Atomization Energy and Standard Heat of Formation of Gaseous Diatomic Arsenic

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Mass spectroscopic investigation of the vapor above gadolinium arsenide in the temperature range 1323–1901K yielded for the equilibrium dissociation reaction $As_2(g) = 2\ As\ (g)$ the enthalpy change of $\Delta H_0° = 90.6 \pm 2.5$ kcal, or $\Delta H_{298}° = 91.3 \pm 2.5$ kcal. In combination with the standard heat of sublimation of arsenic, this gives the standard heat of formation of $As_2(g)$ as $\Delta H_{f,298}° = 52.9 \pm 3.6$ kcal mol^{-1}. Agreement with previous spectroscopic and electron impact studies is very good.

Surprisingly, no previous Knudsen mass spectroscopic studies on the equilibrium dissociation of $As_2(g) = 2\ As(g)$ are reported in the literature, even though the related equilibrium dissociation of $As_4(g) = 2\ As_2(g)$ has been examined independently at least seven times by this method and once by electron impact (*7*). Spectroscopic studies of the atomization of $As_2(g)$ by Kinzer and Almy (*8*) yielded a predissociation value of 31,915 cm^{-1} and, upon a short graphical extrapolation, a vibrational convergence limit of 31,726 cm^{-1}. A more recent spectroscopic study, (*12*) essentially confirms Kinzer and Almy's work, with but a slightly different predissociation value of 31,900 cm^{-1}. Hultgren et al. (*7*) chose to interpret Kinzer and Almy's data, with the inclusion of error limits, as $\Delta H_{298}° = 91.42 \pm 0.54$ kcal mol^{-1} for the atomization of $As_2(g)$. This is in good agreement with an electron impact study of $As_2(g)$ by Hudson (*6*), who obtained $D_0° = 3.94 \pm 0.12$ eV mol^{-1}, or $\Delta H_{298}° = 91.6 \pm 2.8$ kcal mol^{-1}, for the same process. The prospect of an additional confirmation by means of a high-temperature equilibrium study would further enhance confidence in the more precise spectroscopic value for the atomization energy of $As_2(g)$. For such purpose, the Knudsen effusion mass spectroscopic technique is admirably suited.

Experimental

A knife-edge molybdenum Knudsen cell of 0.030 in. orifice diameter, charged with gadolinium arsenide powder, was employed in these studies. The mass spectrometer was operated at a 15-eV ionization energy, 4.5-kV accelerating voltage, and 1.0-mA emission current. The As^+ and As_2^+ species were characterized by their mass/charge ratios, ionization efficiency curves, and shutter profile measurements. Temperature measurements were obtained with a calibrated optical pyrometer focused on a black-body hole at the base of the Knudsen cell. Corrections for window and prism reflector absorptions were applied. The mass spectrometer and experimental procedures used for this work have been described (*1*, *3*).

Results and Discussion

Apart from our interest in the equilibrium dissociation reaction of $As_2(g) = 2\ As(g)$, we wanted also to learn something at the same time about the thermal stability of gadolinium arsenide. The decomposition progressed with the observation of relatively low intensities of As^+ and As_2^+ in the mass spectrum (Table I), and the appearance of the first trace of gadolinium in the vapor did not take place until about 2250K. This points to a high thermal stability of gadolinium arsenide and an arsenic-deficient nonstoichiometric phase. The further increase in temperature to about 2350K, however, brought about a dramatic increase in the pressures of arsenic and gadolinium to the point that the experiment had to be discontinued.

A small known quantity of silver had been also added to the Knudsen cell in the expectation of obtaining an integral calibration constant from the summation of the Ag^+ intensities over time and temperature. However, the silver must have reacted, since it evolved uncustomarily slowly and persisted to temperatures where it was difficult to sort out the extent of shield evaporation contributions to the Ag^+ intensities. Accordingly, after the completion of the gadolinium arsenide study, sufficient silver was added to the Knudsen cell to make it possible to obtain subsequently the silver calibration constant from the known enthalpy change of the reaction $Ag_2(g) = 2\ Ag(g)$ (*4*) in the manner outlined by Grimley (*5*). Care was taken not to disturb the configuration of the Knudsen cell assembly. Also, with a view of repeating the equilibrium dissociation study of $As_2(g) = 2\ As(g)$ with increased As^+ and As_2^+ intensities, a powdered mixture of gadolinium arsenide and graphite was introduced into the cell.

