1. (a) Balance the following redox reaction in acidic solution: $\text{AsH}_3 + \text{Ag}^+ \rightarrow \text{As}_2\text{O}_6 + \text{Ag}$

**oxidation** $4 \text{AsH}_3 + 6 \text{H}_2\text{O} \rightarrow \text{As}_2\text{O}_6 + 24 \text{H}^+ + 24 \text{e}^-$

**reduction** $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$

balanced $4 \text{AsH}_3 + 6 \text{H}_2\text{O} + 24 \text{Ag}^+ \rightarrow \text{As}_2\text{O}_6 + 24 \text{H}^+ + 24 \text{Ag}$

(Note: in this reaction, arsenic is oxidized from the –III to the +III oxidation state)

(b) Balance the following redox reaction in acidic solution: $[\text{MnO}_4^-] + \text{HCN} + \Gamma \rightarrow \text{Mn}^{2+} + \text{ICN}$

**oxidation** $\text{HCN} + \Gamma \rightarrow \text{ICN} + \text{H}^+ + 2 \text{e}^-$

**reduction** $[\text{MnO}_4^-] + 8 \text{H}^+ + 5 \text{e}^- \rightarrow \text{Mn}^{2+} + 2 \text{H}_2\text{O}$

balanced $5 \text{HCN} + 5 \Gamma + 2 [\text{MnO}_4^-] + 11 \text{H}^+ \rightarrow 5 \text{ICN} + 2 \text{Mn}^{2+} + 8 \text{H}_2\text{O}$

(Note: in this reaction, iodine (–I) is being oxidized to iodine (+I) using permanganate)

(c) Balance the following redox reaction in acidic solution: $\text{H}_5\text{IO}_6 + \Gamma \rightarrow \text{I}_2$

**oxidation** $\text{I}^- \rightarrow \frac{1}{2} \text{I}_2 + \text{e}^-$

**reduction** $\text{H}_5\text{IO}_6 + 7 \text{H}^+ + 7 \text{e}^- \rightarrow \frac{1}{2} \text{I}_2 + 6 \text{H}_2\text{O}$

balanced $\text{H}_5\text{IO}_6 + 7 \text{I}^- + 7 \text{H}^+ \rightarrow \frac{1}{2} \text{I}_2 + 6 \text{H}_2\text{O}$

(Note: this is an interesting example of a comproportionation reaction; note the trick to initially balance I$_2$ as $\frac{1}{2}!$)

(d) Balance the following redox reaction in acidic solution: $[\text{UO}]^{2+} + \text{Cr}_2\text{O}_7^{2-} \rightarrow [\text{UO}_2]^{2+} + \text{Cr}^{3+}$

**oxidation** $[\text{UO}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{UO}_2]^{2+} + 2 \text{H}^+ + 2 \text{e}^-$

**reduction** $\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{e}^- \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$

balanced $3 [\text{UO}]^{2+} + \text{Cr}_2\text{O}_7^{2-} + 8 \text{H}^+ \rightarrow 3 [\text{UO}_2]^{2+} + 2 \text{Cr}^{3+} + 4 \text{H}_2\text{O}$

(Note: this is a simple oxidation of uranium from one oxocation to another oxocation using dichromate)

(e) Balance the following redox reaction in basic solution: $\text{Co} + \text{OCl}^- \rightarrow \text{Co(OH)}_3^- + \text{Cl}^-$

**oxidation** $\text{Co} + 3 \text{OH}^- \rightarrow \text{Co(OH)}_3^- + 3 \text{e}^-$

**reduction** $\text{OCl}^- + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{Cl}^- + 2 \text{OH}^-$

balanced $2 \text{Co} + 3 \text{OCl}^- + 3 \text{H}_2\text{O} \rightarrow 2 \text{Co(OH)}_3^- + 3 \text{Cl}^-$

(Note: Cl(+I) in hypochlorite (bleach) is an oxidizing agent, and oxidizes cobalt to the +III state in basic solution.)

(f) Balance the following redox reaction in basic solution: $\text{Au} + \text{CN}^- + \text{O}_2 \rightarrow [\text{Au(CN)}_2]^-$

**oxidation** $\text{Au} + 2 \text{CN}^- \rightarrow [\text{Au(CN)}_2]^- + \text{e}^-$

**reduction** $\text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^-$

balanced $4 \text{Au} + 8 \text{CN}^- + 2 \text{H}_2\text{O} \rightarrow 4 [\text{Au(CN)}_2]^- + 4 \text{OH}^-$

(Note: while gold is not oxidized by oxygen in aqueous solution, addition of cyanide makes this possible. This reaction is heavily used in gold mining operations, especially if the gold concentration of the ores is low. The “cyanide ponds” that are used for this extraction process are serious environmental hazards given the huge quantities of such a toxic substance!)
2. Using Latimer diagram data (Appendix 2 in SAL), suggest chemical reagents which would be suitable for carrying out the following transformations:

(a) oxidation of HCl to chlorine gas: We need to overcome −1.36 V; F₂ would be a good candidate! (F₂/F⁻, +3.05 V).

(b) reducing Cr(III) (aq) to Cr(II) (aq): We need to overcome −0.42 V; most active metals will do this trick, including metallic chromium itself (this would give a nice, clean comproportionation reaction.)

