Practice Exam 3 (the actual third exam last year)

1. (7 + 7 points) Benzene, C_6H_6, is a volatile liquid at room temperature, meaning it has an appreciable vapor pressure. Listed below are thermodynamic data on both the liquid and gaseous forms of benzene at 298.15 K.

	$C_6H_6(l)$	$C_6H_6(g)$
ΔH_f^o/kJ mol^{-1}	49.03	82.93
S^o/J mol^{-1} K^{-1}	172.8	269.2
ΔG_f^o/kJ mol^{-1}	124.50	129.66

Use these data (assuming they are independent of temperature) to answer the following questions. (*Big* hint: consider $C_6H_6(l) \rightleftarrows C_6H_6(g)$ to be a "reaction" at equilibrium.)

(a) What is the vapor pressure of benzene at 298.15 K, the temperature at which the data above hold?

If we think of this vaporization as a "reaction," we can write, where $P_{C_6H_6}$ is the vapor pressure,

$$K = P_{C_6H_6} = e^{-\Delta G_r^o/RT}$$

We can find ΔG_r^o most directly from the ΔG_f^o values:

$$\Delta G_r^o = \Delta G_f^o(g) - \Delta G_f^o(l) = 129.66 \text{ kJ mol}^{-1} - 124.50 \text{ kJ mol}^{-1} = 5.16 \text{ kJ mol}^{-1}$$

and then find the vapor pressure:

$$P_{C_6H_6} = e^{-\Delta G_r^o/RT} = e^{-(5160 \text{ J mol}^{-1})/(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})} = 0.125 \text{ atm}$$

(b) What is the normal boiling point of benzene, i.e., the temperature at which $C_6H_6(g)$ has a vapor pressure of 1 atm?

There are two different ways to think about and solve this problem. First, we recall that at 1 atm, we are at the standard pressure (the pressure to which our tabulated thermodynamic data refer) *and* when the "reaction" (the vaporization) is in equilibrium, that is because the total free energy of the reactants equals the total free energy of the products, making ΔG = 0. Thus, we can write, with T_{vap}^o being the normal boiling point (i.e., the "standard vaporization temperature")

$$\Delta G = 0 = \Delta G_r^o = \Delta H_r^o - T_{vap}^o \Delta S_r^o \quad \text{or} \quad T_{vap}^o = \frac{\Delta H_r^o}{\Delta S_r^o}$$

We find ΔH_r^o from the enthalpy of formation values, and we find ΔS_r^o from the absolute entropies:

$$\Delta H_r^o = (82.93 - 49.03) \text{ kJ mol}^{-1} = 33.90 \text{ kJ mol}^{-1}$$

$$\Delta S_r^o = (269.2 - 172.8) \text{ J mol}^{-1} \text{ K}^{-1} = 96.4 \text{ J mol}^{-1} \text{ K}^{-1}$$

Finally, we calculate T_{vap}^o = (33,900 J mol^{-1})/(96.4 J mol^{-1} K^{-1}) = 351.7 K = 78.5 °C.

The second way to approach this problem considers the temperature and vapor pressure from part (a) as one pair of T, K values and seeks a second pair where $T = T_{vap}^o$ and K = 1 (the value of the equilibrium constant for a partial pressure of 1 atm). These pairs of T, K values are related through the expression

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H_r^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

We know ΔH_r^o, and if we let the values from part (a) represent T_1 and K_1, then we can write

$$\ln\left(\frac{1}{0.125}\right) = -\frac{33{,}900 \text{ J mol}^{-1}}{8.315 \text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{T_{vap}^o} - \frac{1}{298.15 \text{ K}}\right)$$

We solve this expression for T_{vap}^o and find $T_{vap}^o = 351.6$ K = 78.4 °C, essentially the same value we found using the other approach.

