



University of St Andrews

CH3514

# Physical Inorganic Chemistry

## CH3514

Dr. Eli Zysman-Colman

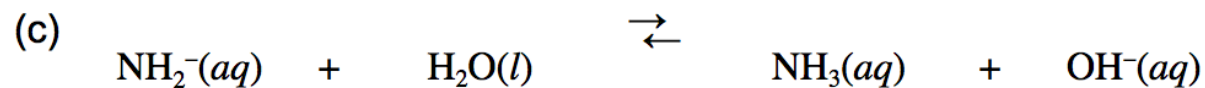
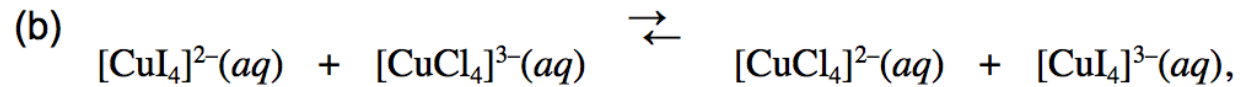
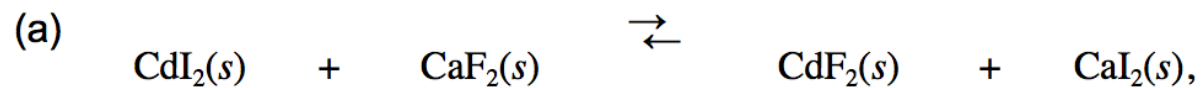
# Transition Metals

1 H Hydrogen 1.0079																	2 He Helium 4.0026
3 Li Lithium 6.941	4 Be Beryllium 9.0122											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.006	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.179
11 Na Sodium 22.989	12 Mg Magnesium 24.305											13 Al Aluminum 26.981	14 Si Silicon 28.085	15 P Phosphorus 30.973	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.955	22 Ti Titanium 47.867	23 V Vanadium 50.941	24 Cr Chromium 51.995	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 68.723	32 Ge Germanium 72.64	33 As Arsenic 74.921	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.8
37 Rb Rubidium 85.467	38 Sr Strontium 87.62	39 Y Yttrium 88.905	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.906	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.905	46 Pd Palladium 106.36	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.757	52 Te Tellurium 127.4	53 I Iodine 126.905	54 Xe Xenon 131.29
55 Cs Cesium 132.905	56 Ba Barium 137.327	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.222	78 Pt Platinum 195.084	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium 209	85 At Astatine 210	86 Rn Radon 222	
87 Fr Francium 223	88 Ra Radium 226	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 264	107 Bh Bohrium 264	108 Hs Hassium 277	109 Mt Meitnerium 268	110 Ds Darmstadtium 285	111 Rg Roentgenium 272	112 Uub Ununbium 285							
57 La Lanthanum 138.905	58 Ce Cerium 140.12	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 145	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.5	67 Ho Holmium 164.930	68 Er Erbium 167.255	69 Tm Thulium 168.934	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.967			
89 Ac Actinium 227	90 Th Thorium 232.037	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237	94 Pu Plutonium 244	95 Am Americium 243	96 Cm Curium 247	97 Bk Berkelium 247	98 Cf Californium 251	99 Es Einsteinium 252	100 Fm Fermium 257	101 Md Mendelevium 258	102 No Nobelium 259	103 Lr Lawrencium 262			



## Some Problems in Class

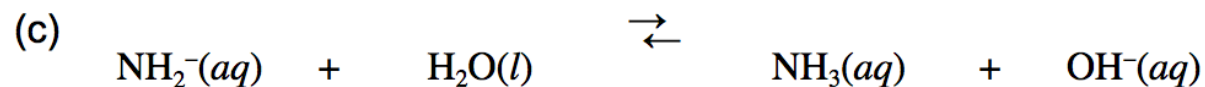
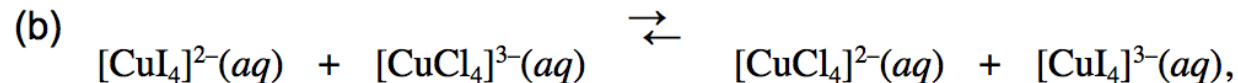
Predict whether the equilibrium constants for the following reactions should be greater than 1 or less than 1:





