# Chemical Engineering (Thermodynamics I) (UCH305)

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# Lecture 13

## First Law of Thermodynamics
## Closed systems (Control mass systems)

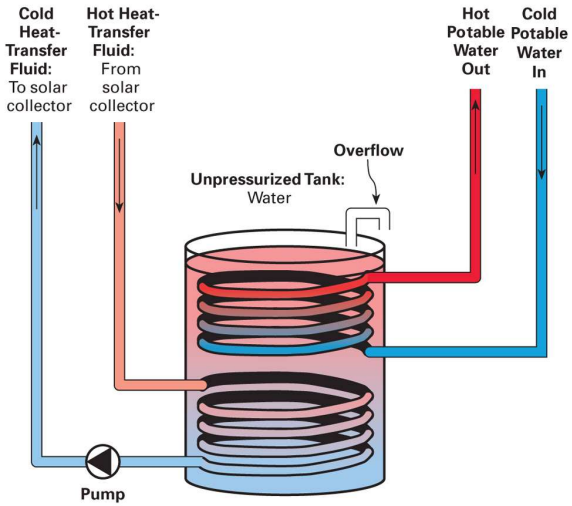
# First Law of Thermodynamics

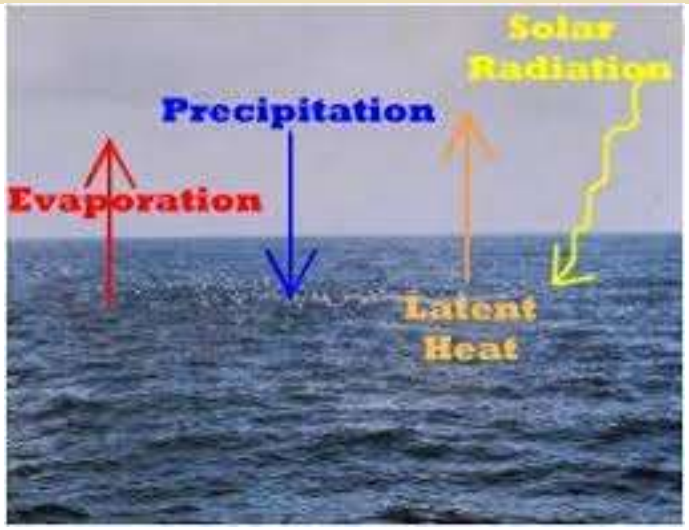
- We have considered various forms of energy such as heat $Q$, work $W$, and total energy $E$ individually.

- No attempt is made to relate them to each other during a process.

# First Law of Thermodynamics

- **First Law of Thermodynamics deals with:**
  - Closed system,
  - Open system,
  - Steady-flow engineering devices.





# Energy balance for systems

- Energy balance for any system undergoing any kind of process is expressed as:
  - Net energy transfer by heat, work, and mass = Change in internal, kinetic, potential, etc., energies

$$E_{in} - E_{out} = \Delta E_{system} \qquad (kJ)$$

$$\begin{pmatrix} \text{Net energy transfer} \\ \text{by heat, work, and mass} \end{pmatrix} = \begin{pmatrix} \text{Change in internal, kinetic,} \\ \text{potential, etc., energies} \end{pmatrix}$$

  - or, in the **rate form,** as:

$$\dot{E}_{in} - \dot{E}_{out} = dE_{system}/dt = \frac{d}{dt}E_{system} \qquad (kW)$$

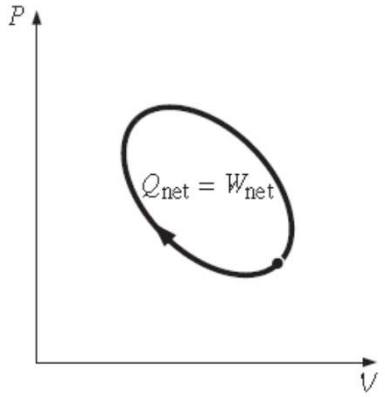
$$\begin{pmatrix} \text{Rate of net energy transfer} \\ \text{by heat, work, and mass} \end{pmatrix} = \begin{pmatrix} \text{Rate of change in internal, kinetic,} \\ \text{potential, etc., energies} \end{pmatrix}$$

