

Professor Glickman, the lab practical joker, deftly places a single drop of hydrochloric acid on the back of Professor Bingham's neck.

## Acids and Bases 🍋

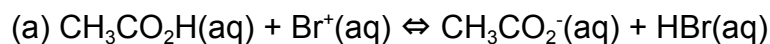
1) Chloroacetic acid ( $\text{ClCH}_2\text{CO}_2\text{H}$ ) has  $K_a = 1.41 \times 10^{-3}$ . What is the value of  $K_b$  for the chloroacetate ion ( $\text{ClCH}_2\text{CO}_2^-$ )?

The  $K_b$  for the chloroacetate ion:

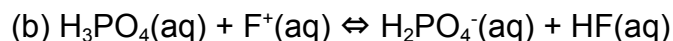
Recall the relationship between acids and their conjugate bases:  $K_a \cdot K_b = K_w$

$K_b$  for the chloroacetate ion will be  $\frac{1.00 \times 10^{-14}}{1.41 \times 10^{-3}} = 7.09 \times 10^{-12}$

2) For each of the following reactions, predict whether the equilibrium lies predominantly to the left or to the right. Explain your predictions briefly.



The equilibrium will favor the weaker acid which can be determined by comparing  $\text{p}K_a$  of the acids on each side of the reaction. On the left side, the acid is acetic acid, which has a  $\text{p}K_a$  of 4.7. On the right side, the acid is hydrobromic acid of -8.7. Therefore, the equilibrium will **favor the left side**.



On the left side, the acid is phosphoric acid, a polyprotic acid. The most acidic proton on phosphoric acid has a  $\text{p}K_a$  of 2.1. On the right side, the acid is hydrofluoric acid, which has a  $\text{p}K_a$  of 3.2. Therefore, the equilibrium will **favor the right side**.

3) Sulfurous acid,  $\text{H}_2\text{SO}_3$ , is a weak acid capable of providing two  $\text{H}^+$  ions.

(a) What is the pH of a 0.45 M solution of  $\text{H}_2\text{SO}_3$ ?

(b) What is the equilibrium concentration of the sulfite ion,  $\text{SO}_3^{2-}$ , in the 0.45 M solution of  $\text{H}_2\text{SO}_3$ ?

(a) pH of 0.45 M  $\text{H}_2\text{SO}_3$ : The equilibria for the diprotic acid are:

$$K_{a1} = \frac{[\text{HSO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{SO}_3]} = 1.2 \times 10^{-2} \text{ and } K_{a2} = \frac{[\text{SO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HSO}_3^-]} = 6.2 \times 10^{-8}$$

For the first step of dissociation:

	$\text{H}_2\text{SO}_3$	$\text{HSO}_3^-$	$\text{H}_3\text{O}^+$
Initial concentration	0.45 M		
Change	-x	+x	+x
Equilibrium	0.45 - x	+x	+x

Substituting into the  $K_{a1}$  expression:  $K_{a1} = \frac{(x)(x)}{(0.45-x)} = 1.2 \times 10^{-2}$

We must solve this expression with the quadratic equation since  $(0.45 < 100 \cdot K_{a1})$ .

The equilibrium concentrations for  $\text{HSO}_3^-$  and  $\text{H}_3\text{O}^+$  ions are found to be 0.0677 M.

The further dissociation is indicated by  $K_{a2}$ .

Using the equilibrium concentrations from the first step, substitute into the  $K_{a2}$  expression.

	$\text{HSO}_3^-$	$\text{SO}_3^{2-}$	$\text{H}_3\text{O}^+$
Initial concentration	0.0677	0	0.0677
Change	-x	+x	+x
Equilibrium	0.0677 - x	+x	0.0677 + x

$$K_{a2} = \frac{[\text{SO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HSO}_3^-]} = \frac{(+x)(0.0677 + x)}{(0.0677 - x)} = 6.2 \times 10^{-8}$$

We note that x will be small in comparison to 0.0677, and we simplify the expression:

$$K_{a2} = \frac{(+x)(0.0677)}{(0.0677)} = 6.2 \times 10^{-8}$$

In summary, the concentrations of  $\text{HSO}_3^-$  and  $\text{H}_3\text{O}^+$  ions have been virtually unaffected by the second dissociation. So  $[\text{H}_3\text{O}^+] = 0.0677 \text{ M}$  and  $\text{pH} = 1.17$

(b) The equilibrium concentration of  $\text{SO}_3^{2-}$ :

From the  $K_{a2}$  expression above:  $[\text{SO}_3^{2-}] = 6.2 \times 10^{-8} \text{ M}$



4) What is the pH of 1.0 L of 0.20 M acetic acid to which 16.4 g of sodium acetate,  $\text{NaCH}_3\text{CO}_2$ , is added?

