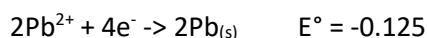
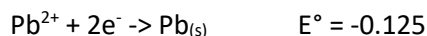


## Study Guide for Electrochemistry

How to find K from  $E^\circ_{\text{cell}}$

1. To review:

- Cell potentials are intensive properties, meaning that they don't depend on the amount of material. For example:



- Standard conditions for electrochemical cells:
  - Pure solids and liquids
  - 1 M solutions
  - 1 bar (~ 1 atm) gases
- Le Chatelier's Principle: Changing the conditions of a reaction at equilibrium will cause the reaction to produce more reactant or product until equilibrium is reestablished.

2. Relating  $E^\circ_{\text{cell}}$  to K

- Standard conditions apply for both  $E^\circ_{\text{cell}}$  and K
- From thermodynamics:

$$\Delta G^\circ = -RT \ln K$$

- From previous electrochemistry discussions:

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

- Putting both together:

$$-RT \ln K = -nFE^\circ_{\text{cell}}$$

$$E^\circ_{\text{cell}} = (RT/nF) \ln K$$

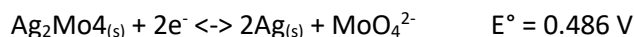
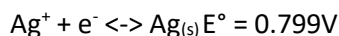
- Where:

- $E^\circ_{\text{cell}}$  is the standard cell potential (in V)
  - R is the thermodynamic form of the gas constant ( $R = 8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ )
  - T is the temperature (in K)
  - n is the number of moles of electrons that are transferred in the reaction
  - F is Faraday's constant ( $F = 96485 \text{ C} \cdot \text{mol}^{-1}$ )
  - K is the equilibrium constant for the reaction
- Usually, the cell is at room temperature (298 K). This reduces the equation to:

$$E^\circ_{\text{cell}} = (0.025693/n) \ln K$$

3. Example:

Using the following standard reduction potentials:



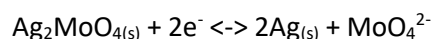
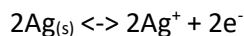
Calculate the solubility product constant for  $\text{Ag}_2\text{MoO}_4(\text{s})$

Solution:

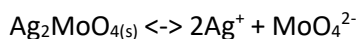
- We know that the solubility product constant equation has this form:



- To get to this equation, we first have to flip one of the half-reactions (changing it from reduction to oxidation) and multiply it by 2. After that we can add the half-reactions.



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We now have the 2 half-reactions. The oxidation half-reaction's  $E^\circ$  becomes  $E^\circ_{\text{anode}}$ . The reduction half-reaction's  $E^\circ$  becomes  $E^\circ_{\text{cathode}}$ . We can then find  $E^\circ_{\text{cell}}$ :

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$E^\circ_{\text{cell}} = 0.486 \text{ V} - 0.799 \text{ V}$$

$$E^\circ_{\text{cell}} = -0.313 \text{ V}$$

- We can now find K:

$$E^\circ_{\text{cell}} = (0.025693/n) \cdot \ln K$$

$$E^\circ_{\text{cell}} \cdot (n/0.025693) = \ln K$$

$$e^{E^\circ_{\text{cell}} \cdot (n/0.025693)} = K$$

$$e^{-0.313 \cdot (2/0.025693)} = K$$

$$K = 2.622 \cdot 10^{-11}$$

- Conceptually, this makes sense. We should expect a non-spontaneous reaction (one with a negative  $E^\circ_{\text{cell}}$ ) to produce very little, if any product at equilibrium (to have a very small K)