

## MATERIAL AND ENERGY BALANCE

The First Law of thermodynamics is a formulation of the law of conservation of energy, adapted for thermodynamic processes. A simple formulation is: "the total energy in a system remains constant.

### Intensive and Extensive Variables; Specific Property

**Intensive Variables** – independent of the size of the system – e.g., temperature, pressure, density, composition (mass or mole fraction).

**Extensive Variables** – depend on the size of the system – e.g., mass, number of moles, volume (mass or molar flow rate and volumetric flow rate), kinetic energy ( $K_E=1/2mv^2$ ) potential energy and internal energy.

**Specific Property** – a quantity that is obtained by dividing an extensive property by the total amount of the material.

– denoted by ‘ $\wedge$ ’ → specific volume ( $\hat{V}$ ) units of  $m^3/kg$

– **enthalpy** and **internal energy** commonly reported as specific values

$$\rightarrow \hat{U} = \left(\frac{kJ}{kg}\right), \hat{H} = \left(\frac{kJ}{kg}\right) \rightarrow \hat{H} = \hat{U} + p\hat{V}$$

### Process Classification:

One of the first things that chemical engineer need to know about processes is the many different ways in which we may operate a process. There are three major classifications of processes:

- **Batch Process:** In a batch process, material is placed in the vessel at the start and (only) removed at the end. --no material is exchanged with the surroundings during the process. Batch Examples: fermentations, small-scale chemicals (pharmaceuticals)
- **Continuous Process:** In a continuous process, material flows into and out of the process during the entire duration of time. Continuous Examples: distillation processes.
- **Semi-batch Process:** A semi-batch process is one that does not neatly fit into either of the other categories (i.e., it is a catch-all classification). Semi-Batch Examples: washing machine, fermentation with purge.

## Energy Balances without Reaction:

### Unsteady-State, Closed Systems:

the general energy balance:-

$$\text{Accumulation} = \text{In} - \text{Out} + \text{Generation} - \text{Consumption}$$

generation=0 and consumption=0 since energy cannot be created or destroyed so the general balance becomes:

$$\text{Accumulation} = \text{In} - \text{Out}$$

the general energy balance without reaction :- for a time interval  $t_1$  to  $t_2$  :-

Accumulation = final system energy – initial system energy = net energy transferred to the system

$$\text{initial system energy} = U_i + E_{ki} + E_{pi}$$

$$\text{final system energy} = U_f + E_{kf} + E_{pf}$$

Net energy transferred to the system =  $Q + W$

$$\Delta E_{inside} = (U_f - U_i) + (EK_f - EK_i) + (PE_f - PE_i) = Q + W$$

**OR**

$$\Delta E_{inside} = \Delta U + \Delta EK + \Delta PE = Q + W$$

**For a closed, unsteady-state system the energy balances in the symbols that we have previously defined are:-**

$$\begin{array}{l} \Delta E_{inside} \quad \equiv \quad \Delta(U + PE + KE)_{inside} = \quad Q \quad + \quad W \\ \text{accumulation} \qquad \qquad \qquad \qquad \qquad \qquad \qquad \text{heat transfer} \quad \text{work} \end{array}$$

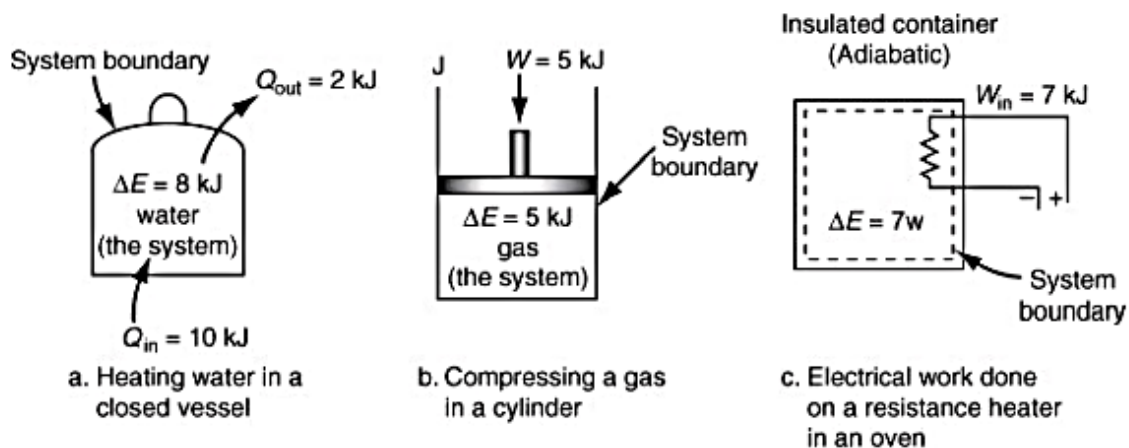
- If several components are involved in the process, then  $U_{inside}$  is the sum of the mass (or moles) of each component  $i$  times the respective specific internal energy of each component  $i$ ,  $\hat{U}_i$ .
- Note that  $(Q + W)$  represents the **total flow of energy** into the closed system.
- We do not put a  $\Delta$  representing the symbol for a change in states before  $Q$  or  $W$  because they are not state variables.

