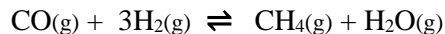


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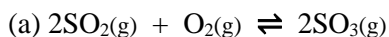
1. (a) At a certain temperature, an equilibrium mixture contains 0.478 mol CH₄, 0.478 mol H₂O, 1.522 mol CO, and 1.566 mol H₂, in a 10.0-L sealed reaction vessel. Calculate the equilibrium constant K_c for the following reaction: $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$

(b) For the same mixture, what is the equilibrium constant K_c for the reaction?

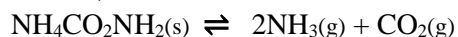


(c) For reaction (b), is the reaction at equilibrium if the same mixture were placed in a 1.00-L vessel at the same temperature? Explain. In which direction the equilibrium would shift if the mixture is not at equilibrium?

2. At a certain temperature, an equilibrium mixture contains the following substances:
[O₂] = 4.2 x 10⁻³ M, [SO₂] = 3.8 x 10⁻³ M, and [SO₃] = 4.1 x 10⁻³ M. Calculate the equilibrium constant K_c for the following reactions:



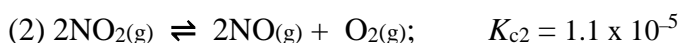
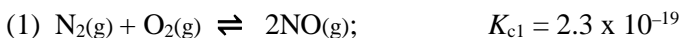
3. Ammonium carbamate (NH₄CO₂NH₄) decomposes when heated and, in a sealed vessel, the following equilibrium is established,



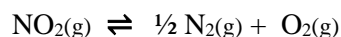
with $K_p = 2.9 \times 10^{-3}$ at 25°C. (a) Calculate the total gas pressure at equilibrium. (c) If 5.00 g NH₄CO₂NH₂ was introduced into an evacuated 5.00-L reaction vessel and the above equilibrium is established at 25°C, how many grams of solid NH₄CO₂NH₂ still remains at equilibrium?

(R = 0.0821 L.atm/mol.K)

4. Given the equilibrium constants for the following reactions:



Calculate K_c for the following reaction at the same temperature.



5. Identify each of the following as strong acid or weak acid:

(a) HBr_(aq): _____ (b) HCl_(aq): _____ (c) HF_(aq): _____

(d) HCOOH: _____ (e) CH₃COOH: _____ (f) HNO₃: _____

(g) H₂SO₄: _____ (h) H₃PO₄: _____ (i) HClO₂: _____

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6. In each of the following pairs of acids, indicate the one with stronger conjugate bases:
- (a) HNO_2 and HNO_3 (b) H_3PO_3 and H_2SO_3 (c) HOCl and HOBr
(d) H_2SO_3 and HClO_3 (e) $\text{CH}_3\text{CO}_2\text{H}$ and $\text{CCl}_3\text{CO}_2\text{H}$ (f) H_2S and H_2Se
7. (a) Determine the pH and percent ionization of 0.20 M nitrous acid, HNO_2 ($K_a = 4.0 \times 10^{-4}$).
(b) A solution of 0.10 M HClO_2 (chlorous acid) has the same pH as that of 0.030 M HCl . What is the K_a of chlorous acid.
8. (a) Calculate the pH of 0.10 M NH_3 solution ($K_{b(\text{NH}_3)} = 1.8 \times 10^{-5}$), which ionizes as follows:
$$\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$$

(b) What is the value of K_a for NH_4^+ in the following equilibrium:
$$\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) ;$$

