ANSWER ALL QUESTIONS IN EXAMINATION BOOKLET SHOWING YOUR WORK
Total Marks = 40

**1.** Common ozone generators convert ~1% of the oxygen in a dry atmosphere to $\mathbf{O_3}$(g). When this is bubbled through a water sample the equilibrium concentration of $\mathbf{O_3}$(aq) is determined to be 1.0 ppm. Calculate the value of $K_H$ for ozone in units M $Pa^{-1}$. [3]

**Answer: $K_H = 2.1 \times 10^{-8}$ M $Pa^{-1}$**

**2.** The attached figure depicts Cadmium speciation in seawater as a function of pH.
a) Estimate the fractional abundance of the three most dominant **Cd** species at pH 9. [2]
b) Explain why the relative contribution of some species increase with increasing pH. [2]

**Answer: Fraction of** **$CdCl_2$ = 0.50**
**$CdCl^+$ = 0.38**
**$CdCl_3^-$ = 0.062**

**The concentration of the corresponding ligands (e.g., $OH^-$ and $CO_3^{2-}$) increase with increased pH.**

**3.** Calculate the pH of pore water at 25$^{o}$C in equilibrium with carbon dioxide at 5000 ppmv, assuming no other sources of proton donors or acceptors. [4]

**Answer: pH = 5.1**

**4.** The stepwise formation constants for $\mathbf{Pb(OH)^+}$ and $\mathbf{PbCO_3}$ are given below. For a solution containing $10^{-6}$ M $\mathbf{Pb_T}$, calculate (show your work) the pH of the speciation boundary between $\mathbf{Pb^{2+}}$ and

a) $\mathbf{PbOH^+}$ in pure water [3]

b) $\mathbf{PbCO_3}$ for a solution containing $10^{-3}$ M $\mathbf{CO_3^{2-}}_T$ [4]

$$Pb^{2+} + OH^- === Pb(OH)^+ \qquad K_{f1} = 2.0 \times 10^6$$

$$Pb^{2+} + CO_3^{2-} === PbCO_3(s) \qquad K_f = 1.3 \times 10^{13}$$

**Answer:** **a) pH = 7.7**
**b) pH = 6.2**

**5.** Briefly describe the difference between any **TWO** of the following pairs, providing *examples* (using chemical or structural formula, where applicable) and commenting on the *environmental significance*. [6]

a) Type A versus Type B metal ions

Difference based on electronic configurations of $d^0$ (Type A, e.g., $Ca^{2+}$) vs $d^{10}$ (Type B, e.g., $Hg^{2+}$).
Type A – generally macro nutrients and non-toxic
Type B – generally non essential and toxic

Type B metal ions are considerably more polarizable and therefore greater tendency to participate in covalent bonding with non-metals, such as carbon. Organometallics are more likely to bio-accumulate.

b) Fulvic acid versus Humic acids

Difference based on water solubility. Fulvic acids are soluble at all pHs, whereas humic acids only at pH > 2.
Fulvics – generally smaller size and greater number of hydrogen bonding functional groups, such as –OH, $-CO_2H$.
Humics – generally larger with fewer –OH and $–CO_2H$ groups. Become water soluble only when carboxylic acids are deprotonated.

Both involved in increasing the solubility and aqueous mobility of metal ions (via complexation) and organics (via hydrophobic interactions, metal ion bridging, H-bonding and electrostatic forces)

c) Soaps versus Detergents

Difference is in the nature of the polar group. Soaps have a carboxylate polar group, whereas detergents have a sulfonate polar end group. Carboxylic acids have a pKa around 4-5, and carboxylates form insoluble precipitates in ‘hard’ water. Sulfonates remain deprotonated at all ambient pHs, but may still form precipitates in ‘hard’ water.

Soaps and detergents increase the water solubility and mobility or organic contaminants. ‘Builders’ are often to raise the pH and form complex ions to effectively remove the $Ca^{2+}$ ions. Some builders contain phosphorus and lead to nutrient enrichment and eutrophication.

**6.** For **TWO** of the following, use appropriate chemical equilibria to predict the affect of specified changes. [6]

a) The presence of STP ($\mathbf{Na_5P_3O_{10}}$) on the precipitation of calcium stearate $\mathbf{Ca(C_{17}H_{35}CO_2^-)_2}$ in '*hard*' water

**Answer: STP lessens tendency to form calcium stearate**

b) Increase in temperature on the solubility of $\mathbf{CaCO_3}$ in the presence of $\mathbf{CO_2}$(aq)

