Atomization Energies of Phosphorus Oxides

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The study by the mass-spectrometric Knudsen-cell method of the vapours in equilibrium with metal oxide+metal phosphide systems at 1000-1700 K made possible the identification of the molecules P_2O_3, P_2O_4, P_2O_5 and P_3O_6. Their atomization energies were determined, as well as those of the phosphorus oxides prevalent at low temperatures. These are: P_2O_3: 2055 ± 15, P_2O_4: 2530 ± 18, P_2O_5: 3020 ± 22, P_3O_6: 4012 ± 24, P_4O_6: 4385 ($+40$, -60), P_4O_7: 4956 ± 23, P_4O_8: 5516 ± 25, P_4O_9: 6066 ± 27 kJ mol^{-1}.

One of the problems in chemistry at high temperatures remains the identification of the molecules present in the gas phase of binary and more complicated systems, and the determination of their thermodynamic properties. Both goals can be achieved by the mass-spectrometric analysis of the ions produced by electron impact from the neutral species in molecular beams formed by the Knudsen effusion method. This procedure indeed gives access to the simultaneous determination of the chemical identity of the molecules and of their partial pressures. These, in turn, permit the calculation of reaction enthalpies, dissociation energies and heats of formation by the relations based on the second and third laws of thermodynamics.

When, as for the phosphorus+oxygen system, the vapour at low temperatures is composed of complex species such as P_4O_{10} through P_4O_7,[1-3] simpler molecules can be formed both by increasing the temperature, and by reducing the chemical activities of the constituent atoms.

When the various molecules can be sequentially made to be of importance in the gas phase, the investigation of their behaviour under electron impact, their identification and the determination of their thermodynamic properties is facilitated. The study of various metal phosphide+metal oxide systems made it possible to realize this and to identify the molecules P_2O_3, P_2O_4, P_2O_5 and P_3O_6 in addition to the already known molecules PO and PO_2,[4] and P_4O_6 to P_4O_{10}.[1-3]

EXPERIMENTAL

The mass spectrometer, Knudsen cell assembly [5] and experimental procedures [6] have already been described. The diaphragm separating the cell from the ion source was cooled by circulating liquid nitrogen. So doing insured that for all molecular ions $P_xO_y^+$, except $P_4O_6^+$, $P_3O_4^+$ and $P_3O_5^+$, the intensity profile measured with the moveable beam defining slit,[5] was the same as for Ag^+. The molybdenum Knudsen cells, used without insert, had cylindrical channel type effusion orifices, 0.8 mm diam., 1.0-1.2 mm long. The condensed phases placed within the cells were MoP, synthesized from the elements and either Fe_2O_3 (mole ratio 1/2, expt 1), CoO(1/2, expt 2) or MoO_3(1/3, expt 3 ; 1/1, expt 4 in consecutive parts *a*, *b* and *c*; 1/1, quantitative vaporization). Pressure calibrations were made by quantitative vaporization of known amounts of silver and integration of the ion currents mostly carried out simultaneously with the study of the phosphorus oxides. In view of the low pressures of the $AgPO_2$ molecule, its contribution to the weight loss was neglected. In the system with

initial nominal composition $MoP+MoO_3$, where the main component of the vapour is P_2O_3, absolute pressure measurements were simultaneously performed, and also by intensity integration and weight loss determination.   For the latter a first weighing was made after the molecules $P_4O_7-P_4O_{10}$ initially present due to slight excess of phosphorus had been vaporized.   The second weighing was made after the complete vaporization of the silver added. These measurements thus yielded an experimental value for the ratio of the sensitivities $S(Ag)/S(P_2O_3)$.   The result is $S(Ag)/S(P_2O_3) = 12.3$ at 14 eV and 7.4 at 19 eV.   It is to be noted that S being proportional to the cross-section and multiplier yield, $S(P_2O_3)$ given above corresponds to the partial cross-section for the process, $P_2O_3+e \rightarrow P_2O_3^+ +2e$, and not to the total ionization cross-section.   The same relative sensitivity was used for P_2O_4, P_2O_5 and P_3O_6, which, by analogy to P_2O_3 and P_4O_6 through P_4O_{10} [1] are expected to also fragment appreciably under electron impact.   For the molecules P_4O_7 through P_4O_{10}, compensation of the sensitivities was assumed in the reactions given in table 2.   For the molecules PO, PO_2 and P_2, relative sensitivities, taking multiplier yields and molecular effects into account, were estimated earlier [4] and for P_4 estimated here in the same fashion. The values are $S(Ag)/S(PO)/S(PO_2) = 1.0/1.2/0.3$ at 14 eV, and $S(Ag)/S(PO)/S(PO_2)/S(P_2)/S(P_4) = 1.0/1.8/1.0/2.2/2.7$ at 19 eV.

