



NATIONAL MATH + SCIENCE INITIATIVE

AP CHEMISTRY

Buffers and Titrations

Presenter Name: _____

Periodic Table of the Elements

1 H 1.0079																	2 He 4.0026				
3 Li 6.941	4 Be 9.012															5 B 10.811	6 C 12.011	7 N 14.007	8 O 16.00	9 F 19.00	10 Ne 20.179
11 Na 22.99	12 Mg 24.30															13 Al 26.98	14 Si 28.09	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.938	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80				
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 93.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	54 Xe 131.29				
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)				
87 Fr (223)	88 Ra 226.02	89 †Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 § (269)	111 § (272)	112 § (277)	§Not yet named									

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

*Lanthanide Series:

†Actinide Series:

AP Chemistry Equations & Constants

Throughout the test the following symbols have the definitions specified unless otherwise noted.

L, mL = liter(s), milliliter(s)

g = gram(s)

nm = nanometer(s)

atm = atmosphere(s)

mm Hg = millimeters of mercury

J, kJ = joule(s), kilojoule(s)

V = volt(s)

mol = mole(s)

ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

E = energy

ν = frequency

λ = wavelength

Planck's constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light, $c = 2.998 \times 10^8$ m s⁻¹

Avogadro's number = 6.022×10^{23} mol⁻¹

Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

EQUILIBRIUM

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}, \text{ where } a A + b B \rightleftharpoons c C + d D$$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$= K_a \times K_b$$

$$\text{pH} = -\log [H^+], \text{ pOH} = -\log [OH^-]$$

$$14 = \text{pH} + \text{pOH}$$

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

$$\text{p}K_a = -\log K_a, \text{ p}K_b = -\log K_b$$

Equilibrium Constants

K_c (molar concentrations)

K_p (gas pressures)

K_a (weak acid)

K_b (weak base)

K_w (water)

KINETICS

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$t_{1/2} = \frac{0.693}{k}$$

k = rate constant

t = time

$t_{1/2}$ = half-life

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

$$n = \frac{m}{M}$$

$$K = ^\circ\text{C} + 273$$

$$D = \frac{m}{V}$$

$$KE \text{ per molecule} = \frac{1}{2}mv^2$$

Molarity, M = moles of solute per liter of solution

$$A = abc$$

P = pressure

V = volume

T = temperature

n = number of moles

m = mass

M = molar mass

D = density

KE = kinetic energy

v = velocity

A = absorbance

a = molar absorptivity

b = path length

c = concentration

Gas constant, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$$= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$$

1 atm = 760 mm Hg

$$= 760 \text{ torr}$$

STP = 0.00°C and 1.000 atm

THERMOCHEMISTRY/ ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -RT \ln K$$

$$= -nFE^\circ$$

$$I = \frac{q}{t}$$

q = heat

m = mass

c = specific heat capacity

T = temperature

S° = standard entropy

H° = standard enthalpy

G° = standard free energy

n = number of moles

E° = standard reduction potential

I = current (amperes)

q = charge (coulombs)

t = time (seconds)

Faraday's constant, $F = 96,485$ coulombs per mole of electrons

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$



NATIONAL
MATH + SCIENCE **BUFFERS AND TITRATIONS**
INITIATIVE
As Easy As It Ever Gets

What I Absolutely Have to Know to Survive the AP Exam

The following might indicate the question deals with buffers and/or titrations:
buffer solution, common ion, conjugate base/acid, equivalence point, ½ equivalence point, end-point, weak acid/base “reacted with a strong..”, titrant, buret, analyte, etc...

Buffers: *All about those “common ions”*

IS: A buffer is a solution of a weak acid or base and its salt [which is its conjugate].

DOES: A buffer resists a change in pH.

HOW IT WORKS: Since a buffer consists of both an acid or base and its conjugate, which differ by an H^+ , both a weak acid and a weak base are present in all buffer solutions.

In order to understand buffers and buffer problems we must be proficient with the following...

