

CHEMICAL ENGINEERING THERMODYNAMICS

CHE F213/ C311

**Chapter 2 : The First Law and
other basic concepts**

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Understanding Energy

- Difficult to define in general, but is defined as capacity of a body to do work (causes an effect)
 - SI units: Joules
- Can be classified as energy in transition and energy in storage
 - Energy transferred as a result of potential difference is **energy is transition**. Loss of identity as soon as soon as energy enters and leaves a system, e.g., gradient of force, and temperature result in transfer of mechanical work, heat respectively
 - **Stored energy** possessed by a system as a result of its position in a force field, its motion, its atomic or molecular structure etc. Examples are kinetic, rotational or vibrational energy, chemical or nuclear energy etc.

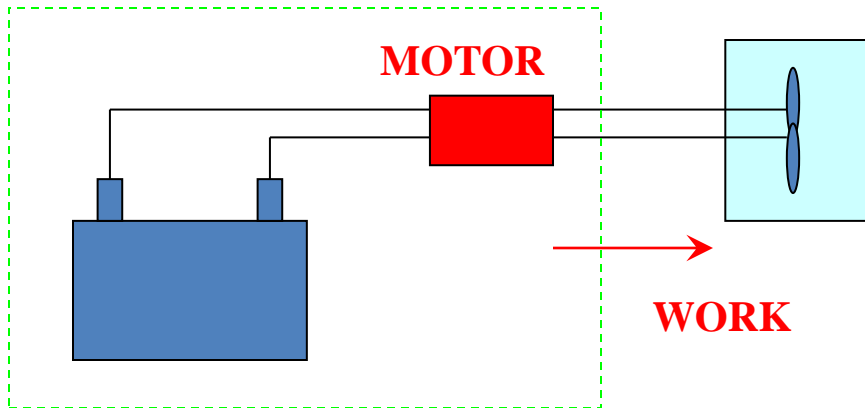
The concept of thermodynamic work

- By definition it is Force times displacement, the latter measured in the direction of the force from the point of application
- In thermodynamic language: *Work is said to be done by a system if the sole effect on the surroundings is reduced to lifting of weight*

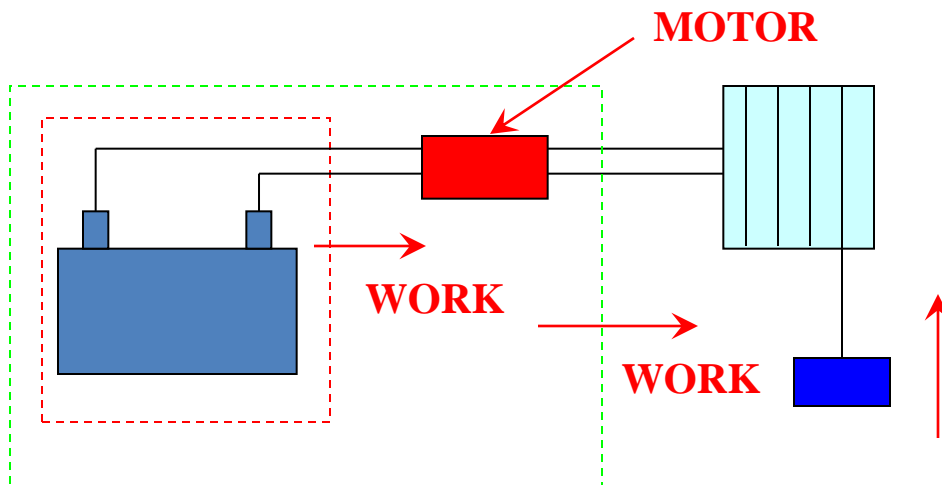
Note The definition does not call for actual raising of a weight, but rather the possibility of a weight being raised

- Thermodynamic work is energy in transition and is manifest at the system boundary only during system-surrounding interaction.

The concept of thermodynamic work



Work crosses system boundary in both cases (green and red boundaries)



Flow of electricity across a system is equivalent to work crossing the system boundary

The concept of heat

- In the case of paddle wheel work, temperature rises, i.e. a change of state occurs
- The same state can be brought about if heat entered the system instead of work
- Heat is energy as work is and has units of work
- Heat is thus defined as energy in transition flowing by a virtue of a temperature difference between two systems or between a system and its surroundings
- It manifests only at the system boundary and cannot be contained

