Enthalpy of solution

* Dissolution of ionic solids:
  + Enthalpy of solution depends on
    - Energies holding solute ions in the crystal lattice
    - Attractive forces holding solvent molecules together
    - Interactions between solute ions and solvent molecules
    - ∆Hsol = ∆Hionic bonds + (∆Hdipole-dipole + ∆Hion-dipole)
    - ∆Hsol = ∆Hionic bonds + ∆Hhydration

Lattice energy (U)

* Energy released when 1 mol of an ionic compound forms from its free ions in the gas phase (A+(g) + B-(g) 🡪 AB(s))
  + Where Q1 and Q­­2are the charges and d is the distance between nuclei and k is a proportionality constant and depends on lattice structure

Enthalpy of ion formation

* Lattice energy (U): energy released when a crystal lattice is formed
* ∆Hionic bonds: energy required to remove ions from a crystal lattice
  + ∆Hionic bonds = -U, ∆Hsol = ∆Hionic bonds + ∆Hhydration
  + Therefore, ∆Hsol = ∆Hhydration - U

Osmosis

* Flow of fluid through a semipermeable membrane to balance the concentration of solutes in solutions on the two sides of the membrane
* Osmotic pressure (∏ = iMRT): pressure applied across a membrane to stop the flow of solvent through membrane where i is the van’t hoff factor (number of ions that it disassociates into)
  + P = (n/v)RT or P=MRT where M is the molarity of solution
  + ∆∏ is the difference in osmotic pressure (how much water diffuses to one side)
* Reverse Osmosis
  + Process in which solvent is forced through a semipermeable membrane, leaving a more concentrated solution behind (used in desalination and water purification)

Colligative Properties & van’t Hoff factor

* Colligative properties: characteristics of solutions that depend upon the concentration and NOT the identity of the particles dissolved in the solvent
* Solutions of electrolytes: need to correct for # of particles formed when ionic substances dissolves
* Van’t Hoff factor (i): number of ions in a formula unit (NaCl, i=2)

Vapor pressure of solutions

* Vapor pressure: pressure exerted by a gas in equilibrium with liquid
  + Rate of evaporation = rate of condensation
* Normal boiling point: boiling point at standard pressure (1atm)
* Factors impacting vapor pressure
  + Temperature/surface area/intermolecular forces
    - Stronger forces = higher kinetic energy needed to enter gas phase
  + Presence of nonvolatile solute
    - Affects rate of evaporation, decreases vapor pressure of solution compared to pure solvent

Clausius-Clapeyron equation: relates vapor pressure of a substance at different temperatures to its heat of vaporization

* + R will usually be 8.314 J/(mol\*K) and ∆Hvap will come out in J/mol
  + Natural log of vapor pressure is inversely proportional to temperature
* Practice
  + Camping fuel: portable lanterns and stoves used for camping and backpacking often use a mixture of C5 and C6 hydrocarbons known as “white gas.” The figure below shows the carbon-skeleton structure of pentane, c5h12, along with its normal boiling point and heat of vaporization. Determine the vapor pressure of pentane on a morning when the temperature is 5˚C. Pentane: boiling point is 36˚C and ∆Hvap is 27.6kj/mol
    - =.3atm (have to change kj/mol ∆H to j/mol)

Solutions of volatile components

* Raoult’s law: total vapor pressure of an ideal solution depends on how much the partial pressure of each volatile components contributes to total vapor pressure of solution
  + Ptotal = X1P1o + X2P2o + X3P3o + X4P4o + …
  + Example for a mixture of water and ethanol (Ptotal=PH2O+PEthanol)
  + A solution contains 100.0 g of water (MW = 18.0 g/mol) and 25.00 g of ethanol (MW = 44.0 g/mol). What are the mole fractions of water and ethanol, and the vapor pressure of the solution at 25°C? (Pwater = 23.8 torr; Pethanol = 58.7 torr)
    - Convert mass of water and ethanol to moles (5.556mol of water and .5682 moles of ethanol)
    - Moles by sum of moles (.907 water and .093 ethanol)
    - Get the mol ratio by dividing mol of (water/ethanol) by total mols
    - Multiply by their individual vapor pressure
    - Add together

Fractional distillation: distilling a liquid that has a higher vapor pressure (lower boiling point) by heating the mixture by an ever-lower temperature to get a purer solution

* The graph is read from right to left

Solvent: the substance that has more moles

Colligative properties

* Set of properties of a solution relative to the pure
* Due to solute-solvent interactions
* Depends on concentration of solute particles, not the identity of particles
* Include: lowering of vapor pressure, boiling point elevation, freezing point depression, osmosis and osmotic pressure

