158. Explain using the HC$_2$H$_3$O$_2$/NaC$_2$H$_3$O$_2$ buffer system how a buffer maintains a relatively constant pH when small quantity of acid (HCl) or base (NaOH) is added.

159. A buffer solution consists of 0.500 M HC$_2$H$_3$O$_2$ and 0.250 M NaC$_2$H$_3$O$_2$. Calculate the pH of the resulting solution if 2.5×10$^{-3}$ mol HClO$_4$ is added to 500. mL of the buffer. The pH of the buffer solution before addition of the HClO$_4$ was 4.44.

160. A buffer solution consists of 0.500 M HC$_2$H$_3$O$_2$ and 0.250 M NaC$_2$H$_3$O$_2$. Calculate the pH of the resulting solution if 0.025 mol NaOH is added to 500. mL of the buffer. The pH of the buffer solution before addition of the NaOH was 4.44.

167. A buffer solution is 0.10 M HC$_2$H$_3$O$_2$ and 0.20 M NaC$_2$H$_3$O$_2$. What is the pH of this buffer solution? Calculate the pH after the addition of 0.0040 mol HCl to 100 ml of the buffer.

170. What is the shape of the titration curve (plot of pH vs. mL of added acid) for titration of a weak base by a strong acid? In a titration, 20 mL of 0.10 M NH$_3$ was titrated with 0.20 M HCl. Calculate the pH of the resulting solution after the addition of the following volumes of acid: 0 mL, 5.0 mL, 10.0 mL, and 15.0 mL. What volume of acid is needed to reach the equivalence point? What species is present at the equivalence point and what is the pH at the equivalence point?

171. What is the difference between the equivalence point and the end point in a titration?

172. An indicator itself is a weak acid or base that has one color in acidic solution and a different color in basic solution. The general equilibria for an indicator can be written as follows:

HIn(aq) + H$_2$O $\rightleftharpoons$ In$^-$ (aq) + H$_3$O$^+$ (aq) \[ K_A \]

For phenolphthalein, HIn is colorless whereas In$^-$ is pink. What is the color of the indicator in basic solution? In acidic solution?

173. For phenolphthalein, $K_A$=7.9×10$^{-10}$. Around what pH will phenolphthalein change color? Could phenolphthalein be used as an indicator during the titration of a strong acid with a strong base (eg. HCl with NaOH)? strong base with a weak acid (eg. NaOH with HC$_2$H$_3$O$_2$)? strong acid with a weak base (eg. HBr with NH$_3$)?

174. Three titrations were to be carried out with the acids and bases indicated below. Choose the best indicator for each titration from the following: phenolphthalein $K_A$=7.9×10$^{-10}$, methyl
orange $K_a = 1.6 \times 10^{-4}$, and bromothymol blue $K_a = 1.6 \times 10^{-7}$.

A. HNO$_3$ with NH$_3$
B. HNO$_3$ with KOH
C. HClO$_3$ with NaOH

**Solubility Product, Factors Affecting Solubility and Ion Product**

175. What is $K_{sp}$? Write the chemical equation for dissolution of Ca$_3$(PO$_4$)$_2$. Write the solubility product constant expression for this equation.
176. How is the numerical value of $K_{sp}$ determined? What does its value depend on?
177. A sample of PbCl$_2$ was dissolved in water until a saturated solution was obtained (until some solid PbCl$_2$ was present). The concentration of Pb$^{2+}$ in the solution was found to be $1.44 \times 10^{-2}$ M. Calculate the numerical value of $K_{sp}$.
178. A saturated solution of Ca$_3$(PO$_4$)$_2$ was prepared and the concentration of Ca$^{2+}$ was found to be $3.43 \times 10^{-7}$ M. Calculate the numerical value of $K_{sp}$.

179. Calculate the solubility (in g/L and in mol/L) of AgBr in water. $K_{sp}(AgBr)=5.4 \times 10^{-13}$.
180. Calculate the solubility (in g/L and in mol/L) of Mg$_3$(AsO$_4$)$_2$ in water. $K_{sp}(Mg_3(AsO_4)_2)=2.1 \times 10^{-20}$.
181. If Ag$_2$SO$_4$ is mixed with water to obtain a saturated solution, what is the concentration of each ion in the resulting solution? $K_{sp}(Ag_2SO_4)=1.2 \times 10^{-5}$.

182. Calculate the solubility of BaF$_2$ in pure water and in 0.30 M KF. NOTE: KF adds a common ion.
183. BaSO$_4$ is only sparingly soluble with $K_{sp}=1.1 \times 10^{-10}$. Will addition of K$_2$SO$_4$ or BaCl$_2$ change the solubility of BaSO$_4$? If so, how? Calculate the solubility of BaSO$_4$ in 0.10 M K$_2$SO$_4$ and in 0.25 M BaCl$_2$.
184. Will addition of an acid or a decrease in pH change the solubility of the following salts? How and why?
   A. CaF$_2$
   B. AgCl
   C. PbI$_2$
   D. Hg$_2$Br$_2$
   E. MnS
   F. ZnCO$_3$

