

FIRST EXAM**With Solutions**

Closed book, one page of notes allowed.

Answer any 4 of the following 5 questions. Please state any additional assumptions you made, and show all work.

Miscellaneous Information:

$$R = 1.987 \text{ cal/mole}^\circ\text{K} = 8.314 \text{ J/mole}^\circ\text{K}$$

$$\text{Absolute zero} = -273.15^\circ\text{C}$$

$$1 \text{ joule} = 0.239 \text{ calories}$$

$$20^\circ\text{C} = 68^\circ\text{F}$$

1. (25%) Use the graphical solution to determine the pH and complete solution composition for 1 liter of pure water to which you've added 10^{-3} moles of Sodium Citrate Dibasic (Na_2HCit). Graph paper is attached to this exam for this purpose.

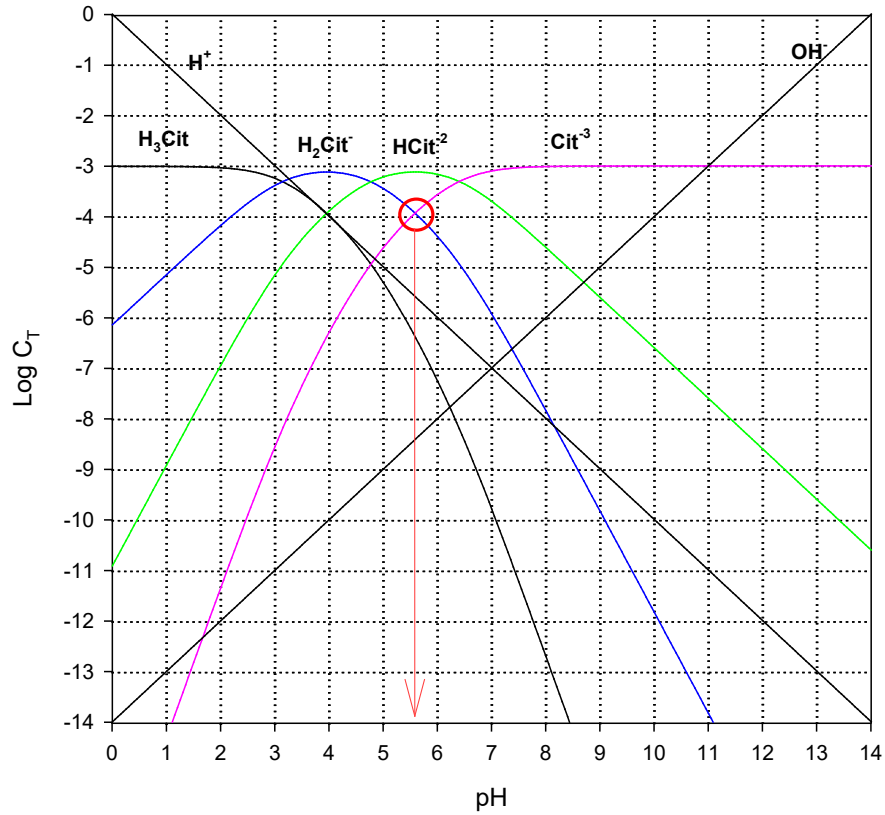
You should notice from the way this is presented (Na_2HCit) and from the presence of three pK_a values in the table, that this is a triprotic acid. The species are usually represented as H_3Cit , H_2Cit^- , HCit^{2-} and Cit^{3-} . Note that you're adding the species, HCit^{2-} .

PBE:

$$2[\text{H}_3\text{Cit}] + [\text{H}_2\text{Cit}^-] + [\text{H}^+] = [\text{OH}^-] + [\text{Cit}^{3-}]$$

