Energy and Energy Balances

The concept of energy conservation as expressed by an **energy balance** equation is central to chemical engineering calculations. Similar to mass balances studied previously, a balance on energy is crucial to solving many problems.

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.

Examples. Discuss each situation below as approximating an isolated, a closed, or an open system.

(i) A river.

(ii) The interior of a closed can of soda.

(iii) The interior of a closed refrigerator that is turned on.

(iv) The interior of a closed refrigerator that is turned off.

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, total amount of material, velocity, and position in order to specify a system's "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

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

In this equation, lets call it 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.

Example. Which of the below examples represent changes in state functions?

(i)	Work done to climb from the bottom (state 1) to the top (state 2) of a mountain.

(ii)	Change in gravitational energy of an object when it is raised from the bottom (state 1) to the top (state 2) of a mountain.

(iii) Change in density of water in a pot when it is heated from 20 $_o$C (state 1) to 50 $_o$C (state 2).

(iv) Amount of heat liberated from burning gas in a stove in order to realize a temperature change of the water in a pot from 20 $_o$C (state 1) to 50 $_o$C (state 2).
(This requires some thought …)

Forms of Energy: The First Law of Thermodynamics

Energy is often categorized as:

A. Kinetic Energy

B. Potential Energy

C. Internal Energy

Kinetic Energy

A system's kinetic energy is associated with directed motion (e.g. translation, rotation) of the system. Translation refers to straight line motion. The kinetic energy E_k of a moving object of mass *m* and travelling with speed *u* is given by,

$$E_k = \frac{1}{2}mu^2 \qquad (2)$$

This is now our second equation, equation 2.

Note that *u (which in our case as I had said earlier is the speed)* is measured relative to a **frame of reference** that defines what is "stationary". E_k (which is the kinetic energy) has units of energy, *m* of mass, and *u* of length/time.
How could the kinetic energy of a system change?
Is kinetic energy a state function? We will find out.

Potential Energy

Potential energy of a system is due to the position of the system in a potential field. There are various forms of potential energy, but only gravitational potential energy will be considered in this course. The gravitational **potential energy** of an object of **mass *m*** at an **elevation *z*** in a gravitational field, relative to its gravitational potential energy at a reference elevation z_0, is given by:

(you will need to write this one down as I will mention the initials of the terms, I have mentioned above which will make sense later if you still do not get)

$$E_p = mg(z - z_0) = mgz - mgz_0 \qquad (3)$$

The quantity *g* is the gravitational acceleration that defines the strength of the gravitational field. Often, the earth's surface is used as the reference and assigned $z_0 = 0$, in which case *mgz* represents the gravitational potential energy of the object relative to its potential energy if it rested on the earth's surface. E_p has units of energy, *m* of mass, *g* of length/time^2, and *z* of length.

How could the gravitational potential energy of a system change?
Is gravitational potential energy a state function?

Internal Energy

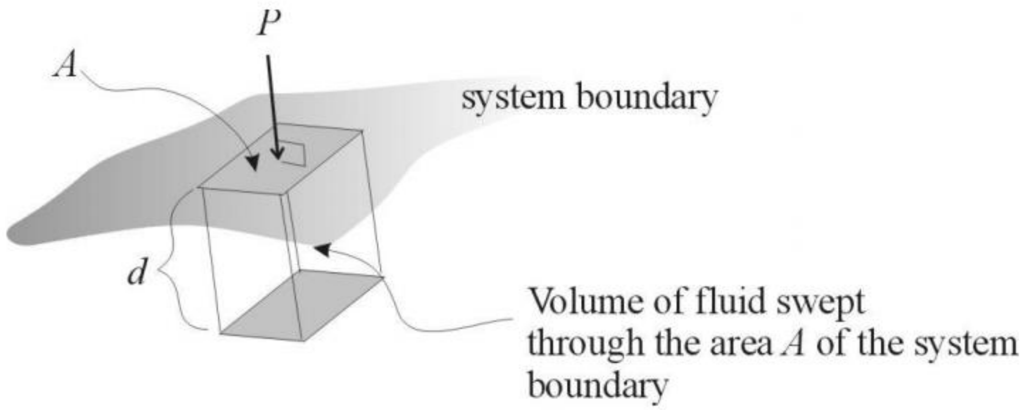
All the energy associated with a system that does not fall under the above definitions of kinetic or potential energy is internal energy. More specifically, internal energy is the energy due to all molecular, atomic, and subatomic motions and interactions. Usually, the complexity of these various contributions means that no simple analytical expression is available from which internal energy can be readily calculated. The internal energy will be represented by the symbol U.
What types of events would bring about a change in a system's internal energy?
Is internal energy a state function?

Enthalpy

The enthalpy H of a system is defined by

$$H = U + PV \quad (4)$$

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, $W = PAd$. 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 (for joules), cal (for calories), and so on.). In a flow diagram which I will attach to the notes folder, we can see the system boundary and the volume of the fluid swept through the area of the system boundary.



What types of events would bring about a change in a system's enthalpy?
Is enthalpy a state function?

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; (you will also need a pen for this one) thus, Vˆ = specific volume (units: volume/mass; e.g. m3/kg, ft3/lbm), Uˆ = specific internal energy (units: energy/mass; e.g. J/kg, BTU/lbm), Hˆ = Uˆ + PVˆ = specific enthalpy (units: energy/mass; e.g. Joules/kg, calories/g), etc.

Given a mass m of a uniform system with a specific property Xˆ , the corresponding

extensive amount of X in the system is found using X = m Xˆ . How would we use this expression to calculate the extensive volume of a system? Or the extensive enthalpy of a system? We are getting there now

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 0^0Celcius 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.

What is the value of $\hat{U}$ or $\hat{H}$ for the material in its 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

change in $\hat{U} = \hat{U}_2 - \hat{U}_1$ and change in $\hat{H} = \hat{H}_2 - \hat{H}_1$

Does the choice of a reference state affect the value of change in $\hat{U}$ or change in $\hat{H}$? 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 change in $\hat{U}$ and change in $\hat{H}$, but not the absolute values of internal energy or enthalpy.

Heat

When there is a difference in temperature between two points, heat is transferred (flows) from high temperature to the low temperature. By convention the numerical value of heat transferred is positive when it is transferred into the system, thereby increasing the energy contained in the system. That is, if Q is the heat transferred from the surroundings to the system, then $Q > 0$ means that net heat is transferred to the system so as to increase the energy of the system. If $Q < 0$, then net heat is transferred from the system to the surroundings, and the system has lost energy. Note that Q has units of energy (e.g. J, cal).

Is the heat transferred in going from state 1 to state 2 a state function? Yes!

What does "transfer of heat" mean, physically? It means that heat lost is the same as heat gained, all external factors such as density kept constant. That is, what are the molecular level processes that give rise to heat transfer? We will discuss that in our next audio lecture as we start a new topic still on energy. We will look at work as an effect of energy. As always, the pleasure has been mine. Have an awesome day and see you in the next lecture