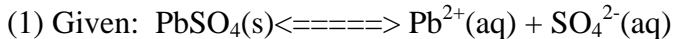


Chem 103 Problem Set #8 Do the problems first without looking at the solutions.



a) Calculate the equilibrium constant if G_f° for $\text{PbSO}_4(\text{s})$ is -811 kJ/mole ; for $\text{Pb}^{2+}(\text{aq})$ is 24.3 kJ/mole and for $\text{SO}_4^{2-}(\text{aq})$ is -742 kJ/mole .

b) Calculate the solubility of PbSO_4 in water.

c) Calculate the solubility of PbSO_4 in a buffer solution if the pH of the solution is 1.73 and the $[\text{HSO}_4^-]$ is 0.100 M. K_a for $\text{HSO}_4^- = 1.02 \times 10^{-2}$

(2) Given: $\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ K_{sp} for $\text{BaSO}_4 = 1.1 \times 10^{-10}$. $\text{Ba}^{2+}(\text{aq})$ is poisonous when ingested. The lethal dosage in mice is about 12 mg per kg of body mass. Despite this fact, BaSO_4 is widely used in medicine to obtain X-ray photographs of the gastrointestinal tract. At Wt of Ba = 137.3; S = 32.1; O = 16.0; Mg = 24.3

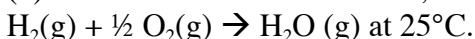
(a) Explain why $\text{BaSO}_4(\text{s})$ is safe to take internally, even though $\text{Ba}^{2+}(\text{aq})$ is poisonous.

(b) What is the concentration of Ba^{2+} , in milligrams per liter, in saturated $\text{BaSO}_4(\text{aq})$?

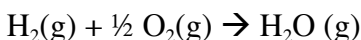
(c) MgSO_4 can be mixed with $\text{BaSO}_4(\text{s})$ in this medical procedure. What function does the MgSO_4 serve?

(d) If the pH of the solution is 1.44 and the $[\text{HSO}_4^-]$ is 0.100 M, what is the solubility of BaSO_4 . K_a for $\text{HSO}_4^- = 1.02 \times 10^{-2}$.

(3) Consider the reaction below, at 25°C .



Given that for water vapor,



Given:

	ΔH_f° (in kJ/mol)	K_p
$\text{H}_2(\text{g})$	0	131
$\text{O}_2(\text{g})$	0	205
$\text{H}_2\text{O}(\text{g})$	-242	189

a) What is the maximum work one can obtain from the formation of 1 mole of water vapor at 298K?[3pts]

b) What is K_p for this reaction under standard conditions?[2 pts]

c) Is K_p greater than K_c ?

d) By how much has the entropy of the universe increased assuming 1 mole of H_2O has been formed by the above reaction?

d) is the sign of ΔG° dependent on the temperature?

Solutions

(1) solution:

a) first, get ΔG° for the dissociation reaction:

$$\Delta G^\circ = \Delta G^\circ_f(\text{Pb}^{2+}) + \Delta G^\circ_f(\text{SO}_4^{2-}) - \Delta G^\circ_f(\text{PbSO}_4(\text{s})) = (24.3 - 742 - (-811))\text{kJ/mol} = +93.3 \text{ kJ/mol};$$

$$K_{\text{sp}} = \exp(-\Delta G^\circ/RT) = \exp(-(93300\text{J/mol}) / ((8.314 \text{ J/molK})(298\text{K})) = 4.42 \times 10^{-17}$$

b) $\text{PbSO}_4(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = x^2 = 4.42 \times 10^{-17} \Rightarrow x = 6.65 \times 10^{-9} \text{ M}$$

c) First, we recognize the presence of a common ion, SO_4^{2-} . To get its concentration we

use the buffer equation: $\text{pH} = \text{pK}_a + \log \frac{[\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$ (where $\text{pK}_a = -\log(1.02 \times 10^{-2}) = 1.99$)

$$10^{\text{pH}-\text{pK}_a} = \frac{[\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} \Rightarrow [\text{SO}_4^{2-}] = [\text{HSO}_4^-](10^{\text{pH}-\text{pK}_a}) = (0.100\text{M})(10^{(1.73-1.99)}) = 0.0550 \text{ M}$$

so we have: $\text{PbSO}_4(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = x(.0550+x) \approx 0.0550x = 4.42 \times 10^{-17} \Rightarrow x = 8.04 \times 10^{-16} \text{ M}$$

(it satisfies the 5% rule).

(2) Solution:

a) BaSO_4 is very insoluble and thus, $[\text{Ba}^{2+}]$ is very low and can be tolerated by the body.

b) $\text{PbSO}_4(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ $K_{\text{sp}} = 1.1 \times 10^{-10}$

$$\text{so, } x^2 = 1.1 \times 10^{-10} \Rightarrow x = 1.0 \times 10^{-5}$$

$$\text{So, \# mg Ba}^{2+}/\text{L} = 1.0 \times 10^{-5} \text{ mol Ba}^{2+}/\text{L} \times (137 \text{ g/mol})(1000\text{mg/g}) = 1.4 \text{ mg/L}$$

c) MgSO_4 is very soluble and provides a common ion (namely SO_4^{2-}) to lower the solubility of BaSO_4 further.

d) Here, we recognize the presence of a common ion, SO_4^{2-} .

From the buffer eq'n: $\text{pH} = \text{pK}_a + \log \frac{[\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$ (where $\text{pK}_a = -\log(1.02 \times 10^{-2}) = 1.991$)

$$10^{\text{pH}-\text{pK}_a} = \frac{[\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} \Rightarrow [\text{SO}_4^{2-}] = [\text{HSO}_4^-](10^{\text{pH}-\text{pK}_a}) = (0.100\text{M})(10^{(1.44-1.99)}) = 0.0282\text{M}$$

so we have: $\text{PbSO}_4(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = x(.0282+x) \approx 0.0282x = 4.42 \times 10^{-17} \Rightarrow x = 1.57 \times 10^{-16} \text{ M}$$

(it satisfies the 5% rule).

(3) solution:

a) $W_{\max} = -\Delta G^{\circ} = -(\Delta H^{\circ} - T\Delta S^{\circ}) = -\{-242 + (298)(-45)\} = +229 \text{ kJ}$

b) solution: $K_p = \exp(-(-229000)/((8.314)(298))) = 1.38 \times 10^{40}$

c) solution: $K_p = K_c(RT)^{\Delta n}$; since, $\Delta n < 0$, ($= -1/2$), then $K_p < K_c$

d) solution: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surroundgs}} = -45 + (812) = \mathbf{767 \text{ J/mol K}}$
(note: $\Delta S_{\text{sys}} = \sum \nu \Delta S_f^{\circ} = 189 - (205)(.5) - 131 = -45 \text{ J/mol}$
and $\Delta S_{\text{surr}} = -\Delta H^{\circ}/T = -(-242000)/298 = 812 \text{ J/mol}$)

e) solution: No since it's both exothermic and increases in entropy.
It's always negative (-)