

1. Calculate ΔS° for the reaction $2\text{Cl}_2(\text{g}) + \text{SO}_2(\text{g}) \rightarrow \text{SOCl}_2(\text{g}) + \text{Cl}_2\text{O}(\text{g})$

Substance:	$\text{Cl}_2(\text{g})$	$\text{SO}_2(\text{g})$	$\text{SOCl}_2(\text{g})$	$\text{Cl}_2\text{O}(\text{g})$
$S^\circ(\text{J/K}\cdot\text{mol})$	223.0	248.1	309.77	266.1

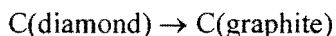
- (a) $-118.2 \text{ J/(K}\cdot\text{mol)}$ (b) $-104.8 \text{ J/(K}\cdot\text{mol)}$ (c) $104.8 \text{ J/(K}\cdot\text{mol)}$
 (d) $118.2 \text{ J/(K}\cdot\text{mol)}$ (e) $1270.0 \text{ J/(K}\cdot\text{mol)}$ (ab) $-233.0 \text{ J/(K}\cdot\text{mol)}$

$$\Delta S^\circ = (S^\circ_{\text{SOCl}_2} + S^\circ_{\text{Cl}_2\text{O}}) - (2S^\circ_{\text{Cl}_2} + S^\circ_{\text{SO}_2}) =$$

$$= 266.1 + 309.77 - 248.1 - 223 \cdot 2 =$$

$$= -118.23 \approx \boxed{-118.2}$$

2. "A diamond is forever" is one of the most successful advertising slogans of all time. But is it true? For the reaction shown below, calculate the standard free energy change at 298 K and determine whether or not a diamond is "forever."



Data: $\Delta H_f^\circ(\text{diamond}) = 1.895 \text{ kJ/mol}$; $S^\circ(\text{diamond}) = 2.337 \text{ J mol}^{-1} \text{ K}^{-1}$; $S^\circ(\text{graphite}) = 5.740 \text{ J mol}^{-1} \text{ K}^{-1}$.

- (a) $\Delta G^\circ = 2.19 \text{ kJ}$; forever (b) -1.90 kJ ; not forever (c) -2.91 kJ ; not forever
 (d) 1.90 kJ ; forever (e) $\Delta G^\circ = < -1000 \text{ kJ}$; not forever

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (0 - 1.895) \frac{\text{kJ}}{\text{mol}} - 298 \cdot \left(\frac{5.74 - 2.337}{1000} \right) \frac{\text{kJ}}{\text{mol}}$$

$$= -2.909 \frac{\text{kJ}}{\text{mol}} \approx -2.91 \frac{\text{kJ}}{\text{mol}}$$

For 1 mol of rxn it is $\boxed{-2.91 \text{ kJ}}$

3. Which one of the following statements would be true for the reaction in the preceding question?

- (a) This reaction is favorable (spontaneous) at high temperatures, but unfavorable (non-spontaneous) at lower temperatures.
 (b) This reaction is favorable (spontaneous) at low temperatures, but unfavorable (non-spontaneous) at higher temperatures.
 (c) This reaction is unfavorable (non-spontaneous) at all temperature.
 (d) This reaction is favorable (spontaneous) at all temperatures.

$$\Delta H < 0 \quad \left(-1.895 \frac{\text{kJ}}{\text{mol}} \right)$$

$$\Delta S > 0 \quad \left(+ 3.4 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right)$$

4. What buffer component ratio would be needed to make a pH 10.00 buffer with the base 4-dimethylaminopyridine (DMAP) and its salt with HCl, 4-dimethylaminopyridine hydrochloride (DMAPH⁺Cl⁻)? Structure of DMAP is shown on page 7.

- (a) 9.7 (b) 3.0 (c) 2.0 (d) 0.50 (e) 0.30

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = \text{p} \frac{K_w}{K_b} + \log \frac{[\text{base}]}{[\text{conj. acid}]} = \\ &= \text{p} \frac{K_w}{K_b(\text{DMAP})} + \log \frac{[\text{DMAP}]}{[\text{DMAPH}^+]} = \text{p} \frac{10^{-14}}{5 \cdot 10^{-5}} + \log \frac{[\text{DMAP}]}{[\text{DMAPH}^+]} = 10.00 \\ \frac{[\text{DMAP}]}{[\text{DMAPH}^+]} &= 10^{10 - 9.699} \approx 2.00 \end{aligned}$$

5. How much solid DMAP ($M_w = 122.17 \text{ g/mol}$) would need to be added to 200. mL of a 0.010 M HCl solution to make a pH 10.00 buffer?