RESULTS

IDENTIFICATION OF THE MOLECULES

The ions formed by electron impact from the species in the molecular beams and their approximate ionization (IP) or appearance potentials (AP) are summarized in table 1, which also gives their relative intensities and the P_2O_3 pressures.   Reaction with silver further led to the observation of $AgPO^+$ (AP = 13.9 eV), $AgPO_2^+$ (IP = 9.3 eV) and impurities to that of $NaPO^+$ (AP = 13.1 eV), $NaPO_2^+$ (IP = 8.6 eV) and KPO_2^+.   During the initial stages of the experiments in the $MoP+MoO_3$ systems, the gaseous species of the MoO_3 system [7] were also observed; at the highest temperatures gaseous $MoPO_4$ and $MoPO_5$ were further identified.

TABLE 1.—APPEARANCE POTENTIALS AND RELATIVE ION INTENSITIES

ion	AP/eV	I(expt 1) [a] 1670 K	I(expt 2) [a] 1317 K	I(expt 3) [a] 1362 K	I(expt 4a) [a] 1032 K	I(expt 4b) [b] 1316 K	I(expt 4c) [b] 1316 K
PO^+	9.5 ± 0.5 and 13.5 ± 1.0	1 [c]	1	1 [d]	1 [e]	1	1
PO_2^+	11.5 ± 0.5 and 15.4 ± 1.0	6.0×10^{-2}	0.10	0.34	8.1×10^{-4e}	5.0×10^{-2}	4.5×10^{-2}
P_2	11.4 ± 0.5		8.6×10^{-3}		1.25		
$P_2O_2^+$	15.4 ± 0.5			2.6×10^{-2}	2.5×10^{-2}		
$P_2O_3^+$	10.4 ± 0.5		2.4×10^{-2}	0.27	0.25	0.55	0.17
$P_2O_4^+$	10.8 ± 1.0			5.9×10^{-3}	$\leqslant 2 \times 10^{-4}$		
$P_2O_5^+$	12.0 ± 1.0			4.8×10^{-4}	$\leqslant 2 \times 10^{-4}$		
$P_3O_6^+$	12.3 ± 1.0			3.6×10^{-4}	7.2×10^{-2}		
$P_3O_7^+$	15.0 ± 1.0			4.5×10^{-3}	2.1×10^{-2}		
P_4^+	10.0 ± 0.5				3.5×10^{-2}		
$P_4O_6^+$				$\leqslant 10^{-2\,f}$	$\leqslant 9.0 \times 10^{-4\,f}$		
$P_4O_7^+$	11.4 ± 0.5			$\leqslant 6 \times 10^{-4\,f}$	4.0×10^{-3}		
$P_4O_8^+$	11.9 ± 0.5			$\leqslant 10^{-4\,f}$	7.3×10^{-2}		
$P_4O_9^+$	12.4 ± 0.5			2.3×10^{-3}	1.5×10^{-1}		
$P_4O_{10}^+$	13.0 ± 0.5			7.0×10^{-3}	1.8×10^{-2}		
$p(P_2O_3)/atm$			9.3×10^{-8}	2.2×10^{-5}	9.5×10^{-6}	1.1×10^{-4}	1.2×10^{-5}

[a] Ionization energy of 19 eV; [b] 14 eV; [c] $I(Fe^+) = 0.9$ and $I(FeO^+) = 1.9 \times 10^{-3}$; [d] corrected for fragmentation, uncorrected 2.1; [e] fragment from P_2O_3 (see fig. 1); [f] interference from re-evaporation.

