

Chemical Engineering Principles 2 (0905212)

Balances on Reactive Processes

Dr.-Ing. Zayed Al-Hamamre

Chemical Engineering Department | University of Jordan | Amman 11942, Jordan
Tel. +962 6 535 5000 | 22888



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Introduction

- In any reaction between stable molecules,
 - Energy is required to break the reactant chemical bonds and energy is released when the product bonds form.
 - If the first process absorbs less energy than the second process releases (as in the water formation reaction), the reaction is **exothermic: the product molecules at a given temperature and pressure have lower internal energies** (and hence lower enthalpies) than the reactant molecules at the same temperature and pressure.
 - The net energy released-the **heat of reaction-must be transferred from the reactor** as heat or work, or else the system temperature increases.
 - If energy is released when the product bonds form than it took to break the reactant bonds, the reaction is **endothermic: energy must be added to the reactor as heat or work to keep the** temperature from decreasing.
- The large internal energy and enthalpy changes commonly associated with chemical reactions can play major roles in the design and operation of chemical processes

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Heat of reaction

- The heat of reaction (or enthalpy of reaction), $\Delta\hat{H}_r(T, P)$ 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.
- Stoichiometric quantities of reactants means molar amounts of the reactants numerically equal to their stoichiometric coefficients
- If stoichiometric quantities of the reactants are fed and the reaction proceeds to completion, both reactants would be completely consumed and stoichiometric quantities of the products would be formed.
- In the reaction, $\text{CaC}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{s}) + \text{C}_2\text{H}_2(\text{g})$

1 mol of $\text{CaC}_2(\text{s})$ react with 2 mol of $\text{H}_2\text{O}(\text{l})$ to form 1 mol $\text{Ca}(\text{OH})_2(\text{s})$ 1 mol $\text{C}_2\text{H}_2(\text{g})$

$$\Delta\hat{H}_r(25^\circ\text{C}, 1 \text{ atm}) = -125.4 \text{ kJ/mol} \longleftrightarrow H_{\text{products}} - H_{\text{reactants}} = -125.4 \text{ kJ.}$$

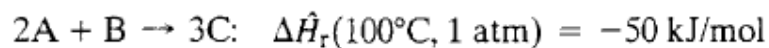
the initial and final temperatures are both 25°C the initial and final pressures are both 1 atm

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Heat of reaction

$\Delta\hat{H}_r$ applies to stoichiometric quantities of each species.



➤ This means that the enthalpy change for the given reaction is

$$\frac{-50 \text{ kJ}}{2 \text{ mol A consumed}} = \frac{-50 \text{ kJ}}{1 \text{ mol B consumed}} = \frac{-50 \text{ kJ}}{3 \text{ mol C generated}}$$

➤ If 150 mol of C/s was generated in the given reaction at 100°C and 1 atm, the associated enthalpy change is

$$\Delta\dot{H} = \frac{-50 \text{ kJ}}{3 \text{ mol C generated}} \left| \frac{150 \text{ mol C generated}}{\text{s}} \right. = -2500 \text{ kJ/s}$$

➤ if ν_A is the stoichiometric coefficient of a reactant or reaction product A (positive if A is a product, negative if it is a reactant) and $n_{A,r}$ moles of A are consumed or generated at $T = T_0$ and $P = P_0$, then the associated enthalpy change is

$$\Delta H = \frac{\Delta\hat{H}_r(T_0, P_0)}{|\nu_A|} n_{A,r}$$

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Heat of reaction

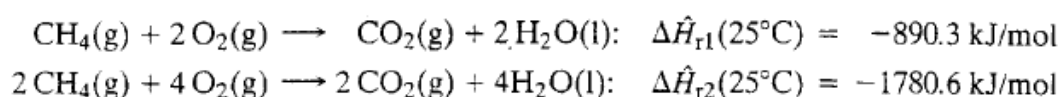
➤ The extent of reaction, ξ , as a measure of how far a reaction has proceeded.

$$\xi = \frac{|n_{A,\text{out}} - n_{A,\text{in}}|}{|\nu_A|} = \frac{n_{A,r}}{|\nu_A|}$$

$$\Rightarrow \Delta H = \xi \Delta\hat{H}_r(T_0, P_0)$$

Remarks

1. If $\Delta\hat{H}_r(T, P)$ is negative the reaction is **exothermic** at temperature T and pressure P , and if $\Delta\hat{H}_r(T, P)$ is positive the reaction is **endothermic** at T and P .
2. At low and moderate pressures, $\Delta\hat{H}_r(T, P)$ is nearly independent of pressure. $\Delta\hat{H}_r(T)$.
3. The value of the heat of a reaction depends on how the stoichiometric equation is written.

