



# AP Chemistry Ultimate Review Packet

## Unit 9: Applications of Thermodynamics

In Unit 6 we talked about **enthalpy (H)**. We must also understand another thermodynamic parameter, **entropy (S)**.

- entropy refers to the dispersal of matter and energy
  - matter/energy become more dispersed → entropy increases
    - melting/vaporization/sublimation, heat flow, decomposition
  - matter/energy become less dispersed → entropy decreases
    - freezing/condensation/deposition, synthesis

Enthalpy and entropy combine to describe **Gibbs free energy**

$$\Delta G = \Delta H - T\Delta S$$

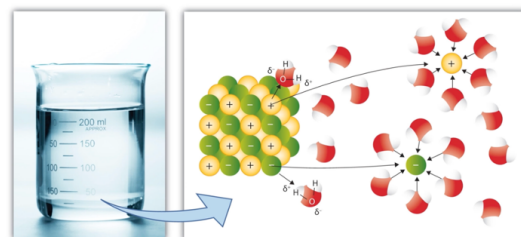
- This parameter determines the *spontaneity* of a process
  - $\Delta G < 0$ : spontaneous
  - $\Delta G > 0$ : nonspontaneous
  - $\Delta G = 0$ : at equilibrium
- A spontaneous process happens on its own without energy input
  - Gas particles spread out to fill their container to increase entropy (dispersal of matter).
  - Heat flows from hot to cold to increase entropy (dispersal of energy)

We can identify how changes in enthalpy/entropy correlate with spontaneity:

- $\Delta H = \text{negative}$  and  $\Delta S = \text{positive}$  → always spontaneous
- $\Delta H = \text{positive}$  and  $\Delta S = \text{negative}$  → always nonspontaneous
- $\Delta H = \text{negative}$  and  $\Delta S = \text{negative}$  → spontaneous at low T
- $\Delta H = \text{positive}$  and  $\Delta S = \text{positive}$  → spontaneous at high T

Spontaneous dissolution of ionic solids is largely due to entropic favorability

- dispersal of ions in solution is entropically favorable
- if the lattice energy is greater than the hydration energy then dissolution of the ionic solid is enthalpically unfavorable (endothermic)
- this can be offset by the entropic favorability to make dissolution spontaneous



Sometimes multiple pathways are possible for a given system:

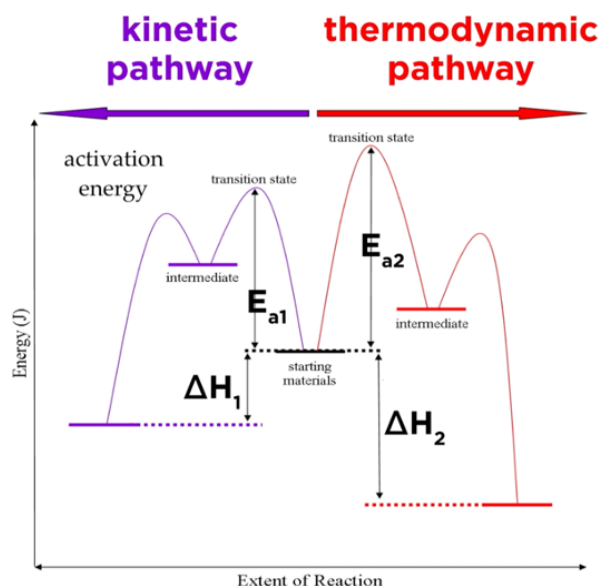
- *thermodynamic control* involves the pathway yielding lowest-energy product
- *kinetic control* involves the pathway with the lowest activation energy

We can relate free energy and equilibria with the following equation:

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

$K > 1$  corresponds with a negative  $\Delta G$  (spontaneous, products favored)

$K < 1$  corresponds with a positive  $\Delta G$  (nonspontaneous, reactants favored)



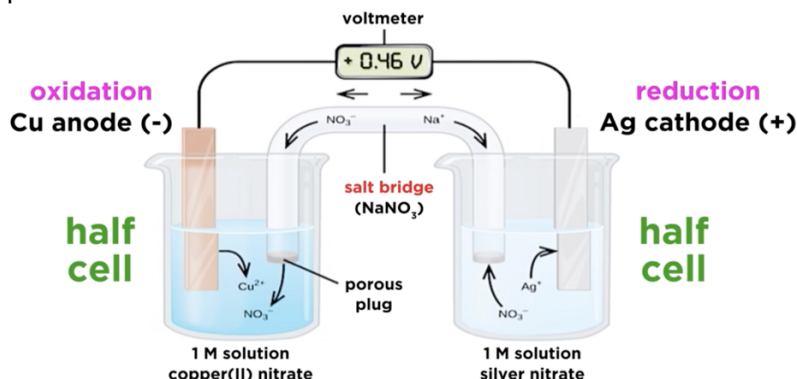


# AP Chemistry Ultimate Review Packet

## Unit 9: Applications of Thermodynamics

### Electrochemistry

Electrochemical cells couple redox reactions with an electric current



A **galvanic cell** uses a spontaneous redox reaction to generate an electric current

- oxidation and reduction half-reactions are split up into separate half cells
- half cells are connected by a wire and salt bridge, each half cell has a metal electrode
- at the **anode** oxidation takes place (neutral metal atoms become ions)
  - these ions leave the electrode and join solution
- at the **cathode** reduction takes place (metal ions become neutral atoms)
  - these atoms leave solution and deposit onto the electrode
- ions from the salt bridge enter/exit half cells to balance charge
- electrons travel from the anode to the cathode through the wire
- the spontaneous flow of these electrons is what generates the current
- each cell has a **cell potential**: energy available per unit charge in volts ( $V = J/C$ )

**Standard reduction potentials** have been tabulated for every potential half cell

- If we want to calculate the cell potential for any hypothetical galvanic cell with two particular substances we consult these tabulated reduction potentials

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

- We plug in the reduction potentials straight from the table without manipulating them whatsoever for sign or stoichiometry. The value that is more positive (further right on number line) is the cathode.

An **electrolytic cell** uses an electric current to drive a nonspontaneous redox reaction

- electrolysis of water to form hydrogen and oxygen gas is an example
- electric car batteries are electrolytic cells
  - these charge up when plugged into a source of electricity and then later power the car

Cell potential correlates with Gibbs free energy according to the following equation:

$$\Delta G^\circ = -nFE^\circ$$

$n$  = moles of electrons transferred

$F$  = Faraday's constant (96,485 C/mol)

- positive cell potential = negative  $\Delta G$  = spontaneous reaction
- negative cell potential = positive  $\Delta G$  = nonspontaneous reaction

We can calculate cell potentials in nonstandard conditions using the **Nernst equation**

$$E_{\text{cell}} = E^\circ - \frac{RT}{nF} \ln Q$$

- $E_{\text{cell}}$  is nonstandard conditions vs.  $E^\circ$  which refers to standard conditions
- $Q$  is the reaction quotient,  $n$  is moles  $e^-$ ,  $F$  is Faraday's constant
- $R$  is the gas constant in J/mol K