

CE59700 008 -- Spring 2009
EXAM 1 Practice (Example) Questions

Some useful equations and constants that will be provided to you:

$$I = 0.5 \sum c_i z_i^2$$

$$-\log \gamma_i = 0.5 z_i^2 (I^{1/2} / (I^{1/2} + 1) - 0.3I)$$

$$K_w = 10^{-14} \text{ M}^2$$

$$\beta (M) = 2.3 ([H^+] + [OH^-] + [HA][A^-]/([HA] + [A^-])) = d[OH^-] / dpH$$

$$\text{alk (eq/L)} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

WHERE APPROPRIATE, GIVE UNITS ON ALL YOUR ANSWERS

If not stated, assume [] = { }

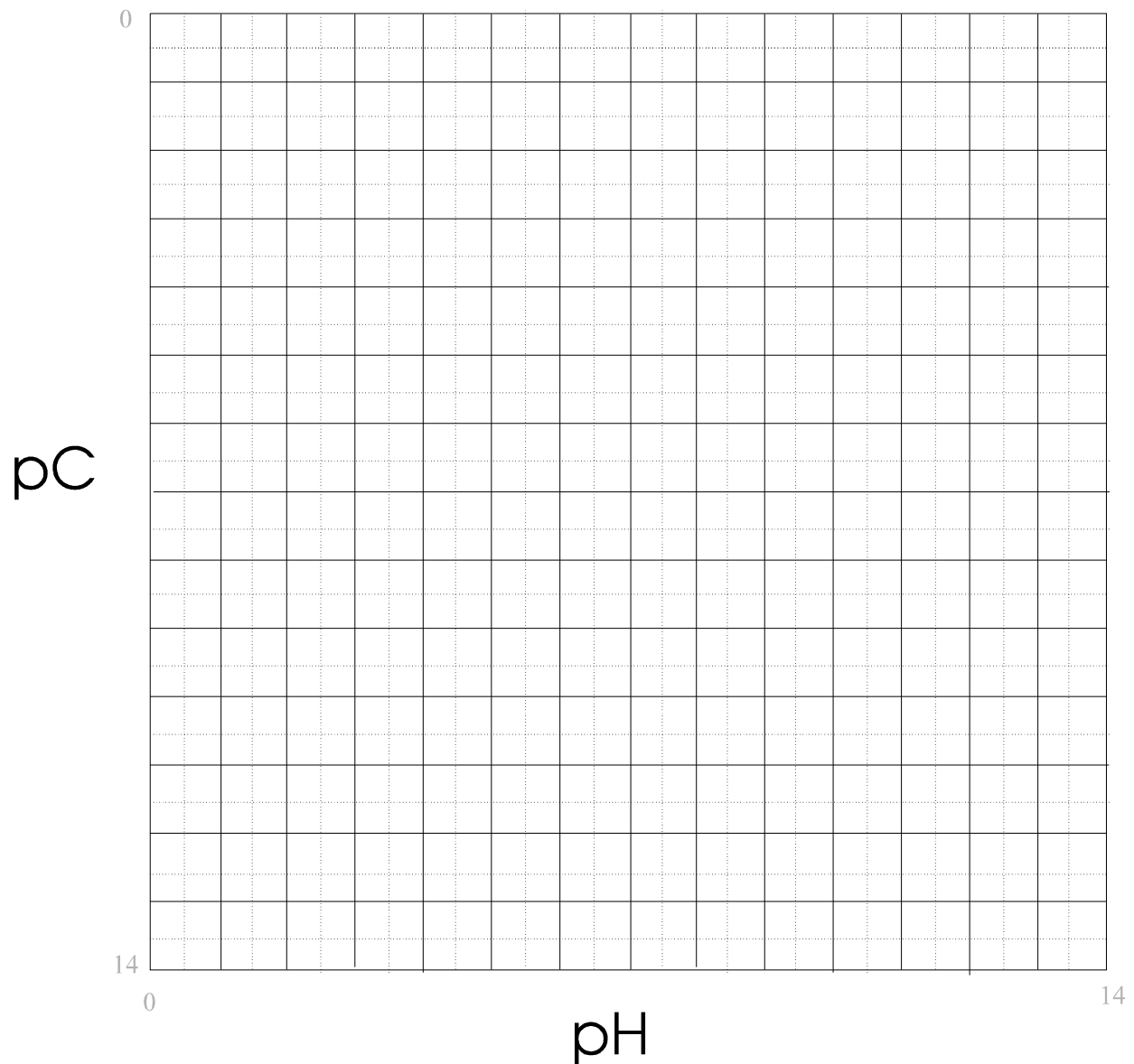
1. What is the pH of pure water that is in equilibrium with carbon dioxide (CO₂) in air. Recall equilibrium with air means [H₂CO₃^{*}]_{aq} = 10^{-4.9} M. Also pK_a (H₂CO₃^{*}) = 6.3, pK_a (HCO₃⁻) = 10.3. Start by writing a set of necessary and sufficient equations. List all unknowns.
2. Write all necessary and non-redundant mass action and mass balance (including the C.B.) equations necessary to solve for all species in a solution composed of pure water to which known amounts of Na₂HPO₄ and H₃PO₄ are simultaneously added. Assume the pK_a values for H₃PO₄, H₂PO₄⁻, and HPO₄²⁻ are all known (and C_t^{Na} is also known). List the unknowns and number the necessary (and nonredundant) equations. You do not need to combine or rearrange – simply list.
3. Aqueous hydrogen sulfide can speciate to form H₂S, HS⁻, and S²⁻ in water. Assume these are the only sulfide species (*i.e.*, no complexes) and calculate α_{HS^-} as a function C_T^{H₂S}, [H⁺], and the K_a's for H₂S and HS⁻. Note: no terms other than C_T, H⁺ and the two K_a's should appear in your answer. Start with necessary mass action and mass balance equations, and then combine.
4. To pure water, 10⁻³ M Na₂CO₃ is added (pK_{a,2} = 10.3 for HCO₃⁻; pK_{a,1} = 6.3 for H₂CO₃^{*}). The system is closed.
 - (a) Write all mass action equations that apply to this water.
 - (b) Write all mass balance equations that apply to this water.
 - (c) Write the proton condition.
 - (d) Solve for the pH making assumptions that only two species concentrations are negligible in equations. What is the CO₃²⁻ concentration?

