

## Thermodynamics 2: Spontaneity, Entropy, and Free Energy.

### Spontaneity:

- A process that occurs in a system that is left to itself; no action from outside the system is necessary.
- If a process is thermodynamically favored, the reverse process is not (and vice versa).
- Note: spontaneity does not predict how fast a reaction occurs. Some processes that are thermodynamically favored will not occur because of kinetic constraints such as high activation energy.
- Exothermic reactions tend to be more spontaneous than endothermic ( $\Delta H < 0$ ) **BUT**
- Spontaneity can only be ascertained by considering both the enthalpy change **AND** whether the system becomes more disordered (entropy change).

### Entropy (S):

- The thermodynamic property that relates to the disorder of the system.
- The greater the degree of disorder, the greater the entropy ie: entropy increases when matter is dispersed.
- A state function.

Entropy generally increases for the following processes:

- Solids  $\rightarrow$  liquids
- Solids or liquids  $\rightarrow$  gases
- Solids or liquids dissolve to form a non-electrolyte solution.
- The number of molecules of gases increases.
- The volume of a gas increases at constant temperature.
- A substance is heated.
- The more atoms in a molecule, the greater the entropy of a substance.

**Second Law of Thermodynamics:** In any spontaneous process, there is an increase in the entropy of the universe.

**Third Law of Thermodynamics:** The entropy of a pure, perfect crystal at 0K can be taken to be zero.

### Standard molar entropies ( $S^\circ$ ):

- The entropy of 1 mole of a substance in its standard state.
- $\Delta S^\circ = \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants})$

**Chemical or physical processes are driven by a decrease in enthalpy or an increase in entropy or both (EU 5.E)**

### Gibbs Free Energy (G):

- $\Delta G = \Delta H - T\Delta S$
- Can be used to predict whether a process is thermodynamically favored.
- $\Delta G < 0$  (negative) the products are favored at equilibrium and the forward reaction is thermodynamically favored ( $K > 1$ ). This is exergonic.
- $\Delta G > 0$  (positive) the reactants are favored at equilibrium and the reverse process is thermodynamically favored ( $K < 1$ ). This is endergonic.
- $\Delta G = 0$  the process is at equilibrium.

### Standard Free Energy Change ( $\Delta G^\circ$ ):

- The free energy change that occurs for a reaction when the reactants and products are in their standard states (as pure substances, as solutions of 1 molar concentration, or as gases at a pressure of 1 bar or 1 atm)..
- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

### Standard Free Energy of Formation ( $\Delta G_f^\circ$ ):

- The free energy change that occurs in the formation of one mole of a substance in its standard state from the reference forms of its elements in their standard states.
- $\Delta G^\circ = \sum G_f^\circ(\text{products}) - \sum G_f^\circ(\text{reactants})$

### Free Energy and Equilibrium:

- At equilibrium,  $\Delta G = 0$  and  $\Delta H = T\Delta S$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

- Remember,  $\Delta G^\circ$  is for a particular temperature where all the reactants and products are in their standard states.
- This can be used to calculate  $\Delta G$  at other temperatures.

$$\Delta G^\circ = -RT \ln K_{eq}$$

- Can be used to calculate the equilibrium constant at that temperature, and therefore equilibrium concentrations or partial pressures.
- **R** is usually expressed as **8.3145 J mol<sup>-1</sup>K<sup>-1</sup>**.
- **T** is in Kelvins
- **ln** is the natural log
- **K<sub>eq</sub>** has to be unitless
- For the equilibrium expression, **K<sub>eq</sub>**, the quantities are expressed as activities, rather than molarities or partial pressures (since units cannot be used).
  - i) A pure solid or liquid has an activity of 1
  - ii) The activity for a gas is the partial pressure with no units.
  - iii) The activity for a solution is the molarity without the units.
- When  $\Delta G^\circ$  is large and negative, the equilibrium lies far to the right and the reaction goes essentially to completion.
- When  $\Delta G^\circ$  is large and positive, the equilibrium lies far to the left and no reaction occurs.
- When  $\Delta G^\circ$  is closer to zero, equilibrium calculations must be done in order to ascertain completeness of the reaction.

### Coupled Reactions and driving reactions that are not thermodynamically favored.

- Two or more simpler reactions can be combined/ coupled to produce a reaction that is thermodynamically favored (the overall reaction has a negative  $\Delta G^\circ$ ).  
Example: A cell can use energy to create order (not thermodynamically favored) via coupling with thermodynamically favored reactions such as the conversion of ATP to ADP in biological systems.
- External sources of energy may be used to drive change when the Gibb's free energy is positive.  
Example: Electricity may be used such as in recharging a battery or electrolysis.  
Example: Light may be used as energy such as in the photoionization of an atom or such as in the conversion of carbon dioxide to glucose through photosynthesis.