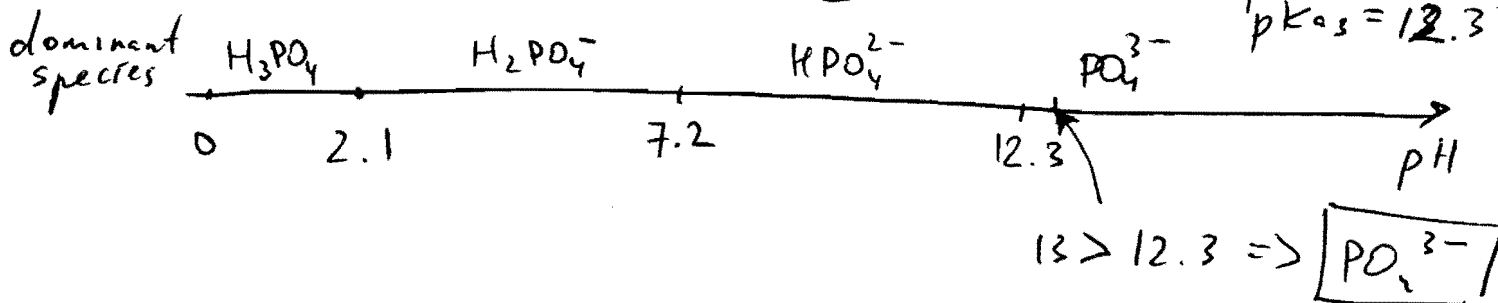
- (a) 0.73 g (b) 3.0 g (c) 0.003 g (d) 1.2 g (e) 7.3 g

$$\begin{aligned} \frac{[\text{DMAP}]}{[\text{DMAPH}^+]} &= 2 \text{ (problem 4)} \\ [\text{DMAP}] &= \frac{m}{M_w V_{\text{HCl}}} - C_{\text{HCl}} \\ [\text{DMAPH}^+] &= C_{\text{HCl}} \\ \frac{[\text{DMAP}]}{[\text{DMAPH}^+]} &= \frac{\frac{m}{M_w V_{\text{HCl}}} - C_{\text{HCl}}}{C_{\text{HCl}}} = 2 \\ \frac{m}{M_w V_{\text{HCl}}} - C_{\text{HCl}} &= 2 C_{\text{HCl}} \\ \frac{m}{M_w V_{\text{HCl}}} &= 3 C_{\text{HCl}} \\ m &= 3 C_{\text{HCl}} \cdot V_{\text{HCl}} \cdot M_w = \\ &= 3 \cdot 0.01 \text{ M} \cdot 0.2 \text{ L} \cdot 122.17 \frac{\text{g}}{\text{mol}} = 0.73302 \text{ g} \approx \boxed{0.73 \text{ g}} \end{aligned}$$

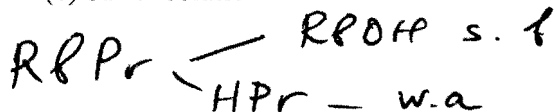
6. The pH of an aqueous H_3PO_4 solution is adjusted to pH=13 by addition of strong base. Which of the following would be the primary species in solution at this pH?

- (a) H_3PO_4 (b) H_2PO_4^- (c) HPO_4^{2-} (d) PO_4^{3-} (e) H_3PO_3

$\text{p}K_{a1} = 2.1$
 $\text{p}K_{a2} = 7.2$
 $\text{p}K_{a3} = 12.3$



7. How is an aqueous solution of rubidium propionate, RbPr, best characterized (propionic acid, HPr=CH₃CH₂COOH)?
- (a) solution of a strong acid
(c) solution of a strong base
(e) buffer solution
- (b) solution of a weak acid
(d) solution of a weak base
(ab) neutral solution



