CEE 680 19 March 2019

# 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 Phosphate Dibasic ($Na_2HPO_4$). 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 Acetic Acid (i.e., $10^{-2}$M HAc plus $10^{-3}$M $Na_2HPO_4$) 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 $10^{-1}$ moles of Sodium Fluoride (NaF) in 1 Liter of water
   b. the same solution in "a" to which you have also added $0.5x10^{-1}$ moles of hydrochloric acid (HCl).

   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.

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

a. _____ The pH of water in equilibrium with atmospheric $CO_2$ is independent of the alkalinity

b. _____ Equilibrium constants can be calculated from the ratio of the forward and backward rate constants

c. _____ The $pK_a$ of an acid can always be calculated from the $pK_b$ of its conjugate base

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. _____ The principle of electroneutrality is always observed in aqueous solutions

g. _____ Non-carbonate weakness is another term for the inverse of the non-carbonate hardness

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

i. _____ Ammonium nitrate a is a very strong base in water

j. _____ The value of $\alpha_o$ plus $\alpha_1$ must always equal 1 for any diprotic acid system.

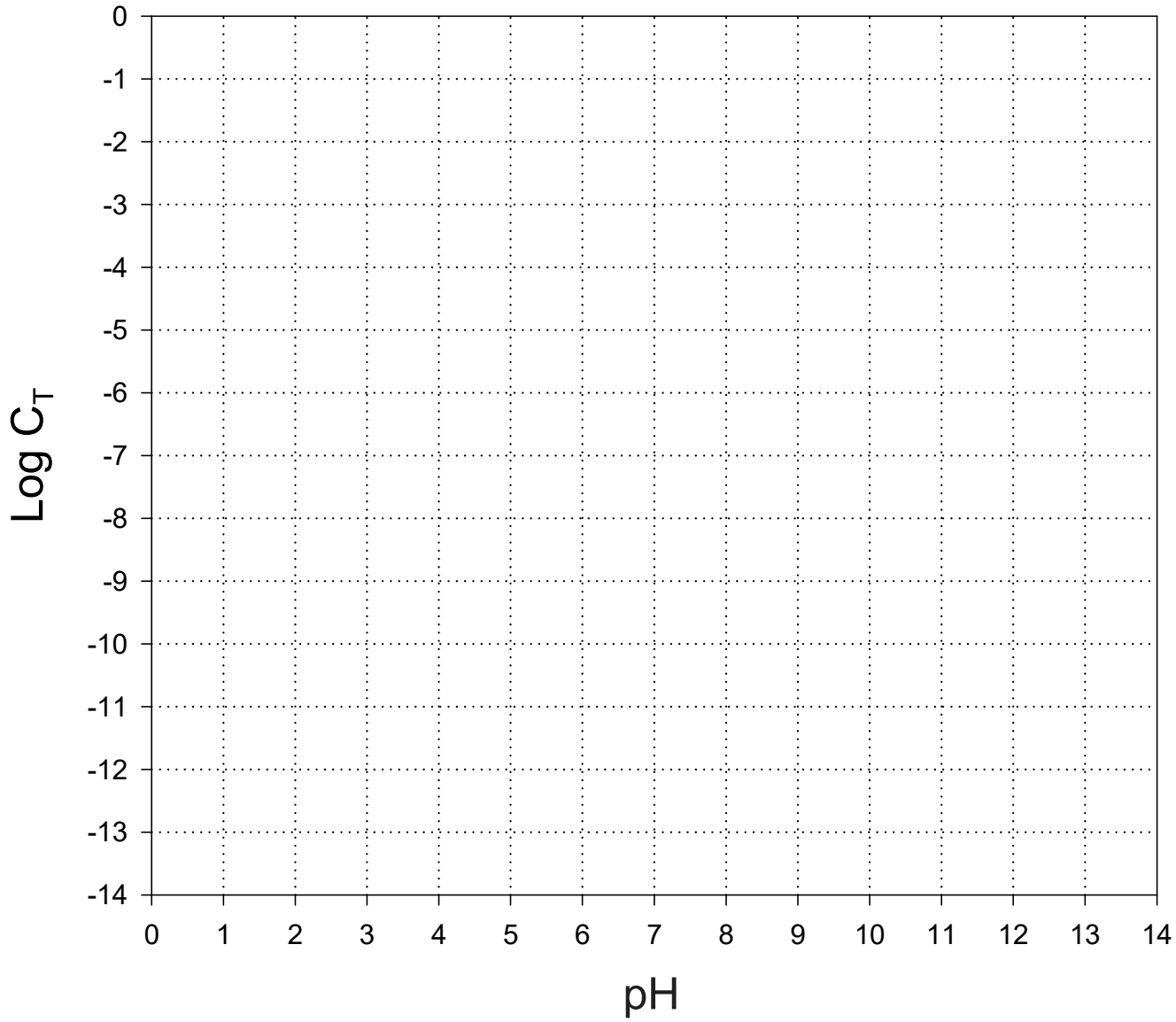
Selected Acidity Constants (Aqueous Solution, 25°C, I = 0)