16.4 g of Sodium Acetate \* (1 mol Sodium Acetate / 82.0343 g) = 0.2 moles Sodium acetate

0.2 M acetic acid \* (1 L) = 0.2 moles acetic acid

$\text{pH} = \text{pK}_a + \log(\text{conjugate base/acid})$

$\text{pH} = 4.7 + \log(0.2 / 0.2)$

$\text{pH} = 4.7$

5) What is the pH of the buffer solution that contains 2.2 g of  $\text{NH}_4\text{Cl}$  in 250 mL of 0.12 M  $\text{NH}_3$ ? Is the final pH lower or higher than the pH of the 0.12 M ammonia solution?

2.2 g  $\text{NH}_4\text{Cl}$  \* (1 mol / 53.491 g) = 0.0411 moles  $\text{NH}_4\text{Cl}$

0.12 M  $\text{NH}_3$  \* (.250 L) = 0.03 moles  $\text{NH}_3$

$\text{pH} = \text{pK}_a + \log(\text{conjugate base/acid})$

$\text{pH} = 9.25 + \log(0.03 / 0.0411)$

$\text{pH} = 9.11$

$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{OH}^-(\text{aq}) + \text{NH}_4^+(\text{aq})$

	$\text{NH}_3$	$\text{H}_2\text{O}$	$\text{OH}^-$	$\text{NH}_4^+$
I (M)	0.12		0	0
C (M)	-x		+x	+x
E (M)	0.12 - x		x	x

$1.8 \times 10^{-5} = x^2 / 0.12 - x$

Assume x to be small relative to 0.12 so this expression simplifies to:

$$1.8 \times 10^{-5} = x^2 / 0.12$$

$$x = 0.0015$$

$$[\text{OH}^-] = 0.0015 \text{ M}$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 14 - (-\log(0.0015))$$

$$\text{pH} = 11.18$$

The final pH is lower than the pH of the 0.12 M ammonia solution.

6) What must the ratio of acetic acid to acetate ion be to have a buffer with a pH value of 4.50?

$$\text{pH} = \text{pK}_a + \log(\text{conjugate base/acid})$$

$$\text{pH} - \text{pK}_a = \log(\text{conjugate base/acid})$$

$$10^{4.50 - 4.74} = \text{conjugate base} / \text{acid}$$

$$0.575 = \text{conjugate base} / \text{acid}$$

$$\text{Acetic acid} / \text{Acetate Ion} = 1.76$$

7) Which of the following combinations would be the best to buffer the pH of a solution at approximately 9?

(a) HCl and NaCl

(b)  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$

(c)  $\text{CH}_3\text{CO}_2\text{H}$  and  $\text{NaCH}_3\text{CO}_2$

17. The best combination to provide a buffer solution of pH 9 is (b) the  $\text{NH}_3/\text{NH}_4^+$  system. Note that  $K_a$  (for  $\text{NH}_4^+$ ) is approximately  $10^{-10}$ . Buffer systems are good when the desired pH is  $\pm 1$  unit from  $\text{p}K_a$  (10 in this case). The HCl and NaCl don't form a buffer. The acetic acid/sodium acetate system would form an acidic buffer ( $\text{p}K_a \approx 5$ ) in the pH range 4 - 6.

8) You titrate 25.0 mL of 0.10 M  $\text{NH}_3$  with 0.10 M HCl.

(a) What is the pH of the  $\text{NH}_3$  solution before the titration begins?

$$0.025 \text{ L} \times 0.10 \text{ M } \text{NH}_3 = 0.0025 \text{ mol } \text{NH}_3$$



	$\text{NH}_3$	$\text{NH}_4^+$	$\text{OH}^-$
I	0.1 M	0	0
C	-x	+x	+x
E	0.1 M	x	x

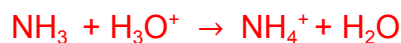
$$K_b = 1.8 \times 10^{-5} = x^2 / (0.1 \text{ M})$$

$$x = [\text{OH}^-] = 0.001342 \text{ M}$$

$$\text{pOH} = 2.87$$

$$\text{pH} = 14 - 2.87 = 11.13$$

(b) What is the pH at the equivalence point?