- MUST know the conjugate A/B concept to be successful at buffer problems. This means understanding that HA has A^- as its conjugate and that NaA is not only a salt, but that any soluble salt releases the common ion, A^-
- $pH = -\log [H^+]$
- $K_a \times K_b = K_w$
- Any titration involving a weak A/B, from the first drop to the last, before equivalence, is a buffer problem. If HA is titrated with NaOH, as soon as the first drop splashes into the container, I've added A^- ions to the solution and the presence of both HA and A^- constitutes a buffer solution.

Buffers: *Calculating pH*

Solving Buffer Problems with the one and only, handy dandy, all I'm ever going to need equation...

$$[H_3O^+] = K_a \frac{[Acid]}{[Base]}$$

Where:

K_a – is the acid dissociation constant

[Acid] – is the concentration of the substance behaving as the **weak** acid in the buffered solution

- Either the weak acid or the salt of the weak base

[Base] – is the concentration of the substance behaving as the **weak** base in the buffered solution

- Either the weak base or the salt of the weak acid

To Solve:

- MUST recognize who's who in the buffered and then solve with the equation
- If the buffer is a weak acid, HA, and its conjugate salt, A^- then HA is the acid and A^- is the base.
- If the buffer is a weak base, B, and its conjugate salt, BH^+ , then B is the base and BH^+ is the acid.
 - You still use the K_a ; thus you must calculate it first using the K_b provided for the weak base
- If concentrations are given plug and chug
- If concentrations of separate solutions are given with volumes and the two are added together you must recalculate the “new concentrations” due to dilution of additive volumes.



Buffers: Calculating pH Con't

Example:

Calculate the pH of a solution containing 0.75 M lactic acid, $\text{HC}_3\text{H}_5\text{O}_3$ ($K_a = 1.4 \times 10^{-4}$), and 0.25 M sodium lactate, $\text{NaC}_3\text{H}_5\text{O}_3$.

- Lactic acid is the weak ACID and lactate ion is its conjugate BASE

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{Acid}]}{[\text{Base}]} = (1.4 \times 10^{-4}) \frac{[0.75]}{[0.25]} = 4.2 \times 10^{-4}$$

$$\text{pH} = -\log(4.2 \times 10^{-4}) = 3.38$$

Example:

A buffered solution contains 0.250 M NH_3 ($K_b = 1.80 \times 10^{-5}$) and 0.400 M NH_4Cl . Calculate the pH of this solution.

- NH_3 is the weak BASE and NH_4^+ is its conjugate ACID
- When you are given a weak base and its salt you will often need to calculate K_a then plug in – don't get in a hurry and mistakenly use the K_b !

$$K_a \times K_b = 1.00 \times 10^{-14}$$

$$K_a = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{Acid}]}{[\text{Base}]} = (5.56 \times 10^{-10}) \frac{[0.400]}{[0.250]} = 8.89 \times 10^{-10}$$

$$\text{pH} = -\log(8.89 \times 10^{-10}) = 9.051$$

Example:

Calculate the pH of a solution prepared by mixing 20.0 mL of 0.300 M acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, with 20.0 mL of 0.350 M $\text{NaC}_2\text{H}_3\text{O}_2$. K_a for acetic acid is 1.80×10^{-5}

- Acetic acid is the weak ACID and acetate ion is its conjugate BASE
- Recalculate molarities OR better yet just calculate the number of moles (volumes are the same as they are all in the same solution so they cancel)....

$$20.0 \text{ mL} \times 0.300 \text{ M} = 6.00 \text{ mmol acid}$$

$$20.0 \text{ mL} \times 0.350 \text{ M} = 7.00 \text{ mmol conjugate base}$$

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{Acid}]}{[\text{Base}]} = (1.80 \times 10^{-5}) \frac{[6.00]}{[7.00]} = 1.54 \times 10^{-5}$$

$$\text{pH} = -\log(1.54 \times 10^{-5}) = 4.812$$



Buffer Attack: *Who Defends?*

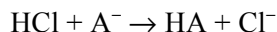
The purpose of a buffer solution is to resist large swings in pH. If a small amount of strong acid is added to the buffer, there is a base component ready and waiting to neutralize the “invader”. The same goes for the addition of a small amount of strong base, there is an acid component ready and waiting to neutralize it...

