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THE THERMODYNAMIC PROPERTIES OF As_2 , As_4 , AND SOME ARSENIC FLUORIDES

by

P. A. G. O'Hare

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Printed in the United States of America

Available from

Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

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P. A. G. O'Hare

Chemical Engineering Division

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November 1968

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ABSTRACT

The thermodynamic functions S° , C_p° , $H^\circ - H_{298}^\circ$, $(H^\circ - H_0^\circ)/T$ and $(G^\circ - H_0^\circ)/T$ have been calculated for gaseous As_4 , As_2 , and AsF_n ($n=1, 2, 3, 4$, and 5) by the formulas of statistical mechanics. In addition, ΔH_f , ΔG_f , and $\log K_f$ values, based on experimental data, are given for As_4 , As_2 , AsF_3 , and AsF_5 ; the corresponding values have been estimated for AsF and AsF_4 . The thermodynamic data have been tabulated at 100° intervals between 0 and 2000°K , and also at 273.15 and 298.15°K . Some thermodynamic aspects of the arsenic-fluorine system are discussed briefly.

I. INTRODUCTION

This report, which is part of a series,¹ deals with the ideal gas molecules As_2 , As_4 , AsF , AsF_2 , AsF_3 , AsF_4 , and AsF_5 . Values for the thermodynamic functions* S° , C_p° , $(H^\circ - H_0^\circ)/T$, $(G^\circ - H_0^\circ)/T$, $(H^\circ - H_{298}^\circ)$, ΔH_f , ΔG_f , and $\log K_f$ have been calculated and are tabulated at 100° intervals between 0 and 2000°K and also at 273.15 and 298.15°K . In some cases, structural, spectral, and enthalpy-of-formation data had to be estimated.

Some thermochemical aspects of the reactions of arsenic fluorides are also discussed in this report.

II. CALCULATIONS

The formulas used to calculate the thermodynamic functions, together with the appropriate constants and their values, have been given previously.^{1,2} The atomic weights of arsenic (74.9216) and fluorine (18.9984) have been taken from the 1961 table of atomic weights.³ The structural and spectral data used in the calculations are summarized in Table I. All the enthalpy-of-formation data in the tables in this report are arbitrarily based on $\text{As}_2(\text{g})$ and $\text{F}_2(\text{g})$ as reference states.

*Most of the symbols used in the present report have been explained in the glossary of terms in Ref. 1.

TABLE I. Data Used in the Calculations

Compound	ω (cm ⁻¹)	M	ℓ (Å)	θ^a	I^b	σ	g_i	ΔH_f^c
As ₂	429.44 ($\omega_{e \times e} = 1.12$ cm ⁻¹)	149.8432	2.285		32.4767×10^{-39}	2	1	0.0
As ₄	350, 250(3), 180(2)	299.6864	2.435	109° 28'	401176×10^{-117}	12	1	-59.8 ± 1.6
AsF	680 ($\omega_{e \times e} = 2.7$ cm ⁻¹)	93.9200	1.743		7.64509×10^{-39}	1	3	-47 ± 5
AsF ₂	600, 280, 745	112.9184	1.71	102°	863.637×10^{-117}	2	2	-138 ± 5
AsF ₃	740.35, 702.2(2), 336.5, 262.3(2)	131.9168	1.706	96° 6'	4132.38×10^{-117}	3	1	-248.1 ± 1.9
AsF ₄	811.4(2), 733, 711, 400.4, 388(2), 369(2)	150.9152	1.71	109° 28'	14883.8×10^{-117}	12	2	-284 ± 10
AsF ₅	811.4(2), 787.4, 733, 642, 400.4, 388(2), 369(2), 123(2)	169.9136	1.692 (ax) 1.667 (eq)	180° (ax) 60° (eq)	25619.9×10^{-117}	6	1	-320.18 ± 1.12

^aInterbond angle.^bMoment of inertia for diatomic molecules (units, g cm²); product of the moments of inertia for polyatomic molecules (units, g³ cm⁶).^cEnthalpy of formation, based on the generic reaction: $\frac{1}{2}\text{As}_2(\text{g}) + n/2\text{F}_2(\text{g}) \rightarrow \text{AsF}_n(\text{g})$; units are kcal mol⁻¹.

III. THERMODYNAMIC PROPERTIES

A. Tetra-atomic Arsenic, As₄(g)

Until recently, no spectroscopic data were available for As₄(g), and therefore some of the thermodynamic properties had to be estimated. Thus, Stull and Sinke's value⁴ for $S_{298}^\circ(\text{As}_4, \text{g})$ was chosen to be consistent with Brewer and Kane's observations⁵ on the vapor pressure of arsenic. However, a paper by Morino, Ukaji, and Ito,⁶ in which an electron-diffraction investigation of As₄(g) was described, also includes estimates of the vibrational frequencies. The estimated values, based on force constant data derived from the observed mean amplitude, were each assigned an uncertainty of ± 30 cm⁻¹. As a result, for example, the present calculated $S_{298}^\circ(\text{As}_4, \text{g})$, 78.83 gibbs mol⁻¹, is uncertain by about 2%. Structural data for As₄(g) were also taken from the work of Morino *et al.*⁶

From the work of Feber and Herrick,⁷ the standard enthalpy of formation, $\Delta H_f^\circ(\text{As}_4, \text{g})$, was taken to be 38.54 ± 0.1 kcal mol⁻¹. When referred to the reaction

$\Delta H_f(\text{As}_4, \text{g}) = -59.8 \pm 1.6$ kcal mol⁻¹. The ΔH_f , ΔG_f , and log K_f values given in Table II refer to Reaction (1).

