Chap.9 Balances on Reactive Processes

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강의록

Introduction

- Heat
  - Sensible Heat $\Delta H = \int C_p dT$
  - Latent Heat : vaporization, sublimation, melting
  - Heat of Reaction
- Heat emitted or absorbed during reaction.
  – Affects economics of the processes
- Topics : Heat of reaction and energy balances of processes

9.1 Heat of Reaction

- Heat of Reaction (Enthalpy of Reaction)

$$\Delta \hat{H}_r(T, P) = H_{\text{products}} - H_{\text{reactants}}$$

  - Reactants : stoichiometric quantities
  - Complete Reaction
  - Reactants are fed at T,P
  - Products are emerging at T,P

Ex) $CaC_2(s) + 2\ H_2O(l) \rightarrow Ca(OH)_2\ (s) + C_2H_2\ (g)$

$$\Delta \hat{H}_r(25^o C, 1\ atm) = -125.4 kJ/mol$$

Heat of Reaction : Per mole of what ?

- Example

  2A + B → 3C

$$\Delta \hat{H}_r = \frac{-50kJ}{2 \text{ mol A reacted}} = \frac{-50kJ}{1 \text{ mol B reacted}} = \frac{-50kJ}{3 \text{ mol C produced}}$$

$$\Delta H = \frac{\Delta \hat{H}_r}{\nu_A} n_A$$

Properties of Heat of Reaction

- "Standard" heat of reaction : at reference T and P (25 ^oC, 1 atm)
- Exothermic (발열반응) : $\Delta\hat{H}_r < 0$

  Endothermic (흡열반응) : $\Delta\hat{H}_r > 0$
- Value depends on stoichiometric eqn.
- Value depends on the state (gas, liquid, solid)

Internal Energy of Raction`

- If a reaction takes place at const. V
  - U = H – PV, assuming ideal gases,

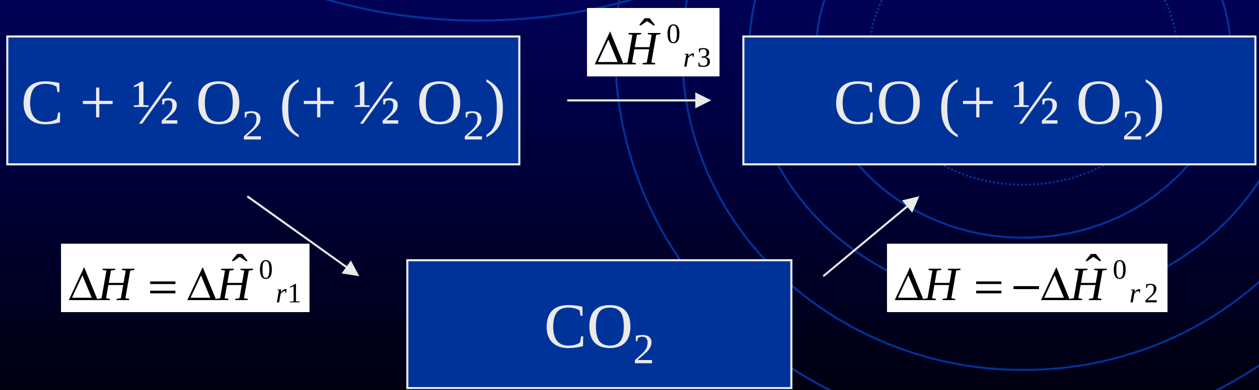
$$\Delta\hat{U}_r = \Delta\hat{H}_r - RT\left(\sum_{\substack{\text{gaseous}\\\text{products}}} \nu_i - \sum_{\substack{\text{gaseous}\\\text{reactants}}} \nu_i \right)$$

9.2 Measurement and Calculation of Heats of Reaction : Hess's Law

- Measurements of heats of reaction : Calorimeter
  - Temperature rise or fall of the fluid can be measured and heat of reactions are determined.