185. Show using equations how addition of an acid increases the solubility of ZnCO$_3$.
186. Will addition of an acid (like HCl) or a decrease in pH change the solubility of MnS?
187. Will addition of an acid or a decrease in pH change the solubility of Fe(OH)$_3$, AgOH, Al(OH)$_3$, and Mg(OH)$_2$? Show using equations how addition of an acid increases the solubility of Mg(OH)$_2$.
188. A. Calculate the pH of a solution saturated with Mg(OH)$_2$. $K_{sp}(Mg(OH)_2)=5.6 \times 10^{-12}$
   B. Calculate the molar solubility of Mg(OH)$_2$ in pure water and in water buffered at a pH of 8.00.
189. Will a precipitate form if 100. mL of 0.075 M Mg(NO$_3$)$_2$ is mixed with 200. mL of 0.010 M Na$_2$CO$_3$? $K_{sp}(MgCO_3)=6.8 \times 10^{-6}$ HINT: Calculate the ion product or reaction quotient (IP or $Q_{sp}$) and compare to $K_{sp}$.
190. If IP($Q_{sp}$)=$K_{sp}$ will a precipitate form and what type of solution is present (saturated, unsaturated or supersaturated)? If IP($Q_{sp}$)$>K_{sp}$ will a precipitate form and what type of solution is present? If IP($Q_{sp}$)$<K_{sp}$ will a precipitate form and what type of solution is present?
191. Will a precipitate form if 500. mL of 0.050 M AgC$_2$H$_5$O$_2$ is mixed with 300. mL of 0.010 M K$_2$SO$_4$? $K_{sp}(Ag_2SO_4)=1.2 \times 10^{-5}$

**Separations via Precipitation and Qualitative Analysis**

191. A solution is 0.0015 M in each of the cations Ag$^+$, Pb$^{2+}$, and Hg$_2^{2+}$. What concentration of chloride ion must be present to precipitate as much of the Hg$_2^{2+}$ (as Hg$_2$Cl$_2$) as possible
227. Amphoteric hydroxides are soluble in both acidic and basic solutions but insoluble in neutral solutions. 

\[ K_{sp}(\text{AgCl}) = 1.4 \times 10^{-10}, \quad K_{sp}(\text{PbCl}_2) = 1.2 \times 10^{-5}, \quad K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10} \]

192. Consider question 191. What concentration of Cl\(^{-}\) is needed to precipitate all of the ions but \(\text{Pb}^{2+}\)? What is the concentration of \(\text{Hg}_2\)\(^{2+}\) ions in the solution at this concentration of Cl\(^{-}\)?

193. A solution with a pH of 0.52 is 0.0010 M in each of the cations \(\text{Pb}^{2+}\), \(\text{Hg}_2\)\(^{2+}\), \(\text{Mn}^{2+}\), \(\text{Ni}^{2+}\), and \(\text{Zn}^{2+}\) and 0.10 M in \(\text{H}_2\text{S}\). Which of these cations will precipitate as the sulfide?

The general equilibrium established for divalent metal cations (+2 charge) is:

\[ \text{MS(s)} + 2 \text{H}_2\text{O}^{+}(aq) \rightleftharpoons \text{H}_2\text{S(aq)} + \text{M}^{2+} + 2 \text{H}_2\text{O} \]

<table>
<thead>
<tr>
<th>MS ( K_{s\text{pa}} )</th>
<th>PbS ( K_{s\text{pa}} )</th>
<th>NiS ( K_{s\text{pa}} )</th>
<th>ZnS ( K_{s\text{pa}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2 \times 10^{-32} )</td>
<td>( 3 \times 10^{-7} )</td>
<td>( 8 \times 10^{-1} )</td>
<td>( 3 \times 10^{-2} )</td>
</tr>
</tbody>
</table>

What pH is needed to precipitate all of the Group III cations as the sulfide?

194. A solution is 0.500 M in each of the ions \(\text{Ni}^{2+}\) and \(\text{Cr}^{3+}\) and has a pH of 4.00. Solid NaOH is added to precipitate the hydroxides. Can these two ions be separated from each other by adjusting the pH of the solution? What pH is needed to precipitate as much of the \(\text{Cr}^{3+}\) as possible without precipitating the \(\text{Ni}^{2+}\)?

\[ \text{Ni(OH)}_2 \quad K_{sp} = 2 \times 10^{-15} \]
\[ \text{Cr(OH)}_3^- \quad K_{sp} = 6.3 \times 10^{-31} \]

195. A solution is 1.0 \times 10^{-3} M in each of the metal cations \(\text{Cu}^+\), \(\text{Pb}^{2+}\), \(\text{Hg}_2\)\(^{2+}\) and \(\text{Ag}^+\). Solid NaBr is added to this solution. In what order will the bromides precipitate?

\[ \text{CuBr} \quad K_{sp} = 6.3 \times 10^{-9} \quad \text{AgBr} \quad K_{sp} = 5.4 \times 10^{-13} \]
\[ \text{PbBr}_2 \quad K_{sp} = 6.6 \times 10^{-6} \quad \text{Hg}_2\text{Br}_2 \quad K_{sp} = 6.4 \times 10^{-23} \]

196. A solution is 0.0050M in \(\text{Sn}^{2+}\) and \(\text{Al}^{3+}\) and has a pH=1.00. Solid NaOH is added to make the solution more basic. Which of these metal cations will precipitate first?

\[ \text{Sn(OH)}_2 \quad K_{sp} = 3 \times 10^{-27} \quad \text{Al(OH)}_3^- \quad K_{sp} = 2.0 \times 10^{-32} \]