B. Diatomic Arsenic, As₂(g)

Stull and Sinke⁴ calculated thermodynamic data for As₂(g); however, the atomic weight of arsenic has since been adjusted,³ and, in addition, more reliable values⁸ for the spectroscopic constants of As₂(g) are now available.

TABLE II. Thermodynamic Properties of Tetra-atomic Arsenic (Gas)

T	$-(G^{\circ}-H_0^{\circ})/T$	$(H^{\circ}-H_0^{\circ})/T$	S°	C_p°
(DEG.K.)	(GIBBS/MOL)	(GIBBS/MOL)	(GIBBS/MOL)	(GIBBS/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	51.675	9.4533	61.129	12.8531
200.00	59.215	12.4561	71.671	17.1976
273.15	63.324	13.8949	77.219	18.3165
298.15	64.558	14.2756	78.833	18.5456
300.00	64.646	14.3020	78.948	18.5606
400.00	68.929	15.4439	84.373	19.1068
500.00	72.462	16.2059	88.668	19.3736
600.00	75.467	16.7474	92.215	19.5225
700.00	78.081	17.1508	95.231	19.6137
800.00	80.392	17.4627	97.855	19.6734
900.00	82.464	17.7107	100.174	19.7146
1000.00	84.340	17.9127	102.253	19.7442
1100.00	86.056	18.0802	104.136	19.7662
1200.00	87.635	18.2214	105.857	19.7829
1300.00	89.099	18.3421	107.441	19.7960
1400.00	90.462	18.4463	108.908	19.8064
1500.00	91.738	18.5373	110.275	19.8148
1600.00	92.937	18.6173	111.554	19.8216
1700.00	94.067	18.6884	112.756	19.8273
1800.00	95.138	18.7518	113.889	19.8321
1900.00	96.153	18.8087	114.962	19.8362
2000.00	97.119	18.8602	115.979	19.8396

T	$(H^{\circ}-H_{298}^{\circ})$	$-\Delta H_f$	$-\Delta G_f$	LOG Kf
(DEG.K.)	(KCAL/MOL)	(KCAL/MOL)	(KCAL/MOL)	
0.00	-4.2563	59.55	59.55	INF
100.00	-3.3109	60.00	56.23	122.89
200.00	-1.7650	59.96	52.45	57.31
273.15	-0.4609	59.84	49.72	39.78
298.15	0.0000	59.80	48.80	35.77
300.00	0.0343	59.80	48.73	35.50
400.00	1.9213	59.61	45.07	24.62
500.00	3.8467	59.42	41.45	18.12
600.00	5.7922	59.22	37.88	13.80
700.00	7.7493	59.02	34.34	10.72
800.00	9.7139	58.82	30.83	8.42
900.00	11.6834	58.63	27.34	6.64
1000.00	13.6564	58.43	23.87	5.22
1100.00	15.6320	58.23	20.43	4.06
1200.00	17.6095	58.03	17.00	3.10
1300.00	19.5884	57.83	13.59	2.28
1400.00	21.5686	57.63	10.19	1.59
1500.00	23.5496	57.44	6.81	0.99
1600.00	25.5315	57.24	3.44	0.47
1700.00	27.5139	57.04	0.08	0.01
1800.00	29.4969	56.84	-3.26	-0.40
1900.00	31.4803	56.64	-6.59	-0.76
2000.00	33.4641	56.44	-9.92	-1.08

The enthalpy of formation of $\text{As}_2(\text{g})$ adopted in the present report is based on the investigation⁹ in which mass spectrometric and weight loss measurements of the species effusing from a Knudsen cell containing GaAs were used to obtain vapor pressures over the range 900-1200°K. A "third-law" treatment of the data yielded an enthalpy value of $-62.5 \text{ kcal mol}^{-1}$ at 298°K for the reaction

However, the free-energy functions used were taken from the compilation of Stull and Sinke.⁴ With the thermodynamic functions for $\text{As}_2(\text{g})$ and $\text{As}_4(\text{g})$ given in the present report, a value of $-59.8 \pm 1.5 \text{ kcal mol}^{-1}$ is obtained for the enthalpy of Reaction (2) at 298°K. Thus,

$$\Delta H_f^\circ(\text{As}_2, \text{g}) = 49.17 \pm 1.1 \text{ kcal mol}^{-1}.$$

According to Arthur,⁹ the pressure measurements reported by Drowart and Goldfinger¹⁰ and by Gutbier,¹¹ on which previous values for $\Delta H_f^\circ(\text{As}_2, \text{g})$ were based, are erroneous because of the likely buildup of arsenic in the mass-spectrometer ionization chambers used in the investigations.

The complete thermodynamic functions for $\text{As}_2(\text{g})$ are given in Table III.

C. Monatomic Arsenic, As(g)

The enthalpy of formation of $\text{As}(\text{g})$ has been calculated by combining the appropriate thermal data for the following processes:

The enthalpy of Reaction (3), $D_0^\circ(\text{As}_2)$, is given by Herzberg¹² and by Gaydon¹³ to be $91.1 \text{ kcal mol}^{-1}$; the enthalpies of Reactions (4) and (5) have been computed from the thermodynamic functions for $\text{As}_2(\text{g})$ and $\text{As}(\text{g})$ given in the present report and in Ref. 14, respectively. Thus, based on the reaction

$\Delta H_f(\text{As}, \text{g})$ is calculated to be $45.9 \pm 1.2 \text{ kcal mol}^{-1}$.

