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Note

THE FORMATION AND STABILITY OF GASEOUS POCl

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The formation of POCl by the reaction

$$POCl_{3(g)} + 2\ Ag_{(s)} = POCl_{(g)} + 2\ AgCl_{(g)} \qquad (1)$$

has been shown by mass-spectrometric and matrix-IR investigations [1]. The heat of formation of $POCl_{(g)}$ has been derived from appearance-potential measurements. In comparison with the heats of formation of the gaseous compounds NOCl [2], AsOCl [3], SbOCl [3], POF [4], POBr [5] and PSCl [6], the value obtained for the heat of atomisation, ΔH^0_{at}(POCl), of 955 kJ mole^{-1} seems somewhat too high. This may be caused by the uncertainty of the appearance-potential measurements. Because the value for the heat of formation of $POCl_{(g)}$ is fundamental to the thermodynamic properties of derived compounds like PO_2Cl [7], we have measured the equilibrium (1) by means of a combination of Knudsen-cell evaporation and mass-spectrometric analysis of the equilibrium gas and derived the heat of reaction (1).

EXPERIMENTS AND EVALUATION OF DATA

The Knudsen cell assembly has been described earlier [8]. Mass-spectrometric analysis of the equilibrium vapour was carried out using an Extranuclear Quadrupol mass-spectrometer (ionisation by electron impact, 70 eV). The reaction of $POCl_3$ with solid silver was carried out in a quartz glass Knudsen cell (diameter of the orifice 1 mm). The temperature was measured by a Pt/Rh-Pt thermocouple.

At room temperature the well-known mass-spectrum of $POCl_3$ was observed [intensities (arbitrary units) in brackets]: P^+ (115), PO^+ (847), PCl^+ (242), $POCl^+$ (207), PCl_2^+ (49), $POCl_2^+$ (3620), $POCl_3^+$ (740). All the ions observed must be formed by fragmentation of $POCl_3^+$. To calculate the pressures from the measured intensities, the assembly must be calibrated. This was done by measurement of the saturation pressure of liquid silver. The values obtained were: $T(Ag) = 1408$ K, $I(Ag) = 1000$, $p(Ag)_{1408} = 8.14 \times 10^{-5}$ atm [9]. From these values, the proportional factor, c, in the equation $p = cIT$ can be calculated at 7.78×10^{-11}. Using this value, calculation of

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equilibrium pressures from the intensities is possible.

At temperatures above 1100 K, ions formed by $POCl_3$ can no longer be observed. Under such conditions, the mass spectrum shows the formation of $POCl_{(g)}$ and $AgCl_{(g)}$ {the identity of POCl was established by appearance-potential measurements, $AP(POCl) = 11.3$ eV, and matrix IR-investigations [1]}. For calculation of the equilibrium constant of reaction (1), one should observe both $POCl_{(g)}$ (and $AgCl_{(g)}$) and $POCl_{3(g)}$ in the mass spectrum. From the mass spectrum at room temperature, the ions which are formed by the fragmentation process of $POCl_3$ are known. Using the basic peak ($POCl_2^+$), the total intensity $\Sigma I(POCl_3)$ of all ions formed by $POCl_3$ is given by $I(POCl_2^+)/f$ [$f = I(POCl_2^+)/\Sigma I(POCl_3)$, where $\Sigma I(POCl_3)$ is the sum of the intensities of all ions formed by fragmentation of $POCl_3^+$; in our case, $f = 3620/5860 = 0.6177$]. The total intensity of all ions formed by fragmentation of POCl must be given by the difference between the sum of the intensities of all P-containing ions and $I(POCl_2^+)/f$. The total intensity of AgCl is given by $I(Ag^+) + I(AgCl^+)$. With the calibration factor, c, the observed mass spectra of the equilibrium vapour lead to the partial pressures of POCl, $POCl_3$ and AgCl and to the equilibrium constant according to reaction (1). We made 18 different measurements at various temperatures between 900 and 1100 K. A second-law evaluation of measurements does not seem suitable in this case, because the error in the intensity of POCl may be too great. We therefore prefer a third-law evaluation of the data. The mean value of log K_p at $1000/T = 1.0000$ was -8.89. Using the entropy and specific heat of POCl, which we have calculated by statistical methods (see later), in combination with the values for $POCl_{3(g)}$ [10], $AgCl_{(g)}$ [11] and $Ag_{(s)}$ [9], we have calculated for reaction (1) $\Delta S^0_{298} = 361.2$ J K^{-1} mole^{-1} and $\Delta C_{p,298} = -18.1$ J K^{-1} mole^{-1}. This result together with $1000/T = 1.0000$ and log $K_p = -8.89$ (p atm) leads to a value for the heat of reaction, $\Delta H^0_T(1) = 509.5$ kJ mole^{-1}, $\Delta H^0_{298}(1) = 522.2$ kJ mole^{-1}. In combination with the heats of formation of $POCl_{3(g)}$ and $AgCl_{(g)}$ given in the literature [2,9], the heat of formation of $POCl_{(g)}$ can be calculated as $\Delta H^0_{298}(POCl_{(g)}) = -215.1$ kJ mole^{-1}. This value, in combination with literature data for $\Delta H^0_{298}(O_l) = 249.4$ kJ mole^{-1} [2], $\Delta H^0_{298}(P_l) = 333.9$ kJ mole^{-1} [2] and $\Delta H^0_{298}(Cl_l) = 121.0$ kJ mole^{-1} [2] leads to a value of 919.4 kJ mole^{-1} for the heat of atomisation: this value is somewhat lower than reported earlier (955 kJ mole^{-1}) [1].

Specific heat and entropy

The specific heat and entropy of $POCl_{(g)}$ have been calculated using: the formula weight of POCl; the interatomic distances d(P–O) = 143.9 pm and p(P–Cl) = 206 pm (ab initio calculation by Ahlrichs [11]); the bond angle 109°C (ab initio calculation by Ahlrichs [11]); and the measured frequencies, 1257.7 cm^{-1}, 489.4 cm^{-1} and 308.0 cm^{-1} [1]. The calculated data for C_p and S^0 are given in Table 1.

TABLE 1

Specific heat and entropy data for $POCl_{(g)}$

T (K)	C_p ($J\ K^{-1}\ mole^{-1}$]	S^0 ($J\ K^{-1}\ mole^{-1}$)
200.00	42.17	257.06
250.00	44.48	266.73
273.16	45.35	270.70
298.16	46.23	274.72
300.00	46.32	275.01
350.00	47.82	282.25
400.00	49.12	288.73
450.00	50.24	294.55
500.00	51.21	299.91
600.00	52.72	309.41
700.00	53.85	317.61
800.00	54.68	324.85
900.00	55.31	331.33
1000.00	55.77	337.19
1100.00	56.15	342.54
1200.00	56.44	347.44
1300.00	56.69	351.96
1400.00	56.90	356.18
1500.00	57.07	360.12
1600.00	57.20	363.80
1700.00	57.28	367.27

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