## Some Problems in Class

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



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



SA-SB

HA-HB

SA-HB

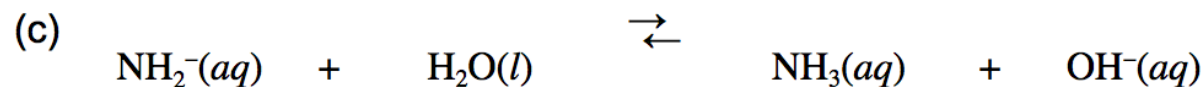
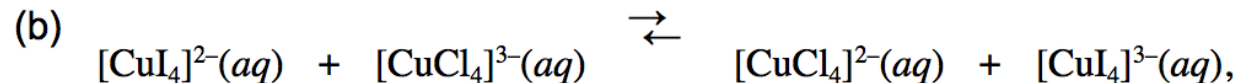
HA-SB

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



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



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

(b)



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SA-HB

HA-HB

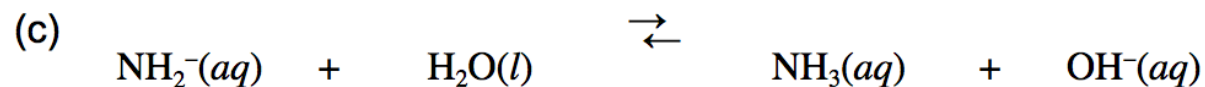
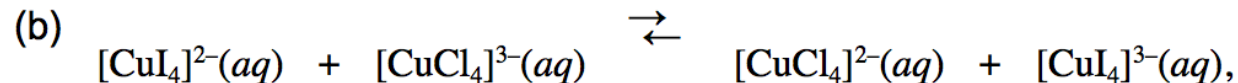
SA-SB

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



## Some Problems in Class

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



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pKa:            15.7                    35

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



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## Some Problems in Class

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Balance the following redox reaction in acid solution:  $\text{MnO}_4^-(aq) + \text{H}_2\text{SO}_3(aq) \rightarrow \text{Mn}^{2+}(aq) + \text{HSO}_4^-(aq)$ . Predict the qualitative pH dependence on the net potential for this reaction (i.e. increases, decreases, remains the same).



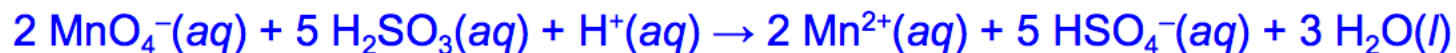
## Some Problems in Class

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



so the net reaction is:





## Some Problems in Class

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

$$\begin{aligned} E &= E^\circ - \frac{2.303RT}{nF} \log \left( \frac{[\text{Mn}^{2+}]^2 [\text{HSO}_4^-]^5}{[\text{MnO}_4^-]^2 [\text{H}_2\text{SO}_3]^5 [\text{H}^+]} \right) \\ &= E^\circ - \frac{2.303RT}{nF} \left[ \log \left( \frac{[\text{Mn}^{2+}]^2 [\text{HSO}_4^-]^5}{[\text{MnO}_4^-]^2 [\text{H}_2\text{SO}_3]^5} \right) - \log[\text{H}^+] \right] \\ &= E^\circ - \frac{2.303RT}{nF} \left[ \log \left( \frac{[\text{Mn}^{2+}]^2 [\text{HSO}_4^-]^5}{[\text{MnO}_4^-]^2 [\text{H}_2\text{SO}_3]^5} \right) + \text{pH} \right] \\ &= E^\circ - \frac{2.303RT}{nF} \left[ \log \left( \frac{[\text{Mn}^{2+}]^2 [\text{HSO}_4^-]^5}{[\text{MnO}_4^-]^2 [\text{H}_2\text{SO}_3]^5} \right) \right] - \frac{2.303RT}{nF} \text{pH} \end{aligned}$$