TABLE III. Thermodynamic Properties of Diatomic Arsenic (Gas)

T	$-(G^{\circ}-H_0^{\circ})/T$	$(H^{\circ}-H_0^{\circ})/T$	S°	C_p°
(DEG.K.)	(GIBBS/MOL)	(GIBBS/MOL)	(GIBBS/MOL)	(GIBBS/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	42.455	6.9805	49.435	7.1165
200.00	47.365	7.2510	54.616	7.9098
273.15	49.660	7.4815	57.141	8.2799
298.15	50.318	7.5521	57.870	8.3661
300.00	50.365	7.5572	57.922	8.3719
400.00	52.573	7.7917	60.364	8.5934
500.00	54.331	7.9648	62.296	8.7098
600.00	55.795	8.0951	63.890	8.7772
700.00	57.051	8.1958	65.247	8.8193
800.00	58.151	8.2756	66.426	8.8473
900.00	59.129	8.3402	67.470	8.8668
1000.00	60.011	8.3936	68.404	8.8809
1100.00	60.813	8.4384	69.251	8.8913
1200.00	61.549	8.4765	70.025	8.8994
1300.00	62.229	8.5093	70.738	8.9056
1400.00	62.860	8.5378	71.398	8.9106
1500.00	63.450	8.5628	72.013	8.9147
1600.00	64.004	8.5849	72.589	8.9180
1700.00	64.525	8.6046	73.129	8.9207
1800.00	65.017	8.6222	73.639	8.9231
1900.00	65.484	8.6381	74.122	8.9250
2000.00	65.927	8.6525	74.580	8.9267

T	$(H^{\circ}-H_{298}^{\circ})$	$-\Delta H_f$	$-\Delta G_f$	LOG Kf
(DEG.K.)	(KCAL/MOL)	(KCAL/MOL)	(KCAL/MOL)	
0.00	-2.2517	0.00	0.00	INF
100.00	-1.5536	0.00	0.00	0.00
200.00	-0.8015	0.00	0.00	0.00
273.15	-0.2081	0.00	0.00	0.00
298.15	0.0000	0.00	0.00	0.00
300.00	0.0155	0.00	0.00	0.00
400.00	0.8650	0.00	0.00	0.00
500.00	1.7307	0.00	0.00	0.00
600.00	2.6054	0.00	0.00	0.00
700.00	3.4854	0.00	0.00	0.00
800.00	4.3688	0.00	0.00	0.00
900.00	5.2545	0.00	0.00	0.00
1000.00	6.1420	0.00	0.00	0.00
1100.00	7.0306	0.00	0.00	0.00
1200.00	7.9201	0.00	0.00	0.00
1300.00	8.8104	0.00	0.00	0.00
1400.00	9.7012	0.00	0.00	0.00
1500.00	10.5925	0.00	0.00	0.00
1600.00	11.4841	0.00	0.00	0.00
1700.00	12.3761	0.00	0.00	0.00
1800.00	13.2683	0.00	0.00	0.00
1900.00	14.1607	0.00	0.00	0.00
2000.00	15.0533	0.00	0.00	0.00

D. Arsenic Monofluoride, AsF(g)

Pannetier, Deschamps, and Guillaumé¹⁵ observed two band systems when an electrical discharge was passed through AsF₃ vapor. The band systems were attributed to the radical AsF; however, because of the absence of isotopic bands, only a relative vibrational analysis was possible. The approximate spectroscopic constants reported by Pannetier *et al.* for the ground (³Σ) state of AsF have been summarized in Table I.

The equilibrium bond length (r_e) in AsF can be estimated by means of Guggenheimer's equation,¹⁶

$$r_e^{1.23} = 2156(z_1 z_2)^{1/4} \mu^{-1/2} \omega_e^{-1}. \quad (7)$$

In Eq. 7, z_1 and z_2 (the number of electrons in the outer shells of the two atoms) are equal to 5 and 7; μ is the reduced mass of the molecule in atomic weight units; and ω_e is the fundamental frequency. The value obtained for r_e is 1.743 Å. For the statistical calculations, the ground-state quantum weight of the AsF molecule was taken to be 3, and the symmetry number was taken to be unity.

There has been no direct determination of the dissociation energy of AsF. However, an approximate value can be deduced from the spectroscopic data by means of a linear Birge-Sponer extrapolation. Thus,

$$D_{LBS} = \frac{\omega_e^2}{4\omega_e X_e} - \frac{1}{2}\omega_e. \quad (8)$$

From Eq. 8, $D_{LBS}(\text{AsF})$ was calculated to be $42,475 \text{ cm}^{-1} = 5.27 \text{ eV}$.

Hildenbrand¹⁷ has shown that the linear Birge-Sponer method can be refined to give more reliable dissociation energies for diatomic molecules, and he proposed the equation

$$\frac{D^\circ}{D_{LBS}} = \frac{5.256}{r_e(\text{IP} - \text{EA})} + 0.448. \quad (9)$$

The symbols in Eq. 9 have the following meanings: D° is the corrected dissociation energy, and (IP - EA) is the difference (in electron volts) between the ionization potential of the more electropositive element and the electron affinity of the more electronegative element. For the calculation of $D^\circ(\text{AsF})$, IP(As) was taken to be 9.81 eV,¹⁸ and EA(F) was taken to be 3.45 eV.¹⁹ From Eq. 9 is derived $D^\circ(\text{AsF}) = 4.86 \text{ eV}$ or $112.1 \text{ kcal mol}^{-1}$. The uncertainty associated with this value, by analogy with other similar molecules, is estimated to be $\pm 0.2 \text{ eV}$ ($\pm 5 \text{ kcal mol}^{-1}$). The enthalpy of formation of AsF can be calculated from

$$\Delta H_f(\text{AsF}, g) = \Delta H_f(\text{As}, g) + \Delta H_f(\text{F}, g) - D^\circ(\text{AsF}) = -47 \pm 5 \text{ kcal mol}^{-1}. \quad (10)$$

The thermodynamic properties of AsF are given in Table IV.