2. (15 points) Magnesium metal, Mg(*s*), forms a dipositive cation in solution with the following standard reduction potential:

$$Mg^{2+}(aq) + 2e^- \rightleftarrows Mg(s) \quad E_{red}^o = -2.363 \text{ V}$$

The standard reduction potential for solid $Mg(OH)_2$ is also known:

$$Mg(OH)_2(s) + 2e^- \rightleftarrows Mg(s) + 2\,OH^-(aq) \quad E_{red}^o = -2.690 \text{ V}$$

Use this information to calculate the solubility product equilibrium constant, K_{sp}, for $Mg(OH)_2(s)$:

$$Mg(OH)_2(s) \rightleftarrows Mg^{2+}(aq) + 2\,OH^-(aq) \quad K_{sp} = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_$$

If we combine the two half reactions as shown below, we end up with the solubility reaction for $Mg(OH)_2$:

$$Mg(OH)_2(s) + 2e^- \rightleftarrows Mg(s) + 2\,OH^-(aq) \quad \text{(reduction, cathode)}$$

$$Mg(s) \rightleftarrows Mg^{2+}(aq) + 2e^- \quad \text{(oxidation, anode)}$$

These half reactions, if coupled in an electrochemical cell, would represent the desired net reaction. Moreover, they would have a standard cell potential given by

$$E_{cell}^o = E_{red}^o + E_{ox}^o = E_{red}^o(\text{cathode}) - E_{red}^o(\text{anode}) = -2.690 \text{ V} - (-2.363 \text{ V}) = -0.327 \text{ V}$$

We note that $n = 2$ in this cell (there are two electrons in the half reactions), and thus we can find the equilibrium constant, K_{sp}:

$$K_{sp} = e^{nFE_{cell}^o/RT} = e^{(2)(96485 \text{ C mol}^{-1})(-0.327 \text{ V})/(8.314 \text{ J mol}^{-1}\text{ K}^{-1})(298.15 \text{ K})} = 8.80 \times 10^{-12}$$

3. (10 + 10 points) Here are a couple of questions about oxidation-reduction reactions.

(a) If "lead shot" (small spheres of Pb(*s*)) is placed in an aqueous solution of red-yellow bromine, $Br_2(aq)$, it is observed that over time, the color disappears. If this now-colorless solution is poured into a fresh, empty container, addition of hydrogen peroxide, $H_2O_2(aq)$, to the solution restores the color. Use half reaction arguments (and data from the back page of the exam) to write and justify balanced, spontaneous net reactions that explain these observations.

The color disappears:

Looking at the data at the end of the exam, we see that $E_{red}^o(Br_2/Br^-) > E_{red}^o(Pb^{2+}/Pb)$. Thus, Br_2 will spontaneously oxidize Pb, and in the process, reddish Br_2 gets turned into colorless Br^-. The net reaction is

$$\mathrm{Pb}(s) + \mathrm{Br_2}(aq) \rightleftarrows \mathrm{Pb^{2+}}(aq) + 2\mathrm{Br^-}(aq)$$

The color reappears:

Here, again using tabulated data at the end of the exam, we note that $E^{\mathrm{o}}_{\mathrm{red}}(\mathrm{H_2O_2/H_2O}) > E^{\mathrm{o}}_{\mathrm{red}}(\mathrm{Br_2/Br^-})$; so, H_2O_2 can oxidize Br^- back to Br_2, according to

$$\mathrm{H_2O_2}(aq) + 2\mathrm{Br^-}(aq) + 2\mathrm{H^+}(aq) \rightleftarrows 2\mathrm{H_2O}(l) + \mathrm{Br_2}(aq)$$

(b) Write the half reactions that add to the balanced net reaction for the following unbalanced reaction, which occurs in a basic aqueous solution:

$$\mathrm{NiO_2}(s) + \mathrm{Fe}(s) \rightarrow \mathrm{Ni(OH)_2}(s) + \mathrm{Fe(OH)_2}(s)$$

