CEE 680 8 March 2018

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
10°F = the new 30°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^{-2} moles of Phenol. Graph paper is attached to this exam for this purpose.

Prepare graph with $pK_a = 9.9$

PBE:

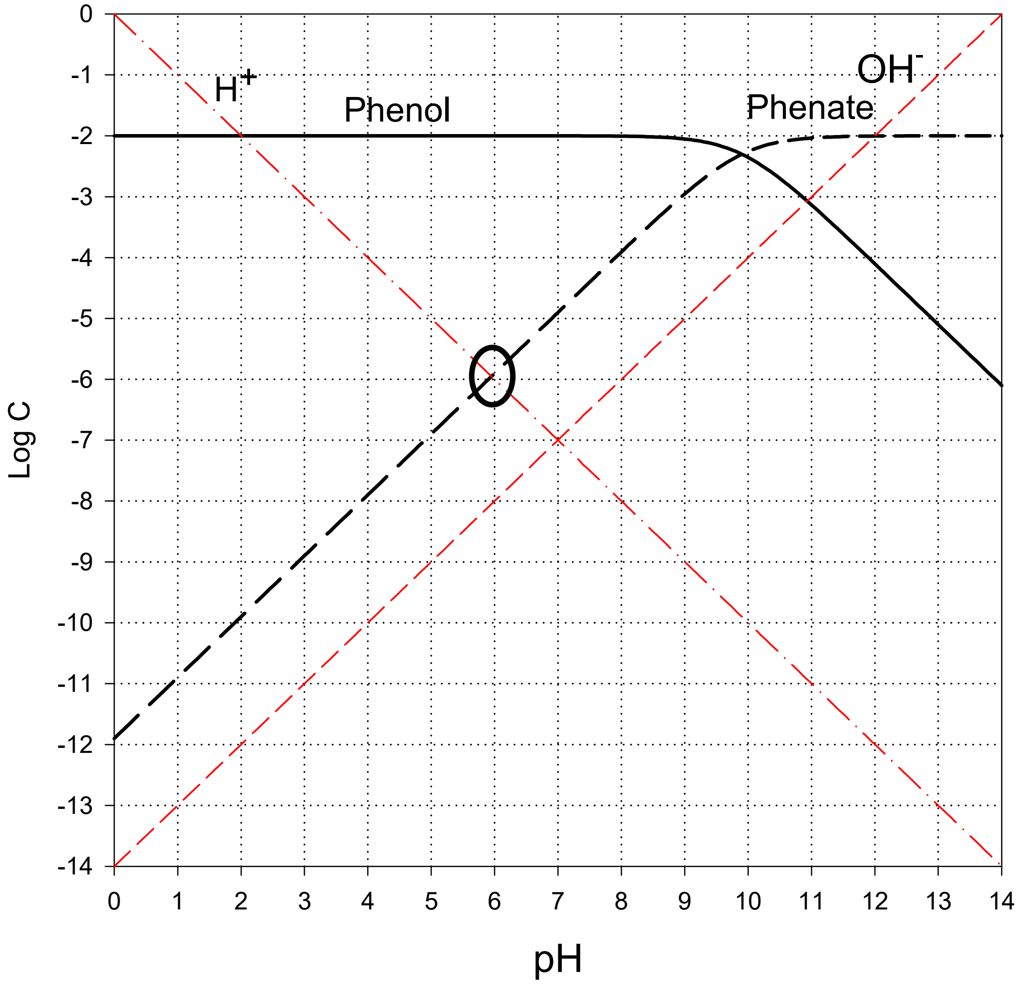
$$[\text{Phenate}^-] + [OH^-] = [H^+]$$

which reduces to:

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

Equality (intersection) occurs at **pH ~ 6.0**

Species	pC	C (Molar)
H^+	6.0	1.0×10^{-6}
OH^-	8.0	1.0×10^{-8}
Phenol	2.0	1.0×10^{-2}
Phenate^-	6.0	1.0×10^{-6}



2. (25%) Determine the pH and solution composition of a mixture of 10^{-2} moles of Phenol plus 10^{-3} moles of Disodium o-Phthalate [$Na_2C_6H_4(COO^-)_2$] in 1 liter of water. Please use a graphical solution for this one too.

Prepare graph with phenol system ($pK_a = 9.9$) and o-phthalic acid system ($pK_1 = 2.89$; $pK_2 = 5.51$).

