Chemistry 2740 Spring 2009 Test 2

Time: 50 minutes
Questions: 4
Marks: 41
Aids allowed: calculator, 8.5×11-inch formula sheet
Useful data is given at the end of this exam paper.

1. Say whether each of the following statements is true or false, and *briefly* (in a few words) explain your reasoning. [2 marks each]

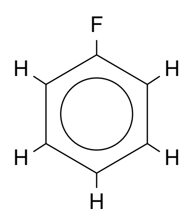
   (a) The Clausius inequality is equivalent to the second law.

   (b) If a reaction is not thermodynamically allowed, we can make it go by adding a catalyst.

   (c) Since the overall reaction is combustion in either case, a fuel cell is no more efficient than a heat engine.

2. In basic solution, Br_2 disproportionates into bromate (BrO_3^-) and bromide ions. Balance the reaction. [6 marks]

3. In crystals, flat aromatic molecules (e.g. benzene) typically stack up with the carbon atoms of one ring directly above the carbon atoms of the ring below due to the interactions between their delocalized π orbitals. For small substituents that lie in the plane of the ring, like fluorine, there is often only a very small energy difference between lining up one fluorine above another, or having a fluorine atom lying above a hydrogen atom. The relative positions of the fluorine atoms in the different layers are therefore essentially random. Calculate the molar residual entropy of fluorobenzene (illustrated below). [6 marks]



4. Strontium is used in a number of applications, for instance as a component of alloys in structural or magnetic materials, as a corrosion inhibitor in coatings, and in fireworks where it is often used for its red emission. The most important strontium ore is celestite ($SrSO_4$). Like most ores, celestite is not a pure material, so the strontium needs to be separated from contaminants. Furthermore, the most convenient starting point for industrial applications is strontium carbonate. Strontium carbonate is much less soluble than strontium sulfate, so in principle we can make the former by reacting the latter with (e.g.) a sodium carbonate solution:

$$\mathrm{SrSO_{4(s)}} + \mathrm{CO^{2-}_{3(aq)}} \rightarrow \mathrm{SrCO_{3(s)}} + \mathrm{SO^{2-}_{4(aq)}}.$$

   (a) Demonstrate how this overall reaction can be broken down into two coupled reactions related to the solubility equilibria of strontium sulfate and of strontium carbonate, and therefore why the relative solubilities of the two compounds determine the direction of equilibrium. [6 marks]

   (b) The solubility products of strontium sulfate and strontium carbonate at 25°C are, respectively, 3.42×10^{-7} and 5.60×10^{-10}. Calculate the equilibrium constant for the above reaction. [2 marks]

   (c) Calculate the standard free energy of formation of an aqueous strontium ion. [5 marks]

   (d) Using Debye-Hückel theory, calculate the solubility of strontium sulfate in water at 25°C. The permittivity of water at this temperature is $6.954 \times 10^{-10}\,\mathrm{C^2 J^{-1} m^{-1}}$. [10 marks]

Useful data

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

$\ln \gamma_i = -A z_i^2 (\varepsilon T)^{-3/2} \sqrt{I_c}$ $\qquad A = 1.107 \times 10^{-10}$

$\ln \gamma_\pm = -A\,|z_+ z_-|\,(\varepsilon T)^{-3/2} \sqrt{I_c}$

To convert degrees Celsius to Kelvin, add 273.15.

Standard thermodynamic data at 1 bar and 298.15 K

Species	$\frac{\Delta_f H^\circ}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\Delta_f G^\circ}{\mathrm{kJ\,mol^{-1}}}$	$\frac{C_{p,m}}{\mathrm{J\,K^{-1}mol^{-1}}}$
$SO^{2-}_{4(aq)}$	−909.34	−744.00	
$SrSO_{4(s)}$	−1453	−1341	