

CHEM 2800

Second Midterm Test Thursday March 22, 2018

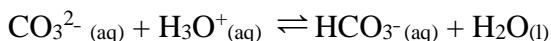
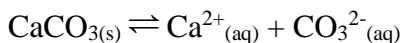
Part A. Answer each question briefly with a few sentences or equations as necessary (5 marks each).

1. State and explain two examples of the properties of water that demonstrate how unique a substance it is.

Many possibilities here.

- Ice floats (the density of ice is lower than that of liquid water, the density of water goes through a maximum at 4°C)
- Liquid water is an excellent solvent for polar or charged species
- Water can act as an acid or a base (it is amphoteric)
- Water can be oxidized or reduced
- Water has a large enthalpy of vapourization
- ...

2. Why are limestone-lined lakes protected from acidification? Show the relevant reactions (2 marks) and explain (3 marks).

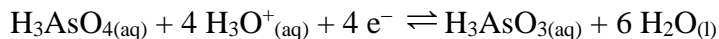


Although the limestone (calcium carbonate) is not very soluble, there are some carbonate ions present. These react with hydronium ions, reducing the acidity, and causing more limestone to dissolve, so the buffering action of the carbonate ion is always present.

3. Why is the alkalinity of 0.05 $\text{Na}_2\text{CO}_{3(aq)}$ greater than that of 0.05 M $\text{NaHCO}_{3(aq)}$? Show the relevant reactions (2 marks) and explain (3 marks).

Alkalinity is a measure of the ability of a water sample to neutralize acidity, i.e. to react with hydronium ions. The $\text{CO}_3^{2-}_{(aq)}$ ion from $\text{Na}_2\text{CO}_{3(aq)}$ can neutralize two hydronium ions according to the reaction $\text{CO}_3^{2-}_{(aq)} + 2 \text{H}_3\text{O}^+_{(aq)} \rightleftharpoons \text{H}_2\text{CO}_{3(aq)} + 2 \text{H}_2\text{O}_{(l)}$. The $\text{HCO}_3^-_{(aq)}$ ion from $\text{NaHCO}_{3(aq)}$ can neutralize only one hydronium ion according to the reaction $\text{HCO}_3^-_{(aq)} + \text{H}_3\text{O}^+_{(aq)} \rightleftharpoons \text{H}_2\text{CO}_{3(aq)} + \text{H}_2\text{O}_{(l)}$.

3. Explain how increasing the pH will affect the toxicity of arsenic in a water sample, knowing that the following reaction happens:



The As atom in $\text{H}_3\text{AsO}_4(\text{aq})$ is at a +5 oxidation state. The As atom in $\text{H}_3\text{AsO}_3(\text{aq})$ is at a +3 oxidation state, which is more toxic. Increasing the pH will shift the reaction to the left, so the toxicity will decrease.

5. Do the following reactions involve acid–base chemistry, redox chemistry, or both? Tick the appropriate boxes.

	Acid–Base Chemistry	Redox Chemistry
$\text{CH}_4(\text{aq}) + 12 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + 9 \text{H}_3\text{O}^+(\text{aq}) + 8 \text{e}^-$	✓	✓
$\text{Fe}^{2+}(\text{aq}) \rightleftharpoons \text{Fe}^{3+}(\text{aq}) + \text{e}^-$		✓
$\text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CO}_3^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$	✓	
$\text{HS}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{H}_2\text{S}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	✓	
$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightleftharpoons \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	✓	✓

6. Why is a free metal ion (e.g. $\text{Cd}^{2+}(\text{aq})$) more toxic than a complexed one (e.g. $\text{CdCl}_3^-(\text{aq})$)?

The free metal ion is able to cross cell membranes more easily.

Part B. Answer B1 and B2. Answer Either B3 or B4 (the best of these two will be counted). 20 marks each.

B1. K_{sp} for $PbCrO_{4(s)}$ in water is 2.8×10^{-13} . Calculate the solubility of $PbCrO_{4(s)}$ (in mol/L) in:

(a) Calculate the solubility of $PbCrO_{4(s)}$ (in mol/L) in pure water.

$$K_{sp} = 2.8 \times 10^{-13} = [Pb^{2+}_{(aq)}][CrO_4^{2-}_{(aq)}]$$

$$\text{But solubility} = [Pb^{2+}_{(aq)}] = [CrO_4^{2-}_{(aq)}] = (2.8 \times 10^{-13})^{1/2} = 5.29 \times 10^{-7} \text{ M}$$