	$\text{NH}_3$	$\text{H}_3\text{O}^+$	$\text{NH}_4^+$	$\text{H}_2\text{O}$
I	0.0025 mol	0.0025 mol	0	—
C	-0.0025 mol	-0.0025 mol	+0.0025 mol	—
E	0 mol	0 mol	0.0025 mol	—



	$\text{NH}_4^+$	$\text{NH}_3$	$\text{H}_3\text{O}^+$
I	0.0025 mol	0	0
C	-x	+x	+x
E	0.0025 mol	x	x

$$K_a = 5.8 \times 10^{-10} = x^2 / (0.0025 \text{ mol} / 0.05 \text{ L})$$

$$x = [\text{H}_3\text{O}^+] = 5.39 \times 10^{-6} \text{ M}$$

$$\text{pH} = 5.28$$

(c) What is the pH at the halfway point of the titration?

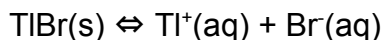
$$\text{pH} = \text{p}K_a$$

$$\text{pH} = -\log(5.8 \times 10^{-10})$$

$$\text{pH} = 9.25$$

## Solubility

9) When 1.55 g of solid thallium(I) bromide is added to 1.00 L of water, the salt dissolves to a small extent.



The thallium(I) and bromide ions in equilibrium with TlBr each have a concentration of  $1.9 \times 10^{-3} \text{ M}$ . What is the value of  $K_{sp}$  for TlBr?

$$K_{sp} = [\text{Tl}^+][\text{Br}^-] = (1.9 \times 10^{-3})^2 = 3.6 \times 10^{-6}$$

10) Calculate the molar solubility of silver thiocyanate, AgSCN, in pure water and in water containing 0.010 M NaSCN.

57. The equilibrium for AgSCN dissolving is:  $\text{AgSCN (s)} \rightleftharpoons \text{Ag}^+ \text{(aq)} + \text{SCN}^- \text{(aq)}$ .

As  $x$  mol/L of AgSCN dissolve in pure water,  $x$  mol/L of  $\text{Ag}^+$  and  $x$  mol/L of  $\text{SCN}^-$  are produced. The expression would be:  $K_{\text{sp}} = [\text{Ag}^+][\text{SCN}^-]$

Substituting  $x$  for the concentrations of the ions:  $x^2 = 1.0 \times 10^{-12}$  and  $x = 1.0 \times 10^{-6} \text{ M}$   
So  $1.0 \times 10^{-6} \text{ mol AgSCN/L}$  dissolve in pure water.

The equilibrium for AgSCN dissolving in NaSCN (0.010 M) is like that above.

Equimolar amounts of  $\text{Ag}^+$  and  $\text{SCN}^-$  ions are produced as the solid dissolves.

However the  $[\text{SCN}^-]$  is augmented by the soluble NaSCN.

$$K_{\text{sp}} = [\text{Ag}^+][\text{SCN}^-] = (x)(x + 0.010) = 1.0 \times 10^{-12}$$

We can simplify the expression by *assuming* that  $x + 0.010 \approx 0.010$ . Note that the value of  $x$  above ( $1.0 \times 10^{-6}$ ) lends credibility to this assumption.

$$(x)(0.010) = 1.0 \times 10^{-12} \quad \text{and } x = 1.0 \times 10^{-10} \text{ M}$$

The solubility of AgSCN in 0.010 M NaSCN is  $1.0 \times 10^{-10} \text{ M}$  -- reduced by four orders of magnitude from its solubility in pure water. LeChatelier strikes again!

11) You have a solution that has a lead(II) ion concentration of 0.0012 M. If enough soluble chloride-containing salt is added so that the  $\text{Cl}^-$  concentration is 0.010 M, will  $\text{PbCl}_2$  precipitate?