(c) reducing Ag⁺ (aq) to Ag(s): This reaction is favorable by +0.799 V. Any oxidation process costing less than 0.8 V will do. For example, Ag⁺ will oxidize sulfur to sulfite (−0.500 V).

(d) reducing I₂ to I⁻: This reaction is favorable by +0.535 V. Any oxidation process costing less than 0.5 V will do. For example, iodine will oxidize dithionite to sulfate (+0.25 V).

3. Use Latimer diagram data (Appendix 2 in SAL) as a guide to write balanced equations for the reactions that might be expected for each of the following species in aerated aqueous acid. If the species is stable, write no reaction.

For the stability in aerated aqueous acids, you have to consider two reactions in water:

- oxidation of your species in question by H⁺: \( H^+ + e^- \rightarrow \frac{1}{2} H_2 \) (\( E^o_{\text{H}_2} = 0 \) V)
- reduction of your species in question by H₂O: \( 4H^+ + O_2 + 4e^- \rightarrow 4H_2O \) (\( E^o_{\text{H}_2O} = +1.23 \) V)

(a) Cr²⁺: (look at the Frost diagram) - we expect oxidation to Cr³⁺ (+0.424 V), just by reaction with water.

\[ \text{Cr}^{2+} + \text{H}^+ \rightarrow \text{Cr}^{3+} + \frac{1}{2} \text{H}_2 \] (\( E^o = +0.42 \) V)

(b) Fe²⁺: (look at the Frost diagram and/or the Pourbaix diagram) - we expect oxidation to Fe(OH)²⁺ by reaction with dissolved oxygen.

\[ \text{Fe}^{2+} + \frac{1}{2} \text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \frac{1}{2} \text{H}_2\text{O} \] (\( E^o = +0.46 \) V)

(c) Cl⁻: We expect no reaction - Cl⁻ is a stable redox product, and is neither and oxidizing or reducing agent.

(d) HClO₂: We expect disproportionation, e.g. to ClO⁻ and HOCl, even though this is a kinetically slow reaction at room temperature.

\[ 2 \text{HClO}_2 \rightarrow \text{ClO}^- + \text{HOCl} + \text{H}^+ \] (\( E^o = +0.49 \) V)

(e) Zn(s): We expect vigorous reaction with hydrogen gas evolution.

\[ \text{Zn} + 2 \text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2 \] (\( E^o = +0.76 \) V)

(f) Ru²⁺: We expect oxidation, probably to RuO₂.4H₂O by reaction with dissolved oxygen.

\[ \text{Ru}^{2+} + \frac{1}{2} \text{O}_2 + 5 \text{H}_2\text{O} \rightarrow \text{RuO}_2.4\text{H}_2\text{O} + 2 \text{H}^+ \] (\( E^o = +0.68 \) V)

(g) Br₂(l): Bromine is stable in acid (it disproportionates in base).

4. Write the Nernst equation for the following, and in each case express the formula in terms of pH. What is the potential for the O₂ reduction at pH = 7 and p(O₂) = 0.20 atm (i.e. neutral water aerated with the oxygen content of the atmosphere)?

\[ E_{\text{actual}} = E^o - \frac{RT}{nF} \ln Q \text{ (general form)} \] or \[ E_{\text{actual}} = E^o - \frac{0.0519V}{n} \log_{10} Q \text{ (at 25°C only)} \]

(Note that this second form of the equation is written in base-10 logarithms, with RT/F supplied with the values corresponding to standard states. This corresponds to the definition of pH, which also uses base 10 logarithms under the same conditions). Hint: remember that pH is defined as the negative of the log of the hydronium ion concentration!)

(a) the reduction of O₂: \( \text{O}_2 \text{ (g)} + 4 \text{H}^+ \text{ (aq)} + 4 e^- \rightarrow 2 \text{H}_2\text{O} \) (l)

\[ E = 1.229 + 0.0591/4 \log[p(O_2) \times [H^+]^4] = 1.229 - 0.0591/4 \{4pH - \log p(O_2)\} \] At pH 7 and p(O₂) 0.2, \( E = 1.30 \)

(b) the reduction of Fe₂O₃ (s): \( \text{Fe}_2\text{O}_3\text{ (s)} + 6 \text{H}^+ \text{ (aq)} + 6 e^- \rightarrow 2 \text{Fe} \text{ (s)} + 3 \text{H}_2\text{O} \) (l)

\[ E = 1.229 + 0.0591/6 \log([H^+]^6) = 1.229 - 0.0591/4 \times pH \]
5. The ligand EDTA forms stable complexes with hard acid centers (HSAB theory). How will complexation with EDTA affect the reduction of $M^{2+}$ to the metal in the first d-series (the elements Sc to Zn)?

Complexation with EDTA should make it more difficult to reduce the ion to the metal form, compared to the aqua ions. That is, the free energy of $[M(EDTA)]^{2-}$ will be lower than that of $[M(OH_2)_6]^{2+}$, hence it should take a greater amount of added energy to raise the system to the energy of the elemental metal.

6. Use the Frost diagram for the first-row d elements in acid solution to describe in point form the redox chemistry of the elements from Ca to Cu.

