CEE 680 10 March 2020

FIRST EXAM

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 cal/mole°K = 8.314 J/mole°K
> Absolute zero = -273.15°C
> 1 joule = 0.239 calories
> 20°C = 68°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.

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.

3. (25%) Determine the complete solution composition of:
   a. a solution of 10^{-2} moles of Hydrogen Sulfide (H_2S) in 1 Liter of water
   b. the same solution in "a" to which you have also added $0.5x10^{-2}$ 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

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

5. (25%) True/False. Mark each one of the following statements with either a "T" or an "F", whichever is most accurate

a. ______ Mass defects are directly proportional to nuclear binding energy

b. ______ The value of α_o plus α_1 must always equal 1 for any triprotic acid system

c. ______ The standard assumption used for developing the Henderson-Hasselbach equation is that all negative ions are negligible

d. ______ The pH of the endpoint of the alkalinity titration is about 4.5

e. ______ Sulfuric acid completely donates its protons to water, regardless of the pH

f. ______ Non-carbonate hardness only exists in water without carbonates

g. ______ Bisulfide is an amphoteric substance

h. ______ Increases in ionic strength have the greatest effect on species with zero charge.

i. ______ The principle of electroneutrality is always observed in aqueous solutions

j. ______ The third most common gas in the atmosphere is carbon dioxide.