-  $E$  represents the sum of ( $U + KE + PE$ ) associated with mass inside the system itself.

- **In closed systems**, the values of  $\Delta PE$  and  $\Delta KE$  in  $\Delta E$  are usually negligible or zero; hence, often you see  $\Delta U = Q + W$  used as the energy balance.

- If the sum of  $Q$  and  $W$  is positive,  $\Delta E$  **increases**; if negative,  $\Delta E$  **decreases**.

Does  $W_{\text{system}} = -W_{\text{surroundings}}$ ? Not necessarily, as you will learn subsequently. For example, in Figure below the electrical work done by the surroundings on the system degrades into the internal energy (increase of temperature) of the system, not in expanding its boundaries.



### Possible Simplifications:-

- if  $T_{\text{system}} = T_{\text{surroundings}}$ , then  $Q = 0$  since no heat is being transferred due to temperature difference
- if the system is perfectly insulated, then  $Q = 0$  (system is adiabatic) since no heat is being transferred between the system and the surroundings
- if system is not accelerating, then  $\Delta Ek = 0$
- if system is not rising or falling, then  $\Delta Ep = 0$
- if energy is not transferred across the system boundary by a moving part (e.g., piston, impeller, rotor), then  $W = 0$
- if system is at constant temperature (system is isothermal), no phase changes or chemical reactions are taking place, and only minimal pressure changes, then  $\Delta U = 0$

### Steady-State, Closed Systems:-

Recall that steady-state means the accumulation in the system is zero, and that closed means that no mass flow occurs across the system boundary. Only  $Q$  and  $W$  may occur during a time interval.

$$\Delta KE = 0$$

$$\Delta PE = 0$$

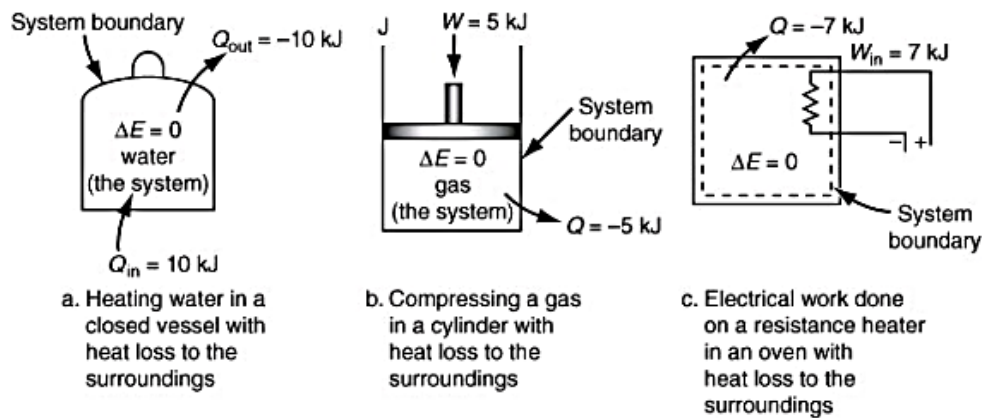
$$\Delta U = 0$$

hence  $\Delta E = 0$

so that

$$Q + W = 0$$

- If you set  $W = -Q$ , you can conclude that all of the work done on a closed, steady-state system must be transferred out as heat ( $-Q$ ) so that the initial and final states of the system are the same. However, ironically, the reverse is false; namely, the heat added to a closed, steady-state system  $Q$  does not always equal the work done by the system ( $-W$ ).