We assign oxidation numbers first. For O and H, they are the usual –2 and +1, respectively. For Ni in NiO_2, it is +4; for Fe, it is 0; for Ni in $Ni(OH)_2$, it is +2, and for Fe in $Fe(OH)_2$, it is also +2. The half reactions are thus (remembering that we're in a *basic* solution)

$$\mathrm{NiO_2}(s) + 2\mathrm{H_2O}(l) + 2e^- \rightleftarrows 2\mathrm{Ni(OH)_2}(s) + 2\mathrm{OH^-}(aq)$$

$$\mathrm{Fe}(s) + 2\mathrm{OH^-}(aq) \rightleftarrows \mathrm{Fe(OH)_2}(s) + 2e^-$$

4. (2 points each) Circle the correct choice from among the italicized choices.

(a) The oxidation number *change* (i.e., final oxidation number – initial oxidation number) for manganese, Mn, in the balanced net reaction below is

$$5\ \mathrm{SO_2}(aq) + 2\ \mathrm{MnO_4^-} + \mathrm{H^+}(aq) + 2\ \mathrm{H_2O}(l) \rightleftarrows 5\ \mathrm{HSO_4^-}(aq) + 2\ \mathrm{Mn^{2+}}(aq)$$

+5 [✓ *–5*] *+10* *–10*

Mn goes from +7 to +2, so the change is –5.

(b) The standard reaction entropy change, $\Delta S^{\mathrm{o}}_{\mathrm{r}}$, for the reaction $\mathrm{SiO_2}(s) \rightarrow \mathrm{Si}(s) + \mathrm{O_2}(g)$ must be

[✓ *large and positive*] *large and negative* *close to zero* *exactly zero*.

The reaction turns one mole of solid into one mole of another solid plus a mole of entropy-rich *gas*. The solids have similar entropies, but the gas has a much larger molar entropy.

(c) If S is the entropy of n moles of an ideal gas in volume V at temperature T, then the expression for the entropy of n moles at T and $2V$ is

2S [✓ *S + nR ln 2*] *S – nR ln 2* *S ln 2*

The entropy change in an ideal gas taken at constant T from V_{i} to V_{f} is $\Delta S = nR \ln(V_{\mathrm{f}}/V_{\mathrm{i}})$. Here, $V_{\mathrm{f}} = 2V_{\mathrm{i}}$.

(d) In the Ag(*s*)/AgCl(*s*) electrode, the species that is reduced is

Ag *Cl*$^-$ $\boxed{\textit{AgCl}}$ *H*$_2$*O*

The half reaction is AgCl(*s*) + e$^-$ $\rightleftarrows$ Ag(*s*) + Cl$^-$(*aq*). The Ag atom is reduced from oxidation state +1 to oxidation state 0.

(e) In 3 Cl_2(*g*) + 6 OH^-(*aq*) $\rightleftarrows$ ClO_3^-(*aq*) + 5 Cl^-(*aq*) + 3 H_2O(*l*), Cl_2 undergoes

reduction *oxidation* $\boxed{\textit{disproportionation}}$ *neutralization*

Disporportionation describes a reaction in which one (or more) element (or elements) simultaneously is (or are) both oxidized and reduced. Here, Cl starts with an oxidation number of 0 in Cl_2, but in Cl^-, it has oxidation number –1, while in ClO_3^-, it has oxidation number +5.

(f) Entropy changes are equal to the heat associated with a process divided by the instantaneous temperature at which the heat was transferred for processes that are

adiabatic *isothermal* $\boxed{\textit{reversible}}$ *at constant P*

The expression that relates an entropy change to a process involving heat is $\Delta S = q_{rev}/T$, so only *reversible* processes have a direct connection between their heat and their entropy change.

(g) The equilibrium constant for the reaction 2 H_2O(*g*) $\rightleftarrows$ 2 H_2(*g*) + O_2(*g*) is less than 1. This tells us that, for H_2O(*g*),

$S^o < 0$ $\Delta G_f^o > 0$ $\Delta S_r^o = 0$ $\boxed{\Delta G_f^o < 0}$

A $K < 1$ means a ΔG_r^o that is positive. For the *reverse* of this reaction, we have a reaction that is twice the formation reaction for H_2O(*g*), and for it, ΔG_r^o would be negative (because we reversed the initial reaction). But this reversed reaction has a ΔG_r^o that is twice ΔG_f^o for water.

