

PROBLEM #4 - 25 points USE UNITS of METERS SECONDS and GRAMS

WRITE ANSWERS TO THE FOLLOWING QUESTIONS ON THE NEXT PAGE, SHOW YOUR WORK. These questions are repeated on the next page for your convenience.

NOTE: THIS IS THE SAME WATER ANALYSIS THAT YOU EVALUATED IN PROBLEM #3

- (5pts) All of the alkalinity is comprised of HCO_3^- . Why does the value for alkalinity differ from the concentration of HCO_3^- ? Provide calculations to support your answer.
- (12pts) Is the water saturated with calcium sulfate (CaSO_4)? Provide calculations to support your answer.
- (5pts) Will calcium carbonate (CaCO_3) precipitate from this sample? Provide calculations to support your answer.
- (3pts) Will this water cause corrosion? Provide calculations to support your answer.

TEMP	15	C
HCO_3^-	198.4	mg/L
Cl^-	114.9	mg/L
K^+	9.9	mg/L
Ca^{+2}	74.4	mg/L
Mg^{+2}	18.1	mg/L
Na^+	130	mg/L
SO_4^{-2}	227.1	mg/L
Total Dissolved Solids	733	mg/L
Alkalinity as CaCO_3	162.6	mg/L
pH	7.37	units

PROVIDE CALCULATIONS AND ANSWERS TO PROBLEM 4 HERE

a) (5pts) All of the alkalinity is comprised of HCO_3^- . Why does the value for alkalinity differ from the concentration of HCO_3^- ? Provide calculations to support your answer.

alkalinity expressed as equivalents of $\text{CaCO}_3 = [\text{HCO}_3^-] \frac{\frac{9}{\text{eq}} \text{CaCO}_3}{\frac{9}{\text{eq}} \text{HCO}_3^-} = 198.4 \frac{\text{mg}}{\text{L}} \frac{50 \frac{\text{g}}{\text{eq}}}{61 \frac{\text{g}}{\text{eq}}} = 163 \frac{\text{mg}}{\text{L}}$

b) (12pts) Is the water saturated with calcium sulfate (CaSO_4)? Provide calculations to support your answer.

Ionic strength = $2.5 \times 10^{-5} (\text{TDS}) = 2.5 \times 10^{-5} (773 \frac{\text{mg}}{\text{L}}) = 0.0183$

divalent $\log \gamma = \frac{-0.5 z^2 \sqrt{I}}{1 + \sqrt{I}} = \frac{-0.5 (2)^2 \sqrt{0.0183}}{1 + \sqrt{0.0183}} = -0.238 \quad \gamma = 0.58$

IAP = (activity Ca^{+2}) (activity SO_4) = $0.58 \cdot 1.86 \times 10^{-3} \frac{\text{M}}{\text{L}} \cdot 0.58 \cdot 2.37 \times 10^{-3} \frac{\text{M}}{\text{L}} = 1.5 \times 10^{-6}$

$\Delta G = \Delta fG_{\text{Ca}^{+2}} + \Delta fG_{\text{SO}_4} - \Delta fG_{\text{CaSO}_4} = 553.6 \frac{\text{kJ}}{\text{M}} + 744.6 \frac{\text{kJ}}{\text{M}} - 1321.8 \frac{\text{kJ}}{\text{M}} = -24.2 \frac{\text{kJ}}{\text{M}}$

$\log K_{sp} = \frac{-\Delta rG}{2,303 RT} = \frac{-23670 \frac{\text{J}}{\text{M}}}{2,303 \cdot 8.314 \frac{\text{J}}{\text{KM}} \cdot 288.15 \text{K}} = -4.29 \quad K_{sp} = 4 \times 10^{-5}$

$IAP < K_{sp}$

$SI < 0 = \log \frac{IAP}{K_{sp}} = -1.45$

} so water is not saturated with Ca

c) (5pts) Will calcium carbonate (CaCO_3) precipitate from this sample? Provide calculations to support your answer.

univalent $\log \gamma = \frac{-0.5 (1) \sqrt{0.0183}}{1 + \sqrt{0.0183}} = \gamma = 0.87$

$pH_s = -\log \left(\frac{K_2 \gamma_{\text{Ca}} [\text{Ca}] \gamma_{\text{HCO}_3} [\text{HCO}_3]}{K_{sp}} \right) = -\log \left(\frac{3.7 \times 10^{-11} (0.58) 1.86 \times 10^{-3} (0.87) 3.75 \times 10^{-3}}{6.03 \times 10^{-9}} \right)$

$= -\log \frac{1.13 \times 10^{-16}}{6.03 \times 10^{-9}} = -\log 1.87 \times 10^{-8} \quad pH_s = 7.73$
 $LI = pH - pH_s = 7.37 - 7.73 = -0.36$ < 0 so scale is not expected

d) (3pts) Will this water cause corrosion? Provide calculations to support your answer.