**Foot-pound force (unit: ft.lbf). Foot-pound force is a derived unit of work and energy. It is equal to the energy transferred to an object when a force of one pound-force (lbf) acts on that object in the direction of its motion through a distance of one foot.**

$$1 \text{ foot-pound force} = 1.356 \text{ J}$$

$$1 \text{ foot-pound force} = 0.324 \text{ cal}$$

$$1 \text{ foot-pound force} = 0.00129 \text{ BTU} / 1 \text{ BTU} = 778 \text{ ft.lbf}$$

$$1 \text{ cal} = 4.187 \text{ J}$$

$$1 \text{ Btu} = 1.055 \text{ KJ}$$

$$1 \text{ lb}_m = 0.454 \text{ Kg}$$

$$1 \text{ kpa} = 0.145 \text{ lb}_f/\text{in}^2$$

**Example .3.1.** Convert 45.0 Btu/lbm to the following:

a. cal/kg b. J/kg c. (ft)(lbf)/lbm

**solution:**

Basis: 1 lb<sub>m</sub>

$$a. \frac{45.0 \text{ Btu}}{\text{lb}_m} \left| \frac{252 \text{ cal}}{1 \text{ Btu}} \right| \frac{1 \text{ lb}_m}{0.454 \text{ kg}} = \boxed{2.5 \times 10^4 \text{ cal / kg}}$$

$$b. \frac{45.0 \text{ Btu}}{\text{lb}_m} \left| \frac{1.055 \times 10^3 \text{ J}}{1 \text{ Btu}} \right| \frac{1 \text{ lb}_m}{0.454 \text{ kg}} = \boxed{1.048 \times 10^5 \text{ J / kg}}$$

c.

$$\frac{45.0 \text{ Btu}}{\text{lb}_m} \left| \frac{7.7816 \times 10^2 \text{ (ft) (lb}_f)}{1 \text{ Btu}} \right| = \boxed{3.5 \times 10^4 \text{ (ft)(lb}_f) / \text{lb}_m}$$

**Example.3.2.** What is the potential energy in joules of a 12 kg mass 25 m above a datum plane?

**solution:**

$$PE = mgh = \frac{12 \text{ kg}}{1} \left| \frac{9.80 \text{ m}}{\text{s}^2} \right| \frac{25 \text{ m}}{1} \left| \frac{1(\text{J})(\text{s}^2)}{1(\text{kg})(\text{m}^2)} \right| = \boxed{2940 \text{ J}}$$

**Example.3.3.** Water is heated in a closed pot on top of a stove while being stirred by a paddle wheel. During the process, 30 kJ of heat are transferred to the water, and 5 kJ of heat are lost to the surrounding air. The work done amounts to 500 J. Determine the final internal energy of the system if its initial internal energy was 10 kJ.

Solution:

Closed system

$$Q + W = \Delta U$$

$$\text{In kJ: } (30-5) + 0.5 = U_f - 10$$

$$U_f = 35.5 \text{ kJ unsteady state}$$

**Example.3.4.** A person living in a  $4\text{m} \times 5\text{m} \times 5\text{m}$  room forgets to turn off a 100 W fan before leaving the room, which is at 100 kPa,  $30^\circ\text{C}$ . Will the room be cooler when the person comes back after 5 hr, assuming zero heat transfer? The heat capacity at constant volume for air is( 30 kJ/kg mol.  $^\circ\text{C}$ )

**Solution:**

Closed unsteady state system

$$Q + W = \Delta U \quad Q = 0$$

$$W = \Delta U = C_v \Delta T$$

$$W = \frac{(100 \text{ W})(5 \text{ hr})}{1000 \text{ W}} \left| \frac{1 \text{ kW}}{1 \text{ kW}} \right| \frac{3.6 \times 10^3 \text{ kJ}}{1 \text{ kW}} = 1.8 \times 10^3 \text{ kJ}$$

$$\text{mols of air} = n = \frac{pV}{RT} = \frac{(100 \text{ kPa})(100 \text{ m}^3)}{303 \text{ K}} \left| \frac{(\text{kg mol})(\text{K})}{(8.314)(\text{kPa})(\text{m}^3)} \right| = 3.97 \text{ kg mol}$$

$$1.8 \times 10^3 = 30(3.97)(T - 30) \quad \boxed{T = 45^\circ\text{C}}$$

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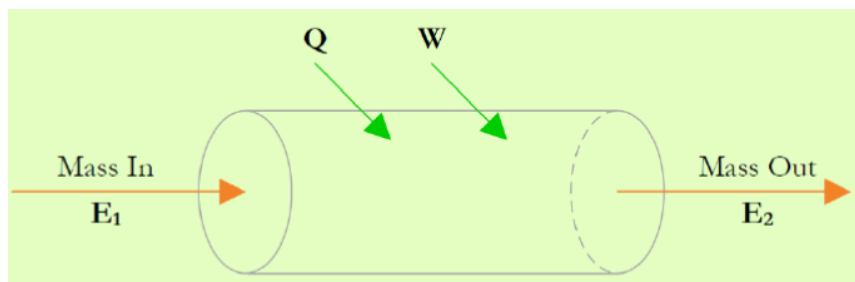
### Energy Balances on Open Systems at Steady-State:

- the preponderance of industrial processes operate under approximately continuous, open, steady-state conditions.