Difficulties for measuring heat of reaction

- Some reactions cannot be accomplished.
- Ex) 2C + $O_2(g) \rightarrow$ 2 CO (incomplete combustion)
  - 주어진 연료를 전부 불완전 연소 시킬수 없다.
  - 낮은 온도 (25도) 에서 반응이 진행되지 않는다.
- Alternative method
  - C + $O_2 \rightarrow CO_2$ $DH_r = -393.51$ kJ/mol
  - CO + ½ O2 $\rightarrow CO_2$ $DH_r = -282.99$ kJ/mol



$$\Delta\hat{H}^0_{r3} = \Delta\hat{H}^0_{r1} + (-\Delta\hat{H}^0_{r2})$$
$$= -393.51 + 282.99$$
$$= -110.52 kJ / mol$$

Hess's Law

- If the stoichiometric equation for a reaction(1) can be obtained by algebraic operations (+,−,*k) on the other stoichiometric equations (2,3,....), then the heat of reaction (1) can be obtained by performing the same operations on the heats of reactions (2,3,...).
- H is state property → Only depends on the initial and final state.

Formation Reactions and Heats of Formation

- Formation reaction :
  - Reaction which the compound is formed from its atomic constituents.
  - Normally occur in nature (O_2 instead of O)
- Examples
  - Ammonium Nitrate :
    - $N_2(g) + 2H_2(g) + 3/2\ O_2(g) \rightarrow NH_4NO_3\ (c\ )$

$$\Delta \hat{H}^0{}_f = -365.14 kJ/mol$$

  - Benzene :
    - $6C\ (s) + 3H_2\ (g) \rightarrow C_6H_6\ (l)$
    - `

$$\Delta \hat{H}^0{}_f = 48.66 kJ/mol$$

Determination of Heats of Reaction using Heats of Formation

- Heats of reactions can be determined from heats of formation using Hess's Law

$$\Delta \hat{H}^0_r = \sum_{\text{products}} \nu_i (\Delta \hat{H}^0_f)_i - \sum_{\text{reactants}} \nu_i (\Delta \hat{H}^0_f)_i$$

- Example
  - $C_5H_{12}(l) + 8O_2\ (g) \rightarrow 5CO_2(g) + 6H_2O\ (l)$

$$\Delta \hat{H}^0_r = 5(\Delta \hat{H}^0_f)_{CO_2(g)} + 6(\Delta \hat{H}^0_f)_{H_2O(l)} - (\Delta \hat{H}^0_f)_{C_5H_{12}(l)}$$

9.4 Heats of Combustion

- Standard Heat of Combustion
  - Heat of reaction of the substance with oxygen to yield specified products
  - Condition : 25 °C, 1 atm
  - Products : CO_2 (g), H_2O (l), SO_2 (g), NO_2 (g)
- Using Hess's Law heat of reaction can be calculated from heats of combustion

$$\Delta\hat{H}^0{}_r = \sum_{\text{products}} \nu_i (\Delta\hat{H}^0{}_c)_i - \sum_{\text{reactants}} \nu_i (\Delta\hat{H}^0{}_c)_i$$

9.5 Energy Balances of Reactive Processes

- General Procedure
  - Choice of reference conditions
    - Choice 1
      - Reactants and products : T_0 where ΔH_r is known
      - Non-reactive species : Any convenient T

$$\Delta H = \frac{n_{AR}\Delta \hat{H}^0{}_r}{\nu_A} + \sum_{\text{outlet}} n_i H_i - \sum_{\text{inlet}} n_i H_i$$

    - Choice 2
      - Reactants and Products :elements at 25 °C
        - Use sum of heats of formation
      - Non-reactive species : Any convenient T

$$\Delta H = \sum_{\text{outlet}} n_i H_i - \sum_{\text{inlet}} n_i H_i$$

Energy Balances of Reactive Processes

- Processes with unknown outlet conditions : adiabatic reactors
  - Trial-and-error solution using Q=DH=0
- Solutions
  - Standard heat of formation for solutions

$$(\Delta \hat{H}^0{}_f)_{solution} = (\Delta \hat{H}^0{}_f)_{solute} + \Delta \hat{H}_s^0(n)$$

9.6 Fuels and Combustion

- Fuels
  - Solid Fuels : coal, coke, solid residue from petroleum
  - Liquid Fuels : hydrocarbons from crude oil, shale oil , alcohols, liquefaction of coal
  - Gas Fuels : natural gas, light hydrocarbons, acetylene, hydrogen
- Heating Values (Caloric Values)
  - Negative value of heat of combustion
  - HHV (higher heating value) : H2O (l)
  - LHV (lower heating value) : H2O (v)

$$HHV = LHV + n\Delta\hat{H}_v^0(H_2O, 25^oC)$$

Adiabatic flame temperature

- Theoretical flame temperature
  - Highest achievable temperature in a adiabatic reactor
  - Calculation procedure :
    - Q=DH =0 for adiabatic reactor

$$\Delta H = n_f \Delta \hat{H}^0{}_c + \sum_{\text{outlet}} n_i H_i(T_{ad}) - \sum_{\text{inlet}} n_i H_i(T_{feed}) = 0$$

