

Multiple Choice (5 points each, Put answers in CAPS in the left margin.)

$R = 8.314 \text{ J/mol}\cdot\text{K} = 0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K}$

- Which of the following would you expect to be **most** acidic?
A) H_2O B) H_2S C) H_2Se D) SiH_4 E) PH_3
- For the equilibrium: $\text{Fe}_3\text{O}_4(\text{s}) + 4 \text{H}_2(\text{g}) \rightleftharpoons 3 \text{Fe}(\text{s}) + 4 \text{H}_2\text{O}(\text{g})$ which of the following will cause no change in the position of the equilibrium?
A) Adding Fe_3O_4 C) Adding H_2 E) A and C
B) Adding NH_3 D) A and B
- The molar solubility for PbF_2 is $2.05 \times 10^{-4} \text{ M}$. What is its K_{sp} ?
A) 3.73×10^{-2} C) 4.20×10^{-8} E) 8.62×10^{-12}
B) 5.90×10^{-2} D) 3.44×10^{-11}
- Which of the following metal ions will yield the **most** acidic solution?
A) Ca^{2+} B) Fe^{3+} C) K^+ D) Li^+ E) Zn^{2+}
- Addition of which of the following would have no effect on the solubility of AgCN ?
A) AgNO_3 B) HCl C) NaCN D) HClO_4 E) NaNO_3
- Which of the following reactions shows the largest increase in entropy?
A) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{HCl}(\text{g})$
B) $\text{BaO}(\text{s}) + \text{CO}_2(\text{g}) \rightarrow \text{BaCO}_3(\text{s})$
C) $\text{SiCl}_4(\text{l}) + 2 \text{H}_2\text{O}(\text{l}) \rightarrow \text{SiO}_2(\text{s}) + 4 \text{HCl}(\text{aq})$
D) $2 \text{CH}_3\text{OH}(\text{l}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{g})$
E) $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{SO}_3(\text{g})$
- Which of the following is a non-spontaneous process?
A) Formation of rust.
B) Hydrolysis of NaCl in water to make HCl and NaOH .
C) Salt dissolving in water.
D) Water evaporating at room temperature.
E) Water freezing at $-10 \text{ }^\circ\text{C}$.

8. Which of the following is a statement of the second law of thermodynamics?
- When reactants are converted into products, the change in enthalpy is independent of the number of steps taken.
 - The entropy of a perfect crystal of any substance at absolute zero is zero.
 - Energy can be converted from one form to another but cannot be created or destroyed.
 - State functions are properties that are determined by the state the system is in.
 - The entropy of the universe is always increasing.

Discussion Questions: (You must show your work to receive credit.)

1. The equilibrium constant for the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI}$ is 55.6 at 425 °C (all are gases). If 1.00 mol of hydrogen and 1.00 mol of iodine are allowed to equilibrate in a 2.00 L vessel, how many moles of hydrogen iodide are produced? What percentage of iodine is converted to hydrogen iodide? (10 points)

$$[\text{H}_2]_i = \frac{1.00 \text{ mol}_{\text{H}_2}}{2.00 \text{ L}} = 0.500 \text{ M} \qquad [\text{I}_2]_i = \frac{1.00 \text{ mol}_{\text{I}_2}}{2.00 \text{ L}} = 0.500 \text{ M}$$

$$[\text{H}_2]_e = 0.500 - x \text{ M} \qquad [\text{I}_2]_e = 0.500 - x \text{ M} \qquad [\text{HI}]_e = 2x$$

$$K_C = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(0.500 - x)^2} = 55.6$$

$$\frac{2x}{0.500 - x} = 7.46$$

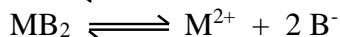
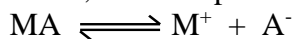
$$x = 0.394 \Rightarrow [\text{HI}]_e = 0.788 \text{ M}$$

$$\text{mol}_{\text{HI}} = \frac{0.788 \text{ mol}_{\text{HI}}}{\text{L}} \times 2.0 \text{ L} = 1.58 \text{ mol}$$

$$\% \text{ conversion} = 100\% - \left(\frac{0.200 \text{ M} - 0.158 \text{ M}}{0.200 \text{ M}} \right) (100\%) = 79.0 \%$$

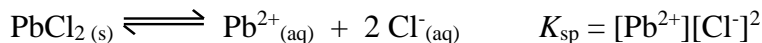
2. Why is it that it is not necessarily correct to say that because the K_{sp} for one salt is larger than that of a different salt, the solubility of the first salt is necessarily higher than the second. (5 points)

For any “insoluble” salt, M_xA_y , where M is the metal and A is the anion, the $K_{sp} = [\text{M}]^x[\text{A}]^y$. For any collection of such salts where all have the same x and y values, a direct comparison of K_{sp} values is possible because the dissociation equations will be the same. However, when they are different, for example MA vs. MB_2 , the equations will be different:



Here the solubility of the first salt goes as the square root of the K_{sp} , while the solubility of the second salt goes as the cube root. As a result, if the K_{sp} values were the same, the second salt would be more, not equally soluble. Thus, it is possible for K_{sp} (MA) to be larger than K_{sp} (MB_2) and be less soluble.