Strong Acid Attack

- If strong acid is added to a buffer solution, the pH will decrease but not nearly as much as it would without the buffer solution.
- When the strong acid is added, the weak base component of the buffer neutralizes the strong acid – thus the strong acid is eliminated, the number of moles of weak base decreases, and the number of moles of weak acid increases.

Example:

- A buffer solution is made using the weak acid HA and its salt A^- (its conjugate base). To the buffer solution you add strong acid, HCl. The buffer “works” because the HCl reacts with the base component of the buffer (A^-) according to the equation below



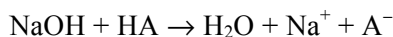
- Thus the buffer solution eliminates **all** of the HCl (or the H^+ or H_3O^+) and sacrifices **some** of the weak base (A^-) making more weak acid, HA.
 - The weak acid HA will ionize in water to make more H_3O^+ ions thus the pH will decrease
- $$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
- However since HA is a weak acid the amount of ionization is very small (less than 5%), it doesn’t produce a large amount of H_3O^+ ions and thus its impact on the pH is not as significant.

Strong Base Attack

- If strong base is added to a buffer solution, the pH will increase but not nearly as much as it would without the buffer solution.
- When the strong base is added, the weak acid component of the buffer neutralizes the strong base – thus the strong base is eliminated, the number of moles of weak acid decreases, and the number of moles of weak base increases.

Example:

- A buffer solution is made using the weak acid HA and its salt A^- (its conjugate base). To the buffer solution you add strong base, NaOH. The buffer “works” because the NaOH reacts with the acid component of the buffer (HA) according to the equation below



- Thus the buffer solution eliminates **all** of the NaOH (or the OH^-) and sacrifices **some** of the weak acid (HA) making more weak base, A^- .
 - The weak base A^- can “react” with water to form more OH^- ions thus the pH will increase
- $$A^- + H_2O \rightleftharpoons OH^- + HA$$
- However since A^- is a weak base the amount of ionization is very small (less than 5%), doesn’t produce a large amount of OH^- ions, and thus its impact on the pH is not as significant

CAUTION:

If the number of moles of the “invader” exceeds the moles present in the buffer then the invader has overrun the buffer and the pH will increase/decrease significantly – the buffer has failed!


 Preparing a Buffer: *It's all about K_a and the Ratio!*

If asked to describe how to prepare a buffer of a certain pH... think $[H_3O^+] = K_a \frac{[Acid]}{[Base]}$

- Use 0.10 M to 1.0 M solutions of reagents & choose an acid whose K_a is near the $[H_3O^+]$ concentration we want. Or its pK_a should be as close to the pH desired as possible. Adjust the ratio of $\frac{[Acid]}{[Base]}$ to fine tune the pH.
- It is the **relative** # of moles (not M) of acid/CB or base/CA that is important since they are in the same solution and share the same solution volume.
 - This allows companies to make concentrated versions of buffer and let the customer dilute--this will not affect the # of moles present--just the dilution of those moles. So on the EXAM, never fall for the trick of “what happens to the pH of the buffer solution after the addition of 250 mL of water. Yes the $[Acid]$ and $[Base]$ are diluted but the $\frac{[Acid]}{[Base]}$ ratio is the same and that is what matters in a buffer!

IMPORTANT NOTE:

- When equal concentrations of Acid and Base are present [which occurs at the $\frac{1}{2}$ equivalence point of a titration] the ratio of acid to base equals ONE and therefore, the $pH = pK_a$.


 Acid-Base Titrations: *It Depends on Where You Are!*

There are 3 types of titrations you will be dealing with.