Calculate the pH of 0.10 M NH_4Cl solution. ($K_w = 1.0 \times 10^{-14}$)
9. Predict whether each of the following solutions is neutral, acidic or basic? In each case, write the chemical equation to support your reasoning.
- (a) $\text{NaF}(\text{aq})$
(b) $\text{KNO}_3(\text{aq})$
(c) $\text{Al}(\text{NO}_3)_3(\text{aq})$
(d) $\text{Na}_2\text{CO}_3(\text{aq})$
10. Buffer solutions of specific pH may be prepared by mixing solutions of weak acid with salts of their conjugate bases in the right proportions. Suppose the following solutions are available to make buffer solutions of various pH's:
0.10 M $\text{CH}_3\text{CO}_2\text{H}$ ($K_a = 1.8 \times 10^{-5}$); 0.10 M NaCH_3CO_2 ;
0.10 M HNO_2 ($K_a = 4.0 \times 10^{-4}$); 0.10 M NaNO_2 ;
0.10 M NH_3 ($K_b = 1.8 \times 10^{-5}$); 0.10 M NH_4Cl ;
0.10 M NaH_2PO_4 ($K_a = 6.3 \times 10^{-8}$); and 0.10 M Na_2HPO_4 ;
- (a) Which pair of solution would you use to prepare buffer solutions with the following pH's?
(i) pH = 3.50; (ii) pH = 5.00; (iii) pH = 7.50; (iv) pH = 9.00
- (b) What is the molar ratio of conjugate base to acid: (i) in a buffer solution with pH = 5.00; (ii) in a buffer solution with pH = 9.00?

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11. A buffer solution is prepared by dissolving 5.1 g sodium acetate (NaCH_3CO_2 ; molar mass = 82.03 g/mol) in 100.0 mL of 0.20 M acetic acid, $\text{CH}_3\text{CO}_2\text{H}$ ($K_a = 1.8 \times 10^{-5}$). (a) Calculate molar ratio of acetate ion to acetic acid, $[\text{CH}_3\text{CO}_2^-]/[\text{CH}_3\text{CO}_2\text{H}]$, and the buffer pH. (b) What is the pH of the resulting solution if 0.012 mole of HCl is added without altering the total volume of solution?

12. A 40.0-mL sample of 0.100 M hypochlorous acid (HClO) is titrated with 0.100 M NaOH. The following pH values were measured at various points in the titration:

Volume of NaOH added (mL):	0.0	10.0	20.0	30.0	40.0
pH of solution mixture:	4.35	7.05	7.50	?	?

- (a) Determine the K_a values of formic acid: (i) using initial pH (that is, pH before NaOH is added), and (ii) using pH value after 20.0 mL of NaOH is added. Calculate the average K_a value. (b) Using the average K_a , predict the pH of the solution after 30.0 mL of 0.100 M NaOH is added. (c) Determine the pH of the solution at equivalent point (after 40.0 mL of 0.100 M NaOH has been added).
13. A 50.0-mL solution of 0.100 M potassium hydrogen phthalate (KHP; (HP^- has $K_a \sim 4.0 \times 10^{-6}$) is titrated with 0.100 M of NaOH. Calculate the pH of the solution:
- before NaOH is added;
 - after 25.0 mL of NaOH is added;
 - after 50.0 mL of NaOH is added, and
 - After 75.0 mL of NaOH is added.
14. For each of the following acid-base titrations in which each solution used is approximately 0.10 M, determine the expected pH at equivalent points, and indicate which acid-base indicator, phenolphthalein ($pK_a \sim 9$) or methyl red ($pK_a \sim 5$) may be used to determine the end-point.
- $\text{HCl(aq)} - \text{NaOH(aq)}$ titration
 - $\text{KHP(aq)} - \text{NaOH(aq)}$ titration; (HP^- has $K_a \sim 4.0 \times 10^{-6}$)
 - $\text{NH}_3\text{(aq)} - \text{HCl(aq)}$ titration; (K_b of $\text{NH}_3 = 1.8 \times 10^{-5}$; K_a of $\text{NH}_4^+ = 5.6 \times 10^{-10}$)
15. Saturated solution of silver phosphate contains 7.4×10^{-3} g of Ag_3PO_4 in 1.00 L of solution. (a) What is the solubility of Ag_3PO_4 in mole per liter? (b) Calculate the K_{sp} for Ag_3PO_4 . (Molar mass of $\text{Ag}_3\text{PO}_4 = 418.67$ g/mol)

