

6. d (cont.)

$$\frac{-\Delta H_{\text{sub}}}{T}$$

neg. b/c endothermic

PS#3 Solns

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i. Above 196 K

$$|\Delta S_{\text{surr}}| < |\Delta S_{\text{sys}}|$$

and  $\Delta S_{\text{univ}} > 0$  So, Sublimation is spontaneous

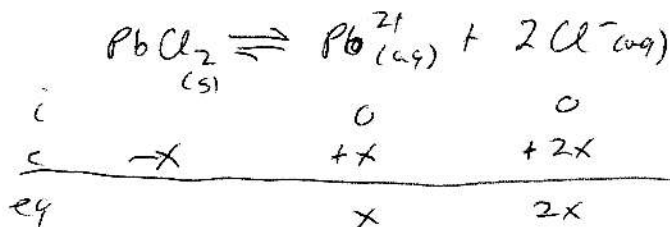
ii. Below 196 K

$$|\Delta S_{\text{surr}}| > |\Delta S_{\text{sys}}|$$

and  $\Delta S_{\text{univ}} < 0$  So, Sublimation is not spontaneous

(The opposite process  $\text{CO}_2(\text{g}) \rightarrow \text{CO}_2(\text{s})$  is spontaneous)

7. a.  $\text{PbCl}_2 \rightarrow K_{\text{sp}} = 1.6 \times 10^{-5}$  at  $25^\circ\text{C}$



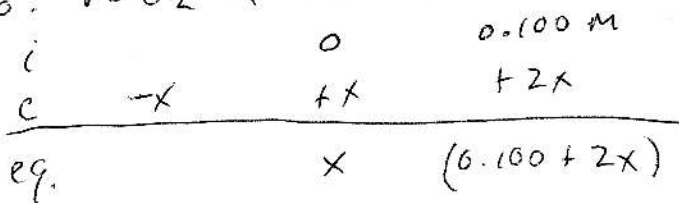
$$K_{\text{sp}} = 1.6 \times 10^{-5} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

$$1.6 \times 10^{-5} = (x)(2x)^2$$

$$1.6 \times 10^{-5} = 4x^3$$

$$x = 1.59 \times 10^{-2} \text{ M}$$

Solubility =  $x = 1.6 \times 10^{-2} \text{ M}$



$$x(0.100 + 2x)^2 = 1.6 \times 10^{-5}$$

approx  $x(0.100) \approx 1.6 \times 10^{-5}$

$$x = 1.6 \times 10^{-4} \text{ M}$$

Approx is ok - this is  $< 5\%$  of 0.100

Solubility =  $1.6 \times 10^{-4} \text{ M}$

(much less than in a, due to the common ion effect)

$$8. \quad [CO_3^{2-}] = 0.0023M, \quad [Cl^-] = 0.00076M$$

a.  $Ag^+$  will precipitate with either of these ions. We must look at the  $K_{sp}$ 's for  $Ag_2CO_3$  and  $AgCl$  and calculate to see which anion precipitates first.

$$K_{sp}(AgCl) = 1.6 \times 10^{-10} \quad K_{sp}(Ag_2CO_3) = 8.1 \times 10^{-12}$$

Comparing the 2  $K_{sp}$ 's, if the conc's of  $CO_3^{2-}$  and  $Cl^-$  were ~~equal~~ <sup>both 1.0M or equal</sup>,  $Cl^-$  would ppt 1st. Since they're not ~~equal~~ <sup>both 1.0M or equal</sup>, we need to go to part b and find  $[Ag^+]$  req'd. to ppt. each ion. (For  $Ag_2CO_3$ , with 2  $Ag^+$ 's, we'd need to take a square root — see below)

b. For  $CO_3^{2-}$   $K_{sp}(Ag_2CO_3) = 8.1 \times 10^{-12}$

$$[Ag^+]^2 [CO_3^{2-}] = 8.1 \times 10^{-12}$$

$$[Ag^+]^2 = \frac{8.1 \times 10^{-12}}{0.0023}$$

$$[Ag^+] = 5.9 \times 10^{-5} M \quad \text{at equilib - for the 1st appearance of ppt.}$$

For  $Cl^-$   $K_{sp}(AgCl) = 1.6 \times 10^{-10}$

$$[Ag^+][Cl^-] = 1.6 \times 10^{-10} \quad \text{at equil.}$$

$$[Ag^+] = \frac{1.6 \times 10^{-10}}{0.000760} = 2.1 \times 10^{-7}$$

for 1st ppt. to form

~~$AgCl$  should ppt first~~ with  $[Ag^+] = 2.1 \times 10^{-7}$ .

$Ag_2CO_3$  won't begin precipitating until  $[Ag^+]$

reached  $5.9 \times 10^{-5} M$ , approximately.