3. Lead(II) chloride has a solubility of 4.45 g/L in aqueous solutions. What is its (i) molar solubility and K_{sp} in pure water and (ii) molar solubility in 1.2 M NaCl solution? (12 points)



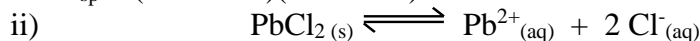
First determine $[\text{PbCl}_2]$.

$$[\text{PbCl}_2] = \left(\frac{4.45 \text{ g}_{\text{PbCl}_2}}{L_{\text{soln}}} \right) \left(\frac{1 \text{ mol}_{\text{PbCl}_2}}{278.1 \text{ g}_{\text{PbCl}_2}} \right) = 1.60 \times 10^{-2} M$$

$$\text{i) } [\text{Pb}^{2+}] = \left(\frac{1.60 \times 10^{-2} \text{ mol}_{\text{PbCl}_2}}{L} \right) \left(\frac{1 \text{ mol}_{\text{Pb}^{2+}}}{1 \text{ mol}_{\text{PbCl}_2}} \right) = 1.60 \times 10^{-2} M$$

$$[\text{Cl}^{-}] = \left(\frac{1.60 \times 10^{-2} \text{ mol}_{\text{PbCl}_2}}{L} \right) \left(\frac{2 \text{ mol}_{\text{Cl}^{-}}}{1 \text{ mol}_{\text{PbCl}_2}} \right) = 3.2 \times 10^{-2} M$$

$$K_{sp} = (1.6 \times 10^{-2})(3.2 \times 10^{-2})^2 = 1.64 \times 10^{-5}$$



Initial $0 M$ $1.2 M$

Change $+x$ $+2x$

Equil x $1.2 + 2x$

$$(x)(1.2 + x)^2 = 1.64 \times 10^{-5}$$

$[\text{Cl}^{-}] \gg 100K_{sp}$, so assume x is negligible in comparison to 1.2

$$(x)(1.2)^2 = 1.64 \times 10^{-5}$$

$$x = 1.14 \times 10^{-5}$$

$$[\text{PbCl}_2] = 1.14 \times 10^{-5} M$$

4. The formation constant of $[\text{M}(\text{CN})_6]^{4-}$ is 2.50×10^{17} , where M is a generic metal. A 0.150 mole quantity of $\text{M}(\text{NO}_3)_2$ is added to a liter of 1.31 M NaCN solution. What is the concentration of M^{2+} ions at equilibrium? (8 points) (Homework 15.14)



initial $0.150 M$ $1.31 M$ $0 M$

react $0 M$ $0.41 M$ 0.150

change $+x$ $+6x$ $-x$

equil x $0.41 + 6x$ $0.150 - x$

$$K_f = \frac{0.150 - x}{(x)(0.41 + 6x)^6} = 2.50 \times 10^{17}$$

Because $K_f \gg 0.41$, assume x is negligible

$$2.50 \times 10^{17} = \frac{0.150}{(x)(0.41)^6}$$

$$x = 7.6 \times 10^{-16} \Rightarrow [\text{M}^{2+}] = 1.3 \times 10^{-16} M$$

5. What is spontaneity and how are enthalpy and entropy related to it? (9 points)

Spontaneity is when processes occur without outside intervention. Energy is released in spontaneous processes, usually as heat. This is a decrease in enthalpy of the system. An increase in energy dispersion also usually occurs in spontaneous processes. This is an increase in entropy.

6. For the reaction $\text{NO}_{2(g)} + \text{CO}_{(g)} \rightleftharpoons \text{NO}_{(g)} + \text{CO}_{2(g)}$ at 25°C:

	ΔH° (kJ/mol)	ΔS° (J/mol·K)
CO	-110.5	197.7
CO ₂	-393.5	213.8
NO	91.3	210.8
NO ₂	33.2	240.1

Calculate $\Delta H^\circ_{\text{rxn}}$, $\Delta S^\circ_{\text{rxn}}$, $\Delta G^\circ_{\text{rxn}}$, K_P (16 points)

$$\Delta H^\circ_{\text{rxn}} = [(1 \text{ mol})(91.3 \frac{\text{kJ}}{\text{mol}}) + (1 \text{ mol})(-393.5 \frac{\text{kJ}}{\text{mol}})] - [(1 \text{ mol})(33.2 \frac{\text{kJ}}{\text{mol}}) + (1 \text{ mol})(-110.5 \frac{\text{kJ}}{\text{mol}})]$$

$$= -224.9 \text{ kJ}$$

$$\Delta S^\circ_{\text{rxn}} = [(1 \text{ mol})(210.8 \frac{\text{J}}{\text{mol}\cdot\text{K}}) + (1 \text{ mol})(213.8 \frac{\text{J}}{\text{mol}\cdot\text{K}})] - [(1 \text{ mol})(240.1 \frac{\text{J}}{\text{mol}\cdot\text{K}}) + (1 \text{ mol})(197.7 \frac{\text{J}}{\text{mol}\cdot\text{K}})]$$

$$= -13.2 \text{ J/K}$$

$$\Delta G^\circ_{\text{rxn}} = -224.9 \text{ kJ} - (298 \text{ K})(-13.2 \frac{\text{J}}{\text{K}})(\frac{1 \text{ kJ}}{1000 \text{ J}})$$

$$= -221.0 \text{ kJ}$$

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

$$(-221.0 \text{ kJ})(1000 \frac{\text{J}}{\text{kJ}}) = -(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(298 \text{ K})(\ln K_P)$$

$$\ln K_P = 89.2$$

$$K_P = 5.48 \times 10^{38}$$