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Module 2 Concept Repository

Reading 1 - Electrochemistry

- Not all oxidation-reduction reactions that have a change in oxidation states have a complete transfer of electrons. For example, in the reaction $\text{Zn(s)} + 2\text{H}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$, there is a clear transfer of electrons between zinc atoms to hydrogen ions as Zn changes oxidation numbers from 0 to +2 and H changes from +1 to 0. In this equation Zn(s) loses electrons (oxidized) and is the reducing agent and H^+ gains electrons (reduced) and is the oxidizing agent. However, in the redox reaction $2\text{H}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$, there is not a complete transfer of electrons because water is not an ionic substance. A more complex example is, $\text{Cd(s)}(0) + \text{Ni(+4)O}_2(-2)(\text{s}) + 2\text{H}_2(+1)\text{O}(-2)(\text{l}) \rightarrow \text{Cd(+2)}(\text{O}(-2)\text{H(+1)})_2(\text{s}) + \text{Ni(+2)}(\text{O}(-2)\text{H(+1)})_2(\text{s})$. Here the oxidation state of Cd increases from 0 to +2 and Ni decreases from +4 to +2. Thus, Cd(s) loses electrons (oxidized) and is the reducing agent and Ni gains electrons as NiO_2 (reduced) and is the oxidizing agent.
- To balance redox reactions conservation of mass must be held. Thus, the amount of each element and number of electrons on each side must be the same. For complex reactions, they are better balance by the method of half-reaction showing electron transfer. For example, the following reaction $\text{Sn}^{2+}(\text{aq}) + 2\text{Fe}^{3+}(\text{aq}) \rightarrow \text{Sn}^{4+}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq})$ can be decomposed into the following oxidation reaction $\text{Sn}^{2+}(\text{aq}) \rightarrow \text{Sn}^{4+}(\text{aq}) + 2\text{e}^-$ and reduction reaction $2\text{Fe}^{3+}(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Fe}^{2+}(\text{aq})$. In acidic aqueous solution, the half reaction can be balanced by balancing atoms other than H and O, balancing O with H_2O , balancing H with H^+ , and then balancing e^- . In a basic solution, the half reaction must be balanced by adding electrons to half reaction based on oxidation state change, balancing with H^+ as if it took place in an acidic solution, adding OH^- to both sides and balance to then combine to form H_2O which are canceled if appeared as both reactants and products, and finally balance the total reaction to finalized as full reaction by adding half reactions that are canceled if appeared as both reactants and products.
- A voltaic cell or electrochemical battery uses a redox reaction to transfer electrons through an external pathway, where the electrodes are the solid conductive metals connected by the external circuit. In the reaction $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$, the electrodes can be Zn(s) and Cu(s) which are materials a part of the reaction. The electrode where oxidation occurs is the anode and the electrode which reduction occurs is the cathode. Based on the half reactions, the anode oxidation half-reaction is $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$ and the cathode electrode half-reaction is $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$. The electrodes Zn(s) and Cu(s) are submerged in ZnSO_4 and CuSO_4 solution, respectively. The solution in the two half cells must remain electrically neutral through ion transfer of Zn^{2+} cations and SO_4^{2-} anions through a salt bridge or porous barrier called a separator.
- The potential difference between two electrodes of a voltaic cell is a voltage difference E_{cell} where the potential associated with each electrode is the potential for reduction at that electrode. This formulates the equation $E_{\text{cell}} = E_{\text{red}}(\text{cathode}) - E_{\text{red}}(\text{anode})$. Standard half-reaction potentials are measured relative to the reduction of $\text{H}^+(\text{aq})$ to $\text{H}_2(\text{g})$ with a potential of 0 V. Potentials are

intensive properties meaning if the amount of substance increases and the energy increases, but volts remain constant. The lower tendency for a half reaction to occur in one direction the greater tendency for it to occur in the other. Meaning, the half-reaction with the most negative reducing potential is the most easily reversed and run as oxidation. To make this formulation pertain to general reduction reactions and spontaneity, $E^\circ = E_{\text{red}}^\circ (\text{reduction}) - E_{\text{red}}^\circ (\text{oxidation})$ where a positive value of E is spontaneous, and a negative value of E is nonspontaneous.

