Environmental Chemistry, Homework 1: Solution

Revision of basic concepts

1) Acid-base reactions: proton transfer

1.a. *Exercises on Key Concepts*

Definitions according to Brönsted-Lowry

1) $H_2CO_3 + H_2O \longleftrightarrow H_3O^+ + HCO_3^-$

$HCO_3^- + H_2O \longleftrightarrow H_3O^+ + CO_3^{2-}$

Acid Conjugate Base

2) $H_2O + SO_4^- \longleftrightarrow HSO_4^- + OH^-$

$H_2O + HSO_4^- \longleftrightarrow H_2SO_4 + OH^-$

Base Conjugate Acid

Protolysis of water

1) A small fraction of water molecules dissociate to hydroxide ion (OH-) and hydronium ion (H_3O^+) which, even in low concentrations (10^{-7} M), are capable of conducting current.

2) $H_2O + H_2O \longleftrightarrow H_3O^+ + OH^-$

Acide + Base <-> Conjugate Acid + Conjugate Base

$K_w = [H_3O^+][OH^-] = 10^{-14}$ is called the ion product of water

Strength of an acid and a base

1) (a) Lactic acid ($K_a = 1.4 \times 10^{-4}$) **X**
(b) Propionic acid ($K_a = 1.4 \times 10^{-5}$) **X**
(c) Acetic acid ($K_a = 1.8 \times 10^{-5}$) **X**
(d) Pyruvic acid ($K_a = 3.2 \times 10^{-3}$) ✓

2)

$K_w = K_a \times K_b$

$-\log K_w = -\log (K_a \times K_b)$

$14 = -\log K_a + - \log K_b$ (with $pK_a = -\log K_a$ and $pK_b = -\log K_b$)

$pK_a + pK_b = 14$

(a) Lactic acid $pK_a = 3.85$ therefore $pK_b = 10.15$

(b) Propionic acid $pK_a = 4.85$ therefore $pK_b = 9.15$

(c) Acetic acid $pK_a = 4.74$ therefore $pK_b = 9.26$

(d) Pyruvic acid $pK_a = 2.49$ therefore $pK_b = 11.51$

The higher the pK_a , the lower the pK_b , so the weaker the acid, the stronger its conjugate base.

Definition of pH

1) (a) pH = -ln [H_3O^+] **X**
   (b) pH = log [H_3O^+] **X**
   (c) pH = log (1/[H_3O^+]) ✓
   (d) pH = -log (10^{-14}/ [OH^-]) ✓
   (e) pH = -log ([H_3O^+]) ✓

2) pH = - log ([H_3O^+]) and [H_3O^+] = K_w/[OH^-]

hence pH = -log (10^{-14}/ [OH^-]) we get [OH^-] = 10^{-8} M

pH = -log (10^{-14}/10^{-8})

pH = 6

3) Weak acids and weak bases do not fully dissociate in solution.

The acid in the presence of water will dissociate according to the equation :

	HA	**+ H_2O**	**—>**	**H_3O^+**	**+ A^-**
At t=0	C_A			0	0
At t_{eq}	C_A - x			+x	+x

This gives : $K_a = \frac{[H_3O^+][A^-]}{[\mathrm{HA}]} = \frac{x^2}{C_A - \mathrm{x}}$ $or\ x = [H_3O^+]$

as the dissociation of the acid is weak, we can consider that x<<C_A , so we can simplify by

$$K_a = \frac{[H_3O^+][A^-]}{[\mathrm{HA}]} = \frac{x^2}{C_A}$$

so $x = [H_3O^+] = \sqrt{K_A C_A}$

-log ([H_3O^+]) = -log $(K_A C_A)^{\frac{1}{2}}$

pH = $-\frac{1}{2} log K_A - \frac{1}{2} log C_A$

pH = $\frac{1}{2}(pK_A - log C_A)$

Using the same reasoning for the weak base, we obtain

x = [OH^-] = $\sqrt{K_b C_B}$

so [H_3O^+] = $\frac{K_w}{\sqrt{K_b C_B}}$

pH = 14 + $\frac{1}{2} log K_b + \frac{1}{2} log C_B$

pH = 14 + $\frac{1}{2} log K_w - \frac{1}{2} log K_a + \frac{1}{2} log C_B$

pH = 7 $-\frac{1}{2}logK_a + \frac{1}{2}logC_B$

pH = 7 $+\frac{1}{2}(pK_a + logC_B)$

1.b. *Calculating the pH of acid solutions*

1) Hydrochloric acid is a strong acid so $[H_3O^+] = n_{HCl}\ V_{HCl} / V_{sol}$

$[H_3O^+]$ = (1x10^{-3} x 1) / 1,001

$[H_3O^+]$ = 9,9 x 10^{-4} M

pH = 3

2) These 3 acids are weak acids, so we use the relationship pH = $\frac{1}{2}(pK_A - logC_A)$

