Key concepts in titrations, buffers, the relationship between pH and pK_a, and determining if an acid or base is ionized

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- **TITRATIONS**

IF A SAMPLE IS AN ACID OR BASE THEN A TITRATION EXPERIMENT WILL DETERMINE THE SAMPLE CONCENTRATION.

ADD TITRANT* FROM BURET TO FLASK CONTAINING SAMPLE.

<u>AT THE STOICHIOMETRIC POINT, VOLUME OF TITRANT ADDED IS KNOWN AND</u>:

MOLES ACID (BASE) TITRANT ADDED = MOLES BASE (ACID) SAMPLE

*TITRANT CONCENTRATION KNOWN. $\text{CONCENTRATION} = \frac{\text{MOLES}}{\text{VOLUME}}$

AT THE STOICHIOMETRIC POINT THE VOLUME OF ADDED TITRANT IS KNOWN. THEREFORE, KNOW MOLES OF TITRANT ADDED (WHICH EQUALS MOLES OF SAMPLE).

AT STOICHIOMETRIC POINT OR EQUIVALENCE POINT SOLUTION CONTAINS A SALT.

IF SALT HAS NO ACIDIC OR BASIC IONS, THEN SOLUTION IS NEUTRAL. pH = 7. E.g. $Na^+Cl^-(aq)$
E.g., HCl (STRONG ACID), NaOH (STRONG BASE) TITRATION

IF SALT HAS ACIDIC IONS, THEN SOLUTION IS ACIDIC. E.g. $NH_4^+Cl^-(aq)$
E.g., HCl (STRONG ACID), NH_3 (WEAK BASE) TITRATION

IF SALT HAS BASIC IONS, THEN SOLUTION IS BASIC. E.g. $Na^+CH_3COO^-(aq)$
E.g., CH_3COOH (WEAK ACID), NaOH (STRONG BASE) TITRATION

PLOT OF SAMPLE pH vs ADDED TITRANT IS CALLED <u>pH CURVE</u>.

USE CLASS EXAMPLES AND PROBLEMS LISTED IN SYLLABUS TO DETERMINE pH OF SALT SOLUTION FOR ACIDIC AND BASIC SALTS.

FOR LAB CLASSSES, CHEM 14BL, etc., REMEMBER TO USE:

AT THE STOICHIOMETRIC POINT: MOLES TITRANT ADDED = MOLES SAMPLE = MOLES SALT

- **HOW TO MAKE AN ACIDIC (OR BASIC) BUFFER?**

BUFFERS ARE NEEDED TO MAINTAIN A CONSTANT pH WHEN DOING EXPERIMENTS WITH BIOLOGICAL MOLECULES.

A BUFFER NEEDS TO ACT AS A SOURCE OR SINK OF H^+.

USE A WEAK ACID (OR BASE). BUT THEY ARE MAINLY IN MOLECULAR FORM.

THEREFORE, ADD THE CONJUGATE BASE (OR CONJUGATE ACID) BY ADDING A SALT WITH THE SAME ANION (OR CATION).

E.g. ACIDIC BUFFER USE ACETIC ACID (CH_3COOH) AND SODIUM ACETATE ($CH_3COO^-Na^+$)

SOLUTION CONTAINING A WEAK ACID (H^+A^-) AND ITS SALT (M^+A^-).
METAL CATION (M^+) IN THE SALT MUST NOT CHANGE THE pH (Na^+, K^+).

E.g. BASIC BUFFER USE AMMONIA (NH_3) AND AMMONIUM CHLORIDE ($NH_4^+Cl^-$).
ANION IN THE SALT MUST NOT CHANGE THE pH (Cl^-, Br^-, I^-).

USE CLASS EXAMPLE AND PROBLEMS LISTED IN SYLLABUS TO DETERMINE pH OF WEAK ACID PLUS ITS SALT IN SOLUTION (OR WEAK BASE PLUS ITS SALT). **THIS IS HOW WE CALCULATE THE pH OF A BUFFER IN CHEM 14B: SETUP AN ICE TABLE, SOLVE FOR X.**

(SEE **FINAL NOTE ON BUFFERS** BELOW.)

- **RELATIONSHIP BETWEEN pH and pK_a**

What is the relationship between pH and pK_a?