- We see that all the metals are potent reducing agents, with the exception of copper, for which the oxidized forms have a higher free energy than the element.
- The reducing strength of the metals goes down smoothly from calcium to nickel, across the period, with nickel being only a mild reducing agent. The jump to copper is fairly large, but its behavior is consistent with the trend towards weaker reducing power - copper simply has none.
- The earlier transition elements favour the +3 oxidation state as the most stable form (bottom of the diagram), while for the latter elements +2 is more stable, sometimes (as for cobalt) considerably more stable.
- The elements in the middle of the series - Mn and Fe - have the largest range of accessible oxidation states.
- The elements at either end of the series have the fewest available oxidation states, and of course zinc (omitted from this diagram) is like calcium in only having one oxidized form, 2+, apart from the elemental form.
- But the free energies of the highest oxidation states of Cr, Mn, Fe and Co are extremely high, and they are all potent oxidizing agents.
- In fact, only Ti in its highest state (+4) has virtually no oxidizing power (here we ignore the calcium and scandium ions, which immediately form stable noble-gas configurations forms and are extremely stable and totally non-oxidizing. They are thus not members of the first-row d-elements.)
- However, Ti is, as expected from its position in the PT, the most similar to Sc in its behaviour.
- Note that virtually all the high-oxidation species are strong oxidizers of similar magnitude: thus the slopes of the lines connecting $\text{CoO}_2$ to $\text{Co}^{2+}$, that of $\text{H}_2\text{FeO}_4$ to $\text{Fe}^{3+}$, that of $\text{HMnO}_4$ to $\text{MnO}_2$ are almost identical. The slope of dichromate ion to chromium(III) is noticeably less steep, consistent with the fact that Cr(VI) is a milder oxidizing agent than Mn(VII) in most applications. On this point, we must recognize that the intermediate species $\text{H}_2\text{MnO}_4$ and $\text{HMnO}_3$ are unstable, short-lived species that, at best, retard the reaction of permanganate in acid briefly, but have little effect on the overall oxidizing ability of permanganate.
- We note that more oxidizing forms of nickel than Ni(II) are not included in this diagram; such forms do exist but are highly reactive (e.g. NiO$_2$ in acid solution has a reduction potential to Ni$^{2+}$ of 1.5 V); this should have been included on the diagram.
- While all the metal ions have the 2+ oxidation as more negative than the element, except Cu$^{2+}$, which is therefore a mild oxidizing agent.
- We note that several species are unstable towards disproportionation: e.g. Cu$^+$, Mn$^{3+}$, MnO$_2$, HMnO$_3$, H$_2$MnO$_4$.
- Comproportionation reactions are most likely for the salts of vanadium and titanium. Although in principle comproportionation could occur with the elemental form of some of these metals, such reactions are likely to be slow. But mixing solutions of V$^{2+}$ and VO$^{2+}$ should lead to the rapid formation of V$^{3+}$ in solution.
7. Consider the Latimer diagrams for lead and tin in acid solution:

\[
\begin{align*}
\text{SnO}_2 & \quad -0.088 \quad \text{Sn}^2+ \quad -0.104 \quad \text{Sn} \\
\text{PbO}_2 & \quad 1.698 \quad \text{Pb}^2+ \quad -0.125 \quad \text{Pb}
\end{align*}
\]

a) Calculate values of \( n_E \) for each oxidation state of lead and tin, and construct a comparative Frost diagram for these two elements in acid solution on the graph paper provided. Ensure the diagram is legible (use a ruler!), including a sensible choice of scale, and that all the points on the diagram are clearly labeled.

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Sn in Acid</th>
<th>Pb in Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>II</td>
<td>-0.208</td>
<td>-0.250</td>
</tr>
<tr>
<td>IV</td>
<td>-0.384</td>
<td>+3.146</td>
</tr>
</tbody>
</table>

b) Which of the six species you have plotted is the strongest oxidizing agent? Justify your answer.

\( \text{PbO}_2 \) – it is in fact the only oxidizing agent, and a strong one, since the line joining \( \text{PbO}_2 \) to \( \text{Pb}^{2+} \) has a steep positive slope.

c) Which of the six species you have plotted is the strongest reducing agent? Justify your answer.

\( \text{Pb}(s) \) metal is a slightly stronger reducing agent than \( \text{Sn}(s) \), since the slope of the line connecting it to \( \text{M}^{2+} \) has a slightly steeper negative slope.

d) Is \( \text{Pb}^{2+} \) stable in acid solution? Justify your answer.

Yes it is stable. It lies well below a line directly connecting its redox neighbours \( \text{PbO}_2 \) and \( \text{Pb}(s) \).

e) What product(s) would form if \( \text{PbO}_2 \) was mixed with \( \text{Sn}^{2+} \) in acidic solution? Write a balanced equation.

