AP Chemistry Unit 5 - Thermodynamics

**Thermochemistry** - the study of heat (=energy) in chemistry

**Thermodynamics** - the study of heat (energy) as it changes

**Kinetic Energy** - energy of motion
- \( E_k = \frac{1}{2} mv^2 \)
  - \( E \) = Energy in Joules (J)
  - \( m \) = mass (kg)
  - \( v \) = velocity (m/s)

**Universe = system + surroundings**
- system – confined to only what is being studied
- surroundings – everything else

**Internal Energy**
- includes all of the potential and kinetic energy of all the parts of the system
- \( \Delta E = E_f - E_i \) (change in internal energy)
- \(+\Delta E\) = the system has gained energy (surroundings lose)
- \(-\Delta E\) = the system has lost energy (surroundings gain)
- \( \Delta E = q + w \)
  - \( q \) = heat (J)
  - \( w \) = work (J)

- \(+q\) = heat added to system
- \(-q\) = heat lost by system
- \(+w\) = work done on system by surroundings
- \(-w\) = work done by system on surroundings

**Endothermic** (heat in) – system gains energy, \(+\Delta E\)
- surroundings lose energy so container often feels cold

**Exothermic** (heat out) – system loses energy, \(-\Delta E\)
- surroundings gain energy so container will feel warm

**State function**
- a property of a system that is determined only by its present state
- does not depend on the pathway it took to reach that state
- Common state functions:
  - pressure, temperature, volume, internal energy, entropy
Enthalpy (H)

- heat flow
- \( \Delta H = \Delta E + P \Delta V \) (at constant pressure)
  - \( H = \) enthalpy (J)
  - \( E = \) internal energy (J)
  - \( PV = \) work done by changing pressure, volume (J)
- \( +\Delta H = \) system has gained heat
- \( -\Delta H = \) system has lost heat

**Determine the sign of \( \Delta H \)**

- ice cube melting
  - \( +\Delta H \) (water gains energy to change from solid to liquid)
- 1 g of butane (C\(_4\)H\(_{10}\)) undergoes complete combustion
  - \( \Delta H \) (heat is released)
- What if the system is contained so no heat can be released? Will a piston rise or fall?
  - 2 C\(_4\)H\(_{10}\) + 13 O\(_2\) \( \rightarrow \) 8 CO\(_2\) + 10 H\(_2\)O
    - volume of products > volume of reactants
    - piston will rise to maintain a constant pressure

Enthalpy of Reactions

\( \Delta H = \Delta H_{\text{products}} - \Delta H_{\text{reactants}} \)

- enthalpy is an extensive property (depends on amount)
- enthalpy change for a reverse reaction will be the same in magnitude, opposite in sign
- enthalpy change depends on state of reactants and products

*How much heat is released when 4.5 g of methane gas is burned in a constant pressure system? \( (\Delta H_{\text{rxn}} = -890 \text{ kJ}) \) (-250 kJ)*

Calorimetry

- measurement of heat flow
- heat capacity - the amount of heat required to raise the temperature of an object by 1K
- molar heat capacity - the amount of heat required to raise 1 mole of a substance by 1K
- specific heat - the amount of heat required to raise 1 g of a substance by 1 K

\[ s = \frac{q}{m\Delta T} \]

- \( s = \) specific heat (J/gK)
- \( q = \) amount of heat exchange (J)
- \( m = \) mass (g)
- \( \Delta T = \) temperature change (K)
Constant Pressure Calorimetry

How much heat is needed to warm 250 g of water from 22 °C to 98°C? The specific heat of water is 4.18 J/g K. (7.9 x 10^4 J)

What is the molar heat capacity of water? (C = 75.2 J/mol K)

A student mixes 50 mL of 1.0 M HCl and 50 mL of 1.0 M NaOH in a calorimeter and notices that the temperature rises from 21.0 °C to 27.5 °C. Calculate the enthalpy change if the total volume is 100 mL, the density is 1.0 g/mL, and the specific heat is 4.18 J/gK. (-2.7 kJ)

Hess's Law

- if a reaction is carried out in a series of steps, the ΔH for the overall reaction will equal the sum of the enthalpy changes for the individual steps.

Calculate ΔH for

- 2 C (s) + H₂ (g) → C₂H₂ (g)

- Given
  - C₂H₂ (g) + 5/2 O₂ (g) + 2 CO₂ (g) + H₂O (l) ΔH = -1299.6 kJ
  - C (s) + O₂ (g) → CO₂ (g) ΔH = -393.5 kJ
  - H₂ (g) + 1/2 O₂ (g) → H₂O (l) ΔH = -285.8 kJ

(ΔH_rxn = 226.8 kJ)

Enthalpy of Formation ΔH_f

- the amount of energy needed to form a 1 mole of a compound from its elements at standard conditions
  - Note: Standard conditions here are 1 atm at 298 K
    - (vs. 1 atm, 0°C for molar volume of a gas)
What is the $\Delta H_f$ for argon?

- 0! There is no formation of a compound.

Which reactions are formations?

