I. (25) Galvanic Cells. Consider the galvanic cell Cu | CuSO$_4$ (1.00 m$^+$) | Hg$_2$SO$_4$(s) | Hg | Cu$'$.  
A. Write the half reactions that occur at each electrode, and the overall cell reaction.  
B. Which electrode is the anode and which the cathode, for the cell as written?  
C. Using data given on the last page, calculate $E^\circ$ for this cell at $P = P^\circ$ and $T = 25^\circ$C.  
D. Calculate the emf $E$ of this cell at 25°C, (1) assuming the stoichiometric activity coefficient of CuSO$_4$ is 1.00, and (2) using the experimental value of 0.043.  
E. Is this a cell with or without transference.
II. (25) **Surface Chemistry.** The surface tension of dilute solutions of phenol in water at 20°C can be represented as an exponential function of the concentration, as illustrated in the accompanying figure.

A. Give the equation that expresses the Gibbs isotherm for $\Gamma_{2(1)}$ (the relative adsorption of phenol with respect to water), in terms of the dependence of the surface tension $\gamma$ on the phenol concentration. (Assume ideal, i.e., take activity coefficients to be 1.00 at all $c$.)

B. Obtain an expression for $\Gamma_{2(1)}$ in terms of the parameters $d$, $f$, and $g$ in the empirical exponential fit illustrated in the figure.

C. Calculate $\Gamma_{2(1)}$ for a 0.200 mol/L solution.

D. What adsorption type does this system illustrate (Type I, II, or III)?
III. (25) **Multicomponent Phase Diagrams.** Liquid substances A and B form a minimum-boiling azeotrope at $x_B = 0.65$ when $P = 1$ bar. B is more volatile than A.

A. Sketch the $T$-$x_B$ diagram for this system in the liquid-vapor regime, properly taking into account the given information, and labeling all regions.

B. A liquid mixture having $x_B = 0.40$ is separated as completely as possible by fractional distillation. What will be the composition of the (1) distillate, and (2) residue?

C. What kind of deviations from ideality (positive or negative) does this system exhibit?

D. Now suppose the system exhibits liquid immiscibility at temperatures slightly below the azeotropic boiling point. Suppose that when the pressure is lowered, the liquid-vapor transition loop intersects the liquid-phase miscibility gap. Sketch the diagram that is appropriate for this situation, again labeling all regions.

E. Using this diagram, describe briefly the phases present and the changes that occur as an $x_B = 0.40$ mixture is warmed, starting below the boiling point and ending with all vapor. (Here assume the experiment is carried out in a large piston, with no removal of A or B, so that $x_B = 0.40$ throughout.)
IV. (30) **Short Sparks.** (Do only 2 of 3).

A. Using the procedure illustrated in class for half-cells involving \( \text{Cr}^{3+}, \text{Cr}^{2+}, \) and \( \text{Cr} \), and data you can find in the table below for half-cells involving \( \text{Fe}^{3+}, \text{Fe}^{2+} \) and \( \text{Fe} \), calculate \( E^\circ \) at 25°C for the half-reaction, \( \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \).

B. Emf data are available for the galvanic cell \( \text{Pt} \mid \text{H}_2(g) \mid \text{HCl(aq)} \mid \text{AgCl(s)} \mid \text{Ag} \mid \text{Pt}' \), for HCl molalities in the range 0.001 \( m^\circ \) to 0.0100 \( m^\circ \), and at 0.300 \( m^\circ \), all at 60°C.

1. Describe in detail how you could analyze these data to obtain \( E^\circ \) and information about the activity coefficients for HCl(aq) as a function of concentration. **Be specific; i.e.,** give equations, and tell what you would plot against what.

2. Could you obtain a reliable estimate of the activity coefficient at 0.300 \( m^\circ \), or only a crude estimate. Explain briefly.
C. For the chemical reaction, $\text{H}_2(g) + 2 \text{AgCl}(s) \rightarrow 2 \text{Ag}(s) + 2 \text{HCl}(aq)$, galvanic cell data give $E^*$ as the following function of the Celsius temperature $\theta$, valid over the range 0–90˚C:

$$E^*(V) = 0.23643 - 4.8621 \times 10^{-4} \theta - 3.4205 \times 10^{-6} \theta^2 + 5.869 \times 10^{-9} \theta^3.$$

Calculate $\Delta G^*$, $\Delta S^*$, and $\Delta H^*$ for this reaction at 30.0˚C.

V. (4) **Bonus.** Give the SI units of (1) charge, (2) length, (3) electric field, (4) emf, (5) electric potential difference, (6) dipole moment, (7) dielectric constant, (8) electrochemical potential.