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Preparation for Buffer Problems – Supplemental Worksheet KEY

Review of Conjugate Acid/Base Pairs

Problem #1: Conjugate acid/base pairs are important to salts and buffers. Complete the following table to practice identifying conjugate acid/base pairs:

Item	Brønsted-Lowry acid or base?	Conjugate partner
Hydronium ion	H_3O^+, acid	Water, H_2O
Cyanide	CN^-, base	Hydrogen cyanide, HCN
Hydroxide	OH^-, base	Water, H_2O
Ammonium ion	NH_4^+, acid	Ammonia, NH_3
Nitrite	NO_2^-, base	Nitrous acid, HNO_2
$H_2PO_4^-$ **	Dihydrogen phosphate ion, acid and base	HPO_4^{2-}, base H_3PO_4, acid
OCl^-	Hypochlorite ion, base	Hypochlorous acid, HClO
$C_6H_5NH_2$	Aniline, base	$C_6H_5NH_3^+$
CH_3NH_2	Methylamine, base	$CH_3NH_3^+$
C_5H_5N (pyridine)	Pyridine, base	$C_5H_5NH^+$

Problem #2: Equilibrium Constants. For each base below, write the reaction for which Kc=Kb. In other words, write the reaction for the base ionizing in water.

a. Ammonia, $K_b = 1.8 \cdot 10^{-5}$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

b. Aniline ($C_6H_5NH_2$), $K_b = 4.2 \cdot 10^{-10}$

$$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$$

c. Dimethylamine $(CH_3)_2NH$, $K_b = 7.4 \cdot 10^{-4}$

$$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$$

d. Hydroxylamine NH_2OH, $K_b = 6.6 \cdot 10^{-9}$

$$NH_2OH + H_2O \rightleftharpoons NH_3OH^+ + OH^-$$

e. Trimethylamine $(CH_3)_3N$, $K_b = 7.4 \cdot 10^{-5}$

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

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Problem #3: For each base above, write its conjugate acid in the corresponding blank, then calculate its pK_a. The first is done for you. (Doing the Lewis Dot diagram can sometimes help with these. Looking at a Kb table can also help.)

Base	Conj Acid	K_b	K_a	pK_a
NH_3	NH_4^+	$1.8 \bullet 10^{-5}$	$5.5 \bullet 10^{-10}$	9.3
$C_6H_5NH_2$	$C_6H_5N_3^+$	$4.2 \bullet 10^{-10}$	$2.4 \bullet 10^{-5}$	4.62
$(CH_3)_2NH$	$(CH_3)_2NH_2^+$	$7.4 \bullet 10^{-4}$	$1.35 \bullet 10^{-11}$	10.87
NH_2OH	NH_3OH^+	$6.6 \bullet 10^{-9}$	$1.5 \bullet 10^{-6}$	5.82
pyridine	$C_5H_5NH^+$	$7.4 \bullet 10^{-5}$	$1.35 \bullet 10^{-10}$	9.87

To calculate the K_a, the following equation is required:

$$K_a = \frac{K_w}{K_b}$$

Sample calculation for $C_6H_5NH_2$

$$K_a(C_6H_5NH_2) = \frac{K_w}{K_b(C_6H_5NH_3^+)} = \frac{1 \times 10^{-14}}{4.2 \times 10^{-10}} = 2.4 \times 10^{-5}$$

To calculate the pKa, the following equation is required:

$$pK_a = -\log(K_a)$$

Sample calculation for $C_6H_5NH_2$

$$pK_a(C_6H_5NH_2) = -\log(2.4 \times 10^{-5}) = 4.62$$

Problem #4: Le Chatelier's Principle. Each of the following actions affects the pH in what way?

