Environmental Chemistry, Homework 1

Revision of basic concepts

1) Acid-base reactions: proton transfer

1.a. Exercises on Key Concepts

Definitions according to Brönsted-Lowry

1) An acid is a chemical compound (molecule or ion) that in aqueous solution, is able to release a proton (H^+). An acid deprotonates to give its conjugated base.

$HA + H_2O <—> H_3O^+ + A^-$

Acid Conjugated Base

Write the equilibrium chemical equation(s) of carbonic acid (H_2CO_3).

2) A base is a chemical compound (molecule or ion) that is able to accept a proton (H^+). A base is protonated to give its conjugated acid.

$H_2O + B <—> BH^+ + OH^-$

Base Conjugated Acid

Write the chemical equilibrium equation(s) for sulfate(SO_4^{2-})

Protolysis of water

A priori, demineralized water does not contain ions. However, it nevertheless has a small electrical conductivity of 5.5 x10^{-6} S[1] at 25 °C Explain why.

Write the water autoproteolysis equation. Indicate which are the basic and acidic forms.

Strength of an acid and a base

The relative strength of acids and bases is given by the value of their equilibrium constant:

$K_a = \frac{[H_3O^+][A^-]}{[\mathrm{HA}]}$ for acids et $K_b = \frac{[\mathrm{B}H^+][OH^-]}{[\mathrm{B}]}$ for bases

Thus, stronger acids have higher K_a values and stronger bases have higher K_b values. Furthermore, $K_w = K_a \times K_b$. Strong acids and bases are completely dissociated in water, while for weak acids and bases a mixture of acidic and basic species will be present in solution.

1) Below are four compounds with an acidic carboxylic function (-COOH), along with their acidity constant K_a. Which of compounds acids is the most acidic?

(a) Lactic acid (K_a = 1.4 x10^{-4})
(b) Propionic acid (K_a = 1.4 x10^{-5})
(c) Acetic acid (K_a = 1.8 x10^{-5})
(d) Pyruvic acid (K_a = 3.2 x10^{-3})

1: Conductivity is measured in Siemens (S); it depends on the ion concentration and the charge of the ions.

2) Acidity or basicity constants are given in tables in the form $pK_a = -\log K_a$ et $pK_b = -\log K_b$. Write a simple relationship to calculate pK_b from pK_a. Calculate the pK_a of the acids from the previous exercise and deduce the pK_b of their conjugated base.

Definition of pH

1) pH is a quantitative measure of the degree of acidity of an aqueous solution. Among the following propositions, which one(s) is/are correct? You can assume a temperature of 25 C.

(a) pH = -ln $[H_3O^+]$

(b) pH = log $[H_3O^+]$

(c) pH = log $(1/[H_3O^+])$

(d) pH = -log $(10^{-14}/ [OH^-])$

(e) pH = -log $([H_3O^+])$

2) If the concentration of hydroxide ions in water at 298 K is 10^{-8} M, what is the pH of the solution?

3) Explain why the following relationships are obtained:

pH = $\frac{1}{2}(pK_A - logC_A)$ where C_A is the total concentration of weak acid in solution.

and pH = $7 + \frac{1}{2}(pK_a + logC_B)$ where C_B is the total concentration of weak base in solution.

1.b. Calculating the pH of acid solutions

1) 1 mL of hydrochloric acid (1 M) is added to 1 liter of pure water. What is the pH of the solution? (Remember: $n_1=n_2$ so $C_1V_1=C_2V_2$)

2) What is the the pH value of an aqueous solution containing 10^{-2} M of lactic acid, pyruvic acid, or acetic acid ? Use the K_a values listed above.

1.c. Calculating the pH of basic solutions

1) 5 mL of sodium hydroxide (1 M) are added to 1 liter of pure water. What is the pH of the solution?

2) What is the pH value of an aqueous solution containing 10^{-2} M of lactate (i.e., the conjugated base of lactic acid), pyruvate and potassium acetate?

2) Oxidation-reduction reactions: electron transfer

2.a. Exercises on Key Concepts

<u>Definition of a redox couple</u>

1) Complete the following sentences :

A **reductant** is a chemical compound (molecule or ion) that is capable of ______ one or more electron (s) (e-). A reductant _____ one or more electron (s) to become oxidized. This is called a ________ reaction.

An **oxidant** is therefore a chemical compound (molecule or ion) that is capable ____ one or more electron (s). An oxidant _________ one or more electron (s) and becomes reduced. This is called a ______ reaction.

The redox couples (Ox/Red) are connected by half-equations:

Ox + ne- <-> Red

2) Each redox couple is associated with a **standard electrochemical potential E° (V)** defined with respect to the couple H^+/H_2 ($E°_{H+/H2}$ = 0.0V). The oxidizing power _____ with decreasing potential.