1. Strong Acid and Strong Base

- Net ionic reaction: $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$
- Only when the acid AND base are both strong is the pH at the equivalence point 7. [Any other conditions and you get to do a nasty equilibrium problem.] This is really a stoichiometry problem with a limiting reactant. The “excess” is responsible for the pH
- Just deal with what is left over. Be sure you are in moles if additive volumes are given and recalculate the M after doing the stoichiometry work – remember, when you add volumes dilution occurs!
- Use $\text{pH} = -\log [\text{H}^+]$ to determine the pH of the solution.

2. Weak Acid and Strong Base

- The equivalence point – the $\text{pH} > 7$
- 4 ZONES OF INTEREST ALONG A TITRATION CURVE for a Weak Acid and Strong Base Titration

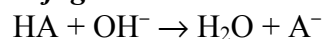
ZONE 1

- The pH before the titration begins.
- This is simply a weak acid problem – before the titration begins all you have is weak acid in the flask!

$$K_a = \frac{x^2}{M} \quad \text{where } x = [\text{H}_3\text{O}^+]$$

ZONE 2

- The pH during the titration but before the equivalence point.
- Once the titration begins the weak acid reacts with the strong base producing salt and water. The salt is the **conjugate base** of the weak acid. This is a BUFFER problem!!!



- Remember that the amount of strong base added = amount of weak acid reacted = amount of salt (conjugate base) produced
- Plug in the amount of weak acid left and the amount of salt produced into the handy, dandy, all I’m ever going to need equation

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{Acid}]}{[\text{Base}]}$$

CAUTION! TIME SAVER: At the $\frac{1}{2}$ equivalence point $[\text{Weak Acid}] = [\text{Conjugate Base formed}]$ thus $[\text{H}_3\text{O}^+] = K_a$


 Acid-Base Titrations: *It Depends on Where You Are! Con't*

ZONE 3: The pH at the Equivalence Point

- This is simply a weak base problem
- At the equivalence point ALL of the WEAK ACID has been reacted with the STRONG BASE – the only species left are H₂O and the SALT – which is the Conjugate Base of the Weak Acid you titrated.
- Remember that the amount of strong base added = amount of weak acid reacted = amount of salt made
- Thus the molarity of the salt in solution is

$$M = \frac{\text{moles of salt formed}}{\text{total L of solution at the equivalence pt.}}$$

- Since this is simply a weak base problem:

$$K_b = \frac{x^2}{M} \quad \text{where } x = [\text{OH}^-]; \text{ find the pOH then convert to pH}$$

CAUTION: Must calculate the K_b of the salt using the K_a of the weak acid

ZONE 4: Beyond the Equivalence Point

- It's all about the excess
- Calculate the amount of excess strong base added beyond the equivalence point and then recalculate its M . This is a strong base so $\text{pOH} = -\log [\text{OH}^-]$

3. Weak Base and Strong Acid

- Just like the Weak Acid/Strong Base above, just flip flop the process...
- The equivalence point < pH 7

IMPORTANT NOTES:

There is a distinction between the equivalence point and the end point.

- The end point is when the indicator changes color.
- The equivalence point is when the number of moles of acid = number of moles of base in the titration
- If you've made a careful choice of indicator or are using a pH probe, the equivalence point and the end point of the titration will be achieved at the same time
- When choosing an indicator, determine the pH at the equivalence pt., then, pick the indicator that has a $\text{p}K_a$ close to the pH at the equivalence point