(h) A concentration cell is constructed using Zn electrodes and solutions in which $[Zn^{2+}]$ = 0.05 M for one half-cell and $[Zn^{2+}]$ = 0.50 M in the other. The *magnitude* of E_{cell} is

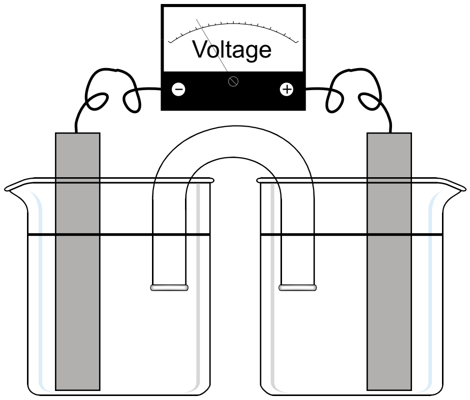
0.0591 V $\boxed{\textit{0.0296 V}}$ *0.591 V* *0.7628 V*

For a concentration cell (one for which $E^o_{cell} = 0$), the magnitude of E_{cell} is given by

$$|E_{cell}| = \left| \frac{0.0591\ \text{V}}{n} \log \frac{\text{(one concentration)}}{\text{(other concentration)}} \right|$$

Here, $n = 2$, and the concentration ratio is 10 (or 0.1—it doesn't matter).

5. (20 points) Shown below is a simple electrochemical cell: two solutions with metal electrodes connected to a voltmeter and a salt bridge completing the circuit. The voltmeter is reading a *positive* voltage.



One beaker holds a 0.013 M solution of $CdCl_2$ and a Cd electrode, while the other holds a 0.530 M solution of $AgNO_3$ and a silver metal electrode.
(a) What is the spontaneous net reaction represented by this cell?

We consult the standard reduction potential table at the end of the exam and conclude that the spontaneous reaction must be $\mathrm{Cd}(s) + 2\mathrm{Ag}^+(aq) \rightleftarrows \mathrm{Cd}^{2+}(aq) + 2\mathrm{Ag}(s)$ because the half reaction for the reduction of Ag^+ is above (has a higher value) that for the reduction of Cd^{2+}.

(b) What is in the beaker on the right, i.e., the beaker connected to the positive terminal of the voltmeter, and *how can you tell*?

The net reaction involves the reduction of Ag^+, and reduction reactions appear in the right-hand, positive, cathode electrode in a conventional cell diagram.

(c) What voltage does the voltmeter indicate?

We first calculate $E^{\mathrm{o}}_{\mathrm{cell}}$ from the standard reduction potentials tabulated at the end of the exam:

$$E^{\mathrm{o}}_{\mathrm{cell}} = \underset{\mathrm{Ag/Ag^+}}{0.7991\ \mathrm{V}} - \underset{\mathrm{Cd/Cd^{2+}}}{(-0.4029\ \mathrm{V})} = 1.202\ \mathrm{V}$$

We note that $n = 2$ for this cell, and that the ion concentrations are $[\mathrm{Ag}^+] = 0.530$ M and $[\mathrm{Cd}^{2+}] = 0.013$ M. The reaction quotient, Q, for our net reaction is thus

$$Q = \frac{[\mathrm{Cd}^{2+}]}{[\mathrm{Ag}^+]^2} = \frac{0.013}{(0.530)^2} = 4.63 \times 10^{-2}$$

and the full Nernst equation is

$$E_{\mathrm{cell}} = E^{\mathrm{o}}_{\mathrm{cell}} - \frac{0.0591\ \mathrm{V}}{n}\log Q = 1.202\ \mathrm{V} - \frac{0.0591\ \mathrm{V}}{2}\log(4.63 \times 10^{-2}) = 1.241\ \mathrm{V}$$

(d) If pure water is added to the beaker containing Ag, the voltage (circle one)

increases. *is unchanged.* [✓ *decreases.*]

Adding water lowers $[\mathrm{Ag}^+]$, which increases Q, which increases $\log Q$, which decreases E_{cell}.