PBE:

$$[\text{Phenate}^-] + [OH^-] = [H^+] + [\text{Hphthalate-}] + 2[H_2\text{Phthalate}]$$

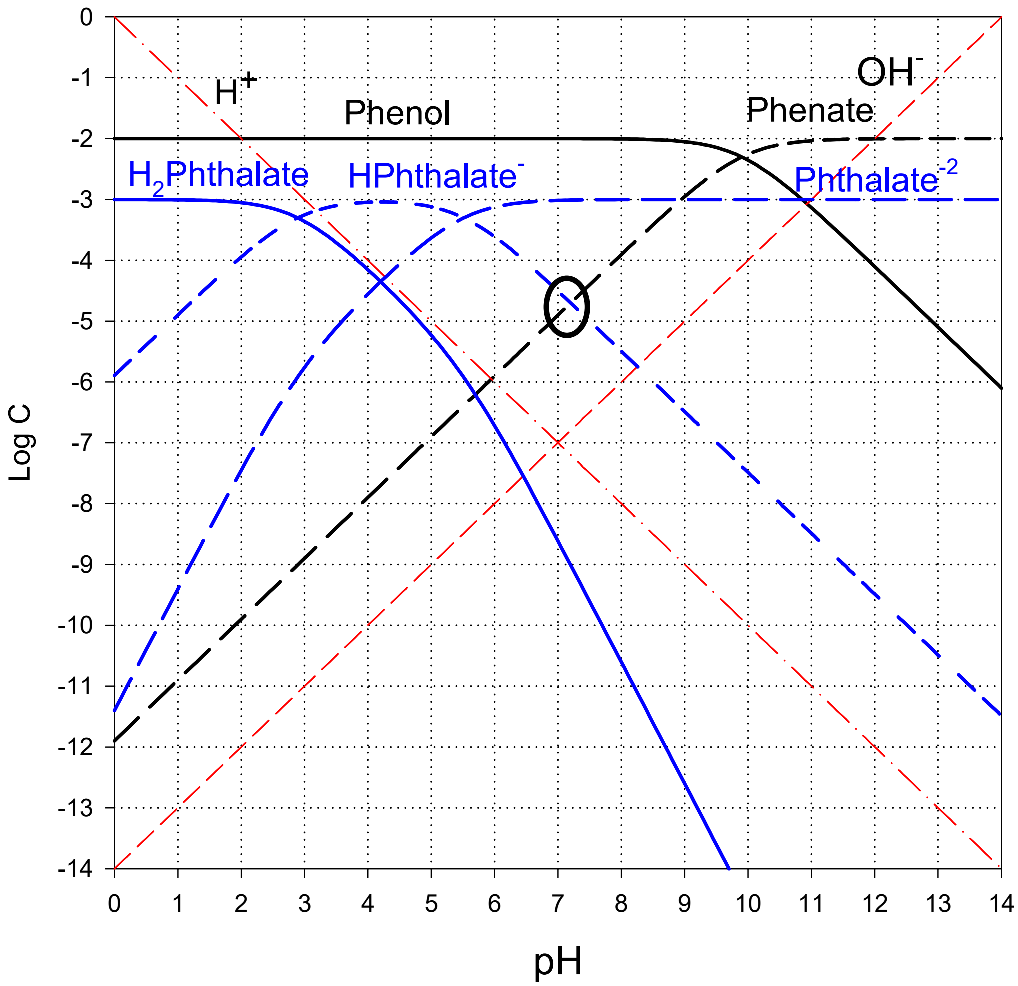
which reduces to:

$$[\text{Phenate}^-] = [\text{Hphthalate-}]$$

Equality (intersection) occurs at **pH ~ 7.2**

Species	pC	C (Molar)
H^+	7.2	6.3×10^{-8}
OH^-	6.8	1.6×10^{-7}
Phenol	2.0	1.0×10^{-2}
Phenate$^-$	4.7	2.0×10^{-5}
Phthalate^{-2}	3.0	1.0×10^{-3}
HPhthalate$^-$	4.7	2.0×10^{-5}
H_2Phthalate	9.0	1.0×10^{-9}

PBE Solution



3. (25%) Determine the complete solution composition of:
    a. a solution of 10^{-2} moles of Sodium Hypochlorite (NaOCl) in 1 Liter of water
    b. a solution of 10^{-2} moles of the conjugate acid [i.e., Hypochlorous Acid (HOCl)] in 1 Liter of water.