Buffers and Titrations Cheat Sheet

Relationships

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{Acid}]}{[\text{Base}]}$$

$$K_a = \frac{x^2}{M} \quad \text{where } x = [\text{H}_3\text{O}^+]$$

$$K_b = \frac{x^2}{M} \quad \text{where } x = [\text{OH}^-]$$

$$K_a \times K_b = 1 \times 10^{-14}$$

$$\text{pH} = -\log[\text{H}^+]$$

$$\text{pOH} = -\log[\text{OH}^-]$$

4 ZONES OF INTEREST ALONG A TITRATION CURVE for a Weak Acid and Strong Base

- Initial pH – simply a weak acid/weak base problem $K_a = \frac{x^2}{M}$ where $x = [\text{H}_3\text{O}^+]$ or $K_b = \frac{x^2}{M}$ where $x = [\text{OH}^-]$
- During the titration – BUFFER, BUFFER, IT'S A BUFFER! $[\text{H}_3\text{O}^+] = K_a \frac{[\text{Acid}]}{[\text{Base}]}$ where the weak and its conjugate salt are what we need to know about.
- Equivalence Pt. – only salt and water left; the salt is either a weak base (if a weak acid was titrated) or a weak acid (if a weak base was titrated); work it as such: $K_a = \frac{x^2}{M}$ where $x = [\text{H}_3\text{O}^+]$ or $K_b = \frac{x^2}{M}$ where $x = [\text{OH}^-]$
 BUT you have to convert K_a to K_b or vice versa!!!
- Beyond the Equivalence Pt. – This is a stoichiometry problem; find out how much STRONG (acid or base) is left after equivalence, recalculate its molarity (remember the volume increased during the titration), and use $\text{pH} = -\log[\text{H}^+]$ or $\text{pOH} = -\log[\text{OH}^-]$

Be aware of where the volume of STRONG added in the titration is $\frac{1}{2}$ way to equivalence point!

- Here $[\text{H}_3\text{O}^+] = K_a$ because the $\frac{[\text{Acid}]}{[\text{Base}]}$ is 1 (same amount of weak acid (base) and its conjugate are present. HUGE time saver and easy way to find the K_a or K_b of the weak acid or base.
- In a titration problem ALWAYS know where the equivalence point is!!!!!!

BUFFERS: Only need to use the equation: $[\text{H}_3\text{O}^+] = K_a \frac{[\text{Acid}]}{[\text{Base}]}$; read carefully and know who is the weak acid (base) and who is the conjugate salt (it plays the other role!).

Don't be tricked – NEVER select a strong acid or base as a part of a buffer solution; it HAS TO BE WEAK

When a buffered solution is “attacked” remember:

- If the attacker is a strong acid; the base component of the buffer “sacrifices” and reacts with the invading acid, converting it to water and more weak acid – thus resisting large decreases in the pH
- If the attacker is a strong base; the acid component of the buffer “sacrifices” and reacts with the invading base, converting it to water and more weak base – thus resisting large increases in the pH

Connections

Equilibrium

Stoichiometry

Potential Pitfalls and Things to Watch For

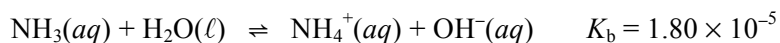
 Knowing when you need K_a or K_b

Recognizing the weak organic bases

BE AWARE of when a weak acid (base) is present with its conjugate salt – HELLO! YOU ARE IN THE BUFFER ZONE!!!!