Although the addition of graphite had the desired effect of substantially increasing the intensities of As^+ and As_2^+ by promoting the decomposition of gadolinium arsenide, it also resulted unfortunately in the complete closure of the orifice of the cell and the opening up of the cell on its side, evidently through an alloying process. Analysis of the data would indicate that this could have occurred already at about 1350K, whereafter an abrupt

Table I. Observed Intensities of As^+ and As_2^+ at 15 eV, Equilibrium Constants, Free Energy Function Changes, and Standard Enthalpy Change for Reaction $As_2(g) = 2As(g)$

T, K	Intensities[a] (A) × 10^{12}		$-\log K$	$-\Delta(G_T° - H_{298}°)/T$, cal K^{-1}	$\Delta H_{298}°$, kcal
	As^+	As_2^+			
1368	4.55	15.6	8.94	26.64	92.4
1353	2.40	5.40	9.04	26.63	92.0
1323	1.20	3.00	9.40	26.61	92.1
1398	15.3	32.5	8.20	26.66	89.7
1449	40.0	96.0	7.82	26.69	90.5
1507	141	280	7.17	26.73	89.7
1570	390	1080	6.86	26.77	91.3
1616	930	1800	6.31	26.79	90.0
1779	900	330	5.56	26.89	93.1
1835	660	49.0	4.99	26.92	91.3
1661	39.0	3.20	6.30	26.82	92.4
1835	165	3.50	5.05	26.92	91.8
1901	390	5.70	4.50	26.95	90.4

$\Delta H_{298}° = 91.3 \pm 1.1$
$\Delta H_0° = 90.6 \pm 1.1$

[a] $P_{As} = 0.447 \times I(As^+) \times T \times 10^{-12}$ atm. $P_{As_2} = 0.318 \times I(As_2^+) \times T \times 10^{-12}$ atm.

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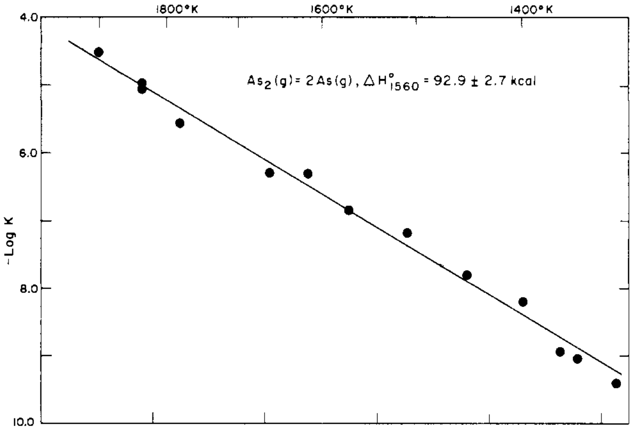

Figure 1. Second-law plot for reaction $As_2(g) = 2\,As(g)$

decrease in the As^+ and $As_2{}^+$ intensities was observed. However, well prior to this temperature it had been possible to obtain relatively strong Ag^+ and $Ag_2{}^+$ intensities for the determination of the silver calibration constant, which permitted us to salvage our main objective in this subsidiary run.

