

Stability of Phosphorus Species in Seawater

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Received 25 May 1984; revised received 18 October 1984

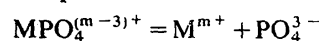
Relative stabilities of various oxidation states, oxyacids and dissolved inorganic complexes of phosphorus in anoxic and oxic marine environments are elucidated. H_3PO_2/P^0 and $H_2PO_2^-/P^0$ are the strong reducing couples in acidic and basic solutions, respectively, in anoxic conditions. $H_3PO_4/H_4P_2O_6$ and H_3PO_2/P^0 are the important reducing couples in seawater. HPO_4^{2-} and H_3PO_4 are the stable ones in oxic and anoxic seawaters, respectively. $UO_2(HPO_4)_2^{2-}$ and $Fe(HP_2O_7)_2^{2-}$ are the most stable complexes in oxic seawater. Among the PO_4^{3-} complexes $CaPO_4^-$ is more stable.

Besides the stability of different oxidation states of an element, relative stabilities among the species of an oxidation state are significant in determining elemental behaviour in the environment. This is of interest, particularly in understanding the biogeochemical processes occurring in natural systems¹. Phosphorus contributes to the biological and geological chemistry of the oceans² and has also become significant owing to its role as a pollutant. Hence, the need to find the stable, metastable and unstable species of phosphorus in seawater need not be stressed. This study attempts to throw some light on relative stabilities of various oxidation states, oxyacids and dissolved inorganic complexes of phosphorus in anoxic and oxic marine environments.

Methods

Oxidation state diagrams were constructed and volt-equivalents for complexes calculated according to Wong³. Calculations were based on thermodynamic data available in literature⁴⁻⁹. Stability constants of various species available at zero ionic strength at 25°C ($\log \beta$) were converted to ionic strength of 0.72 i.e. $\log K$. From K values, volt-equivalents of dissolved species were calculated in 2 steps.

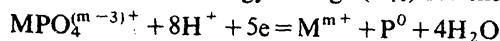
(1) Calculation of free energy of dissociation of the complex



$$G_{r(1)}^0 = -RT \ln K = +1.3643 \log K$$

(k cal. mole⁻¹) at 25°C

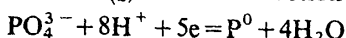
(2) Total free energy change (G_{rT}^0) for the reaction



can be written

$$G_{rT}^0 = G_{r(1)}^0 + G_{r(2)}^0 + G_{M^{m+}}^0 \quad (\text{k cal. mole}^{-1})$$

where $G_{r(2)}^0$ is for the reaction



The estimated total free energy of the reaction was

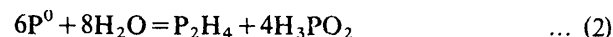
utilised in the computation of redox potential, E^0 , at unit molal activities of individual species present. Since, stability trends remained unaltered for different sulphur species in seawater while using both O_2/H_2O and O_2/H_2O_2 couples as controllers of seawater redox potential¹⁰, O_2/H_2O couple alone was considered in this study.

Results and Discussion

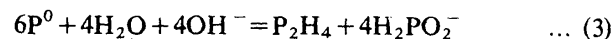
Anoxic Environment—The 5+ oxidation state is the most stable species of phosphorus in both acidic and basic solutions (Fig. 1) which is present as H_3PO_4 and PO_4^{3-} , respectively. The 3- and 2- oxidation states as in PH_3 and $P_2H_4^0$ respectively, are highly unstable in both the solutions even under anoxic conditions, in contrast to that of nitrogen³ and sulphur¹⁰. Berner¹¹ reported that phosphorus does not directly participate in redox reactions like nitrogen or sulphur. However, if by some means hydrogen diphosphide (P_2H_4) is introduced into an anoxic solution, it disproportionates in both the solutions yielding phosphine (PH_3) and elemental phosphorus (P^0).