- $2 \text{Na (s)} + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{Na}_2\text{O (s)}$
  - yes
- $2 \text{K (l)} + \text{Cl}_2 (g) \rightarrow 2 \text{KCl (s)}$
  - no, K would be a solid under standard conditions
  - two moles of product are formed
  - K (s) + $\frac{1}{2}$ Cl$_2$ (g) $\rightarrow$ KCl (s)
- C$_6$H$_{12}$O$_6$ (s) $\rightarrow$ 6 C (diamond) + 6 H$_2$ (g) + 3 O$_2$ (g)
  - No, decomposition
  - 6 C (graphite) + 6 H$_2$ (g) + 3 O$_2$ (g) $\rightarrow$ C$_6$H$_{12}$O$_6$ (s)

- $\Delta H_{\text{rxn}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$

Calculate the enthalpy of reaction for the combustion of 1 mole of methanol (CH$_3$OH, -1367 kJ)

Strength of Covalent Bonds

- Bond enthalpy $- \Delta H$ for the breaking of a bond in one mole of a gaseous substance
  - Always positive
  - As $\Delta H$ increases, bond strength increases
  - Generally, as the number of bonds between two atoms increases, strength increases and the bond length decreases

$\Delta H_{\text{rxn}} = \sum (-\Delta H_{\text{bonds broken}}) - \sum (-\Delta H_{\text{bonds formed}})$

Estimate the enthalpy of reaction for the combustion of ethane (C$_2$H$_6$) gas. ($\Delta H_{\text{rxn}} = -1416$ kJ)

<table>
<thead>
<tr>
<th>TABLE 8.4 Average Bond Enthalpies (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Single Bonds</strong></td>
</tr>
<tr>
<td>C—H 413</td>
</tr>
<tr>
<td>C—C 348</td>
</tr>
<tr>
<td>C—N 293</td>
</tr>
<tr>
<td>C—O 378</td>
</tr>
<tr>
<td>C—F 485</td>
</tr>
<tr>
<td>C—Cl 328</td>
</tr>
<tr>
<td>C—Br 276</td>
</tr>
<tr>
<td>C—I 240</td>
</tr>
<tr>
<td>C—S 239</td>
</tr>
<tr>
<td>Si—H 323</td>
</tr>
<tr>
<td>Si—Si 226</td>
</tr>
<tr>
<td>Si—C 361</td>
</tr>
<tr>
<td>Si—O 464</td>
</tr>
</tbody>
</table>

| **Multiple Bonds**                        |
| C=C 614                                   |
| C==C 839                                  |
| C==N 615                                  |
| C==O 799                                  |
| N==N 418                                  |
| N==N 941                                  |
| N==O 607                                  |
| S==O 523                                  |
| S==S 418                                  |


First Law of Thermodynamics
- Energy cannot be created or destroyed.

Spontaneous process
- One that proceeds on its own without outside assistance
- The reverse reaction will be non-spontaneous

Predict which are spontaneous...
- When a piece of metal at 150 °C is added to water at 40°C, the water gets hotter.
  - Spontaneous
- Water at room temperature decomposes into H₂ and O₂ gas.
  - Not spontaneous; reverse is spontaneous once ignited by a spark or flame
- Benzene (C₆H₆) vapor at 1 atm condenses to become a liquid at the normal boiling point.
  - Process is at equilibrium – neither forward or reverse reaction is spontaneous

Entropy
- S (J/K) – the extent of randomness in a system

Mercury is a silvery liquid at room temperature. The normal freezing point is -38.9 °C, and its ΔH_fus is 2.29 kJ/mol. What is the entropy change when 50.0 g of liquid mercury freezes at the normal freezing point? (-2.44 J/K (negative entropies tend to be non-spontaneous)

Second Law of Thermodynamics
- Any irreversible process results in an overall increase in entropy, whereas a reversible process results in no change in entropy.
  - i.e. The entropy of the universe is always increasing
- Entropy increases for...
  - Gases formed from liquids or solids
  - Liquids or solutions formed from solids
  - Reactions where there are more product gas molecules than reactant molecules

Is ΔS + or -?
- H₂O (l) → H₂O (g)
  - positive
- Ag⁺ (aq) + Cl⁻ (aq) → AgCl (s)
  - negative
- 4 Fe (s) + 3 O₂ (g) → 2 Fe₂O₃ (s)
  - negative
- N₂ (g) + O₂ (g) → 2 NO (g)
  - Need more information
Third Law of Thermodynamics
- The entropy of a pure crystalline solid at 0K is 0.

Entropy Changes in Reactions
- $\Delta S^0 = \Sigma S^0_{\text{products}} - \Sigma S^0_{\text{reactants}}$

*Using Appendix C, calculate the change in entropy for the formation of ammonia gas from hydrogen and nitrogen gas. (-198.3 J/K)*

Gibbs Free Energy
- Determines the spontaneity of a reaction
- Exothermic reactions and those that increase in entropy tend to be spontaneous, but they could be competing factors (endothermic, increase in entropy)
- $\Delta G = \Delta H - T\Delta S$
  - $\Delta G < 0$, reaction is spontaneous
  - $\Delta G > 0$, reaction is not spontaneous (reverse rxn will occur)
  - $\Delta G = 0$, reaction is at equilibrium (btw. reactants & products)

Effect of Temperature on Spontaneity of Reactions

<table>
<thead>
<tr>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>$-T\Delta S$</th>
<th>$\Delta G$ = $\Delta H$ - $T\Delta S$</th>
<th>Reaction Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>+</td>
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<td>Spontaneous at all temperatures</td>
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<tr>
<td>+</td>
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<td>+</td>
<td>+</td>
<td>Non-spontaneous at all temperatures</td>
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<td>-</td>
<td>-</td>
<td>+</td>
<td>+ or -</td>
<td>Spontaneous only at low T</td>
</tr>
<tr>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+ or -</td>
<td>Spontaneous only at high T</td>
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</tbody>
</table>

*Using Appendix C, determine whether or not the reaction of forming ammonia gas from nitrogen and hydrogen gas is spontaneous at 25°C and at 500°C. (-33.3 kJ, 61 kJ)*