#### Precipitation Reactions

65. Given the equation for  $\text{PbCl}_2$  dissolving in water:  $\text{PbCl}_2 \text{(s)} \rightleftharpoons \text{Pb}^{2+} \text{(aq)} + 2 \text{Cl}^-$   
we can write the  $K_{\text{sp}}$  expression:  $K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = 1.7 \times 10^{-5}$

Substituting the ion concentrations into the  $K_{\text{sp}}$  expression we get:

$$Q = [\text{Pb}^{2+}][\text{Cl}^-]^2 = (0.0012)(0.010)^2 = 1.2 \times 10^{-7}$$

Since  $Q$  is less than  $K_{\text{sp}}$ , no  $\text{PbCl}_2$  precipitates.

12) If the concentration of  $\text{Zn}^{2+}$  in 10.0 mL of water is  $1.63 \times 10^{-4} \text{ M}$ , will zinc hydroxide,  $\text{Zn(OH)}_2$ , precipitate when 4.0 mg of NaOH is added?

If  $\text{Zn(OH)}_2$  is to precipitate, the reaction quotient ( $Q$ ) must exceed the  $K_{\text{sp}}$  for the salt.

4.0 mg of NaOH in 10. mL corresponds to a concentration of:

$$[\text{OH}^-] = \frac{4.0 \times 10^{-3} \text{ g NaOH}}{0.0100 \text{ L}} \cdot \frac{1 \text{ mol NaOH}}{40.0 \text{ g NaOH}} = 0.010 \text{ M}$$

The value of  $Q$  is:  $[\text{Zn}^{2+}][\text{OH}^-]^2 = (1.6 \times 10^{-4})(1.0 \times 10^{-2})^2 = 1.6 \times 10^{-8}$

The value of  $Q$  is greater than the  $K_{\text{sp}}$  for the salt ( $4.5 \times 10^{-17}$ ), so  $\text{Zn(OH)}_2$  precipitates.



## Thermodynamics

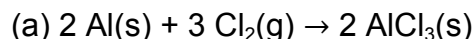
13) Which substance in each pair has the higher entropy?

- (a) Dry ice (solid  $\text{CO}_2$ ) at  $-78^\circ\text{C}$  or  $\text{CO}_2(\text{g})$  at  $0^\circ\text{C}$ .
- (b) Liquid water at  $25^\circ\text{C}$  or liquid water at  $50^\circ\text{C}$ .
- (d) One mole of  $\text{N}_2(\text{g})$  at 1 bar pressure or one mole of  $\text{N}_2(\text{g})$  at 10 bar pressure (both at 298 K).

Compound with the higher entropy:

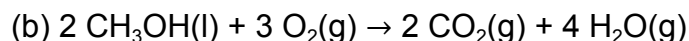
- (a)  $\text{CO}_2(\text{s})$  at  $-78^\circ$  vs  $\text{CO}_2(\text{g})$  at  $0^\circ\text{C}$ : Entropy increases with temperature.
- (b)  $\text{H}_2\text{O}(\ell)$  at  $25^\circ\text{C}$  vs  $\text{H}_2\text{O}(\ell)$  at  $50^\circ\text{C}$ : Entropy increases with temperature.
- (c)  $\text{Al}_2\text{O}_3(\text{s})$  (pure) vs  $\text{Al}_2\text{O}_3(\text{s})$  (ruby): Entropy of a solution (even a solid one) is greater than that of a pure substance.
- (d) 1 mol  $\text{N}_2(\text{g})$  at 1 bar vs 1 mol  $\text{N}_2(\text{g})$  at 10 bar: With the increased P, molecules have greater order.

14) Calculate the standard entropy change for the following reactions at  $25^\circ\text{C}$ .



$$\Delta_r S^\circ = (2\text{ mol})(109.29\text{ J/K}\cdot\text{mol}) - [(3\text{ mol})(223.08\text{ J/K}\cdot\text{mol}) + (2\text{ mol})(28.3\text{ J/K}\cdot\text{mol})]$$

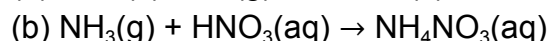
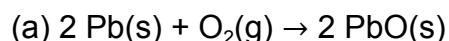
$$\Delta_r S^\circ = -507.26\text{ J/K}$$



$$\Delta_r S^\circ = [(4\text{ mol} \cdot 188.84\text{ J/K}\cdot\text{mol}) + (2\text{ mol} \cdot 213.74\text{ J/K}\cdot\text{mol})] - [(2\text{ mol} \cdot 127.19\text{ J/K}\cdot\text{mol}) + (3\text{ mol} \cdot 205.07\text{ J/K}\cdot\text{mol})]$$

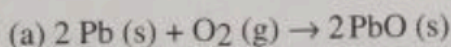
$$\Delta_r S^\circ = 313.25\text{ J/K}$$

15) Using values of  $\Delta_f H^\circ$  and  $S^\circ$ , calculate  $\Delta_r G^\circ$  for each of the following reactions at  $25^\circ\text{C}$ .