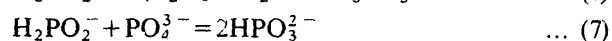
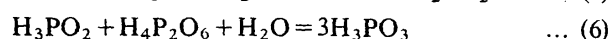
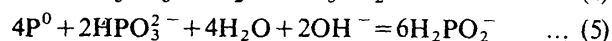
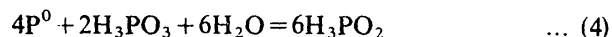
P^0 in turn decomposes to give P_2H_4 and hypophosphorus acid (H_3PO_2) in acidic solutions



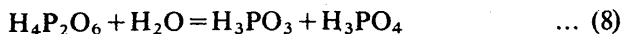
Its disproportionation in basic solutions is shown as



Metastable species are H_3PO_2 and H_3PO_3 in acid solutions (Eqs 4 and 6) and $H_2PO_2^-$ and HPO_3^{2-} in basic solutions (Eqs 5 and 7).

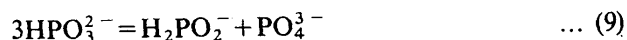


Hypophosphoric acid ($H_4P_2O_6$) is relatively unstable in acidic solutions and dissociates as in Eq. 8.



In acidic solutions H_3PO_2/P^0 and $H_2PO_2^-/P^0$ are the strong reducing couples (Fig. 1). In both the solutions 1+ and 0 oxidation states of phosphorus participate as end members in reducing couples. From Fig. 1, it is obvious that there is no oxidizing couple in basic solution but the only one in acidic solution is $H_3PO_3/H_4P_2O_6$. The 5+ state acts as the strong reducing agent in oxygen deficient waters (Fig. 1).

Oxic environment—Stability sequence of different oxidation states is same in oxic as in the anoxic environment (Fig. 2). But, in the oxic solution (Fig. 2) HPO_3^{2-} disproportionates (Eq. 9) in basic solution.



whereas it is metastable in acidic solutions (Eq. 7). Significantly the metastability and disproportionation intensities of phosphorus oxyacids, P^0 and P_2H_4 are more in anoxic environment (Fig. 1), than in oxic environment (Fig. 2), as can be derived from slopes between various oxidation states. However, the reactions in oxic environment occur in the same way as in anoxic environment (Eqs 1 to 8). In addition Fig. 2 shows the enhancement in either stability or instability of any species, in both the solutions with an increase in oxygen concentration. The single oxidizing couple $H_3PO_3/H_4P_2O_6$ in anoxic waters, transforms to an additional reducing couple in oxic waters. In basic solutions PO_4^{3-}/HPO_3^{2-} is the strong reducing

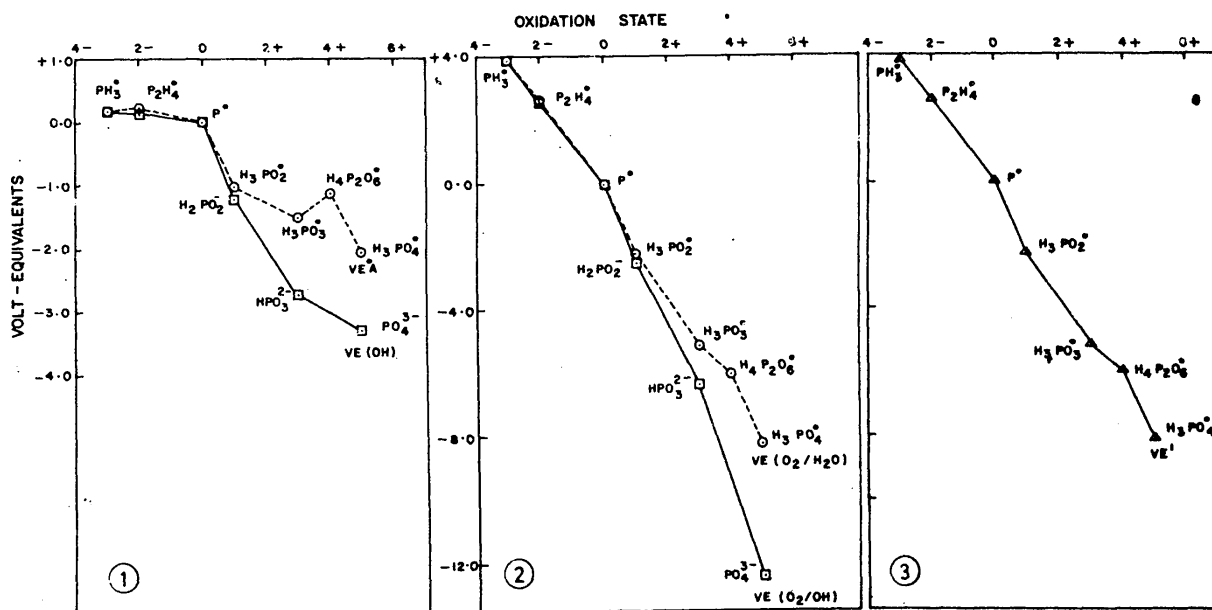
couple, wherein, both $H_3PO_4/H_4P_2O_6$ and H_3PO_2/P^0 are of similar magnitude in acidic solutions (Fig. 2).

