

Essay Questions

1986

Average score = 2.90

a) four points

1. As effective nuclear charge on central atom increases, acid strength increases.

OR

As number of lone oxygen atoms (oxygen atoms not bonded to hydrogen) increases, acid strength increases.

OR

As electronegativity of central atom increases, acid strength increases.

2. Loss H^+ by neutral acid molecules reduces acid strength.

OR

 K_a of $H_2SO_3 > K_a$ of HSO_3^-

b) four points

 $H_3BO_3 < HSO_3^- < H_2SO_3 < HClO_3 < HClO_4$ H_3BO_3 or HSO_3^- weakest (must be together) $HClO_3$ weaker than $HClO_4$ HSO_3^- weaker than H_2SO_3

Both S acid weaker than both Cl acids

Note: if acids in exactly in exactly reverse, one point

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3. Give a brief explanation for each of the following.

1990

- (a) For the diprotic acid H_2S , the first dissociation constant is larger than the second dissociation constant by about 10^5 ($K_1 \approx 10^5 K_2$).
- (b) In water, NaOH is a base but HOCl is an acid.
- (c) HCl and HI are equally strong acids in water but, in pure acetic acid, HI is a stronger acid than HCl .
- (d) When each is dissolved in water, HCl is a much stronger acid than HF .

a) After the first H^+ is lost from H_2S the remaining species, HS^- , has a negative charge. This ^{increases} the attraction of the S atom for the bonding electrons in $[\text{HS}^-]$. The bond is therefore stronger, H is harder to remove, and K_2 would be lower. (1)

b) Polar H_2O can separate ionic ~~NaOH~~ ^{NaOH} into $\text{Na}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ giving a basic solution. (1)
In HOCl chlorine has a high attraction for electrons due to its greater charge density. This draws electrons in the $\text{H}-\text{O}$ bond towards it and weakens the bond. H^+ can be removed making an acid solution. (1)

c) in H_2O , water is a more basic solvent (greater attraction for H^+) and removes H^+ from Cl^- and I^- equally. In HAc , acetic acid has little attraction for H^+ but can separate H^+ from the larger I^- easier than smaller Cl^- . (1)

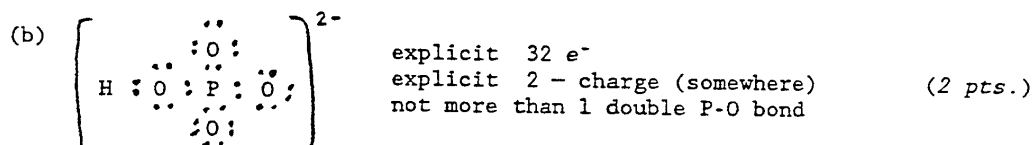
d) The bond between H and Cl is weaker than the bond between H and F . HCl is therefore a stronger acid. (2)

1994

Question 7



Note: any proton transfer to any P_xO_y species earns 1 point.



Note: HPO_4^{2-} (formula only) or other P_xO_y species with correct diagram earns 1 point.

(c) Graph goes from upper left to lower right (pH decreases) (1 pt.)

Two protons transferred $\left\{ \begin{array}{l} \text{Two "buffers"} \\ \text{Two "equivalence"} \end{array} \right\}$ in either direction (1 pt.)

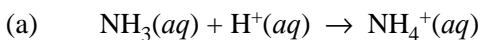
Explain/correctly label at least one "buffer" or "equivalence" region (1 pt.)



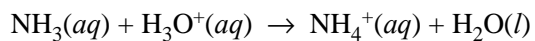
Note: other proton transfer earns 1 point if consistent with product in part (a)

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Question 8
(8 points)