Practice Exam 3 (the actual third exam last year)

6. (9 + 6 points) In three separate experiments, excess $HCl(aq)$ was reacted, in turn, with $Al(s)$, $Li(s)$, and the compound lithium aluminum hydride, $LiAlH_4(s)$. In each reaction, $H_2(g)$ is evolved, and the metal ions are produced in solution. The standard molar enthalpies of reactions were measured for each reaction, as indicated below. Each of these values assumes *one mole of the reactants listed below appears in its corresponding net reaction*.

Reactant	ΔH_r^o/kJ mol^{-1}
$Al(s)$	544.1
$Li(s)$	284.0
$LiAlH_4(s)$	713.6

(a) Write the balanced net reactions that represent these experiments and the data above.

(1) with Al:

$$Al(s) + 3H^+(aq) \rightleftarrows Al^{3+}(aq) + \frac{3}{2} H_2(g)$$

(2) with Li:

$$Li(s) + H^+(aq) \rightleftarrows Li^+(aq) + \frac{1}{2} H_2(g)$$

(3) with $LiAlH_4$:

$$LiAlH_4(s) + 4H^+(aq) \rightleftarrows Li^+(aq) + Al^{3+}(aq) + 4\, H_2(g)$$

(b) Calculate the standard molar enthalpy of formation of $LiAlH_4(s)$.

The formation reaction for $LiAlH_4$ is

$$Li(s) + Al(s) + 2H_2(g) \rightleftarrows LiAlH_4(s)$$

and this reaction is, using the reactions from part (a), the combination (1) + (2) – (3). Thus

$$\begin{aligned}\Delta H_f^o(LiAlH_4(s)) &= \Delta H_r^o(1) + \Delta H_r^o(2) - \Delta H_r^o(3)\\ &= 544.1 \text{ kJ mol}^{-1} + 284.0 \text{ kJ mol}^{-1} - 713.6 \text{ kJ mol}^{-1}\\ &= 114.5 \text{ kJ mol}^{-1}\end{aligned}$$

Practice Exam 3 (the actual third exam last year)

This exam included the following information:

$R = 0.08206$ L atm mol^{-1} K^{-1} = 8.314 J mol^{-1} K^{-1} $F = 96485$ C mol^{-1}

$\Delta G = \Delta H - T\Delta S$ $\Delta G_r = \Delta G_r^o + RT \ln Q$ $\Delta G_r^o = -RT \ln K = -nFE_{\text{cell}}^o$

$\ln \frac{K_2}{K_1} = -\frac{\Delta H_r^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ $T/\text{K} = t/°\text{C} + 273.15$ $1 \text{ V} = 1 \text{ J C}^{-1}$

$E_{\text{cell}}^o = E_{\text{red}}^o(\text{cathode}) - E_{\text{red}}^o(\text{anode})$

$E_{\text{cell}} = E_{\text{cell}}^o - \frac{RT}{nF} \ln Q = E_{\text{cell}}^o - \frac{0.0591 \text{ V}}{n} \log Q$ (at 298.15 K)

Selected Standard Reduction Potentials, E_{red}^o, at 298.15 K

$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$	+1.776 V
$Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$	+1.3595 V
$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$	+1.087 V
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.7991 V
$I_2(aq) + 2e^- \rightarrow 2I^-(aq)$	+0.536 V
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.337 V
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0 V
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	–0.126 V
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	–0.250 V
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	–0.4029 V
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–0.4402 V
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.7628 V
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	–2.363 V

Standard Electrochemical Notation

left	right
negative	positive
anode	cathode
oxidation	reduction