E. Arsenic Difluoride, AsF₂(g)

The molecular data for AsF₂(g) given in Table I are based on the results of spectral²⁰ and structural²¹ investigations of AsF₃.

The dissociation energy of the primary bond in AsF₃, $D(\text{AsF}_2\text{-F})$, is estimated to be equal to $1.1\bar{D}(\text{AsF}_3)$. This relationship is valid for PCl_3 ^{22a} and SbCl_3 .^{22b} Thus,

$$D(\text{AsF}_2\text{-F}) = 1.1\bar{D}(\text{AsF}_3) = 128.6 \pm 5 \text{ kcal mol}^{-1}. \quad (11)$$

Therefore, for the reaction

$\Delta H = 128.6 \pm 5 \text{ kcal mol}^{-1}$, and $\Delta H_f^\circ(\text{AsF}_2)$ is calculated to be $-113.8 \pm 5 \text{ kcal mol}^{-1}$. For the reaction

$\Delta H_f(\text{AsF}_2, g)$ is calculated to be $-138 \pm 5 \text{ kcal mol}^{-1}$.

The thermodynamic properties of AsF₂ are given in Table V.

F. Arsenic Trifluoride, AsF₃(g)

The infrared and Raman spectra of AsF₃ are in accord with C_{3v} symmetry for the molecule; spectral data used in the calculations (see Table I) are based on the investigations reported by Hoskins and Lord^{20a} and by de Mandirola.^{20b} The As-F bond length and the FAsF bond angle have been determined by Bartell and Clippard.²¹ The value calculated for $S_{298}^\circ(\text{AsF}_3, g)$, 68.97 gibbs mol⁻¹, is in close agreement with the experimental value, $69.05 \pm 0.15 \text{ gibbs mol}^{-1}$, obtained by Russell, Rundle, and Yost.²³

Yost and Sherborne²⁴ measured the enthalpies of the following reactions by solution calorimetry:

$$\Delta H = -64.5 \pm 0.8 \text{ kcal mol}^{-1};$$

$$\Delta H = -10.7 \pm 0.8 \text{ kcal mol}^{-1}.$$

TABLE IV. Thermodynamic Properties of Arsenic Monofluoride (Gas)

T	$-(G^{\circ}-H_0^{\circ})/T$	$(H^{\circ}-H_0^{\circ})/T$	S°	C_p°
(DEG.K.)	(GIBBS/MOL)	(GIBBS/MOL)	(GIBBS/MOL)	(GIBBS/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	41.747	6.9528	48.700	6.9665
200.00	46.581	7.0292	53.611	7.3261
273.15	48.791	7.1619	55.953	7.7163
298.15	49.420	7.2134	56.634	7.8337
300.00	49.465	7.2172	56.682	7.8419
400.00	51.570	7.4215	58.991	8.1988
500.00	53.246	7.6008	60.846	8.4203
600.00	54.645	7.7499	62.395	8.5602
700.00	55.849	7.8727	63.722	8.6523
800.00	56.907	7.9743	64.882	8.7154
900.00	57.851	8.0593	65.911	8.7604
1000.00	58.704	8.1311	66.836	8.7933
1100.00	59.482	8.1925	67.675	8.8182
1200.00	60.198	8.2455	68.443	8.8374
1300.00	60.859	8.2916	69.151	8.8525
1400.00	61.475	8.3321	69.808	8.8645
1500.00	62.051	8.3680	70.419	8.8743
1600.00	62.593	8.3999	70.992	8.8824
1700.00	63.103	8.4285	71.531	8.8891
1800.00	63.585	8.4542	72.039	8.8948
1900.00	64.043	8.4775	72.520	8.8996
2000.00	64.478	8.4987	72.977	8.9037

T	$(H^{\circ}-H_{298}^{\circ})$	$-\Delta H_f$	$-\Delta G_f$	LOG Kf
(DEG.K.)	(KCAL/MOL)	(KCAL/MOL)	(KCAL/MOL)	
0.00	-2.1507	46.97	46.97	INF
100.00	-1.4554	46.97	47.33	103.45
200.00	-0.7448	46.99	47.69	52.12
273.15	-0.1944	47.00	47.96	38.38
298.15	0.0000	47.00	48.04	35.21
300.00	0.0145	47.00	48.04	35.00
400.00	0.8179	47.01	48.39	26.44
500.00	1.6497	47.01	48.73	21.30
600.00	2.4993	47.01	49.08	17.88
700.00	3.3602	47.02	49.42	15.43
800.00	4.2288	47.03	49.76	13.60
900.00	5.1027	47.03	50.11	12.17
1000.00	5.9805	47.04	50.45	11.03
1100.00	6.8611	47.05	50.79	10.09
1200.00	7.7439	47.06	51.13	9.31
1300.00	8.6284	47.07	51.47	8.65
1400.00	9.5143	47.09	51.80	8.09
1500.00	10.4013	47.10	52.14	7.60
1600.00	11.2891	47.12	52.47	7.17
1700.00	12.1777	47.13	52.81	6.79
1800.00	13.0669	47.15	53.14	6.45
1900.00	13.9566	47.17	53.47	6.15
2000.00	14.8468	47.19	53.81	5.88

TABLE V. Thermodynamic Properties of Arsenic Difluoride (Gas)