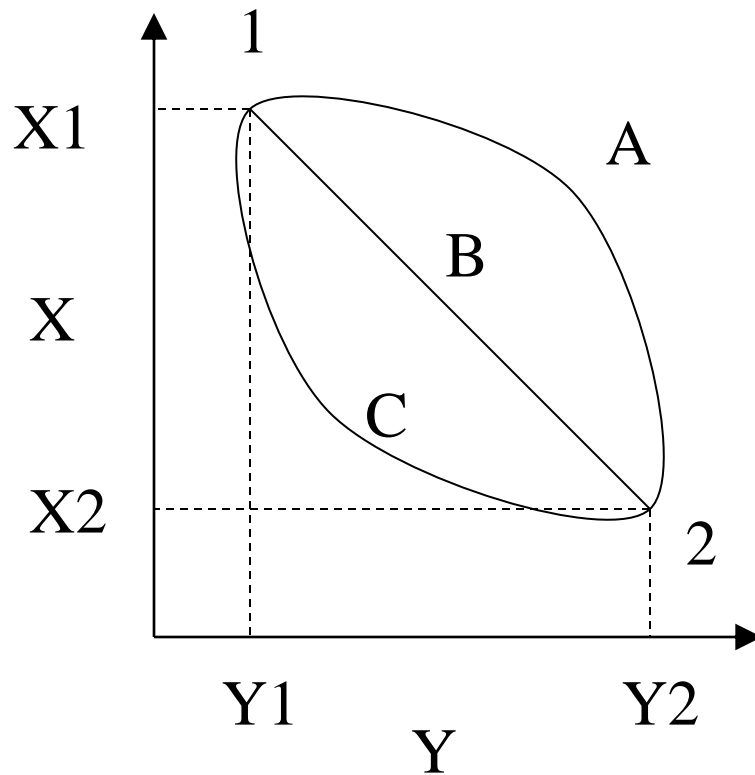
The concept of heat

- Heat entering a system is positive (added to) and leaving a system is negative
- A process in which no heat transfer takes place is an adiabatic process
- In a closed system an application of work or heat can cause a change of state
 - When heat is added to a pure substance it is seen that either the phase changes with temperature remaining constant (saturation state) or temperature changes with substance remaining in the same phase
 - In the former case it is called latent heat and in the latter sensible heat
 - Heat transfer by 3 modes: conduction, convection or radiation

Sign convention

- Conventions important when solving problems
- System and surroundings do equal, but opposite work and heat interactions
 - $W_{\text{by the system}} = -W_{\text{on the system}}$
 - $Q_{\text{into system}} = -Q_{\text{out from the system}}$
- Heat Q and work W always refer to the system, and modern sign convention makes the numerical values of both the quantities positive for transfer into the system from the surroundings.

State function & Path function



Note 1-C-2-A-1 is a cycle

State/Point function Independent of path followed by system. State 2 is a point function

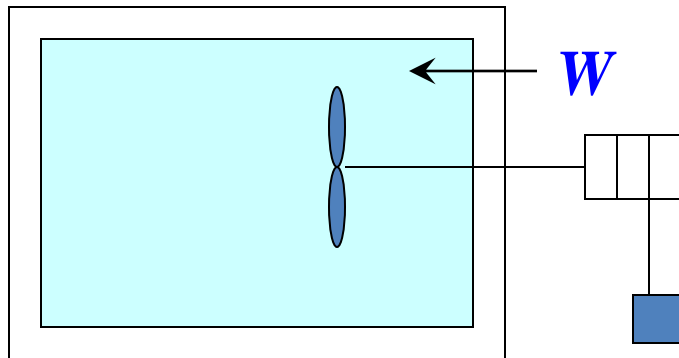
Change in state = Final value of property – initial value

Path function Path dependent (1-C-2, 1-A-2, 1-B-2)

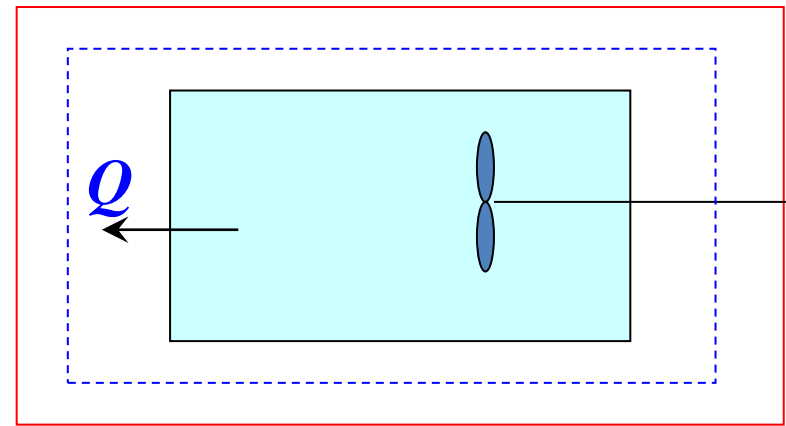
Integration required to determine the quantity which is path dependent.