$pH = -LOG\,[H_3O^+]$

SETUP WEAK ACID FOR K_A: $HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$

$$K_A = \frac{[A^-][H_3O^+]}{[HA]}$$

$$[H_3O^+] = K_A \frac{[HA]}{[A^-]} \qquad \text{(REARRANGE)}$$

$$-LOG\,[H_3O^+] = -LOG\,K_A - LOG\frac{[HA]}{[A^-]} \qquad \text{(TAKE -LOG BOTH SIDES)}$$

$$pH = pK_A + LOG\frac{[A^-]}{[HA]}$$

THIS EQUATION IS RELATED TO 1) **DETERMINING IF AN ACID OR BASE IS CHARGED OR**

NEUTRAL AND 2) **BUFFERS**.

- **DETERMINING IF AN ACID OR BASE IS CHARGED OR NEUTRAL**

CHEM 14A:
BIOLOGICAL ACID, HA, HAS A $pK_A = 4.22$.
IS THE ACID NEUTRAL OR NEGATIVELY CHARGED AT pH = 6?

$pH > pK_A$ SOLUTION IS MORE ALKALINE AND THE ACID WILL GIVE OFF H^+ TO FORM A^- AND IS NEGATIVELY CHARGED.

CHEM 14B:

USE ABOVE EQUATION TO ANSWER (AND CAN CALCULATE EXPLICITLY THE RATIO $\frac{[A^-]}{[HA]}$).

$$pH = pK_A + LOG\frac{[A^-]}{[HA]}$$

IF $pH > pK_A$ THEN THE RATIO $\frac{[A^-]}{[HA]} > 1$ AND $[A^-] > [HA]$.

GIVES SAME ANSWER: THE ACID IS NEGATIVELY CHARGED AT pH = 6.

USING ABOVE NUMBERS:

$$6 = 4.22 + LOG\frac{[A^-]}{[HA]}$$

$$1.78 = LOG\frac{[A^-]}{[HA]}$$

$$10^{1.78} = \frac{[A^-]}{[HA]} = 60$$ CONCENTRATION OF $[A^-]$ IS 60x HIGHER.

CHEM 14A:
UNDER ACIDIC CONDITIONS ($pH < pK_A$), BIOLOGICAL ACID IS PROTONATED AS HA.

THE SOLUTION IS MORE ACIDIC THAN THE BIOLOGICAL ACID.
BIOLOGICAL ACID STAYS PROTONATED AS HA.

CHEM 14B:

SAME ANSWER USING:

$$pH = pK_A + LOG\frac{[A^-]}{[HA]}$$

IF $pH < pK_A$ THEN THE RATIO $\frac{[A^-]}{[HA]} < 1$ AND $[A^-] < [HA]$.

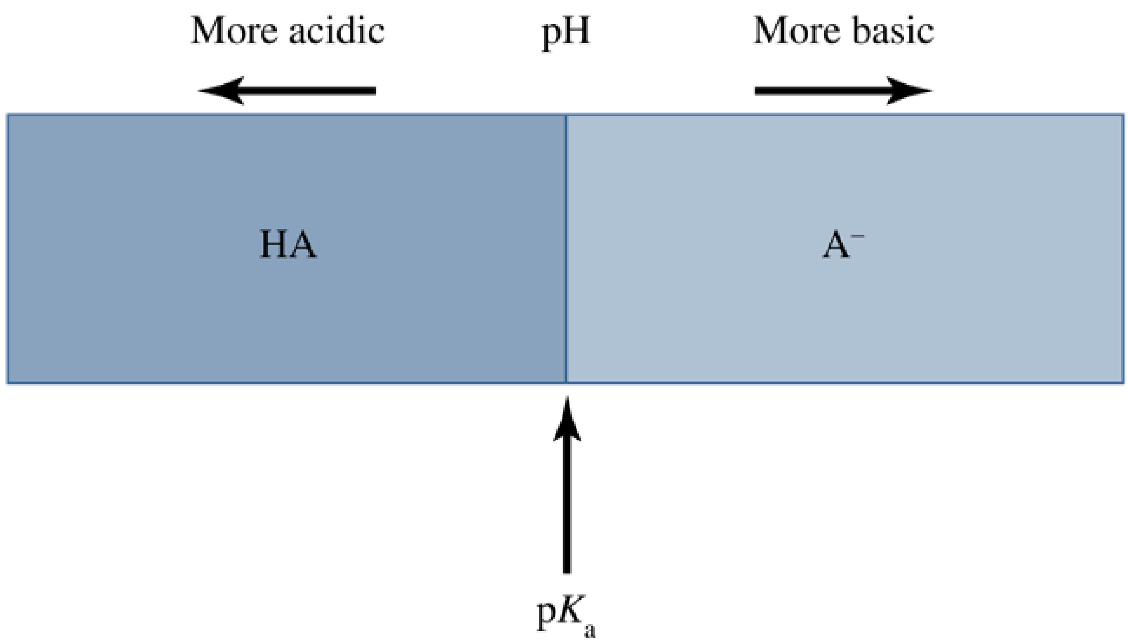
E.g. pH = 2

$$2 = 4.22 + LOG\frac{[A^-]}{[HA]}$$

$$-2.22 = LOG\frac{[A^-]}{[HA]}$$

$$10^{-2.22} = \frac{[A^-]}{[HA]} = 0.0060$$ CONCENTRATION OF [HA] IS 166x HIGHER.