| 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 | $C_3H_5O(COOH)_3 = H^+ + C_3H_5O(COOH)_2COO^-$ | 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 |
| Propionic acid | $C_2H_5COOH = H^+ + C_2H_5COO^-$ | 4.87 |
| o-Phthalate | $C_6H_4(COOH)COO^- = H^+ + C_6H_4(COO\text{-})_2$ | 5.51 |
| 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:

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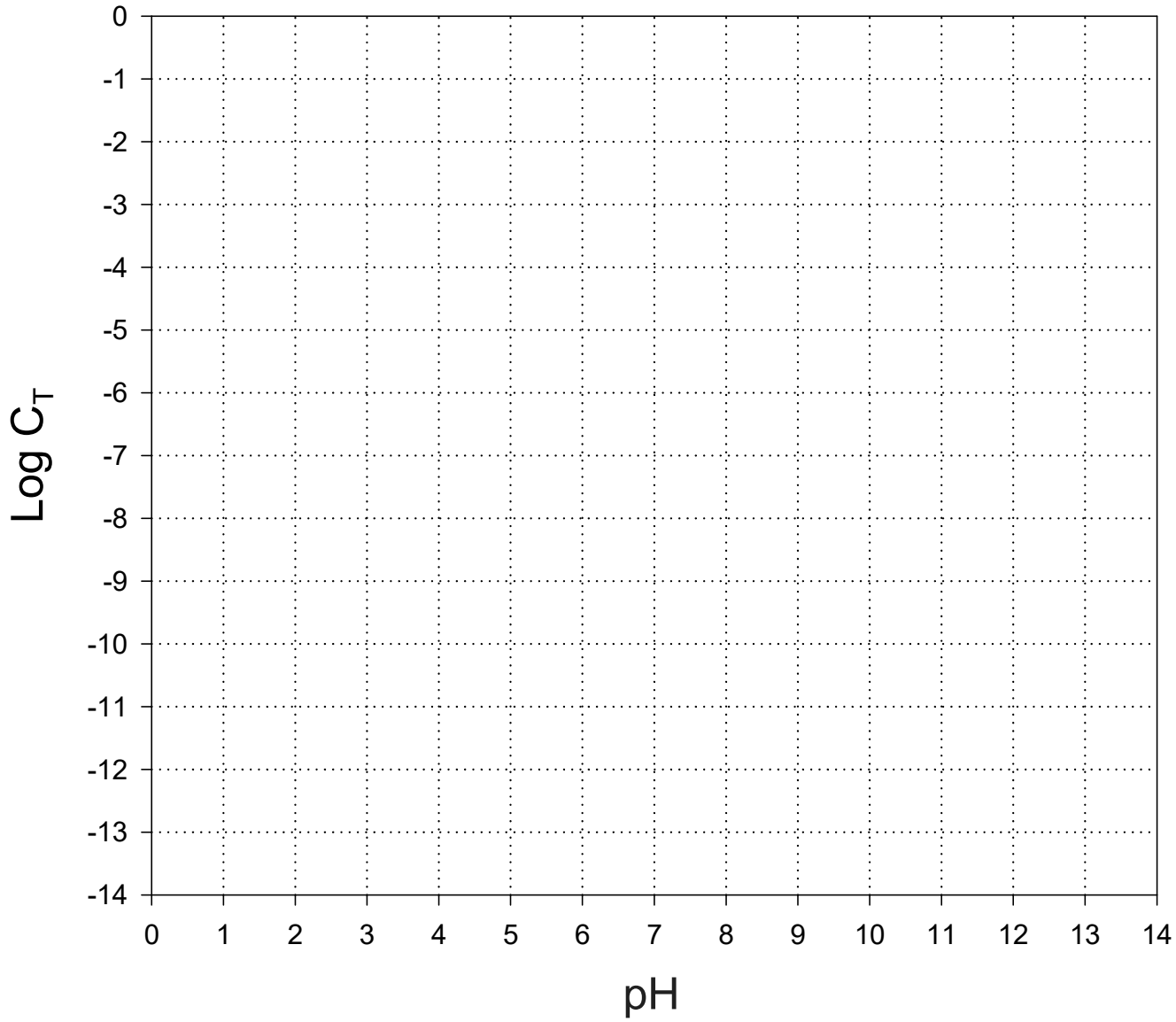
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Log $C_T$
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