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

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^{-3} moles of Sodium Phosphate Dibasic (Na_2HPO_4). Graph paper is attached to this exam for this purpose.

Prepare graph with pK_s = 2.15, 7.2 and 12.3; and $C_T = 10^{-3}$

PBE:

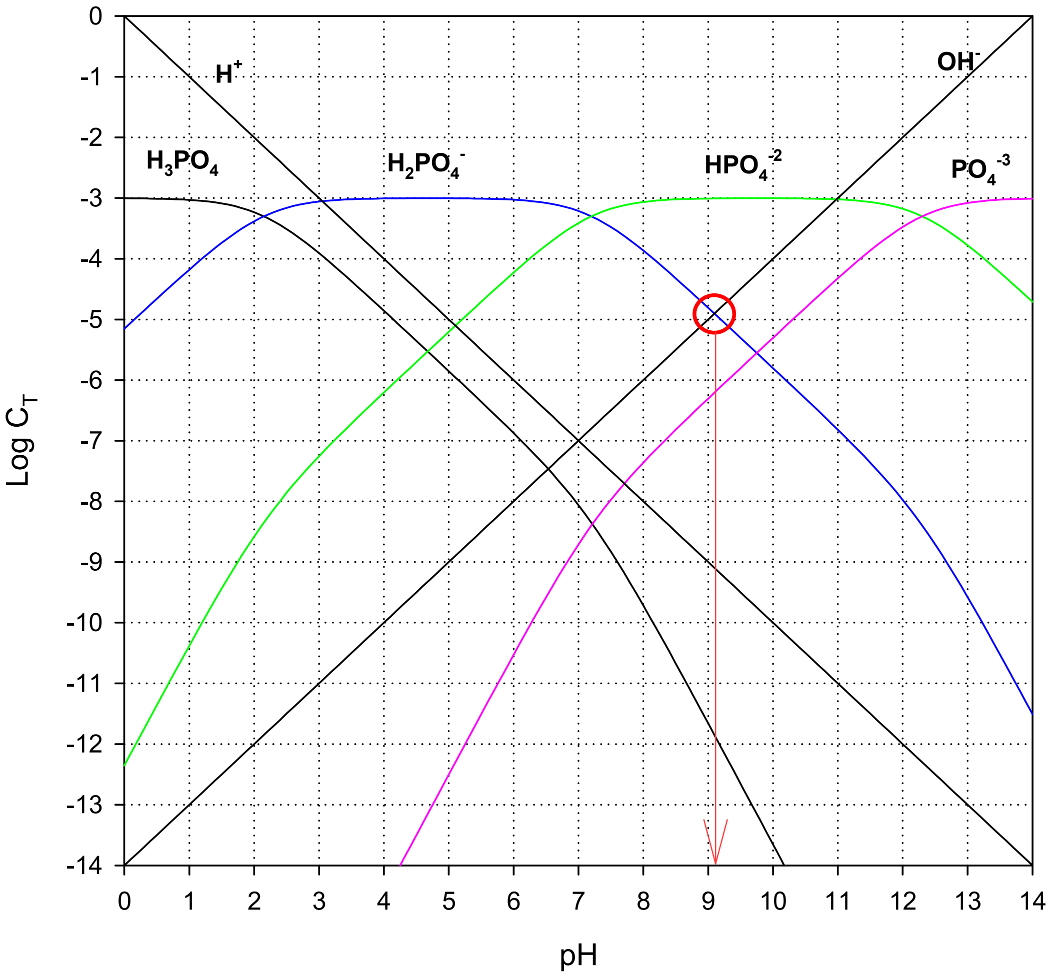
$$2[H_3PO_4] + [H_2PO_4^-] + [H^+] = [OH^-] + [PO_4^{-3}]$$

which reduces to:

$$[H_2PO_4^-] = [OH^-]$$

Equality (intersection) occurs at **pH ~ 9.1**

Species	pC	C (Molar)
H^+	9.1	7.9E-10
OH^-	4.9	1.3E-05
H_3PO_4	11.85	1.4E-12
$H_2PO_4^-$	4.9	1.3E-05
HPO_4^{-2}	3.0	1.0E-03
PO_4^{-3}	6.2	6.3E-07
Na^+	2.7	2.0E-03



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.