   But this time use an algebraic solution. You can ignore ionic strength effects (i.e., assume infinite dilution). Remember to make simplifying assumptions

For this case, we have an acid and then its conjugate base. The pK_a is 7.5, and the pC is 2.

a. a solution of 10^{-2} moles of Sodium Hypochlorite (NaOCl) in 1 Liter of water

note that from the attached table: $pK_a = 7.5$, so that $pK_b = 14-7.5 = 6.5$
pC = 2

A. Make basic solution assumption, which leads to:

$$[OH^-] \approx \frac{-K_b + \sqrt{K_b^2 + 4K_bC}}{2}$$

$[OH^-] = 5.6076 \times 10^{-5}$
pOH = 4.2512
pH = 9.7488

but easier to make the combined basic solution and weak base assumption, which leads to:

$$[OH^+] \approx \sqrt{K_bC}$$

$[OH^-] = 5.6234 \times 10^{-5}$
pOH = 4.2500
pH = 9.7500

some textbooks use pKa = 7.6, instead of 7.5. In this case we get:
$pK_b = 14-7.6 = 6.4$

A. Make basic solution assumption, which leads to:

$$[OH^-] \approx \frac{-K_b + \sqrt{K_b^2 + 4K_bC}}{2}$$

$[OH^-] = 6.2897 \times 10^{-5}$
pOH = 4.2013

pH = 9.7986

but easier to make the combined basic solution and weak base assumption, which leads to:

$$[OH^{+}] \approx \sqrt{K_b C}$$

$[OH^{-}]$ = 6.3096 x 10^{-5}
pOH = 4.2000
pH = 9.8000

b. a solution of 10^{-2} moles of the conjugate acid [i.e., Hypochlorous Acid (HOCl)] in 1 Liter of water.

B. Make acidic solution assumption, which leads to:

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

$[H^{+}]$ = 1.7767 x 10^{-5}
pH = 4.75038

but easier to make the combined acidic solution and weak acid assumption, which leads to:

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

$[H^{+}]$ = 1.7783 x 10^{-5}
pH = 4.75000

and again, if you use pKa – 7.6, you would get:

A. Make acidic solution assumption, which leads to:

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

$[H^{+}]$ = 1.5836 x 10^{-5}

pH = 4.80034

but easier to make the combined acidic solution and weak acid assumption, which leads to:

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

$[H^+] = 1.5849 \times 10^{-5}$
pH = 4.80000

4. (25%) Repeat problem #3a, but this time add 0.1 M of NaCl as well as the 10^{-2} moles of NaOCl to your liter of water. Also this time, do not ignore ionic strength effects.

$$K_b = \frac{\{HOCl\}\{OH^-\}}{\{OCl^-\}} = \frac{[HOCl]\gamma_{HOCl}[OH^-]\gamma_{OH^-}}{[OCl^-]\gamma_{OCl^-}}$$
$$= \left(\frac{[HOCl][OH^-]}{[OCl^-]}\right)\left(\frac{\gamma_{HOCl}\gamma_{OH^-}}{\gamma_{OCl^-}}\right)$$

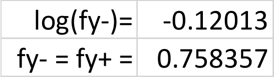
$$K_b = \frac{\{HOCl\}\{OH^-\}}{\{OCl^-\}} = \frac{[HOCl]\gamma_{HOCl}[OH^-]\gamma_{OH^-}}{[OCl^-]\gamma_{OCl^-}}$$
$$\left(\frac{[HOCl][OH^-]}{[OCl^-]}\right) = K_b\left(\frac{\gamma_{OCl^-}}{\gamma_{OH^-}}\right)$$
$$K_b' = K_b\left(\frac{\gamma_{OCl^-}}{\gamma_{OH^-}}\right)$$
$$K_b' = K_b$$

And with the Guntelberg approximation, both activity corrections are identical so that K_b does not change. However, the K_w will change

$$[H^+]\gamma_{H^+}[OH^-]\gamma_{OH^-} = K_w$$
$$K_w' \equiv [H^+][OH^-] = {}^{K_w}\!/_{\gamma_{H^+}\gamma_{OH^-}}$$

Use the Guntelberg approximation:

