

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY
CHEMICAL ENGINEERING DEPARTMENT
CHE 252: CHEMICAL PROCESS CALCULATIONS II

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COURSE DESCRIPTION

Course Objectives: This course is to enable students understand and apply the basics of calculations related to material and energy flow in chemical processes.

Topics to be covered include:

Energy sources, concepts from the First law of thermodynamics. General energy balance on flow systems. Energy balance on closed systems. Fuels and combustion. Combustion calculations. Heats of formation, reaction, combustion. Hess's law. Balances on mixing, heating, cooling, and reactive processes. Humidity and humidity charts.

Learning Outcomes: Upon completion of this course, a student should be able to:

1. Apply the First Law of Thermodynamics to perform energy balances on steady-state non-reactive and reactive processes.
2. Determine enthalpy and internal energy changes associated with changes in temperature, pressure, mixing, phase change, and chemical reaction from appropriate heat capacities, heats of solution, latent heats, and heats of formation or combustion.
3. Solve materials and energy balances simultaneously on chemical process systems.
4. Use Hess Law
5. Solve combustion problems
6. Understand the concept of humidity and usage of psychrometric chart

Reference Texts

David M. Himmelblau, & James B. Riggs (2004): Basic Principles and Calculations in Chemical Engineering, 7th Edition, Prentice Hall International Series,

Richard M. Felder and Ronald W. Rousseau (2005): Elementary Principles of Chemical Processes (3rd Edition), John Wiley & Sons Inc.

LECTURE 1: INTRODUCTION TO ENERGY SOURCES, CONCEPTS FROM THE FIRST LAW OF THERMODYNAMICS.

Learning Objectives

At the end of the lecture the student is expected to be able to do the following:

- Define or explain the following terms: energy, system, closed system, nonflow system, open system, flow system, surroundings, property, extensive property, intensive property,
- List and define the three components of the total energy of a process system
- List and define the two forms of energy transfer between a system and its surroundings.
- State the conditions under which heat and work are positive.
- Convert an energy or power (energy/time) expressed in any unit (e.g., J, dyne.cm, Btu, ft.lbf/h, kW, hp) to its equivalent in any other dimensionally consistent units.

1.1 SYSTEM

A “system” is an object or a collection of objects that an analysis is done on. The system has a definite boundary, called the system boundary that is chosen and specified at the BEGINNING of the analysis. Once a system is defined, through the choice of a system boundary, everything external to it is called the **surroundings**. All energy and material that are transferred out of the system enter the surroundings, and vice versa. In the general case there are very few restrictions on what a system is; a system can have a nonzero velocity, a nonzero acceleration, and a system can even change in size with time.

An **isolated system** is a system that does not exchange heat, work, or material with the surroundings.

If heat and work are exchanged across a system’s boundary, but material is not, it is a **closed system**.

An **open system** can exchange heat, work, and material with the surroundings.

State of a System

Once a system is defined, a certain number of variables will specify its state fully.

For example, one may need to provide the temperature, pressure, composition, “state.” The exact information that is needed to specify the state of a system depends on the type of system and the analysis to be performed.

State Functions and State Properties

The state of a system can be changed, for example by increasing its temperature or changing its composition. Properties of the system, whose change depends only on the initial (before) and final states of the system, but not on the manner used to realize the change from the initial to the

final state, are referred to as **state properties** or **state functions**. In other words, the change in a state function or state property X , between some final (state 2) and initial (state 1) situations, can be expressed as

$$\Delta X = \underbrace{X_{\text{final}} - X_{\text{initial}}}_{\text{change in } X} \equiv X_{\text{state 2}} - X_{\text{state 1}} \quad (1)$$

In equation 1, X_{final} only depends on the final state of the system, and X_{initial} only on the initial state of the system. Equation 1 does not require any information whatsoever as to how the system got from the initial to the final state, since X does not depend on the details of the path followed.

The total energy of a system has three components:

- 1. Kinetic energy:** Energy due to the translational motion of the system as a whole relative to some frame of reference (usually the earth's surface) or to rotation of the system about some axis.
- 2. Potential energy:** Energy due to the position of the system in a potential field (such as a gravitational or electromagnetic field). In this text, we will deal only with gravitational potential energy.
- 3. Internal energy:** All energy possessed by a system other than kinetic and potential energy, such as energy due to the motion of molecules relative to the center of mass of the system, to the rotational and vibrational motion and the electromagnetic interactions of the molecules, and to the motion and interactions of the atomic and subatomic constituents of the molecules.

Suppose a process system is **closed**, meaning that no mass is transferred across its boundaries while the process is taking place. Energy may be transferred between such a system and its surroundings in two ways:

- 1. As heat**, or energy that flows as a result of temperature difference between a system and its surroundings. The direction of flow is always from a higher temperature to a lower one. *Heat is defined as positive when it is transferred to the system from the surroundings.*
- 2. As work**, or energy that flows in response to any driving force other than a temperature difference, such as a force, a torque, or a voltage. For example, if a gas in a cylinder expands and moves a piston against a restraining force, the gas does work on the piston (energy is transferred as work from the gas to its surroundings, which include the piston). *In this* The terms "work" and "heat" refer only to energy that is being transferred: you can speak of the heat or work added to a system or given off by a system, but it is meaningless to speak of the heat or work possessed by or contained within a system.