T	$-(G^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	S°	C_p°
(DEG.K.)	(GIBBS/MOL)	(GIBBS/MOL)	(GIBBS/MOL)	(GIBBS/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	47.150	8.0973	55.247	8.5751
200.00	52.944	8.7313	61.675	10.1597
273.15	55.743	9.2535	64.997	11.1588
298.15	56.561	9.4252	65.986	11.4366
300.00	56.619	9.4376	66.057	11.4558
400.00	59.421	10.0526	69.474	12.2711
500.00	61.720	10.5497	72.270	12.7645
600.00	63.680	10.9465	74.626	13.0734
700.00	65.392	11.2657	76.658	13.2757
800.00	66.914	11.5261	78.440	13.4142
900.00	68.284	11.7417	80.026	13.5126
1000.00	69.531	11.9226	81.454	13.5848
1100.00	70.675	12.0763	82.751	13.6391
1200.00	71.731	12.2083	83.940	13.6811
1300.00	72.713	12.3229	85.036	13.7140
1400.00	73.630	12.4233	86.054	13.7404
1500.00	74.490	12.5118	87.002	13.7619
1600.00	75.301	12.5905	87.891	13.7795
1700.00	76.066	12.6609	88.727	13.7942
1800.00	76.791	12.7242	89.516	13.8065
1900.00	77.481	12.7815	90.262	13.8170
2000.00	78.138	12.8335	90.971	13.8260

T	$(H^\circ - H_{298}^\circ)$	$-\Delta H_f$	$-\Delta G_f$	LOG Kf
(DEG.K.)	(KCAL/MOL)	(KCAL/MOL)	(KCAL/MOL)	
0.00	-2.8101	137.57	137.57	INF
100.00	-2.0004	137.81	136.79	298.96
200.00	-1.0639	137.95	135.71	148.30
273.15	-0.2825	138.00	134.92	107.95
298.15	0.0000	138.00	134.60	98.67
300.00	0.0212	138.00	134.58	98.04
400.00	1.2109	138.01	133.44	72.91
500.00	2.4647	137.99	132.30	57.83
600.00	3.7578	137.97	131.16	47.78
700.00	5.0759	137.94	130.03	40.60
800.00	6.4108	137.91	128.90	35.21
900.00	7.7574	137.89	127.78	31.03
1000.00	9.1125	137.86	126.66	27.68
1100.00	10.4738	137.83	125.54	24.94
1200.00	11.8399	137.81	124.42	22.66
1300.00	13.2097	137.79	123.31	20.73
1400.00	14.5825	137.77	122.19	19.08
1500.00	15.9576	137.75	121.08	17.64
1600.00	17.3347	137.73	119.97	16.39
1700.00	18.7134	137.72	118.86	15.28
1800.00	20.0935	137.71	117.75	14.30
1900.00	21.4747	137.70	116.64	13.42
2000.00	22.8568	137.69	115.54	12.63

To calculate $\Delta H_f^\circ(\text{AsF}_3, l)$ from Eqs. 14 and 15, the following auxiliary data (kcal mol^{-1}) were required: $\Delta H_f^\circ(1N\text{-NaOH}) = -112.36$; ^{25,26b} $\Delta H_f^\circ(\text{NaF}, c) = -137.78 \pm 0.3$; ^{26c} $\Delta H_f^\circ(\text{H}_2\text{O}, l) = -68.32$; ²⁵ and $\Delta H_f^\circ(\text{As}_2\text{O}_3, c) = -160.30 \pm 0.22$. ²⁷ Combination of Eqs. 14 and 15 yields

$$\Delta H_f^\circ(\text{AsF}_3, l) = -231.99 \pm 1.76 \text{ kcal mol}^{-1}.$$

The enthalpy of vaporization, $\Delta H_v^\circ(\text{AsF}_3, l)$, is equal to $8.51 \text{ kcal mol}^{-1}$. ²³ Therefore,

$$\Delta H_f^\circ(\text{AsF}_3, g) = -223.5 \pm 1.8 \text{ kcal mol}^{-1}.$$

Consequently, based on the reaction

$\Delta H_f(\text{AsF}_3, g)$ is calculated to be $-248.1 \pm 1.9 \text{ kcal mol}^{-1}$.

The thermodynamic functions for AsF_3 are given in Table VI.

G. Arsenic Tetrafluoride, $\text{AsF}_4(g)$

For the statistical calculations, the vibrational frequencies and structural data were estimated by analogy with AsF_5 (see Section H below); the structure of AsF_4 was assumed to be tetrahedral by analogy with PF_4 . ^{28,29}

The enthalpy of formation of $\text{AsF}_4(g)$ was estimated by assuming that the enthalpies of the following reactions are equal:

The value for $\Delta H_f^\circ(\text{AsF}_5, g)$ given in Section H was used in Eq. 18. Thus,

$$\Delta H_f^\circ(\text{AsF}_4, g) = -259 \pm 10 \text{ kcal mol}^{-1}.$$

For the reaction

$\Delta H_f(\text{AsF}_4, g)$ is calculated to be $-284 \pm 10 \text{ kcal mol}^{-1}$.

The thermodynamic functions of AsF_4 are given in Table VII.

TABLE VI. Thermodynamic Properties of Arsenic Trifluoride (Gas)

T	$-(G^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	S°	C_p°
(DEG.K.)	(GIBBS/MOL)	(GIBBS/MOL)	(GIBBS/MOL)	(GIBBS/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	47.058	8.3799	55.438	9.7058
200.00	53.332	9.9381	63.270	13.1079
273.15	56.597	11.0447	67.641	14.9389
298.15	57.579	11.3926	68.972	15.4388
300.00	57.650	11.4176	69.067	15.4734
400.00	61.107	12.6296	73.737	16.9341
500.00	64.032	13.5860	77.618	17.8172
600.00	66.578	14.3407	80.919	18.3703
700.00	68.836	14.9440	83.780	18.7330
800.00	70.865	15.4341	86.299	18.9813
900.00	72.707	15.8385	88.545	19.1578
1000.00	74.393	16.1773	90.571	19.2873
1100.00	75.949	16.4646	92.414	19.3849
1200.00	77.393	16.7112	94.104	19.4602
1300.00	78.739	16.9251	95.664	19.5194
1400.00	80.000	17.1121	97.112	19.5668
1500.00	81.186	17.2771	98.464	19.6053
1600.00	82.306	17.4236	99.730	19.6369
1700.00	83.367	17.5546	100.921	19.6633
1800.00	84.373	17.6724	102.046	19.6855
1900.00	85.332	17.7789	103.111	19.7043
2000.00	86.246	17.8756	104.122	19.7205