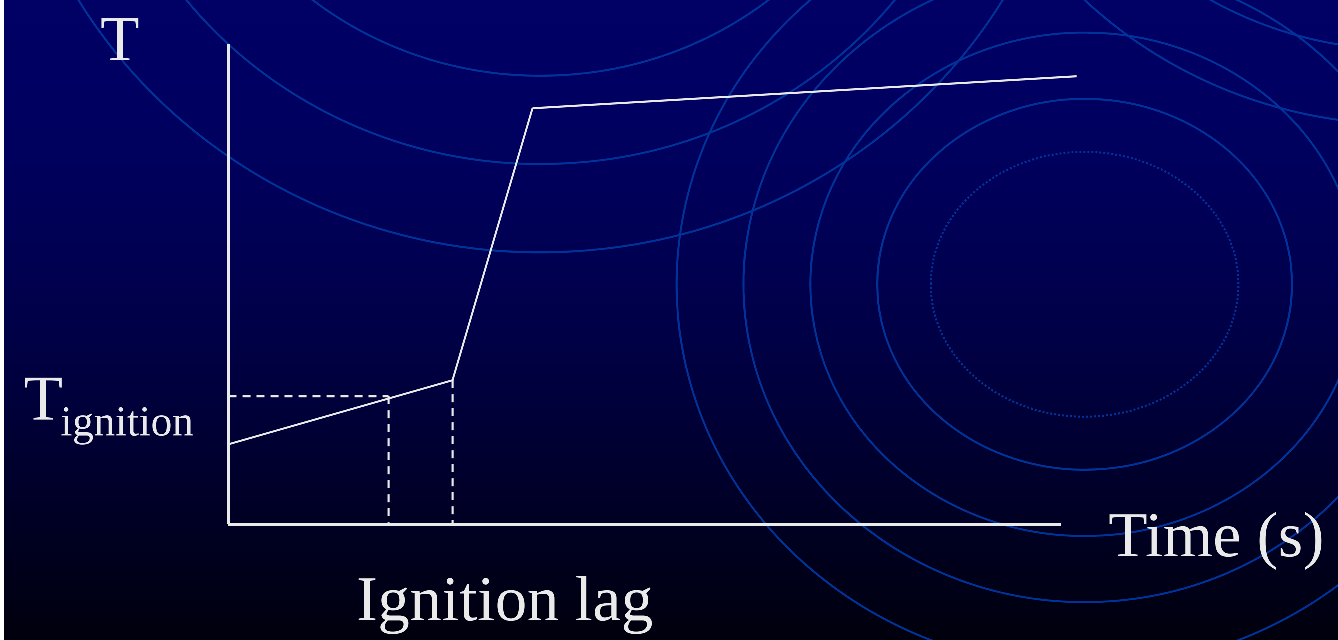
    - Trial-and error calculation to find T_{ad}.

Flammability and Ignition

- Chemical reaction kinetics
  - Rate of chemical reactions
  - Depends on T, concentration, ...
- Combustion (연소): rapid, high temperature oxidation reaction
- Ignition (발화, 착화)
  - The rate of reaction increases abruptly when the reaction mixtures exceeds a certain T.
  - T : Ignition temperature (발화온도)

Flammability and Ignition

- Ignition temperature, ignition lag
- Ignition temperature depends on air-fuel ratio, pressure, shape of the reactor,...
- Minimum value : Spontaneous ignition temperature



Flammability Limits

- Highest available T : when air-fuel ratio is nearly stoichiometric ratio
- Excess O2 or excess fuel reduces flame temperature
- Flammability Limits (explosive range)
  - Upper flammability limit
  - Lower flammability limit
  - Explosion or ignition is impossible outside this range.
- Flash temperature
  - The temperature at which the liquid gives off enough vapor to form ignitable mixture.

Flames and Detonations

- Visible flame
- Flame velocity
- Stationary flame
- Flash back
- Detonation