Which reduces to:

$$[\text{H}_2\text{Cit}^-] = [\text{Cit}^{3-}]$$



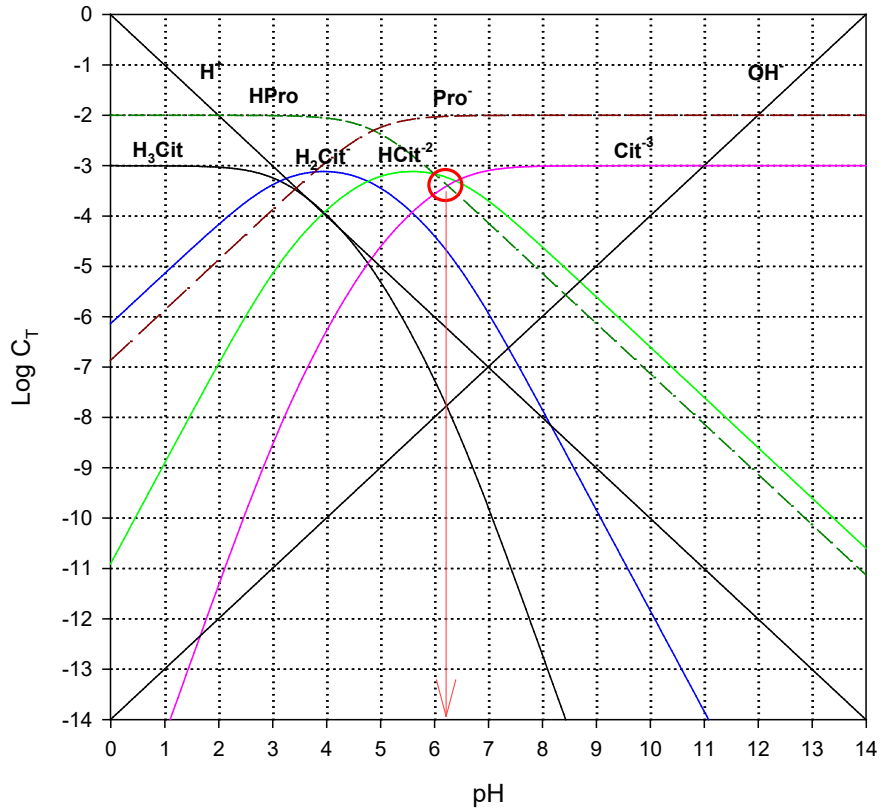
2. (25%) Determine the pH and solution composition of the above solution after you have added 10^{-2} moles of the potassium salt of Propionic Acid (i.e., 10^{-2} M KProp plus 10^{-3} M Na_2HCit) in 1 liter of water. Please use a graphical solution for this one too.

PBE:



Which reduces to:

$$[\text{HPro}] = [\text{Cit}^{3-}]$$



3. (25%) Determine the complete solution composition of:
- a solution of 10^{-2} moles of Hydrogen Sulfide (H_2S) in 1 Liter of water
 - the same solution in "a" to which you have also added 0.5×10^{-2} moles of Sodium Hydroxide (NaOH).
- But this time use an algebraic solution. Please ignore ionic strength effects (i.e., assume infinite dilution). Remember to make simplifying assumptions

Part a

Since H₂S is a fully-protonated diprotic acid, it might be reasonable to assume it gives rise to an **Acidic Solution**. Based on this assumption, the simplified algebraic solution is:

$$[H^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_a C}}{2}$$

$$[H^+] = \frac{-10^{-7.02} + \sqrt{10^{-7.02} + 4(10^{-7.02})10^{-2}}}{2}$$

$$[H^+] = 3.085 \times 10^{-5}$$

$$\text{pH} = 4.5107$$

now check assumption:

- $[H^+] \gg [OH^-]$

In addition, since H₂S has a first pK that is fairly high (7.02), you could also assume it is a **Weak Acid** in addition to using the **Acidic Solution** assumption. Based on this assumption, the simplified algebraic solution is:

$$[H^+] = \sqrt{K_a C}$$

If you didn't remember this, you could derive it using the PBE or ENE

$$[H^+] = [OH^-] + [HS^-] + 2[S^{2-}]$$

And simplifying

$$[H^+] \approx [HS^-]$$

And recognizing that the pK_a is 7.02, so that under acidic conditions

$$\text{pH} \ll \text{pK}_a$$

or

$$[H^+] \gg K_a$$

Which means that

$$C \approx [H_2S]$$

And since

$$K_1 = \frac{[HS^-][H^+]}{[H_2S]}$$
$$[HS^-] \approx \frac{K_1 C}{[H^+]}$$

So:

$$[H^+] \approx \frac{K_1 C}{[H^+]}$$

And:

$$[H^+] = \sqrt{K_1 C}$$

Either way, substituting gives:

$$\begin{aligned} [H^+] &= \sqrt{10^{-7.02} 10^{-2}} \\ [H^+] &= \sqrt{10^{-9.02}} \\ [H^+] &= 10^{-4.51} \end{aligned}$$

$$\mathbf{pH = 4.51}$$

now check assumptions:

- $[H^+] \gg [OH^-]$
- $[H_2S] \gg [HS^-]$

Part b

Since this is an acid to which you've added a strong base, you cannot use a PBE, but you can use an ENE (CBE). You can also make the assumptions:

- $[HS^-] \gg [OH^-]$
- $[Na^+] \gg [H^+]$

Which when combined with the ENE, gives you the H-H Equation.

You might also recognize this right from the start. In this case, you've added half as much strong base as you had H_2S to begin. This is equivalent to a titration to the mid-point, where you are left with equal amounts of H_2S and HS^- . This is the perfect application for the Henderson-Hasselbalch (H-H) equation.

$$pH = pK_a + \log \left(\frac{[A]}{[HA]} \right)$$

So in this case:

$$\begin{aligned} pH &= 7.02 + \log \left(\frac{[HS^-]}{[H_2S]} \right) \\ pH &= 7.02 + \log(1) \end{aligned}$$

$$\mathbf{pH = 7.02}$$

now check assumptions:

- $[HS^-] \gg [OH^-]$
- $[Na^+] \gg [H^+]$

4. (25%) Repeat problem #3a, but this time consider ionic strength effects, using the Güntelberg Approximation.

Recall the Güntelberg Approximation is:

$$\log f = -0.5z^2 \frac{\sqrt{I}}{1 + \sqrt{I}}$$

Which requires calculation of ionic strength (I):

$$I = \frac{1}{2} \sum M_i C_i$$

Since in 3a, you can use the ENE or PBE to approximate the major charged species

$$[HS^-] = [H^+]$$

So:

$$I = \frac{1}{2} \sum (3.085 \times 10^{-5} + 3.085 \times 10^{-5}) = 3.085 \times 10^{-5}$$

Then

$$\log f = -0.5 \frac{\sqrt{3.085 \times 10^{-5}}}{1 + \sqrt{3.085 \times 10^{-5}}} = -0.00276$$

$$f = 0.994$$

Now going back to problem we had

$$[H^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_a C}}{2}$$

And we need to adjust for the new Ka based on ionic strength corrections

$$K_a = \frac{\{HS^-\}\{H^+\}}{\{H_2S\}} = \frac{[HS^-]f_{HS^-}\{H^+\}}{[H_2S]f_{H_2S}}$$

You could go back to the original simplified equation from assuming an acidic solution and a weak acid

$$[HS^-] \approx \frac{K_1 C}{[H^+]}$$

And

$$[HS^-] \approx \frac{K_1 C f_{H^+}}{\{H^+\}}$$

And

$$[H^+] \approx \frac{K_1 C f_{H^+}}{\{H^+\}}$$

And

$$\frac{\{H^+\}}{f_{H^+}} \approx \frac{K_1 C f_{H^+}}{\{H^+\}}$$

So:

$$\{H^+\} = \sqrt{K_1 C (f_{H^+})^2} = f_{H^+} \sqrt{K_1 C}$$

$$\{H^+\} = 0.994 \sqrt{10^{-7.02} 10^{-2}}$$

$$\{H^+\} = 3.066 \times 10^{-5}$$

$$\mathbf{pH = 4.513}$$

in other words, almost no difference with the ionic strength correction

5. (25%) True/False. Mark each one of the following statements with either a “T” or an “F”, whichever is most accurate
- a. **T** Mass defects are directly proportional to nuclear binding energy
 - b. **F** The value of α_0 plus α_1 must always equal 1 for any triprotic acid system
 - c. **F** The standard assumption used for developing the Henderson-Hasselbach equation is that all negative ions are negligible
 - d. **T** The pH of the endpoint of the alkalinity titration is about 4.5
 - e. **F** Sulfuric acid completely donates its protons to water, regardless of the pH
 - f. **F** Non-carbonate hardness only exists in water without carbonates
 - g. **T** Bisulfide is an amphoteric substance
 - h. **F** Increases in ionic strength have the greatest effect on species with zero charge.
 - i. **T** The principle of electroneutrality is always observed in aqueous solutions
 - j. **F** The third most common gas in the atmosphere is carbon dioxide.