**Amphotericism, Ammonia Complexes and Calculations Involving Complex Formation**

223. Does formation of a metal complex usually increase or decrease the solubility of a salt?

224. Write the equations for the formation of the following metal complexes.

\[ [\text{Ag(NH}_3)_2]^{+} \quad K_f = 1.7 \times 10^7 \quad [\text{Al(OH)}_3]^- \quad K_f = 2.1 \times 10^{34} \]
\[ [\text{Cu(NH}_3)_2]^{2+} \quad K_f = 1.1 \times 10^{13} \quad [\text{Cr(OH)}_4]^- \quad K_f = 8 \times 10^{29} \]
\[ [\text{Ag(CN)}_2]^- \quad K_f = 1 \times 10^{21} \quad [\text{Zn(OH)}_4]^{2-} \quad K_f = 2.8 \times 10^{15} \]

225. Is AgCl more soluble in pure water or a solution of aqueous ammonia? Why?

Write the NET equation that shows how solid AgCl can be dissolved by aqueous ammonia to form an ammonia complex. Calculate the value of the equilibrium constant for this equation. \(K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10} \); \(K_{f}([\text{Ag(NH}_3)_2]^{+}) = 1.7 \times 10^7 \)

226. The metal cations, \(\text{Cd}^{2+}\), \(\text{Zn}^{2+}\), \(\text{Cu}^{2+}\), \(\text{Ag}^+\) and \(\text{Ni}^{2+}\) form soluble ammonia complexes of \([\text{Cd(NH}_3]_4]^{2+}\), \([\text{Zn(NH}_3]_4]^{2+}\), \([\text{Cu(NH}_3]_2]^{2+}\), \([\text{Ag(NH}_3]_2]^{+}\) and \([\text{Ni(NH}_3]_6]^{2+}\). The test for formation of an ammonia complex is to add a limited amount of ammonia and then to add an excess of ammonia to a solution containing one of these ions. Give equations for the reaction that occurs with each of these metal cations in limited and excess ammonia.

227. Amphoteric hydroxides are soluble in both acidic and basic solutions but insoluble in neutral solutions. The metal cations \(\text{Al}^{3+}\), \(\text{Zn}^{2+}\), \(\text{Pb}^{2+}\), \(\text{Cr}^{3+}\) and \(\text{Sn}^{2+}\) are amphoteric and form soluble complexes of \([\text{Al(OH)}_3]^-\), \([\text{Zn(OH)}_2]^-\), \([\text{Pb(OH)}_3]^-\), \([\text{Cr(OH)}_4]^-\) and \([\text{Sn(OH)}_3]^-\) at high pH (pH>10). The test for amphoteric nature is to add a limited amount of NaOH and then to add an excess of NaOH to a solution containing one of these ions. Give equations for the reaction that occurs for each of these ions in limited and excess NaOH.
228. Calculate the solubility of AgBr ($K_{sp}=5.4 \times 10^{-13}$) in 0.75 M NH$_3$. Compare the solubility of AgBr in pure water and in 0.75 M NH$_3$.

\[ K_f([Ag(NH_3)_2]^+)=1.7 \times 10^7 \]

229. A solution is 0.60 M in [Cu(NH$_3$)$_4$]$^{2+}$ ($K_f=1.1 \times 10^{13}$). Calculate the concentration of free Cu$^{2+}$ and NH$_3$ in this solution.

230. Calculate the solubility of Cu(OH)$_2$ in a solution of 1.2 M NH$_3$.

\[ K_{sp}(Cu(OH)_2)=1.6 \times 10^{-19} \]

231. Calculate the equilibrium concentrations of Ni$^{2+}$ and NH$_3$ in the solution when 0.050 mol Ni(NO$_3$)$_2$ is added to 1000. mL of 1.0 M NH$_3$.

\[ K_f([Ni(NH_3)_6]^{2+})=5.6 \times 10^8 \]

232. The complex ion [Ag(NH$_3$)$_2]^+$ ($K_f=1.7 \times 10^7$) is formed from a solution that is 0.10 M Ag$^+$ and 1.0 M NH$_3$. After the complex is formed, the solution is made 0.030 M in NaCl. Will any AgCl precipitate? $K_{sp}$(AgCl)=$1.8 \times 10^{-10}$

### Spontaneity, Enthalpy, Entropy and Gibbs Free Energy

233. Define the following terms: spontaneous process and nonspontaneous process.

234. If a reaction is exothermic does that automatically mean that it is spontaneous in the forward direction? If a reaction is endothermic, does that automatically mean that it is nonspontaneous in the forward direction?

235. Given the standard heats of formation below, calculate the standard enthalpy of the reaction:

\[
4 \text{NH}_3(g) + 5 \text{O}_2(g) \rightarrow 4 \text{NO(g)} + 6 \text{H}_2\text{O(g)}
\]

\[
\Delta H_f(\text{NO(g)})=+90.37 \text{kJ/mol; } \Delta H_f(\text{H}_2\text{O(g)})=-241.8 \text{kJ/mol; } \Delta H_f(\text{NH}_3(g))=-46.19 \text{kJ/mol}
\]

236. Define entropy, $S$. Can $S$ have a negative value? Can $S$ have a negative value?

237. If $S$ is positive during a reaction or process, is entropy increasing or decreasing during the process? If $S$ is negative during a reaction or process, is entropy increasing or decreasing during the process?