Joule's experiment

- In 1840's, Joule performed a series of experiments in which he measured the heat produced from measured amount of work
- This experiment led to the formulation of the first law of thermodynamics
- A two process cycle carried out on a system with a fluid



Insulated system



Insulated system

Experiments designed to prove the energy equivalence of heat & work

Form in which energy is transferred to water	Mechanism used	Form of energy supplied to mechanism	Method of measuring energy input	Corrections that must be made to energy input data
Mechanical Energy	Stirring: Paddle wheel driven by electrical motor	Electrical energy	Product of voltage, current and time	Electrical energy loss in motor and circuit, temperature rise of paddle wheel
Mechanical Energy	Stirring: Paddle wheel driven by pulley and falling weight	Mechanical energy	Change in potential energy of weight: $m g h$	Temperature rise of paddle wheel
Heat flow	Electrical energy converted to heat in a resistor	Electrical energy	Product of voltage, current and time	Temperature rise in resistor and electrical losses in circuit

Joule's experiment

- Joule repeated his experiment for various systems and for different amount of work interactions and measuring the corresponding amount of heat transfer in each case for bringing system back to original state.
- He found that net work input W was always equal to the net amount heat transfer Q from the system (equal in magnitude when same units are used)
- From the experiments, it was found that a fixed quantitative relationship existed between the heat and work for a cyclical process.

First Law for a system undergoing a thermodynamic cycle

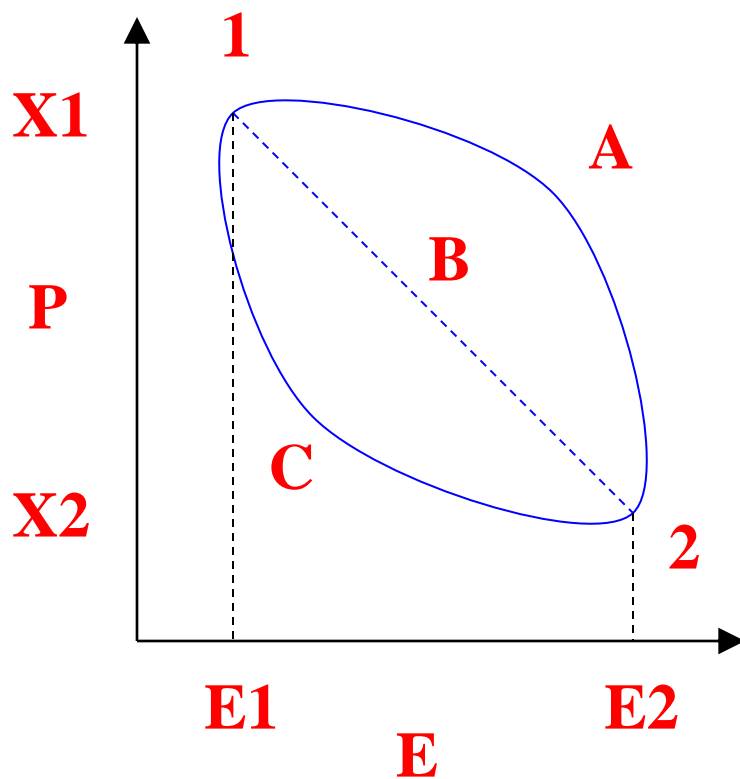
Since system at the end is restored to its original state he concluded that the algebraic sum of heat and work interactions during a thermodynamic cycle is zero, thus

During a cycle, a system undergoes, the cyclic integral of heat added is equal to the cyclic integral of work done

$$\oint \delta Q + \oint \delta W = 0$$

- The symbol δ is used to indicate that W and Q are inexact differentials
- Note the constraints of this law: **applies to a closed system and only to a thermodynamic cycle**
- Both heat and work have same units

First Law for a process in a closed system



Path 1-A-2-B-1

$$\int_{1-2} \delta Q_A + \int_{2-1} \delta Q_B + \int_{1-2} \delta W_A + \int_{2-1} \delta W_B = 0$$

Path 1-A-2-C-1

$$\int_{1-2} \delta Q_A + \int_{2-1} \delta Q_C + \int_{1-2} \delta W_A + \int_{2-1} \delta W_C = 0$$

Subtracting and rearranging

$$\int_{1-2} (\delta Q + \delta W)_B = \int_{1-2} (\delta Q + \delta W)_C$$

First Law for a process in a closed system

- It is seen that for any change in the state of a system, the quantity $(\delta Q + \delta W)$ is always the same for any path
- It is independent of the path followed for this change of state. It is a point or state function and hence a property
- The source of this energy lies within the system itself, where energy is stored in some fashion. This property is called **Stored** energy

$$\delta Q + \delta W = dE$$

dE used because it is an exact differential. *Integrating,*

$$Q_{1-2} + W_{1-2} = E_2 - E_1 = \Delta E$$

First law for a closed system where $E_2 - E_1$ is change in stored energy.