-An open system involves mass flow in the energy balance. If mass flows in and out of a system, the mass carries energy along with it.

**shaft work ( $W_s$ )** – rate of work done by the process fluid on a moving part within the system (e.g., piston, turbine, rotor).

**flow work ( $W_f$ )** – rate of work done by the fluid at the system outlet minus the rate of work done on the fluid at the system inlet.



Since:  $(E=K_E+P_E+U)$

$$\Delta E = Q + W$$

$$E_2 - E_1 = Q + W$$

If there are multiple inlets and outlets:

$$\sum E_2 - \sum E_1 = Q + W$$

The work appearing in the equation is the combined flow work and shaft work:

$$W = W_f + W_s$$

Hence:

$$\sum E_2 - \sum E_1 = Q + (W_f + W_s)$$

The net flow work is determined as:

- Flow work done on the system by the surroundings to introduce material into the system=  
 $m_1(p_1\widehat{V}_1) = (W_f)_1$

- Flow work done by the system on the surroundings to remove material from the system =  
 $-m_2(p_2\widehat{V}_2) = (W_f)_2$

The flow work is usually expressed in terms of pressure and volume:

$$W_f = (pV)_1 - (pV)_2$$

For multiple inlets and outlets:

$$W_f = \sum (pV)_1 - \sum (pV)_2$$

The energy balance becomes:

$$\sum E_2 - \sum E_1 = Q + \left[ \left( \sum (pV)_1 - \sum (pV)_2 \right) + W_s \right]$$

$E = KE + PE + U$ , then:

$$\sum (KE + PE + U)_2 - \sum (KE + PE + U)_1 = Q + \left[ \left( \sum (pV)_1 - \sum (pV)_2 \right) + W_s \right]$$

$H = U + pV$ , then

$$\sum (KE + PE + H)_2 - \sum (KE + PE + H)_1 = Q + W_s$$

$$\Delta(KE + PE + H)_{flows} = Q + W$$

the equation most commonly applied to open, steady-state processes does not include any potential and kinetic energy changes:

$$\Delta H_{flows} = Q + W$$



**In an open, unsteady-state system,** the accumulation term ( $\Delta E$ ) in the energy balance can be nonzero:

$$\Delta E_{inside} = \Delta(KE + PE + U)_{inside} = -\Delta(KE + PE + H)_{flow} + Q + W$$

**Example .3.5.** A closed vessel contains saturated steam at 1000.0 psia in a 4-to-1 vapor volume-to-liquid volume ratio. What is the steam quality?

**Solution:**

Basis: 5 ft<sup>3</sup> vessel

Vapor = 4 ft<sup>3</sup>, Liquid = 1 ft<sup>3</sup>

Steam tables: Sat'd steam at 1000 psia

$$\hat{V}_v = 0.44596 \frac{\text{ft}^3}{\text{lb}}$$

$$\hat{V}_l = 0.02159 \frac{\text{ft}^3}{\text{lb}}$$

lb

mass fr.

$$m_l = \frac{1 \text{ ft}^3}{0.02159 \text{ ft}^3/\text{lb}} =$$

46.32

0.838

$$m_v = \frac{4 \text{ ft}^3}{0.44596 \text{ ft}^3/\text{lb}} =$$

8.97

0.162

$m_t =$

55.29

1.000

|                 |
|-----------------|
| Quality = 0.162 |
|-----------------|

**Example .3.6.** Is it possible to compress an ideal gas in a cylinder with a piston isothermally in an adiabatic process? Explain your answer briefly.

**Solution:** No. The energy balance is  $Q + W = \Delta U$ , and for  $Q = 0$  and since  $\Delta U = 0$  for an isothermal process  $W = 0$ .

**Example .3.7.** A vertical cylinder capped by a piston weighing 990 g contains 100 g of air at 1 atm and 25°C. Calculate the maximum possible final elevation of the piston if 100 J of work are used to raise the cylinder and its contents vertically. Assume that all of the work goes into raising the piston.