238. Arrange the phases liquid, solid and gas according to decreasing entropy. Predict the sign of $\Delta S$ (the change in entropy) for the following processes

A. $\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)}$
B. $\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}$
C. $\text{H}_2\text{O(g)} \rightarrow \text{H}_2\text{O(s)}$
D. $\text{NaCl(s)} \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$
E. $\text{FeSO}_4(s) \rightarrow \text{Fe}^{2+}(aq) + \text{SO}_4^{2-}(aq)$
F. $\text{I}_2(s) \rightarrow \text{I}_2(aq)$

239. For the reaction given in question 235, predict the sign for the entropy change ($\Delta S$).

For the reaction $2 \text{H}_2\text{O(g)} + \text{N}_2(g) \rightarrow \text{N}_2\text{H}_4(l) + \text{O}_2(g)$, predict the sign for the entropy change ($\Delta S$).

240. Show how the entropy of a substance depends on temperature. What is the entropy of a perfectly ordered crystalline solid at absolute zero? State the third law of thermodynamics.

241. Calculate the change in entropy from tabulated values of the standard molar entropies for the reaction given in Question 235.

\[ S^o(\text{NH}_3(g))=192.3 \text{ J/K-mol} \quad S^o(\text{NO(g)})=210.7 \text{ J/K-mol} \]

\[ S^o(\text{O}_2(g))=205.0 \text{ J/K-mol} \quad S^o(\text{H}_2\text{O(g)})=188.7 \text{ J/K-mol} \]

242. State the second law of thermodynamics. Show how the expression for Gibbs Free Energy is obtained from the second law of thermodynamics. If during a reaction, the total entropy of the system and surroundings ($\Delta S_{net}$) is increasing what is the sign of $\Delta G$ and is the reaction spontaneous in the forward direction?

243. Give the equation used to calculate the Gibbs Free Energy change ($\Delta G$) for a reaction or process. What values of $\Delta G$ lead to spontaneous processes? nonspontaneous processes?

244. For the following signs of $\Delta H$ and $\Delta S$ predict the sign of $\Delta G$ and decide whether or not
sign of $\Delta G$ will depend on temperature.

CASE#1: $\Delta H = +$; $\Delta S = +$

CASE#2: $\Delta H = +$; $\Delta S = -$  

CASE#3: $\Delta H = -$; $\Delta S = +$

CASE#4: $\Delta H = -$; $\Delta S = -$  

What is the crossover temperature and how is it calculated? Can a crossover temperature be calculated for CASE #2 and CASE #3? Why or why not?

245. For the reaction $C_2H_5OH(l) + 3 O_2(g) \rightarrow 2 CO_2(g) + 3 H_2O(l)$

Calculate the standard Gibbs free energy change. Decide whether the reaction is spontaneous in the forward direction. Calculate at what temperature the reaction will change in behavior from spontaneous to nonspontaneous or from nonspontaneous to spontaneous (ie. calculate the crossover temperature).

$G_f^\circ$(kJ/mol) $H_f^\circ$(kJ/mol) $S_f^\circ$(J/K-mol)

$C_2H_5OH(l)$ -277.7 161

$O_2(g)$ 205.0

$CO_2(g)$ -393.5 213.6

$H_2O(l)$ -285.8 69.9

246. Calculate the standard Gibbs Free energy ($\Delta G^\circ$) from tabulated values of the standard Gibbs Free energy of formation ($\Delta G_f^\circ$) for the reactions below and decide whether the reaction is spontaneous or nonspontaneous in the forward direction.

A. $CH_4(g) + 4 Cl_2(g) \rightarrow CCl_4(l) + 4 HCl(g)$

B. $2 CH_3OH(l) \rightarrow 2 CH_4(g) + O_2(g)$

$\Delta G_f^\circ$(kJ/mol) $\Delta H_f^\circ$(kJ/mol) $S_f^\circ$(J/K-mol)

$CH_4(g)$ -50.75

$CCl_4(l)$ -60.63

$HCl(g)$ -95.30

$CH_3OH(l)$ -166.3

$CO(g)$ -137.2 -110.5 197.6

$H_2O(g)$ -228.6 -241.8 188.7

$H_2(g)$ 0 0 130.6

C(s,gr) 0 0 5.7

Gibbs Free Energy and Equilibrium

247. $\Delta G$ is the Gibbs Free Energy under nonstandard conditions. How is $\Delta G$ different from $\Delta G^\circ$? Give the equation used to calculate $\Delta G$ from $\Delta G^\circ$ and Q (the reaction quotient). NOTE: If a reaction consists of primarily gas phase reactants and products $Q_p$ should be used. If a reaction consists of primarily solution phase reactant and products $Q_c$ should be used.

248. Consider the reaction below. Initially a vessel contained 0.500 atm CO(g), 0.150 atm $H_2O(g)$ and $4.25 \times 10^{-2}$ atm $H_2(g)$. Is the reaction spontaneous in the forward direction at 25 C? at 800 C? HINT: Calculate the value of $\Delta G$. Values of $\Delta G_f^\circ$ are given in question 246.

$C(s) + H_2O(g) \leftrightarrow CO(g) + H_2(g)$

249. Use the facts that $i$. when a reaction is at equilibrium $\Delta G=0$ and $ii$. when a reaction is at equilibrium $Q=K$ to derive the relationship between $\Delta G^\circ$ and $K$.