(b) Calculate the solubility of $PbCrO_{4(s)}$ (in mol/L) in 0.1 M $Na_2SO_{4(aq)}$.

$$\begin{aligned} I &= \frac{1}{2} \sum b_i z_i^2 \\ &= \frac{1}{2} (0.2(+1)^2 + 0.1(-2)^2) = 0.3 \end{aligned}$$

$$\begin{aligned} \log_{10} \gamma_{\pm} &= -0.51 |z_+ z_-| \left[\frac{I^{1/2}}{1 + I^{1/2}} - 0.3(I) \right] \\ &= -0.51 |(2)(-2)| \left[\frac{0.3^{1/2}}{1 + 0.3^{1/2}} - 0.3(0.3) \right] \\ &= -0.538 \end{aligned}$$

$$\gamma_{\pm} = 10^{-0.538} = 0.290$$

$$\begin{aligned} K_{sp} &= a_{Pb^{2+}} a_{CrO_4^{2-}} \\ &= \gamma_{\pm} b_{Pb^{2+}} \gamma_{\pm} b_{CrO_4^{2-}} \\ &= \gamma_{\pm}^2 b_{Pb^{2+}} b_{CrO_4^{2-}} \end{aligned}$$

$$\begin{aligned} b_{Pb^{2+}} b_{CrO_4^{2-}} &= \frac{K_{sp}}{\gamma_{\pm}^2} \\ &= \frac{2.8 \times 10^{-13}}{(0.290)^2} \\ &= 3.34 \times 10^{-12} \end{aligned}$$

$$\begin{aligned} \text{solubility} &= b_{Pb^{2+}} = (3.34 \times 10^{-12})^{1/2} \\ &= 1.83 \times 10^{-6} \text{ m} \\ &= 1.83 \times 10^{-6} \text{ M} \end{aligned}$$

B2. H₂S is a weak acid with $K_{a1} = 1.0 \times 10^{-7}$ and $K_{a2} = 1.0 \times 10^{-19}$. Calculate the fractions of H₂S(aq), HS⁻(aq) and S²⁻(aq) present in water at pH = 7.5

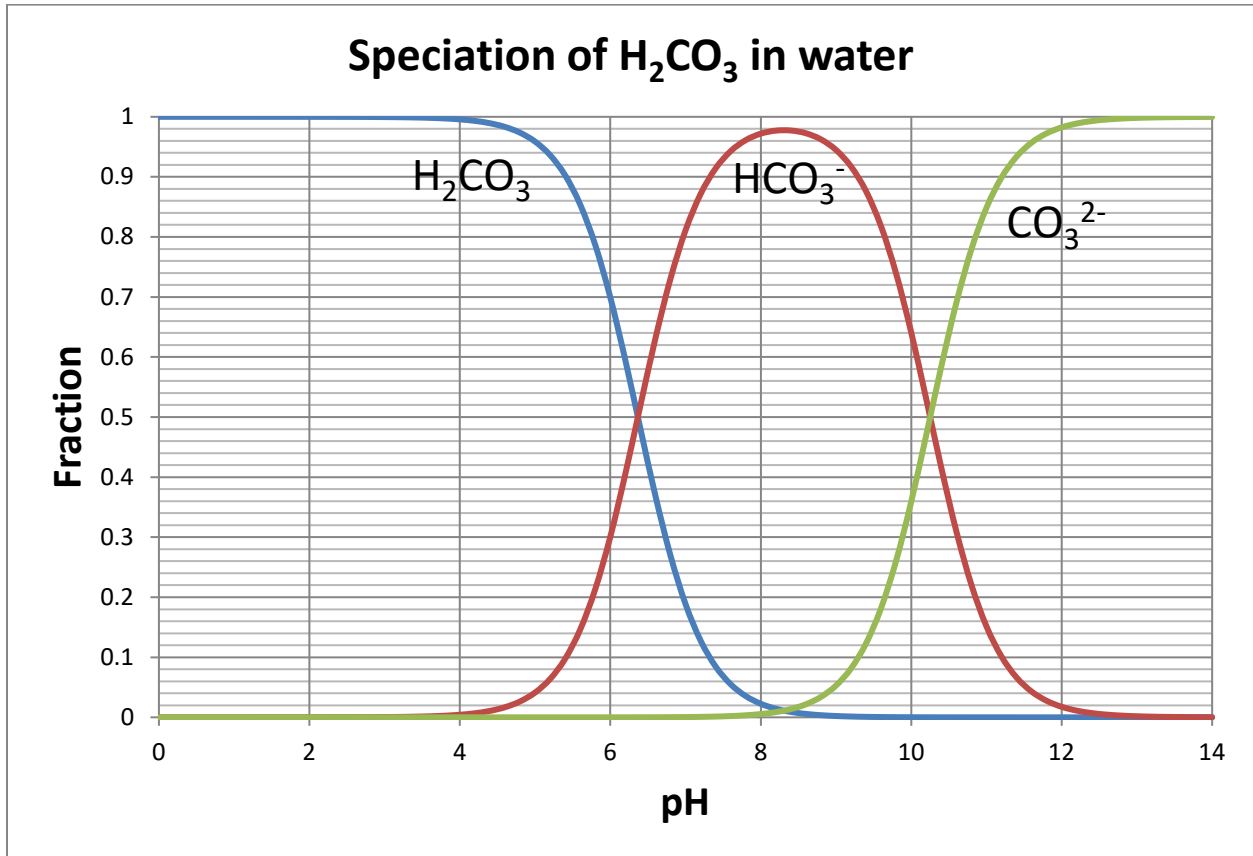
At pH = 7.5, $[\text{H}_3\text{O}^+_{(\text{aq})}] = 10^{-7.5} = 3.16 \times 10^{-8} \text{ M}$