Mutual comparison of the ionization potentials and comparison with the ioniza-tion and appearance potentials in the literature [1] indicates that PO^+ and PO_2^+ (except in expt 4a), P_2^+, $P_2O_3^+$, $P_2O_4^+$, $P_2O_5^+$, $P_3O_6^+$ (except in expt 4a), P_4^+, $P_4O_7^+$ through $P_4O_{10}^+$, $NaPO_2^+$ KPO_2^+ and $AgPO_2^+$ are parent ions formed by direct ionization from the corresponding neutral molecules. $P_2O_2^+$ and $P_3O_7^+$ are considered to be fragment ions.
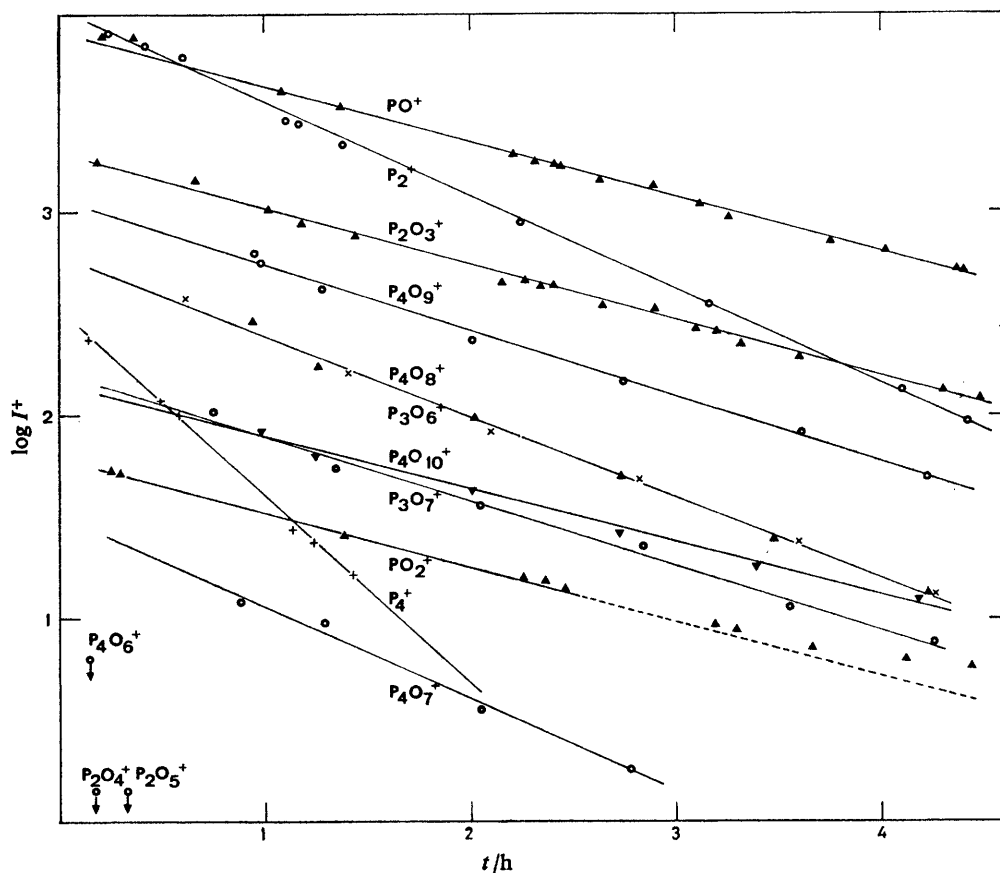

FIG. 1.—Time dependence of the ion intensities at 1032 K (expt 4a).

Identification of the neutral molecules P_4O_9, P_4O_8, P_4O_7 and in particular P_2O_3 could be confirmed, accepting P_2^+, P_4^+ and $P_4O_{10}^+$ to be parent ions, from the variation of their intensity I(at 19 eV) as function of the evolution with time t of the activities of phosphorus and oxygen at constant temperature.   Fig. 1 shows that log I varies linearly with t with the following relative coefficients a: P_2^+, 1.00; P_4^+, 2.00; $P_4O_{10}^+$, 0.57, set equal to $4a(P)+10a(O)$; $P_4O_9^+$, 0.70 (calc. 0.71); $P_4O_8^+$, 0.87 (calc. 0.86); $P_4O_7^+$, 0.99 (calc. 1.00); $P_3O_7^+$, 0.69 (calc. 0.50); $P_3O_6^+$, 0.87 (calc. 0.64); $P_2O_3^+$, 0.59 (calc. 0.57); PO_2^+, 0.58, during the first two hours, (calc. 0.21); PO, 0.58 (calc. 0.36).   Simultaneously, it is shown that, *under the conditions of the experiment,* $P_3O_7^+$ and $P_3O_6^+$ are fragment ions formed mainly from P_4O_9 and P_4O_8 respectively and that PO^+ and PO_2^+ are fragment ions from P_2O_3. (The appearance potentials [1] of $P_2O_3^+$, PO_2^+ and PO^+ from P_4O_{10} are 28, 23 and 24 eV respectively and can therefore