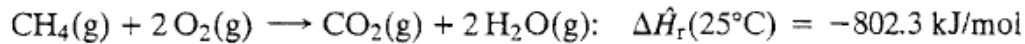
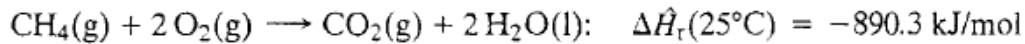


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Heat of reaction

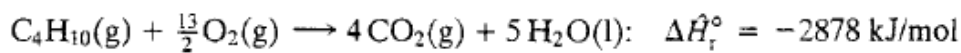
4. The value of a heat of reaction depends on the states of aggregation (gas, liquid, or solid) of the reactants and products.



5. The **standard heat of reaction**, $\Delta \hat{H}_r^\circ$, 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 Calculation of Heats of Reaction

1. The standard heat of the combustion of *n*-butane vapor is



Calculate the rate of enthalpy change, $\Delta \hat{H}$ (kJ/s), if 2400 mol/s of CO_2 is produced in this reaction and the reactants and products are all at 25°C.

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Example Cont.

2. What is the standard heat of the reaction



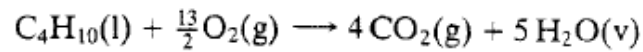
Calculate $\Delta \hat{H}$ if 2400 mol/s of CO_2 is produced in *this* reaction and the reactants and products are all at 25°C.

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Example Cont.

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 $\Delta\dot{H}$ if 2400 mol/s of CO_2 is produced in this reaction and the reactants and products are all at 25°C.

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Example Cont.

- 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**, $\Delta\hat{U}_r(T)$,

$$\Delta\hat{U}_r(T) = U_{\text{products}} - U_{\text{reactants}}$$

if stoichiometric quantities of reactants react completely at temperature T

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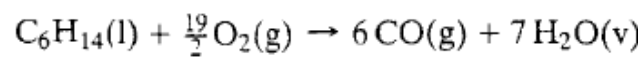


Heat of reaction

- If ν_A is the stoichiometric coefficient of the i^{th} gaseous reactant or product.
- If ideal gas behavior is 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 by

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

for the reaction



$$\begin{aligned} \Delta \hat{U}_r(T) &= \Delta \hat{H}_r(T) - RT(6 + 7 - \frac{19}{2}) \\ &= \Delta \hat{H}_r(T) - \frac{7}{2}RT \end{aligned}$$

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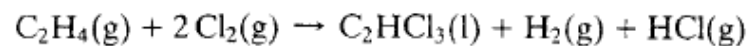
Heat of reaction

- If there are no gaseous reactants or products, then

$$\Delta \hat{U}_r = \Delta \hat{H}_r.$$

Example Evaluation of $\Delta \hat{U}_r$

The standard heat of the reaction



is $\Delta \hat{H}_r^\circ = -420.8 \text{ kJ/mol}$. Calculate $\Delta \hat{U}_r^\circ$ for this reaction.



Hess's law

- The heat of reaction can be measured in a **calorimeter: a closed reactor immersed in a fluid** contained in a well-insulated vessel.
- The rise or fall of the fluid temperature can be measured and used to determine the energy released or absorbed by the reaction,
- The value of $\Delta\hat{H}_r^\circ$ may then be calculated from that energy and known reactant and product heat capacities.

Hess's law

- 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 $\Delta\hat{H}_{r1}^\circ$ can be obtained by performing the same operations on the heats of reactions $\Delta\hat{H}_{r2}^\circ, \Delta\hat{H}_{r3}^\circ, \dots$

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Example

Hess's Law

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

1. $\text{C}_2\text{H}_6 + \frac{7}{2}\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$: $\Delta\hat{H}_{r1}^\circ = -1559.8 \text{ kJ/mol}$
2. $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$: $\Delta\hat{H}_{r2}^\circ = -393.5 \text{ kJ/mol}$
3. $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$: $\Delta\hat{H}_{r3}^\circ = -285.8 \text{ kJ/mol}$

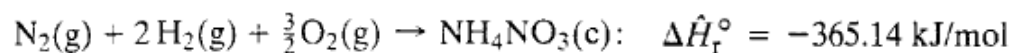
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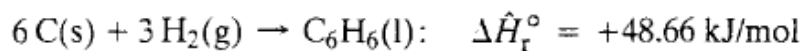
Formation reaction and heat of formation