or

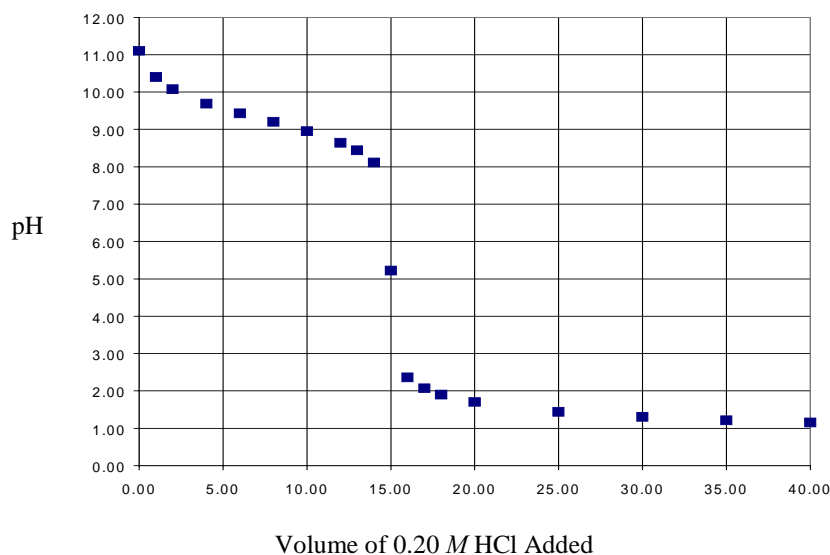


1 pt.

Note: phase designations not required to earn point

(b) Sketch of Titration Curve:

3 pts.



- 1st pt. \Rightarrow initial pH must be > 7 (calculated pH ≈ 11)
- 2nd pt. \Rightarrow equivalence point occurs at $15.0 \text{ mL} \pm 1 \text{ mL}$ of HCl added (equivalence point must be detectable from the shape of the curve or a mark on the curve)
- 3rd pt. \Rightarrow pH at equivalence point must be < 7 (calculated pH ≈ 5).

Note: a maximum of 1 point earned for any of the following:

- a line without an equivalence point
- a random line that goes from high pH to low pH
- an upward line with increasing pH (equivalence point **MUST** be at 15.0 mL)

AP[®] Chemistry 2000 – Scoring Standards

Question 8

(continued)

- (c) Methyl Red would be the best choice of indicator, **1 pt.**

because

the pK_a for Methyl Red is closest to the pH at the equivalence point. **1 pt.**

Notes:

- explanation must agree with equivalence point on graph
- alternative explanation that titration involves strong acid and weak base (with product an acidic salt) earns the point

- d) The resulting solution is basic. **1 pt.**

K_b for NH_3 (1.8×10^{-5}) and K_a for NH_4^+ (5.6×10^{-10}) indicate that NH_3 is a stronger base than NH_4^+ is an acid

or

1 pt.

$[\text{OH}^-] = K_b = 1.8 \times 10^{-5}$ because of the equimolar and equivolume amounts of ammonium and ammonia \Rightarrow cancellation in the buffer pH calculation. Thus $\text{pOH} \approx 5$ and $\text{pH} \approx 9$ (i.e., recognition of buffer, so that $\log\left(\frac{0.05}{0.05}\right) = 0 \Rightarrow \text{pOH} = \text{p}K_b \approx 5 \Rightarrow \text{pH} = 14 - \text{pOH} \approx 9$)

Problems

1987

a) three points

$$1.518 \text{ g KHC}_8\text{H}_4\text{O}_4 \div (204.2 \text{ g / mole}) = 7.434 \times 10^{-3} \text{ moles KHP}$$

$$7.434 \times 10^{-3} \text{ mol KHP} = 7.434 \times 10^{-3} \text{ mol NaOH}$$

$$7.434 \text{ millimole NaOH} \div 26.90 \text{ mL NaOH} = 0.2764 \text{ M NaOH}$$

OR

$$7.434 \times 10^{-3} \text{ mol NaOH} / 0.02690 \text{ L} = 0.2764 \text{ M NaOH}$$

b) three points

$$(28.35 \text{ mL NaOH} / 25.00 \text{ mL HNO}_3) \times (0.2764 \text{ moles NaOH} / \text{L}) \times (1 \text{ mole HNO}_3 / 1 \text{ mole NaOH}) = 0.3134 \text{ M HNO}_3 \text{ solution}$$

$$0.3134 \text{ M} \times 500 \text{ ml dilute soln} = x (10.00 \text{ mL conc. HNO}_3 \text{ soln})$$

$$x = (0.3134) (500) \div (10.00) = 15.67 \text{ M HNO}_3$$

c) three points

$$\% = (\text{g HNO}_3 \div \text{g soln}) \times 100$$

to get numerator:

$$(15.67 \text{ HNO}_3 / \text{L soln}) \times (63.02 \text{ g HNO}_3 / \text{mole}) = 987.5 \text{ g HNO}_3 \text{ (in a L)}$$

to get denominator:

$$(1.42 \text{ g soln} / \text{mL soln}) \times (1000 \text{ mL} / \text{L}) = 1,420 \text{ g HNO}_3 \text{ soln (in a L)}$$

then:

$$\% = (987.5 \text{ g HNO}_3 / 1,420 \text{ g soln}) \times 100 = 69.5\% \text{ HNO}_3$$

