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PART II

VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE

Part II. Mass Spectrometric Studies of the Vaporization of Sulphides and the Dissociation Energy of S_2

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ABSTRACT

The equilibria $S_2 \rightleftharpoons 2S$ and $CaS \rightleftharpoons Ca + S$ have been observed in the vapor phase above CaS. $D_o^o(S_2) = 4.4 \pm 0.2$ e.v., $D_o^o(SO) = 5.4 \pm 0.2$ e.v., $D_o^o(CaS) = 3.7 \pm 0.2$ e.v., and $\Delta H_{298}^{vap}(CaS) = 5.9 \pm 0.2$ e.v. have been determined mass spectrometrically.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

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MASS SPECTROMETRIC STUDIES OF THE VAPORIZATION OF SULPHIDES AND THE DISSOCIATION ENERGY OF S_2.

DISCUSSION

The disagreement between second and third law values of the dissociation energy of S_2 ($D_c^o(S_2)$) obtained from equilibrium measurements has been emphasized many years ago[1]. A relationship was also pointed out between the heat of combustion of SO, $D_o^o(O_2)$, $D_o^o(SO)$, and $D_o^o(S_2)$, which should permit one to choose one of the values allowed by observed predissociations for $D_o^o(S_2)$ and $D_o^o(SO)$. Recent measurements[2] do not seem to settle the question[3].

In the vapour phase above CaS we have observed by mass spectrometry[4] the dissociation $S_2 \rightleftharpoons 2S$, and $CaS \rightleftharpoons Ca + S$ and have calculated $D_o^o(S_2) = 4.4 \pm 0.2$ e.v., $D_o^o(SO) = 5.4 \pm 0.2$ e.v. $D_o^o(CaS) = 3,7 \pm 0.2$ e.v. and $\Delta H_{298}^{vap}(CaS) = 5.9 \pm 0,2$ e.v.

The mass spectrometric method has been described previously [4,5]. The sample was heated in a molybdenum Knudsen cell ; provisions were made to distinguish between residual gas molecules and those of the beam which passes through a cooled collimation system : ion intensities were measured with an electron multiplier. Absolute values of partial vapour pressures were obtained from $P_i = I_i T/S_i$; I_i is the measured current corresponding to a species i, T the absolute temperature of the Knudsen cell, and S_i the sensitivity for i :

$$(6) \quad S_i = (M_i/2\pi R)^{1/2}(s/G_i) \sum_i I_i T^{1/2} \Delta t;$$

M_i is its molecular mass, R the gas constant, s the area of the effusion orifice and t the time necessary to evaporate the weight G_i of species i . Brightness temperatures of a small threaded hole at the bottom of the Knudsen cell have been measured with an optical pyrometer; emissivity and window corrections were made. [7]

Dissociation energies were calculated from:

$$D_0^O = - RT\ln K + T\Delta((F_T^O - H_O^O)/T) \text{ (3d law) and :}$$

$$D_T^O = Rd\ln K/d(1/T) \text{ (2d law) using free energy fun-}$$

ctions taken from Stull and Sinke[8], or for CaS,

calculated by comparison of oxides and sulphides,

assuming $\omega_e = 390 \text{ cm}^{-1}$, $r_e = 2.3$ A and that only

the $^1\Sigma$ ground state is important.

Ionization cross sections were taken from
Otvos and·Stevenson[9] and it was assumed that
those of molecules are equal to the sum of those of
the constituent atoms. The mass effect and the
molecular effect of the multiplier[10] were considered
to compensate each other. A possible error of 20°
in the temperature measurement would lead to an
uncertainty of 12 % in the second law and of 1%
in the third law values ; instead of the assump-
tions made above, it may be reasonable that the
product of ionization cross section and multiplier
gain is the same for the atom and for the molecule[11]:

in that case the 3d law D_O^O values of Table I are
increased by about $+$ 3.5 kcal. and $\Delta H_{298}^{vap}(CaS)$
diminished by the same amount.

The data of Table I and $\Delta H_{298}^{vap}(Ca)^{(8)}$ = 42.2 kcal.
$\Delta H_{298}^O (1/2\ S_2)$ = 15.4 kcal, the standard heat of
formation $\Delta H_{298\ f.}^O (CaS)$ = 110.0 $\pm$ 2 kcal[12] permit
one to calculate $\Delta H_{298}^{vap}(CaS)$ = 136 kcal. The value
obtained from this cycle is considered as more
reliable than that given in table I (see remark
table I).

$D_O^O(S_2)$ obtained here, combined with $\Delta H_O^O(SO)^{(2b)}$
for the reaction $1/2\ S_2 + 1/2\ O_2 \rightleftharpoons SO$ definitely
rules out a value $D_O^C(SO)$ smaller than 5.2 e.v.
There are good spectroscopic arguments for
$D_O^O(SO)$ = 5.358 e.v.[13] rather than 5.027 e.v.[3].
Our measurements are not accurate enough to permit
one to settle the question whether the predi-
ssociation at 4.41 e.v. gives the exact dissociation
of S_2[14] or an upper limit[15]; a value $D(S_2)$ $\approx$ 4.2 e.v.
would agree with our results[16]. Within the
accuracy quoted in Table I, all available data

on $D(S_2)$ and $D(SO)$ [3] except appearance potential
measurements [17] and older equilibrium measurements
(cf. 1,2,3,14) seem to be in agreement.

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Table I. Heats of Vaporization and Dissociation Energies of S_2 and CaS

$T^\circ K$	$\log p(S)$[*]	$\log p(S_2)$	$\log p(Ca)$	$\log p(CaS)$	$D_0^o(S_2)$ kcal	$D_0^o(CaS)$ kcal	$H_{298}^{vap}(CaS)$ kcal
1922	-5.96	-6.56	-6.15	-	100	-	-
1975	-5.46	-6.25	-5.79	-	96.5	-	-
2026	-5.34	-6.01	-5.54	-	98.0	-	-
2048	-5.04	-5.82	-5.35	-	96.4	-	-
2053	-5.03	-5.83	-5.32	-7.26	96.4	79.8	151.9
2070	-5.18	-5.88	-5.42	-7.03	98.8	84.9	149.0
2098	-4.86	-5.63	-5.13	-6.99	97.3	80.7	151.5
2143	-4.76	-5.48	-5.03	-6.66	98.9	83.7	151.6
2144	-4.60	-5.38	-4.90	-6.72	96.7	80.3	152.2
2154	-4.71	-5.44	-4.99	-	98.8	-	-
2156	-4.64	-5.38	-4.86	-6.71	96.8	80.1	152.9
2190	-4.52	-5.28	-4.75	-6.55	98.3	81.5	153.6
2223	-4.27	-5.02	-4.58	-6.27	97.4	81.3	153.7
2297	-3.98	-4.82	-4.24	-5.99	96.8	80.3	155.6
			average		97.6	81.4	152.4[**]
			slope method		108	95	129
			proposed values		101 ± 5	86 ± 5	136 ± 10

[*] Decimal logarithms of pressures in atmospheres.

[**] $F_T - H_{298}/T$ for this process in based on very scanty data on C_p (CaS) (K. K. Kelley, U.S. Bureau of Mines Bulletin 476, Washington D. C. , 1949)