NMSI SUPER PROBLEM

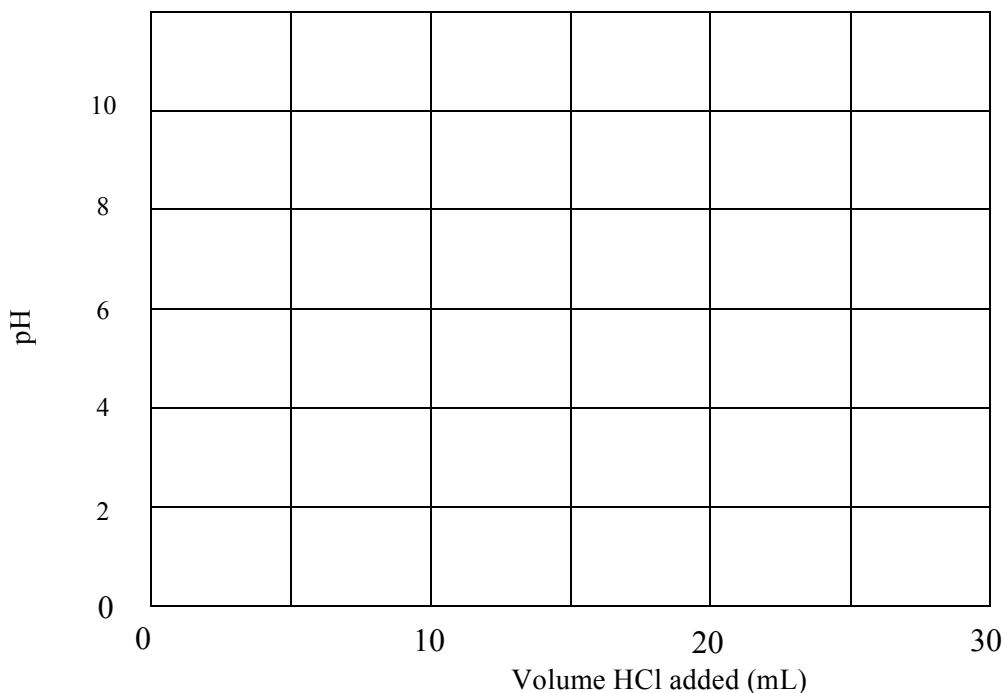


Ammonia reacts with water as indicated in the reaction above.

- (a) Write the equilibrium constant expression for the reaction represented above.
- (b) Calculate the pH of a 0.150 M solution of NH_3

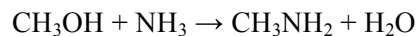
A 20 mL sample of the 0.150 M solution of NH_3 is titrated with 0.100 M HCl

- (c) Determine the volume of HCl required to reach the equivalence point.
- (d) Calculate the pH of the solution after the addition of 15 mL of HCl.
- (e) Calculate the pH of the solution at the equivalence point of the titration.
- (f) Using the axes provided below, sketch the titration curve that would result if the student had used 0.200 M HCl instead of the 0.100 M used above, to perform the titration. The equivalence point must be clearly marked.

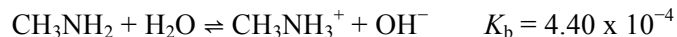




When ammonia is reacted with methanol with a specific catalyst, the colorless gas methylamine (along with dimethylamine and trimethylamine) can be produced. While trimethylamine is the favored product, adjusting the reactant ratios can help alter the amount of the three 'amines' produced. The process is complex but is used to industrially produce methylamine – which is listed as a controlled substance by the US Drug Enforcement Agency, because of its uses in the production of methamphetamine.



When methylamine is isolated and dissolved in water it acts as a weak base according to the reaction below.



The methylamine above was dissolved in 150 mL of water, resulting in a solution had a methylamine concentration of 0.150 *M*.

- (g) Calculate the pH of the methylamine solution
- (h) To the above solution of methylamine, 0.0120 mole of methylammonium chloride was added. Calculate the pH of the solution after the addition of the methylammonium chloride, $\text{CH}_3\text{NH}_3\text{Cl}$.
- (i) Draw the Lewis structure for
- methylamine, CH_3NH_2 .
 - methylammonium ion, CH_3NH_3^+ .

2009 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS**CHEMISTRY****Section II****(Total time—95 minutes)****Part A****Time—55 minutes****YOU MAY USE YOUR CALCULATOR FOR PART A.**

CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures.

Be sure to write all your answers to the questions on the lined pages following each question in the booklet with the pink cover. Do NOT write your answers on the green insert.

Answer Questions 1, 2, and 3. The Section II score weighting for each question is 20 percent.

1. Answer the following questions that relate to the chemistry of halogen oxoacids.

(a) Use the information in the table below to answer part (a)(i).