**Answer: Higher temperature increases tendency to form calcite**

c) Decrease in pH on mobilization of $\mathbf{Pb^{2+}}$ by NTA

**Answer: Decrease in pH decreases mobilization by NTA**

**7.** What mass (kg) of soluble biodegradable organic matter represented by the formula $\{\mathbf{CH_2O}\}$ will consume all of the $\mathbf{O_2}$ dissolved in an air-saturated 5.0 x $10^6$ L pond at 25$^o$C. Estimate the DOC (in mg **C**/L) of this water. [5]

$$\{\mathbf{CH_2O}\} \quad + \quad \mathbf{O_2} \quad \rightarrow \quad \mathbf{CO_2} \quad + \quad \mathbf{H_2O}$$

**Answer:** **mass of $\{CH_2O\}$ consumed = 41 kg**
**[DOC] = 3.3 mg C/L**

**8.** In a lake water sample containing 1.0 x $10^{-3}$ mol $L^{-1}$ calcium and 50 μg $L^{-1}$ fulvic acid, determine the fraction of the fulvic acid that is bound to calcium. Assume that calcium is the only metal present in significant concentration at a pH of 5. Use 5.0 mmol $FA_{CO2}$- per gram of FA and $K_f$' = 1.2 x $10^3$. [5]

**Answer: Fraction of FA bound to calcium = 56%**

Distribution of chemical species for cadmium in seawater at 25°C as a function of pH

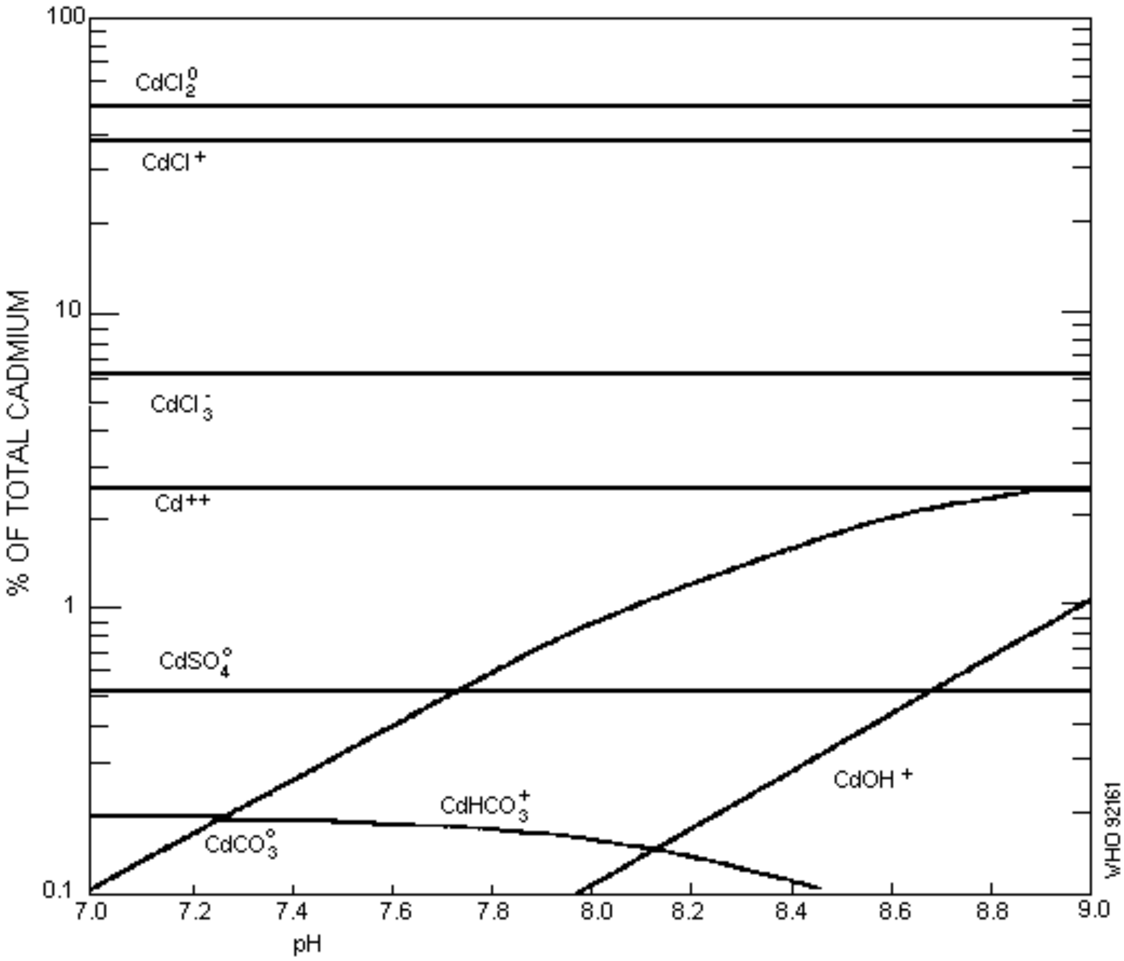


**Fig. 3. Calculated distribution of the chemical species of cadmium in sea water at 25°C and 1 atm as a function of pH.**

pe – pH speciation for lead under two conditions a) $10^{-6}$ M $\mathbf{Pb}_T$ and b) $10^{-6}$ M $\mathbf{Pb}_T$ and $10^{-3}$ M $\mathbf{CO_3^{2-}}_T$