- The energy balance can be expressed on a **per unit mass** basis as:

$$e_{in} - e_{out} = \Delta e_{system} \qquad (kJ/kg)$$

# Cyclic process or closed system

**Cyclic process or closed system**:




- For a closed system undergoing a **cycle,**
  - the initial and final states are identical, and thus

$$\Delta E_{system} = E_2 - E_1 = 0.$$

- Then the energy balance for a cycle simplifies to:

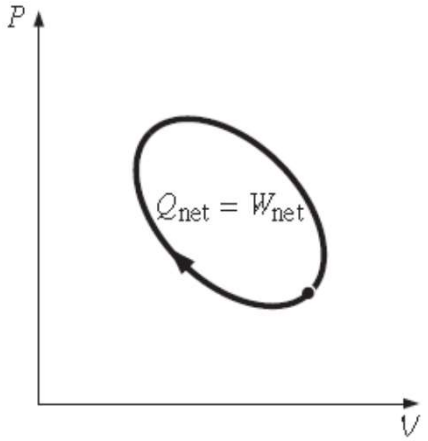
$$E_{in} - E_{out} = 0, \text{ or}$$

$$E_{in} = E_{out}.$$

- Noting that a closed system does not involve any mass flow across its boundaries, the energy balance for a cycle can be expressed in terms of heat and work interactions as:

$$(For\ a\ cycle)$$
$$Q_{net,in} = W_{net,out}$$
$$\dot{Q}_{net,in} = \dot{W}_{net,out}$$

- That is, the net work output during a cycle is ***equal*** to net heat input, as shown in figure:




For a cycle, $\Delta E = 0$, thus $Q_{net} = W_{net}$.

- The energy balance relation in that case for a closed system becomes:

$$Q_{\text{net,in}} - W_{\text{net,out}} = \Delta E_{\text{system}}$$

or

$$Q - W = \Delta E$$

where $Q = Q_{\text{net,in}} = Q_{\text{in}} - Q_{\text{out}}$ is the *net heat input,* and

$W = W_{\text{net,out}} = W_{\text{out}} - W_{\text{in}}$ is the *net work output.*

# First law of Thermodynamics

- Energy neither created nor destroyed, changes the forms during interactions between system and surroundings.

- The first law states that the amount of energy added to a system is ***equal*** to the sum of its increase in heat energy and the work done on the system. $[\Delta E = Q + W\ ]$

- The *first law* is an example of the principle of conservation of energy.

## First Law of Thermodynamics (Energy balance)

- The energy balance (or the first-law) relations already given are intuitive in nature and are easy to use when the magnitudes and directions of heat and work transfers are known.
  - (**Intuitive means** having the ability to understand or know something without any direct evidence or reasoning process or proof)

- When performing a general analytical study or solving a problem that involves an unknown heat or work interaction,
  - we need to assume a direction for the heat or work interactions.

# Classical thermodynamics

- In such cases, it is common practice to use the classical thermodynamics sign convention and to assume:
  - the heat to be transferred *into the system* in the amount of $Q$ (heat input), and
  - the work to be done *by the system* in the amount of $W$ (work output), and
    * then to solve the problem.

# Various forms of the first-law relation for closed systems

- General : $Q - W = \Delta E$
- Stationary Systems : $Q - W = \Delta U$
- Per unit mass : $q - w = \Delta e$
- Differential form : $\delta q - \delta w = de$

# Specific Heats/Heat capacities

- The ***specific heat*** is defined as *the energy required to raise the temperature of a unit mass of a substance by one degree*.

- Unit: J/(kg.K) = J/(kg.°C) or kJ/(kg.K) = kJ/(kg.°C)

- In general, this energy depends on how the process is executed.

- In thermodynamics, we are interested in two kinds of specific heats:
  - specific heat at constant volume $c_v$ and
  - specific heat at constant pressure $c_p$.

- The specific heat at constant volume $\boldsymbol{c_v}$ can be viewed as *the energy required to raise the temperature of the unit mass of a substance by one degree as the volume is maintained constant.*

- The *energy required* to do the same as the pressure is maintained constant is the specific heat at constant pressure $c_p$.
  - (Volume changes to maintain the pressure).

- The specific heat at constant pressure $c_p$ is always greater than $c_v$ .