250. Consider the reaction for the formation of the cobalt ammonia complex $[Co(NH_3)_6]^{3+}$ below.

$Co^{3+}(aq) + 6 NH_3(aq) \leftrightarrow [Co(NH_3)_6]^{3+} (aq)$

$K_f=2.0 \times 10^7$ at 25 C

A. Calculate the Gibbs Free Energy under standard conditions for this reaction.

B. If $[Co^{3+}]=0.00500M$, $[NH_3]=0.10 M$ and $[Co(NH_3)_6]^{3+}=1.00 M$ initially, is the reaction spontaneous in the forward direction?
251. For the reaction \( \text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \) \( \Delta G^\circ = +37.2 \text{ kJ} \)
Calculate the equilibrium constant at 25 C. Calculate the equilibrium constant at 200 C.

<table>
<thead>
<tr>
<th>( \Delta H^\circ (\text{kJ/mol}) )</th>
<th>( S^\circ (\text{J/K-mol}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{PCl}_5(\text{g}) )</td>
<td>-374.9</td>
</tr>
<tr>
<td>( \text{PCl}_3(\text{g}) )</td>
<td>-287.0</td>
</tr>
<tr>
<td>( \text{Cl}_2(\text{g}) )</td>
<td>223.0</td>
</tr>
</tbody>
</table>

252. For the reaction \( \text{C}_2\text{H}_4(\text{g}) + 3 \text{O}_2(\text{g}) \rightleftharpoons 2 \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g}) \) \( \Delta H^\circ = -1323 \text{ kJ} \)
Decide whether or not the reaction is spontaneous in the forward direction under the following conditions: \( p(\text{C}_2\text{H}_4) = 20 \text{ atm}; p(\text{O}_2) = 0.020 \text{ atm}; p(\text{CO}_2) = 0.010 \text{ atm}; \) and \( p(\text{H}_2\text{O}) = 0.010 \text{ atm at 25 C.} \) Under the same conditions, is the reaction spontaneous in the forward direction at 750 C?

<table>
<thead>
<tr>
<th>( S^\circ (\text{J/K-mol}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2(\text{g}) )</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}(\text{g}) )</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4(\text{g}) )</td>
</tr>
<tr>
<td>( \text{O}_2(\text{g}) )</td>
</tr>
</tbody>
</table>

253. The substance \( \text{P}_4\text{O}_{10}(\text{s}) \) is often used to adsorb water vapor in dry boxes by the following reaction: \( 6 \text{H}_2\text{O}(\text{g}) + \text{P}_4\text{O}_{10}(\text{s}) \rightleftharpoons 4 \text{H}_3\text{PO}_4(\text{s}) \)
A. Calculate \( \Delta G^\circ \) and \( K \) at 25 C and decide whether the reaction is spontaneous in the forward direction.

<table>
<thead>
<tr>
<th>( \Delta H^\circ (\text{kJ/mol}) )</th>
<th>( S^\circ (\text{J/K-mol}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_3\text{PO}_4(\text{s}) )</td>
<td>-1279</td>
</tr>
<tr>
<td>( \text{P}<em>4\text{O}</em>{10}(\text{s}) )</td>
<td>-2984</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}(\text{g}) )</td>
<td>-241.8</td>
</tr>
</tbody>
</table>

B. The \( \text{P}_4\text{O}_{10} \) is regenerated by heating the \( \text{H}_3\text{PO}_4 \) and removing the water. To what temperature should the \( \text{H}_3\text{PO}_4 \) be heated (i.e. at what temperature does the reaction become spontaneous in the reverse direction)? What is the value of \( K \) at this temperature?

C. The vapor pressure of water at 25 C is 17.5 mm Hg. Will the \( \text{P}_4\text{O}_{10} \) spontaneously adsorb the water vapor at 25 C?
CHEM 116-Dr. Babb’s Sections
Answer Key to Exam #4 Review Sheet

159. pH = 4.43
160. pH = 4.56
167. pH of original buffer solution = 5.04
pH after addition of 0.0040 mol HCl = 4.80
pH after addition of 0.0060 mol NaOH = 5.6

168. After addition of 0 mL of 0.25 M KOH: pH = 0.30
After addition of 25 mL of 0.25 M KOH: pH = 0.9 (prior to eq. pt.; excess strong acid present)
After addition of 50 mL of 0.25 M KOH: pH = 7 (at eq. pt; only neutral salt present)
After addition of 60 mL of 0.25 M KOH: pH = 12.5 (after eq. pt; excess strong base present)
Volume of base needed to reach eq. pt = 50. mL

169. After addition of 0 mL of 0.20 M KOH: pH = 2.23
After addition of 2.5 mL of 0.20 M KOH: pH = 3.46 (½ way to eq. pt; buffer present)
After addition of 5.0 mL of 0.20 M KOH: pH = 8.14 (at eq. pt; only basic salt present)
After addition of 6.0 mL of 0.20 M KOH: pH = 12.1 (after eq. pt; excess strong base present)
Volume of base needed to reach eq. pt = 5.0 mL
pH ½ way to eq. pt is equal to pK_A

170. After addition of 0 mL of 0.20 M HCl: pH = 11.13
After addition of 5.0 mL of 0.20 M HCl: pH = 9.26 (½ way to eq. pt; buffer present)
After addition of 10.0 mL of 0.20 M HCl: pH = 5.22 (at eq. pt; only acidic salt present)
After addition of 15.0 mL of 0.20 M HCl: pH = 1.54 (after eq. pt; excess strong acid present)
Volume of acid needed to reach eq. pt = 10. mL
pH ½ way to eq. pt is equal to pK_A for NH_3

172. For phenolphthalein: color in acidic solution is colorless; color in basic solution is pink.
173. Phenolphthalein will change color around its pK_A value which is 9.10. Phenolphthalein could be used in titration of strong acid with strong base since pH around eq. pt. changes from 4-10 with addition of 1 drop of base. Phenolphthalein could also be used in titration of weak acid with strong base since at eq. pt a basic salt with a basic pH is present. However, phenolphthalein could NOT be using in titration of a weak base with a strong acid since at eq. pt. an acidic salt with an acidic pH is present.

