# CH3041 Tutorial 3 Water Chemistry B Answers

1. Define the $E_H$ of a solution and the pE of a solution and explain how they are related.

$E_H = E_{1/2}$ for the dominant redox couple in solution ($E = E^o - (RT/nF)\ lnQ$), this is referred to as the redox potential of the solution the units are volts. It may be measured using a Pt working electrode and a reference electrode (eg. Calomel) and the value then referenced back to the SHE. There are large errors associated with this measurement and reliable values are typically found in acid-mine drainage waters and swimming pools. A positive $E_H$ indicates that the dominant redox system is an oxidising one eg. $O_2 + 4e^- \rightarrow 2O^{2-}$ and the size of the potential indicates the strength of this oxidising reagent relative to SHE.

The pE is a measure of the electron activity in solution. $pE = -log\{a(e^-)\}$.
A high positive pE defines an oxidising environment in much the same manner as a high positive $E_H$ value. The pE value is an indicator of the intensity of electrons in solution.
$aA + ne- \rightarrow bB$
$Q = \{B\}^b / \{A\}^a$
$pE^o = 1/n\ log\ K = E^o{½} / 0.0591$
$pE = pE^o - 1/n\ logQ$ $E_H = E^o - (RT/nF)\ lnQ$ (put in 8.314, 298, 96.5 x 103, 2.303 (ln to log)

Most pE values are calculated by measuring the quantities of the various species present in solution to find Q and then using tabulated $E^o_{½}$ values to calculate $pE^o$.

Both $E_H$ and pE parameters are therefore used to indicate the redox characteristics of a natural water.
$pE = E_H / 0.0591$

2. Calculate the ion activity product for $CaSO_4$ in seawater using the concentrations $Ca^{2+}$ 10 mmol $l^{-1}$ and $SO_4^{2-}$ 28 mmol $l^{-1}$, the activity coefficients are $\gamma Ca^{2+} = 0.73$ and $\gamma SO_4^{2-} = 0.49$. At 25°C the value of $K_{SP}$ for $CaSO_4$ is $2.6 \times 10^{-5}$. Calculate the degree of saturation of $CaSO_4$ and predict if this compound is under-saturated or over-saturated in seawater.

$a_i = \gamma_i [i]$
$IAP = aCa^{2+} \times aSO_4^{2-} = (0.73 \times 10 \times 10^{-3}) \times (0.49 \times 28 \times 10^{-3}) = 1.01 \times 10^{-4}$

$\Omega = IAP / K_{SP} = 1.00 \times 10^{-4} / 2.6 \times 10^{-5} = 3.89$ $CaSO_4$ is supersaturated in seawater using activities

[ To show the effect of activities:
$Q = [cation]^m[anion]^n = [Ca^{2+}] \times [SO_4^{2-}] = 10 \times 10^{-3} \times 28 \times 10^{-3}\ mol^2\ l^{-2} = 2.8 \times 10^{-4}\ mol^2\ l^{-2}$

$\Omega = Q / K_{SP} = 2.8 \times 10^{-4} / 2.6 \times 10^{-5} = 10.77$ $CaSO_4$ is supersaturated in seawater using concs.]

Remember the activities are just the real available concentrations that include the effects of deviations from ideality.
Another book suggests a $K_{SP}$ of $4.2 \times 10^{-5}$ which gives $\Omega = 2.38$

3. Using the Nernst equation, $pE = pE^o - 1/n \times log(\{red\}/\{ox\})$, calculate the pE value for an anoxic water containing $10^{-6}M\ Fe^{2+}$ in equilibrium with $Fe(OH)_3(s)$ at a pH of 4. Use concentrations as they closely approximate activities in this situation. The value of the equilibrium constant for the dominant redox 1/2 reaction: $Fe(OH)_{3(s)} + 3H^+ + e^- \leftrightarrows Fe^{2+} + 3H_2O$ is $K = 1 \times 10^{16}$. Recall that $pE^o = 1/n\ log\ K$.

$pE^o = 1/n\ log\ K = 1/1 \times log\ (1 \times 10^{16}) = 16$

$pE = pE^o - 1/n \times log(\{red\}/\{ox\})$

$\{ox\} = [H^+]^3 = (10^{-pH})^3 = (1 \times 10^{-4})^3 = 1 \times 10^{-12}M$ - the $Fe(OH)_3$ is omitted as it is a solid.

$\{red\} = [Fe^{2+}] = 1 \text{ x } 10^{-6}$ M - the water is omitted as it is a essentially a pure liquid as it is in vast excess.

$pE = pE^{o} - 1/n \text{ x } \log(\{red\}/\{ox\}) = 16 - \log(1\text{x } 10^{6}) = 16 - 6 = 10$

4. Colourless sulphur bacteria may be classed as chemotrophs, autotrophs and lithotrophs which use $O_2$ as an oxidant. Explain what these terms mean and how this will effect where these organisms exist in the water column and the chemistry in their vicinity.

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|---|---|
| Chemotrophs | Organisms which use chemical for their metabolic energy<br>(as opposed to phototrophs which use sunlight) |
| Autotrophs | Organisms which build their chemical building blocks from $CO_2$<br>(as opposed to heterotrophs which use existing organic matter from other organisms) |
| Lithotrophs | Organisms which use inorganic chemicals as their electron donors in metabolism.<br>(as opposed to organotrophs which use organic matter as an electron donor) |

Colourless sulphur bacteria use $CO_2$ as a carbon source as they are autotrophs (they build the organic molecules they require from this inorganic source). They use energy from the oxidation of $H_2S$ to form $SO_4^{2-}$ and the electrons from this process are accepted by oxygen which make them chemotrophs (using chemical energy with $O_2$ as an oxidant). The inorganic source of electrons is $H_2S$ which is oxidised from S(II) to S(VI) and so they are lithotrophs. The organism will exist where there are reasonable concentrations of $CO_2$ . There must be available $O_2$ and available $H_2S$. The latter is generally formed by bacterial action under anoxic conditions where the *Desulfovibrio* bacteria oxidise organic matter using electrons supplied by a S(VI) $SO_4^{2-}$ to S(II) $H_2S$ transformation. The colourless sulphur bacteria are to be found on the oxic side of the oxic-anoxic boundary. The organisms generate sulphate which in an oxic environment will tend to oxidise to sulphuric acid and so they will need to be acid tolerant. They are important in the sulphur cycle as they help return the reduced S back to oxidised S for other organisms to use as an electron acceptor.

5. What is redox cycling at an oxic-anoxic boundary? Explain using an example.

Photosynthesis and turbulent mixing of $O_2$ saturated surface waters ensure that the top layers of water in a stratified water column have a high dissolved oxygen content. Microorganisms will use $O_2$ in the first instance in respiration as they consume the available dead biomass in this topmost part of the water profile. This results in a gradual lowering of the dissolved oxygen content and eventually as the microorganisms switch to the use of $NO_3^-$ as an electron acceptor the DO content drops to zero. The region where the DO drops to zero is referred as the oxic-anoxic boundary. It is important in redox cycling as the compounds below the boundary will be metabolising using redox couples which operate at steadily more negative (ie. reducing) values. Above the boundary there is sufficient oxygen and so the characteristic redox potential is that of the $O_2/H^+$ couple.
An element as it descends in the water column will pass from a highly oxidised state above the boundary to a reduced one below the boundary. Organisms around the boundary will use the various different oxidation states of the element for their metabolic processes. This ensures that each element will be cycled many times in the aquatic environment before it is lost to sedimentation.