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16. Saturated solution of magnesium hydroxide, Mg(OH)_2 , has $\text{pH} = 10.42$. (a) Determine the solubility (in mol/L) and the K_{sp} of Mg(OH)_2 . (b) What is the solubility of Mg(OH)_2 in solution that is buffered at $\text{pH} = 9.00$? (c) How many grams of Mg(OH)_2 will dissolve in 1.00 L of solution buffered at $\text{pH} = 9$?
17. A 25.0 mL solution of 0.100 M $\text{Pb(NO}_3)_2$ is added to 25.0 mL of 0.200 M NaBr . (a) How many grams of PbBr_2 precipitate will form? (b) What are the concentrations of Pb^{2+} , NO_3^- , Na^+ , and Br^- , respectively, in the saturated solution containing PbBr_2 precipitate? (PbBr_2 has $K_{\text{sp}} = 4.6 \times 10^{-6}$)
18. For the following equilibrium: $\text{Cu}^{2+}(\text{aq}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons \text{Cu(NH}_3)_4^{2+}(\text{aq}); \quad K_{\text{f}} = 1.12 \times 10^{13}$
- (a) If 5.0 mL of 0.10 M $\text{Cu(NO}_3)_2$ is added to 20.0 mL of 2.0 M NH_3 solution, and the above equilibrium is established, calculate the molar concentration of Cu^{2+} , $\text{Cu(NH}_3)_4^{2+}$, NH_3 , and NO_3^- , respectively, in the equilibrium mixture?
- (b) If the solubility equilibrium: $\text{Cu(OH)}_2(\text{s}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$, has $K_{\text{sp}} = 2.2 \times 10^{-20}$, what is the value of K_{c} for the following equilibrium:
- $$\text{Cu(OH)}_2(\text{s}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons \text{Cu(NH}_3)_4^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$$
19. Given the following equilibria in aqueous solution:
- $$\text{AgBr}(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}); \quad K_{\text{sp}} = 5.0 \times 10^{-13}$$
- $$\text{Ag}^+(\text{aq}) + 2\text{S}_2\text{O}_3^{2-}(\text{aq}) \rightleftharpoons \text{Ag(S}_2\text{O}_3)_2^{3-}(\text{aq}); \quad K_{\text{f}} = 2.9 \times 10^{13}$$
- (a) What is K_{c} for the following equilibrium?
- $$\text{AgBr}(\text{s}) + 2\text{S}_2\text{O}_3^{2-}(\text{aq}) \rightleftharpoons \text{Ag(S}_2\text{O}_3)_2^{3-}(\text{aq}) + \text{Br}^-(\text{aq});$$
- (b) Determine the molar solubility of AgBr in solution of 0.50 M $\text{Na}_2\text{S}_2\text{O}_3$.
- (c) How many grams of AgBr will dissolve in 5.0×10^2 mL of 0.50 M $\text{Na}_2\text{S}_2\text{O}_3$?
20. You are provided with the following reagents for cations analysis: 6 M HCl , 6 M NaOH , 6 M NH_3 , and 3 M H_2SO_4 . Which reagent would you use to separate cations in the following mixtures? With the help of relevant chemical equations, explain briefly how each pair of cations would be separated using your reagent of choice? (*Hint*: check the Solubility Rules and determine which cations form complex ions with NH_3 and/or OH^- .)
- (a) Ag^+ and Ba^{2+} (b) Ba^{2+} and Cu^{2+} (c) Cu^{2+} and Fe^{3+} (d) Cr^{3+} and Fe^{3+}

