

Key for Review Problems for Equilibrium Unit

Problem 1. Many small, highly charged cations are slightly acidic when dissolved in water. For example, a 0.10 M solution of AlCl_3 has a pH of 2.9. The reaction responsible for the acidity is



where $\text{Al}(\text{H}_2\text{O})_6^{3+}$ is a metal-ligand complex of Al^{3+} and H_2O . Determine the K_a value for $\text{Al}(\text{H}_2\text{O})_6^{3+}$.

Answer. Set this problem up with an ICE table, taking the initial concentration of $\text{Al}(\text{H}_2\text{O})_6^{3+}$ as 0.10 M and the equilibrium concentration of H_3O^+ as 1.26×10^{-3} M (a pH of 2.9). Knowing that $[\text{H}_3\text{O}^+]_{\text{eq}}$ gives the change in concentration for $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and $\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}$ and gives their respective equilibrium concentrations as 9.87×10^{-2} M and 1.26×10^{-3} M. Substituting into the K_a expression gives its value as 1.61×10^{-5} .

Problem 2. Quinine, $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$, is an alkaloid derived from a tree that grows in tropical rain forests. In addition to being an ingredient in tonic water, quinine also is used in the treatment of malaria. Like all alkaloids, quinine is a sparingly soluble weak base; its $\text{p}K_b$ is 5.1 and its solubility is 1.00 g in 190 L of water. What is the pH of a saturated solution of quinine?

Answer. This problem is simply finding the pH of a weak base. The initial concentration of quinine is given by its solubility and is 1.62×10^{-5} M. The K_b for quinine is 7.94×10^{-6} . Setting up an ICE table leaves you with

$$7.94 \times 10^{-6} = \frac{x^2}{1.62 \times 10^{-5} - x}$$

A simplification here will not work (try it and see). Solving exactly via the quadratic equation gives $x = [\text{OH}^-] = 8.05 \times 10^{-6}$ M and a pH of 8.91.

Problem 3. Magnesium hydroxide, $\text{Mg}(\text{OH})_2$, is a slightly soluble ionic compound with a K_{sp} of 1.8×10^{-11} . It is often used in antacid products, such as milk of magnesia, to reduce stomach acidity. It is also an important industrial source of magnesium. (a) What is the molar solubility of $\text{Mg}(\text{OH})_2$ in pure water? (b) Sea water is an important industrial source of magnesium with typical concentrations of 5.4×10^{-2} M. What is the minimum pH at which $\text{Mg}(\text{OH})_2$ begins to precipitate from sea water?

Answer. For part (a), an ICE table leads to $K_{sp} = (x)(2x)^2 = 4x^3$. Solving for x gives 1.65×10^{-4} M, which is the concentration of Mg^{2+} at equilibrium. This also is the molar solubility since each mole of $\text{Mg}(\text{OH})_2$ produces a mole of Mg^{2+} . For part (b), the question is what $[\text{OH}^-]$ is needed to initiate precipitation when the concentration of Mg^{2+} is 5.4×10^{-2} M. Here we work directly from the K_{sp} ; thus

$$K_{sp} = 1.8 \times 10^{-11} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (5.4 \times 10^{-2})[\text{OH}^-]^2$$

Solving gives $[\text{OH}^-]$ as 1.83×10^{-5} M or a pH of 9.26. Note that you are not setting up an ICE table because there is no equilibrium in the absence of $\text{Mg}(\text{OH})_2$.

Problem 4. An important industrial reaction is the Haber process in which N_2 and H_2 react to make ammonia. What is frustrating about this reaction is that at low temperatures, where the reaction's equilibrium constant is very large, the reaction's rate is too slow to be of practical use. At higher temperatures the reaction is faster, but the equilibrium constant is less favorable. (a) Based on the above statement, do you expect that the Haber process is exothermic or endothermic? Briefly explain and then check your answer by calculating ΔH . (b) An inventor claims to have discovered a new catalyst that increases the percentage of nitrogen and hydrogen that is converted to ammonia by the Haber process without needing to change the temperature. A member of your family is eager to invest in the inventor's discovery. Explain to your relative why this is a bad idea. (c) To maximize the yield of ammonia, would it be better to run this reaction in a small volume container or a large volume container? Explain.

Answer For (a), K is smaller at higher temperatures, which makes heat a product and the reaction is exothermic. The value of ΔH° for $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$ is $-92.2 \text{ kJ/mol}_{\text{rxn}}$. For (b), a catalyst can make a reaction go faster (kinetics) but it cannot change the reaction's equilibrium constant (thermodynamics). For (c), a smaller container is the best choice. Decreasing volume has the effect of increasing the concentration of all three gases. This makes Q smaller than K and the reaction responds by shifting toward the product side.