Acid	K_a at 298 K
HOCl	2.9×10^{-8}
HOBr	2.4×10^{-9}

- (i) Which of the two acids is stronger, HOCl or HOBr? Justify your answer in terms of K_a .
- (ii) Draw a complete Lewis electron-dot diagram for the acid that you identified in part (a)(i).
- (iii) Hypoiodous acid has the formula HOI. Predict whether HOI is a stronger acid or a weaker acid than the acid that you identified in part (a)(i). Justify your prediction in terms of chemical bonding.
- (b) Write the equation for the reaction that occurs between hypochlorous acid and water.
- (c) A 1.2 M NaOCl solution is prepared by dissolving solid NaOCl in distilled water at 298 K. The hydrolysis reaction $\text{OCl}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HOCl}(aq) + \text{OH}^-(aq)$ occurs.
- (i) Write the equilibrium-constant expression for the hydrolysis reaction that occurs between $\text{OCl}^-(aq)$ and $\text{H}_2\text{O}(l)$.
- (ii) Calculate the value of the equilibrium constant at 298 K for the hydrolysis reaction.
- (iii) Calculate the value of $[\text{OH}^-]$ in the 1.2 M NaOCl solution at 298 K.

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(d) A buffer solution is prepared by dissolving some solid NaOCl in a solution of HOCl at 298 K. The pH of the buffer solution is determined to be 6.48.

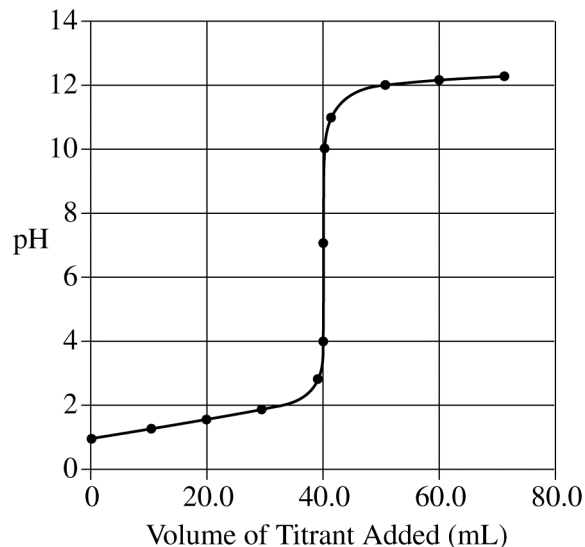
(i) Calculate the value of $[\text{H}_3\text{O}^+]$ in the buffer solution.

(ii) Indicate which of $\text{HOCl}(aq)$ or $\text{OCl}^-(aq)$ is present at the higher concentration in the buffer solution. Support your answer with a calculation.

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Answer Question 5 and Question 6. The Section II score weighting for these questions is 15 percent each.

Your responses to these questions will be scored on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

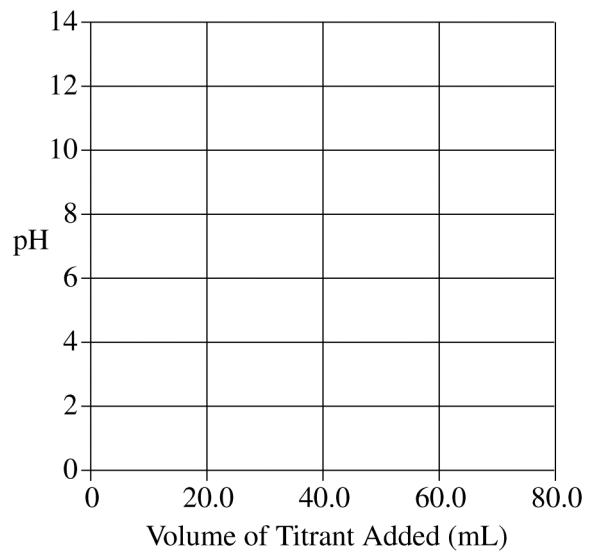


5. A solution of 0.100 M HCl and a solution of 0.100 M NaOH are prepared. A 40.0 mL sample of one of the solutions is added to a beaker and then titrated with the other solution. A pH electrode is used to obtain the data that are plotted in the titration curve shown above.
- Identify the solution that was initially added to the beaker. Explain your reasoning.
 - On the titration curve above, circle the point that corresponds to the equivalence point.
 - At the equivalence point, how many moles of titrant have been added?
 - The same titration is to be performed again, this time using an indicator. Use the information in the table below to select the best indicator for the titration. Explain your choice.