Prepare graph for acetate system with $pK_a = 4.75$; and $C_T = 10^{-2}$, and superimpose this on the prior phosphate graph with $pK_s = 2.15$, 7.2 and 12.3; and $C_T = 10^{-3}$

PBE:

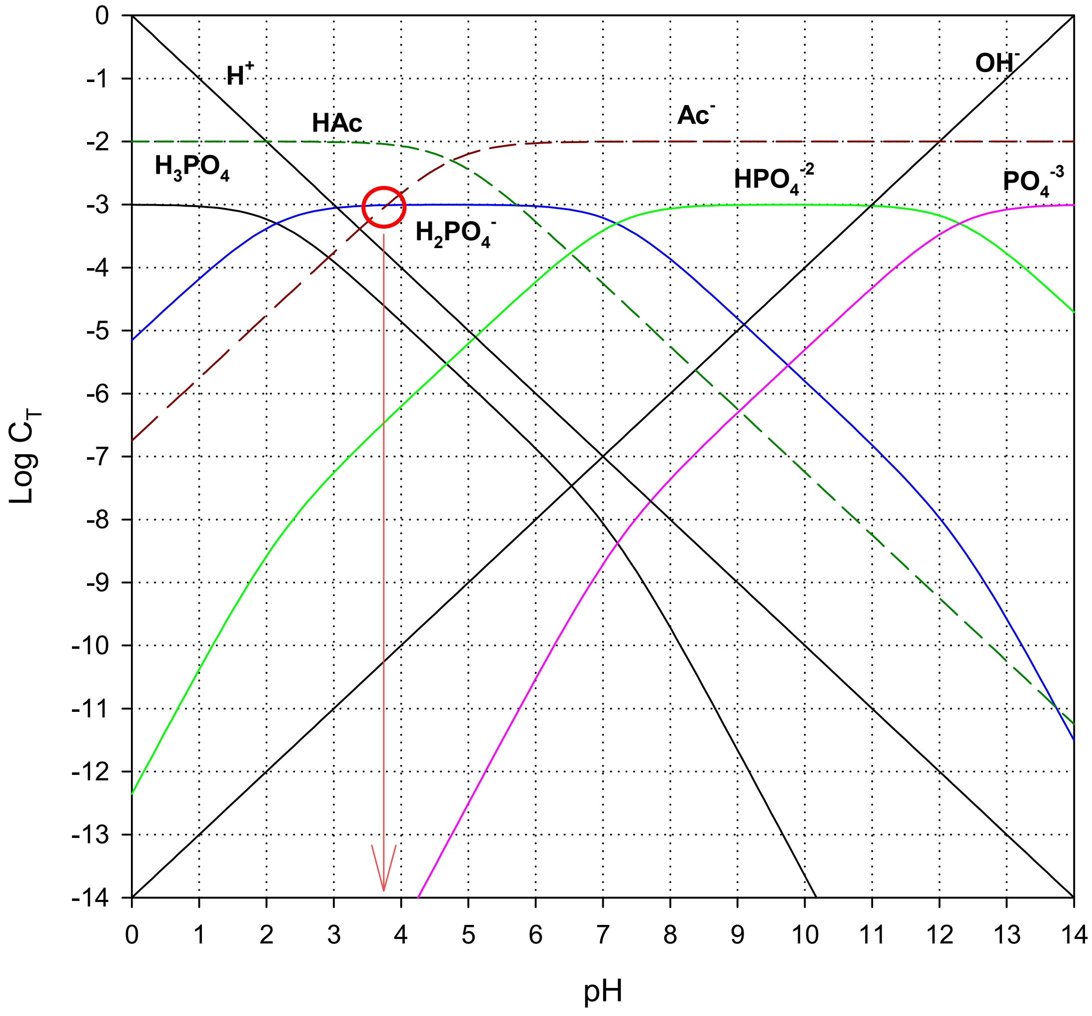
$$2[H_3PO_4] + [H_2PO_4^-] + [H^+] = [OH^-] + [PO_4^{-3}] + [Ac^-]$$

which reduces to:

$$[H_2PO_4^-] = [Ac^-]$$

Equality (intersection) occurs at **pH ~ 3.8**

Species	pC	C (Molar)
H^+	3.8	1.6E-04
OH^-	10.2	6.3E-11
H_3PO_4	4.65	2.2E-05
$H_2PO_4^-$	3.0	1.0E-03
HPO_4^{-2}	6.4	4.0E-07
PO_4^{-3}	14.0	1.0E-14
Na^+	2.7	2.0E-03
HAc	2.0	1.0E-02
Ac^-	3.0	1.0E-03



