Chemistry 2720 Fall 2002 Test 2

Answer all questions.

Write all answers in the booklets provided.

Aids allowed: $8\frac{1}{2} \times 11$-inch information sheet, calculator.

Time: 75 min

Questions: 5

Marks: 56

Useful data:

$$R = 8.314472 \, \text{J}\,\text{K}^{-1}\text{mol}^{-1}$$

To convert degrees Celsius to Kelvin, add 273.15.

Standard Thermodynamic Properties at 25°C and 1 bar			
Species	$\Delta \bar{H}_f^\circ$ (kJ/mol)	$\Delta \bar{G}_f^\circ$ (kJ/mol)	$\bar{C}_p$ ($\text{J}\,\text{K}^{-1}\text{mol}^{-1}$)
$N_{2(g)}$	0	0	28.87
$Pb^{2+}_{(aq)}$	0.92	-24.24	
$PbSO_{4(s)}$	-919.97	-813.04	
$SO^{2-}_{4(aq)}$	-909.34	-744.00	
$ZnO_{(s)}$	-350.46	-320.48	40.3

Standard Entropies at 25°C and 1 bar	
Species	$\bar{S}^\circ$ $\text{J}\,\text{K}^{-1}\text{mol}^{-1}$
$C_{(s)}$ (graphite)	5.74
$C_5H_4N_4O_{2(s)}$ (xanthine)	161.1
$H_{2(g)}$	130.680
$N_{2(g)}$	191.609
$O_{2(g)}$	205.152

1. Calculate the entropy of nitrogen at 400 K. [4 marks]

2. 20 mL of a 0.04 mol/L solution of lead (II) nitrate is mixed with 15 mL of a 0.003 mol/L solution of ammonium sulfate at 25°C. Is a lead (II) sulfate precipitate formed? [10 marks]

3. Zinc-air batteries are commonly used in miniature batteries of the sort used for instance in hearing aids. The overall reaction is very simple:

$$2Zn_{(s)} + O_{2(g)} \rightarrow 2ZnO_{(s)}.$$
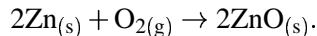
The oxygen is provided from the ambient air. A typical miniature zinc-air battery stores about 500 J of energy. This is enough to power a hearing aid for a week or so. Assuming that the pressure of oxygen is about 0.2 bar, what is the initial mass of zinc in such a battery? Assume that the battery operates at 25°C and that it produces the maximum possible electrical work. The molar mass of zinc is 65.38 g/mol. [9 marks]

4. Ice fog occurs when the condensation of water vapor into ice becomes spontaneous. If the partial pressure of water is 0.004 bar, below what temperature would you predict ice fog to form? Report your final answer in degrees Celsius. The vapor pressure of ice at 0°C is 6.025×10^{-3} bar. The enthalpy of vaporization of liquid water at 0°C is 44.91 kJ/mol while the enthalpy of fusion at this temperature is 6.007 kJ/mol. [9 marks]

5. Xanthine is an intermediate in purine metabolism.
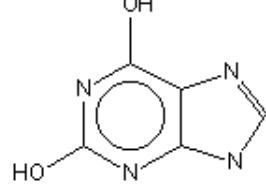
It is only slightly soluble, and so tends to precipitate out of solution at higher concentrations, leading to urinary stones.[1] The hydroxyl protons are ionizable so xanthine is a diprotic acid. Two processes are important in the solubilization of xanthine:

$$H_2Xan_{(s)} \overset{K_1}{\rightleftharpoons} H_2Xan_{(aq)}$$

$$H_2Xan_{(aq)} \overset{K_2}{\rightleftharpoons} H^+_{(aq)} + HXan^-_{(aq)}$$
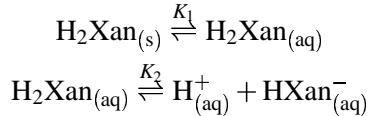
(The second proton is too weakly acidic to be physiologically relevant.)

(a) The equilibrium constants have recently been measured.[2] Their values at 298.15 K are $K_1 = 1.29 \times 10^{-4}$ and $K_2 = 2.95 \times 10^{-8}$. What is the solubility of xanthine in aqueous solution at a fixed (buffered) pH of 6.5 (a typical pH for urine)? [8 marks]
    Hint: The solubility includes all forms of xanthine in solution.

(b) At 310.15 K, $K_1 = 2.04 \times 10^{-4}$. The standard enthalpy of formation of solid xanthine is -379.6 kJ/mol. Estimate the standard enthalpy of formation of aqueous xanthine. [5 marks]

(c) Estimate the standard free energy of formation of solid xanthine. [6 marks]

(d) Estimate the standard free energy of formation of aqueous xanthine ($H_2Xan_{(aq)}$). [5 marks]

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[1] This is only one insoluble compound which can be involved in the formation of stones.
[2] E. Königsberger et al., J. Chem. Thermodyn. **33**, 1 (2001).