with $logC_A$ = log (10^{-2}) = -2

Lactic acid: pH = (3.85 + 2) = 2.9 3

Pyruvic acid: pH = (2.49 + 2) = 2.25

Acetic acid: pH = (4.74 + 2) = 3.37

1.c. *Calculating the pH of basic solutions*

1) Sodium hydroxide, NaOH, is a strong base, completely dissociated into Na^+ and OH^- , so

pH = $-\log\left(\frac{K_w}{[\mathrm{OH}^-]}\right) = -\log\left(\frac{10^{-14}}{5\ x\ 10^{-3}}\right)$

pH =11.7

2) These 3 conjugated bases are weak (based on the K_b values calculated) above. We can write:

pH = 7 $+\frac{1}{2}(pK_a + logC_B)$

Lactic acid: pH = 7 + (3.85 - 2) = 7.9 3

Pyruvic acid: pH = 7 + (2.49 - 2) = 7.25

Acetic acid: pH = 7 + (4.74 - 2) = 8.37

2) Oxidation-reduction reactions: electron transfer

2.a. *Exercises on Key Concepts*

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

1) A reductant is a chemical compound (molecule or ion) which is able to give up one or more electrons (e-). A reductant loses one or more electrons to become oxidized This is called a oxidation reaction.

An oxidant is therefore a chemical compound (molecule or ion) that is capable of acquiring one or more electron(s). An oxidant acquires one or more electrons and becomes reduced. This is called a reduction reaction.

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

3)

Reactions	Ox1	Red1	Ox2	Red2
$Cu(s) + 2AgNO_3 \rightarrow Cu(NO_3)_2 + Ag(s)$	Ag^+	Cu(0)	Cu^{2+}	Ag(0)
$3Cl_2 + 2Al(s) \rightarrow 6Cl^- + 2\ Al^{3+}$	Cl_2 (0)	Al(0)	Al^{3+}	Cl^-

2.b. *Equilibrating redox reactions*

1) $NO^-_2 + MnO_4^- + H_3O^+ \longrightarrow NO^-_3 + Mn^{2+} + H_2O$

-Determination of the pairs involved in the reaction

MnO_4^- / Mn^{2+} et NO^-_3 / NO^-_2

-Determination of oxidation numbers and half-reactions

MnO_4^- : N.O. = +VII

Mn^{2+} : N.O. = +II

This reaction requires 5e- and the charges are balanced by H+:

$\underline{MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O}$ eq (1)

NO^-_3 : N.O. = +V

NO^-_2 : N.O. = +III

This reaction requires 2e- and the charges are balanced by H+:

$\underline{NO^-_3 + 2e^- + 2H^+ \rightarrow NO^-_2 + H_2O}$ eq (2)

-Electronic transfer equilibration : x2 for eq (1) and x5 for eq (2)

$2\ MnO_4^- + \mathbf{10\ e^-} + 16\ H^+ \rightarrow 2\ Mn^{2+} + 8\ H_2O$

$5\ NO^-_2 + 5\ H_2O \rightarrow 5\ NO^-_3 + \mathbf{10\ e^-} + 10\ H^+$

-Combination of the 2 equations

$5\ NO^-_2 + 2\ MnO_4^- + 6\ H^+ \rightarrow 5\ NO^-_3 + 2\ Mn^{2+} + 3\ H_2O$

ou $5\ NO^-_2 + 2\ MnO_4^- + 6\ H_3O^+ \rightarrow 5\ NO^-_3 + 2\ Mn^{2+} + 9\ H_2O$

3) Precipitation/dissolution reactions

$M_nX_m(s) \leftrightarrow nM(aq) + mX(aq)$

Ks = $[M]^n[X]^m$ and S = $\sqrt[n+m]{\frac{Ks}{n^n m^m}}$

(a)	$CaCO_3$	Ks = $3.3*10^{-9}$ M^2	S = $5.75*10^{-5}$ M
(b)	$Mn(OH)_2$	Ks = $2.0*10^{-13}$ M^3	S = $3.68*10^{-5}$ M
(c)	$Cu(OH)_2$	Ks =$4.8*10^{-20}$ M^3	S = $2.28*10^{-7}$ M
(d)	CdS	Ks = $1.0*10^{-27}$ M^2	S = $3.16*10^{-14}$ M

$CaCO_3$ is the most soluble.