Thermochimica Acta, 63 (1983) 251–253
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

Note

IDEAL GAS THERMODYNAMIC PROPERTIES OF HYPOIODOUS ACID

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(Received 23 September 1982)

Hypoiodous acid (HOI), which is formed by the hydrolysis of elemental iodine

$$I_2(\text{aq.}) + H_2O \leftrightharpoons \text{HOI}(\text{aq.}) + H^+(\text{aq.}) + I^-(\text{aq.}) \qquad (1)$$

is an important species in dilute aqueous iodine solutions for certain pH and oxidation conditions [1]. Although evidence for the existence of HOI in the gas phase is not conclusive, it has been of some concern in analyses of postulated loss-of-coolant accidents in nuclear power plants [1–3]. The prediction of the partition of HOI between the solution and gas phases [1–3], or of the concentration of HOI in high-temperature iodine–steam mixtures [4], is of particular importance in nuclear safety studies. Such predictions can be made if the thermodynamic properties of HOI(g) are known.

The ideal gas heat capacity, $C_p^0(T)$, entropy, $S^0(T)$, enthalpy, $H^0(T) - H^\circ(0)$, and Gibbs energy function, $\phi^0(T) \equiv -[G^0(T) - H^0(0)]/T$, of HOI in the temperature range 298.15–2000 K at a pressure of 101 kPa, are listed in Table 1. These functions were calculated in the rigid rotator-harmonic oscillator approximation, using standard statistical thermodynamic methods [5,6]. The spectroscopic and molecular constants used in the calculation were: (i) the vibrational frequencies, 575, 1103 and 3597 cm^{-1}, and (ii) the principal moments of inertia, 1.25, 101.81 and 103.06×10^{-47} kg m^2. The vibrational frequencies are those for an HOI molecule trapped in a rare gas matrix [7], and the moments of inertia were calculated from the molecular structure of HOI. By analogy with similar molecules [8], HOI is nonlinear, with a bond angle of approximately 110°. The OH and OI bond lengths are 0.096 and 0.20 nm, respectively.

Thermodynamic equilibrium calculations require data on the Gibbs energy of formation, $\Delta G_f^0(T)$. Values of $\Delta G_f^0(T)$, with respect to the elements at 298.15 K, can be calculated from the expression

$$\Delta G_f^0(T) = \Delta G_f^0(298.15) - \left[T\phi^0(T) - 298.15\phi^0(298.15)\right] \qquad (2)$$

0040-6031/83/$03.00

TABLE 1

Ideal gas thermodynamic properties of HOI at 101 kPa

Temp. (K)	$C_p^0(T)$ (J K^{-1} mole^{-1})	$\phi^0(T)$ (J K^{-1} mole^{-1})	$S^0(T)$ (J K^{-1} mole^{-1})	$H^0(T) - H^0(0)$ (kJ mole^{-1})
298.15	38.96	219.66	254.67	10.44
300	39.02	219.88	254.91	10.51
400	41.72	230.14	266.52	14.55
500	43.75	238.40	276.06	18.83
600	45.27	245.37	284.18	23.29
700	46.46	251.43	291.25	27.88
800	47.46	256.80	297.52	32.57
900	48.35	261.64	303.16	37.36
1000	49.16	266.06	308.30	42.24
1100	49.90	270.12	313.02	47.19
1200	50.58	273.88	317.39	52.22
1300	51.21	277.39	321.47	57.31
1400	51.78	280.66	325.28	62.46
1500	52.30	283.76	328.87	67.66
1600	52.77	286.69	332.26	72.91
1700	53.19	289.47	335.47	78.21
1800	53.58	292.11	338.52	83.55
1900	53.93	294.63	341.43	88.93
2000	54.24	297.04	344.20	94.33

Reliable experimental values of $\Delta G_f^0(298.15)$ for HOI(g) are not available. An estimated value can, however, be obtained using $\Delta G_f^0[\text{HOI(aq.)}, 298.15] = -98.7 \pm 1$ kJ mole^{-1} [1] and Gelles' estimate [9] that the Gibbs energy of vaporization of HOI(aq.) is 8.3 ± 5 kJ mole^{-1}. Thus, $\Delta G_f^0(298.15)$ for HOI(g) is equal to -90.6 ± 6 kJ mole^{-1}, and $\Delta G_f^0(T)$ can be calculated using eqn. (2). Although the function $\phi^0(T)$ is affected by the use of the rigid rotator-harmonic oscillator approximation, and uncertainties in the spectroscopic and molecular constants (the error is estimated to be less than 1% at 2000 K), the greatest uncertainty in $\Delta G_f^0(T)$ results from the large uncertainty in $\Delta G_f^0(298.15)$.

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