Seawater—The stability of phosphorus oxyacids in seawater (Fig. 3) is similar to that exhibited in oxic acidic solutions (Fig. 2) a behaviour also exhibited by sulphur oxyacids¹⁰. P^0 disproportionates in seawater according to the equation,



As shown earlier $H_4P_2O_6$ is also unstable (Fig. 3 and Eq. 8). H_3PO_2 and H_3PO_3 show metastability, as they can be formed from their respective neighbouring oxyacids (Eqs 4 and 6). Though, both H_3PO_2 and H_3PO_3 exhibit metastability, H_3PO_3 is more stable because of lower volt-equivalents. Nevertheless, H_3PO_4 (5+) exhibits the highest stability, in agreement with the published reports^{1,2,12,13}. As in oxic acidic solutions, $H_3PO_4/H_4P_2O_6$ and H_3PO_2/P^0 couples are important as reducing couples in seawater.

Volt-equivalents of different species of phosphorus, oxyacids and anions, are incorporated in Table 1. In accordance with the earlier works^{1,12,14}, HPO_4^{2-} shows the highest stability in oxic seawater. Further the present study shows that $H_3PO_4^0$ is the most stable one in anoxic acidic waters (Fig. 1, Table 1). Next to HPO_4^{2-} , $H_2PO_4^-$ has the higher volt-equivalents in oxic seawater followed by $HP_2O_7^{3-}$, $H_2P_2O_7^{2-}$, PO_4^{3-} and $H_3PO_4^0$ (Table 1). It is shown^{1,12,14} that approximately 86, 13 and 0.75% of phosphoric acid shall exist as HPO_4^{2-} , PO_4^{3-} and $H_2PO_4^-$ ions, respectively in seawater. In spite of its complexation in seawater, HPO_4^{2-} is reported to be the major



Figs 1 to 3—Oxidation state diagrams of phosphorus system in (1) anoxic environment [VE^A (acidic solutions) and $VE(OH)$ (basic solutions)]; (2) oxic environment [$VE(O_2/H_2O)$ (acidic solutions) and $VE(O_2/OH)$ (basic solutions)]; and (3) seawater of pH 8 and $pO_2 = 0.21$ atm

oxyanion. The occurrence of PO_4^{3-} in high concentration than the thermodynamically more stable $H_2PO_4^-$ (Table 1) is ascribed to the impact of specific and non specific interaction¹². $HP_2O_7^{3-}$ and $H_2P_2O_7^{2-}$ have higher stability than PO_4^{3-} and might present in natural waters, because of their active participation in energy transformations in biological systems¹⁵. Table 1 shows that stability of PO_4^{3-} is followed by $H_3P_2O_7^-$, $H_3PO_4^0$, HPO_3^0 and $H_4P_2O_7^0$ for 5+ oxidation state. It is also seen that the stability of other species decreases as the oxidation number decreases (Fig. 3). Moreover, in seawater, the existence of phosphorus species with oxidation states other than 5+ are practically unknown¹¹.