Which of these reactions is (are) predicted to be product-favored at equilibrium? Are the reactions enthalpy or entropy-driven?

. Calculate  $\Delta_r G^\circ$  for:



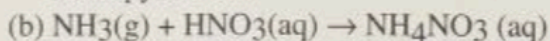
$$\Delta_r H^\circ = (2 \text{ mol})(-219 \frac{\text{kJ}}{\text{mol}}) - [0 + 0] = -438 \text{ kJ}$$

$$\Delta_r S^\circ = (2 \text{ mol})(66.5 \frac{\text{J}}{\text{K}\cdot\text{mol}}) -$$

$$[(2 \text{ mol})(64.81 \frac{\text{J}}{\text{K}\cdot\text{mol}}) + (1 \text{ mol})(205.07 \frac{\text{J}}{\text{K}\cdot\text{mol}})] = -201.7 \text{ J/K}$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = -438 \text{ kJ} - (298.15 \text{ K})(-201.7 \text{ J/K})(\frac{1.000 \text{ kJ}}{1000 \text{ J}}) = -378 \text{ kJ}$$

Reaction is product-favored since  $\Delta G < 0$ . With the very large negative  $\Delta H$ , the process is enthalpy driven.



$$\Delta_r H^\circ = (1 \text{ mol})(-339.87 \frac{\text{kJ}}{\text{mol}}) - [(1 \text{ mol})(-45.90 \frac{\text{kJ}}{\text{mol}}) + (1 \text{ mol})(-207.36 \frac{\text{kJ}}{\text{mol}})] = -86.61 \text{ kJ}$$

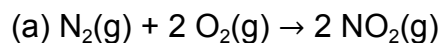
$$\Delta_r S^\circ = (1 \text{ mol})(259.8 \frac{\text{J}}{\text{K}\cdot\text{mol}}) -$$

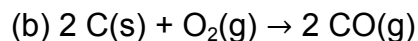
$$[(1 \text{ mol})(192.77 \frac{\text{J}}{\text{K}\cdot\text{mol}}) + (1 \text{ mol})(146.4 \frac{\text{J}}{\text{K}\cdot\text{mol}})] = -79.4 \frac{\text{J}}{\text{K}\cdot\text{mol-rxn}}$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = -86.61 \text{ kJ} - (298.15 \text{ K})(-79.4 \text{ J/K})(\frac{1.000 \text{ kJ}}{1000 \text{ J}}) = -62.9 \frac{\text{kJ}}{\text{mol-rxn}}$$

Reaction is product-favored since  $\Delta G < 0$ . With the very large negative  $\Delta H$ , the process is enthalpy driven.

16) Determine whether the reactions listed below are entropy-favored or disfavored under standard conditions. Predict how an increase in temperature will affect the value of  $\Delta_r G^\circ$ .





(a)  $\text{N}_2(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow 2 \text{NO}_2(\text{g})$

$$\Delta_r H^\circ = (2 \text{ mol})(+33.1 \frac{\text{kJ}}{\text{mol}}) - [0 + 0] = +66.2 \frac{\text{kJ}}{\text{mol-rxn}}$$

$$\Delta_r S^\circ = (2 \text{ mol})(+240.04 \frac{\text{J}}{\text{K} \cdot \text{mol}}) - [(1 \text{ mol})(191.56 \frac{\text{J}}{\text{K} \cdot \text{mol}}) + (2 \text{ mol})(+205.07 \frac{\text{J}}{\text{K} \cdot \text{mol}})] = -121.62 \frac{\text{J}}{\text{K} \cdot \text{mol-rxn}}$$

$$\Delta_r G^\circ = (2 \text{ mol})(51.23 \frac{\text{kJ}}{\text{mol}}) - [(1 \text{ mol})(0 \frac{\text{kJ}}{\text{mol}}) + (1 \text{ mol})(0 \frac{\text{kJ}}{\text{mol}})] = 102.5 \text{ kJ}$$

The reaction is entropy-disfavored *and* enthalpy-disfavored.  
There is *no*  $T$  at which  $\Delta G < 0$ .

