surface of the sample by cutting off 1-3 mm of surface with an end cutter. It is believed that the vaporization rate was retarded in these cases by an oxide layer.

The effect of the residual oxygen in the vacuum system on the vaporization rate was found to be small by carrying out runs in which zirconium discs were placed inside the susceptor to act as getters.

Table 1 gives the average third law heat of vaporization data for seven runs which were acceptable; i.e., there was apparently no oxide layer. (The uncertainties listed are simply the standard deviation.) The runs in which the vaporization rate was retarded by such an oxide layer yield a third law heat of about $79.7_5 \pm 0.15$. The cell parameters are given in Table 2. Since there is no trend of ΔH_{298} with temperature, it is presumed that the second-law heat of vaporization for these runs will be in reasonable agreement with the third law results.

Also finished during the quarter were the measurements of the decomposition pressure of Al_4C_3. A problem arises in measuring the equilibrium vaporization rate of this compound since there appears to be a barrier to transport of the aluminum from the interior of the crystal to the vapor phase. When a fresh sample of stoichiometric Al_4C_3 is heated at a fixed temperature in a torsion-effusion cell, one observes first, a high deflection, which is coupled with a high system pressure, both of which slowly drop off with time. X-ray analysis of the material in the cell at this stage shows the presence of Al_4C_3 and Al_2O_3 (trace).

Further heating leads to the loss of Al_2O_3 by reaction of the oxide with the carbide (or by decomposition of an intermediate oxy-carbide phase) to form

Al(g) + CO. When the oxide has all been removed from the cell as shown by x-ray diffraction, the system pressure is much lower than at the beginning of the heating and stays about constant with further heating. The cell deflection stays constant for a comparatively short period after the sample has been degassed of oxide. At this point the cell contains only the yellow Al_4C_3 and, perhaps, some graphite. With further heating, the deflection drops off slowly but continuously. Still, the cell contains only Al_4C_3 and graphite. There is no evidence of change of lattice constants as the sample is depleted in the aluminum, and thus, there is no evidence for a crystalline phase that is substoichemetric in aluminum. Also during this period, the yellow color, characteristic of Al_4C_3, disappears. Grinding such an all-black sample uncovers again the yellow Al_4C_3. If such a ground sample is again heated to the decomposition temperature, one observes again, the constant deflection that was observed with the sample just after all the oxide was removed. It is believed that this short plateau is the pressure which is characteristic of the equilibrium decomposition pressure of Al_4C_3.

The decomposition pressure of Al_4C_3 was measured in three different graphite cells (Table 2). All measurements were made such that there was an easily observable yellow color on the surface of the sample at the completion of the run. At that time, enough more aluminum was added to the cell to make up for that aluminum that had been lost, through vaporization. The cell was heated at a constant temperature until it reached a constant deflection and then a new run was started. Analysis showed that there was no free aluminum in the cell after the cell had reached a constant deflection.

The results of these measurements are tabulated in Table 3. It is apparent that when the experiments are carried out in this manner, there is no "hole-size" effect such as was observed by Searcy and Meschi[5] and also by us when no attempt was made to keep plenty of Al_4C_3 on the vaporizing surfaces. At present, we will take as the heat of the reaction, the average of the second and third law values, 92.2 Kcal/mole. This, combined with the average of the three heats of formation for Al_4C_3,[2,3,4] $\Delta Hf^o_{298}\left[Al_4C_3(c)\right]$ = 51.2 Kcal/mole, yields $\Delta Hv_{298}\left[Al(l)\right]$ = 79.4 Kcal/mole. This is fortuitously in very good agreement with the aluminum vapor pressure measurements. The second-law heat of reaction, ΔH_{298} = 91.0 Kcal/mole, yields a $\Delta Hv_{298}\left[Al(l)\right]$ = 78.2 Kcal/mole while the third law heat of reaction, 93.5 Kcal/mole yields $\Delta Hv_{298}\left[Al(l)\right]$ = 80.7 Kcal/mole.

To augment the above measurements, the vapor pressure of aluminum is being measured by a torsion-free-evaporation method. Preliminary measurements yield for Al, the third law heat of vaporization of 78.8 Kcal/mole.

Beam Modulation

All of the mechanical and electronic parts of the beam modulation apparatus have been mounted and tested on the mass spectrometer. While it is possible to observe a modulated beam, the amplified beam signal is rather weak. The low signal appears to be due to fact that the chopper is not driven at a constant speed. This is apparently caused by "whipping" in the drive cable. A right-angle drive is being installed in place of the drive cable to overcome this difficulty.

Major Accomplishments

New data have been obtained relevant to the heat of vaporization of aluminum. Thus, we favor the heat of vaporization at 298° of 79.4 ± 1.8 Kcal/mole. Work has continued on the beam modulation modification for the mass spectrometer. This latter, it is believed, will greatly enhance the usefulness of the instrument for our studies.

Problems Encountered

No major problems were encountered.

Future Plans

The work on the mass spectrometer modifications will continue. Further work is planned on measuring the vapor pressure of aluminum by the torsion-free evaporation technique. Studies of the combination of gravimetric-effusion and torsion-effusion measurements to yield vapor molecular weight data are planned.

Action Required of Government

None.

Table 1. The Heat of Vaporization of Aluminum

Run No.	No. of Points	Cell No.	Heat of Vaporization ± Standard Dev., Kcal/mole
IV	14	1	79.41 ± 0.09
V	37	2	79.47 ± 0.16
VI	15	1	79.48 ± 0.23

Table 2. Effusion Cell Constants

Cell	$\bar{a}$, cm.^{2}	ℓ/r	$\bar{C}$	$\overline{ac}$, cm.^{2}	Σafq, cm.^{3}
BeO-1[a]	0.0152	1.40	0.598	0.00909	.02211
BeO-2[b]	0.00755	1.88	0.529	0.00399	.00493
G-30[c]	0.0178	1.35	0.606	0.0108	.0357
G-39[d]	0.00407	2.75	0.441	0.00180	.00293
G-40[c]	0.00827	2.20	0.493	0.00408	.01264

a. 4 chambers of ~.5 cm.^{2} cross-sectional area each
b. 2 chambers of ~.5 cm.^{2} cross-sectional area each
c. 4 orifices, one chamber of ~3 cm.^{2} cross-sectional area
d. 2 orifices, one chamber of ~3 cm.^{2} cross-sectional area

Table 3. The Heat of the Reaction: $1/4\ Al_4C_3(c) = Al(g) + 3/4\ C(graph.)$

Cell No.	No. of Points	$\Delta H_T^{a,b}$	T, °K	$\Delta H_{298}^{a,b}$	$\Delta H_{298} \pm \sigma^{b,c}$
30	10	91.1	1660	89.0	93.46 ± 0.10
39	22	93.9	1750	91.6	93.37 ± 0.16
40	25	96.0	1590	94.0	93.55 ± 0.19
overall	57	93.[illegible]6	1682	91.0	93.46 ± 0.16

a. Second law
b. ΔH is in Kcal/mole
c. Third law

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