174. To answer find pK_A for each indicator which gives pH around which indicator changes color. Phenolphthalein, pK_A = 9.10; methyl orange, pK_A = 3.80; bromothymol blue, pK_A = 6.80. Now decide the relative pH for each of the titrations in A-C.

<table>
<thead>
<tr>
<th>Titration</th>
<th>Eq. Pt. Salt</th>
<th>pH at Eq. Pt.</th>
<th>Indicator</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. HNO_3 with NH_3</td>
<td>NH_4NO_3</td>
<td>pH&lt;7</td>
<td>methyl orange</td>
</tr>
<tr>
<td>B. HNO_3 with KOH</td>
<td>KNO_3</td>
<td>pH = 7</td>
<td>bromothymol orange</td>
</tr>
<tr>
<td>C. HClO_2 with NaOH</td>
<td>NaClO_2</td>
<td>pH &gt; 7</td>
<td>phenolphthalein</td>
</tr>
</tbody>
</table>

177. K_{sp} = 1.19\times10^{-5}
178. K_{sp} = 2.11\times10^{-33}
179. Solubility: 7.3\times10^{-7} M; 1.4\times10^{-4} g/L
180. Solubility: 4.5\times10^{-5} M; 1.6\times10^{-2} g/L
181. \([\text{Ag}^+] = 2.9 \times 10^{-2} \text{ M; } [\text{SO}_4^{2-}] = 1.4 \times 10^{-2} \text{ M}\]
182. Solubility in pure water: \(3.6 \times 10^{-3} \text{ M}\)
    Solubility in 0.30 M KF: \(2.0 \times 10^{-6} \text{ M}\)
183. Both K₂SO₄ and BaCl₂ will decrease the solubility of BaSO₄ in water due to addition of
    common ion. Solubility in 0.10 M K₂SO₄: \(1.1 \times 10^{-9} \text{ M}\); Solubility in 0.25 M BaCl₂:
    \(4.4 \times 10^{-10} \text{ M}\); Solubility in pure water: \(1.0 \times 10^{-5} \text{ M}\)
184. Any salt that contains the conjugate base of a weak acid will have its solubility increased
    by addition of a strong acid (i.e. the salt will be more soluble at lower or acidic solution
    pH).
    Salts more soluble in acidic solution than in pure water are CaF₂, MnS, and ZnCO₃.
186. Any salt that is a metal hydroxide will have its solubility increased by addition of a strong
    acid (i.e. the salt will be more soluble at lower or acidic solution pH).
187. A. pH = 10.35
    B. Solubility in pure water: \(1.12 \times 10^{-4} \text{ M}\); Solubility in soln buffered at pH 8.00 =
    \(5.6 \text{ M}\).
188. Precipitate of MgCO₃ will form because IP > Ksp.
189. If IP = Ksp, no precipitate will form and the solution is saturated.
    If IP > Ksp, a precipitate will form and the solution is supersaturated.
    If IP < Ksp, a precipitate will not form and the solution is unsaturated.
190. Precipitate of Ag₂SO₄ will not form because IP < Ksp.
192. To precipitate as much Hg²⁺ and Ag⁺ as possible without precipitating Pb²⁺ need \([\text{Cl}^−] = 0.089 \text{ M}\).
    At this \([\text{Cl}^−]\), the \([\text{Hg}_2^{2+}]\) left in solution is \(1.8 \times 10^{-16} \text{ M}\). Therefore, most of the
    Hg²⁺ has been precipitated.
193. A solution with a pH=0.52 will precipitate Pb²⁺ and Hg²⁺.
    A pH of slightly higher than 7.2 is needed to precipitate all of the Group III ions.
194. Yes, these two ions can be separated by adjusting the solution pH. To precipitate as
    much of the Cr³⁺ as possible without precipitating the Ni²⁺ the solution pH should be
    adjusted to 6.8.
195. Hg₂Br₂ (ppts. first): AgBr: CuBr: PbBr₂ (ppts. last)
196. Sn²⁺ will precipitate first.
223. Formation of a metal complex usually increases the solubility of a salt because Kf for
    formation of most metal complexes is >>1.
224. Ag⁺(aq) + 2 NH₃(aq) ⇌ [Ag(NH₃)₂]⁺(aq) \(K_f = 1.7 \times 10^7\)
    Cu²⁺(aq) + 4 NH₃(aq) ⇌ [Cu(NH₃)₄]²⁺(aq) \(K_f = 1.1 \times 10^{13}\)
    Ag⁺(aq) + 2 CN⁻(aq) ⇌ [Ag(CN)₂]⁻(aq) \(K_f = 1 \times 10^{31}\)
    Al³⁺(aq) + 4 OH⁻(aq) ⇌ [Al(OH)₄]⁻(aq) \(K_f = 2.1 \times 10^{34}\)
    Cr³⁺(aq) + 4 OH⁻(aq) ⇌ [Cr(OH)₄]⁻(aq) \(K_f = 8 \times 10^{29}\)
    Zn²⁺(aq) + 4 OH⁻(aq) ⇌ [Zn(OH)₄]²⁻(aq) \(K_f = 2.8 \times 10^{15}\)
225. AgCl is more soluble in a solution of aqueous ammonia than in pure water due to
    formation of the very stable metal complex ion, [Ag(NH₃)₂]⁺.
    \[\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^−(aq)\]
    \(K_{sp} = 1.8 \times 10^{-10}\)
    \[\text{Ag}^+(aq) + 2 \text{NH}_3(aq) \rightleftharpoons [\text{Ag(NH}_3)_2]^+(aq)\]
    \(K_f = 1.7 \times 10^7\)
    Net Eq: \[\text{AgCl(s)} + 2 \text{NH}_3(aq) \rightleftharpoons [\text{Ag(NH}_3)_2]^+(aq) + \text{Cl}^−(aq)\]
    \(K = K_{sp} \times K_f = 3.1 \times 10^{-3}\)
226. Limited NH₃: Cd²⁺(aq) + 2 NH₃(aq) + 2 H₂O ⇌ Cd(OH)₂(s) + 2 NH₄⁺(aq)
    Excess NH₃: Cd(OH)₂(s) + 4 NH₃(aq) ⇌ [Cd(NH₃)₄]²⁺(aq) + 2 OH⁻(aq)
    Limited NH₃: Zn²⁺(aq) + 2 NH₃(aq) + 2 H₂O ⇌ Zn(OH)₂(s) + 2 NH₄⁺(aq)
Excess NH₃: Zn(OH)₂(s) + 4 NH₃(aq) ⇌ [Zn(NH₃)₄]²⁺(aq) + 2 OH⁻(aq)

