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Calculation of the Thermodynamic Functions of Tetrafluorodiphosphine

Olivera Nešković

The Boris Kidrič Institute of Nuclear Sciences, Vinča, Belgrade, Yugoslavia

The heat capacity, free energy function, heat content function and the absolute entropy of tetrafluorodiphosphine (P_2F_4) have been calculated.

INTRODUCTION

The homolytic dissociation of tetrafluorodiphosphine, which is of fundamental importance in the chemistry of this compound, has been investigated by some workers.[1-4] The occurrence of dissociation has been demonstrated, but the entropy of dissociation has not been determined. The derived enthalpy of dissociation from mass spectrometric data has been determined as $\Delta H^{\circ}_{diss,298} = (239 \pm 42)$ kJ mol^{-1}.[5] This value is based on electron impact investigation of the appearance potential of PF_2^+ ion from P_2F_4 molecule using the estimated value of the ionization potential of PF_2 radical from the appearance potential of PF_2^+ ion from PF_3, PF_2I and PF_2H molecules. Recently, $\Delta H^{\circ}_{diss,0}$ has been determined[6] as $(170 \ldots 176)$ kJ mol^{-1}. These values are based on the photoionization mass spectrometric investigation of the ionization potential of PF_2 radical and appearance potential of PF_2^+ ion from P_2F_4 molecule. As an estimated value, $\Delta H^{\circ}_{diss,0} = (173 \pm 5)$ kJ mol^{-1} is adopted (see Appendix I).

CALCULATIONS

Since there are no published data on the entropy of dissociation for the reaction of dissociation and the total statistical thermodynamic functions for P_2F_4 molecule, it was deemed worthwhile to obtain these value by statistical calculation.

Using the ideal-gas harmonic oscillator approximation and structural parameters,[7] together with the observed infrared and Raman fundamental frequencies,[1] translational, rotational and vibrational contributions to the total statistical thermodynamic functions for P_2F_4 molecule were calculated[8] (see Appendix II).

By varying bond lengths, bond angles and vibrational frequencies, within the experimental error limits, and repeating calculations with adjusted data, the maximum relative errors over the temperature range considered were

found to be $\pm 0.3\%$ for C_p°, $\pm 0.2\%$ for $(H_T^\circ - H_0^\circ)/T$, $\pm 0.4\%$ for $-(G_T^\circ - H_0^\circ)/T$ and $\pm 0.4\%$ for S°.

TABLE I

Computed thermodynamic functions for P_2F_4 molecule (ideal gas at 101.3 kN m^{-2})

T K	C_p° J K^{-1} mol^{-1}	$(H_T^\circ - H_0^\circ)/T$ J K^{-1} mol^{-1}	$-(G_T^\circ - H_0^\circ)/T$ J K^{-1} mol^{-1}	S° J K^{-1} mol^{-1}
100.0	48.5	37.8	214.0	251.8
200.0	71.0	50.5	244.3	294.8
298.2	92.4	62.4	265.0	327.5
300.0	97.8	62.6	267.4	330.0
400.0	103.7	72.6	287.0	359.6
500.0	115.3	80.4	304.2	384.7
600.	117.4	86.7	319.6	406.2
700.0	123.1	91.7	333.4	425.1
800.0	124.2	95.8	346.0	441.7
900.0	127.0	99.6	357.5	457.1
1000.0	128.0	102.0	368.1	470.1

APPENDIX I

We found[6] $\Delta H^\circ_{diss,0}$ (P_2F_4) from the ionization potential of PF_2 radical and the appearance potential of PF_2^+ ion from P_2F_4 molecule, *i. e.*,

I. P. (PF_2) = 8.84_7 $\pm$ 0.01) eV, and

A. P. (PF_2^+/P_2F_4) = (10.606 to 10.670) eV ($\pm$ 0.01 eV)

$\Delta H^\circ_{diss,0}$ (P_2F_4) = 1.76 to 1.82 eV, or 170 to 176 kJ mol^{-1}. The estimated value for ΔH°_{diss} is 173 kJ mol^{-1} and the absolute error in the determination of the enthalpy of dissociation arises from the error in the determination of *I. P.* and *A. P.*, and from the indeterminacy for *A. P.* values. This value was found to be $\pm$ 5 kJ mol^{-1}.

APPENDIX II

The structural parameters for P_2F_4 were published[7] as

$$r \,(P—P) = (2.81 \pm 0.006) \text{ Å}$$

$$r \,(P—F) = (1.587 \pm 0.003) \text{ Å}$$

$$< PPF = (95.4 \pm 0.3)^\circ$$

$$< FPF = (99.1 \pm 0.4)^\circ$$

Using these data, the product of three principal moments of inertia is 6.893168 $\times$ $\times$ 10^{-113} g^3 cm^6.

The vibrational contribution to the total statistical thermodynamic functions was computed using the fundamental vibrational frequencies, which were listed as (in cm^{-1}): 825 (ν_1), 541 (ν_2), 377 (ν_3), 214 (ν_4), 843 (ν_5), 803 (ν_8), 453 (ν_9), 813 (ν_{10}), 365 (ν_{11}) and 361 (ν_{12}), by Rudolph *et al.*[1] In this work no evidence for ν_6 and ν_7 bands was found in the gas phase infrared and Raman spectra of P_2F_4. These values were estimated as 348 cm^{-1} (ν_6) and 157 cm^{-1} (ν_7) from the similar spectrum of P_2Cl_4 molecule.[9]

NOMENCLATURE

T	temperature
H	enthalpy
S	entropy
C_p	heat capacity
$-(G_T^\circ - H_0^\circ)/T$	free energy function
$(H_T^\circ - H_0^\circ)/T$	heat content function
$I.P.$	ionization potential
$A.P.$	appearance potential
ν	vibrational frequency

SUPERSCRIPTS

o	standard state

SUBSCRIPTS

diss	dissociation
0 or 298	reference temperature

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SAŽETAK

Izračunavanje termodinamičkih funkcija i disocijacijske ravnoteže tetrafluorodifosfina

Olivera Nešković

Izračunati su toplotni kapacitet, funkcija slobodne energije i apsolutna entropija za tetrafluorodifosfin. Na osnovu eksperimentalno određene entalpije disocijacije i izračunatih statičkih vrednosti termodinamičkih funkcija, izračunate su konstante ravnoteže i stepeni disocijacije za ravnotežu $P_2F_4 \rightleftharpoons 2PF_2$.