\[
\begin{align*}
\text{PbO}_2 & + 4 \text{H}^+ + 2 \text{e}^- \rightarrow \text{Pb}^{2+} + 2 \text{H}_2\text{O} \quad 1.698 \text{V} \\
\text{Sn}^{2+} & + 2 \text{H}_2\text{O} \rightarrow \text{SnO}_2 + 4 \text{H}^+ + 2 \text{e}^- \quad 0.088 \text{V} \\
\text{PbO}_2 & + \text{Sn}^{2+} \rightarrow \text{Pb}^{2+} + \text{SnO}_2 \quad 1.786 \text{V}
\end{align*}
\]

f) Demonstrate what the lead-containing species would be if \( \text{PbO}_2 \) were reacted with Mg, given that the standard reduction potential of Mg: \( \text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg} \ E = -2.36 \text{V} \) \( E^o \)

\[
\begin{align*}
\text{Mg} & \rightarrow \text{Mg}^{2+} + 2\text{e}^- \\
\text{PbO}_2 & + 4 \text{H}^+ + 2 \text{e}^- \rightarrow \text{Pb}^{2+} + 2 \text{H}_2\text{O} \quad 1.698 \text{V} \\
\text{PbO}_2 & + \text{Mg} + 4 \text{H}^+ \rightarrow \text{Pb}^{2+} + \text{Mg}^{2+} \quad 4.06 \text{V}
\end{align*}
\]

\[
\begin{align*}
\text{(Mg} & \rightarrow \text{Mg}^{2+} + 2\text{e}^- \text{)} \times 2 \quad 2.36 \text{V} \\
\text{PbO}_2 & + 8 \text{H}^+ + 4 \text{e}^- \rightarrow \text{Pb}(s) + 4 \text{H}_2\text{O} \quad = 3.146 / 4 = 0.787 \text{V} \\
\text{PbO}_2 & + 2 \text{Mg} + 8 \text{H}^+ \rightarrow \text{Pb}(s) + 2 \text{Mg}^{2+} \quad 3.15 \text{V}
\end{align*}
\]

The answer depends on how much magnesium were added; one equivalent of Mg would convert all the lead(IV) oxide into lead(II) aqua ion, since this is the preferred reaction (more positive \( E^o \)); however, any excess Mg would result in the reduction of lead(II) to metallic lead, since the second reaction also has a favourable redox potential.

g) Is this reaction an inner-sphere redox or an outer-sphere redox reaction? Justify your answer.

Definitely inner-sphere, as the lead loses covalently bound oxygen atoms as it is reduced.

h) Use the Frost diagram to contrast the chemical behavior of tin and lead in aqueous solution. Elemental tin and lead are expected to be very similar – both are very mild reducing agents. Also the chemistry of the metal \( +2 \) ions are expected to be highly similar, as the redox potentials leading to them are very similar. Their sizes are also likely to be more or less identical as a result of the lanthanide contraction. However, with respect to the \( +4 \) oxidation state, these compounds could hardly be more different. \( \text{SnO}_2 \) is very stable, the most stable form of the elements in the aqua/oxo system. But \( \text{PbO}_2 \) is a very powerful oxidizing agent.
8. Consider the Latimer diagram for titanium in acidic and basic solutions:

**Acidic Solution**

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>II</td>
<td>-3.26</td>
<td>-4.26</td>
</tr>
<tr>
<td>III</td>
<td>-3.63</td>
<td>-6.21</td>
</tr>
<tr>
<td>IV</td>
<td>-3.5</td>
<td>-7.59</td>
</tr>
</tbody>
</table>

**Basic Solution**

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>II</td>
<td>-1.38</td>
<td>-1.95</td>
</tr>
<tr>
<td>III</td>
<td>-1.63</td>
<td>-2.13</td>
</tr>
<tr>
<td>IV</td>
<td>-1.95</td>
<td>-2.13</td>
</tr>
</tbody>
</table>

The resulting Frost diagram is shown at right:

b) *Is any species in the titanium Frost diagram an oxidizing agent? Explain.*

TiO\(_{2}^{2+}\) in acid solution is an extremely mild oxidizing agent. The line connecting it to Ti\(_{3}^{+}\) has a positive slope. All other lines have negative slope, hence are not oxidizing agents.

c) *Is titanium metal a stronger reducing agent under acidic or basic conditions? Explain.*

Stronger under basic conditions. The line connecting Ti to the Ti(II) species has a steeper negative slope under basic than under acidic conditions.

d) *What reaction do you expect to occur if dilute acidic solutions of Ti\(_{2}^{+}\) and TiO\(_{2}^{2+}\) are mixed? Write balanced redox half reactions and a balanced overall redox reaction.*

We would expect a comproportionation reaction between Ti\(_{2}^{+}\) and TiO\(_{2}^{2+}\) when they are mixed. The equations are:

\[
\begin{align*}
\text{Ti}^{2+} & \rightarrow \text{Ti}^{3+} + e^- & E^\circ = 0.37 \text{ V} \\
\text{TiO}_{2}^{2+} + 2 \text{H}^+ + e^- & \rightarrow \text{Ti}^{3+} + \text{H}_2\text{O} & E^\circ = 0.1 \text{ V} \\
\text{Ti}^{3+} + \text{TiO}_{2}^{2+} + 2 \text{H}^+ & \rightarrow 2 \text{Ti}^{3+} + \text{H}_2\text{O} & E^\circ = 0.5 \text{ V}
\end{align*}
\]

e) *You are an employee of a paint company, and are asked to produce TiO\(_{2}\) as economically as possible starting with metallic titanium. Burning the metal in oxygen is not allowed for environmental reasons. Propose a method using the Frost diagram for data, and write a balanced redox half reaction for the process.*

I would stir finely divided Ti into a 1 M (or stronger) solution of sodium or potassium hydroxide and add oxidizing agent in the form of dioxygen or peroxide. The expected reaction would be:

\[
\text{Ti} + 4 \text{OH}^- \rightarrow \text{TiO}_2 + 2 \text{H}_2\text{O} + 4 e^- \quad E^{\circ/2} = 7.59 / 4 = 1.90 \text{ V}
\]
Consider the Latimer diagram for manganese in acidic and basic solution.

a) Calculate values of $n_E$ for each redox couple connecting a given oxidation state of manganese in acid and base solution to the elemental form, and construct a comparative Frost diagram for this element under the two sets of conditions on the graph paper provided. Ensure the diagram is legible (use a ruler!), including a sensible choice of scale, and that all the points on the diagram are clearly labeled.