Limited NH₃: Cu²⁺(aq) + 2 NH₃(aq) + H₂O ⇌ Cu(OH)₂(s) + 2 NH₄⁺(aq)
Excess NH₃: Cu(OH)₂(s) + 4 NH₃(aq) ⇌ [Cu(NH₃)₄]²⁺(aq) + 2 OH⁻(aq)

Limited NH₃: Ag⁺(aq) + NH₃(aq) + H₂O ⇌ AgOH(s) + NH₄⁺(aq)
Excess NH₃: AgOH(s) + 2 NH₃(aq) ⇌ [Ag(NH₃)₂]⁺(aq) + OH⁻(aq)

Limited NH₃: Ni²⁺(aq) + 2 NH₃(aq) + H₂O ⇌ Ni(OH)₂(s) + 2 NH₄⁺(aq)
Excess NH₃: Ni(OH)₂(s) + 6 NH₃(aq) ⇌ [Ni(NH₃)₆]²⁺(aq) + 2 OH⁻(aq)

Limited NaOH: Al⁺³(aq) + 3 OH⁻(aq) ⇌ Al(OH)₃(s)
Excess NaOH: Al(OH)₃(s) + OH⁻(aq) ⇌ [Al(OH)₄]⁻(aq)

Limited NaOH: Zn⁺²(aq) + 2 OH⁻(aq) ⇌ Zn(OH)₂(s)
Excess NaOH: Zn(OH)₂(s) + 2 OH⁻(aq) ⇌ [Zn(OH)₄]²⁻(aq)

Limited NaOH: Pb⁺²(aq) + 2 OH⁻(aq) ⇌ Pb(OH)₂(s)
Excess NaOH: Pb(OH)₂(s) + 2 OH⁻(aq) ⇌ [Pb(OH)₄]²⁻(aq)

Limited NaOH: Cr⁺³(aq) + 3 OH⁻(aq) ⇌ Cr(OH)₃(s)
Excess NaOH: Cr(OH)₃(s) + OH⁻(aq) ⇌ [Cr(OH)₄]⁻(aq)

Limited NaOH: Sn⁺²(aq) + 2 OH⁻(aq) ⇌ Sn(OH)₂(s)
Excess NaOH: Sn(OH)₂(s) + OH⁻(aq) ⇌ [Sn(OH)₃]⁻(aq)

227. Solubility of AgBr in 0.75 M NH₃ = 2.3×10⁻³ M.
Solubility of AgBr in pure water = 7.3×10⁻⁷ M. Note that AgBr in 3200 times more soluble in 0.75 M NH₃ than in pure water due to formation of the very stable complex ion, [Ag(NH₃)₂]⁺.

228. [Ni⁺²]=7.6×10⁻¹⁰ M; [NH₃] = 0.70 M

229. Yes, AgCl will precipitate.

230. pH=10.1

234. ΔH= - (exothermic); this favors spontaneous process in forward direction but does not mean that overall the reaction is spontaneous.
ΔH= +(endothermic); this favors nonspontaneous process in forward direction but does not mean that overall the reaction is nonspontaneous.

235. -904.56 kJ

236. Entropy = S = amount of randomness or disorder in a system. As amount of randomness/disorder increases, S increases. S does not have negative values but ΔS, which is the change in entropy during a process, can have negative values.

237. ΔS= +; entropy is increasing and this favors spontaneous process in forward direction.
ΔS= -; entropy is decreasing and this favors nonspontaneous process in forward direction.