T	$(H^\circ - H_{298}^\circ)$	$-\Delta H_f$	$-\Delta G_f$	LOG Kf
(DEG.K.)	(KCAL/MOL)	(KCAL/MOL)	(KCAL/MOL)	
0.00	-3.3967	247.21	247.21	INF
100.00	-2.5587	247.76	244.73	534.85
200.00	-1.4091	248.04	241.56	263.97
273.15	-0.3798	248.10	239.23	191.41
298.15	0.0000	248.10	238.37	174.73
300.00	0.0286	248.10	238.31	173.61
400.00	1.6552	248.05	235.05	128.43
500.00	3.3963	247.96	231.81	101.32
600.00	5.2077	247.83	228.59	83.27
700.00	7.0641	247.69	225.40	70.37
800.00	8.9505	247.54	222.23	60.71
900.00	10.8580	247.39	219.07	53.20
1000.00	12.7806	247.24	215.93	47.19
1100.00	14.7144	247.09	212.81	42.28
1200.00	16.6568	246.94	209.70	38.19
1300.00	18.6059	246.79	206.60	34.73
1400.00	20.5603	246.64	203.51	31.77
1500.00	22.5189	246.49	200.44	29.20
1600.00	24.4811	246.35	197.37	26.96
1700.00	26.4462	246.21	194.31	24.98
1800.00	28.4136	246.07	191.27	23.22
1900.00	30.3831	245.93	188.23	21.65
2000.00	32.3544	245.80	185.19	20.24

TABLE VII. Thermodynamic Properties of Arsenic Tetrafluoride (Gas)

T	$-(G^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	S°	C_p°
(DEG.K.)	(GIBBS/MOL)	(GIBBS/MOL)	(GIBBS/MOL)	(GIBBS/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	47.288	8.1752	55.463	9.2048
200.00	53.446	9.9953	63.441	14.4215
273.15	56.802	11.6121	68.414	17.4858
298.15	57.842	12.1404	69.982	18.3211
300.00	57.917	12.1787	70.096	18.3790
400.00	61.687	14.0602	75.747	20.8261
500.00	64.994	15.5743	80.568	22.3160
600.00	67.944	16.7819	84.726	23.2551
700.00	70.607	17.7537	88.360	23.8738
800.00	73.031	18.5469	91.578	24.2989
900.00	75.254	19.2037	94.458	24.6017
1000.00	77.307	19.7552	97.062	24.8243
1100.00	79.212	20.2240	99.436	24.9923
1200.00	80.990	20.6270	101.617	25.1220
1300.00	82.655	20.9768	103.632	25.2241
1400.00	84.221	21.2832	105.504	25.3059
1500.00	85.699	21.5537	107.253	25.3723
1600.00	87.098	21.7941	108.892	25.4271
1700.00	88.426	22.0092	110.435	25.4726
1800.00	89.689	22.2027	111.892	25.5110
1900.00	90.894	22.3777	113.272	25.5435
2000.00	92.046	22.5367	114.583	25.5714

T	$(H^\circ - H_{298}^\circ)$	$-\Delta H_f$	$-\Delta G_f$	LOG Kf
(DEG.K.)	(KCAL/MOL)	(KCAL/MOL)	(KCAL/MOL)	
0.00	-3.6196	282.27	282.27	INF
100.00	-2.8021	283.20	278.13	607.85
200.00	-1.6206	283.79	272.80	298.10
273.15	-0.4478	283.98	268.80	215.07
298.15	0.0000	284.00	267.35	195.97
300.00	0.0339	284.00	267.25	194.69
400.00	2.0044	284.00	261.66	142.96
500.00	4.1675	283.88	256.08	111.93
600.00	6.4495	283.70	250.54	91.26
700.00	8.8080	283.48	245.03	76.50
800.00	11.2179	283.25	239.56	65.44
900.00	13.6637	283.00	234.11	56.85
1000.00	16.1355	282.74	228.69	49.98
1100.00	18.6267	282.47	223.30	44.37
1200.00	21.1327	282.21	217.93	39.69
1300.00	23.6502	281.94	212.58	35.74
1400.00	26.1769	281.67	207.26	32.35
1500.00	28.7109	281.41	201.95	29.42
1600.00	31.2509	281.14	196.67	26.86
1700.00	33.7960	280.88	191.39	24.61
1800.00	36.3452	280.62	186.14	22.60
1900.00	38.8980	280.36	180.90	20.81
2000.00	41.4538	280.11	175.66	19.20

H. Arsenic Pentafluoride, AsF₅(g)

The vibrational spectrum of AsF₅ has been extensively investigated;³⁰ the frequencies given in Table I have been taken from the paper by Hoskins and Lord.^{30a} The structure of AsF₅ has been investigated by Bartell and Clippard,²¹ who found the symmetry to be D_{3h}.

The standard enthalpy of formation of AsF₅(g) has been determined to be -295.59 ± 0.19 kcal mol⁻¹.³¹ Therefore, for the reaction

$\Delta\text{Hf}(\text{AsF}_5, \text{g})$ is calculated to be -320.18 ± 1.12 kcal mol⁻¹.

