**KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY**

**CHEMICAL ENGINEERING DEPARTMENT**

**CHE 252: CHEMICAL PROCESS CALCULATIONS II**

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**LECTURE 7:** ENERGY BALANCE ON REACTIVE PROCESSES

**Learning Objectives**

At the end of this lecture the students are expected to do the following:

1. Explain the concepts of heat of reaction; heat of formation; combustion; heat of combustion; standard heats of formation, combustion, and reaction;
2. Calculate the total enthalpy change, given (a) the amount of any reactant consumed or any product generated in a reaction at a given temperature and pressure and (b) the heat of the reaction at that temperature and pressure.
3. Determine a heat of reaction from heats of other reactions using Hess's law. Determine standard enthalpies and internal energies of reaction from known standard heats of formation and heats of combustion.
4. Solve reactive-system energy balance problems for (a) the heat transfer required for specified inlet and outlet conditions, (b) the outlet temperature corresponding to a specified heat input (e.g., for an adiabatic reactor), and (c) the product composition corresponding to a specified heat input and a specified outlet temperature.

**8.1 HEATS OF REACTION**

The heat of reaction (or enthalpy of reaction), (T, P), is the enthalpy change for a process in which stoichiometric quantities of reactants at temperature T and pressure P react completely in a single reaction to form products at the same temperature and pressure.

Consider the reaction between solid calcium carbide and liquid water to form solid calcium hydroxide and gaseous acetylene,

the heat of reaction for this at 25°C and 1 atm is (25°C, 1 atm) = -125.4 kJ/mol

From the above it means that if 1 mol of solid calcium carbide reacts completely with 2 mol of liquid water to form 1 mol of solid calcium hydroxide and 1 mol of gaseous acetylene, and the initial and final temperatures are both 25°C and the initial and final pressures are both 1 atm, then Hproducts - Hreactants = -125.4 kJ. If the reaction is run under conditions such that the energy balance reduces to *,* then 125.4 kJ of heat must be transferred from the reactor in the course of the reaction.

If a reaction takes place at a temperature Toand pressure Poand the extent of reaction is ξ, the associated enthalpy change is

For a continuous process, nA,r (mol) would be replaced by *(mol/s)* in this expression, ξ(mol) would be replaced by (mol/s),and (kJ)would be replaced by (kJ/s)*.*

Following are several important terms and observations related to heats of reaction:

1. If  *(T, P)* is negative the reaction is exothermic at temperature *T* and pressure *P,* and if

*(T, P)* is positive the reaction is endothermic at *T* and *P.* These definitions of exothermic and endothermic are equivalent to the ones given earlier in terms of chemical bond strengths.

*2.* At low and moderate pressures, (T, P) is nearly independent of pressure. We will presume this independence in the balance of in this lecture and write the heat of reaction as (T).

3. The value of the heat of a reaction depends on how the stoichiometric equation is written.

For example,

The first line states that the combined enthalpy of 1 gram-mole of CO2 plus 2 gram-moles of liquid water is 890.3 kJ lower than the combined enthalpy of 1 gram-mole of methane plus 2 gram-moles of oxygen at 25°C. Doubling the quantity of reactants at a given condition doubles the total enthalpy of the reactants at that condition, and similarly for the products.

The difference between the product and reactant enthalpies in the second reaction (by definition,

must therefore be double the enthalpy difference in the first reaction .

*4. The value of a heat of reaction depends on the states of aggregation (gas, liquid, or solid) of the reactants and products.* For example,

The only difference between the reactions is that the water formed is a liquid in the first one and a vapor in the second. Since enthalpy is a state function, the difference between the two heats of reaction must be the enthalpy change associated with the vaporization of 2 mol of water at 25°C-that is, (25°C).

1. The standard heat of reaction, is the heat of reaction when both the reactants and products are at a specified reference temperature and pressure, usually *25°C* and 1 atm.

**Example 7.1 Calculation of Heats of Reaction**

The standard heat of the combustion of n-butane vapor is

Calculate the rate of enthalpy change, (kJ/s)*,* if 2400 *mol/s* of CO2 is produced in this reaction and the reactants and products are all at *25°C.*

2. What is the standard heat of the reaction

Calculate if 2400 mol/sof CO2 is produced in thisreaction and the reactants and products are all at 25OC.

3. The heats of vaporization of n-butane and water at *25°C* are 19.2 kJ/mol and 44.0 kJ/mol respectively.

What is the standard heat of the reaction

Calculate if 2400 mol/sof CO2 is produced in this reaction and the reactants and products are all at *25°C.*

***Solution***

1. Since doubling the stoichiometric coefficients of a reaction must double the heat of reaction

The enthalpy change associated with the production of 2400 mol/s of *CO2* at 25°C cannot depend on how the stoichiometric equation is written (the same quantities of reactants and products at the same temperatures must have the same enthalpies), and so must be the value calculated in question 1 (a). Let us do the calculation and prove it, however.

