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# Thermodynamics

## Review Notes

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### Introduction

- Thermodynamics describes whether a reaction will occur and how easily it will do so.
  - About energy exchanges
  - Kinetics describes speed of a reaction. Not Thermodynamics.
- Terminology
  - System: the particular part of the universe being studied
    - Isolated: cannot exchange energy or matter
    - Closed: can exchange energy but not matter
    - Open: can exchange energy and matter
  - Processes by which properties of a system change:
    - Isothermal: temperature is constant
    - Adiabatic: when no heat exchange occurs
    - Isobaric: when pressure is constant
- There are different forms of energy:
  - Heat:
  - Enthalpy:  $\Delta H$  is a measure of the heat absorbed by a system under constant pressure.
  - Entropy:  $\Delta S$  is a measure of a system's capacity for storing energy at a particular temperature
- Gibb's Free Energy
  - $\Delta G$  is a total combination of the different forms of energy so that comparisons and calculations can be made.
    - If  $\Delta G < 0$ , then a reaction will occur spontaneously.

- **3 Laws of Thermodynamics**

- **1<sup>st</sup> law:** Energy can neither be created nor destroyed; only converted into different forms.
- **2<sup>nd</sup> law:** All processes spontaneously proceed toward a state of greater entropy.
- **3<sup>rd</sup> law:** As a system approaches absolute zero, all processes cease and the entropy of the system approaches a minimum value.

- **Phase Diagrams**

- Three phases: solid, liquid, gas
- Standard phase diagrams usually have Pressure as Y-axis and Temperature as X-axis
  - **Triple point** – the specific temperature / pressure combination at which a gas, liquid, and solid can coexist in equilibrium
  - **Critical point** – point at which no increase in pressure will convert a gas into a liquid.

## Heat and Enthalpy

- Heat
  - just a form of energy...it is measured through the temperature of an object
  - transfer occurs spontaneously from warmer → cooler objects (3rd Law of Thermodynamics)
  - measured in Joules or calories (1 cal = 4.184 K)
- Calorimetry:
  - Heat absorbed or released is given by:
$$q = Mc\Delta T$$
    - c is the specific heat, which measures how much heat a mass of object can absorb for a specific temperature change
  - 2 Types
    - Constant volume - bomb calorimeter used to measure the heat released during the reaction (the heat of reaction)
    - Constant pressure
- Enthalpy
  - $\Delta H$  is a measure of the heat absorbed by a system under constant pressure.
$$\Delta H_{rxn} = H_{products} - H_{reactants}$$
  - Implies a few things:
    - Individual molecules have their enthalpy values
    - If products have less energy, then  $\Delta H_{rxn} < 0$ .
      - $\Delta H_{rxn} < 0$ , exothermic
        - reaction doesn't need additional heat energy
      - $\Delta H_{rxn} > 0$ , endothermic
        - reaction needs heat input
  - Standard Heat of Formation -  $\Delta H^{\circ}_f$ 
    - Enthalpy change that would occur if molecule were created from its elemental components. (at standard state ... 25°C)
  - Standard Heat of Reaction -  $\Delta H^{\circ}_{rxn}$ 
    - Enthalpy change that occurs during a reaction. (at standard state ... 25°C)
    - aka: Heat of Vaporization, Heat of Condensation, Heat of Combustion

- Hess' Law

- Enthalpies of reactions are additive.



- Bond Dissociation Energy – energies associated with breaking and forming bonds

- Specifically: the positive value associated with the energy absorbed when bonds are broken



- Bond energies can be used to estimate enthalpies of reactions. Simply calculate the energy in all the bonds of the products and subtract all the energies in the bonds of the reactants. The difference is how much heat energy the reaction lost or absorbed during the reaction.

## Entropy

- Typically defined as “randomness” of a system
  - More appropriately, it’s a measure of the energy capacity of a system at a certain temp.  
→ units: (kJ / mol) / Kelvin
  - $\Delta S \rightarrow \text{gas} > \text{liquid} > \text{solid}$  - because of more freedom of movement of molecules.  
Therefore, can store more kinetic energy
- Two ways entropy changes:
  - Phase changes: molecules with greater freedom of movement can store more kinetic energy...therefore, have higher entropy.
  - Change in # of molecules: more molecules = more individual sources of kinetic energy storage ... sum of more molecules is greater than sum of fewer molecules.
- Entropy is a state function:  $\Delta S^{\circ}_{\text{rxn}} = (\sum S^{\circ}_{\text{products}}) - (\sum S^{\circ}_{\text{reactants}})$
- 2<sup>nd</sup> law: All processes spontaneously proceed toward a state of greater entropy.
  - a system reaches maximum entropy at equilibrium

## Gibb's Free Energy

- entropy and enthalpy are different forms of energy → Gibb's Free Energy formula combines them
$$\Delta G = \Delta H - T\Delta S$$
- used to determine spontaneity (not kinetics.....i.e speed of reaction. That depends on activation energy, not  $\Delta G$ .)
  - $\Delta G > 0$ , not spontaneous
  - $\Delta G < 0$ , spontaneous
  - $\Delta G = 0$ , at equilibrium
- $\Delta G^\circ = \text{Standard Free Energy}$  →  $\Delta G$  at 25°C and 1 atm
- $\Delta G_f = \text{Standard Free Energy of Formation}$  → free energy change when 1 mol of a molecule is created from elements in their standard states under standard conditions
  - $\Delta G_f$  of an element = 0
- Free Energy is a state function:  $\Delta G^\circ_{rxn} = (\Sigma G^\circ_{products}) - (\Sigma G^\circ_{reactants})$ 
  - \* note the similarity of this equation to Hess' Law. Almost any state function could be substituted for  $\Delta G$  here.

### Free energy and Equilibrium

- $\Delta G^\circ_{rxn} = -RT \ln Q$ . When  $Q = K_{eq}$ ,  $\Delta G^\circ_{rxn} = 0$  and the reaction is at equilibrium.