The thermodynamic functions for AsF₅ are given in Table VIII.

I. Some Observations on the Thermodynamics of the Arsenic-Fluorine System

The thermodynamic data given in the present report have been applied to some reactions that involve arsenic fluorides. The reactions considered are given in Table IX together with the Gibbs energy values at selected temperatures.

The most significant reaction, perhaps, is the decomposition of arsenic pentafluoride, and therefore the thermal stability of AsF₅ is of some interest. The present calculations show that (a) at ~1900°K, the ΔG value for Reaction a of Table IX is approximately zero; (b) significant decomposition of AsF₅ starts at about 1400°K; and (c) fluorination of AsF₃ to AsF₅ is thermodynamically favored at room temperature. AsF₅ is probably stable to at least 1000°C; this is in contrast to the analogous fluorides, PF₅ and SbF₅, which are stable up to temperatures in excess of 2500°C. The observation that AsF₃ should undergo spontaneous fluorination at room temperature is in accord with experimental facts.³² The data in Table IX also indicate that AsF₃ should be thermally stable to at least 1700°C, and that decomposition of AsF₂ and AsF₄ becomes significant at about 1200°C.

The thermodynamic values in Table X are in accord with experimental observations that Reactions a and b of Table X occur spontaneously at room temperature. Although Reactions c and d could be expected to proceed similarly, cursory observations³⁰ indicate that little or no reaction takes place when AsF₅ and PF₃ are combined at room temperature. Either the thermodynamic data are seriously in error, or the activation energy for Reaction d is substantial. The latter explanation is regarded as being more plausible.

TABLE VIII. Thermodynamic Properties of Arsenic Pentafluoride (Gas)

T	$-(G^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	S°	C_p°
(DEG.K.)	(GIBBS/MOL)	(GIBBS/MOL)	(GIBBS/MOL)	(GIBBS/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	48.923	9.6210	58.544	12.2982
200.00	56.469	12.5365	69.006	18.4795
273.15	60.691	14.6257	75.317	22.0184
298.15	62.000	15.2871	77.288	22.9884
300.00	62.095	15.3348	77.430	23.0557
400.00	66.836	17.6513	84.488	25.9099
500.00	70.981	19.4914	90.472	27.6555
600.00	74.668	20.9507	95.619	28.7583
700.00	77.989	22.1214	100.111	29.4859
800.00	81.007	23.0751	104.082	29.9861
900.00	83.772	23.8639	107.636	30.3428
1000.00	86.322	24.5255	110.847	30.6050
1100.00	88.686	25.0876	113.774	30.8030
1200.00	90.890	25.5705	116.461	30.9559
1300.00	92.954	25.9896	118.944	31.0763
1400.00	94.894	26.3565	121.250	31.1727
1500.00	96.724	26.6802	123.404	31.2510
1600.00	98.455	26.9680	125.423	31.3156
1700.00	100.098	27.2254	127.323	31.3693
1800.00	101.660	27.4569	129.117	31.4146
1900.00	103.151	27.6662	130.817	31.4530
2000.00	104.575	27.8564	132.431	31.4859

T	$(H^\circ - H_{298}^\circ)$	$-\Delta H_f$	$-\Delta G_f$	LOG Kf
(DEG.K.)	(KCAL/MOL)	(KCAL/MOL)	(KCAL/MOL)	
0.00	-4.5578	318.34	318.34	INF
100.00	-3.5957	319.46	312.67	683.34
200.00	-2.0505	320.04	305.61	333.95
273.15	-0.5628	320.18	300.38	240.34
298.15	0.0000	320.18	298.49	218.80
300.00	0.0426	320.18	298.35	217.35
400.00	2.5027	320.07	291.09	159.04
500.00	5.1879	319.84	283.87	124.08
600.00	8.0126	319.53	276.70	100.79
700.00	10.9272	319.18	269.59	84.17
800.00	13.9022	318.81	262.53	71.72
900.00	16.9196	318.43	255.52	62.05
1000.00	19.9677	318.04	248.55	54.32
1100.00	23.0385	317.64	241.62	48.01
1200.00	26.1268	317.24	234.72	42.75
1300.00	29.2286	316.84	227.86	38.31
1400.00	32.3412	316.44	221.03	34.51
1500.00	35.4625	316.04	214.23	31.21
1600.00	38.5910	315.65	207.46	28.34
1700.00	41.7253	315.25	200.71	25.80
1800.00	44.8645	314.86	193.99	23.55
1900.00	48.0080	314.48	187.28	21.54
2000.00	51.1550	314.09	180.59	19.73

TABLE IX. Gibbs Energy Values (kcal mol⁻¹) for Some Decomposition Reactions of Arsenic Fluorides at Selected Temperatures (°K)

Reaction	298.15	400	600	800	1000	1200	1400	1600	1800	2000
a. AsF ₅ (g) → AsF ₃ (g) + F ₂ (g)	60.1	56.0	48.1	40.3	32.6	25.0	17.5	10.1	2.7	-4.6
b. AsF ₂ (g) → AsF(g) + $\frac{1}{2}$ F ₂ (g)	86.6	85.1	82.1	79.1	76.2	73.3	70.4	67.5	64.6	61.7
c. AsF ₃ (g) → AsF ₂ (g) + $\frac{1}{2}$ F ₂ (g)	103.8	101.6	97.4	93.3	89.3	85.3	81.3	77.4	73.5	69.7
d. AsF ₅ (g) → AsF ₄ (g) + $\frac{1}{2}$ F ₂ (g)	31.1	29.4	26.0	23.0	19.9	16.8	13.8	10.8	7.9	4.9

TABLE X. Thermodynamic Data (298.15°K) for Some Reactions Involving AsF₃ and AsF₅^a