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



log(fy-)=	-0.12013
fy- = fy+ =	0.758357

$$K_w' \equiv \{H^+\}[OH^-] = {}^{K_w}\!/_{(0.758)} = 1.318K_w$$

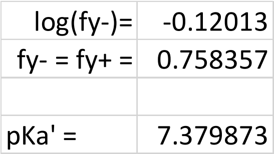
or

$$pK_w' = -0.12 + pK_w = 13.88$$

Since pH = pKw-pOH, and since the pOH is unchanged by the increase in ionic strength, then the increase in ionic strength drops the pH by 0.24 log units

pH = 9.75-0.12
pH = 9.63

Alternatively, you could simply start with the pK_a and modify that. You would get the same answer:



log(fy-)=	-0.12013
fy- = fy+ =	0.758357
pKa' =	7.379873

pH = 9.75-0.12
pH = 9.63

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

a. **T** The pH of pure water in equilibrium with atmospheric CO_2 is below 6

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

c. **F** The pK_a of an acid is always equal to the pK_b of its conjugate base

d. **F** pH = 7 at the end-point of a titration

e. **F** Nitric acid always completely donates its proton to the solvent it is dissolve in, regardless of the nature of that solvent

f. **T** The principle of electroneutrality is always observed in aqueous solutions

g. **F** Non-carbonate hardness is equal to the magnesium concentration minus the sulfate concentration

h. **F** Increases in ionic strength have no effect on species with zero charge.

i. **F** Hypochlorite is a very strong base in water

j. **T** The value of α_o plus α_1 must always equal 1 for any monoprotic acid system.

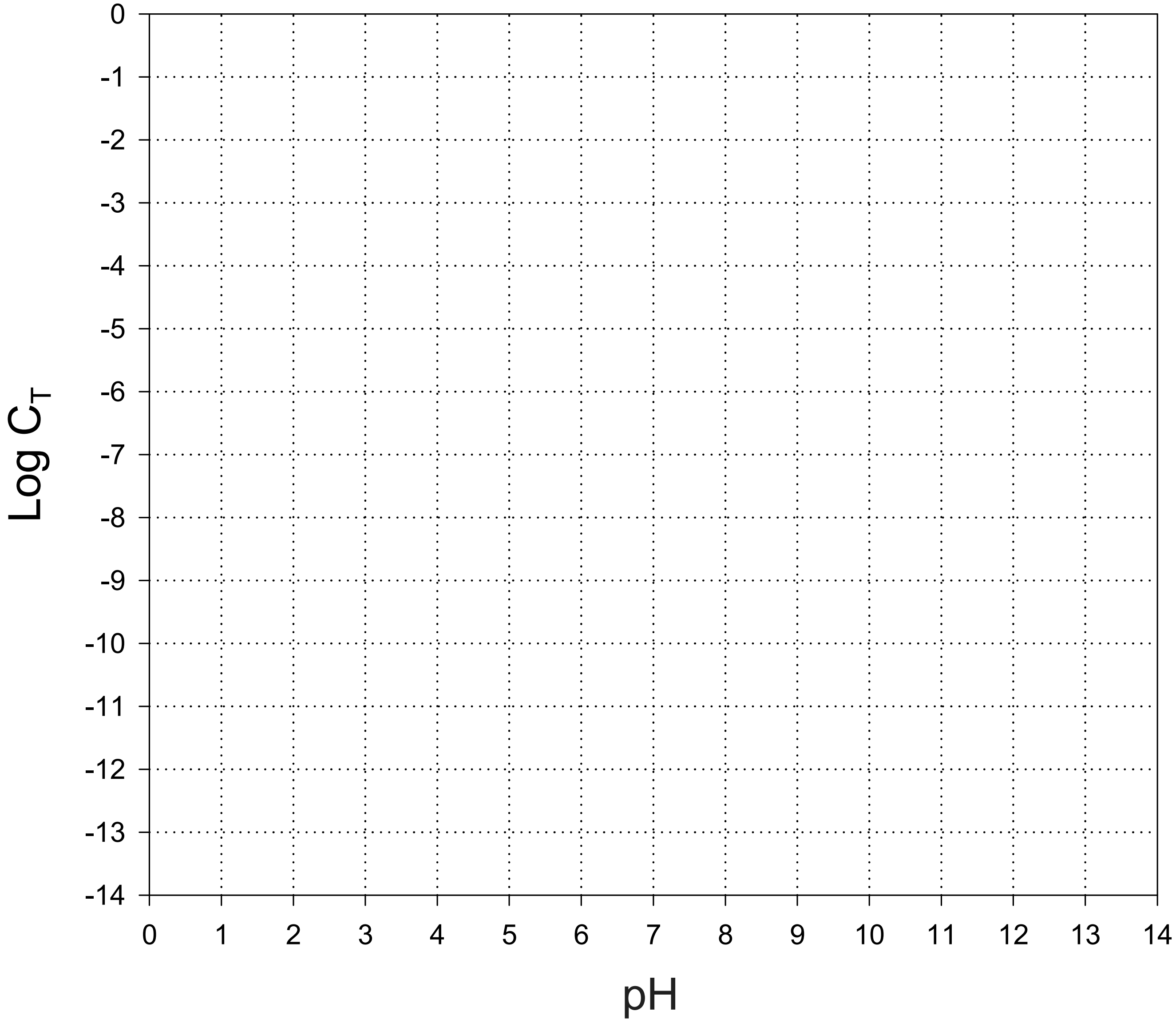
Selected Acidity Constants (Aqueous Solution, 25°C, I = 0)

