Vanadium Lab Notes.

These are rough lecture notes which correspond to the Vanadium lab, and will probably only make sense if read alongside the lab.

In this lab, $V^{5+}$ is reduced to $V^{4+}$, $V^{3+}$, $V^{2+}$. The different oxidation states of vanadium are evident due to color changes, and can be separated by ion-exchange chromatography. Concepts of coordination complexes, d-d transitions, redox potentials, and the Nernst equation are involved.

### Coordination complexes

Each oxidation state of vanadium exists as an aquo complex, where $H_2O$ or $OH^-$ fills the coordination shell to make a tetrahedral or octahedral complex. Under our experimental conditions (acidic water), the species in solution are as follows:

<table>
<thead>
<tr>
<th>oxidation state</th>
<th>short-hand notation</th>
<th>complex</th>
<th>rough symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V^{5+}$</td>
<td>$VO_3^-$</td>
<td>$[V(OH)O_3]^{2-}$</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>$V^{4+}$</td>
<td>$VO^{2+}$</td>
<td>$[V(H_2O)_5O]^{2+}$</td>
<td>octahedral</td>
</tr>
<tr>
<td>$V^{3+}$</td>
<td>$V^{3+}$</td>
<td>$[V(H_2O)_6]^{3+}$</td>
<td>octahedral</td>
</tr>
<tr>
<td>$V^{2+}$</td>
<td>$V^{2+}$</td>
<td>$[V(H_2O)_6]^{2+}$</td>
<td>octahedral</td>
</tr>
</tbody>
</table>

**Figure 1.** Vanadate, vanadyl, and vanadium(III) ions in acidic water.

Metals in general will form complexes with water, through coordinate bonds with the an electron pair from the Oxygen atom of water: metals are Lewis acids, while water is a Lewis base. The high charge of the metal ion makes the coordinated water more acidic – in other words, the proton is easily lost. You can think of this in terms of a competition between the metal and the proton for electron pairs. This is why one of the coordinated waters in the $[V(H_2O)_6O]^{2+}$ complex is deprotonated twice. Also, the ability of transition metals to accept two pairs of electrons (form a double bond) allows the water to be doubly deprotonated; this is why the coordinated waters in $[V(OH)O_3]^{2-}$ are highly deprotonated. But don’t forget that some of the other protons, especially in the $V$(III) complex, can be lost if the water becomes less acidic.
**d-d transitions**

A d-d transition arises due to the absorption of a photon of light with energy \((E = h \nu)\) equal to the ligand-field splitting, \(10Dq\), as shown in figure 2. Since each vanadium complex in the current experiment absorbs a different wavelength of light, it is reasonable to think that each has a different d-d energy splitting, \(10Dq\).

\[
\Delta E = h \nu = 10Dq
\]

**Figure 2.** Schematic of a d-d transition in V(III).

**Redox potentials.**

Below is a Latimer diagram, which summarizes the reduction potentials for vanadium complexes in acidic water. The numbers above each arrow indicates the standard reduction potential, \(E^0\), for each reduction process.

\[
\begin{align*}
[\text{VO}_3^-] & \rightarrow [\text{VO}]^{2+} & E^0 = 1.00 \\
 & \rightarrow \text{V}^{3+} & E^0 = 0.34 \\
 & \rightarrow \text{V}^{2+} & E^0 = -0.26 \\
 & \rightarrow \text{V}^{(s)} & E^0 = -1.13
\end{align*}
\]

**Figure 3.** Latimer diagram for vanadium in acidic water.

A Latimer diagram is a great way to summarize free energy information, as the Gibbs free energy \((\Delta G^0)\) is derived from the product of the reduction potential \((E^0)\), the number of electrons transferred \((n)\), and the Faraday constant \((F = 96,500 \text{ C/mol})\):

\[
\Delta G^0 = -nFE^0
\]

For example, is reducing \(\text{V}^{5+}\) to \(\text{V}^{4+}\) energetically favorable? If the free energy change is negative, then yes, it is energetically favorable. And remember to convert: \(1 \text{J} = (1 \text{V})(1 \text{C})\).

\[
\Delta G^0 = -(1 \text{ e}^-/\text{mol})(96,500 \text{ C/mol})(+1.00\text{V})(1/\text{VC}) = -96.5 \text{ kJ/mol}
\]

Yes, this half-reaction is energetically favored.