Reaction	ΔH° (kcal mol ⁻¹)	ΔS° (gibbs mol ⁻¹)	ΔG° (kcal mol ⁻¹)
a. PCl ₃ (l) + AsF ₃ (l) → AsCl ₃ (l) + PF ₃ (g)	6.1	19.5	0.3
b. 3PCl ₅ (g) + 5AsF ₃ (g) → 5AsCl ₃ (g) + 3PF ₅ (g)	-65.1	-5.3	-63.5
c. AsF ₅ (g) + PF ₃ (g) → AsF ₃ (l) + PF ₅ (g)	-87.8	-29.1	-79.1
d. AsF ₅ (g) + PF ₃ (g) → AsF ₃ (g) + PF ₅ (g)	-79.3	-3.4	-78.3

^aThermochemical values used in this table have been taken from this report and from Refs. 25 (PCl₃, PCl₅, and AsCl₃), 32 (PF₃), and 33 (PF₃ and PF₅).

ACKNOWLEDGMENT

We wish to thank H. M. Feder for his helpful criticism of this report. We are also grateful to Professor L. S. Bartell of The University of Michigan for permission to use some of his unpublished data.

REFERENCES

1. P. A. G. O'Hare, *The Thermodynamic Properties of Some Chalcogen Fluorides*, ANL-7315 (July 1968).
2. J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, John Wiley & Sons, Inc., New York (1940).
3. A. E. Cameron and E. Wichers, *J. Am. Chem. Soc.* **84**, 4175 (1962).
4. D. R. Stull and G. C. Sinke, *Thermodynamic Properties of the Elements*, No. 18, Advances in Chemistry Series, Amer. Chem. Soc., Washington (1956).
5. L. Brewer and J. S. Kane, *J. Phys. Chem.* **59**, 105 (1955).
6. Y. Morino, T. Ukaji, and T. Ito, *J. Chem. Soc. Japan* **39**, 64 (1966).
7. C. C. Herrick and R. C. Feber, *J. Phys. Chem.* **72**, 1102 (1968).
8. J. d'Incan, P. Perdigon, and J. Janin, *Compt. Rend. Ser. B* **262**, 951 (1966).
9. J. R. Arthur, *J. Phys. Chem. Solids* **28**, 2257 (1967).
10. J. Drowart and P. Goldfinger, *J. Chim. Phys.* **55**, 721 (1958).
11. H. Gutbier, *Z. Naturforsch* **16a**, 268 (1961).
12. G. Herzberg, *Spectra of Diatomic Molecules*, D. Van Nostrand Co., New York (1950).
13. A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules*, 2nd Ed., Chapman Hall, London (1953).
14. R. Hultgren, R. L. Orr, and K. K. Kelley, *Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys*, University of California, Berkeley, California (April 1965).
15. G. Pannetier, P. Deschamps, and J. Guillaume, *Compt. Rend., Ser. B* **261**, 3396 (1965).
16. K. M. Guggenheimer, *Proc. Phys. Soc. (London)* **58**, 456 (1946).
17. D. L. Hildenbrand, *Calculation of Dissociation Energies from Spectroscopic Data*, Chemical Propulsion Information Agency, Publication No. 146, Vol. I (May 1967), p. 63.
18. C. E. Moore, *Atomic Energy Levels*, Vol. II, National Bureau of Standards Circular 467, Washington, D.C. (1958).
19. R. S. Berry and C. W. Reimann, *J. Chem. Phys.* **38**, 1540 (1963).

20. (a) L. C. Hoskins and R. C. Lord, *J. Chem. Phys.* **43**, 155 (1965).
(b) O. B. de Mandirola, *J. Mol. Struct.* **1**, 203 (1967-1968).
21. L. S. Bartell and F. B. Clippard, The University of Michigan, private communication (1968).
22. (a) M. Halmann and Y. Klein, *J. Chem. Soc.*, 4324 (1964).
(b) V. E. Grob, *J. Chem. Phys.* **39**, 972 (1963).
23. H. Russell, Jr., R. E. Rundle, and D. M. Yost, *J. Am. Chem. Soc.* **63**, 2825 (1941).
24. D. M. Yost and J. E. Sherborne, *J. Am. Chem. Soc.* **57**, 700 (1935).
25. D. D. Wagman *et al.*, *Selected Values of Chemical Thermodynamic Properties*, National Bureau of Standards Technical Note 270-3, Washington, D.C. (1968).
26. (a) *JANAF Thermochemical Tables*, The Dow Chemical Company, Midland, Michigan (March 1961).
(b) *Ibid.* (March 1966).
(c) *Ibid.* (Dec 1963).
27. A. E. Beezer, C. T. Mortimer, and E. G. Tyler, *J. Chem. Soc.* 4471 (1965).
28. J. R. Morton, *Can. J. Phys.* **41**, 706 (1963).
29. P. W. Atkins and M. C. R. Symons, *J. Chem. Soc.*, 4363 (1964).
30. (a) L. C. Hoskins and R. C. Lord, *J. Chem. Phys.* **46**, 2402 (1967).
(b) L. K. Akers, *Diss. Abstr.* **15**, 1638 (1955).
(c) E. A. Vondrak, *Ibid.* **26**, 2278 (1965).
(d) S. Blanchard, Rapport CEA-R3195 (1967).
31. P. A. G. O'Hare and W. N. Hubbard, *J. Phys. Chem.* **69**, 4358 (1965).
32. E. Rudzitis, Argonne National Laboratory, private communication.
33. P. A. G. O'Hare, *The Thermodynamic Properties of P₂, P₄, and Some Phosphorus Fluorides*, ANL-7459 (Dec 1968).