Under anoxic conditions, either due to mineralisation of organic matter in marine sediments or by pollution, $H_3PO_4^0$ stability is followed by HPO_3^0 , $H_2PO_4^-$ and $H_4P_2O_7^0$ (Table 1). Further Table 1 shows relatively higher stability of neutral phosphorus oxyacids of 5+ state than their oxyanions, in contrast to their stability in oxidic seawater. After the $H_4P_2O_7^0$, stability of its anions increases as the charge of the ion decreases, i.e. $HP_2O_7^{3-}$, $H_2P_2O_7^{2-}$ and $H_3P_2O_7^-$. The rest of the acids and anions are more unstable than the 5+ state species (Table 1), as discussed above.

It was estimated^{1,12,14} that phosphate anions were mainly present as ionic pairs, with cations present in seawater. This complexation was shown to essentially depend on ionic charge of the anion¹² while Wedborg¹ found its dependence on the charge to radius ratio of the cations. The concentrations of various cationic species, used in the present calculations are listed in Table 2. Where the concentration of the ion A is mentioned as $pA = -\log[A]$, the equation for evaluation of volt-equivalents in seawater, becomes

$$VE' = VE_A^0 - 0.472nh - 0.746n + 0.059cnpA \quad (Eq. 7)$$

at a pH of 8 and pO_2 of 0.21 atm. In the above equation c is the stoichiometric coefficient of ion A. Volt-equivalents for the considered dissolved complexes are given in Table 3. In addition to major ions of seawater some minor elements are also considered and of all the complexes, $UO_2(HPO_4)_2^{2-}$ shows the maximum stability followed by $Fe(HP_2O_7)_2^{3-}$, $NaHPO_4^-$, $MgHPO_4^0$ and $CaHPO_4^0$ in oxidic seawater. Though $UO_2(HPO_4)_2^{2-}$ and $Fe(HP_2O_7)_2^{3-}$ occur in negligible amounts because of the very low concentrations of UO_2^{2+} , Fe^{3+} and perhaps of $HP_2O_7^{3-}$ ions in seawater in comparison to major cations, the relative stability cannot be ignored in view of environmental problems. $MgHPO_4^0$ is having high percentage (47.6%) than the $NaHPO_4^-$ (13%) which may be due to the increase in the product of interacting ionic charges $(Z_+ \cdot Z_-)^1$. In

Table 1—Stabilities of Dissolved Phosphorus Species in Acidic Anoxic (VE_A^0) and Oxidic (VE' at a pH of 8 and a pO_2 of 0.21 atm) Seawater

Oxidation state	Dissolved species	VE_A^0	VE'
3 ⁻	PH_3	+0.195	+3.849
2 ⁻	P_2H_4	+0.200	+2.636
1 ⁺	$H_3PO_2^0$	-1.020	-2.238
	$H_2PO_2^-$	-0.391	-2.081
3 ⁺	$H_3PO_3^0$	-1.500	-5.154
	$H_2PO_3^-$	-1.401	-5.527
	HPO_3^0	-1.038	-5.636
4 ⁺	$H_4P_2P_6^0$	-1.120	-5.992
	$H_3P_2O_6^-$	-1.060	-6.168
	$H_2P_2O_6^{2-}$	-0.976	-6.314
	$HP_2O_6^{3-}$	-0.764	-6.334
5 ⁺	$P_2O_5^0$	-0.468	-6.284
	$H_3PO_4^0$	-2.060	-8.150
	$H_2PO_4^-$	-1.930	-8.492
	HPO_4^{2-}	-1.505	-8.539
	PO_4^{3-}	-0.795	-8.301
	HPO_3^0	-1.985	-8.075
	$H_4P_2O_7^0$	-1.925	-8.015
	$H_3P_2O_7^-$	-1.885	-8.211
$H_2P_2O_7^{2-}$	-1.815	-8.377	
	$HP_2O_7^{3-}$	-1.620	-8.418