- Because at constant pressure the system is allowed to expand and the energy for this expansion work must also be supplied to the system.

- Now we attempt to express the specific heats in terms of other thermodynamic properties.

- First, consider a fixed mass in a stationary closed system undergoing a constant-volume process (and thus no expansion or compression work is involved).

- The conservation of energy principle ($e_{in} - e_{out} = \Delta e_{system}$) for this process can be expressed in the differential form as:
  - $\delta e_{in} - \delta e_{out} = du$

- The left-hand side of this equation represents the net amount of energy transferred to the system.

- From the definition of $c_v$, this energy must be equal to $c_v\, dT$, where $dT$ is the differential change in temperature.

- Thus: $c_v\, dT = du$ at constant volume

or $$c_v = \left( \frac{\partial u}{\partial T} \right)_v$$

- Similarly, an expression for the specific heat at constant pressure $c_p$ can be obtained by considering a constant-pressure expansion or compression process.

- It yields

$$c_p\, dT = dh \qquad \text{at constant pressure}$$

or

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p$$

- A common unit for ***specific heats*** is kJ/(kg·°C) or kJ/(kg·K).

- Notice that these two units are ***identical*** since $\Delta T(°C) = \Delta T(K)$,
- That means 1°C change in temperature is equivalent to a change of 1 K.

- The specific heats are sometimes given on a ***molar basis***.

- They are then denoted by $c_v$ and $c_p$ and have the unit kJ/(kmol·°C) or kJ/(kmol·K).

- Using the definition of ***enthalpy*** and the ***equation of state*** of an ideal gas, we have:
  - $h = u + pv$
    * According to ideal gas law: $pv = RT$
      - Therefore,
        - $h = u + RT$
        - $dh = du + R.dT$

- Hence, then the differential changes in the ***internal energy*** and ***enthalpy*** of an ideal gas can be expressed as:
  - $du = c_v\, dT$
  - $dh = c_p\, dT$

- Then substitute these relations in the following equation:
  - $dh = du + R.dT$
- But, we know that
  - $du = c_v\, dT$
  - $dh = c_p\, dT$
- Then:
  - $c_p\, dT = c_v\, dT + R.dT$
- or
  - $c_p = c_v + R$
  - $c_p - c_v = R$

- The change in internal energy or enthalpy for an ideal gas during a process from state 1 to state 2 is determined by integrating these equations:

$$\Delta u = (u_2 - u_1) = \int_1^2 c_v \, dT \quad (kJ/kg)$$

*and*

$$\Delta h = (h_2 - h_1) = \int_1^2 c_p \, dT \quad (kJ/kg)$$

$$c_p = a + bT + cT^2 + dT^3 + eT^4$$

- Where,

  a, b, c, d, e = constants and are given in tabular form in thermodynamics.

  T = absolute temperature, K

## Ideal Gas Heat Capacity ( Specific Heat ) As Function of Temperature

$$C_p^o\ (J / mol.K) = a + b\,T + c\,T^2 + d\,T^3 + e\,T^4$$

where a, b, c, d, e are constants given below

| Name | a | b | c | d | e |
|---|---|---|---|---|---|
| ACETALDEHYDE | 24.06 | 0.07 | 1.253e-04 | -1.876e-07 | 7.104e-11 |
| ACETIC ACID | 12.13 | 0.19 | -3.184e-05 | -1.068e-07 | 6.05e-11 |
| ACETONE | 24.64 | 0.13 | 1.681e-04 | -2.791e-07 | 1.106e-10 |
| ACETYLENE | 2.67 | 0.22 | -3.888e-04 | 3.37e-07 | -1.116e-10 |
| AMMONIA | 27.26 | 2.313e-04 | 2.243e-07 | -2.169e-10 | 5.41e-14 |
| BENZENE | -55.00 | 0.59 | -5.293e-04 | 2.429e-07 | -4.523e-11 |
| BUTADIENE-1,2 | 11.23 | 0.26 | -1.408e-04 | 2.774e-08 | 4.091e-13 |
| BUTADIENE-1,3 | -27.22 | 0.47 | -4.532e-04 | 2.238e-07 | -4.43e-11 |
| BUTANE | -2.48 | 0.39 | -2.204e-04 | 5.543e-08 | -4.105e-12 |
| BUTYL ACETATE | 13.62 | 0.54 | -2.278e-04 | 7.91e-10 | 0 |
| CARBON DIOXIDE | 17.46 | 0.09 | -1.008e-04 | 6.539e-08 | -1.845e-11 |
| CARBON MONOXIDE | 31.37 | -0.01 | 4.139e-05 | -2.903e-08 | 6.878e-12 |
| CARBON TETRACHLORIDE | 38.54 | 0.22 | -2.977e-04 | 1.796e-07 | -4.06e-11 |
| CHLORINE | 26.55 | 0.03 | -5.072e-05 | 3.14e-08 | -7.219e-12 |
| CHLOROFORM | 22.08 | 0.20 | -2.293e-04 | 1.263e-07 | -2.696e-11 |
| CHLOROMETHANE | 13.30 | 0.10 | -4.193e-05 | 1.082e-09 | 2.424e-12 |