Energy, like work, has units of force times distance: for example, joules (Nm), ergs (dyne·cm), and ft.lbf. It is also common to use energy units defined in terms of the amount of heat that must be transferred to a specified mass of water to raise the temperature of the water by a specified temperature interval at a constant pressure of 1 atm. The most common of these units are tabulated here.

Unit	Symbol	Mass of Water	Temperature Interval
Kilogram-calorie or kilocalorie	kcal	1 kg	15°C to 16°C
Gram-calorie or calorie	cal	1 g	15°C to 16°C
British thermal unit	Btu	1 lb _m	60°F to 61°F

Conversion between these and other energy units may be performed using the conversion factors in reference books.

The principle that underlies all energy balances is the law of conservation of energy, which states that energy can neither be created nor destroyed. This law is also called the first **law of thermodynamics**. In its most general form, the first law states that the rate at which energy (kinetic + potential + internal) is carried into a system by the input streams, plus the rate at which it enters as heat, minus the rate at which it is transported out of the system by the output streams, minus the rate at which it leaves as work, equals the rate of accumulation of energy in the system.

Enthalpy

The enthalpy H of a system is defined by

$$H = U + PV$$

where P is the pressure and V is volume. Let's think about the PV term. We know that PA , where A is the area subjected to a pressure P , is the force acting on that area. If a fluid inside a system is displaced through a distance d by the force PA , then the resultant work W done on the system can be calculated as the product of this force times the displacement. In other words, $W = PA d$. Now note that $Ad = V$, the volume swept out by the displacement. Thus, an alternate way to write the displacement work is $W = PV$. This type of work, where pressure results in the displacement of a fluid, will be referred to as **flow work**. If an amount of fluid of volume V is inserted into a system against a pressure P , the work required to accomplish this is PV . Enthalpy, therefore, can be viewed as the sum of the internal energy of this fluid volume added to the system plus the flow work performed on the system in order to insert the fluid. Enthalpy has units of energy (e.g. J, cal, BTU).

Specific Properties

The total internal energy, enthalpy, kinetic energy, and potential energy of a system are extensive properties. An extensive property depends on the total number of molecules present in the

system and on the system's total size. Often, it is more convenient to refer to the amount of a property per mass of the system. For example, if the system is a fluid phase, one may want to express the amount of internal energy or enthalpy contained in a unit mass of the fluid. If one refers to an amount of a property per mass, one is speaking about a **specific property**. Specific properties are intensive. Thus, specific volume is volume per mass, specific internal energy is internal energy per mass, and specific enthalpy is enthalpy per mass. Specific properties will be identified by a “^” symbol above them; thus, \hat{V} = specific volume (units: volume/mass; e.g. m³/kg, ft³/lbm), \hat{U} = specific internal energy (units: energy/mass; e.g. J/kg, BTU/lbm), $\hat{H} = \hat{U} + P\hat{V}$ = specific enthalpy (units: energy/mass; e.g. J/kg, cal/g), etc.

Reference States

The specific internal energy and specific enthalpy of a material are always defined relative to a **reference state**. The reference state can be chosen to refer to any set of conditions, although often it is chosen to be 0 °C and 1 atm. Then, one speaks of \hat{U} or \hat{H} of a material relative to the value of \hat{U} or \hat{H} of that material in the reference state.

Now imagine that a system passes from state 1 to state 2. In general, \hat{U} or \hat{H} will change when the state of the system changes, with the difference being

$$\Delta\hat{U} = \hat{U}_2 - \hat{U}_1 \quad \Delta\hat{H} = \hat{H}_2 - \hat{H}_1$$

Note that, in calculations, we will only be interested in how much the internal energy or enthalpy changed. That is, we will only need to calculate $\Delta\hat{U}$ and $\Delta\hat{H}$, but not the absolute values of internal energy or enthalpy.

Rates vs Amounts

Chemical processes use process streams to transport material from one point to another. Consider a stream with a mass flowrate \dot{m} (note that we could equivalently have used molar units). The material in the stream carries its kinetic, potential, and internal energy with it. Therefore, the mass transport is perforce accompanied by energy transport. The rates of energy transport (units: energy/time, e.g. J/s, BTU/h) that accompany the material flow in a process stream can be calculated as follows:

$$\dot{E}_k = \frac{1}{2}\dot{m}u^2 \quad \dot{E}_p = \dot{m}gz \quad \dot{U} = \dot{m}\hat{U}$$

Heat transport and work can be also expressed as rates, with symbols \dot{Q} and \dot{W} , respectively. The units of \dot{Q} and \dot{W} are energy/time. Note that units of energy/time are equivalently called units of **power**.