System: $CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+$

Change	Reaction shifts	At new Equilibrium, pH will
Adding more moles of acetic acid	Right, towards the products	pH with decrease because [H+] will increase since the reaction shifts towards the products
Adding H_3O^+	Left, towards the reactants	pH will decrease because [H+] will increase due to the addition of H_3O^+, the decrease in H+ ions from the rxn shifting left is negligible compared to the effect of adding the strong acid
Adding strong base	Right, towards the products	pH will increase because the OH- and H+ ions will neutralize and [H+] will decrease, the increase in H+ ions from the rxn shifting right is negligible compared to the effect of adding the strong base
Adding a small amount of a strong acid like HCl	Left, towards the reactants	pH with decrease because [H+] will increase due to the addition of H_3O^+, the decrease in H+ ions from the rxn shifting left is negligible compared to the effect of adding the strong acid
Adding sodium acetate	Left, towards the reactants	pH with increase because [H+] will decrease since the reaction shifts towards the reactants

Problem #5: Challenge Calculation Problem. You locate a vial of formic acid and need to know its molarity. A pH meter measures its pH to be 2.70. Calculate the molarity of formic acid. (Ka = 1.8e-4)

Step 1:

$$pH = -\log[H^+]$$
$$[H^+] = 10^{-pH} = 10^{-2.7} = 2.00 \times 10^{-3}\ M$$

Step 2:

R	$HCOOH$	$+ H_2O \leftrightarrow$	$HCOO^-$ +	H_3O^+
I	x	----	0	0
C	$-2\bullet10^{-3}$	------	$+2\bullet10^{-3}$	$+2\bullet10^{-3}$
E	~x	----	$2\bullet10^{-3}$	$2\bullet10^{-3}$

Step 3:

$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$$

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$$[HCOOH] = \frac{(2.00 \times 10^{-3})^2}{1 \times 10^{-4}} = 0.0221\ M$$

*This problem is a "backwards" problem to the usual problem, however, the same steps are followed but in a different order. We fill in the information we know the RICE table as usual, except this time it is different information that we know.

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**For problem #6, salts that form ions that are weak acids or bases produce H^+ ions or OH^- ions respectively and make acidic or basic solutions respectively.*

Salts

Problem #6: Before we continue to the next topic, you need to understand the effect of salts and ions in water. They influence pH. You need to know how to determine what influence they will have and what reactions will (and won't) occur. To practice, complete the following table. The first one is done for you.

Salt	Predicted salt type	Cation	Cation reaction w/H_2O	Anion	Anion reaction w/H_2O	Solution will become
NaI	Neutral	Na^+	$Na^+ + H_2O \leftarrow NaOH + H^+$ Equil far left, so no H+ produced	I-	$I^- + H_2O \leftarrow HI + OH^-$ Equil far left, so no OH^- produced	Neutral
NH_4Br	Acidic	NH_4^+	$NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+$ Some H_3O^+ produced	Br^-	$Br^- + H_2O \leftarrow HBr + OH^-$ Equil far left, so no OH^- produced	Acidic
$C_6H_5NH_3NO_3$	Acidic	$C_6H_5NH_3^+$	$C_6H_5NH_3^+ + H_2O \leftrightarrow C_6H_5NH_2 + H_3O^+$ H_3O^+ produced	NO_3^-	$NO_3^- + H_2O \leftarrow HNO_3 + OH^-$ Equil far left, so no OH^- produced	Acidic
NaOCl	Basic	Na^+	$Na^+ + H_2O \leftarrow NaOH + H^+$ No H^+ produced	OCl^-	$OCl^- + H_2O \leftrightarrow HOCl + OH^-$ OH^- is produced	Basic
$CaBr_2$	Neutral	Ca^{2+}	$Ca^{2+} + 2\,H_2O \leftarrow Ca(OH)_2 + 2\,H^+$ No H^+ produced	Br^-	$Br^- + H_2O \leftarrow HBr + OH^-$ Equil far left, so no OH^- produced	Neutral
KNO_2	Basic	K^+	$K^+ + H_2O \leftarrow KOH + H^+$ No H^+ produced	NO_2^-	$NO_2^- + H_2O \leftrightarrow HNO_2 + OH^-$ OH- is produced	Basic
NH_4ClO_4	Acidic	NH_4^+	$NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+$ Some H_3O^+ produced	ClO_4^-	$ClO_4^- + H_2O \leftarrow HClO_4 + OH^-$ No OH^- produced	Acidic
NH_4NO_2	Acidic	NH_4^+	$NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+$ H^+ is produced	NO_2^-	$NO_2^- + H_2O \leftrightarrow HNO_2 + OH^-$ OH- is produced	Slightly Acidic*

Problem #7: A few problems.