8. What is the pH of a 1.2 M aqueous solution of RbPr?

- (a) 8.48 (b) 9.48 (c) 5.28 (d) 4.52 (e) 0.18

$$\text{Pr}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{HPr}$$

$$[\text{OH}^-] \approx \sqrt{\frac{K_w}{K_a} C_{\text{Pr}^-}} = \sqrt{\frac{10^{-14}}{1.3 \cdot 10^{-5}} \cdot 1.2} \approx 3.04 \cdot 10^{-5} \text{ M}$$

$$\text{pH} = \text{p} \frac{K_w}{[\text{OH}^-]} = 9.482 \approx \boxed{9.48}$$

9. What is the pH of an aqueous mixture of 0.50 M RbPr and 0.30 M HPr?

- (b) 8.89 (b) 10.96 (c) 4.89 (d) 5.93 (e) 5.11

$$\text{pH} = \text{p} K_a + \log \frac{[\text{Pr}^-]}{[\text{HPr}]} =$$

$$= 4.886 + \log \frac{0.5}{0.3} = 5.1079 \approx \boxed{5.11}$$

Consider the following titration for the next 4 questions.

10.0 mL of 0.250 M $\text{HClO}_4(\text{aq})$ (in flask) is titrated with 0.100 M $\text{NaOH}(\text{aq})$ (in buret).

10. What is the overall reaction occurring in the titration?

- (a) $\text{Na}^+(\text{aq}) + \text{ClO}_4^-(\text{aq}) \rightarrow \text{NaClO}_4(\text{aq})$
(b) $\text{HClO}_4(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{NaClO}_4(\text{aq})$
(c) $\text{NaOH}(\text{aq}) \rightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq})$
(d) $2\text{HClO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + 2\text{ClO}_4^-(\text{aq})$
(e) $\text{HClO}_4(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaH}(\text{aq}) + \text{HOClO}_4(\text{aq})$

11. How many mL's of the NaOH solution need to be added to reach the equivalence point of the titration?

- (a) 250. mL (b) 2.50 mL (c) 15.0 mL (d) 20.0 mL (e) 25.0 mL

$$C_{\text{HClO}_4} V_{\text{HClO}_4} = C_{\text{NaOH}} V_{\text{NaOH}}$$

$$V_{\text{NaOH}} = \frac{10 \text{ mL} \cdot 0.25 \text{ M}}{0.1 \text{ M}} = 25 \text{ mL}$$

12. Which combination of ions of the following is present in the flask after 10.0 mL of the NaOH(aq) solution have been added? (Be sure to consider your answer to the above question in answering this question. Take into account only the ions with concentration greater than 10^{-7} M.)

- (a) $\text{ClO}_4^-; \text{H}_3\text{O}^+$ (b) $\text{ClO}_4^-; \text{Na}^+; \text{H}_3\text{O}^+$ (c) $\text{ClO}_4^-; \text{OH}^-; \text{Na}^+; \text{H}_3\text{O}^+$ (d) $\text{ClO}_4^-; \text{OH}^-; \text{Na}^+$
(e) $\text{ClO}_4^-; \text{Na}^+$ (ab) $\text{ClO}_4^-; \text{Na}^+; \text{CO}_3^{2-}$

13. What is the pH of the solution in the flask after 10.0 mL of the NaOH(aq) have been added?

- (a) 1.215 (b) 0.602 (c) 0.075 (d) 7.500 (e) 1.125

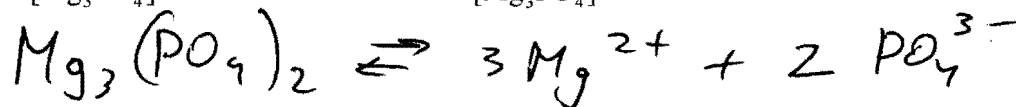
$$[\text{H}^+] \approx [\text{HClO}_4] = \frac{V_{\text{HClO}_4} - V_{\text{NaOH}}}{V_{\text{HClO}_4} + V_{\text{NaOH}}} =$$
$$= \frac{C_{\text{HClO}_4} V_{\text{HClO}_4} - C_{\text{NaOH}} V_{\text{NaOH}}}{V_{\text{HClO}_4} + V_{\text{NaOH}}} = \frac{0.25 \text{ M} \cdot 10 \text{ mL} - 0.1 \text{ M} \cdot 10 \text{ mL}}{10 \text{ mL} + 10 \text{ mL}} =$$

$$= 0.075 \text{ M}$$

$$\text{pH} = -\log(0.075) \approx 1.125$$

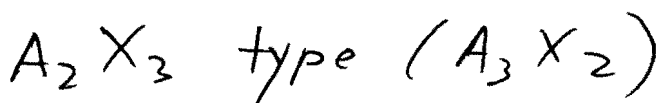
14. What is the K_{sp} expression for $Mg_3(PO_4)_2$? (Look at all answers carefully. Some of them are very similar.)