$$\begin{aligned}\alpha_{\text{H}_2\text{S}} &= \frac{[\text{H}_3\text{O}^+_{(\text{aq})}]^2}{[\text{H}_3\text{O}^+_{(\text{aq})}]^2 + K_{a1}[\text{H}_3\text{O}^+_{(\text{aq})}] + K_{a1}K_{a2}} \\ &= \frac{(3.16 \times 10^{-8})^2}{(3.16 \times 10^{-8})^2 + 1.0 \times 10^{-7}(3.16 \times 10^{-8}) + 1.0 \times 10^{-7}(1.0 \times 10^{-19})} \\ &= \frac{9.99 \times 10^{-16}}{4.16 \times 10^{-15}} \\ &= 0.240\end{aligned}$$

$$\begin{aligned}\alpha_{\text{HS}^-} &= \frac{K_{a1}[\text{H}_3\text{O}^+_{(\text{aq})}]}{[\text{H}_3\text{O}^+_{(\text{aq})}]^2 + K_{a1}[\text{H}_3\text{O}^+_{(\text{aq})}] + K_{a1}K_{a2}} \\ &= \frac{1.0 \times 10^{-7}(3.16 \times 10^{-8})}{4.16 \times 10^{-15}} \\ &= 0.760\end{aligned}$$

$$\begin{aligned}\alpha_{\text{S}^{2-}} &= \frac{K_{a1}K_{a2}}{[\text{H}_3\text{O}^+_{(\text{aq})}]^2 + K_{a1}[\text{H}_3\text{O}^+_{(\text{aq})}] + K_{a1}K_{a2}} \\ &= \frac{1.0 \times 10^{-7}(1.0 \times 10^{-19})}{4.16 \times 10^{-15}} \\ &= 0.00\end{aligned}$$

- B3.** A water sample has a total carbonate species concentration of 0.1 M, pH = 10.0, $[\text{HS}^-_{(\text{aq})}] = 0.05 \text{ M}$ and $[\text{Al}^{3+}] = 0.005 \text{ M}$. Use this information and the speciation graph below to calculate the alkalinity of this sample.



At pH 10.0, we see from the graph that $\alpha(\text{HCO}_3^-_{(\text{aq})}) = 0.64$ and $\alpha(\text{CO}_3^{2-}_{(\text{aq})}) = 0.36$. If the total carbonate species concentration is 0.1 M, then

$$[\text{HCO}_3^-_{(\text{aq})}] = 0.1(0.64) = 0.064 \text{ M}$$

and

$$[\text{CO}_3^{2-}_{(\text{aq})}] = 0.1(0.36) = 0.036 \text{ M}$$

$$\text{At pH} = 10.0, [\text{H}_3\text{O}^+_{(\text{aq})}] = 1.0 \times 10^{-10} \text{ M}$$