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

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^{-1} moles of Sodium Fluoride (NaF) in 1 Liter of water

note that from the attached table: $pK_a = 3.2$ for HF, so that $pK_b = 14-3.2 = 11.8$
and thus $K_b = 1.58x10^{-12}$
pC = 1

A. Make basic solution assumption, which leads to:

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

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

$$[OH^-] = \frac{-1.58x10^{-12} + \sqrt{(1.58x10^{-12})^2 + 4x1.58x10^{-12}(0.1)}}{2}$$

$[OH^-] = 3.98 \text{ x } 10^{-7}$
pOH = 6.4
pH = 7.6

and to get the HF and F- concentrations, you can use the alpha values or re-derive them as follows:

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

$$K_a = \frac{[H^+](C - [HF])}{[HF]}$$

$$K_a[HF] = [H^+]C - [H^+][HF]$$
$$K_a[HF] + [H^+][HF] = [H^+]C$$
$$[HF] = \frac{[H^+]C}{K_a + [H^+]}$$

Species	pC	C (Molar)
H^+	8.1	7.9E-9
OH^-	5.9	1.2E-06
HF	5.9	1.2E-06
F^-	1.0	1.0E-01
Na+	1.0	1.0E-01

this looks OK, but you could also have made the strong acid/weak base assumption

$$[OH^-] = \sqrt{K_b C + K_w}$$

$$[OH^-] = \sqrt{K_b C + K_w}$$

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

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

$[OH^-] = 1.2589 \times 10^{-6}$
pOH = 5.90
pH = 8.10

b. the same solution in "a" to which you have also added 0.5×10^{-1} moles of hydrochloric acid (HCl).

Now recognize that this is addition of a strong acid to a base, and the ratios are 0.5 M/1 M, so that you have titrated half of the F- to HF (i.e., f=0.5). From here you can use the Henderson Hasslebach equation. The simple answer is that the pH is just the pKa:

Species	pC	C (Molar)
H^+	3.2	6.3E-4

OH^-	10.8	1.6E-11
HF	1.3	5.0E-02
F^-	1.3	5.0E-02
Cl^-	1.3	5.0E-02

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

First determine the ionic strength.

Species	pC	C (Molar)	Mz^2
H^+	8.1	7.9E-9	7.9E-9
OH^-	5.9	1.2E-06	1.2E-06
HF	5.9	1.2E-06	0
F^-	1.0	1.0E-01	1.0E-01
Na^+	1.0	1.0E-01	1.0E-01
		Sum	2.0E-01
		Ionic Strength	1.0E-01

Use the Guntelberg approximation:

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

log f = -0.5*(0.01/1.01) =

$$logf = -0.5\frac{\sqrt{0.1}}{1+\sqrt{0.1}}$$

$$logf = -1.2x10^{-1}$$

$$f = 0.758$$

so, taking the simplest solution to 3a.

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

$$K_b = \frac{\{HF\}\{OH^-\}}{\{F^-\}}$$

And now parsing the activities into the product of the molar concentration and the activity coefficients

$$K_b = \frac{[HF]\gamma_{HF}[OH^-]\gamma_{OH-}}{[F^-]\gamma_{F-}}$$

And we define conditional constants:

$$cK_b \equiv \frac{[HF][OH^-]}{[F^-]}$$

So that

$$cK_b \equiv \frac{[HF][OH^-]}{[F^-]} = K_b \frac{\gamma_{F-}}{\gamma_{OH-}}$$

But both activities coefficients are the same using extended DH, so OH- is unchanged by the ionic strength, now consider the other values:

$$K_w = \{H^+\}\{OH^-\}$$

$$K_w = [H^+]\gamma_{H+}[OH^-]\gamma_{OH-}$$

$$[H^+] = \frac{K_w}{[OH^-]\gamma_{OH-}\gamma_{H+}}$$

Molar concentration

So, this means [H+] = $7.9\text{x}10^{-9}/(0.758)^2 = 1.37\text{x}10^{-8}$

pH = 7.86 when expressed as molar conc

Activity

So, this means [H+] = $7.9\text{x}10^{-9}/0.758 = 1.04\text{x}10^{-8}$

pH = 7.98 when expressed as activity

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

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

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

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

d. __F__ 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. __T__ The principle of electroneutrality is always observed in aqueous solutions

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

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

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

j. __F__ The value of α_o plus α_1 must always equal 1 for any diprotic acid system.