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

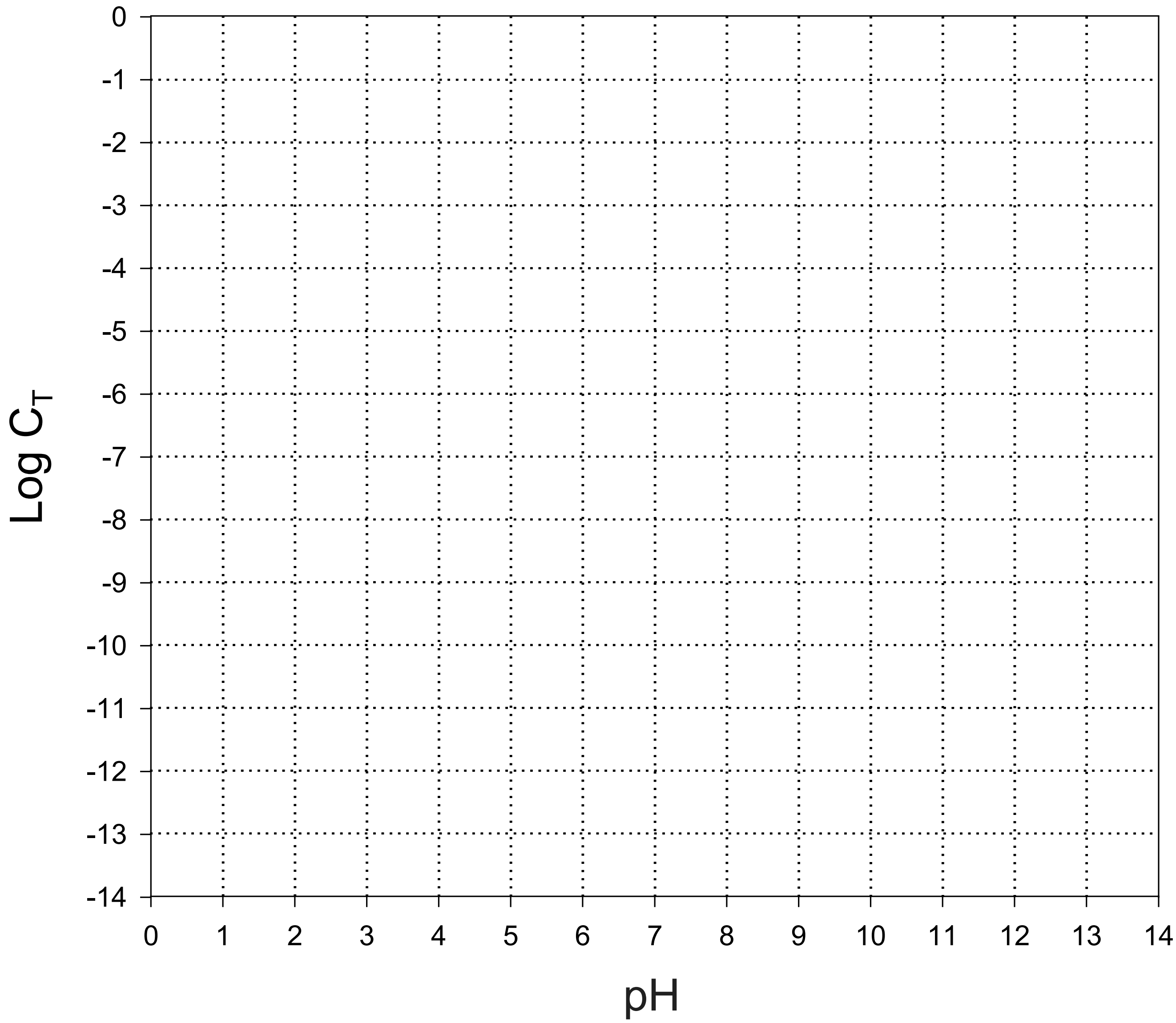
NAME	FORMULA	pK_a
Perchloric acid	$HClO_4 = H^+ + ClO_4^-$	-7 STRONG
Hydrochloric acid	$HCl = H^+ + Cl^-$	-3
Sulfuric acid	$H_2SO_4 = H^+ + HSO_4^-$	-3 (&2) ACIDS
Nitric acid	$HNO_3 = H^+ + NO_3^-$	-0
Hydronium ion	$H_3O^+ = H^+ + H_2O$	0
Trichloroacetic acid	$CCl_3COOH = H^+ + CCl_3COO^-$	0.70
Iodic acid	$HIO_3 = H^+ + IO_3^-$	0.8
Bisulfate ion	$HSO_4^- = H^+ + SO_4^{-2}$	2
Phosphoric acid	$H_3PO_4 = H^+ + H_2PO_4^-$	2.15 (&7.2,12.3)
o-Phthalic acid	$C_6H_4(COOH)_2 = H^+ + C_6H_4(COOH)COO^-$	2.89 (&5.51)
Citric acid (H_3Cit)	$C_3H_4OH(COOH)_3 = H^+ + C_3H_4OH(COOH)_2COO^-$	3.14 (&4.77, 6.4)
Hydrofluoric acid	$HF = H^+ + F^-$	3.2
Aspartic acid	$C_2H_6N(COOH)_2 = H^+ + C_2H_6N(COOH)COO^-$	3.86 (&9.82)
m-Hydroxybenzoic acid	$C_6H_4(OH)COOH = H^+ + C_6H_4(OH)COO^-$	4.06 (&9.92)
p-Hydroxybenzoic acid	$C_6H_4(OH)COOH = H^+ + C_6H_4(OH)COO^-$	4.48 (&9.32)
Nitrous acid	$HNO_2 = H^+ + NO_2^-$	4.5
Acetic acid	$CH_3COOH = H^+ + CH_3COO^-$	4.75
Citrate Monobasic (H_2Cit^{-1})	$C_3H_4OH(COOH)_2COO^- = H^+ + C_3H_4OHCOOH(COO)_2^{-2}$	4.77
Propionic acid	$C_2H_5COOH = H^+ + C_2H_5COO^-$	4.87
o-Phthalate	$C_6H_4(COOH)COO^- = H^+ + C_6H_4(COO-)_2$	5.51
Citrate Dibasic ($HCit^{-2}$)	$C_3H_4OHCOOH(COO)_2^{-2} = H^+ + C_3H_4OH\ (COO)_3^{-3}$	6.4
Carbonic acid	$H_2CO_3 = H^+ + HCO_3^-$	6.35 (&10.33)
Hydrogen sulfide	$H_2S = H^+ + HS^-$	7.02 (&13.9)
Dihydrogen phosphate	$H_2PO_4^- = H^+ + HPO_4^{-2}$	7.2
Hypochlorous acid	$HOCl = H^+ + OCl^-$	7.5
Boric acid	$B(OH)_3 + H_2O = H^+ + B(OH)_4^-$	9.2 (&12.7,13.8)
Ammonium ion	$NH_4^+ = H^+ + NH_3$	9.24
Hydrocyanic acid	$HCN = H^+ + CN^-$	9.3
p-Hydroxybenzoic acid	$C_6H_4(OH)COO^- = H^+ + C_6H_4(O)COO^{-2}$	9.32
Phenol	$C_6H_5OH = H^+ + C_6H_5O^-$	9.9
m-Hydroxybenzoic acid	$C_6H_4(OH)COO^- = H^+ + C_6H_4(O)COO^{-2}$	9.92
Bicarbonate ion	$HCO_3^- = H^+ + CO_3^{-2}$	10.33
Monohydrogen phosphate	$HPO_4^{-2} = H^+ + PO_4^{-3}$	12.3
Bisulfide ion	$HS^- = H^+ + S^{-2}$	13.9
Water	$H_2O = H^+ + OH^-$	14.00
Ammonia	$NH_3 = H^+ + NH_2^-$	23