(b)  $2 \text{C(s)} + \text{O}_2(\text{g}) \rightarrow 2 \text{CO(g)}$

$$\Delta_r H^\circ = (2 \text{ mol})(-110.525 \frac{\text{kJ}}{\text{mol}}) - [0 + 0] = -221.05 \frac{\text{kJ}}{\text{mol-rxn}}$$

$$\Delta_r S^\circ = (2 \text{ mol})(+197.674 \frac{\text{J}}{\text{K} \cdot \text{mol}}) - [1 \text{ mol}(205.07 \frac{\text{J}}{\text{K} \cdot \text{mol}}) + 2 \text{ mol}(5.69 \frac{\text{J}}{\text{K} \cdot \text{mol}})] = 179.078 \frac{\text{J}}{\text{K}}$$

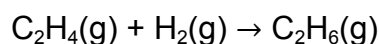
$$\Delta_r S^\circ = [2 \text{ mol} \cdot 197.674 \text{ J/(K} \cdot \text{mol)}] - [1 \text{ mol} \cdot 205.07 \text{ J/(K} \cdot \text{mol)} + 2 \text{ mol} \cdot 5.69 \text{ J/(K} \cdot \text{mol)}] = 179.078 \text{ J/K}$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$

$$\Delta_r G^\circ = -221.05 \text{ kJ} - 298 \text{ K} (179.078 \cdot 10^{-3} \text{ kJ/K})$$

$$\Delta_r G^\circ = -274.45 \text{ kJ/mol}$$

17) Calculate  $\Delta_r G^\circ$  at  $25^\circ\text{C}$  for the formation of 1.00 mol of  $\text{C}_2\text{H}_6(\text{g})$  from  $\text{C}_2\text{H}_4(\text{g})$  and  $\text{H}_2(\text{g})$ . Use this value to calculate  $K_p$  for the equilibrium.



Comment on the sign of  $\Delta_r G^\circ$  and the magnitude of  $K_p$ .

$$\Delta_r G^\circ = \sum \Delta_f G^\circ_{\text{products}} - \sum \Delta_f G^\circ_{\text{reactants}}$$

$$= -31.89 - (68.35 + 0) = -100.24 \text{ kJ/(mol} \cdot \text{rxn)}$$

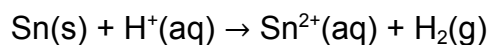
$$\Delta G^\circ = -RT \ln(K)$$

$$-100.24 \text{ kJ/(mol*rxn)} = -8.314 \text{ J/(mol*K)} * 298 \text{ K} * \ln(K)$$

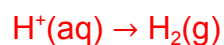
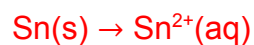
$$K = 3.7 * 10^{17} \dots \text{Large } K \text{ value means product favored.}$$

### Electrochemistry

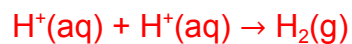
18) Balance the following redox equation in acidic conditions.



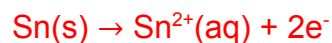
Step 1)



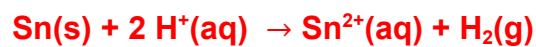
Step 2)



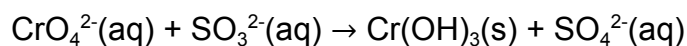
Step 3)



Step 4)

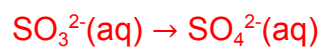
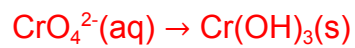


19) Balance the following redox equation in basic conditions.

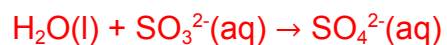


Step 1)

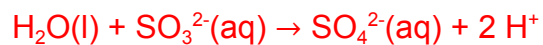
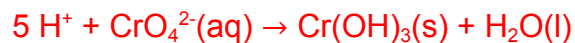




Step 2)



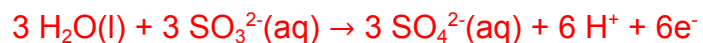
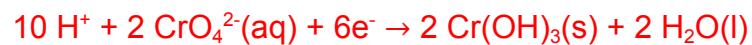
Step 3)



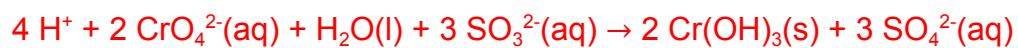
Step 4)