TABLE 2.—REACTION ENTHALPIES AND ATOMIZATION ENERGIES (kJ mol⁻¹)

expt	reaction	T/K interval	$\log K_p$	$\Delta H_0^\circ(\mathrm{II})$ [a]	$\Delta H_0^\circ(\mathrm{III})$ [b]	molecule	$D_0^\circ(\mathrm{III})$ [c]
1	$FeO + PO = Fe + PO_2$	1590–1696	—	—	85 ± 12 [f]	FeO	412 ± 14 [f]
2	$PO_2 + 0.5P_2 = 2PO$	1197–1377	$-8530 \pm 550/T + 4.9 \pm 0.4$ [d]	159 ± 13 [e]	149 ± 8	PO_2	1092 ± 11
4a	$P_4 = 2P_2$	1032	-3.9	—	232 ± 7	P_4	1202 ± 10
	$P_4O_6 = 0.6P_4O_{10} + 0.4P_4$	1032	$\geqslant 1.4$	—	$\leqslant -23 \pm 9$	P_4O_6	$\leqslant 4416 \pm 18$
	$P_4O_7 = 0.7P_4O_{10} + 0.3P_4$	1032	0.7	—	23 ± 14	P_4O_7	4956 ± 23
	$P_4O_8 = 0.8P_4O_{10} + 0.2P_4$	1032	-0.5	—	-1 ± 15	P_4O_8	5516 ± 25
	$P_4O_9 = 0.9P_4O_{10} + 0.1P_4$	1032	-0.9	—	6 ± 16	P_4O_9	6066 ± 27
	$P_2O_3 = 0.3P_4O_{10} + 0.4P_2$	1032	1.0	—	-113 ± 17	$P_2O_3\ C_{2v}$	2061 ± 18
					-123 ± 17	C_s	2051 ± 18
2	$P_2O_3 = PO + PO_2$	1197–1377	$-18\,920 \pm 550/T + 7.5 \pm 0.4$	369 ± 18	387 ± 14	$P_2O_3\ C_{2v}$	2067 ± 15
				368 ± 18	377 ± 14	C_s	2056 ± 15
3		1151–1374	$-19\,780 \pm 560/T + 8.5 \pm 0.5$	385 ± 18	379 ± 14	$P_2O_3\ C_{2v}$	2058 ± 15
				384 ± 18	369 ± 14	C_s	2048 ± 15
4b		1149–1315	$-20\,000 \pm 350/T + 8.7 \pm 0.3$	389 ± 16	379 ± 14	$P_2O_3\ C_{2v}$	2058 ± 15
				387 ± 16	369 ± 14	C_s	2048 ± 15
4c		1186–1386	$-19\,350 \pm 300/T + 8.1 \pm 0.2$	377 ± 16	380 ± 14	$P_2O_3\ C_{2v}$	2059 ± 15
				376 ± 16	370 ± 14	C_s	2049 ± 15
3	$P_2O_4 = 2PO_2$	1215–1374	$-18\,700 \pm 710/T + 9.2 \pm 0.5$	368 ± 20	364 ± 14	$P_2O_4\ D_{2h}$	2536 ± 17
				369 ± 20	345 ± 14	C_s	2517 ± 18
3	$P_2O_5 = 0.5P_4O_{10}$	1272–1374	see fig. 3		-280 ± 18	P_2O_5	3020 ± 22
3	$P_3O_6 = 3PO_2$	1295–1344	see fig. 2		753 ± 20	P_3O_6	4012 ± 24

[a] Reaction enthalpy at 0 K obtained by the second law; [b] reaction enthalpy at 0 K obtained by the third law; [c] dissociation or atomization energy obtained from $\Delta H_0^\circ(\mathrm{III})$; [d] the uncertainties cited are twice the standard deviation; [e] the uncertainties in $\Delta H_0^\circ(\mathrm{II})$ include those in $\Delta H_f^\circ(\mathrm{II})$, in the temperature (0.5 %) and in $H_T^\circ - H_0^\circ$; [f] the uncertainties take into account, for $\Delta H_0^\circ(\mathrm{III})$, twice the standard deviation from the mean, the uncertainty in the temperature, the estimated uncertainty in the product of the cross sections (100 %) and in the free energy functions and for D_0°, the uncertainty in the atomization energies of the reference molecules.

not be formed from the latter at 19 eV, even if $a(P_2O_3) = a(P_4O_{10})$. Towards the right in fig. 1, PO_2^+ tends to become a parent ion.

