HIGH TEMPERATURE RESEARCH

VOL 13

SUMMARY:

Why do we know more today than we did yesterday? One reason is that scientists engage in research. The excitement of discovering new knowledge through research is illustrated by studying the bond strength of gaseous titanium monosulfide. Gaseous TiS molecules as well as gaseous titanium and sulfur atoms are produced by the vaporization of the high melting crystalline titanium monosulfide at temperatures near 2000°K. The procedures for producing and measuring temperatures in this region are shown. Analysis of the mass spectrum gives the relative concentrations of atomic Ti and S, and of TiS molecules. A torsion effusion apparatus gives data on the toal gas pressure at a series of temperatures. From these data, we calculate the bond strength of gaseous TiS. But at least as many new questions are raised as are answered. We don't run out of questions in research.

PURPOSE:

To stimulate interest in pure research by showing some experimental procedures used in high temperature chemistry to determine the bond strength of gaseous titanium monosulfide.

OUTLINE:

1. *Explaining the properties of substances with high melting points.*
Substances such as tungsten (VI) boride WB_2, boron carbide B_4C, cerium (III) sulfide Ce_2S_3, titanium (III) oxide Ti_2O_3, titanium (II) oxide TiO, and titanium (II) sulfide TiS all have high melting temperatures (near 2000°C). This behavior arises because the atoms are strongly bonded to one another in a three-dimensional network. The structure of solid TiS is explained with the aid of a model. The question is then raised as to what gas species will form when the TiS is heated to a sufficiently high temperature.

2. *Identifying the various gas species and determining their ratios.*
The solid TiS sample is placed in a tungsten crucible and after a vacuum of about one-billionth of an atmosphere is achieved, the sample is heated to about 1300°K by a tungsten ribbon. Electron bombardment increases the temperature to 1805°K, (well below the melting point of 2203°K) as shown by an optical pyrometer. A shutter is opened to allow gas species escaping from the crucible to reach the detector of a mass spectrometer. With the shutter closed, residual gases in the system are recorded and later subtracted from the spectrum. The mass spectrum reveals that the gas species are Ti and S atoms and TiS molecules in the ratio of 1.00 : 1.00 : 2.10. The experiment is performed at other temperatures to determine the corresponding ratios.

3. *Measuring the vapor pressure and calculating partial pressures.*
With the aid of animation, the operation of a torsion effusion apparatus is explained. From the observed twist of the effusion cell, the total vapor pressure of the equilibrium gas may be determined. From the relative gas pressures as determined with the mass spectrometer, the actual gas pressure of each species is calculated. Performing the experiment at other temperatures gives vapor pressures as a function of temperature.

4. *Calculating the bond strength of gaseous TiS molecules.*
The strength of the TiS bond is the energy required to separate *gaseous* TiS into *gaseous* Ti and S atoms. This quantity must be calculated from the data of the two experiments performed, namely, vaporization of solid TiS to gaseous TiS and dissociation of solid TiS into gaseous Ti and S atoms. The data from the reactions is maipulated as follows:

	ΔH (kcal/mol)
(1) Ti(s) $\longrightarrow$ Ti(g) + S(g)	+240
(2) TiS (g) $\longleftarrow$ TiS(s)	-117
TiS(g) $\longrightarrow$ Ti(g) +S(g)	+123 (514 kJ/mol)

Note that reaction (2) is the reverse of the vaporization reaction, hence the sign of ΔH is reversed.

The fundamental equation relating changes in vapor pressure to changes in temperature is as follows:

$$\log P_2 - \log P_1 = \frac{-\Delta H}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\frac{\log P_2 - \log P_1}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = \text{slope of the plotted line} = -\Delta H\left(\frac{(1)}{2.303R}\right)$$

R is the gas-law constant and 2.303 is the numerical factor relating $\log_{10}$ to natural logarithms. Thus one obtains the equation ΔH=Ks where s is the slope of the plot and K is a constant of value -4.58×10^{-3} to give ΔH values in kilocalories. From the above equation, the numerical value of the constant K is calculated as follows:

$$K = \frac{2.303 \times 1.987}{1{,}000} = -4.58 \times 10^{-3}$$

Note that the line plotted slopes downward from left to right, so the slope will have a minus value:

$$\text{slope} = \frac{-1.28}{5.00 \times 10^{-5}} = -2.56 \times 10^{4}$$

Thus ΔH for the vaporization has the value:

$(-2.56 \times 10^4)(-4.58 \times 10^{-3}) = 117$ kcal, 489 kjoule.

It is interesting to note that the plot of log P vs. 1/T is not really quite a straight line. In other words, ΔH, the heat of reaction, varies with temperature, normally decreasing as temperature increases.

Determining the bond strength of TiS was the immediate goal of this high temperature research. However, as with most research, more new questions are raised than are answered.

SUPPLEMENTARY MATERIAL:

Note that three methods of heating samples are illustrated in the film. These are radiation from a hot filament, electron bombardment, and high frequency induction. The essential use of a bound notebook will be recognized, since a vital piece of information on a loose page could be lost. A nylon glove is necessary during the assembly of the crucible and heating apparatus to avoid contamination.

The techniques demonstrated in this presentation are constantly being modified and are finding new applications both in research laboratories and in industrial plants. Among the most exciting are the high-temperature syntheses of the variety of newly developed superconductors and the preparation of less brittle, highly refractory ceramic materials. New methods employing lasers or concentrated solar radiation have given much greater range and flexibility to attaining high temperatures. Methods involving zone refining and chemical vapor deposition can produce the ultra-pure, high-melting materials demanded by the electronics industry. Even films of diamond (sublimation temperature nearly 4000°C) are made by vapor deposition.

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