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





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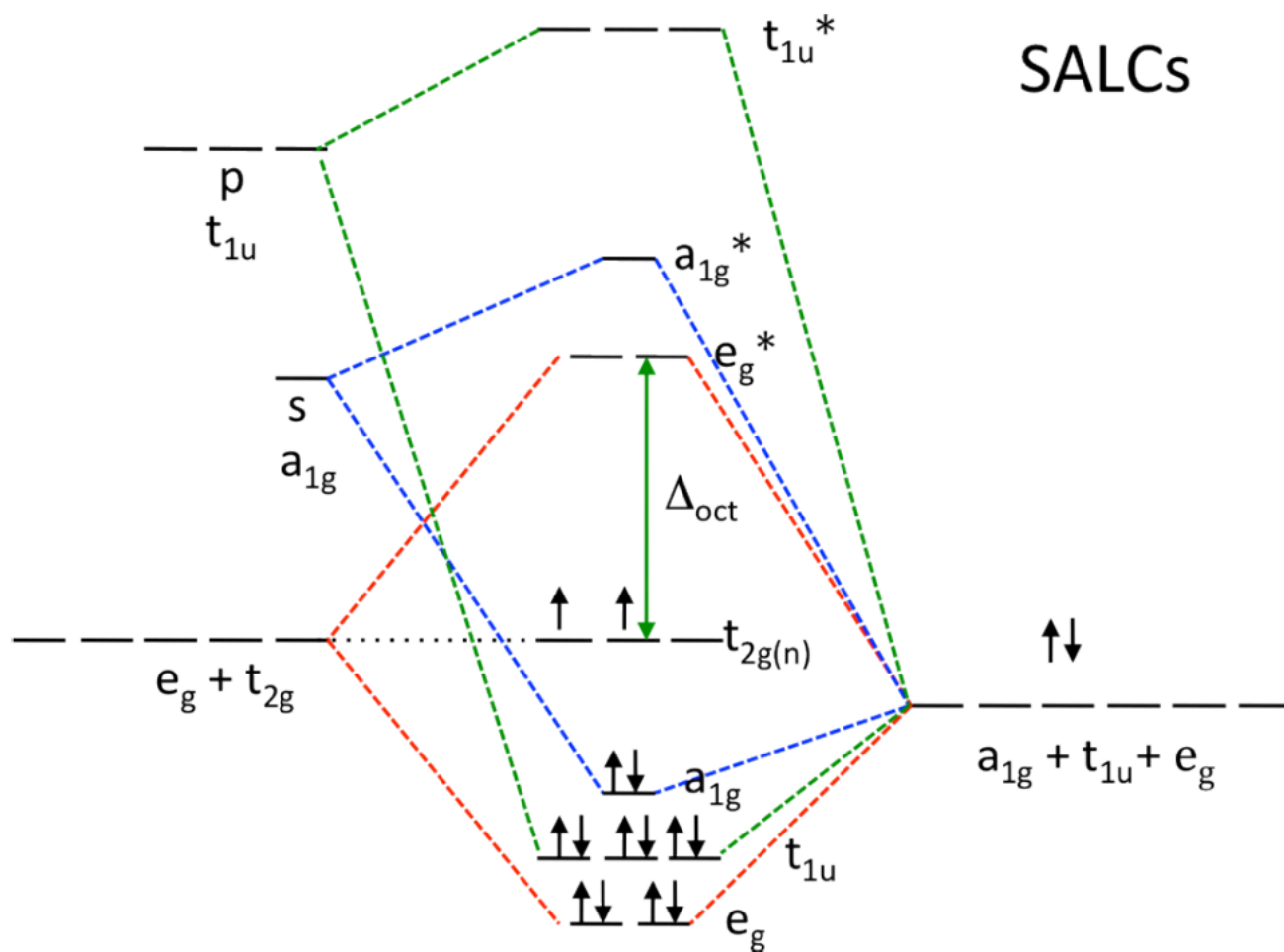
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Draw an MO diagram for  $[\text{V}(\text{NH}_3)_6]^{3+}$ . Indicate  $\Delta_o$  on the diagram.



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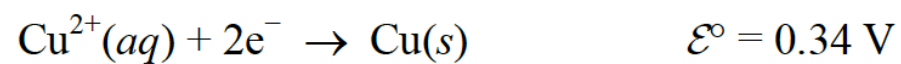
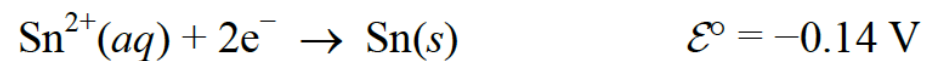
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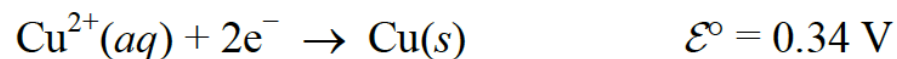
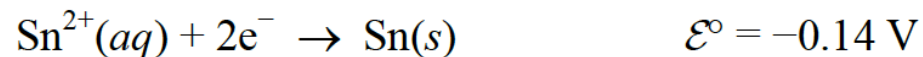
The following two half-reactions take place in a galvanic cell. At standard conditions, what species are produced at each electrode?