Answers

- (a) $K_c = 0.256$; (b) $K_c' = 3.91$;
(c) No. Reducing the volume will increase pressure and equilibrium will shift to the left;
- (a) $K_c = 280$; (b) $K_c' = 6.0 \times 10^{-2}$
- (a) $K_p = 2.92 \times 10^{-3}$; (b) $P_{\text{total}} = 0.270 \text{ atm}$; (c) 3.56 g of $\text{NH}_4\text{CO}_2\text{NH}_2$ remains;
- $K_c = 6.9 \times 10^6$
- (a) strong (b) strong; (c) weak; (d) weak; (e) weak (f) strong
(g) strong (h) weak (i) weak
- (a) HNO_2 (b) H_3PO_3 (c) HOBr (d) H_2SO_3 (e) $\text{CH}_3\text{CO}_2\text{H}$ (f) H_2S
- (a) $\text{pH} = 2.05$; % ionization = 4.5%; (b) HClO_2 has $K_a = 1.3 \times 10^{-2}$
- (a) $\text{pH} = 11.13$; (b) $K_a = 5.6 \times 10^{-10}$; $\text{pH} = 5.13$
- (a) basic (b) neutral (c) acidic (d) basic
- (a) (i) $\text{HNO}_2\text{-NaNO}_2$ (ii) $\text{CH}_3\text{CO}_2\text{H- NaCH}_3\text{CO}_2$ (iii) $\text{NaH}_2\text{PO}_4\text{- Na}_2\text{HPO}_4$
(iv) $\text{NH}_4\text{Cl-NH}_3$ (b) (i) $[\text{CH}_3\text{CO}_2^-]/[\text{CH}_3\text{CO}_2\text{H}] = 1.8/1$; (ii) $[\text{NH}_3]/[\text{NH}_4^+] = 0.56/1$
- (a) $\text{pH} = 5.23$; (b) $\text{pH} = 4.93$
- (a) (i) $K_a = 2.0 \times 10^{-8}$ (ii) $K_a = 3.2 \times 10^{-8}$; (iii) Average $K_a = 2.6 \times 10^{-8}$;
(b) $\text{pH} = 8.06$; (c) $\text{pH} = 10.14$
- (a) initial $\text{pH} = 3.20$; (b) $\text{pH} = 5.40$; (c) At equivalent point, $\text{pH} = 9.05$;
- Suitable indicators: (a) Phenolphthalein or Methyl Red; (b) Phenolphthalein (c) Methyl Red
- (a) solubility of $\text{Ag}_3\text{PO}_4 = 1.8 \times 10^{-5} \text{ mol/L}$; (b) $K_{\text{sp}} = 2.8 \times 10^{-18}$;
- (a) Solubility of $\text{Mg(OH)}_2 = 1.3 \times 10^{-4} \text{ mol/L}$; $K_{\text{sp}} = 8.8 \times 10^{-12}$ (b) 0.090 mol/L
- (a) precipitate = 0.92 g of PbBr_2 ;
(b) $[\text{Pb}^{2+}] = 0.0105 \text{ mol/L}$; $[\text{Br}^-] = 0.0210 \text{ mol/L}$; $[\text{Na}^+] = [\text{NO}_3^-] = 0.10 \text{ M}$
- (a) $[\text{Cu}^{2+}] = 3.3 \times 10^{-16} \text{ M}$; $[\text{Cu(NH}_3)_4^{2+}] = 0.020 \text{ M}$; $[\text{NH}_3] = 1.5 \text{ M}$
(b) $K_c = 2.5 \times 10^{-7}$;
- (a) $K_c = 14.5$; (b) solubility of $\text{AgBr} = 0.22 \text{ mol/L}$; (c) mass of AgBr dissolved = 21 g
- (a) Add 6 M HCl : AgCl will form precipitate; Ba^{2+} remains in solution (BaCl_2 is soluble)
(b) Add 3 M H_2SO_4 : BaSO_4 will form precipitate; CuSO_4 is soluble;
(c) Add 6 M NH_3 : Fe(OH)_3 will form precipitate; Cu^{2+} forms complex ion $\text{Cu(NH}_3)_4^{2+}$ and remains in solution;
(d) Add excess 6 M NaOH : Fe(OH)_3 will form precipitate; Cr^{3+} forms complex ion Cr(OH)_4^- and remains in solution.