Chemistry 2720 Fall 2005 Test 2

Time: 75 min

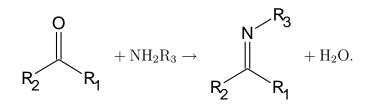
Marks: 53

Aids permitted: calculator, one 8.5×11 -inch formula sheet

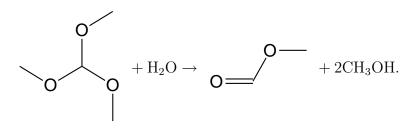
Write all answers in the booklets provided.

Useful data is given at the end of this exam paper.

1. Imines (organic compounds containing a carbon-nitrogen double bond) can be synthesized by condensation of an aldehyde or ketone with an amine:



This reaction is often carried out using trimethylorthoformate (trimethoxymethane) as the solvent. In other solvents, it often fails. Trimethylorthoformate reacts with water as follows:



Explain why this reaction might work in trimethylorthoformate when it fails in other solvents. Discuss what the qualitative information given above tells us about the thermodynamics of the reactions mentioned. [8 marks]

2. The solubility of calcium fluoride (molar mass 78.07 g/mol) in water at 26°C is 0.017 g/L. What is the standard free energy of formation of calcium fluoride? What approximations, if any, did you have to make in your calculation? [10 marks]

- 3. Many microorganisms derive energy by fermenting glucose, $C_6H_{12}O_6$. The products vary, but in one variation they are ethanol, C_2H_5OH and carbon dioxide. This is actually a redox reaction in which glucose is both the oxidizing and reducing agent.
 - (a) Use the redox reaction balancing procedure to balance this reaction. [6 marks] Note: Yes, this reaction can be balanced by inspection, but humor me.
 - (b) Calculate the maximum non-PV work which could be done at 25°C in aqueous medium per mole of glucose fermented if the concentrations are [glucose] = 0.7 mol/L, [ethanol] = 1.3 mol/L, and [CO₂] = 0.03 mol/L. [6 marks]
 - (c) Calculate the voltage generated if this reaction were carried out in an electrochemical cell under the conditions given in the previous part of this question. [2 marks]
- 4. Calculate the equilibrium constant for the reaction

$$2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + I_{2(s)}$$

at 25° C. [7 marks]

- 5. What is the vapor pressure of a 0.4 mol/L aqueous solution of sodium sulfate at 60°C? [6 marks]
- 6. (a) Recall that in the biochemists' standard state, the pH is fixed at 7. Derive an equation relating $\Delta \bar{G}^{\circ}$ and $\Delta \bar{G}^{\circ'}$ for the general reaction

Reactants \rightarrow Products + $\nu H^+_{(aq)}$,

where ν is a stoichiometric coefficient. [4 marks]

Hint: Write down the equation for $\Delta \bar{G}$ and note that $\Delta \bar{G}^{\circ'}$ is $\Delta \bar{G}$ under the special condition that everything is in its (chemists') standard state *except* for H⁺.

Note: The equation you will derive will also work if H^+ appears on the reactant side of the equation provided we take ν in that case to be a negative quantity.

- (b) Use your equation to calculate $\Delta \bar{G}_{f}^{\circ\prime}$ for the chloride ion. [4 marks]
- **Bonus:** One of the potential questions for the Oct. 27 quiz asked you to calculate the vapor pressure of SO_3 over a 1.5 mol/L sulfuric acid solution due to the reaction

$$HSO_{4(aq)}^- + H_{(aq)}^+ \rightleftharpoons SO_{3(g)} + H_2O_{(l)}.$$

I was tempted to use this as the quiz question until I realized there was a problem: You can't calculate the vapor pressure from this reaction alone because another reaction would likely be important. What is this reaction?

 $\mathcal{F} = 96\,485.342\,\mathrm{C/mol}$

 $R=8.314\,472\,{\rm J\,K^{-1}mol^{-1}}$

To convert degrees Celsius to Kelvin, add 273.15.

Species	$\Delta \bar{H}_{f}^{\circ}$	$\Delta \bar{G}_{f}^{\circ}$	\bar{C}_P
	(kJ/mol)	(kJ/mol)	$(\mathrm{J}\mathrm{K}^{-1}\mathrm{mol}^{-1})$
$Ca^{2+}_{(aq)}$	-543.0	-552.8	
$C_2H_5OH_{(aq)}$	-288.3	-181.64	
$C_6H_{12}O_{6(s)}$ (α -D-glucose)	-1274.4	-910.23	218.16
$CO_{2(aq)}$	-413.26	-386.05	
$\mathrm{Cl}^{-}_{\mathrm{(aq)}}$	-167.080	-131.218	
$F_{(aq)}$	-335.35	-281.52	
$H_2\tilde{O}_{(1)}$	-285.830	-237.140	75.40
$H_2O_{(g)}$	-241.826	-228.582	33.58

Reduction process	$\mathcal{E}^{\circ}(\mathbf{V})$
$\operatorname{Fe}_{(\mathrm{aq})}^{3+} + e^{-} \rightarrow \operatorname{Fe}_{(\mathrm{aq})}^{2+}$	+0.771
$I_{2(s)} + 2e^- \rightarrow 2I_{(aq)}$	+0.5355

Properties of liquid water

		Mole	Vapor	Heat of	Molar
Temperature	Density	density	pressure	vaporization	entropy
$(^{\circ}C)$	(g/cm^3)	$(\mathrm{mol/L})$	(Torr)	(J/g)	$(\mathrm{J}\mathrm{K}^{-1}\mathrm{mol}^{-1})$
0	0.9999	55.49	4.579	2493	63.2
4	1.0000	55.49	6.101	2485	
20	0.9982	55.39	17.535	2447	
25	0.9971	55.33	23.756	2435	69.95
40	0.9922	55.06	55.324	2402	
60	0.9832	54.56	149.38	2356	
80	0.9718	53.93	355.1	2307	
100	0.9584	53.19	760.000	2257	86.9