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]

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]

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

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]

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

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

5. Briefly describe the difference between any **<u>TWO</u>** 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

b) Fulvic acid versus Humic acids

c) Soaps versus Detergents

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

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

c) Decrease in pH on mobilization of $\mathbf{Pb^{2+}}$ 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 5.0×10^6 L pond at 25°C. Estimate the DOC (in mg **C**/L) of this water. [5]

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

8. In a lake water sample containing 1.0×10^{-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 $K_f' = 1.2 \times 10^3$. [5]

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

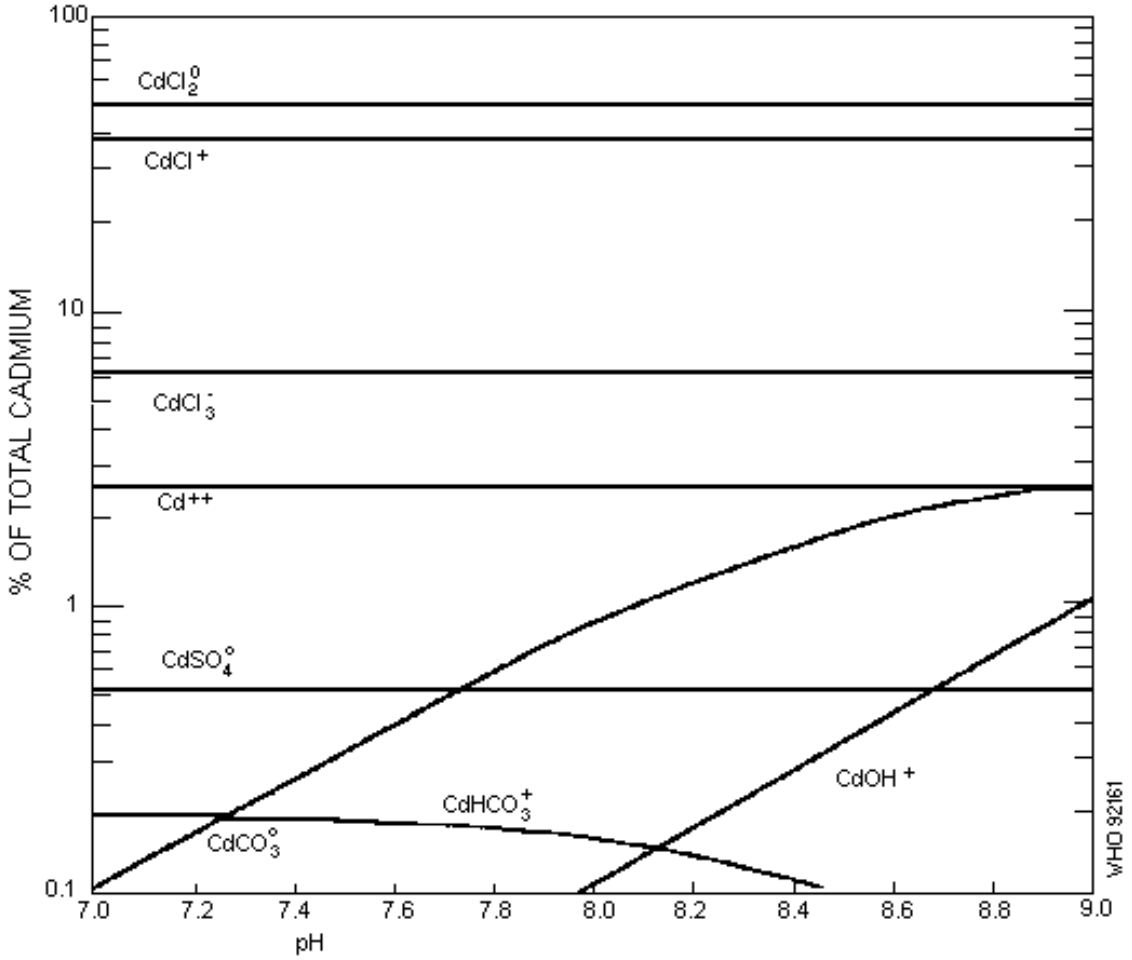

Fig. 3. Calculated distribution of the chemical species of cadmium in sea water at 25°C and 1 atm as a function of pH.