Selected Acidity Constants (Aqueous Solution, 25°C, I = 0)

NAME	FORMULA	pK _a
Perchloric acid	$\text{HClO}_4 = \text{H}^+ + \text{ClO}_4^-$	-7 STRONG
Hydrochloric acid	$\text{HCl} = \text{H}^+ + \text{Cl}^-$	-3
Sulfuric acid	$\text{H}_2\text{SO}_4 = \text{H}^+ + \text{HSO}_4^-$	-3 (&2) ACIDS
Nitric acid	$\text{HNO}_3 = \text{H}^+ + \text{NO}_3^-$	-0
Hydronium ion	$\text{H}_3\text{O}^+ = \text{H}^+ + \text{H}_2\text{O}$	0
Trichloroacetic acid	$\text{CCl}_3\text{COOH} = \text{H}^+ + \text{CCl}_3\text{COO}^-$	0.70
Iodic acid	$\text{HIO}_3 = \text{H}^+ + \text{IO}_3^-$	0.8
Bisulfate ion	$\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$	2
Phosphoric acid	$\text{H}_3\text{PO}_4 = \text{H}^+ + \text{H}_2\text{PO}_4^-$	2.15 (&7.2,12.3)
o-Phthalic acid	$\text{C}_6\text{H}_4(\text{COOH})_2 = \text{H}^+ + \text{C}_6\text{H}_4(\text{COOH})\text{COO}^-$	2.89 (&5.51)
Citric acid (H ₃ Cit)	$\text{C}_3\text{H}_4\text{OH}(\text{COOH})_3 = \text{H}^+ + \text{C}_3\text{H}_4\text{OH}(\text{COOH})_2\text{COO}^-$	3.14 (&4.77, 6.4)
Hydrofluoric acid	$\text{HF} = \text{H}^+ + \text{F}^-$	3.2
Aspartic acid	$\text{C}_2\text{H}_6\text{N}(\text{COOH})_2 = \text{H}^+ + \text{C}_2\text{H}_6\text{N}(\text{COOH})\text{COO}^-$	3.86 (&9.82)
m-Hydroxybenzoic acid	$\text{C}_6\text{H}_4(\text{OH})\text{COOH} = \text{H}^+ + \text{C}_6\text{H}_4(\text{OH})\text{COO}^-$	4.06 (&9.92)
p-Hydroxybenzoic acid	$\text{C}_6\text{H}_4(\text{OH})\text{COOH} = \text{H}^+ + \text{C}_6\text{H}_4(\text{OH})\text{COO}^-$	4.48 (&9.32)
Nitrous acid	$\text{HNO}_2 = \text{H}^+ + \text{NO}_2^-$	4.5
Acetic acid	$\text{CH}_3\text{COOH} = \text{H}^+ + \text{CH}_3\text{COO}^-$	4.75
Citrate Monobasic (H ₂ Cit ⁻¹)	$\text{C}_3\text{H}_4\text{OH}(\text{COOH})_2\text{COO}^- = \text{H}^+ + \text{C}_3\text{H}_4\text{OHCOOH}(\text{COO})_2^{2-}$	4.77
Propionic acid	$\text{C}_2\text{H}_5\text{COOH} = \text{H}^+ + \text{C}_2\text{H}_5\text{COO}^-$	4.87
o-Phthalate	$\text{C}_6\text{H}_4(\text{COOH})\text{COO}^- = \text{H}^+ + \text{C}_6\text{H}_4(\text{COO}-)_2$	5.51
Citrate Dibasic (HCit ⁻²)	$\text{C}_3\text{H}_4\text{OHCOOH}(\text{COO})_2^{2-} = \text{H}^+ + \text{C}_3\text{H}_4\text{OH}(\text{COO})_3^{3-}$	6.4
Carbonic acid	$\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$	6.35 (&10.33)
Hydrogen sulfide	$\text{H}_2\text{S} = \text{H}^+ + \text{HS}^-$	7.02 (&13.9)
Dihydrogen phosphate	$\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{2-}$	7.2
Hypochlorous acid	$\text{HOCl} = \text{H}^+ + \text{OCl}^-$	7.5
Boric acid	$\text{B}(\text{OH})_3 + \text{H}_2\text{O} = \text{H}^+ + \text{B}(\text{OH})_4^-$	9.2 (&12.7,13.8)
Ammonium ion	$\text{NH}_4^+ = \text{H}^+ + \text{NH}_3$	9.24
Hydrocyanic acid	$\text{HCN} = \text{H}^+ + \text{CN}^-$	9.3
p-Hydroxybenzoic acid	$\text{C}_6\text{H}_4(\text{OH})\text{COO}^- = \text{H}^+ + \text{C}_6\text{H}_4(\text{O})\text{COO}^{2-}$	9.32
Phenol	$\text{C}_6\text{H}_5\text{OH} = \text{H}^+ + \text{C}_6\text{H}_5\text{O}^-$	9.9
m-Hydroxybenzoic acid	$\text{C}_6\text{H}_4(\text{OH})\text{COO}^- = \text{H}^+ + \text{C}_6\text{H}_4(\text{O})\text{COO}^{2-}$	9.92
Bicarbonate ion	$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$	10.33
Monohydrogen phosphate	$\text{HPO}_4^{2-} = \text{H}^+ + \text{PO}_4^{3-}$	12.3
Bisulfide ion	$\text{HS}^- = \text{H}^+ + \text{S}^{2-}$	13.9
Water	$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	14.00
Ammonia	$\text{NH}_3 = \text{H}^+ + \text{NH}_2^-$	23

