Chem 116 Lecture 23 notes
12/9/08 (LL)

E^{O}_{Cell}- look at reduction potentials

positive voltage- runs spontaneously in that direction

^{o} –standard for thermodynamics and electrochemistry: 25C=298K, 1.00atm and solution concentrations all 1.0M

Non standard conditions- Temp that is not 25c or 298k, and concentrations that aren't at 1M

If you increase the concentration of the reactants you increase the voltage

<u>Example</u>:

Cu | Cu^{2+} (.001M) || Ag(2.00M) | Ag

Oxidation Reduction

Oxidation Cu ⍰ Cu^{2+} + $2e^{-}$ E^{o} = -3.37V

Reduction 2e (Ag^{+} + 1e- ⍰ Ag) E^{o} = +.779V

Overall Rxn 2Ag(aq) + Cu (s) -⍰ Cu^{2+} (aq) + 2Ag(s) E^{O}_{Cell}= + 4.62V

Voltage Meter Reads: +0.57V

At 25C the equation is:

E_{cell}= E^{O}_{Cell} - (0.0592 / n) (log Q)

n= least common multiple of e-

n= 2, least common multiple of e- when adding the half rxns

Q= [products] / [reactants]

Q= [Cu^{2+}] / [Ag^{2+}]^{2} = (.001) / (2.00)^{2}

Q= .0025

E cell= (.462V) - .0592/2 (log .0025) = .569V (matches the voltage meter)

Electroplating- Can be done by running a cell non-spontaneously

Current- can think of it as the speed of the e- flowing thru wire (moles of e- per second)

Voltage- Difference between half cell rxns

Electrolysis Example

$2H_2O \rightarrow 2H_2 + O_2$

element H - reduced goes from + 1 charge to 0 charge, a total of four H atoms do this, so n=4 electrons are exchanged

element O - oxidized goes from -2 charge to 0 charge, a total of two O atoms do this, so n=4 electrons are exchanged

When you separate the reduction and oxidation half reactions, you would find that you need to add some H^+ during the SOHe balancing. But then when you add up the half-reactions, the H^+ will cancel out. Actually what's happening is that H+ is a catalyst bc it gets used during the oxidation step (where the 4 electrons are produced) and regenerated at the reduction step (where the 4 electrons are used).

E^o_{Cell}= -1.229 V, not spontaneous in the direction that the rxn is written bc # is negative

- Can force rxn to happen by placing a current across

1) Amperes(A) = Coulumbs / Seconds
   Coulumbs= amount of e-
2) 96,500 C= 1 mole e- (conversion factor, also called the Faraday constant)
   Time = 45 min= 2700 sec
   Amt of Coulombs= (.445 C/s) (2700s)= 1201.5C
   Moles e- = (1201.5) (1 mol e- / 96500 C)= .0125 moles e-
   Moles O_2 = (.01245 moles e-) (1 mol O_2 / 4 moles of e-) = .003113 mols O_2
   Mass O_2 = .003113 mol O_2 (32.0g / 1 mol O_2)= .097g = .10g O_2

   In the overall rxn: Oxygen was changing from -2 to 0 oxidation state two atoms of O did this so it takes n= 4e- per 1 mole O_2

Thermodynamics= Brings together equilibrium, kinetics & enthalpy, entropy

When any process occurs: disorder (entropy) in the entire universe is increased. The universe = the system + surroundings. In a given system, the entropy can increase or decrease during a change. Just so long as the universe's entropy increases. The universe's entropy can increase if the surroundings entropy increases more than the system decreases.

Absolute 0= 0K

Temp= Measure of kinetic energy (motion)

Exothermic - system is going from a higher energy state to a lower energy state, and giving off heat when it changes

Endothermic- system is going from a lower energy state to a higher energy state, and taking in heat when it changes

Because q (heat) = enthalpy change when the pressure is constant, when it's an endothermic change (ΔH is positive), the temperature of the system increases (remember $q = m\ C\ \Delta T$). And when it's an exothermic change, the temperature of the system decreases.

The absolute entropy of a system depends on what state (phase) the system is in and its temperature. Also depends on the degrees of freedom. The change in entropy of a system is the difference between the entropy at the end minus the entropy at the beginning. For example, if a solid increases in temperature but stays a solid, the entropy at the beginning is lower and the entropy at the end (higher temperature) is higher. This is because there is more disorder as the particles move around more at higher temperature. So, going from the lower temperature to the higher temperature, the change in entropy in this case is positive.

More degrees of freedom - more entropy

Compare absolute entropies:

a) O_2 (g) vs O_3 (g) O_3 higher entropy bc more degrees of freedom

a) NH_4 Cl (aq) – higher entropy bc (aq) is more disordered than (s)

b) Cl_2 (g) higher entropy bc it is a larger molecule and has more degrees of freedom than F_2 (g). For the others, Br_2 (l) is lower entropy than Cl_2 (g) and F_2 (g) because (l) is lower entropy than (g). And I_2 (s) is the lowest entropy because (s) is lower entropy than (l) or (g).

c) MgO - lower entropy bc the ions are held together more tightly because combination of +2 and -2 charge. Also MgO is smaller, so less space taken up than NaCl, so fewer degrees of freedom in MgO.