5. $C_T^{\text{HOCl}} = 0.001 \text{ M}$.

(a) Draw lines for $p[\text{H}^+]$, $p[\text{OH}^-]$, $p[\text{HOCl}]$, $p[\text{OCl}^-]$, and C_T^{HOCl} on the pC-pH diagram. $pK_a(\text{HOCl}) = 7.5$

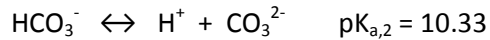
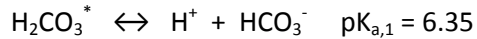
(b) What is the proton condition of pure water to which only HOCl has been added? Solving graphically, what is the pH of this water?

(c) What is the proton condition of pure water to which only NaOCl (bleach) has been added? Solving graphically, what is the pH of this water?



6. Find the concentrations of all species in a 0.01 M solution of NH_4Cl . A line through a species is a good statement of an assumption; however, check all assumptions. NH_4^+ has a pK_a of 9.3. Neglect ionic strength effects.

7. The following equilibria apply to the carbonate system:



A 100 mL sample of a natural water has a pH of 8.0, and requires 5 mL of 0.02 M H_2SO_4 to reach pH 4.5 (the methyl orange end-point).

(a) Calculate the total alkalinity in units of meq/L.

(b) Assuming that the carbonate species account for most of the anions in this water, and assuming that Ca^{2+} and Mg^{2+} are the predominant cations, what is a good estimate of the ionic strength?

9. To 1 L pure water, 10 mmoles CaCl_2 and 10 mmoles NaCl are added. Calculate (1) the ionic strength, and (2) the activity of Calcium ions in this solution.

10. Known amounts of Na_2HPO_4 and CaHCO_3 are added to the same 1 L of pure water. Write the set of necessary and sufficient equations that can be used to solve for all unknown species in this water sample. List and number the unknown species and number the necessary equations. Assume both salts completely dissolve and that no aqueous phase metal-ligand complexes form.