

WHERE APPROPRIATE, GIVE UNITS ON ALL YOUR ANSWERS  
and assume  $[ ] = \{ \}$  in all cases

Some useful equations and constants:

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

$$-\log \mathbf{g}_i = 0.5 z_i^2 \left( I^{1/2} / (I^{1/2} + 1) - 0.3I \right)$$

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

$$A = ECl$$

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

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


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**1. (10 pts)** What is the pH of pure water that is in equilibrium with carbon dioxide (CO<sub>2</sub>) in air. Recall equilibrium with air means  $[H_2CO_3^*]_{\text{aq}} = 10^{-5} \text{ M}$ . Also  $pK_a(H_2CO_3^*) = 6.3$ ,  $pK_a(HCO_3^-) = 10.3$ . Start by writing a set of necessary and sufficient equations. List all unknowns.

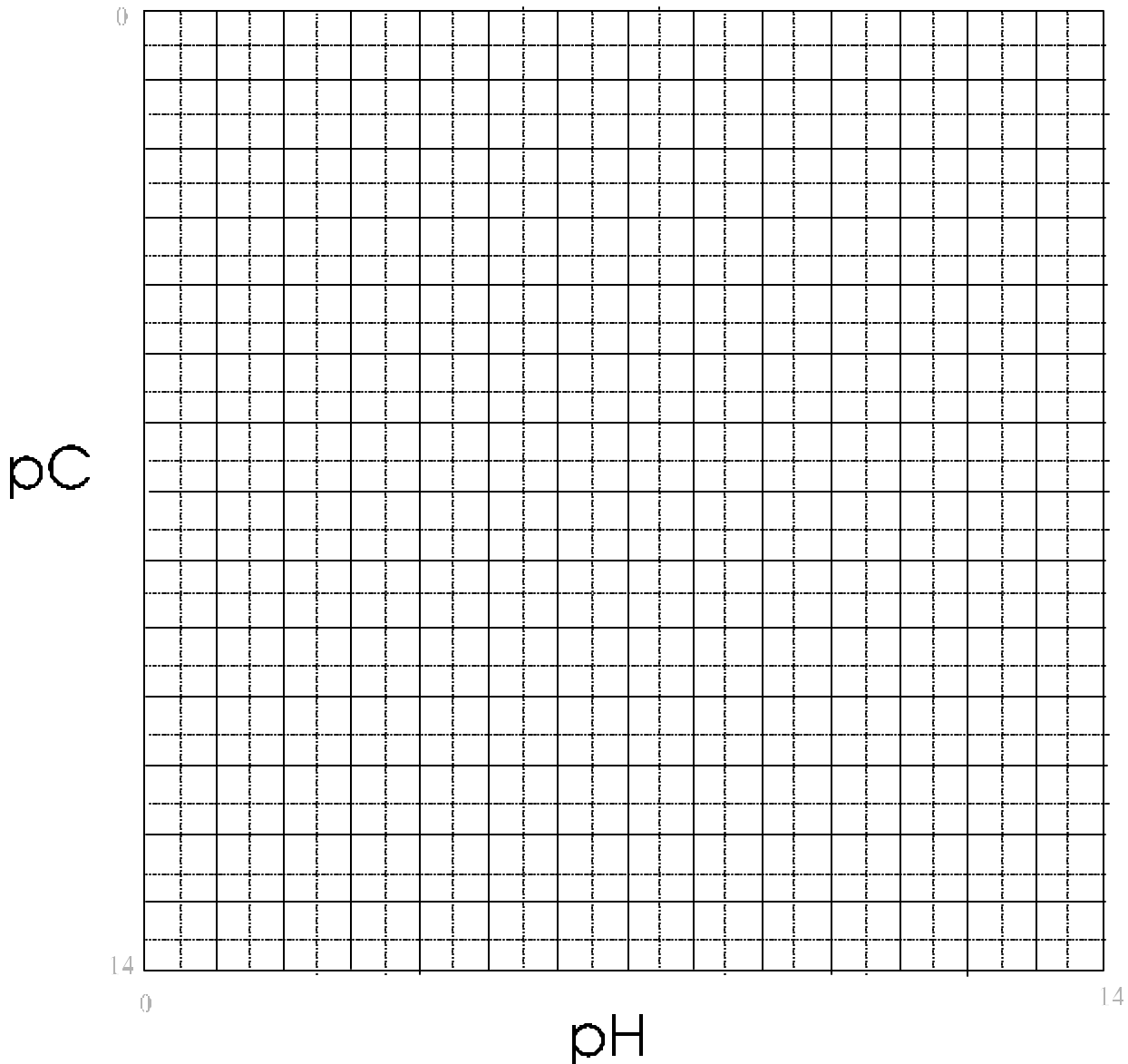
**2. (20 pts)** Write all necessary and non-redundant mass action and mass balance (including the C.B.) equations necessary to solve for all species in a solution composed of pure water to which known amounts of  $\text{Na}_2\text{HPO}_4$  and  $\text{H}_3\text{PO}_4$  are simultaneously added. Assume the  $\text{pK}_a$  values for  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{HPO}_4^{2-}$  are all known (and  $C_t^{\text{Na}}$  is also known). List the unknowns and number the necessary (and nonredundant) equations. You do not need to combine or rearrange – simply list.

3. (20 pts)  $C_T^{\text{HOCl}} = 0.001 \text{ M}$ .

(a) Draw lines for  $p[\text{H}^+]$ ,  $p[\text{OH}^-]$ ,  $p[\text{HOCl}]$ ,  $p[\text{OCl}^-]$ , and  $C_T^{\text{HOCl}}$  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?



**4. (15 pts)** Aqueous hydrogen sulfide can speciate to form  $\text{H}_2\text{S}$ ,  $\text{HS}^-$ , and  $\text{S}^{2-}$  in water. Assume these are the only sulfide species (*i.e.*, no complexes) and calculate  $\alpha_{\text{HS}^-}$  as a function  $C_{\text{T}}^{\text{H}_2\text{S}}$ ,  $[\text{H}^+]$ , and the  $K_{\text{a}}$ 's for  $\text{H}_2\text{S}$  and  $\text{HS}^-$ . Note: no terms other than  $C_{\text{T}}$ ,  $\text{H}^+$  and the two  $K_{\text{a}}$ 's should appear in your answer. Start with necessary mass action and mass balance equations, and then combine.

**5. (5 pts)** What is the beer-Lambert law (define all terms) and what are its applications?

**6. (20 pts)** To pure water,  $10^{-3}$  M  $\text{Na}_2\text{CO}_3$  is added ( $\text{pK}_{\text{a},2} = 10.3$  for  $\text{HCO}_3^-$ ;  $\text{pK}_{\text{a},1} = 6.3$  for  $\text{H}_2\text{CO}_3^*$ ). 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  $\text{CO}_3^{2-}$  concentration?