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Acid $n_E$</th>
<th>Base $n_E$</th>
<th>Acid $n_E$</th>
<th>Base $n_E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>0.90</td>
<td>0.56</td>
<td>0.95</td>
<td>0.146</td>
</tr>
<tr>
<td>I</td>
<td>-1.18</td>
<td>-1.56</td>
<td>-0.234</td>
<td>-1.56</td>
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<tr>
<td>II</td>
<td>-2.36</td>
<td>-3.12</td>
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<td>-3.12</td>
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<tr>
<td>III</td>
<td>-0.86</td>
<td>-3.354</td>
<td>-2.36</td>
<td>-3.12</td>
</tr>
<tr>
<td>IV</td>
<td>0.09</td>
<td>-3.208</td>
<td>-2.36</td>
<td>-3.12</td>
</tr>
<tr>
<td>V</td>
<td>2.99</td>
<td>-2.278</td>
<td>0.09</td>
<td>-3.208</td>
</tr>
<tr>
<td>VI</td>
<td>4.27</td>
<td>-2.008</td>
<td>2.99</td>
<td>-2.278</td>
</tr>
<tr>
<td>VII</td>
<td>5.17</td>
<td>-1.448</td>
<td>4.27</td>
<td>-2.008</td>
</tr>
</tbody>
</table>

b) Which species, under what conditions, is the strongest oxidizing agent?

$H_3MnO_4$ in acid (has the steepest line with positive slope).

c) Which species, under what conditions, is the strongest reducing agent? Mn in base (has steepest line with negative slope).

d) Is $Mn^{2+}$ in acidic solution stable towards disproportionation? Explain. Yes. It lies below the line connecting it to any of its neighbors. It is in a thermodynamic well, and is the most stable form of manganese in acidic solution.

e) What is the most stable form of manganese in acid solution? In basic solution? How can you explain the difference? $Mn^{2+}$ in acid, but $Mn_2O_3$ in base. From our study of Bronsted acidity, we recognize that $Mn$(III) cations are more acidic than $Mn$(II). In basic solution this leads to an oxide with a much higher affinity for oxide ions. (You could also argue this from lattice energy considerations). Thus the enhancement of the free energy in the presence of high hydroxide/oxide ion concentration stabilizes the $Mn$(III) state dramatically (over 2 V difference in acid and base).

f) What reaction is expected to occur if $Mn$ and $MnO_2$ are added to a 1.0 M solution of a non-coordinating acid? Would anything have to be done to make this reaction occur at a reasonable rate? Provide a balanced equation and a cell voltage.

We expect a comproportionation reaction: $Mn + MnO_2 + 4 H^+ \rightarrow 2 Mn^{2+} + 2 H_2O$ (you can see why the acid is needed for this reaction to proceed smoothly, since four moles of $H^+$ are consumed per mole of reactants).

g) Aqueous permanganate (usually obtained from its potassium salt) is a common reagent in analytical chemistry, despite the fact that it lies outside the stability field for water. How is this possible? On the other hand, why cannot permanganate solutions be stored for any length of time? What happens to such solutions? Given:

$$2 H_2O \rightarrow O_2 + 4 H^+ + 4 e^- \quad E_{0}^{\circ} = -1.229,$$

provide a balanced redox reaction for the expected process.

The metastability of permanganate depends on the overpotential for oxygen production from water. On long standing we nonetheless expect this reaction to occur. Certain impurities also catalyze this decomposition and make it rapid. On long standing, permanganate solutions in neutral water tend to deposit brown solid, therefore $MnO_2$. The balanced reaction is:

$$4 MnO_4^- + 4 H^+ \rightarrow 4 MnO_2 + 3 O_2 + 2 H_2O$$
10. a) Calculate the \( pK_a \) values for Mn\(^{n+} \) for Mn(II), Mn(III) and Mn(IV) oxidation states. Use this data to explain what forms these oxidation states take on the Frost diagram. [Hint: Take manganese aqua ions to be high spin for these calculations.] The equation to use requires knowledge of the electronegativity, which for Mn is 1.55, so we use:

\[
pK_a = 15.14 - 0.8816 \left( \frac{Z^2}{r} + 9.60 \left( \chi_{\text{Pauling}} - 1.50 \right) \right)
\]

We assume a hexaaqua complex as the original species in solution from which a given species derives, i.e. the undissociated form of the “acid”, so \([\text{Mn(OH}_2)_6]^2+\). The radii are taken from the table in Section 5.2.

