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AEC-NASA TECH BRIEF

Mass-Spectrometric Study of the Rhenium-Oxygen System

Rhenium, having the second-highest melting point (3180°C) among metals, invites many applications for use both for refractory containers used in high-temperature studies, and in technologies. Its growing utilization for high-temperature applications has generated immediate need for knowledge of the thermodynamic properties of its compounds. Thus the thermodynamic values for rhenium oxide systems have been determined by mass spectrometry and x-ray diffraction. The experimental procedure, resultant data, and other results are reported (see ref.).

Three solid oxides of rhenium are well established: the dirhenium heptoxide (Re_2O_7), the trioxide (ReO_3), and the dioxide (ReO_2). The thermodynamic properties of $Re_2O_7(s)$ have been well established from low-temperature heat capacity, bomb calorimetry, and vapor-pressure measurements, whereas the properties of $ReO_2(s)$ and $ReO_3(s)$ are incomplete or uncertain. In particular the low-temperature heat capacities of $ReO_2(s)$ and $ReO_3(s)$ have not been measured, and the results of vapor-pressure studies have shown considerable disagreement.

The purpose of this investigation was to examine in detail the equilibrium vapors over thermodynamically defined systems. The vaporization behaviors of the two-phase solid systems ($Re + ReO_2$) and (ReO_3) were studied by means of the Knudsen effusion method and mass-spectrometric observations, followed by x-ray-diffraction identification of the residual phase after cooling of the material to room temperature.

The vapor phase in equilibrium with each of the two systems is the same, primarily $Re_2O_7(g)$ with only a minor amount (<5%) of $ReO_3(g)$. The condensed phases were identified before and after vaporization by x-ray-diffraction analysis. Mass-spectrometric data were combined with the mass-loss effusion data to yield the following equations for the vapor pressure (calculated as Re_2O_7):

For reaction $3ReO_3(s) \rightleftharpoons ReO_2(s) + Re_2O_7(g)$,

$$\log P(\text{atm}) = 12.529 \pm 0.270 - [(11{,}913 + 173)/T]$$

(612°–710°K) with $\Delta H_t^\circ = 54.5 \pm 0.8$ kcal/mole

For reaction $7/2\ ReO_2(s) \rightleftharpoons 3/2\ Re(s) + Re_2O_7(g)$,

$$\log P(\text{atm}) = 14.442 \pm 0.145 - [(20{,}447 + 143)/T]$$

(961°–1087°K) with $\Delta H_t^\circ = 93.5 \pm 0.7$ kcal/mole

The thermodynamic properties were recalculated to 298°K by estimation of a constant $\Delta C_p \approx -4$ cal/deg. mole for the sublimation reactions

$$\Delta H_f^\circ 298\,[ReO_2(s)] = -102.8 \pm 2.0 \text{ kcal/mole}$$

$$S^\circ 298\,[ReO_2(s)] = 13.5 \pm 1.6 \text{ eu}$$

$$\Delta H_f^\circ 298\,[ReO_3(s)] = -140.7 \pm 2.0 \text{ kcal/mole}$$

$$S^\circ 298\,[ReO_3(s)] = 19.3 \pm 1.5 \text{ eu}$$

In the course of the study, the appearance potential of $Re_2O_7(g)$ was found to be 13.0 ± 0.5 eV.

Reference:

Battles, J. E.; Gundersen, G. E.; Edwards, R. K.: J. Phys. Chem., vol. 72, 1968, p. 3963. Edwards, R. K.: A Mass Spectrometric Study of the Rhenium Oxide System. Argonne National Laboratory, 15 Dec. 1967.

(continued overleaf)

Notes:

1. This information may interest the metals industry.
2. Inquiries concerning this information may be directed to:

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