- (a) $[Mg^{2+}]^3[PO_4^{3-}]^2$ (b) $[Mg^{2+}]^2[PO_4^{3-}]^3$ (c) $[Mg]^3[PO_4]^4$
 (d) $\frac{[Mg]^3[PO_4]^2}{[Mg_3PO_4]^2}$ (e) $\frac{[Mg^{2+}]^3[PO_4^{3-}]^2}{[Mg_3PO_4]}$



15. The solubility of $Mg_3(PO_4)_2$ in pure water is 8.6×10^{-6} M in pure water at $25^\circ C$. What is the value of the K_{sp} for this compound at $25^\circ C$?

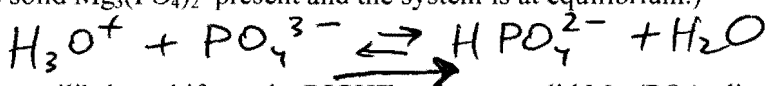
- (a) 2.9×10^{-3} (b) 2.5×10^{-15} (c) 1.3×10^{-30} (d) 5.1×10^{-24} (e) 4.7×10^{-26}



$$K_{sp} = (2s)^2 (3s)^3 = 108s^5 \approx 5.08 \cdot 10^{-24} \approx \boxed{5.1 \cdot 10^{-24}}$$

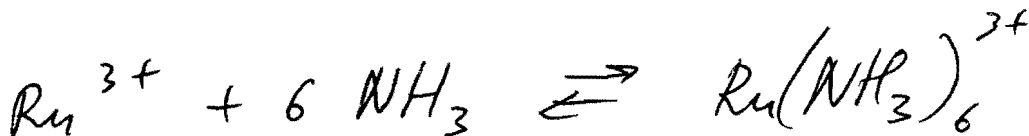
16. What will happen if HCl is added to a saturated aqueous solution of $Mg_3(PO_4)_2$ in water? ("Saturated solution" means that there is solid $Mg_3(PO_4)_2$ present and the system is at equilibrium.)

- (a) Nothing happens.
 (b) The $Mg_3(PO_4)_2$ solubility equilibrium shifts to the RIGHT and more solid $Mg_3(PO_4)_2$ dissolves.
 (c) The $Mg_3(PO_4)_2$ solubility equilibrium shifts to the LEFT and more $Mg_3(PO_4)_2$ precipitates out of solution.
 (d) The $Mg_3(PO_4)_2$ solubility equilibrium shifts to the RIGHT and more $Mg_3(PO_4)_2$ precipitates out of solution.
 (e) The $Mg_3(PO_4)_2$ solubility equilibrium shifts to the LEFT and more solid $Mg_3(PO_4)_2$ dissolves.



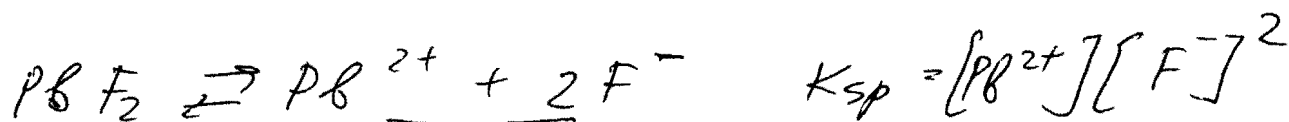
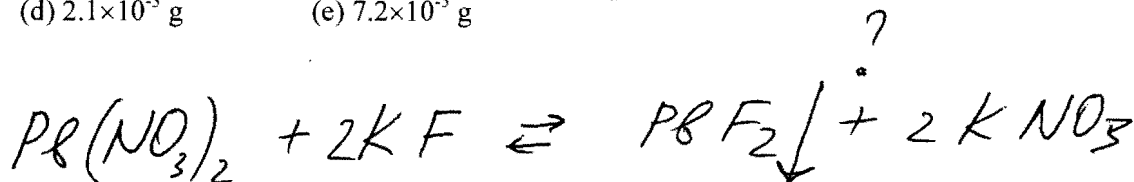
17. Ru^{3+} ion forms a complex ion with 6 ammonia molecules. What is the K_f expression for the formation this complex ion?