## 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?



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

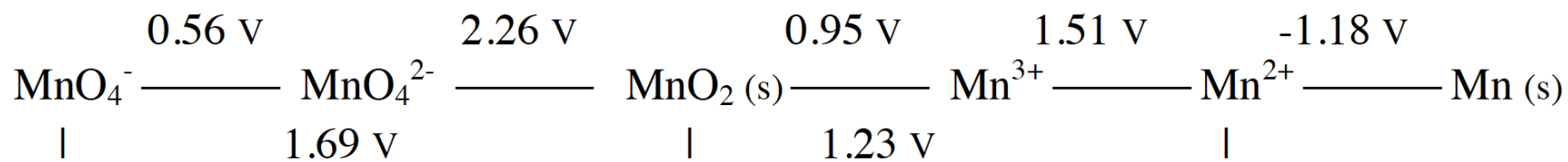
*Reaction is spontaneous in the direction which results in a positive  $E^{\circ}$ .*

*A positive  $E^{\circ}$  can be obtained by reversing the first reaction, which means that Sn is oxidized and  $\text{Cu}^{2+}$  is reduced. Reduction occurs at the cathode.*



## Some Problems in Class

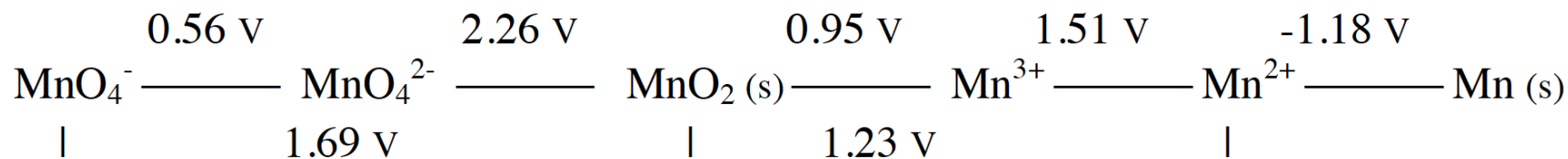
The Latimer diagram for manganese in acidic solution is given below at 25°C. Find the standard reduction potential for the reduction of permanganate ion,  $\text{MnO}_4^-$ , to  $\text{Mn}^{2+}$  from the potentials listed.



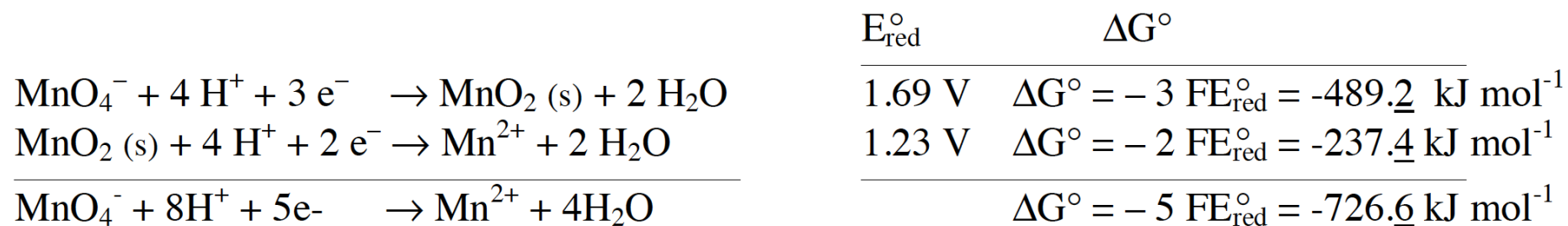


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*Answer:* The following two half cells add to give the desired reaction. The Gibbs free energies add to give the Gibbs free energy of the overall reaction:



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

$$E_{\text{red}}^\circ = \frac{\Delta G^\circ}{-5 F} = \frac{-726.6 \times 10^3 \text{ J mol}^{-1}}{-5 (96485 \text{ C mol}^{-1})} = 1.51 \text{ V} \quad \text{with } 1 \text{ J} = 1 \text{ C V}$$