Real vs ideal solutions

* Deviations from raoult’s law:
  + Due to differences in solute-solvent and solvent-solvent interactions
    - Ideal solutions have no preferences for interactions, adhesive forces = cohesive forces
    - Ideally the vapor pressures increase linearly, real solutions deviate further from the ideal the further it gets from either endpoint
      * If two particles have a stronger interactive force with each other than either would have with themselves, then the vapor pressure would be lower than expected
      * If two particles have a weaker interactive force with each other than either would have with themselves, then the vapor pressure would be higher than expected

Solute concentration: molality (m)

* Changes in boiling point/freezing point of solutions depend on molality
  + Preferred for properties involving temp change b/c it’s independent of temp

Colligative properties

* Boiling point elevation (∆Tb):
  + Where Kb = boiling point elevation constant of the solvent, m = molality
* Freezing point depression (∆Tf):
  + Where Kf = freezing point depression constant, m = molality
* Kf or Kb is usually in ˚C/m

Henry’s law

* Cgas = kH \* Pgas
* Where C is the maximum concentration of gas in a particular solvent (M), k is henry’s law constant for the gas (mol/(L\*atm)), and P is the partial pressure of the gas in the solvent (atm)
* Pressure and temperature are inversely proportional so the solubility of a gas in a liquid decrease as temperature increases
* 1.3E-3 is the k constant

Thermodynamics

* System: the part of the universe that is the focus of a thermodynamic study (isolated, open, closed)
* Surroundings: everything that is not the system
* Universe = system + surroundings
* Spontaneous process: a process that, once started, occurs without outside intervention
* Nonspontaneous process: a process that only occurs as long as energy is continually added to the system
* Entropy (S)
  + A measure of how dispersed the energy in a system is at a specific temperature

Spontaneity and enthalpy (∆H)

* Endothermic reactions can also be spontaneous

Laws of thermodynamics

* Law of conservation of energy: energy cannot be created or destroyed
  + But it can be converted from one form to another
  + ∆E=q+w change in energy equals heat/thermal energy + work
* Second law of thermodynamics: entropy in the universe increases in any spontaneous process ∆Suni = ∆Ssys + ∆Ssurr > 0
  + Nonspontaneous reactions can be made spontaneous by making the system have a really high ∆S, and viceversa
* Third law of thermodynamics: the entropy of a perfect crystal is zero at absolute zero
  + Provides a point of reference or baseline for entropy
* Zeroth law of thermodynamics: (= is thermal equilibrium) if A=B and B=C, then A=C

Boltzmann Equation: S = kB In(W)

* S= entropy kB = boltzmann constant (1.38e-23) W=# of microstates

Standard molar entropy

* The absolute entropy of 1 mol of a substance in its standard state at 298.15K and 1 bar
* Calculated from measurements of molar heat capacities as a function of temperature

Entropy

* There is a jump when phase changing from solid to liquid and liquid to gas
  + The jump is greater from liquid to gas
* Factors that increase entropy
  + Increasing temperature (more kinetic energy, more dispersion)
  + Increasing volume (think about gasses)
  + Increasing number of independent particles (greater distribution of energy across particles)
  + Complexity of molecular structure (greater molecular weight = more energy in bonds)
    - This allows for more internal motion (more vibrational motion)

Types of molecular motion

* Translational: movement through space
* Rotational: spinning motion around an axis perpendicular to the bond
* Vibrational: movement of atoms toward/away from each other

Thermodynamic entropy

* ∆S Suni = ∆Ssys + ∆Ssurr
  + When using the isothermic equation, remember qsystem = -qsurroundings
  + Make sure you have a balanced equation
* For an isothermal process
  + qrev = reversible flow of heat caused by difference in temperature between system and surroundings
* reversible process
  + a process that can run in the reverse direction in a way that the system can be restored to its original state, no net energy has flowed either to the system or to its surroundings (like phase changes)

Gibbs free energy (G)

* maximum energy released by a process occurring at a constant temperature and pressure that is available to do useful work
  + Usually ∆G is kJ (kJ/mol)
* ∆G = ∆H – T∆S

|  |  |  |  |
| --- | --- | --- | --- |
| ∆H | ∆S | ∆G | Spontaneity |
| - | + | Always < 0 | Always spontaneous |
| - | - | < 0 at lower temp | Spontaneous at lower temp |
| + | + | < 0 at higher temp | Spontaneous at higher temp |
| + | - | Always > 0 | Never spontaneous |

* + Easier to just remember that ∆G < 0 is spontaneous and figure out if ∆S is positive or negative
  + If ∆G = 0 then the system is at equilibrium
* To find the point where a reaction

Metabolism

* In living systems
  + Breaking down food and generating heat is spontaneous
    - ∆G < 0 (catabolic)
  + Building muscles is not spontaneous
    - ∆G > 0 (anabolic)
  + Living systems couple catabolic reactions to anabolic reactions (usually ATP)
    - The net result has to be spontaneous