- The **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 **standard heat of formation** of the compound $\Delta\hat{H}_f^\circ$ is 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)
- Standard heats of formation for many compounds are listed in Table B.1
- For crystalline ammonium nitrate NH₄NO₃(c)

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



for liquid benzene $\Delta\hat{H}_f^\circ = 48.66 \text{ kJ/mol}$,



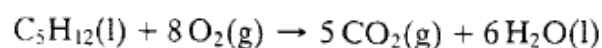
Formation reaction and heat of formation

- The standard heat of formation of an elemental species (e.g., O₂) is zero.
- If ν_A is the stoichiometric coefficient of the i^{th} species participating in a reaction (+ for products, - for reactants) and $\Delta\hat{H}_f^\circ$ is the standard heat of formation of this species, then the standard heat of the reaction is

$$\Delta\hat{H}_r^\circ = \sum_i \nu_i \Delta\hat{H}_{fi}^\circ = \sum_{\text{products}} |\nu_i| \Delta\hat{H}_{fi}^\circ - \sum_{\text{reactants}} |\nu_i| \Delta\hat{H}_{fi}^\circ$$

Example *Determination of a Heat of Reaction from Heats of Formation*

Determine the standard heat of reaction for the combustion of liquid *n*-pentane, assuming H₂O(l) is a combustion product.



Heat of combustion

- The **standard heat of combustion of a substance**, $\Delta\hat{H}_c^\circ$, is the heat of the combustion of **that** substance with oxygen to yield specified products [e.g., $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$], with both reactants and products at 25°C and 1 atm (the arbitrary but conventional reference state).
- Table B.1 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 $\text{CO}_2(\text{g})$,
 - (b) All hydrogen forms $\text{H}_2\text{O}(\text{l})$,
 - (c) All sulfur forms $\text{SO}_2(\text{g})$, and
 - (d) All nitrogen forms $\text{N}_2(\text{g})$.
- Standard heats of reactions that involve only combustible substances and combustion products can be calculated from tabulated standard heats of combustion.
- For CO_2 , H_2O and SO_2 , the standard heats of combustion is equal to zero.

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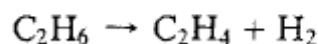
Heat of combustion

- For combustion reaction,

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

Example *Calculation of a Heat of Reaction from Heats of Combustion*

Calculate the standard heat of reaction for the dehydrogenation of ethane:



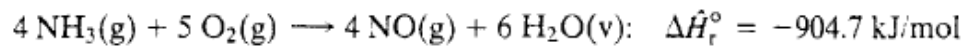
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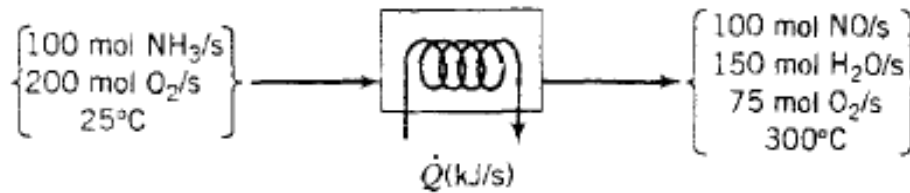
Energy balance on reactive processes

Example *Energy Balance About an Ammonia Oxidizer*

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



One hundred mol NH_3/s and 200 mol O_2/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.



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Example Cont.

Example Cont.



Example Cont.





Example

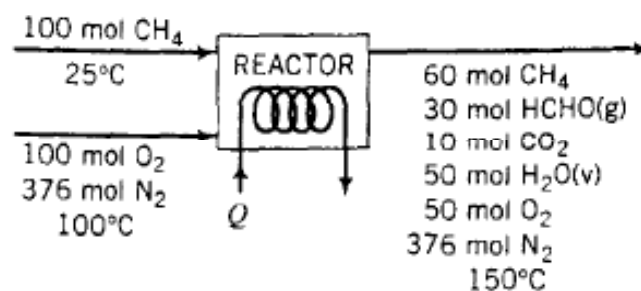


Energy Balance on a Methane Oxidation Reactor

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

1. $\text{CH}_4(\text{g}) + \text{O}_2 \rightarrow \text{HCHO}(\text{g}) + \text{H}_2\text{O}(\text{v})$
2. $\text{CH}_4(\text{g}) + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}(\text{v})$

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



Example Cont.