Exemples de potentiels standard à 25°C pH = 0

Ox / Réd	E^0 (V)	Ox / Réd	E^0 (V)
Oxydants forts		SO_4^{2-}/SO_3^{2-}	+0.17
F_2/F^-	+2.87	Cu^{2+}/Cu^+	+0.15
O_3/O_2	+2.07	NO_3^-/NO_2^-	+0.01
$S_2O_8^{2-}/SO_4^{2-}$	+2.10	$H_3O^+/H_{2\,(g)}$	0.00
H_2O_2/H_2O	+1.78	O_2/O_2^{2-}	-0.08
Au^+/Au	+1.69	CH_3CO_2H/CH_3CHO	-0.12
MnO_4^-/Mn^{2+}	+1.51	Pb^{2+}/Pb	-0.13
Mn^{3+}/Mn^{2+}	+1.50	Sn^{2+}/Sn	-0.14
$Cl_{2\,(aq)}/Cl^-$	+1.36	Ni^{2+}/Ni	-0.23
$Cr_2O_7^{2-}/Cr^{3+}$	+1.33	Cd^{2+}/Cd	-0.40
$O_{2\,(g)}/H_2O$	+1.23	Fe^{2+}/Fe	-0.44
Br_2/Br^-	+1.09	S/S^{2-}	-0.48
$NO_3^-/NO_{(g)}$	+0.96	O_2/O_2^-	-0.56
NO_3^-/NO_2	+0.80	Zn^{2+}/Zn	-0.76
Ag^+/Ag	+0.80	H_2O/H_2	-0.83
Fe^{3+}/Fe^{2+}	+0.77	Al^{3+}/Al	-1.66
MnO_4^{2-}/MnO_2	+0.60	Mg^{2+}/Mg	-2.37
$I_{2\,(aq)}/I^-$	+0.62	Na^+/Na	-2.71
Cu^{2+}/Cu	+0.34		
CH_3CHO/CH_3CH_2OH	+0.19	Réducteurs forts	

3) A redox reaction involves two redox couples. The strongest oxidant reacts with the strongest reductant. Using the table of standard potentials above, complete the following table indicating the direction of the reaction.

Réactions	Ox1	Red1	Ox2	Red2
$Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + Ag$				
$6Cl^- + 2\,Al^{3+} \rightarrow 3Cl_2 + 2Al$				

2.b. Equilibrating redox reactions

Let us take the case of the oxidation of copper by silver nitrate. The two couples involved in the reaction are:

	Cu^{2+}/Cu	Ag^{+}/Ag
oxidation number:	+II/0	+I/0
So the oxidation half-equation is	$Cu^{0} \rightarrow Cu^{2+} + 2e^{-}$	$Ag^{+} + e^{-} \rightarrow Ag$

The number of electrons involved is not balanced, i.e., the number of electrons given must be equal to the number of electrons received

$$\begin{array}{rl} Cu^{0} \rightarrow Cu^{2+} + 2e^{-} & \times 1 \\ Ag^{+} + e^{-} \rightarrow Ag & \times 2 \\ \hline Cu + 2\,AgNO_3 \rightarrow Cu(NO_3)_2 + 2\,Ag & \end{array}$$

During a redox reaction, the compounds undergo changes in oxidation number (O.N.). To balance the half-equations, it is also necessary to balance the charges, using the self-protolysis of water.

Balance the following equation: $NO^{-}_{2} + MnO_4^{-} + H_3O^{+} \longrightarrow NO^{-}_{3} + Mn^{2+} + H_2O$

1. **The sum of the oxidation numbers of all atoms in the molecule or ion is equal to its total charge. Useful for determining the O.N. of the organic compounds**
2. For atoms in their ground state. O.N. = 0
3. For elements of
   - group I: O.N. = +1
   - group II: O.N. = +2
   - group III (excl. Bor): O.N. = +3 for M^{3+}; O.N. = +1 for M^{+}
   - group IV (excl. C & Si): O.N. = +4 for M^{4+}; O.N. = +2 for M^{2+}
4. **For hydrogen,** **O.N. = +1 in combination with nonmetals**
   O.N. = -1 in combination with metals
5. **For fluorine, and halogens,**
   O.N. = -1 in all compounds
4. **For oxygen,** O.N. = -1 in peroxydes (O_2^{2-})
   O.N. = -1/2 in superoxydes (O_2^{-})
   O.N. = -1/3 in ozonides (O_3^{-})
   O.N. = -2 unless combined with F

3) Precipitation/dissolution reactions

Calculate the molar solubility in pure water of:

(a) $CaCO_3$ $K_s = 3.3*10^{-9}\ M^2$

(b) $Mn(OH)_2$ $K_s = 2.0*10^{-13}\ M^3$

(c) $Cu(OH)_2$ $K_s = 4.8*10^{-20}\ M^3$

(d) CdS $K_s = 1.0*10^{-27}\ M^2$

Which of these salts is the most soluble in water?