- $c_p - c_v = R$ **or** $c_p = c_v + R$ (kJ/kg.K)

- Ideal-gas property called the **specific heat ratio** $\gamma$, defined as:

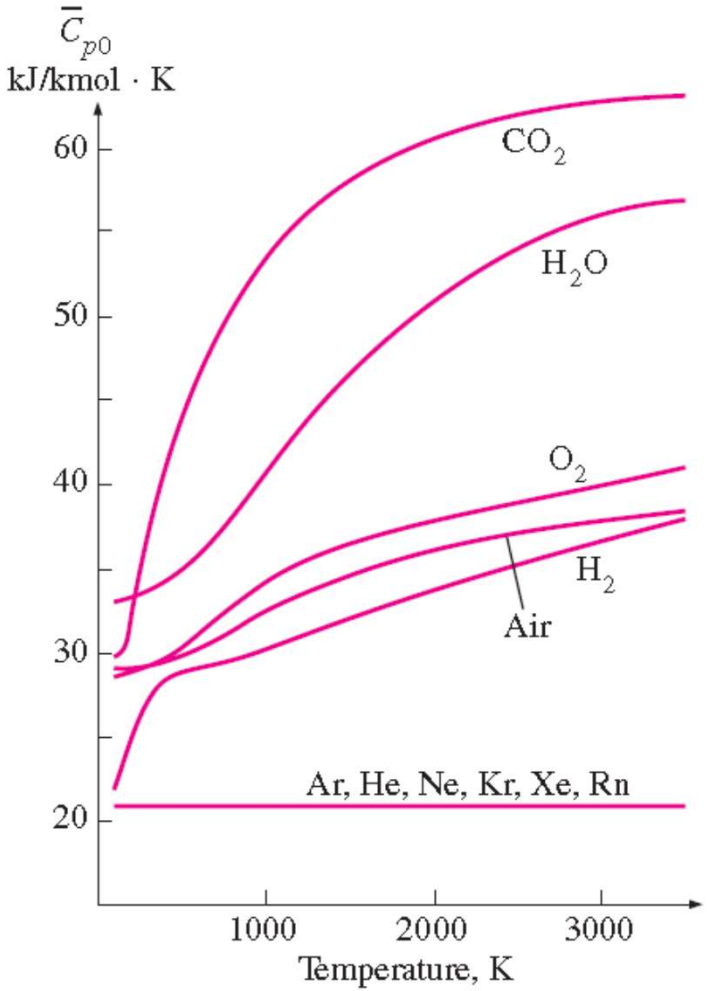
$$\gamma = \frac{c_p}{c_v}$$

- The specific ratio also varies with temperature, but this variation is very mild.

- For monatomic gases, its value is essentially constant at 1.667.

- Many diatomic gases, including air, have a specific heat ratio of about 1.4 at room temperature.

# Ideal-gas constant-pressure specific heats for some gases



## Internal energy, enthalpy, and specific heats of solids and liquids

- It can be mathematically shown that the constant-volume and constant-pressure specific heats are identical for ***incompressible substances***.

- Therefore, for solids and liquids, the subscripts on $c_p$ and $c_v$ can be dropped, and both specific heats can be represented by a single symbol $c$.

$$c_p = c_v = c$$

# References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4. *Cengel, Y. A. and Boles, M., Thermodynamics: An Engineeing Approach, Tata McGraw Hill (2008).*

***Thank you for your Patience***