Closed unsteady state process

$$Q + W = \Delta U + \Delta(\text{PE})$$

Ignore change in center of mass of the air

$$Q = 0 \quad \text{assumed}$$

$$\Delta U = 0 \quad \text{assumed (to get maximum elevation)}$$

$$W = 100 \text{ J}$$

$$100 = \Delta(\text{PE}) = mg\Delta h = (0.990 \text{ kg}) (9.80 \text{ m/s}^2) \Delta h \text{ (m)}$$

$$\boxed{\Delta h = 10.3 \text{ m}}$$

**Example.3.8.** Two tanks are suspended in a constant temperature bath at 200°F. The first tank contains 1 ft<sup>3</sup> of dry saturated steam. The other tank is evacuated. The two tanks are connected. After equilibrium is reached, the pressure in both tanks is 1 psia. Calculate (a) the work done in the process, (b) the heat transfer to the two tanks, (c) the internal energy change of the steam, and (d) the volume of the second tank.

**Solution:**

Closed, unsteady state process

Initial conditions

$V = 1 \text{ ft}^3$  saturated dry satd. steam (the basis)

Look up

$$\hat{V} = 33.610 \text{ ft}^3/\text{lb}$$

$$\hat{H} = 1145.72 \text{ Btu/lb}$$

$$\hat{U} = 1073.96 \text{ Btu/lb}$$

$$p = 11.548 \text{ psia}$$

Calculate the lb of steam

$$m = \frac{1 \text{ lb}}{33.610 \text{ ft}^3} \left| \frac{1 \text{ ft}^3}{1} \right| = 0.02975 \text{ lb}$$

$$Q + W = \Delta U$$

a.  $\boxed{W = 0}$  (fixed boundary)

$$Q = \Delta U$$

b&c.  $\Delta U = U_2 - U_1 = (1077.48) (0.02975) - (1073.96) (0.02975) = \boxed{0.105 \text{ Btu}} = Q$

d. The volume of the second tank is  $V_{\text{final}} = (392.713) (0.02975) = 11.68$   
 $V_2 = 11.68 - 1 = 10.68 \text{ ft}^3$

Final conditions

$$V = 1 \text{ ft}^3 (\text{known}) + V_2$$

At  $p = 1 \text{ psia}$   $T = 200^\circ\text{F}$ . The water is vapor

From the steam tables:

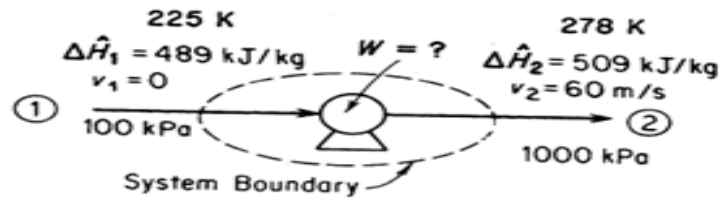
$$\hat{H} = 1150.15 \text{ Btu/lb}$$

$$\hat{U} = 1077.48 \text{ Btu/lb}$$

$$\hat{V} = 392.713 \text{ ft}^3/\text{lb}$$

**Example 3.9.** Air is being compressed from 100 kPa and 255 K (where it has an enthalpy of 489 kJ/kg) to 1000 kPa and 278 K (where it has an enthalpy of 509 kJ/kg). The exit velocity of the air from the compressor is 60 m/s. What is the power required (in kilowatts) for the compressor if the load is 100 kg/hr of air? (Assume that: the entering velocity of the air is zero,  $Q = 0$ , steady state).

**Solution:**



flow process (open system).

Basis: 100 kg of air = 1 hr

$$\Delta(KE + PE + H)_{flows} = Q + W$$

$$m_1 = m_2 = m = 100 \text{ kg}$$

$$\Delta PE = 0, Q = 0$$

$$\Delta KE + \Delta H = W$$

$$\Delta H = \frac{(509 - 489) \text{ kJ}}{\text{kg}} \Big| \frac{100 \text{ kg}}{1} = 2000 \text{ kJ}$$

$$\Delta KE = \frac{1}{2} m (v_2^2 - v_1^2)$$

$$= \left( \frac{1}{2} \right) \frac{100 \text{ kg}}{1} \Big| \frac{(60 \text{ m/s})^2}{\text{s}^2} \Big| \frac{1 \text{ kJ}}{\frac{1000(\text{kg})(\text{m}^2)}{(\text{s})^2}} = 180 \text{ kJ}$$

$$W = (2000 + 180) = 2180 \text{ kJ}$$

(Note: The positive sign indicates work is done on the air.)

To convert to power (work/time),

$$\text{kW} = \frac{2180 \text{ kJ}}{1 \text{ hr}} \Big| \frac{1 \text{ kW}}{1 \text{ kJ}} \Big| \frac{1 \text{ hr}}{3600 \text{ s}} = \boxed{0.61 \text{ kW}}$$