Methane	$CH_4 = H^+ + CH_3^-$	34

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_2CO_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_3COOH	-116.79	-95.5
CH_3COO^-, 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_2O (g)	-57.7979	-54.6357
H_2O (l)	-68.3174	-56.690
PO_4^{-3} (aq)	-305.30	-243.50
HPO_4^{-2} (aq)	-308.81	-260.34
$H_2PO_4^-$ (aq)	-309.82	-270.17
H_3PO_4 (aq)	-307.90	-273.08
SO_4^{-2}	-216.90	-177.34
HS^- (aq)	-4.22	3.01
H_2S(g)	-4.815	-7.892
H_2S(aq)	-9.4	-6.54

Guntelberg Approximation:

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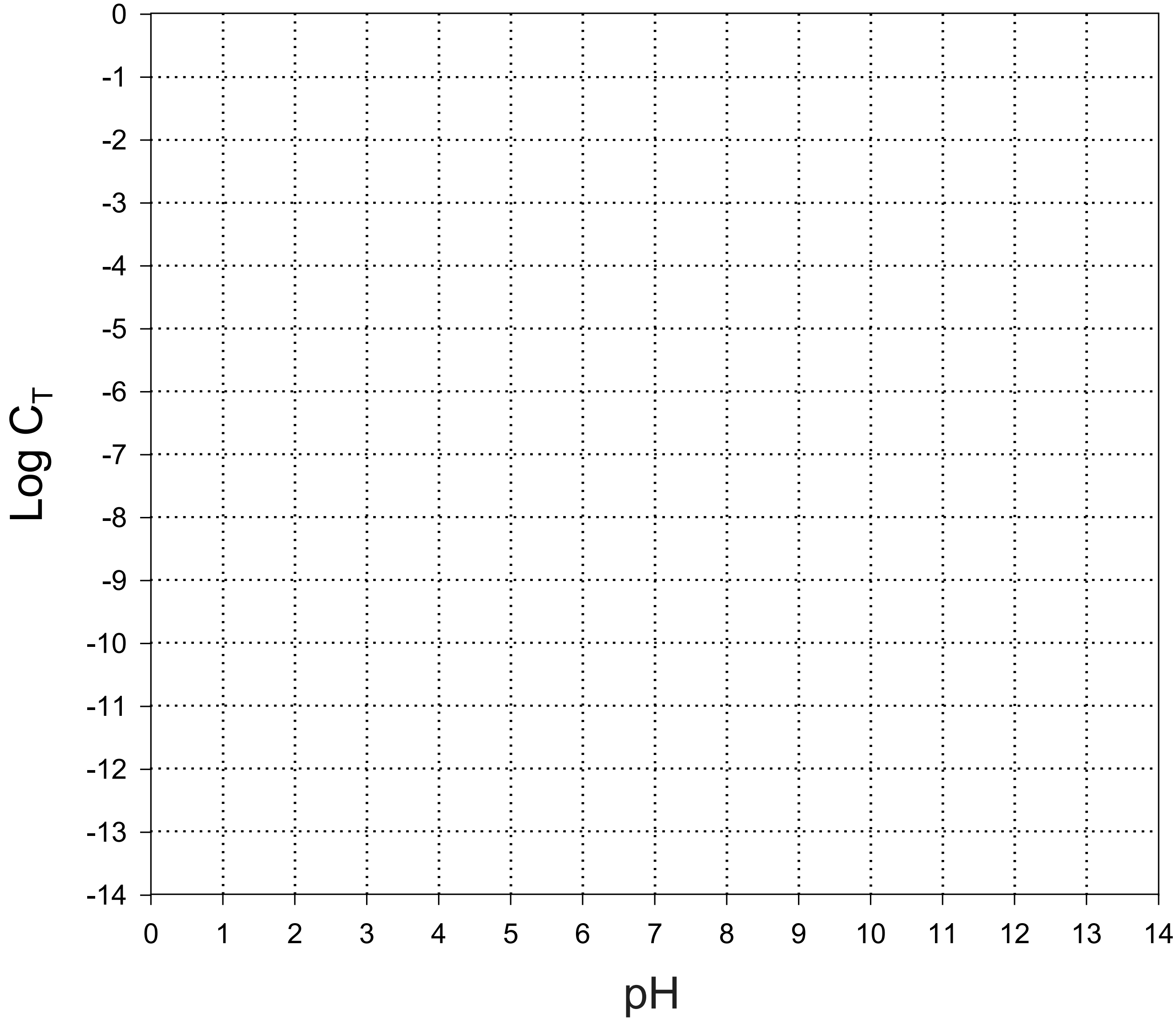
pH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pH