EQUILIBRIUM CONSTANTS, REACTION ENTHALPIES AND ATOMIZATION ENERGIES

Because of the absence of information on the thermodynamic properties of the condensed phases actually present and of the bivariant behaviour of the systems investigated, only homogeneous gas-phase reactions are considered (table 2). The
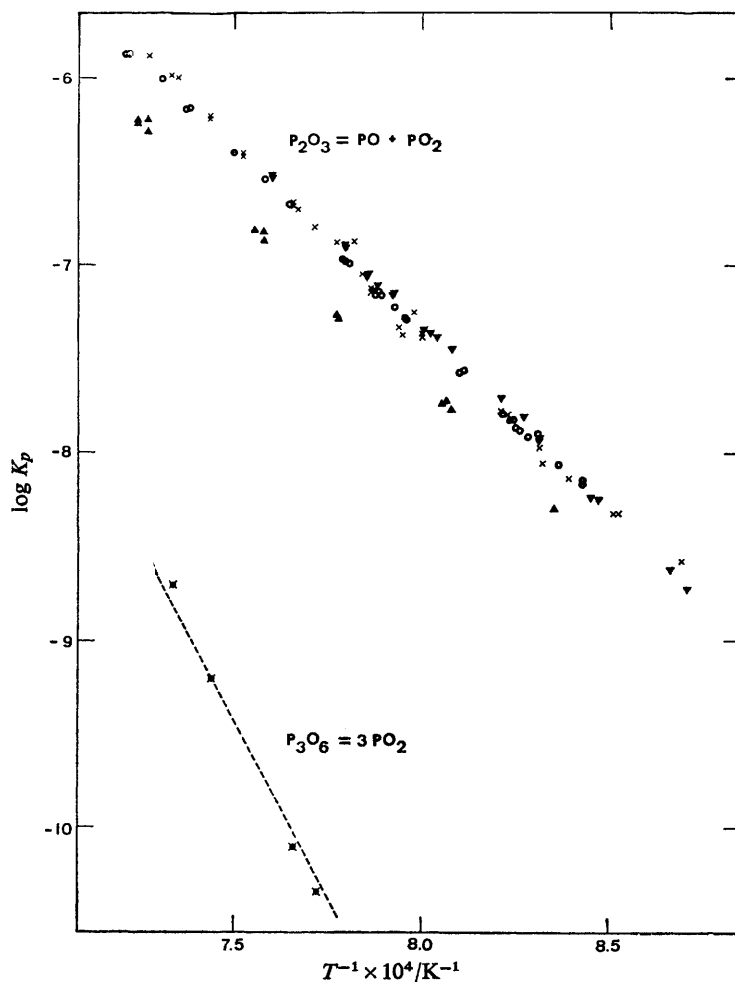

FIG. 2.—Temperature dependence of the equilibrium constants △, expt 2 ; ×, expt 3 ; ▽, expt 4b ; ○, expt 4c.

equilibrium constants are summarized in fig. 2 and 3, typical individual pressures or ratios of pressures being given in table 1 and in fig. 1. The numerical values of the free energy functions and enthalpies used in the calculation of the reaction enthalpies are taken from the literature or estimated as discussed in the appendix. The Van t'Hoff relation is used only if the equilibrium in question could be studied over a
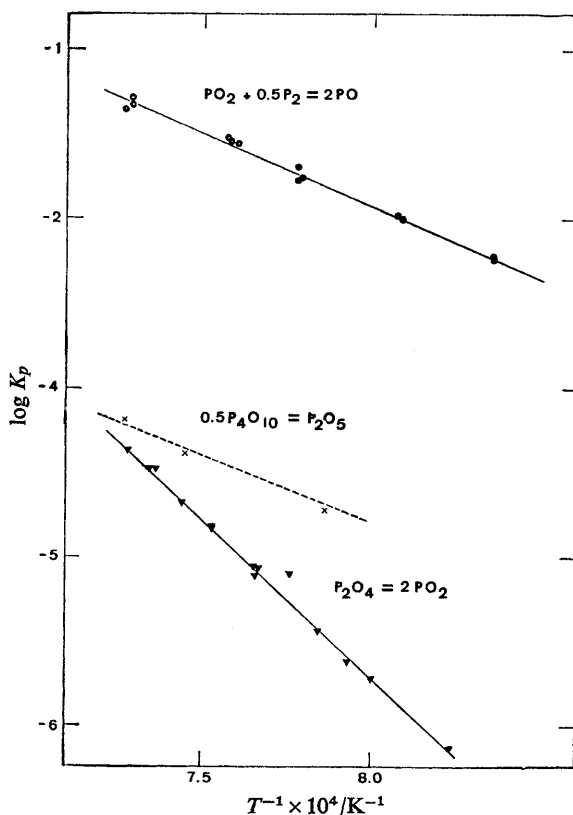
FIG. 3.—Temperature dependence of the equilibrium constants.

sufficiently extended temperature interval and is not corrected for possible variation of the ionization cross-sections with temperature.