<table>
<thead>
<tr>
<th>( Z )</th>
<th>( r )</th>
<th>( pK_a )</th>
<th>Classification</th>
<th>Acid species</th>
<th>Base species</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.96</td>
<td>11.0</td>
<td>Weakly acidic</td>
<td>( \text{Mn}^{2+} ) (aq)</td>
<td>( \text{Mn} ) (OH)(_2)</td>
</tr>
<tr>
<td>3</td>
<td>0.72</td>
<td>3.7</td>
<td>Moderately acidic</td>
<td>( \text{Mn}^{3+} ) (aq)</td>
<td>( \text{Mn}_2\text{O}_3 )</td>
</tr>
<tr>
<td>4</td>
<td>0.67</td>
<td>-6.3</td>
<td>Very strongly acidic</td>
<td>( \text{MnO}_2 )</td>
<td>( \text{MnO}_2 )</td>
</tr>
</tbody>
</table>

The weakly acidic 2+ state is predominantly present as the non-ionized aqua ion in 1 M acid, but precipitates as the hydroxides in 1 M base. Much the same is true for the moderately acidic 3+ state, except that the hydroxide gets dehydrated to the oxide \( \text{Mn}_2\text{O}_3 \) due to the increased lattice energy of a 3+/2− combination. But the very strongly acidic 4+ state is fully hydrolised and dehydrated to \( \text{MnO}_2 \) over the full \( pH \) range.

b) Calculate the \( pK_a \) values for the parent acids of MnO\(_n^–\) anions for the Mn(V), Mn(VI) and Mn(VII) oxidation states. Use the results to discuss the forms that these three oxidation states take in acid and base solution on the Frost diagram.

The equation to use is the Pauling estimate, For \( \text{O}_q^p\text{E(OH)}_p \), \( pK_a \sim 8 - 5p \)

<table>
<thead>
<tr>
<th>Parent acid formula</th>
<th>( q )</th>
<th>( pK_a )</th>
<th>Classification</th>
<th>Acid species</th>
<th>Base species</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_3\text{MnO}_4 )</td>
<td>1</td>
<td>3</td>
<td>Moderately acidic</td>
<td>( \text{H}_3\text{MnO}_4 )</td>
<td>( \text{MnO}_4^– )</td>
</tr>
<tr>
<td>( \text{H}_2\text{MnO}_4 )</td>
<td>2</td>
<td>-2</td>
<td>Strongly acidic</td>
<td>[( \text{HMnO}_4 )](^–)</td>
<td>( \text{MnO}_4^3– )</td>
</tr>
<tr>
<td>( \text{HMnO}_4 )</td>
<td>3</td>
<td>-7</td>
<td>Very strongly acidic</td>
<td>( \text{MnO}_4^2– )</td>
<td>( \text{MnO}_4^2– )</td>
</tr>
</tbody>
</table>

Here again the influence of the inherent tendency to hydrolise is observed in the forms present in 1 M acid or base solution. The strongly acidic \( \text{HMnO}_4 \) is fully dissociated throughout the \( pH \) range (compare \( \text{HClO}_4 \)), whereas the strongly acidic Mn(VI) acid is mono-dissociated in strong acid, and fully dissociated in base, as expected. Finally, the weak Mn(V) aqua ion is fully protonated in strong acid solution, but fully deprotonated in strong base, in full agreement with its \( pK_a \) value.

11. (a) Note that several oxidation states which are present on the Frost diagram, under both acidic and basic conditions, are not shown in the Pourbaix diagram. Provide a clear explanation of why this might be the case for each missing species!

- **In acid solution:** present are \( \text{Mn}^{2+} \), \( \text{Mn}_2\text{O}_3 \) and \( \text{MnO}_4^2– \); absent are \( \text{Mn}^{3+} \), \( \text{H}_3\text{MnO}_4 \) and \( \text{HMnO}_4 \).
- **In base solution:** present are \( \text{Mn(OH)}_2 \), \( \text{Mn}_2\text{O}_3 \), \( \text{MnO}_2 \) and \( \text{MnO}_4^2– \); absent are \( \text{MnO}_4^3– \) and \( \text{MnO}_4^2– \).
- The absent species are in each case species that lie above the lines connecting their neighbours, i.e. they are unstable w.r.t. disproportionation. In actual fact, \( \text{MnO}_4^2– \), which is the least unstable species on the Frost diagram, as it lies almost directly on the line connecting the \( \text{Mn}(IV) \) and \( \text{Mn}(VII) \) species in basic solution, is actually found on more extended Pourbaix diagrams at very high \( pH \), i.e. in solutions approaching 10 M hydroxide ion concentration.
- Finally, on this Pourbaix diagram elemental manganese does not show up. This metal is readily oxidised, and is therefore only found at much more negative potentials than are displayed on this diagram.

(b) The Pourbaix diagram contains one additional species which is not on the Frost diagram. Identify this compound, and discuss why it is not shown on the Frost diagram. (Hint: this compound exists as a solid, only.)

This “extra” species is in fact solid \( \text{Mn}_2\text{O}_3 \) under strongly basic conditions. From the four oxide ions we get a 8− charge, implying at total of 8+ charges from the three manganese ions. How can this be? Well, we can get it by assigning oxidation states of 3+, 3+ and 2+ to the three manganese ions in the empirical formula, i.e. it is a mixed-oxidation state metal oxide. Such mixed systems are in fact fairly common for the transition metal oxides in their solid state forms. In solution this distinction is not maintained. The alternative explanation, i.e. that there are superoxide or peroxide ions present in this solid has been disproven using X-ray crystallography. Recall that these two ions are *diatomic* molecular ions, whereas the structure obtained only contains isolated oxide ions, consistent with the interpretation give above.
(c) What form(s) will manganese take in lake and stream water, where the pH = 6-8 and $E^\circ = 0.6-0.7$ V?
In lake and stream water in the given $E$/pH range, manganese is predominantly in the insoluble MnO$_2$ form, and thus is found in the sludge at the bottom of the lake or stream. However, the border to soluble Mn$^{2+}$ is not so terribly far away, so that a small amount of dissolved Mn$^{2+}$ is expected to remain in equilibrium with the precipitated dioxide.