Indicator	pH Range of Color Change
Methyl violet	0 – 1.6
Methyl red	4 – 6
Alizarin yellow	10 – 12

- What is the difference between the equivalence point of a titration and the end point of a titration?
- On the grid provided on the next page, sketch the titration curve that would result if the solutions in the beaker and buret were reversed (i.e., if 40.0 mL of the solution used in the buret in the previous titration were titrated with the solution that was in the beaker).

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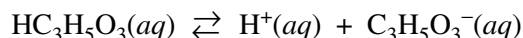


2002 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)**CHEMISTRY****Section II****(Total time—90 minutes)****Part A****Time—40 minutes****YOU MAY USE YOUR CALCULATOR FOR PART A.**

CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures.

Be sure to write all your answers to the questions on the lined pages following each question in the booklet with the goldenrod cover. Do NOT write your answers on the lavender insert.

Answer Question 1 below. The Section II score weighting for this question is 20 percent.



- Lactic acid, $\text{HC}_3\text{H}_5\text{O}_3$, is a monoprotic acid that dissociates in aqueous solution, as represented by the equation above. Lactic acid is 1.66 percent dissociated in 0.50 M $\text{HC}_3\text{H}_5\text{O}_3(\text{aq})$ at 298 K. For parts (a) through (d) below, assume the temperature remains at 298 K.
 - Write the expression for the acid-dissociation constant, K_a , for lactic acid and calculate its value.
 - Calculate the pH of 0.50 M $\text{HC}_3\text{H}_5\text{O}_3$.
 - Calculate the pH of a solution formed by dissolving 0.045 mole of solid sodium lactate, $\text{NaC}_3\text{H}_5\text{O}_3$, in 250. mL of 0.50 M $\text{HC}_3\text{H}_5\text{O}_3$. Assume that volume change is negligible.
 - A 100. mL sample of 0.10 M HCl is added to 100. mL of 0.50 M $\text{HC}_3\text{H}_5\text{O}_3$. Calculate the molar concentration of lactate ion, $\text{C}_3\text{H}_5\text{O}_3^-$, in the resulting solution.

2003 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS

CHEMISTRY

Section II

(Total time—90 minutes)

Part A

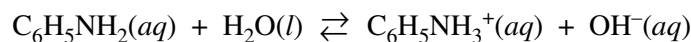
Time—40 minutes

YOU MAY USE YOUR CALCULATOR FOR PART A.

CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures.

Be sure to write all your answers to the questions on the lined pages following each question in the booklet with the pink cover. Do NOT write your answers on the green insert.

Answer Question 1 below. The Section II score weighting for this question is 20 percent.



- Aniline, a weak base, reacts with water according to the reaction represented above.
 - Write the equilibrium constant expression, K_b , for the reaction represented above.
 - A sample of aniline is dissolved in water to produce 25.0 mL of a 0.10 M solution. The pH of the solution is 8.82. Calculate the equilibrium constant, K_b , for this reaction.
 - The solution prepared in part (b) is titrated with 0.10 M HCl. Calculate the pH of the solution when 5.0 mL of the acid has been added.
 - Calculate the pH at the equivalence point of the titration in part (c).
 - The $\text{p}K_a$ values for several indicators are given below. Which of the indicators listed is most suitable for this titration? Justify your answer.

Indicator	$\text{p}K_a$
Erythrosine	3
Litmus	7
Thymolphthalein	10