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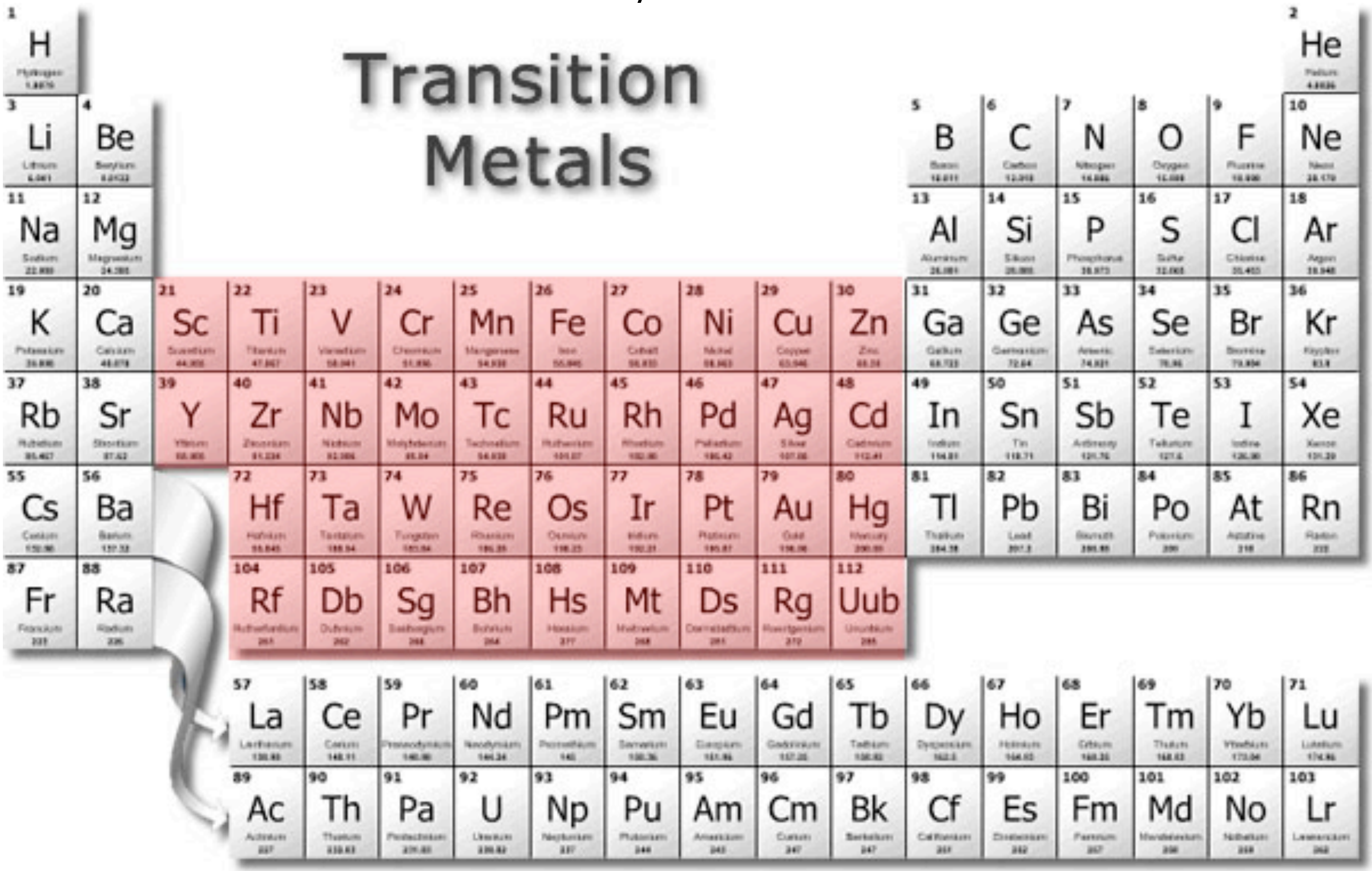
Physical Inorganic Chemistry
CH3514

Dr. Eli Zysman-Colman



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Some Problems in Class

Predict whether the equilibrium constants for the following reactions should be greater than 1 or less than 1:

(a) $CdI_2(s) + CaF_2(s) \rightleftarrows CdF_2(s) + CaI_2(s)$,

(b) $[CuI_4]^{2-}(aq) + [CuCl_4]^{3-}(aq) \rightleftarrows [CuCl_4]^{2-}(aq) + [CuI_4]^{3-}(aq)$,

(c) $NH_2^-(aq) + H_2O(l) \rightleftarrows NH_3(aq) + OH^-(aq)$

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Use hard-soft acid base theory to approach the problem:

(a) $CdI_2(s) + CaF_2(s) \rightleftarrows CdF_2(s) + CaI_2(s)$

SA-SB HA-HB SA-HB HA-SB

The preferred direction is reactants so the equilibrium constant is less than 1.