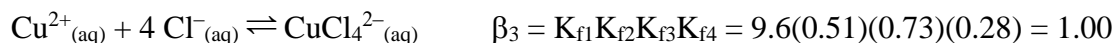
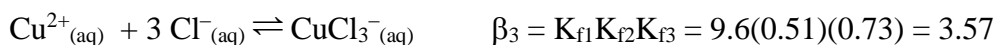
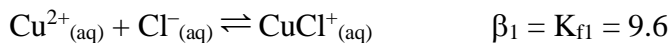
$$\text{pOH} = 14 - \text{pH} = 4.0, \text{ thus } [\text{OH}^-] = 1.0 \times 10^{-4} \text{ M}$$

$$\text{Alkalinity} = [\text{OH}^-] + [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{HS}^-] - [\text{H}_3\text{O}^+] - 3 [\text{Al}^{3+}]$$

$$= 10^{-4} \text{ M} + 0.064 \text{ M} + 2 (0.036 \text{ M}) + 0.05 \text{ M} - 10^{-10} \text{ M} - 3(0.005 \text{ M}) = 0.17 \text{ M}$$

B4. Formation constants for complexes between the $\text{Cu}^{2+}_{(\text{aq})}$ ion and the chloride ion are:

$K_{f1} = 9.6$, $K_{f2} = 0.51$, $K_{f3} = 0.73$, $K_{f4} = 0.28$. If the total copper concentration in a water sample is 0.001 M, and $[\text{Cl}^{-}_{(\text{aq})}] = 0.2$ M, calculate the concentrations of $\text{Cu}^{2+}_{(\text{aq})}$, $\text{CuCl}^{+}_{(\text{aq})}$, $\text{CuCl}_{2(\text{aq})}$, $\text{CuCl}_{3}^{-}_{(\text{aq})}$ and $\text{CuCl}_{4}^{2-}_{(\text{aq})}$ (all in mol/L).



As shown in class, the concentration of uncomplexed metal ion is:

$$\begin{aligned} [\text{Cu}^{2+}_{(\text{aq})}] &= \frac{C_{\text{Cu}}}{1 + \beta_1[\text{Cl}^{-}_{(\text{aq})}] + \beta_2[\text{Cl}^{-}_{(\text{aq})}]^2 + \beta_3[\text{Cl}^{-}_{(\text{aq})}]^3 + \beta_4[\text{Cl}^{-}_{(\text{aq})}]^4} \\ &= \frac{0.001 \text{ M}}{1 + 9.6(0.2) + 4.90(0.2)^2 + 3.57(0.2)^3 + 1.00(0.2)^4} \\ &= 3.18 \times 10^{-4} \text{ M} \end{aligned}$$

$$[\text{CuCl}^{+}_{(\text{aq})}] = \beta_1[\text{Cu}^{2+}_{(\text{aq})}][\text{Cl}^{-}_{(\text{aq})}] = 9.6(3.18 \times 10^{-4})(0.2) = 6.11 \times 10^{-4} \text{ M}$$

$$[\text{CuCl}_{2(\text{aq})}] = \beta_2[\text{Cu}^{2+}_{(\text{aq})}][\text{Cl}^{-}_{(\text{aq})}]^2 = 4.90(3.18 \times 10^{-4})(0.2)^2 = 6.23 \times 10^{-5} \text{ M}$$

$$[\text{CuCl}_{3}^{-}_{(\text{aq})}] = \beta_3[\text{Cu}^{2+}_{(\text{aq})}][\text{Cl}^{-}_{(\text{aq})}]^3 = 3.57(3.18 \times 10^{-4})(0.2)^3 = 9.08 \times 10^{-6} \text{ M}$$

$$[\text{CuCl}_{4}^{2-}_{(\text{aq})}] = \beta_4[\text{Cu}^{2+}_{(\text{aq})}][\text{Cl}^{-}_{(\text{aq})}]^4 = 1.00(3.18 \times 10^{-4})(0.2)^4 = 5.09 \times 10^{-7} \text{ M}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$1 \text{ bar} = 10^5 \text{ Pa}$$

$$g_0 = 9.80 \text{ m s}^{-2}$$

$$0^\circ\text{C} = 273.15 \text{ K}$$

$$N_{\text{Av}} = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$1 \text{ Pa m}^3 = 1 \text{ J}$$

$$c = 3.00 \times 10^8 \text{ m s}^{-1}$$

$$h = 6.63 \times 10^{-34} \text{ J s}$$

IA (1)												VIIIA (18)					
1 H 1.008	IIA (2)											III A (13)	IV A (14)	VA (15)	VIA (16)	VII A (17)	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	III B (3)	IV B (4)	VB (5)	VIB (6)	VII B (7)	(8)	VIII B (9)	(10)	IB (11)	II B (12)	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.70	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (269)	109 Mt (268)	110 Ds (269)	111 Rg (280)	112 Cp (277)	113 Nh (286)	114 Fl (289)	115 Mc (290)	116 Lv (293)	117 Ts (294)	118 Og (294)

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)