CH3041 Tutorial 3 Water Chemistry B Answers

1. Define the terms **sensible heat** and **latent heat** as they are applied to a parcel of air.

Sensible heat is the heat energy in the air due to the kinetic energy of the air molecules.
Latent heat is the stored heat energy in water vapour that is released as the water condenses.
ΔH_{vap} = 40.7 kJ / mol is used in vaporising water and so the negative of this is released as water condenses.

2. A sample of lake water is analysed and contains the following concentrations of ions (mg / L) :

Na^+	Cl^-	Ca^{2+}	CO_3^{2-}	Mg^{2+}	SO_4^{2-}
46	71	401	600	243	961

The activity coefficients for Mg^{2+} and SO_4^{2-} at 25°C are both $\gamma = 0.630$.

- Calculate the ion product, Q, for magnesium sulphate.
- Calculate the ion activity product, IAP, for magnesium sulphate and predict whether this compound is likely to precipitate from the lake water when it is left to stand at 25°C. ($K_{SP\,(MgSO4)}$ = 5.9×10^{-3} at 25°C)
- Calculate the ionic strength, *I* , of the water sample.

	Na^+	Cl^-	Ca^{2+}	CO_3^{2-}	Mg^{2+}	SO_4^{2-}
M	23.0	35.45	40.08	60.01	24.31	96.06
[X]	0.002	0.002	0.0100	0.0100	0.0100	0.0100

- Calculate the ion product Q for magnesium sulphate.

$MgSO_4 \leftrightarrows Mg^{2+} + SO_4^{2-}$

$Q_{MgSO4} = [cation]^m[anion]^n = [Mg^{2+}] \times [SO_4^{2-}] = 10.0 \times 10^{-3} \times 10.0 \times 10^{-3}\ mol^2\ l^{-2} = \mathbf{1.00 \times 10^{-4}\ mol^2\ l^{-2}}$

- Calculate the ion activity product for magnesium sulphate where the activity coefficients for γMg^{2+} and γSO_4^{2-} are both 0.630 at the given concentration.

$a_{Mg2+} = \gamma Mg^{2+}[Mg^{2+}] = 0.630 \times 0.0100 = 6.30 \times 10^{-3}$

$a_{SO42-} = \gamma SO_4^{2-}[SO_4^{2-}] = 0.630 \times 0.0100 = 6.30 \times 10^{-3}$

$IAP = a_{Mg2+} \times a_{SO42-} = 6.30 \times 10^{-3} \times 6.30 \times 10^{-3} = \mathbf{3.97 \times 10^{-5}\ mol^2\ L^{-2}}$

Neither the **Ion Product** or **Ion Activity Product** exceed the solubility product for magnesium sulphate and so magnesium sulphate will not precipitate. $\Omega = IAP / K_{SP} = 6.7 \times 10^{-3}$

- Calculate the ionic strength of the water sample.

	c cation	c anion	cation c z^2	anion c z^2
NaCl	2.00e-3	2.00e-3	2.00e-3	2.00e-3
$CaCO_3$	1.00e-2	1.00e-2	4.00e-2	4.00e-2
$MgSO_4$	1.00e-2	1.00e-2	4.00e-2	4.00e-2

$I = ½\ \Sigma\ (c_i\ z_i^2)$

I = 1/2 ([Na].1 + [Cl].1 + [Ca].4 + $[CO_3^{2-}]$.4 + [Mg].4 + $[SO_4]$.4)
= 1/2 (2.00e-3 + 2.00e-3 + 4.00e-2 + 4.00e-2 + 4.00e-2 + 4.00e-2)
= 1/2 (1.64e-1)
= $\mathbf{8.20 \times 10^{-2}\ mol\ l^{-1}}$.

3. Calculate the pE of a swamp water which has a considerable amount of organic matter floating about in it and which upon chemical analysis indicates that the following redox coupple is dominant:

$$\underset{+IV}{CO_{2(aq)}} + 8H^+_{(aq)} + 8e- \rightarrow \underset{-IV}{CH_4} + 2H_2O_{(l)}$$

The $E^o_{1/2}$ value for this redox couple is 0.170 V.
The pH of the water is 4.00 and the aqueous concentrations of carbon dioxide and methane are 1.00 mmol/L and 2.00 μmol/L, respectively.

$[H^+] = 10^{-4.00} = 1 \times 10^{-4}$ mol / L

$pE^o = E^o_{1/2} / 0.0591 = 0.170 / 0.0591 = 2.876$

$$\begin{aligned} pE &= pE^o - 1/n \log ([Red] / [Ox]) \\ &= 2.876 - 1/8 \log ([CH_4] /[CO_2] [H^+]^8) \\ &= 2.876 - 1/8 \log ([2 \times 10^{-6} / 1 \times 10^{-3} [1 \times 10^{-4}]^8] \\ &= 2.876 - 3.663 \\ &= \mathbf{-0.79} \end{aligned}$$

4. A variety of bacteria have evolved to use the biomass that is floating around in natural waters as a carbon source.

- Using a stratified lake with a reasonably high [SO_4] as an example explain which bacteria you would expect to find around the oxic-anoxic boundary.
- Explain how these bacteria may alter the electron activity of the water body.

A lake will tend to have reasonably high oxygen and biomass concentrations at the surface where the phytoplankton are active. Under these conditions most bacteria are able to operate using oxygen as the electron acceptor and {CH_2O} as their carbon source and electron donor. As the biomass descends in the water column the amount of oxygen decreases and at the oxic-anoxic boundary organisms must choose a different electron acceptor. Bacteria may choose either sulphate or organic matter {CH_2O} and use either sulphate reduction (to form H_2S) or methanogenesis (to form CH_4) as alternative sources of metabolic energy.

Colourless sulphur bacteria will exist on the oxic side of the oxic-anoxic boundary. They 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. These organism will exist where there are reasonable concentrations of CO_2 . There must be available O_2 and available H_2S. 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.
Green and purple sulphur bacteria will exist on the anoxic side of the anoxic boundary. They 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 photons to build up complex organic molecules from CO_2 and so they are photoautotrophs, the electrons from the process H_2S to SO_4^{2-} are accepted by carbon dioxide which makes them (CO_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.

H_2S is generally formed by bacterial action under anoxic conditions where **sulphur reducing bacteria** (such as *Desulfovibrio* bacteria**)** oxidise organic matter suppling electrons to the S(VI) SO_4^{2-} to S(-II) H_2S

transformation.   These organisms use organic matter for their source of carbon, energy and as an electron donor and so they are heterotrophs, chemotrophs and organotrophs.

The electron activity will be highly reducing on the anoxic side of the boundary and oxidising on the oxic side of the boundary. As these microorganisms are all using chemicals based around sulphate reduction / H_2S oxidation you would expect that this redox couple will control the pE of the water around the boundary and hence the pE will be around 4 - 5.

(pE^{o}_{W} 4.5)