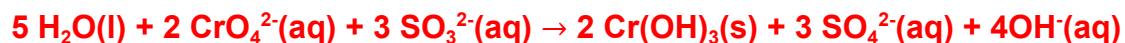
Step 5)



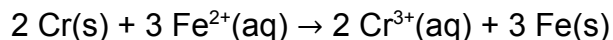
Step 6)



Step 7)



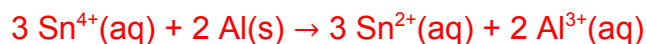
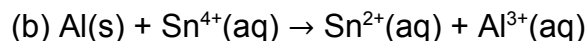
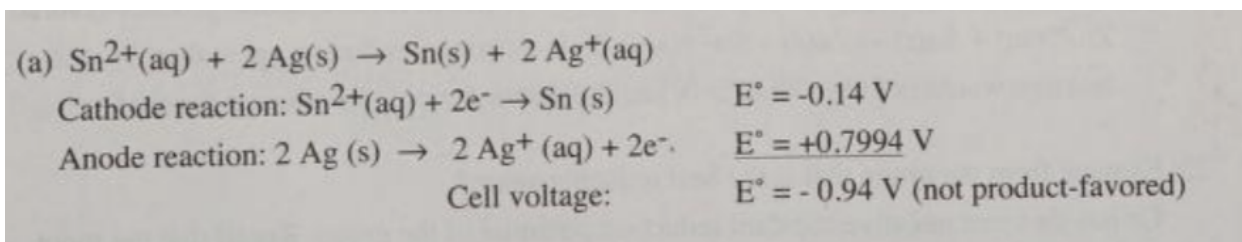
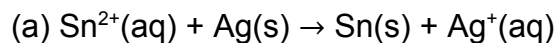
20) A voltaic cell is constructed using the reaction of chromium metal and iron(II) ions.



Complete the following sentences: Electrons in the external circuit flow from the **Cr** electrode to the **Fe** electrode. Negative ions move in the salt bridge from the **Fe|Fe<sup>2+</sup>** half-cell to the **Cr|Cr<sup>3+</sup>** half-cell. The half-reaction at the anode is **Cr(s) → Cr<sup>3+</sup>(aq) + 3e<sup>-</sup>**, and that at the cathode is **Fe<sup>2+</sup>(aq) + 2e<sup>-</sup> → Fe(s)**.

21) Balance each of the following unbalanced equations; then calculate the standard potential,  $E^\circ_{\text{cell}}$ , and decide whether each is product-favored at equilibrium as written.

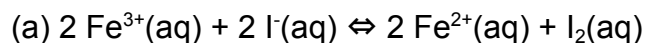
(All reactions are carried out in acid solution.)



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.15 \text{ V} - (-1.66 \text{ V}) = 1.81 \text{ V}$$

Product favored at equilibrium

22) Calculate  $\Delta_r G^\circ$  and the equilibrium constant for the following reactions.



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.771 \text{ V} - 0.621 \text{ V} = 0.15 \text{ V}$$

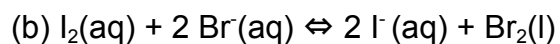
$$\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$$

$$\Delta_r G^\circ = -2 * 96,000 \text{ C} * 0.15 \text{ V} = -28.8 \text{ kJ}$$

$$E^\circ_{\text{cell}} = (0.0257/n) * \ln K$$

$$0.15 = 0.0257/2 * \ln(K)$$

$$K = 1.2 * 10^5$$



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.621 \text{ V} - 1.08 \text{ V} = -0.46 \text{ V}$$

$$\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$$

$$\Delta_r G^\circ = -2 * 96,000 \text{ C} * -0.46 \text{ J} = 88.3 \text{ kJ}$$

$$E^\circ_{\text{cell}} = (0.0257/n) * \ln K$$

$$-0.46 = (0.0257/2) * \ln K$$

$$K = 2.8 * 10^{-16}$$

23) The standard potential,  $E^\circ_{\text{cell}}$ , for the reaction of  $\text{Zn}(\text{s})$  and  $\text{Cl}_2(\text{g})$  is +2.12 V. What is the standard free energy change,  $\Delta_r G^\circ$ , for the reaction?

$$\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$$

$$\Delta_r G^\circ = -2 * 96000 * 2.12 = -407 \text{ kJ}$$