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Example Cont.



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Example Cont.



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Example Cont.



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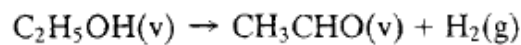


Processes with Unknown Outlet Conditions: Adiabatic Reactors

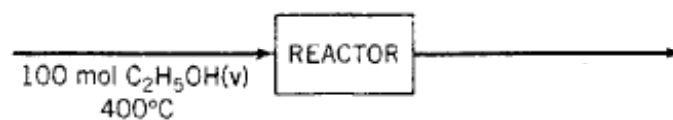


Example *Energy Balance on an Adiabatic Reactor*

The dehydrogenation of ethanol to form acetaldehyde



is carried out in a continuous adiabatic reactor. Ethanol vapor is fed to the reactor at 400°C, and a conversion of 30% is obtained. Calculate the product temperature.



Example Cont.



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Example Cont.



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Example Cont.



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Example Cont.



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Example



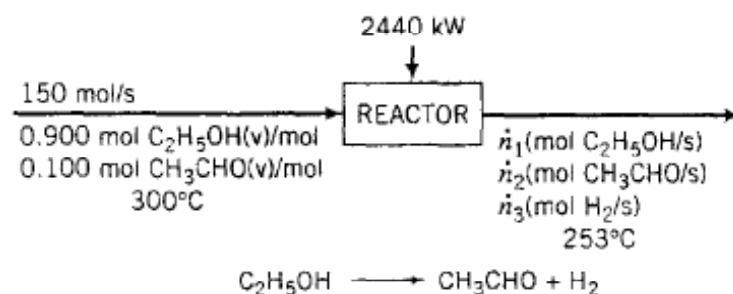
Simultaneous Material and Energy Balances

The ethanol dehydrogenation reaction



is carried out with the feed entering at 300°C.

The feed contains 90.0 mole% ethanol and the balance acetaldehyde and enters the reactor at a rate of 150 mol/s. To keep the temperature from dropping too much and thereby decreasing the reaction rate to an unacceptably low level, heat is transferred to the reactor. When the heat addition rate is 2440 kW, the outlet temperature is 253°C. Calculate the fractional conversion of ethanol achieved in the reactor.



Example cont.



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Example cont.



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Example cont.



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Example cont.



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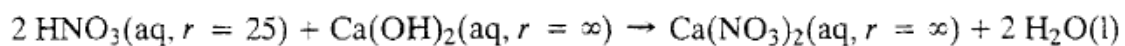
Thermochemistry of Solutions

- The enthalpy change associated with the formation of a solution from the solute elements and the solvent at 25°C is called the **standard heat of formation of the solution**
- If a solution contains n moles of solvent per mole of solute, then

$$(\Delta\hat{H}_f^\circ)_{\text{solution}} = (\Delta\hat{H}_f^\circ)_{\text{solute}} + \Delta\hat{H}_s^\circ(n) \quad (\text{energy})/(\text{mole of solute}).$$

where $\Delta\hat{H}_s^\circ$ is the heat of solution at 25°C

- The standard heat of a reaction involving solutions may be calculated from heats of formation of the solutions
- For the reaction



the standard heat of reaction

$$\begin{aligned} \Delta\hat{H}_r^\circ &= (\Delta\hat{H}_f^\circ)_{\text{Ca}(\text{NO}_3)_2(\text{aq})} + 2(\Delta\hat{H}_f^\circ)_{\text{H}_2\text{O}(\text{l})} - 2(\Delta\hat{H}_f^\circ)_{\text{HNO}_3(\text{aq}, r=25)} - (\Delta\hat{H}_f^\circ)_{\text{Ca}(\text{OH})_2(\text{aq}, r=\infty)} \\ &= -114.2 \text{ kJ/mol} \end{aligned}$$

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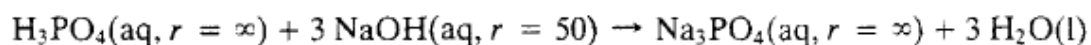


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Example

Standard Heat of a Neutralization Reaction

1. Calculate $\Delta\hat{H}_r^\circ$ for the reaction



2. If 5.00 mol of NaOH dissolved in 250 mol of water is neutralized completely at 25°C with dilute phosphoric acid, what is the attendant enthalpy change?

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Example cont.



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Example



Energy Balance on a Neutralization Process

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Problem 9.30



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Problem 9.30 cont.



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