The dissociation or atomization energies are derived from the reaction enthalpies using $D_0^\circ(P_2) = 485.3 \pm 4$,[8] $D_0^\circ(PO) = 593.0 \pm 8$,[4] both based on spectroscopic and thermodynamic determinations, $D_{0,at}^\circ(PO_2) = 1086.2 \pm 11$,[4] $D_{0,at}^\circ(P_4) = 1195 \pm 8$,[8] and $D_{0,at}^\circ(P_4O_{10}) = 6601 \pm 8$ kJ mol^{-1}.[8]

DISCUSSION

Among the atomization energies determined in this study, comparison with literature results can be made for the molecules P_4, PO_2, P_4O_6 through P_4O_{10}.
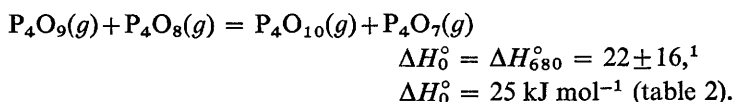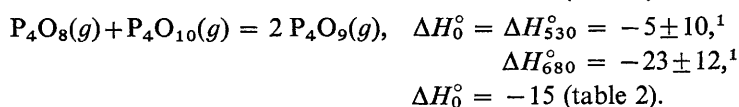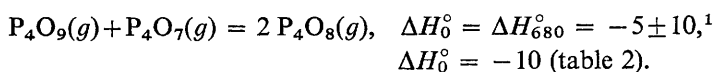
$D_0^\circ(P_4) = 1202 \pm 10$, $D_0^\circ(PO_2) = 1092 \pm 11$, determined both by the second and third laws and $D_0^\circ(FeO) = 412 \pm 14$ kJ mol^{-1} compare very favourably with $D_0^\circ(P_4) = 1195 \pm 8$,[8] $D_0^\circ(PO_2) = 1086 \pm 11$,[4] and $D_0^\circ(FeO) = 406 \pm 12$,[10] and 414 ± 20 kJ mol^{-1}.[9] (The latter value is corrected to the same free energy function as used here). Simultaneously, the exchange reaction $FeO(g) + PO(g) = Fe(g) + PO_2(g)$ shows the consistency between the dissociation energies of the molecules PO, PO_2 and FeO.

For P_4O_7, P_4O_8 and P_4O_9 the determination of the atomization energies is based on the reactions,

$$P_4O_n(g) = (n/10)P_4O_{10}(g) + (1 - n/10)P_4(g), \quad n = 7, 8, 9.$$
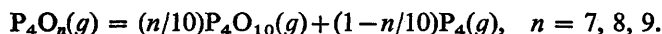
The calculation of the atomization energies of these molecules depends thus on $D^\circ_{0,at}(P_4O_{10})$ given in the JANAF Tables. The value, 6601 ± 8 kJ mol^{-1} is, however, confirmed by the consistency in the atomization energy of P_2O_3 deduced from the reactions $P_2O_3(g) = PO(g)+PO_2(g)$, and $P_2O_3(g) = 0.3\,P_4O_{10}(g)+0.4\,P_2(g)$, and from the reaction $P_4O_{10}(g)+2PO(g) = 6PO_2(g)$, which yields $D^\circ_{0,at}(P_4O_{10}) = 6587\pm 40$ kJ mol^{-1}.

For P_4O_7, P_4O_8 and P_4O_9, a first comparison can be made between the second law reaction enthalpies measured in ref. (1) and those calculated from the atomization energies in table 2 for the reactions :

$$P_4O_9(g)+P_4O_7(g) = 2\,P_4O_8(g), \quad \Delta H^\circ_0 = \Delta H^\circ_{680} = -5\pm10,^1$$
$$\Delta H^\circ_0 = -10 \text{ (table 2)}.$$

$$P_4O_8(g)+P_4O_{10}(g) = 2\,P_4O_9(g), \quad \Delta H^\circ_0 = \Delta H^\circ_{530} = -5\pm10,^1$$
$$\Delta H^\circ_{680} = -23\pm12,^1$$
$$\Delta H^\circ_0 = -15 \text{ (table 2)}.$$

$$P_4O_9(g)+P_4O_8(g) = P_4O_{10}(g)+P_4O_7(g)$$
$$\Delta H^\circ_0 = \Delta H^\circ_{680} = 22\pm16,^1$$
$$\Delta H^\circ_0 = 25 \text{ kJ mol}^{-1} \text{ (table 2)}.$$

In fact, the calculation of the enthalpy differences associated with the reactions employed for these molecules in table 2 requires only relative pressures, i.e., ion intensities, so that the data in ref. (1) can also be used to calculate the same reaction enthalpies. The important point thereby is that the temperature in ref. (1) (423-673 K), differs markedly from that here. The result, with $D^\circ_{0,at}(P_4O_{10}) = 6601\pm8$, is respectively $D^\circ_{0,at} = 4969, 5498$ and 6051 kJ mol^{-1} for P_4O_7, P_4O_8 and P_4O_9, in satisfactory agreement with the present results.