- (a) $\frac{[Ru^{3+}][NH_3]^6}{[Ru(NH_3)_6^{3+}]}$ (b) $[Ru^{3+}][NH_4^+]^6$ (c) $[Ru^{3+}][NH_3]_6$
 (d) $\frac{[Ru(NH_4)_6^{3+}]}{[Ru^{3+}][NH_4^+]^6}$ (e) $\frac{[Ru(NH_3)_6^{3+}]}{[Ru^{3+}][NH_3]^6}$



18. What is the maximum amount of potassium fluoride ($M_w=58.1\text{g/mol}$) that can be added to 100. mL of a $1.0 \times 10^{-4}\text{ M}$ solution of lead(II) nitrate without precipitating out lead(II) fluoride? K_{sp} of lead(II) fluoride = 3.6×10^{-8}

- (a) 0.080 g (b) $1.5 \times 10^{-3}\text{ g}$ (c) 0.11 g
(d) $2.1 \times 10^{-3}\text{ g}$ (e) $7.2 \times 10^{-5}\text{ g}$



$$\text{MAXIMUM } [\text{F}^-] = \sqrt{\frac{K_{sp}}{[\text{Pb}^{2+}]}} = \frac{m_{\text{KF}}}{M_{\text{KF}} V}$$

$$m_{\text{KF}} = M_{\text{KF}} \cdot V \cdot \sqrt{\frac{K_{sp}}{[\text{Pb}^{2+}]}} = 58.1 \frac{\text{g}}{\text{mol}} \cdot 0.1 \text{ L} \cdot \sqrt{\frac{3.6 \cdot 10^{-8}}{1 \cdot 10^{-4}}} = \boxed{0.11 \text{ g}}$$

19. The Three Laws of Thermodynamics are as follows:

1. The total energy of the universe is constant.
2. The total entropy of the universe increases for a spontaneous process.
3. The entropy of a perfectly ordered crystal at 0 K is 0.

The answers in order are

- (a) energy, energy, energy (b) energy, entropy, energy (c) entropy, energy, energy
(d) entropy, energy, entropy (e) energy, entropy, entropy

20. Which of the following should have the greatest molar entropy at 300 K?

- (a) $\text{CH}_4(\text{g})$ (b) $\text{H}_2\text{O}(\text{l})$ (c) $\text{NaCl}(\text{s})$ (d) $\text{N}_2\text{O}_4(\text{g})$ (e) $\text{H}_2(\text{g})$

a) gas

b) highest molar mass

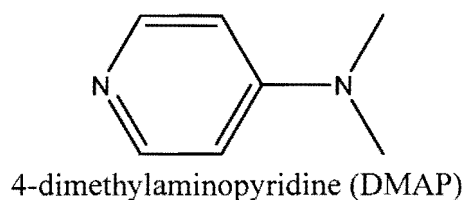
ADDITIONAL INFORMATION and EQUATIONS

Some K_a Values at 25°C

	K_{a1}	K_{a2}	K_{a3}
CH_3COOH	1.8×10^{-5}		
$\text{C}_6\text{H}_5\text{COOH}$	6.3×10^{-5}		
$\text{CH}_3\text{CH}_2\text{COOH}$	1.3×10^{-5}		
H_3BO_3	5.8×10^{-10}		
H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
$\text{H}_2\text{C}_2\text{O}_4$	5.6×10^{-2}	5.4×10^{-5}	
HCO_2H	1.8×10^{-4}		
H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
H_2SO_4	very large	1.2×10^{-2}	
HF	3.5×10^{-4}		

Some K_b values at 25°C

	K_b
NH_3	1.8×10^{-5}
CH_3NH_2	4.4×10^{-4}
4-dimethylaminopyridine (DMAP)	5.0×10^{-5}
$\text{C}_5\text{H}_5\text{N}$	1.7×10^{-9}



$$K_a K_b = K_w = 1.008 \times 10^{-14} \quad R = 8.314 \times 10^{-3} \text{ kJ/(mol}\cdot\text{K)} \quad 0^\circ\text{C} = 273.15 \text{ K}$$

$$pH = pK_a + \log \frac{[\text{conj. base}]}{[\text{acid}]} \quad pK_a = -\log K_a$$

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants} \quad \Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

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