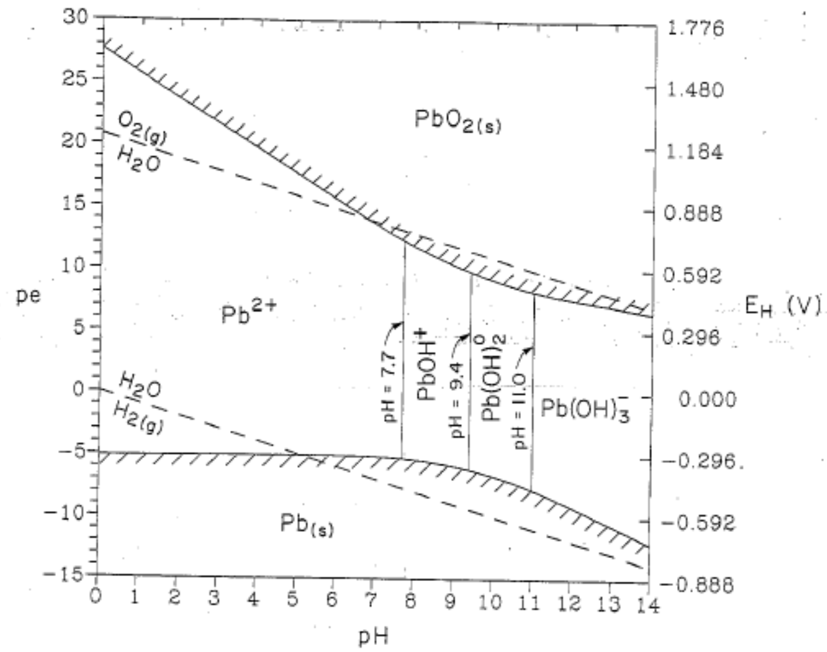


**Figure 21.8** pe-pH diagram for $Pb_T = 10^{-6}$ $M$ at 25°C/1 atm. The only assumptions are: 1) unit activity for all solids when present; and 2) unit activity coefficients for all solution species.

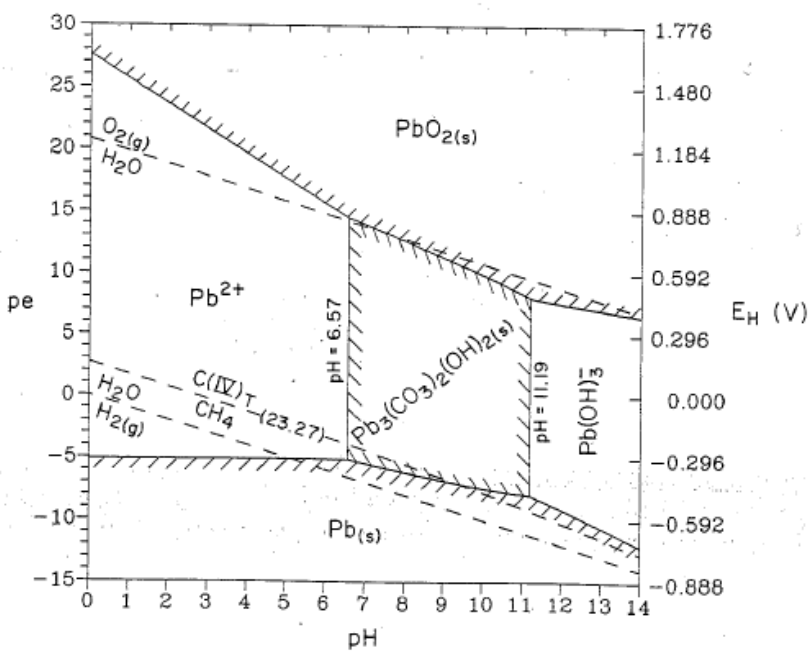


**Figure 22.9** pe-pH diagram for $Pb_T = 10^{-6}$ $M$ and $C_T = 10^{-3}$ $M$ at 25°C/1 atm. Unit activity coefficients in the aqueous phase, and unit activities for the solids (when present) are assumed. The predominance boundaryline between total dissolved C(IV) and $CH_4$ (i.e., Eq. (23.27)) is included.

Fractional abundance for $H_2CO_3$ and $H_3PO_4$ as a function of pH