PAGE 3 IS SUMMARIZED IN THIS CHEM 14A DIAGRAM:



TITRATIONS AND BUFFERS ARE COVERED IN DETAIL IN LAB AND BIOCHEM/BIOSCIENCE CLASSES.

SINCE WE HAVE COVERED THE CONCEPTS AND MATH TO SOLVE THESE PROBLEMS I DISCUSS THEM IN CHEM 14B TO MAKE THE CONNECTIONS AND ASSIST STUDENTS WHEN THEY TAKE OTHER CLASSES.

- **FINAL NOTE ON BUFFERS**

(WE ARE NOT USING THE HENDERSON-HASSELBALCH EQUATION IN CHEM 14B.)

INSTEAD OF SETTING UP AN EQUILIBRIUM TABLE AND <u>EXPLICITELY SOLVING FOR X (AS WE DO IN CHEM 14B)</u>, MANY BIOCHEM/BIOSCIENCE CLASSES WILL USE THIS EQUATION:

$$pH = pK_A + LOG\frac{[A^-]}{[HA]}$$

AND APPROXIMATE: $[A^-]$ = INITIAL BASE CONCENTRATION
[HA] = INITIAL ACID CONCENTRATION

THIS GIVES THE HENDERSON-HASSELBALCH EQUATION:

$$pH = pK_A + LOG\frac{[A^-]_{INITIAL\ BASE}}{[HA]_{INITIAL\ ACID}}$$

AN IDEAL BUFFER HAS EQUAL CONCENTRATIONS OF A^{-} (TAKE UP PROTONS) AND HA (GIVE OFF PROTONS) AND CAN THEN NEUTRALIZE AN ADDED ACID OR BASE SO THAT THE pH STAYS CLOSE TO ITS ORIGINAL VALUE.

$$\text{IF} \quad [A^{-}]_{\text{INITIAL BASE}} = [HA]_{\text{INITIAL ACID}}$$

$$\text{THEN} \quad pH = pK_A + \text{LOG}\,\frac{[A^{-}]_{\text{INITIAL BASE}}}{[HA]_{\text{INITIAL ACID}}} = pK_A$$

OPTIMUM BUFFER CAPACITY: pH = pK_A

<u>TO MAKE AN ACIDIC BUFFER</u>: SELECT WEAK ACID WITH pK_A CLOSE TO DESIRED pH AND ADD ITS CONJUGATE BASE IN THE FORM OF A SALT WITH THE SAME CONCENTRATION.

E.g. $[CH_3COOH] = [CH_3COO^{-}Na^{+}]$

CH_3COOH $pK_A = 4.75$ CAN BE USED AS A BUFFER IN SOLUTIONS WITH pH 3.75 TO 5.75 AND WORKS BEST AS A BUFFER AT pH 4.75.

USING THE HENDERSON-HASSELBALCH EQUATION FOR AN ACIDIC BUFFER:
INITIAL [BASE] IS THE INITIAL [SALT]
INITIAL [ACID] IS JUST THE INITIAL [ACID]

<u>TO MAKE A BASIC BUFFER</u>: SELECT WEAK BASE SUCH THAT ITS CONJUGATE ACID HAS A pK_A CLOSE TO DESIRED pH AND ADD ITS CONJUGATE ACID IN THE FORM OF A SALT.

E.g. $[NH_3] = [NH_4^{+}Cl^{-}]$

NH_4^{+} $pK_A = 9.25$ CAN BE USED AS A BUFFER IN SOLUTIONS WITH pH 8.25 TO 10.25 AND WORKS BEST AS A BUFFER AT pH 9.25.

USING THE HENDERSON-HASSELBALCH EQUATION FOR A BASIC BUFFER:
INITIAL [BASE] IS JUST THE INITIAL [BASE]
INITIAL [ACID] IS THE INITIAL [SALT]

HOPE THIS HELPS YOU IN CHEM 14B AND IN YOUR LAB AND BIOCHEM/BIOSCIENCE CLASSES.
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