- The Gibbs free energy is the measure of the spontaneity of a process that occurs at constant temperature and pressure. A positive value of E and a negative value of G indicate a spontaneous reaction. This is formulated as $G^\circ = -nFE^\circ = -RT \ln K$ where n is number of moles of electrons and $F = 96,485 \text{ C/mol}$. This can be reformulated to derive $E = (RT/nF) \ln K$
- When under nonstandard conditions we can examine concentration of cell emf under the Nernst equation where free energy change G is related to standard free energy change G° . $G = G^\circ + RT \ln Q$, where Q is the reaction quotient in the equilibrium constant form where concentration is the reaction mixture at given moment. This can be reformulated as $-nFE = -nFE^\circ + RT \ln Q$ and $E = E^\circ - (RT/nF) \ln Q$. A reaction quotient example from voltaic cell example is $(0.050 \text{ Zn}^{2+}/5.0 \text{ Cu}^{2+})$.
- Voltaic cells can be based solely on emf generated by difference in concentration is a concentration cell. An example of this is the anode half reaction $\text{Ni(s)} \rightarrow \text{Ni}^{2+}(\text{aq}) + 2e^-$ and the cathode half reaction $\text{Ni}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Ni(s)}$ and $E = 0 - (0.592 \text{ V} / 2 n e^-) \log[\text{Ni}^{2+} \text{dilute} / \text{Ni}^{2+} \text{concentrated}]$
- Redox reactions can lead the unfavorable corrosion of metals due to oxidation.

Reading 2 – Materials

- Gibbs free energy can be denoted as $G_r^\circ = \sum G_f^\circ(\text{products}) - \sum G_f^\circ(\text{reactants})$ and for a formation reaction where the formation of the elements is zero from simple elements A and B, $G_r^\circ = G_f^\circ(\text{AB})$
- The value of G_r° in J/ mol Reaction is $G_r^\circ = -zFE$ where z is the charge number of the mobile ionic species, E is the voltage between the electrodes, and F is the Faradays constant.
- Important chemical and electrochemical reactions exist with growing and disappearing phases. This is where an electrode material is reconstituted. Phase diagrams represent changes in identity or number of phases. Two types of these reactions are formation reactions and displacement reactions.
- In a formation reaction such as $\text{A} + \text{B} = \text{AB}$ a new phase AB is formed. For example, electrochemical experiments at 350°C of a reaction of lithium with antimony changed the electrical potential of the positive electrode and E_{cell} .
- In a displacement reaction $\text{A} + \text{BX} = \text{AX} + \text{B}$ the A species displaces the B species in the BX binary phase. A new phase of B is formed, and a driving force is if AX has greater stability/greater negative value G_f° than phase B.
- An insertion reaction or intercalation reactions occurs by inserting a guest species into unoccupied interstitial sites of host materials crystal structure. This does not cause changes in the identity, crystal structure, or phases in the microstructure, but does cause volume change mechanical stress and mechanical energy. Mechanical energy related to insertion and extraction of interstitial species plays role is hysteresis and energy loss observed in battery electrode reactions. This is $x\text{A} + \text{BX} = \text{A}_x\text{BX}$ where an amount x of species A with phase BX produces product A_xBX .

- Important parameters of energy storage systems are energy and power per unit weight, called specific energy and specific power, energy and power per unit volume, called energy density and power density, and cycle life do determine number of recharge cycle before failure, and finally, cost. Characteristics of batteries are often visualized through Ragone plots.
- Another important parameter is operating voltage at discharge, at electrical supply, and recharge. The equilibrium cell voltage is primarily determined by thermodynamics of chemical reaction between components in electrode.
- High voltage energy is more useful as $P=V^2/R$ in applications such as auto manufacturers need to operate systems at over 200V but applications like portable devices and semiconductors need lower voltages.
- Energy contained in system is integral of voltage by the charge capacity do. Charge is measured in C per mol/g/N/m³. State of charge is value of fraction of maximum capacity still available to be supplied.
- Insertion or formation reaction $x\text{A} + \text{R} = \text{A}_x\text{R}$ has maximum theoretical specific energy in J/g as $\text{MTSE} = (xE/W_t)F$ where W_t is sum of weight of reactants, F is faradays constant, and E is volts. MTSE can be express in Wh/kg where $\text{MTSE} = 26805(xE/W_t)$
- Variation of voltage occurs as batteries are charged and discharged. Cell voltage and state of charge under or near equilibrium conditions. Coulometric titration can provide information of this behavior.
- Charge capacity is expected to be maintain over many cycles however initial capacity is reduced during cycling. Coulombic efficiency measures the fraction of prior charge capacity that is available following discharge.
- Self-discharge implies increase of available capacity with time without any discharge. This is a problem with some systems and negligible with others. Self-discharge involves the transport of neutral species or charged species. This transport can occur through adjacent vapor phase, cracks in electrolyte, or dissolved gas in liquid electrolyte. Also, impurities can react to reduce capacity over time.
- Equivalent of cell voltage is $E = -G_r^\circ/zF$, however this is not account for impedance to resist ionic transport, electrode interface, or time dependent diffusion in and out of electrode microstructure.