Problem 5. Virtually all investigations in cell biology and biochemistry are carried out in buffered aqueous solutions. Imagine you are studying an enzyme that is active only between a pH of 7.1 and 7.4 and that you need to prepare 1.50 L of a phosphate buffer at a pH of 7.25, limiting the total concentration of phosphate species to 0.085 M. The following compounds are available to you: 14.75 M H_3PO_4 , KH_2PO_4 and K_2HPO_4 . Which two phosphate species will you use? What quantities of each will you use? How many moles of H_3O^+ and of OH^- can this buffer absorb without the pH falling below 7.1 or above 7.4?

Answer. The $\text{p}K_a$ values for H_3PO_4 are 2.15, 7.20 and 12.38. A buffer with a pH of 7.25 requires using $\text{p}K_{a2}$, or a mixture of H_2PO_4^- and HPO_4^{2-} . Using the Henderson-Hasselbach equation

$$7.25 = 7.20 + \log \left(\frac{\text{moles HPO}_4^{2-}}{\text{moles H}_2\text{PO}_4^-} \right)$$

and solving gives the ratio $\frac{\text{moles HPO}_4^{2-}}{\text{moles H}_2\text{PO}_4^-}$ as 1.122. The maximum concentration of phosphate species is 0.085 M. Since the buffer is to be 1.5 liters, this is 0.1275 moles, or

$$\text{moles HPO}_4^{2-} + \text{moles H}_2\text{PO}_4^- = 0.1275$$

Solving the last two equations simultaneously gives moles H_2PO_4^- as 0.06008 and moles HPO_4^{2-} as 0.06742, which corresponds to 8.18 g of KH_2PO_4 and 11.7 g of K_2HPO_4 .

Moving the pH to 7.1 requires the addition of a strong acid (H_3O^+), converting some HPO_4^{2-} to H_2PO_4^- ; thus

$$7.1 = 7.20 + \log \left(\frac{\text{moles HPO}_4^{2-} - x}{\text{moles H}_2\text{PO}_4^- + x} \right)$$

where x is the moles of H_3O^+ . Solving gives the moles of H_3O^+ as 0.0110.

Moving the pH to 7.4 requires the addition of a strong base (OH^-), converting some H_2PO_4^- to HPO_4^{2-} ; thus

$$7.4 = 7.20 + \log \left(\frac{\text{moles HPO}_4^{2-} + x}{\text{moles H}_2\text{PO}_4^- - x} \right)$$

where x is the moles of OH^- . Solving gives the moles of OH^- as 0.0721.

Problem 6. The solubility of the mineral Ag_2CrO_4 depends upon pH because chromate, CrO_4^{2-} is a weak base. For this problem limit yourself to the following equilibrium reactions:

- $\text{Ag}_2\text{CrO}_4(s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{CrO}_4^{2-}(aq)$ for which $K_{sp} = 2.57 \times 10^{-12}$
- $\text{H}_2\text{CrO}_4(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCrO}_4^-(aq)$ for which $K_{a1} = 1.6$
- $\text{HCrO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CrO}_4^{2-}(aq)$ for which $K_{a2} = 3.1 \times 10^{-7}$

Calculate the molar solubility for Ag_2CrO_4 at pH levels buffered to 4.0, 5.0, 8.0, and 9.0. Be sure to clearly indicate the reaction responsible for the molar solubility of Ag_2CrO_4 at each pH level and to clearly show your work.

Answer. The $\text{p}K_a$ values for H_2CrO_4 are -0.204 and 6.51, so at pH levels of 8.0 and 9.0 the solubility is controlled by the K_{sp} reaction only; thus

$$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (2x)^2(x) = 2.57 \times 10^{-12}$$

$$4x^3 = 2.57 \times 10^{-12}$$

$$x = [\text{CrO}_4^{2-}] = S_{\text{Ag}_2\text{CrO}_4} = 8.63 \times 10^{-5}$$

At pH levels of 4.0 and 5.0, the important species is HCrO_4^- and solubility is controlled by the reaction



for which

$$K_{eq} = \frac{[\text{Ag}^+]^2[\text{HCrO}_4^-]}{[\text{H}_3\text{O}^+]} = \frac{K_{sp}}{K_{a2}} = 8.29 \times 10^{-6}$$

At a pH of 4.0, we have

$$8.29 \times 10^{-6} = \frac{(2x)^2(x)}{1.00 \times 10^{-4}}$$

which gives

$$x = [\text{HCrO}_4^-] = S_{\text{Ag}_2\text{CrO}_4} = 5.92 \times 10^{-4}$$

and at a pH of 5.0 we have

$$8.29 \times 10^{-6} = \frac{(2x)^2(x)}{1.00 \times 10^{-5}}$$

which gives

$$x = [\text{HCrO}_4^-] = S_{\text{Ag}_2\text{CrO}_4} = 2.75 \times 10^{-4}$$