(d) What is the environmental consequence for manganese when water from fresh-water bogs (pH = 4, $E^\circ = 0.1$ V) in contact with manganese ores are allowed to drain into a lagoon in the ocean (pH = 9, $E^\circ = -0.4$ V)?
In the bog, we are well into the soluble aqua ion Mn$^{2+}$, whereas in the lagoon the manganese would be expected to precipitate without oxidation to Mn(OH)$_2$, from whence dehydration might eventually occur to give MnO.

(e) People often find that clear well water that they draw from wells will deposit a black manganese-containing solid on standing in their toilet bowls. Explain what that solid is and why it forms in the toilet bowl and not underground.
From the Pourbaix diagram, we see that at pH 6-7, at 0.7 V Mn is predominantly in the soluble aqua ion state, which is colourless (the colour of [Mn(OH$_2$)$_6$]$^{2+}$ is among the palest of the transition metal aqua ions, and at natural concentrations results in colourless solutions.) But at 0 V in the same pH range, Mn is predominantly in the MnO$_2$ range, and manganese(II) oxide is indeed a black solid. We propose therefore that the well water far from exposure to the atmosphere is under reducing conditions, giving clear water. But on aeration of the water in the toilet tank and bowl, the Mn(II) is oxidised to the insoluble Mn(IV) oxide.

(f) In section 6.4.1 we learned about the essential trace elements, and find that Mn has a quite high concentration in mammalian tissue (ca. 1ppm), but very low concentration in ocean water (10$^{-3}$ ppm). Explain.
In ocean water, i.e. pH 8 and +0.4 to +0.6 V, Mn is divided between Mn$_2$O$_3$ and MnO$_2$, both of which are insoluble. Except from a very small amount of dissolved metal in equilibrium with these solids, including the reduced Mn$^{2+}$ aqua ion, most of the manganese will precipitate from ocean waters. Hence the much lower concentration of this element in sea water.
Another implication of this analysis is that mammalian systems need efficient Mn absorption, storage and transport mechanisms.

12. As mentioned in lecture and in some of the problems above, coordination of a metal ion will alter its redox chemistry. When the element ruthenium is combined with a chelating tetradentate nitrogen donor, “L”, it forms a stable aquachlorocomplex cis-[RuLCl(OH$_2$)]$^+$.
Answer the following questions with respect to the Pourbaix diagram for this metal complex. A molecular model of the complex has also been included, as well as a sketch of the ligand.
(a) Which oxidation states of ruthenium are found on the diagram?
Ru(II), Ru(III), Ru(IV) and Ru(V), the latter only at very high potentials in strong acid solution.

(b) What is the standard reduction potential of cis-[RuLCl(OH$_2$)$_2$]$^{+2}$?
This is the intercept of the line separating Ru(III) and Ru(II) at pH = 0. The value is therefore ~ +0.4 V.

(c) Why are there two different Ru(III) species on the diagram?
There is a vertical acid-base predominance boundary. To the left is found the acid form, to the right the base form. Since there is only one aqua ion in this complex, which is stabilised by the large tetradentate ligand and the strongly...
bound chloride ion, the chemical consequences of hydrolysis are most obvious. The process that occurs can be represented:

\[
cis-[\text{RuLCl(OH}_2\text{)]}^{2+} + \text{H}_2\text{O} \rightarrow [\text{RuLCl(OH)}^+] + \text{H}_3\text{O}^+
\]

We expect Ru\(^{3+}\) to be moderately acidic, and to be strongly affected by the ligand environment.

(d) Throughout the pH range there is only one form of Ru(IV) on the diagram. Explain the nature of this complex. Contrast it to the single Ru(II) species over the indicated pH range.

We expect Ru(IV) to be strongly acidic. In fact, the species that is observed is the special case of an oxo-anion (section 4.3.4 (c)), caused by the double dissociation of a coordinated water molecule. The parent aqua ion is expected to be very strongly acidic, so it spontaneously ionizes to release 2 H\(^+\) to the solvent environment. This situation is true over the whole pH 0 – 10 range displayed in the diagram.

On the other hand, the Ru(II) species cis-[RuLCl(OH\(_2\)])^+ is expected to be mildly acidic, and indeed it is found in the undissociated form over the displayed 0 – 10 pH unit displayed.

(e) What is the reduction potential of cis-[RuLCl(O)]\(^+\) at pH = 6?

We draw intersects on the diagram at pH 6 to the line crossing from the Ru(IV) species to the Ru(II) species; the intercept lies at ~ +0.65 V.

(f) What is the highest oxidation state of Ru that can be achieved with this ligand set in strongly acidic solution?

Ru(V) is accessed in the complex cis-[Ru(O)LCl]\(^2+\), which apparently has only been characterized in the pH 0–3 range.

(g) Write balanced redox half reactions connecting the two forms of Ru(III) with the Ru(IV) species. Use these equations to explain the different slopes in the lines forming the III/IV boundary.