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QUESTION 4

(9 points)

4. Concentrated sulfuric acid (18.4-molar H_2SO_4) has a density of 1.84 grams per milliliter. After dilution with water to 5.20-molar, the solution has a density of 1.38 grams per milliliter and can be used as an electrolyte in lead storage batteries for automobiles.
- Calculate the volume of concentrated acid required to prepare 1.00 liter of 5.20-molar H_2SO_4 .
 - Determine the mass percent of H_2SO_4 in the original concentrated solution.
 - Calculate the volume of 5.20-molar H_2SO_4 that can be completely neutralized with 10.5 grams of sodium bicarbonate, NaHCO_3 .
 - What is the molality of the 5.20-molar H_2SO_4 ?

Scoring Guide

- (a) $V_1M_1 = V_2M_2$
 $(1.00 \text{ L})(5.20 \text{ mol/L}) = (x)(18.4 \text{ mol/L})$
 $x = \frac{5.2 \text{ mol}}{18.4 \text{ mol/L}} = 0.283 \text{ L (or 283 mL)}$ **1 point**
- (b) mass 1 liter of concentrated $\text{H}_2\text{SO}_4 = 1 \text{ L} \times (1.84 \text{ g/mL}) \times (1,000 \text{ mL/L})$
 $= 1,840 \text{ g } \text{H}_2\text{SO}_4$
 $18.4 \text{ mol } \text{H}_2\text{SO}_4 \times \frac{98.1 \text{ g}}{1 \text{ mol}} = 1,805 \text{ g } \text{H}_2\text{SO}_4$ } *either one* **1 point**
- mass percent $\text{H}_2\text{SO}_4 = \frac{1,805 \text{ g}}{1,840 \text{ g}} \times 100 = 98.1\%$ **1 point**
- (c) Stoichiometric ratio of NaHCO_3 to $\text{H}_2\text{SO}_4 = 2:1$ **1 point**
- $10.5 \text{ g } \text{NaHCO}_3 \times \frac{1 \text{ mol } \text{NaHCO}_3}{84.0 \text{ g } \text{NaHCO}_3} = 0.125 \text{ mol } \text{NaHCO}_3$ **1 point**
- Since 1 mol H_2SO_4 reacts with 2 mol NaHCO_3 , 0.125 mol NaHCO_3 reacts with 0.0625 mol H_2SO_4
- $0.0625 \text{ mol } \text{H}_2\text{SO}_4 = V \times M = (V)(5.20 \text{ M})$
 $V = \frac{0.0625 \text{ mol}}{5.20 \text{ mol/L}} = 0.0120 \text{ L (or 12.0 mL)}$ **1 point**

(d) $\text{molality} = \frac{\text{moles solute}}{1,000 \text{ g solvent}} = \frac{\text{moles solute}}{1 \text{ kg solvent}}$

$$\text{mass of 1 L of } 5.20 \text{ M H}_2\text{SO}_4 = 1 \text{ L} \times \frac{1,000 \text{ mL}}{1 \text{ L}} \times \frac{1.38 \text{ g}}{1 \text{ mL}} = 1,380 \text{ g}$$

$$\text{mass of H}_2\text{SO}_4 \text{ in 1 L} = (5.20 \text{ mol/L})(98.1 \text{ g/mol}) = 510 \text{ g}$$

$$\text{mass of H}_2\text{O in 1 L} = 1,380 - 510 = 870 \text{ g}$$

$$\text{molality} = \frac{5.20 \text{ mol H}_2\text{SO}_4}{870 \text{ g}} \times \frac{1,000 \text{ g}}{1 \text{ kg}} = 5.98 \text{ m}$$

1 point

1 point

1 point

(Note: no credit earned for $\frac{5.20 \text{ mol}}{1.38 \text{ kg}} = 5.77 \text{ m}$)