Table 2—Concentrations of Different Ions ($pX = -\log[X]_{sw}$ in M) Used in Calculation of Volt-Equivalents

Ion	PX
Na^+	0.33
K^+	1.99
Ca^{2+}	2.07
Mg^{2+}	1.36
Cu^{2+}	8
Cd^{2+}	8
Fe^{3+}	8
Ni^{2+}	8
UO_2^{2+}	8

contrast, the $Z_+ \cdot Z_-$ increases for Mg^{2+} from $H_2PO_4^-$ to PO_4^{3-} whereas the stability is in reverse order (Table 3). High percentage of $MgHPO_4^0$ (47.6%) than $CaHPO_4^0$ (5%) can be ascribed to the charge to radius ratio of the cations¹ as also revealed in the present computation (Table 3). The complexing capacity is more for PO_4^{3-} ion than for the other species, but its complexes are relatively less stable than those of $H_2PO_4^-$, HPO_4^{2-} and $HP_2O_7^{3-}$, except calcium complexes. $CaPO_4^-$ is more stable than $CaHP_2O_7^-$ and $CaH_2PO_4^+$. Cd, Cu and Ni complexes of PO_4^{3-} exhibit almost the same magnitude of stability in seawater. The stabilities of P(5+) complexes in oxidic seawater follow the order: $UO_2(HPO_4)_2^{2-} > Fe(HP_2O_7)_2^{3-} > NaHPO_4^- > MgHPO_4^0 > CaHPO_4^0 > MgH_2PO_4^+ > KHPO_4^- > CaPO_4^-$. Also, $UO_2(HPO_4)_2^{2-}$ is the most stable one under anoxic conditions (Table 3). $CaH_2PO_4^+$ is the next followed by $MgH_2PO_4^+$, $Fe(HP_2O_7)_2^{3-}$ and

Table 3—Stabilities of Dissolved Metal-Phosphate Complexes in Acidic Anoxic (VE_a) and Oxidic (VE_o), at a pH of 8 and a pO₂ of 0.21 atm.) Seawater

Complex	VE _a	VE _o	% Species*
MgH ₂ PO ₄ ⁺	-1.965	-8.447	0.07
CaH ₂ PO ₄ ⁺	-1.975	-8.415	0.01
NaHPO ₄ ⁻	-1.530	-8.544	12.80
KHPO ₄ ⁻	-1.520	-8.436	—
MgHPO ₄ ⁰	-1.560	-8.514	47.60
CaHPO ₄ ⁰	-1.570	-8.487	4.98
UO ₂ (HPO ₄) ₂ ²⁻	-2.047	-8.845	—
MgPO ₄ ⁻	-0.955	-8.381	6.46
CaPO ₄ ⁻	-1.050	-8.434	3.52
CdPO ₄ ⁻	-1.125	-8.159	—
CuPO ₄ ⁻	-1.190	-8.224	—
NiPO ₄ ⁻	-1.140	-8.171	—
CaHP ₂ O ₇ ⁻	-1.680	-8.417	—
Fe(HP ₂ O ₇) ₂ ³⁻	-1.945	-8.625	—

*% of phosphate species estimated by Wedborg¹ by including free H₂PO₄⁻ (0.62%), HPO₄²⁻ (23.8%), PO₄³⁻ (0.006%) and the species tabulated above.

CaHP₂O₇⁻, CaHPO₄⁰ and MgHPO₄⁰ are after the above 5 species. Adsorption of these two latter ion pairs on to hydrous ferric oxides or other suspended matter in oxidic seawater enhances the phosphate concentration in anoxic marine pore water by their dissolution along with oxides¹¹.

Acknowledgement

The authors thank Dr V V R Varadachari, Director, for his constant encouragement and Dr R Sen Gupta,

for kindly going through the manuscript and making suggestions and to Mr S P Anand for his encouragement.

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