For P_4O_6, re-evaporation, probably due to recombination of P_2O_3, made it possible to determine only an upper limit to the true pressure and thus an upper limit to the atomization energy. A number of conclusions can, however, already be drawn therefrom.

The JANAF Tables give, on the basis of the heat of formation of $P_4O_6(l)$ and the heat of vaporization of $P_4O_6(g)$, the value $D^\circ_{0,at}(P_4O_6) = 4934$ kJ mol^{-1}, which is difficult to reconcile with the present information. By using the heat of combustion of P_4O_6 (c) to $P_4O_{10}(c)$, $\Delta H^\circ_{298} = -1343$ kJ mol^{-1},^{11} $\Delta H^\circ_{298,f}(P_4O_{10}, c)$,^{8} and the heat of vaporization of P_4O_6, there results $D^\circ_{0,at}(P_4O_6) = 4318\pm35$ kJ mol^{-1}. This may, however, be a lower limit since combustion^{11} of P_4O_6 was incomplete. From the appearance potential for the process, $P_4O_{10}(g)+e\rightarrow P_4O_6^+(g)+4O(g)+2e$, 32.6 ± 0.5 eV and the ionization potential of P_4O_6, 10.6 ± 0.5 eV, there follows $D^\circ_{0,at}(P_4O_6) = 4477\pm75$ kJ mol^{-1}.^{1} Finally, extrapolation of the atomization energies of P_4O_{10} through P_4O_7 yields $D^\circ_{0,at}(P_4O_6) = 4385$ kJ mol^{-1}. It is thus probable that the upper limit derived here is quite close to the atomization energy of P_4O_6, for which the value $D^\circ_{0,at}(P_4O_6) = 4385$ $(+40, -60)$ kJ mol^{-1} is proposed, which implies $\Delta H^\circ_{298,f}(P_4O_6,c) = -1662$ $(+40, -60)$ kJ mol^{-1}.

Important results in this investigation are considered to be the identification and the determination of the atomization energies of the molecules P_2O_3, P_2O_4, P_2O_5 and P_3O_6. P_2O_3 and P_2O_5 are, if not necessarily structurally, at least formally, the monomers of the molecules P_4O_6 and P_4O_{10}. As mentioned above, $P_4O_6(g)$ was observed as a re-evaporation product, whenever P_2O_3 was important in the vapour. There is thus reason to believe that there are little or no kinetic limitations to the dimerization of P_2O_3 to P_4O_6, which is thermodynamically highly favoured at low

TABLE 3.— FREE ENERGY FUNCTIONS $(-(G^\circ - H^\circ)/T)$/J mol⁻¹ K⁻¹) AND ENTHALPIES $((H_T^\circ - H_0^\circ)$/J mol⁻¹)

T/K	$P_2O_3(C_s)$	$P_2O_3(C_{2v})$	$P_2O_4(D_{2h})$	$P_2O_4(C_s)$	P_2O_5	P_3O_6	P_4O_7	P_4O_8	P_4O_9
298	258.5	250.5	254.7	268.7	270.7	277.1	287.4	298.8	303.5
1000	339.5	331.1	347.0	361.1	376.7	407.0	446.2	470.0	487.0
1200	354.5	346.1	364.7	378.9	397.5	433.7	479.4	505.9	525.7
1400	367.6	359.4	380.4	394.6	416.0	457.5	509.1	538.1	560.4
$H_{298}^\circ - H_0^\circ$	16 100	15 600	17 300	17 200	19 200	21 500	25 100	27 100	29 000
$H_{1300}^\circ - H_0^\circ$	110 800	111 800	132 300	132 800	155 800	200 600	250 200	271 200	292 400

temperatures. Likewise, P_2O_4 and P_3O_6 may be considered to be the dimer and the trimer of PO_2, of which P_4O_8 is the tetramer.