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 $\mathbf{CO_3^{2-}}_T$

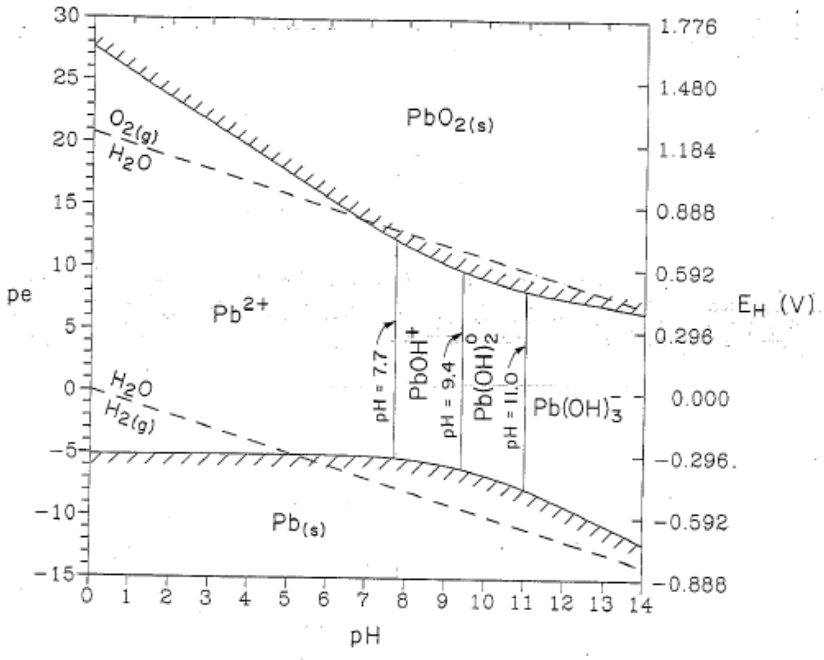

Figure 21.8 pe-pH diagram for $Pb_T = 10^{-6}$ *M* at 25°C/1 atm. The only assumptions are: 1) unit activity for all solids when present; and 2) unit activity coefficients for all solution species.

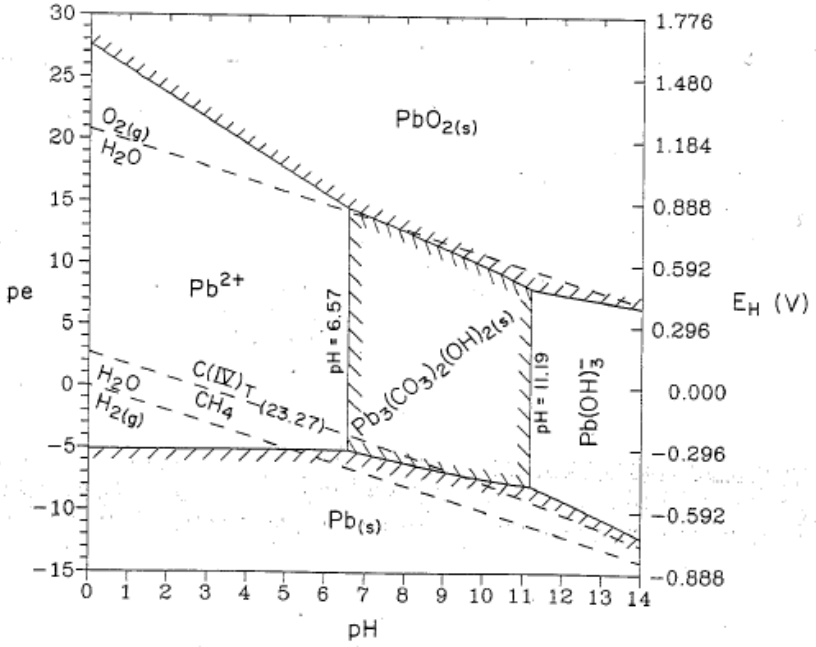

Figure 22.9 pe-pH diagram for $Pb_T = 10^{-6}$ *M* and $C_T = 10^{-3}$ *M* at 25°C/1 atm. Unit activity coefficients in the aqueous phase, and unit activities for the solids (when present) are assumed. The predominance boundaryline between total dissolved C(IV) and CH_4 (i.e., Eq. (23.27)) is included.

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