From the silver calibration constant, $k_{\rm Ag}$, of 0.561 atm $A^{-1}K^{-1}$ the corresponding values for $k_{\rm As}$ and $k_{\rm As2}$ were obtained by the general relationship, $k_i = k_{\rm Ag}(\sigma_{\rm Ag}\gamma_{\rm Ag})/(\sigma_i\gamma_i)$, where the σ's are maximum ionization cross sections and the γ's are multiplier gains of secondary electrons. The maximum cross sections of the singly ionized atomic species were taken from Mann (*11*). The value of $\sigma_{\rm As2}$ was taken to be 1.5 times that of $\sigma_{\rm As}$ (*2*). The observed intensities of As^+ and $As_2{}^+$ at 15 eV (Table I) were adjusted to their required maximum values by an empirical factor $I_{\rm max}/I$ of 1.11 and 1.14, respectively. The relative multiplier gain, $\gamma_{\rm As2}/\gamma_{\rm Ag} = 1.35$, was obtained experimentally. That of $\gamma_{\rm As}/\gamma_{\rm Ag} = 1.40$ was obtained from a comparison with the relative values of $\gamma_{\rm Sb}/\gamma_{\rm Sb2}$ (*9*).

The second-law and third-law enthalpy changes were obtained, respectively, from the standard relationships: $\log K = -\Delta H^\circ/4.576T + \Delta S^\circ/4.576$ and $\Delta H_{298}{}^\circ/T = -4.576 \log K - \Delta(G_T{}^\circ - H_{298}{}^\circ)/T$. The pressures in atmospheres were obtained by the relationship $P_i = k_i I_i{}^+ T$, where $I_i{}^+$ is expressed in amperes and T in K. The free energy functions, $-(G_T{}^\circ - H_{298})/T$, of As(g) and $As_2(g)$, and other ancillary thermodynamic data, were taken from Hultgren et al. (*7*), but as these are cited only to 1200K, additional values at higher temperatures, calculated from identical premises as used by Hultgren et al., were taken from Stull and Sinke (*13*) for As(g) and from Hudson (*6*) for $As_2(g)$.

The second-law plot for the equilibrium dissociation of $As_2(g) = 2\,As(g)$ is shown in Figure 1. The equilibrium constants, free energy function changes, and the third-law enthalpy change for this reaction are shown in Table I. The second-law enthalpy and entropy changes when reduced to the standard temperature of 298K, $\Delta H_{298}{}^\circ = 91.5 \pm 2.7$ kcal and $\Delta S_{298}{}^\circ = 25.8 \pm 1.8$ cal K^{-1}, respectively, agree very well with the corresponding third-law values, $\Delta H_{298}{}^\circ = 91.3 \pm 1.1$ kcal and $\Delta S_{298}{}^\circ = 25.68$ cal K^{-1}. Error limits refer to standard deviations only.

We give preference to the third-law enthalpy change in view of the possibility of slight fragmentation of $As_2(g)$, since it is relatively immune to such perturbations. However, we had here no such indications of fragmentation as was the case in the equilibrium dissociation of $P_2(g) = 2\,P(g)$ examined at 22 eV (*10*), but then again for the equilibrium dissociation of $Sb_2(g) = 2\,Sb(g)$ at 22 eV (*10*) no fragmentation could be deduced either. Nor did we observe any $As_3{}^+$ and $As_4{}^+$ intensities in the temperature region of our study that could have made fragment contributions to the As^+ and $As_2{}^+$ intensities. Furthermore, the relative intensities of As^+ and $As_2{}^+$ (Figure 1) are such that significant fragmentation of $As_2(g)$ would have to have occurred before its influence would be definitely noticeable in the derived thermodynamic data. The low ionization energy of 15 eV employed here would further minimize the possibility of fragmentation.

With the inclusion of all possible sources of error, we take the final enthalpy change value for the dissociation of $As_2(g) = 2\,As(g)$ to be $\Delta H_{298}{}^\circ = 91.3 \pm 2.5$ kcal, or $\Delta H_0{}^\circ = 90.6 \pm 2.5$ kcal. In combination with the standard heat of sublimation of arsenic (*7*), this leads to the standard heat of formation of $As_2(g)$, $\Delta H_{f,298}{}^\circ = 52.9 \pm 3.6$ kcal mol^{-1}. As is seen from a comparison with the spectroscopically (*8*, *12*) and electron impact (*6*) derived enthalpy changes, the agreement with the present study is very good.

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