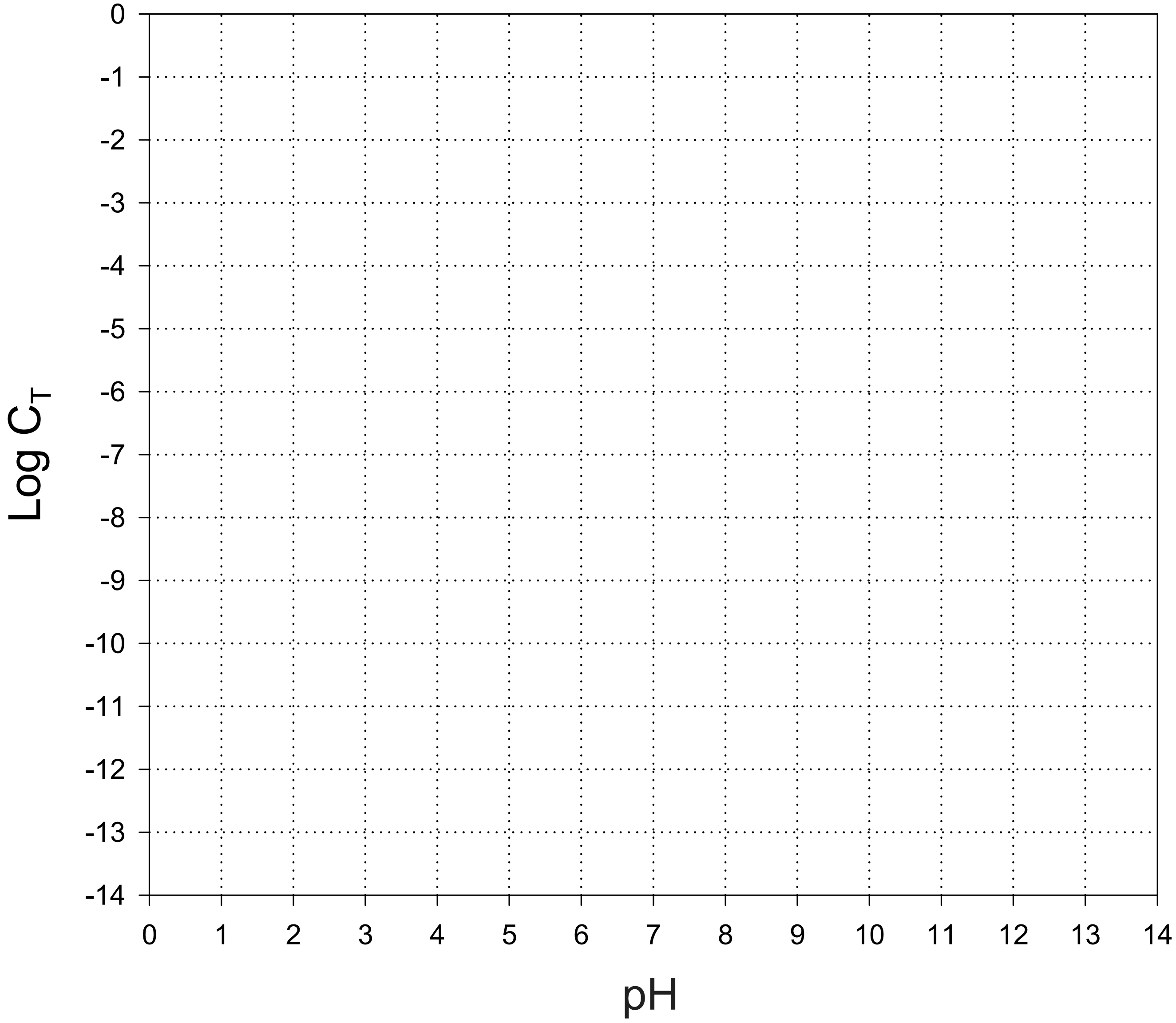
Selected Acidity Constants (Aqueous Solution, 25°C, I = 0)