Species	$\Delta \overline{H}_f^o$ kcal/mole	$\Delta \overline{G}_f^o$ kcal/mole
Ca ⁺² (aq)	-129.77	-132.18
CaCO ₃ (s), calcite	-288.45	-269.78
CaO (s)	-151.9	-144.4
C(s), graphite	0	0
CO ₂ (g)	-94.05	-94.26
CO ₂ (aq)	-98.69	-92.31
CH ₄ (g)	-17.889	-12.140
H ₂ CO ₃ (aq)	-167.0	-149.00
HCO ₃ ⁻ (aq)	-165.18	-140.31
CO ₃ ⁻² (aq)	-161.63	-126.22
HOCl (aq)	-28.90	-19.10
OCl ⁻ (aq)	-25.60	-8.80
CH ₃ COOH	-116.79	-95.5
CH ₃ COO ⁻ , acetate	-116.84	-89.0
H ⁺ (aq)	0	0
H ₂ (g)	0	0
HF (aq)	-77.23	-71.63
F ⁻ (aq)	-80.15	-67.28
Fe ⁺² (aq)	-21.0	-20.30
Fe ⁺³ (aq)	-11.4	-2.52
Fe(OH) ₃ (s)	-197.0	-166.0
NO ₃ ⁻ (aq)	-49.372	-26.43
NH ₃ (g)	-11.04	-3.976
NH ₃ (aq)	-19.32	-6.37
NH ₄ ⁺ (aq)	-31.74	-19.00
HNO ₃ (aq)	-49.372	-26.41
O ₂ (aq)	-3.9	3.93
O ₂ (g)	0	0
OH ⁻ (aq)	-54.957	-37.595
H ₂ O (g)	-57.7979	-54.6357
H ₂ O (l)	-68.3174	-56.690
PO ₄ ⁻³ (aq)	-305.30	-243.50
HPO ₄ ⁻² (aq)	-308.81	-260.34
H ₂ PO ₄ ⁻ (aq)	-309.82	-270.17
H ₃ PO ₄ (aq)	-307.90	-273.08
SO ₄ ⁻²	-216.90	-177.34
HS ⁻ (aq)	-4.22	3.01
H ₂ S(g)	-4.815	-7.892
H ₂ S(aq)	-9.4	-6.54

Guntelberg Approximation:

$$\log f = -0.5z^2 \frac{\sqrt{I}}{1 + \sqrt{I}}$$