1. Compare the two reactions:

The total enthalpy of the products in the second reaction [4 mol *CO2(g)* + 5 mol H2O(g) at 25°C] is greater than that of the products in the first reaction [4 mol *CO2(g)* + 5 mol H2O(l) at 25°C] by five times the heat of vaporization of water. Similarly, the total enthalpy of the reactants in the second reaction is lower than that of the reactants in the first reaction by the heat of vaporization of butane.

Since= Hproducts - Hreactants, it follows that

**For a closed System**

If a reaction takes place in a closed reactor at constant volume, the heat released or absorbed is determined by the change in internal energy between reactants and products. The **internal energy of reaction,**  *(T),* is the difference *U*products - Ureactants if stoichiometric quantities of reactants react completely at temperature *T.*

Suppose a reaction occurs, and *vi* is the stoichiometric coefficient of the *i*th gaseous reactant or product. If ideal gas behavior can be assumed and specific volumes of liquid and solid reactants and products are negligible compared with those of the gases, the internal energy of reaction is related to the heat of reaction bv

For example

The internal energy of reaction is

If there are no gaseous reactants or products then to a good approximation .

***Example 7.2 Evaluation of***

The standard heat of reaction

is . Calculate for this reaction.

**Solution**

From stoichiometric equation

**7.2 MEASUREMENT AND CALCULATION OF HEATS OF REACTION: HESS' LAW**

Hess's law states that if the stoichiometric equation for reaction 1 can be obtained by algebraic operations (multiplication by constants, addition, and subtraction) on stoichiometric equations for reactions 2,3, ... , then the heat of reaction can be obtained by performing the same operations on the heats of reactions ...

***Example 7.3 Hess’ Law***

The standard heats of the following combustion reactions have been determined experimentally:

Use Hess’s law and the given heats of reaction to determine the standard heat of the reaction

Since form equations above (1-4) it can be seen that (4

From Hess’s law

(

This heat of reaction could not have been measured directly, since you cannot react carbon and hydrogen in such a way that ethane is the only reaction product.

***Example 7.4***

Calculate the heat of combustion for C2H6 from the following reactions:

The reaction for combustion of ethane is as follows:



**7.3 FORMATION REACTIONS AND HEATS OF FORMATION**

A formation reaction of a compound is the reaction in which the compound is formed from its elemental constituents as they normally occur in nature (e.g., O2 rather than O). The enthalpy change associated with the formation of 1 mole of the compound at a reference temperature and pressure (usually 25°C and 1 atm) is the standard heat of formation of the compound, .

Standard heats of formation for many compounds are listed in Table B.1 (Felder and Rosseau) and on pp. 2-187 through 2-198 of *Perry's Chemical Engineers' Handbook.* For example, for crystalline ammonium nitrate is given in Table B.1 as - 365.14 *kJ/mol,* signifying

Similarly, for liquid benzene = 48.66 *kJ/mol* or

*The standard heat of formation of an elemental species (e.g.,* O2) *is zero.*

It may be shown using Hess's law that if v*i is the stoichiometric coefficient of the ith species participating in a reaction* (+ *for products,* - *for reactants) and*  *is the standard heat of formation of this species, then the standard heat of the reaction is*

***Example 7.5***

Consider the combustion of liquid ethanol as shown in the following reaction scheme:

Use heat of formation to determine the standard heat of reaction.

Substitute the values of the standard heat of formation:

**7.4 HEATS OF COMBUSTION**

The **standard heat of combustion** of a substance,, is the heat of the combustion of that substance with oxygen to yield specified products [e.g., *CO2(g)* and H2O(l)], with both reactants and products at 25oC and 1 atm (the arbitrary but conventional reference state).

Table B.l (Felder and Rosseau) lists standard heats of combustion for a number of substances. The given values are based on the following assumptions: (a) all carbon in the fuel forms CO2(g), (b) all hydrogen forms H2O(I), (c) all sulfur forms *SO2(g),* and (d) all nitrogen forms *NO2(g).* The standard heat of combustion of liquid ethanol, for example, is given in Table B.l as *=* *1366.9 kJ/mol,* which signifies

: (25°C, 1 atm) = -1366.9 *kJ/mol*

Additional heats of combustion are given on pp. 2-195 through 2-199 of *Perry's Chemical Engineers' Handbook*.