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The preferred direction is products so the equilibrium constant is greater than 1.

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pKa: 15.7 35

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Some Problems in Class

Balance the following redox reaction in acid solution: $MnO_4^-(aq) + H_2SO_3(aq) \rightarrow Mn^{2+}(aq) + HSO_4^-(aq)$. Predict the qualitative pH dependence on the net potential for this reaction (i.e. increases, decreases, remains the same).

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Split the reaction into the two half-reactions and balance each separately:

$$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$$

$$H_2SO_3(aq) + H_2O(l) \rightarrow HSO_4^-(aq) + 3\ H^+(aq) + 2\ e^-$$

so the net reaction is:

$$2\ MnO_4^-(aq) + 5\ H_2SO_3(aq) + H^+(aq) \rightarrow 2\ Mn^{2+}(aq) + 5\ HSO_4^-(aq) + 3\ H_2O(l)$$

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This can be thought of in terms of the Nernst equation, as well:

$$E = E° - \frac{2.303RT}{nF}\log\left(\frac{[Mn^{2+}]^2[HSO_4^-]^5}{[MnO_4^-]^2[H_2SO_3]^5[H^+]}\right)$$

$$= E° - \frac{2.303RT}{nF}\left[\log\left(\frac{[Mn^{2+}]^2[HSO_4^-]^5}{[MnO_4^-]^2[H_2SO_3]^5}\right) - \log[H^+]\right]$$

$$= E° - \frac{2.303RT}{nF}\left[\log\left(\frac{[Mn^{2+}]^2[HSO_4^-]^5}{[MnO_4^-]^2[H_2SO_3]^5}\right) + pH\right]$$

$$= E° - \frac{2.303RT}{nF}\left[\log\left(\frac{[Mn^{2+}]^2[HSO_4^-]^5}{[MnO_4^-]^2[H_2SO_3]^5}\right)\right] - \frac{2.303RT}{nF}pH$$

That is, increasing the pH subtracts from the standard potential so the net potential decreases with increasing pH.

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Draw an MO diagram for $[V(NH_3)_6]^{3+}$. Indicate Δ_o on the diagram.

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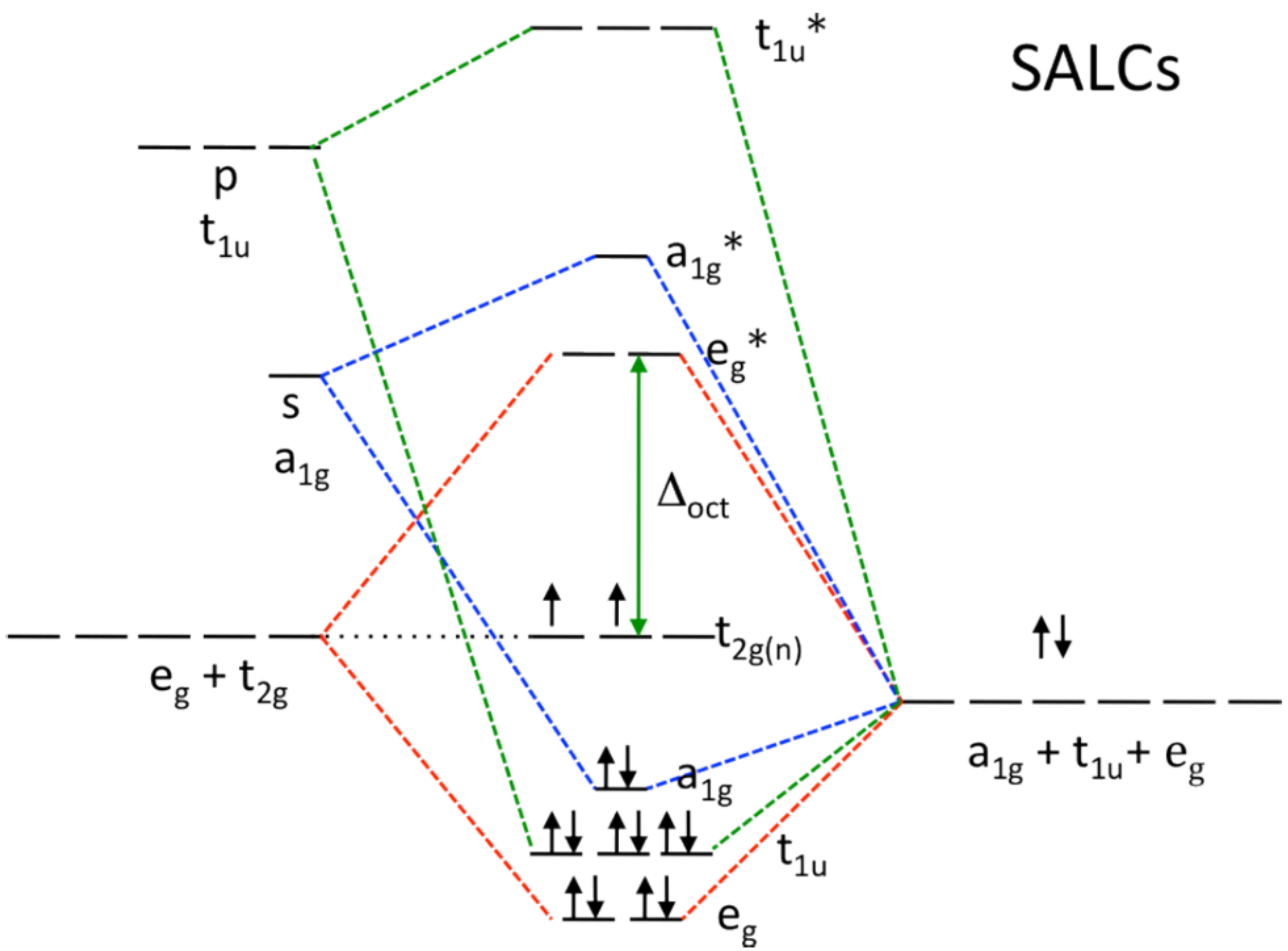