Circle the acidic salts from the following list: $CaCO_3$, NH_4Cl, $NaNO_3$, KBr, $Ca(HCO_3)_2$.
For reasons similar to that above.
(Challenge) How does an acidic salt make pH more acidic (lower pH)?

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Acid salts dissociate into a weak acid and spectator ions. The weak acid then reaches its equilibrium which results in the production of some H+ ions since it is an acid. The presence of H+ ions makes the solution acid.
*H^+ and OH^- is produced, but slightly more H^+ is produced because NH_4^+ is a slightly stronger weakacid than NO_2^- is of a weak base.

$$K_a(NH_4^+) = 5.6 \times 10^{-10} > 1.4 \times 10^{-11} = K_b(NO_2^-)$$

Calculate the pH of a 10.0 mM solution of ammonium chloride. pH is _____5.6_______

Step 0:
Recognize 10.0 mM = 0.010 M
Ammonium Chloride: $NH_4Cl \rightarrow NH_4^+(aq) + Cl^-(aq)$

Step 1:

R	NH_4^+ +	H_2O	↔	NH_3	+	H_3O^+
I	0.01	-----		0		0
C	-x	-----		+x		+x
E	~0.01	-----		x		x
	(b/c x is so small)					

Step 2:

$$K_a(NH_4^+) = 5.6 \times 10^{-10} = \frac{x^2}{0.01}$$
$$x = \sqrt{(5.6 \times 10^{-10})(0.01)} = 2.37 \times 10^{-6}$$
$$[H^+] = 2.37 \times 10^{-6}$$

Step 3:

$$pH = -\log[H^+] = 5.6$$

Next, calculate the pH of a 0.13 M NH_4Br solution. The pH is ____5.07___________.

Step 0:
Ammonium Bromide: $NH_4Br \rightarrow NH_4^+(aq) + Br^-(aq)$

Step 1:

R	NH_4^+ +	H_2O	↔	NH_3	+	H_3O^+
I	0.13	-----		0		0
C	-x	-----		+x		+x
E	~0.13	-----		x		x
	(b/c x is so small)					

Step 2:

$$K_a(NH_4^+) = 5.6 \times 10^{-10} = \frac{x^2}{0.01}$$
$$x = \sqrt{(5.6 \times 10^{-10})(0.13)} = 8.5 \times 10^{-6}$$
$$[H^+] = 8.5 \times 10^{-6}$$

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Step 3:

$$pH = -\log[H^+] = 5.07$$

Neutralization Reactions

Problem #8: Complete Ionic and Net ionic Equations. Identify the spectator ions for the reactions below. (One method is to write the balanced chemical reaction, then write the complete ionic reaction, then write the net ionic reaction. Recall that the complete ionic equation writes strong electrolytes as dissociated ions. Strong electrolytes are soluble salts, strong acids, strong bases.)

a. Sodium hydroxide reacts with hydrobromic acid Spectator ions are: Na^+ and Br^- because OH^- and H^+ react to form H_2O. These Na^+ and Br^- remain in solution and do not react to form anything new.

$$NaOH(s) + HBr(s) \rightarrow$$
$$\boldsymbol{Na^+(aq)} + OH^-(aq) + H^+(aq) + \boldsymbol{Br^-(aq)} \rightarrow$$
$$\boldsymbol{NaBr(aq)} + H_2O(l)$$

b. Sodium hydroxide reacts with nitrous acid Spectator ions are: Na^+ because Na^+ is the only ion that never reacts to form something new like H2) or HNO2 like H^+, OH^-, and HNO_2 ions. It just watches and stays in solution.

Step 1:

$$NaOH(s) + HNO_2 \rightarrow$$
$$Na^+(aq) + OH^-(aq) + H^+(aq) + NO_2^-(aq) \rightarrow$$
$$NaNO_2(aq) + H_2O\ (l)$$

Step 2:

$$NaNO_2(aq) \rightarrow Na^+(aq) + NO_2^-(aq)$$

Step 3:

$$NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq)$$