*Standard heats of reactions that involve only combustible substances and combustion products can be calculated from tabulated standard heats of combustion,* in another application ofHess's law. A hypothetical reaction path may be constructed in which (a) all combustible reactantsare burned with O2 at 25°C and (b) CO2 and H2O combine to form the reaction products plus O2. Step (b) involves the reverse of the combustion reactions of the reaction products.Since both steps involve only combustion reactions, the total enthalpy change-which equalsthe desired heat of reaction-can be determined entirely from heats of combustion as

If any reactants or products are combustion products (i.e., CO2, H2O, SO2), their heats of combustion are equal to zero.

Consider the formation of pentane:

Carbon, hydrogen, and pentane can all be burned, and their standard heats of combustion can be determined experimentally. Therefore,

***Example 7.6***

Consider the combustion of liquid ethanol as shown in the following reaction scheme:

Use heat of formation to determine the standard heat of combustion.

The standard heat of reaction is calculated from the standard heat of combustion as

Substitute the values of the standard heat of combustion, knowing that the magnitudes of the standard heat of combustion of oxygen, water, and carbon dioxide are zero:

**7.5 Energy Balance for Reactive Processes**

For energy balances with reaction, we have two methods for solving these types of problems: the heat of reaction method (extent of reaction) and the heat of formation method (element balance). These two methods differ in the choice of the reference state.

**7.5.1Heat of Reaction Method**

The heat of reaction method is ideal when there is a single reaction for which is known. This method requires calculation of the extent of reaction, ξ. The extent of reaction can be obtained by performing material balance for any reactant or product for which the feed and product flow rates are known. The reference state is such that all reactant and product species are at 25°C and 1 atm in the states for which the heat of reaction is known (Figure 7.1).



Figure 7.1: Rate of change in enthalpy for a reactive process.

For a single reaction at a reference state of 25°C and 1 atm while reactant and product are at different inlet and exit temperatures

For multiple reactions where the reference state is 25°C and 1 atm and the inlet and exit streams are at temperatures other than the reference states,

**7.5.2 Heat of Formation or Element Balance Method**

In the heat of formation method, the heats of reaction terms () are not required as they are implicitly included when heats of formation of the reactants are subtracted from the products. For single and multiple reactions



Figure 7.2 Heat of formation or element balance method.

where the specific molar enthalpy of component *i* in the inlet streams is

Specific molar enthalpy of component *i* in the exit streams is

**Example 7.7 *Energy Balance About an Ammonia Oxidizer***

The standard heat of reaction for the oxidation of ammonia is given below:

One hundred mol NH3/s and 200 mol *O2/s* at 25°C are fed into a reactor in which the ammonia is completely consumed. The product gas emerges at 300°C. Calculate the rate at which heat must be transferred to or from the reactor, assuming operation at approximately 1 atm.

**Solution**



Since only one reaction takes place and is known, we will use the heat of reaction method for the energy balance, choosing as references the reactant and product species in the states for which the heat of reaction is given. The enthalpy table appears as follows:

References: at 25oC and 1 atm

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Substance** | **(mol/s)** | **(kJ/mol)** | **(mol/s)** | **(kJ/mol)** |
|  | 100 | 0 | - | - |
|  | 200 | 0 | 75 |  |
|  | - | - | 100 |  |
|  | - | - | 150 |  |





Thus, 19,700 kW of heat must be transferred from the reactor to maintain the product temperature at 300°C. If less heat were transferred, more of the heat of reaction would go into the reaction mixture and the outlet temperature would increase.

**Example 7.8 *Energy Balance on a Methane Oxidation Reactor***

Methane is oxidized with air to produce formaldehyde in a continuous reactor. A competing reaction is the combustion of methane to form CO2.

A flowchart of the process for an assumed basis of 100 mol of methane fed to the reactor is shown below:



***Basis: 100 mol CH4 Fed***

Since the component amounts of all streams are known, we may proceed directly to the energy balance. We choose as references the elemental species that form the reactants and products at 25°C and I atm (the state for which heats of formation are known) and the nonreactive species N2 (g) also at 25°C and I atm (the reference state for Table B.8). The inlet-outlet enthalpy table is shown below.



***Calculate Unknown Enthalpies***

In the following calculations, values of come from Table B.1, formulas for *Cp(T)* come from Table B.2, and values of *H(T)* for O2 and N2 are specific enthalpies relative to the gaseous species at 25°C taken from Table B.8. Effects of any pressure changes on enthalpies are neglected and the details of the calculations are not shown.



As each of these values is calculated, it should be substituted in the inlet-outlet enthalpy table. The table finally appears as follows:



***Evaluate***

***Energy Balance***

Remember that we are dealing with a continuous process and hence an open system. [The reason we use *n (mol)* and not (mol/s) is that we took 100 mol CH4 as a basis of calculation.] With , and *Ws* neglected, the open system energy balance yields

Q = = -15,300 kJ