We choose to write these as reductions in standard electrochemical form, as follows:

Acid solution: \[ [\text{Ru(O)LCl}]^+ + 2\text{H}^+ + e^- \rightarrow [\text{RuLCl(OH}_2\text{)]}^{2+} \]

Base solution: \[ [\text{Ru(O)LCl}]^+ + \text{H}_2\text{O} + e^- \rightarrow [\text{RuLCl(OH}_2\text{)]}^{2+} + \text{OH}^- \]

We find that the IV/III reduction in acid involves two equivalents of hydronium ion, while the same reaction in a basic solvent requires the change in one equivalent of hydroxide, which is the conjugate of one unit of acid. Thus we expect a greater pH dependence of the cell potential \( E_{\text{cell}} \) in the acid redox process as we do in the base redox process. Thus the acid condition line slopes more steeply than the base condition lines (a vertical predominance diagram separates these two forms at pH = 4.

(i) Contrast the result for cis-[RuLCl(OH\(_2\)])^+ with that obtained for ruthenium in the aqua/oxo system (next question). For the answer to this question, see #14(b).
13. The “blank” Pourbaix diagram below belongs to the element ruthenium in the pure aqua/oxo environment.

(a) Without reference to your notes, fill in the following chemical forms on Ru in the predominance areas of this diagram: Ru, RuO₄, RuO₄⁻, RuO₄₂⁻, Ru(OH)₃, Ru(OH)₄, RuO₅²⁻.

(b) Contrast the chemical behaviour of ruthenium in the absence and presence of ligand “L”. Which oxidation states are present/absent in each system? Which species are likely to be soluble, which insoluble? Which oxidation states predominate (use caution here: reference must be made to the scale values for $E^0$ for valid comparisons.

If we superimpose the Pourbaix diagram of cis-[RuLCl(OH₂)]⁺ onto the one above (green rectangle is the area of comparison), we find some interesting comparisons:

- Ru is a noble metal, and is not readily oxidized in water and air (metallic Ru is found well above the H₂O/H₂ line of water), but in the presence of “L” and “Cl” ligands, it is more easily oxidized, so that in the range where the aqua system is elemental Ru, the complex is in the Ru(II) form.
- Ru(II) is not stable in the aqua system, so that oxidation of metallic ruthenium gives directly the Ru(III) hydroxide at all pH.
- In the presence of “L” and “Cl” ligands, Ru is stable in this oxidation state.
- Whereas Ru(III) is present as the hydroxide in the aqua system at all pH, the complexed Ru(III) has well-defined acid-base chemistry, with a predominance boundary at pH = 6.
- The ligand causes the oxidation of ruthenium to Ru(IV) to lie at slightly higher energy than the aqua system at all pH values studied.
- On the other hand, oxidation to Ru(V) is possible with the “L” and “Cl” ligands, but this oxidation state is not even observed in the aqua system, where Ru(IV) is oxidized directly to Ru(VIII) as RuO₄.
- Under basic conditions, Ru(VI) and Ru(VII) are known in the aqua system, but for the ligand complex we have no data at such high pH.

(c) Contrast the chemical behaviour of Ru with its lighter group member Fe. The Pourbaix diagram for iron was discussed in class in detail. From the two diagrams, discuss in detail the similarities/differences in the chemical behaviour of these two elements.

- Ru is more noble than Fe. The standard reduction potential of Fe²⁺ is −0.5 V in acid solution, but is +0.7 V for Ru(OH)₃, a difference of 1.2 V, which is very large.
- Fe³⁺ is present in the aqua system, but this is not the case for Ru²⁺.
Ru(III) exists over only a narrow E range, but Fe(III) is stable of a very wide range of redox energies. Ru exists in +4, +5, +6 and +8 oxidation states, while Fe exists as 2+, 3+ and 6+ oxidation states only.

(d) Not all species that are typically displayed on a Latimer or Frost diagram necessarily are present on a Pourbaix diagram. For example, species that rapidly disproportionate may never be predominant, and Pourbaix diagrams are E vs. pH predominance diagrams. Use the Latimer diagram for ruthenium to discuss which species do, and which do not, show up on both. Are any oxidation states represented by different species on the two kinds of diagrams? Why might this be?

- The Pourbaix diagram only has the oxidation states 0, +3, +4 and +8 present in acid solution, while there is redox potential information present on the Latimer diagram for 0, +2, +3, +4, +6, +7 and +8 states. Clearly many of these must be unstable towards disproportionation (here construction of a Frost diagram is to be strongly recommended).
- In base solution, the Pourbaix diagram displays the additional oxidation states +6 and +7.
- Ru(III) is predominant as Ru(OH)₃ over the full pH range, while the Latimer diagram has potential data for apparently Ru³⁺(aq).
- Ru(IV) is predominant as Ru(OH)₄ over the full pH range, while the Latimer diagram has potential data for [Ru(OH)₂]²⁺. This is of course the form of this molecule that has two of the hydroxides protonated in 1 M acid.
- We can understand the existence of different species on Latimer and Pourbaix diagrams by recognizing that the presence of a potential for any redox species does not necessarily mean that the species has to be the dominant one under those conditions. This is especially true when one of the two species precipitate. Thus [Ru(OH)₂(OH₂)₃]²⁺ is the doubly protonated conjugate of Ru(OH)₄. 