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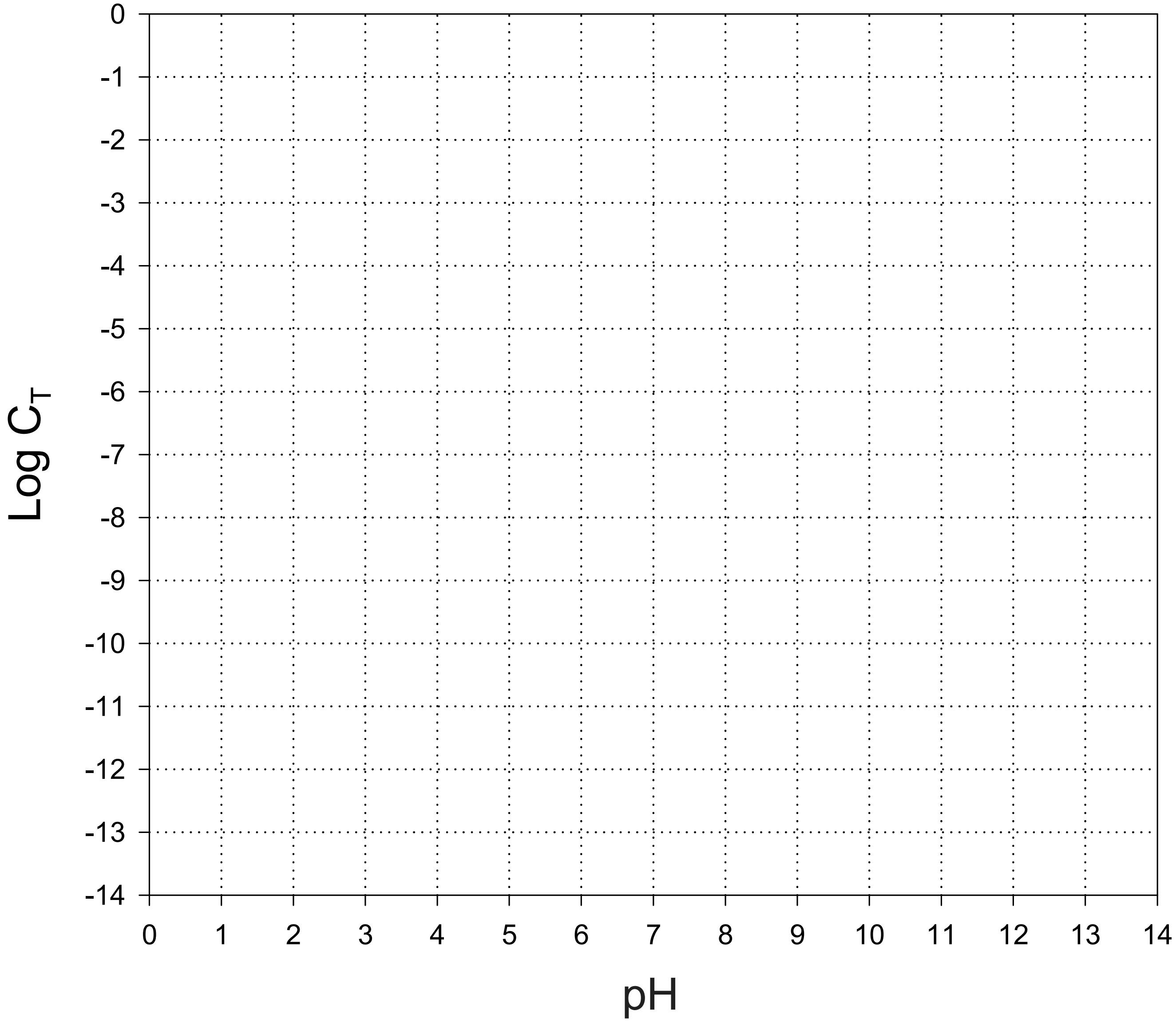

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