An important concept to keep in mind: the symbol \(^{0}\) indicates that the reaction is run under **standard conditions**, in which each reactant has a concentration of 1 mol/L, and each gas has a partial pressure of 1 atm.
If standard conditions are not operative, then the equilibrium for a reaction may change (recall LeChatelier’s principle???). Consider the following two reactions, and whether they are energetically favored. The first example is pretty straightforward, while the second incorporates the effects of non-standard states on reaction energies.

1. The reaction between KMnO₄ and V⁴⁺, in which V⁴⁺ is oxidized to V⁵⁺.

   Compare the two half-reactions:
   \[ \text{MnO}_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \quad 1.52 \text{ V} \]
   \[ 5(\text{VO}_2^+ + 2H_2O) \rightleftharpoons 5\text{VO}_3^- + 4H^+ + e^-) \quad -1.00 \text{ V} \]

   Net: \[ \text{MnO}_4^- + 5\text{VO}_2^+ + 6H_2O \rightleftharpoons Mn^{2+} + 5\text{VO}_3^- + 12H^+ \quad +0.52 \text{ V} = E^0 \]

   \[ \Delta G^0 = -(5e-/mol)(96.5 \text{ kC/mol})(0.52\text{V})(J/VC) = -250 \text{ kJ/mol} \]

   Yes, this reaction is energetically favored.

   Note that the reduction potential for the oxidation half-reaction was NOT multiplied!! Multiplying the oxidation half-reaction by 5 was done to obtain a balanced equation only. The voltage change for each half-reaction is that for standard conditions, in which every species is present at 1M concentration, and is therefore independent of the number of moles involved.

2. The reaction between VO₃⁻ and Cl⁻, which is the first step of your lab. VO²⁺ is produced.

   Compare the half reactions, and balance them:
   \[ 2(\text{VO}_3^- + 4H^+ + e^-) \rightleftharpoons \text{VO}^{2+} + 2H_2O) \quad 1.00 \text{ V} \]
   \[ 2\text{Cl}^- \rightleftharpoons \text{Cl}_2 + 2e^- \quad -1.36 \text{ V} \]

   net: \[ 2\text{VO}_3^- + 8H^+ + 2 \text{Cl}^- \rightleftharpoons 2\text{VO}^{2+} + 4H_2O + \text{Cl}_2 \quad -0.36 \text{ V} = E^0 \]

   \[ \Delta G^0 = -(2e-/mol)(96.5 \text{ kC/mol})(-0.36\text{V})(J/VC) = + 70 \text{ kJ/mol} \]

   No, this reaction is not energetically favored. And note that, again, multiplying the equations to obtain stoichiometric balance does not lead to a multiplied reduction potential.

The above conclusion presents a problem, since this reaction definitely does occur. How to reconcile reality with our computations?

Well, the first place to look is at our assumptions. This reaction is not energetically favored under standard conditions. Our reaction is, in fact, not done even close to standard conditions. The brief answer is: Cl₂ gas escapes, thereby pulling the equilibrium to the right. – this makes the above reaction favored under laboratory conditions. A more quantitative view is shown next.
**The Nernst Equation**

The Nernst equation (check your GenChem or Inorganic text for further details) accounts for electrochemical potentials under *conditions that are not standard state*. The observed potential \( E \) deviates from the standard-state potential \( E^0 \) by a factor involving the gas constant \( R \), temperature \( T \), the number of electrons and Faraday’s constant, and the natural logarithm of the reaction quotient \( Q \):

\[
E = E^0 - \frac{RT}{nF} \ln Q
\]

where \( Q = \frac{[\text{products}]}{[\text{reactants}]} \)

At 298K, this simplifies to

\[
E = E^0 - (0.059V/n)\log Q
\]

A reaction for which \( E^0 \) is negative will have a positive potential *under non-standard conditions* anytime that the following relationship is found:

\[
|\frac{(0.059V/n)\log Q}{|E^0|} > 1\]

Applying the Nernst equation to example 2:

\[
E = -0.36V - \left( \frac{0.059V}{2} \log \frac{[VO_3^-]^2[H^+]^9[Cl^-]^2}{[VO^{2+}]^2(P_{Cl_2})} \right)
\]

Inspection shows that, should the partial pressure of \( Cl_2 \) decrease, the reaction quotient \( Q \) will become less than 1, and \( \log Q \) will therefore eventually become a negative number. For example, \( \log(0.9) = -0.046 \). This will cause the second term of the Nernst equation to become positive in value, and greater in magnitude that the first term (\( E^0 \)). Once this happens, the overall potential under non-standard conditions can become a positive value.

So, Cl- can reduce \( VO_3^- \) *under non-standard conditions*, since the reaction quotient deviates below unity.