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

(1) Given: $PbSO_4(s) \Longleftrightarrow Pb^{2+}(aq) + SO_4^{2-}(aq)$
a) Calculate the equilibrium constant if $\Delta G°_f$ for $PbSO_4(s)$ is -811 Kj/mole; for $Pb^{2+}(aq)$ is 24.3 kJ/mole and for SO_4^{2-} (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 $[HSO_4]$ is 0.100 M. K_a for $HSO_4^- = 1.02 \times 10^{-2}$

(2) Given: $BaSO_4$ (s) $\Longleftrightarrow$ Ba^{2+} (aq) + SO_4^{2-} (aq) K_{sp} for $BaSO_4 = 1.1 \times 10^{-10}$. Ba^{2+} (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 $BaSO_4$ (s) is safe to take internally, even though Ba^{2+}(aq) is poisonous.
(b) What is the concentration of Ba^{2+}, in milligrams per liter, in saturated $BaSO_4$ (aq)?
(c) $MgSO_4$ can be mixed with $BaSO_4$ (s) in this medical procedure. What function does the $MgSO_4$ serve?
(d) If the pH of the solution is 1.44 and the $[HSO_4^-]$ is 0.100 M, what is the solubility of $BaSO_4$. K_a for HSO_4- = 1.02×10^{-2}.

(3) Consider the reaction below, at 25°C.
$H_2(g) + ½ O_2(g) \rightarrow H_2O$ (g) at 25°C.
Given that for water vapor,

$H_2(g) + ½ O_2(g) \rightarrow H_2O$ (g)

Given:

	$\Delta H°_f$ (in kJ/mol)	K_p
$H_2(g)$	0	131
$O_2(g)$	0	205
H_2O (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?

e) is the sign of $\Delta G°$ dependent on the temperature?

Solutions

(1) solution:

a) first, get $\Delta G°$ for the dissociation reaction:

$\Delta G° = \Delta G°_f(Pb^{2+}) + \Delta G°_f(SO_4^{2-}) - \Delta G°_f(PbSO_4(s)) = (24.3 - 742 - (-811))$kJ/mol =

= + 93.3 kJ/mol;

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

b) $PbSO_4(s) \text{<=====>} Pb^{2+}(aq) + SO_4^{2-}(aq)$

x x

$K_{sp} = [Pb^{2+}][SO_4^{2-}] = x^2 = 4.42\text{x}10^{-17} \Rightarrow x = 6.65\text{x}10^{-9}$M

c) First, we recognize the presence of a common ion, SO_4^{2-}. To get it's concentration we use the buffer equation: $pH = pK_a + \log\frac{[SO_4^{2-}]}{[HSO_4^-]}$ (where $pK_a = -\log(1.02 \text{ x } 10^{-2}) = 1.99$)

$10^{pH-pKa} = \frac{[SO_4^{2-}]}{[HSO_4^-]} \Rightarrow [SO_4^{2-}] = [HSO_4^-](10^{pH-pKa}) = (0.100M)(10^{(1.73-1.99)}) = 0.0550$ M

so we have: $PbSO_4(s) \text{<=====>} Pb^{2+}(aq) + SO_4^{2-}(aq)$

x 0.0550M+x

$K_{sp} = [Pb^{2+}][SO_4^{2-}] = x(.0550+x) \approx 0.0550x = 4.42\text{x}10^{-17} \Rightarrow x = 8.04 \text{ x } 10^{-16}$M

(it satisfies the 5% rule).

(2) Solution:

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

b) $PbSO_4(s) \text{<=====>} Pb^{2+}(aq) + SO_4^{2-}(aq)$ $K_{sp} = 1.1 \text{ x } 10^{-10}$

x x

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

So, # mg Ba^{2+}/L = $1.0\text{x}10^{-5}$ mol Ba^{2+}/L x (137 g/mol)(1000mg/g) = 1.4 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: $pH = pK_a + \log\frac{[SO_4^{2-}]}{[HSO_4^-]}$ (where $pK_a = -\log(1.02 \text{ x } 10^{-2}) = 1.991$)

$10^{pH-pKa} = \frac{[SO_4^{2-}]}{[HSO_4^-]} \Rightarrow [SO_4^{2-}] = [HSO_4^-](10^{pH-pKa}) = (0.100M)(10^{(1.44-1.99)}) = 0.0282$M

so we have: $PbSO_4(s) \text{<=====>} Pb^{2+}(aq) + SO_4^{2-}(aq)$

x 0.0282M+x

$K_{sp} = [Pb^{2+}][SO_4^{2-}] = x(.0282+x) \approx 0.0282x = 1.1 \text{ x } 10^{-10} \Rightarrow x = 3.90 \text{ x } 10^{-9}$M

(it satisfies the 5% rule).

(3) solution:
a) $W_{max} = -\Delta G° = -(\Delta H°-T\Delta S°) = -\{-242 + (298)(-45)\}=+229$ kJ

b) solution: $K_p = \exp(-(-229000/((8.314)(298)) = 1.38x10^{40}$

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

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

e) solution: YES since it's exothermic and but decreases in entropy.
It's always negative (-)