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	$C_6H_4(COOH)COO^- = H^+ + C_6H_4(COO-)_2$	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:

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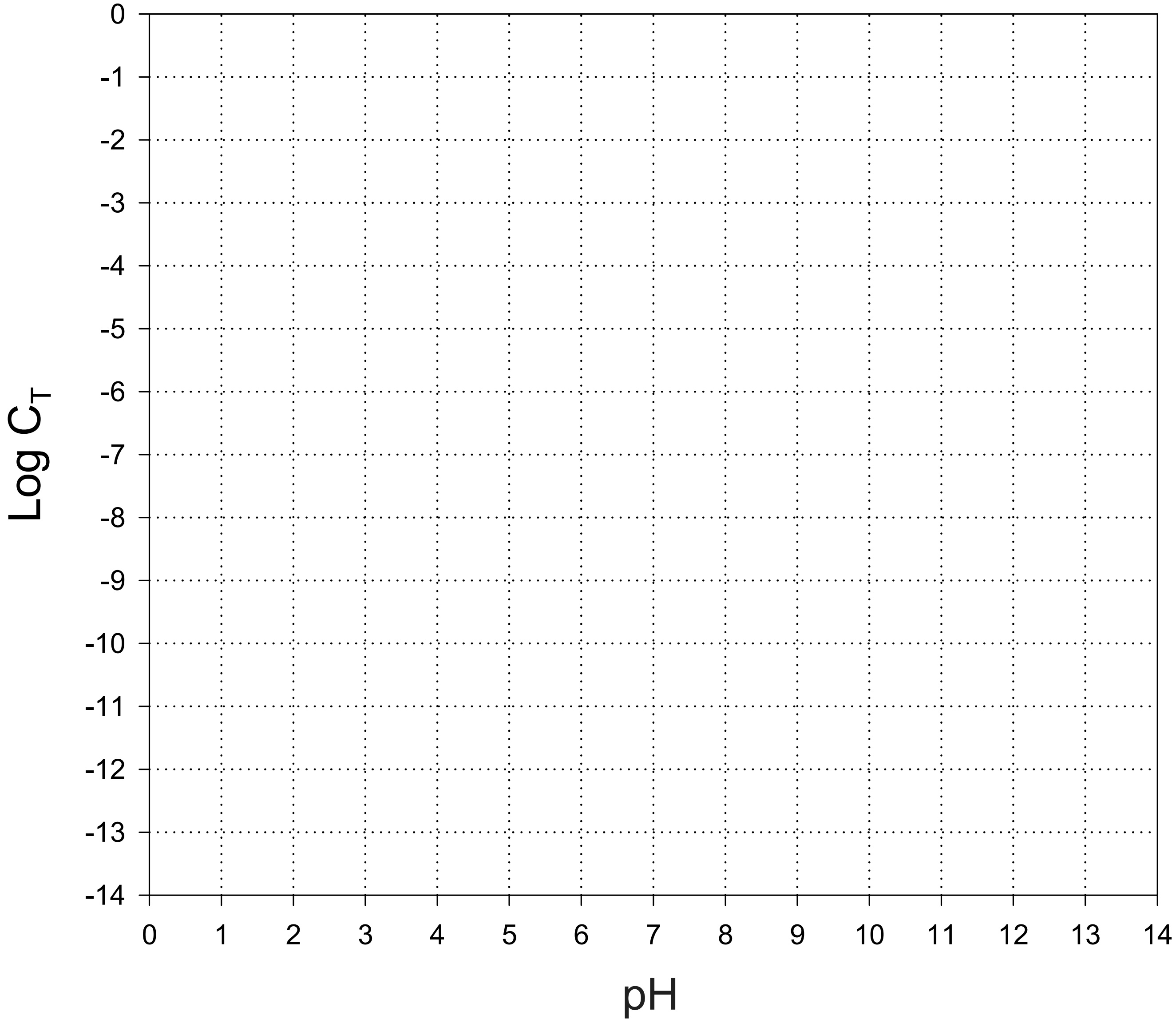
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