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Some Problems in Class

The following two half-reactions take place in a galvanic cell. At standard conditions, what species are produced at each electrode?

$$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s) \qquad \mathcal{E}^\circ = -0.14\ \text{V}$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad \mathcal{E}^\circ = 0.34\ \text{V}$$

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Cu is produced at the cathode and Sn^{2+} is produced at the anode.

Reaction is spontaneous in the direction which results in a positive E°.
A positive E° can be obtained by reversing the first reaction, which means that Sn is oxidized and Cu^{2+} is reduced. Reduction occurs at the cathode.

Some Problems in Class

The Latimer diagram for manganese in acidic solution is given below at 25°C. Find the standard reduction potential for the reduction of permanganate ion, MnO_4^-, to Mn^{2+} from the potentials listed.

$$MnO_4^- \xrightarrow{0.56\ V} MnO_4^{2-} \xrightarrow{2.26\ V} MnO_2\,(s) \xrightarrow{0.95\ V} Mn^{3+} \xrightarrow{1.51\ V} Mn^{2+} \xrightarrow{-1.18\ V} Mn\,(s)$$

$$MnO_4^- \xrightarrow{1.69\ V} MnO_2\,(s) \xrightarrow{1.23\ V} Mn^{2+}$$

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$MnO_4^- \to MnO_2\,(s)$: 1.69 V; $MnO_2\,(s) \to Mn^{2+}$: 1.23 V

Answer: The following two half cells add to give the desired reaction. The Gibbs free energies add to give the Gibbs free energy of the overall reaction:

	E°_{red}	ΔG°
$MnO_4^- + 4\,H^+ + 3\,e^- \rightarrow MnO_2\,(s) + 2\,H_2O$	1.69 V	$\Delta G^\circ = -\,3\,FE^\circ_{red} = -489.\underline{2}\ kJ\ mol^{-1}$
$MnO_2\,(s) + 4\,H^+ + 2\,e^- \rightarrow Mn^{2+} + 2\,H_2O$	1.23 V	$\Delta G^\circ = -\,2\,FE^\circ_{red} = -237.\underline{4}\ kJ\ mol^{-1}$
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$		$\Delta G^\circ = -\,5\,FE^\circ_{red} = -726.\underline{6}\ kJ\ mol^{-1}$

After adding the Gibbs free energies, the overall voltage is given by solving $\Delta G^\circ = -\,5\,FE^\circ_{red}$:

$$E^\circ_{red} = \frac{\Delta G^\circ}{-\,5\,F} = \frac{-726.\underline{6}\times 10^3\ J\ mol^{-1}}{-\,5\,(96485\ C\ mol^{-1})} = 1.51\ V$$

with $1\ J = 1\ C\ V$