CM 1111 Tutorial 5

Question 1

a) Complete and balance the following reactions and state which species is the acid and which the base.

(i) $H_2O_{(l)} + HNO_{3(g)}$

$H_2O_{(l)} + HNO_{3(g)} \rightarrow H_3O^+_{(aq)} + NO_3^-{}_{(aq)}$
B A A B

(ii) $H_2O_{(l)} + NH_{3(g)}$

$H_2O_{(l)} + NH_{3(g)} \rightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$
A B A B

(iii) $H_2SO_{4(l)} + NaOH_{(aq)}$

$H_2SO_{4(l)} + NaOH_{(aq)} \rightarrow NaHSO_{4(aq)} + H_2O_{(l)}$ or
A B B A
$H_2SO_{4(l)} + 2\ NaOH_{(aq)} \rightarrow Na_2SO_{4(aq)} + 2\ H_2O_{(l)}$
A B B A

(iv) $NaOH_{(aq)} + CO_{2(g)}$

$NaOH_{(aq)} + CO_{2(g)} \rightarrow Na^+_{(aq)} + HCO_3^-{}_{(aq)}$
B A adduct (already Lewis adduct)

b) Acid rain contains mainly sulfuric acid (at concentrations as high as 10^{-2} M), and in many parts of the world it is destroying marble statuary at an alarming rate. Marble is mainly calcium carbonate, and the reaction is acid-base. Give a balanced chemical equation for the reaction and state which is the acid, and which is the base.

$H_2SO_{4(aq)} + CaCO_{3(s)} \rightarrow CaSO_{4(aq)} + \cancel{H_2CO_{3(aq)}}$

$\cancel{H_2CO_{3(aq)}} \rightarrow H_2O_{(l)} + CO_{2(g)}$

$H_2SO_{4(aq)} + CaCO_{3(s)} \rightarrow CaSO_{4(aq)} + H_2O_{(l)} + CO_{2(g)}$

H_2SO_4 = acid, $CaCO_3$ = base.

Question 2

Arrange the Brønsted acidity of the following compounds and ions in water in increasing order and briefly explain your answer.

Mg^{2+}, Li^{+}, H_2CO_3 (carbonic acid), CF_3CO_2H (trifluoroacetic acid)

Li^{+} (pk_a ~13.6) < Mg^{2+} (pk_a ~11.4) < H_2CO_3 (pk_a ~6.4) < CF_3CO_2H (pk_a ~0.23)

Li^{+} and Mg^{2+} form aqua complexes in solution, in which H_2O interacts with the ion via the oxygen atom leading to a polarization of the O-H bond. The amount of polarization and thus the acidity of the bond water molecule is dependent on the charge/size ratio of the ion. Mg^{2+} with its greater charge and smaller size therefore gives rise to a stronger acid compared to Li^{+}.

Carbonic acid can be considered as an oxoacid (e.g. CO(OH)2), in which the presence of an electronegative "oxo" on a carbon(IV) central atom leads to greater O-H bond polarization compared to those of the hydrated ions above thus giving rise to an increased acidity.

Trifluoroacetic acid can be derived from carbonic acid by replacing one O-H group with a much more electron-withdrawing CF_3 group, which leads to a substantial increase in acidity.

Question 3

Look up the pk_a values of the relevant acids, and comment on the feasibility of the following acid/base reactions:

a) $H_2SO_{4(conc)} + NaO_2CCH_{3(s)} \rightarrow NaHSO_{4(s)} + CH_3CO_2H_{(l)}$

Yes, this reaction is feasible, because the stronger acid (H_2SO_4, pK_a ~–2) will react with the salt to form the weaker acid (HOAc, pk_a ~4.76) and the salt of the weaker base.

b) $H_2SO_{4(conc)} + NaCl_{(s)} \rightarrow NaHSO_{4(s)} + HCl_{(g)}$

Purely based on the pk_a values {pK_a (H_2SO_4) = ~ –2; pk_a (HCl) = ~ –7} this reaction should not be favorable, i.e. equilibrium is on the left side (K is small). However, all acid-base reactions are equilibrium reactions and any small amount of gaseous HCl that forms is removed from the equilibrium via evaporation pushing the equilibrium to the product side. With this consideration, the reaction becomes feasible too.

Question 4

Addition of NH_3 solution to an aqueous solution of $AlCl_3$ leads to the precipitation of $Al(OH)_3$.

a) Derive the complete equation for this chemical reaction.

$$AlCl_{3(aq)} + 3\ NH_{3(aq)} + 3\ H_2O_{(l)} \rightarrow Al(OH)_{3(s)} + 3\ NH_4Cl_{(aq)}$$

b) Treatment of the $Al(OH)_3$ precipitate with NaOH solution leads to dissolution. Briefly explain this observation using chemical equations.

$$Al(OH)_{3(s)} + NaOH_{(aq)} \rightarrow Na[Al(OH)_4]_{(aq)}$$

c) Treatment of the $Al(OH)_3$ precipitate with HCl solution leads to dissolution. Briefly explain this observation using chemical equations.

$$Al(OH)_{3(s)} + 3\ HCl_{(aq)} \rightarrow AlCl_{3(aq)} + 3\ H_2O_{(l)}$$

d) What is the correct term to describe the behaviour of $Al(OH)_3$?

Amphoteric/amphiprotic