Ryzner Index = $2pH_s - pH = 2(7.73) - 7.37 = 8.08$
 somewhat corrosive

Substance (form)	Gibbs $\Delta_f G$ (kJ)mol ⁻¹
Al (s)	0
Al ₂ SiO ₅ (kyanite)	-2443.88
Al ₂ SiO ₅ (andalusite)	-2442.66
Al ₂ SiO ₅ (sillimanite)	-2440.99
Ar (g)	0
C (graphite)	0
C (diamond)	2.9
CH ₄ (g)	-50.72
C ₂ H ₆ (g)	-32.82
C ₃ H ₈ (g)	-23.49
C ₂ H ₅ OH (l)	-174.78
C ₆ H ₁₂ O ₆ (glucose)	-910
CO (g)	-137.17
CO ₂ (g)	-394.36
CO ₃ ²⁻ (aq)	-527.81
H ₂ CO ₃ (aq)	-623.08
HCO ₃ ⁻ (aq)	-586.77
Ca ²⁺ (aq)	-553.58
CaCO ₃ (calcite)	-1128.8
CaSO ₄ (anhydrite)	-1321.8
CaCO ₃ (aragonite)	-1127.8
CaCl ₂ (s)	-748.1
Cl ₂ (g)	0
Cl ⁻ (aq)	-131.23
Cu (s)	0
Fe (s)	0
H ₂ (g)	0
H (g)	203.25
H ⁺ (aq)	0
H ₂ O (l)	-237.13
H ₂ O (g)	-228.57
He (g)	0
Hg (l)	0
N ₂ (g)	0
NH ₃ (g)	-16.45
Na ⁺ (aq)	-261.91
NaCl (s)	-384.14
NaAlSi ₃ O ₈ (albite)	-3711.5
NaAlSi ₂ O ₆ (jadeite)	-2852.1
Ne (g)	0
O ₂ (g)	0
O ₂ (aq)	16.4
OH ⁻ (aq)	-157.24
Pb (s)	0
PbO ₂ (s)	-217.33
PbSO ₄ (s)	-813
SO ₄ ²⁻ (aq)	-744.53
HSO ₄ ⁻ (aq)	-755.91
SiO ₂ (α quartz)	-856.64
H ₄ SiO ₄ (aq)	-1307.67

Values of R	Units (V·P·T ⁻¹ ·n ⁻¹)
8.314472	J·K ⁻¹ ·mol ⁻¹
0.0820574587	L·atm·K ⁻¹ ·mol ⁻¹
83.14472	cm ³ ·bar·mol ⁻¹ ·K ⁻¹
8.20574587 × 10 ⁻⁵	m ³ ·atm·K ⁻¹ ·mol ⁻¹
8.314472	cm ³ ·MPa·K ⁻¹ ·mol ⁻¹
8.314472	L·kPa·K ⁻¹ ·mol ⁻¹
8.314472	m ³ ·Pa·K ⁻¹ ·mol ⁻¹
62.36367	L·mmHg·K ⁻¹ ·mol ⁻¹
62.36367	L·Torr·K ⁻¹ ·mol ⁻¹
83.14472	L·mbar·K ⁻¹ ·mol ⁻¹
0.08314472	L·bar·K ⁻¹ ·mol ⁻¹
1.987	cal·K ⁻¹ ·mol ⁻¹
6.132440	lbf·ft·K ⁻¹ ·g·mol ⁻¹
10.73159	ft ³ ·psi·°R ⁻¹ ·lb·mol ⁻¹
0.7302413	ft ³ ·atm·°R ⁻¹ ·lb·mol ⁻¹
998.9701	ft ³ ·mmHg·K ⁻¹ ·lb·mol ⁻¹
8.314472 × 10 ⁷	erg·K ⁻¹ ·mol ⁻¹

heavy scale	scale	neutral	corrosive	very corrosive
5.5	6.2	6.8	8.5	
RI				

Carbonate Equilibrium Constants as a Function of Temperature

T, °C	K _m	K ₁	K ₂	K _{sp}
5		3.02 x 10 ⁻⁷	2.75 x 10 ⁻¹¹	8.13 x 10 ⁻⁹
10		3.46 x 10 ⁻⁷	3.24 x 10 ⁻¹¹	7.08 x 10 ⁻⁹
15		3.80 x 10 ⁻⁷	3.72 x 10 ⁻¹¹	6.03 x 10 ⁻⁹
20		4.17 x 10 ⁻⁷	4.17 x 10 ⁻¹¹	5.25 x 10 ⁻⁹
25	1.58 x 10 ⁻³	4.47 x 10 ⁻⁷	4.68 x 10 ⁻¹¹	4.57 x 10 ⁻⁹
40		5.07 x 10 ⁻⁷	6.03 x 10 ⁻¹¹	3.09 x 10 ⁻⁹
60		5.07 x 10 ⁻⁷	7.24 x 10 ⁻¹¹	1.82 x 10 ⁻⁹

$$K_m = \frac{[H_2CO_3]}{[CO_2]_{aq}} \quad K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \quad K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

K_{sp} = Solubility product for CaCO₃

1 H Hydrogen 1.00794	2 He Helium 4.002602						
3 Li Lithium 6.941	4 Be Beryllium 9.012182	5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050	13 Al Aluminum 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973761	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29
55 Cs Cesium 132.90545	56 Ba Barium 137.327	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)