238. S_gas >> S_liquid > S_solid
A. ΔS = +  E. ΔS = -
B. ΔS = +  F. ΔS = +
C. ΔS = -
D. ΔS = +

239. 4 NH₃(g) + 5 O₂(g) → 4 NO(g) + 6 H₂O(g); ΔS = + because n_gas=+1
\[2 \text{H}_2\text{O}(g) + \text{N}_2(g) \rightarrow \text{N}_2\text{H}_4(l) + \text{O}_2(g); \quad \Delta S = - \text{ because } n_{\text{gas}} = -2\]

241. \(+180.8 \text{ J/K}\)

243. \(\Delta G = \text{Gibbs Free Energy}; \quad \Delta G = \Delta H - T\Delta S; \quad \Delta G = -\), spontaneous \(\Delta G = +\), nonspontaneous

244. CASE#1: \(\Delta H= +; \quad \Delta S= +; \quad \Delta G = \pm, \text{ dependent on temperature}\)

CASE#2: \(\Delta H= +; \quad \Delta S= -; \quad \Delta G = +, \text{ independent of temperature}\)

CASE#3: \(\Delta H= -; \quad \Delta S= +; \quad \Delta G = -, \text{ independent of temperature}\)

CASE#4: \(\Delta H= -; \quad \Delta S= -; \quad \Delta G = \pm, \text{ dependent on temperature}\)

Crossover temperature: temperature at which reaction can be made to change spontaneity (i.e. spontaneous→nonspontaneous or nonspontaneous→spontaneous).

To calculate crossover temperature: \(T = \frac{\Delta H}{\Delta S}\).

Crossover temperatures cannot be calculated for Cases #2 and #3 because these reactions are always either spontaneous or nonspontaneous at all temperatures.

245. \(\Delta G^* (25 \text{ C}) = -1325.2 \text{ kJ}; \text{ This reaction is spontaneous at 25 C. This reaction can be made nonspontaneous at any temperature above the crossover temperature of 9825 K.}\)

246. A. \(-391.08 \text{ kJ}; \text{ spontaneous at 25 C}\)

B. \(+231.10 \text{ kJ}; \text{ nonspontaneous at 25 C}\)

247. \(\Delta G^* = \text{Gibbs free energy under standard conditions and at specified temperature.}\)

Standard Conditions: all gases having partial pressure of 1 atm; all solutes having concentrations of 1 M; solids, liquids and gases in pure form.

\(\Delta G = \text{Gibbs free energy under nonstandard conditions and at specified temperature.}\)

Equation relating \(\Delta G^*\) to \(\Delta G:\)

\(\Delta G = \Delta G^* + RT\ln Q\)

248. At 25 C: \(\Delta G = +86.6 \text{ kJ}; \text{ nonspontaneous}\)

At 800 C: \(\Delta G = -29.68 \text{ kJ}; \text{ spontaneous}\)

NOTE: To calculate \(\Delta G\) at 25 C, \(\Delta G^*\) (at 25 C) could be calculated from standard Gibbs free energies of formation \(\Delta G^*_f\) since these are tabulated specifically at a temperature of 25 C. However to calculate \(\Delta G\) at 800 C, \(\Delta G^*\) (at 800 C) had to be calculated from the equation \(\Delta G^* = \Delta H^* - T \Delta S^*\).

249. Derivation of equation relating \(\Delta G^*\) to \(K:\)

\(\Delta G = \Delta G^* + RT\ln Q;\)

However at equilibrium the following conditions apply: 1. \(\Delta G = 0;\) 2. \(Q=K;\)

Therefore, the original equation becomes: \(0 = \Delta G^* + RT\ln K;\)

Rearranging for \(\Delta G^*:\)

\(\Delta G^* = -RT\ln K;\)

Rearranging for \(K:\)

\(K = \exp(-\Delta G^*/RT)\)

250. A. \(\Delta G^*(at \ 25 \text{ C}) = -42 \text{ kJ/mol}\)

B. Under the conditions given in Part B, the reaction is nonspontaneous in the forward direction. To determine this fact, either 1.) calculate \(\Delta G = +5 \text{kJ under this set of nonstandard conditions OR 2.) calculate Q=2.0×10^8 and compare it to K.}\)

251. \(K(at \ 25 \text{ C}) = 3.01×10^{-7}; \ K(at \ 200 \text{ C}) = 0.15\)

NOTE: To calculate \(K\) at 200 C, \(\Delta G^*\) at 200 C must first be calculated from the equation \(\Delta G^* = \Delta H^* - T \Delta S^*\).

252. At 25 C, \(\Delta G = -1388 \text{ kJ}; \text{ reaction is spontaneous}\)

At 750 C, \(\Delta G = -1374 \text{ kJ}; \text{ reaction is spontaneous}\)

253. A. \(\Delta G(at \ 25 \text{ C}) = -407 \text{ kJ and } K = 2.2×10^{71}; \text{ reaction is spontaneous under standard conditions.}\)

B. A temperature of 741 K (468 C) or above is needed to regenerate the \text{P}_4\text{O}_{10}. This temperature is the crossover temperature. At the crossover temperature the numerical value of \(K\) is 1.

C. Yes, at 25 C the \text{P}_4\text{O}_{10} will spontaneously adsorb the water vapor. To determine
this calculate $\Delta G = -351$ kJ under this set of nonstandard conditions.

NOTE: To calculate $\Delta G$, $Q$ must first be calculated. For this reaction, $Q = 1/(p_{\text{water}})^6$ where the $p_{\text{water}}$ must be in units of atmospheres.