Although the agreement between the second and third law enthalpies for the reactions leading to the atomization energies of P_2O_3 and P_2O_4 are satisfactory, it can not be used to choose between the two structures envisaged, nor to exclude completely free rotations analogous to those attributed to N_2O_3, N_2O_4 and N_2O_5.[8] Until further information becomes available, $D^\circ_{0,at}(P_2O_3) = 2055 \pm 15$, $D^\circ_{0,at}(P_2O_4) = 2530 \pm 18$, $D^\circ_{0,at}(P_2O_5) = 3020 \pm 22$, $D^\circ_{0,at}(P_3O_6) = 4012 \pm 24$ kJ mol^{-1} are retained.
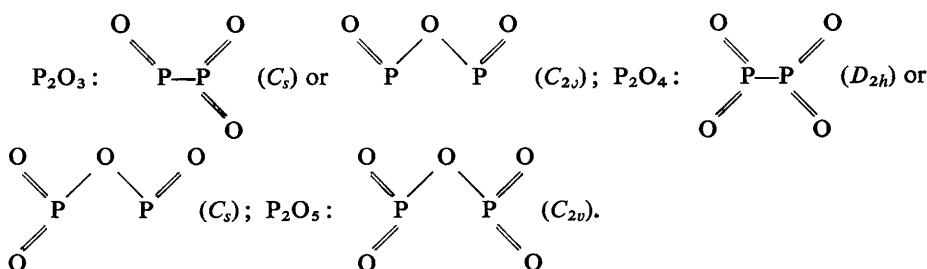
Another result of interest is the observation of gaseous ternary compounds of high stabilities, for which the preliminary values are: $D^\circ_{0,at}(NaPO_2) = 1395 \pm 40$, $D^\circ_{0,at}(KPO_2) = 1375 \pm 40$, $D^\circ_{0,at}(AgPO_2) = 1345 \pm 40$, $D^\circ_{0,at}(SnPO_2) = 1450 \pm 40$ kJ mol^{-1} (observed in connection with the study of $PO(g)$ [4]). It is likely that similar molecules occur in many other high temperature systems, such as flames.

APPENDIX

THERMODYNAMIC FUNCTIONS

For the atom Fe [8] and for the molecules P_2,[8] P_4,[8] PO,[8] PO_2,[4, 8] P_4O_6,[8] P_4O_{10},[8] and FeO,[8] the thermodynamic functions given in the references cited were used. For the remaining molecules, the thermodynamic functions were calculated with the usual statistical mechanical formulae for the rigid rotor, harmonic oscillator, using estimated structures and vibration frequencies. These structures were estimated by analogy with those of the corresponding N—O molecules, taking angles and interatomic distances in P_4O_6 and P_4O_{10} into account:

$$P_2O_3: \quad \begin{array}{c} O \qquad O \\ \diagdown \quad \diagup \\ P-P \\ \downarrow \\ O \end{array} \ (C_s) \text{ or } \begin{array}{c} O \quad O \quad O \\ \diagdown \diagup \diagdown \diagup \\ P \qquad P \end{array} \ (C_{2v}); \quad P_2O_4: \quad \begin{array}{c} O \qquad O \\ \diagdown \quad \diagup \\ P-P \\ \diagup \quad \diagdown \\ O \qquad O \end{array} \ (D_{2h}) \text{ or}$$

$$\begin{array}{c} O \quad O \quad O \\ \diagdown \diagup \diagdown \diagup \\ P \qquad P \\ \diagup \\ O \end{array} \ (C_s); \quad P_2O_5: \quad \begin{array}{c} O \quad O \quad O \\ \diagdown \diagup \diagdown \diagup \\ P \qquad P \\ \diagup \quad \diagdown \\ O \qquad O \end{array} \ (C_{2v}).$$

The O=P=O, O=P—O, O=P—P and P—O—P angles are respectively 134, 117, 110 and 105°. The P=O distance adopted is 143 or 148 pm depending on whether P is tri or pentavalent; while the P—O and P—P distances are 165 and 205 pm. For P_3O_6 a plane hexagonal P_3O_3 structure was used with an apical oxygen atom on each phosphorus atom and distances as above. The vibration frequencies adopted, by comparison with those in the N—O, P_4O_6 and P_4O_{10} molecules are:

$P_2O_3(C_s)$: 150, 130, 110, 65, 50, 30, 25 (2), 20 mm^{-1}; $P_2O_3(C_{2v})$: 130, 110, 80, 65, 50 (2), 40, 30, 10 mm^{-1}; $P_2O_4(D_{2h})$: 150, 130, 110 (2), 65 (2), 50, 40, 30, 25 (2), 20 mm^{-1}; $P_2O_4(C_s)$: 150, 130, 110, 80, 65 (2), 50(2), 40, 30, 25, 10 mm^{-1}; $P_2O_5(C_{2v})$: 150, 130, 110 (2), 80, 65 (2), 50 (3), 40, 30, 25, 10 mm^{-1}; $P_3O_6(D_{3h})$: 140 (3), 97 (3), 65 (2), 60 (2), 45 (2), 40 (3), 35 (3), 300 (3) mm^{-1}.

For the molecules P_4O_7 through P_4O_9, the thermodynamic functions were linearly interpolated between those for P_4O_6 and P_4O_{10}, taking differences in symmetry numbers into account. The numerical values of the thermodynamic functions are given in table 3.

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