Symbol Δ always indicate final condition minus initial condition

First Law of thermodynamics for a process in a closed system

- Heat added to a system goes to increase stored energy and can result in work

The basis of first law is thus the law of conservation of energy

Net energy added to a system = Energy in – Energy out = increase in stored energy

- For isolated system W and $Q = 0$. Hence $E_2 = E_1$. The stored energy of an isolated system remains constant
- For a cycle no change in state so stored energy change is zero

The concept of internal energy

- Stored energy represents energy present in macroscopic and microscopic forms
- Macroscopic: KE and PE
- Microscopic: Energy associated with motion, position and chemical bonding and configuration of individual molecules
- In absence of electrical, magnetic, surface tension effects

$$\Delta E = \Delta U + \Delta KE + \Delta PE$$

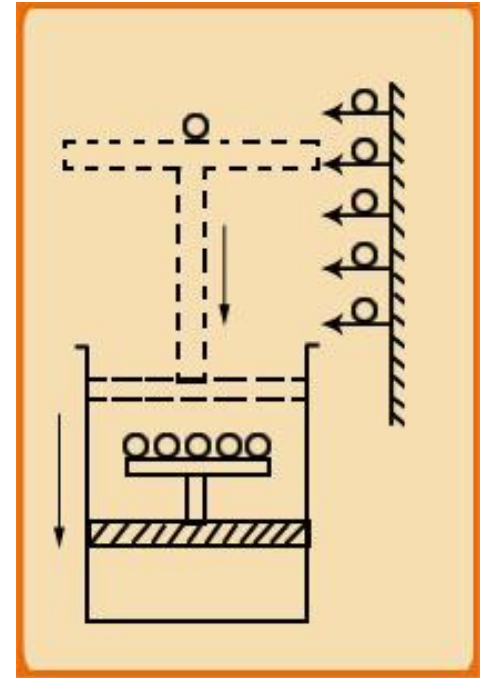
- For stationary systems ΔKE and $\Delta PE = 0$ and $\Delta E = \Delta U$
- U is known as internal energy
- Units are the same as the units of heat and work (Joule)
- Internal energy per unit mass is specific internal energy (Tables give this value)

Reversible Process

- A process is reversible if it can be completely reversed, i.e. when carried out in the opposite direction the system follows the same succession of states as it followed in the forward direction (very crude definition)
- *A process is reversible if after the process occurs, the system can be restored to its original state without any effect on its surroundings i.e. both system and surroundings are restored to initial conditions*
- *This effect occurs only when the driving force is infinitesimally small*
- A reversible process leaves no history of the process after it is reversed

Reversibility

- Take the example of the simple gas-in-piston-and-cylinder system as shown in figure
 - No friction involved
 - Putting succession of infinitesimal masses to piston : Potential energy to compression work into the system
 - If the direction of transfer of mass is reversed, the process reverses and proceeds backward along with it's original path.
- A reversible process is one in which all potential are always in balance and the system is never more than differentially away from an equilibrium state.



Example of reversible processes are:

Frictionless motion of solids

Slow frictionless adiabatic expansion/compression of a gas

Slow isothermal compression/expansion of a gas

Irreversibility

- A process which is not reversible is irreversible
- If a system in this case is restored to its original state, surroundings must be altered
- Irreversible processes have friction and are carried out with finite driving forces
- All processes carried out in finite time with real substances are accompanied in some degree by dissipative effects of one kind or another.
- Caused by friction, unrestrained expansion, mixing of substances, combustion, flow of electricity through a resistor, heat transfer over a finite temperature difference etc.

Reversible Work Calculation

- The work of expansion or compression of a gas caused by differential displacement of a piston in cylinder

$${}_1W_2 = \int \delta W = -\int P dV$$

This equation is valid within limits of reversible process:

- The system should be in internal equilibrium
- Mechanical equilibrium (internal pressure should balance with the external force)

- The integral represents the area under the $P - V$ diagram
- Work done can be found by integration provided a relationship between P and V is known

Energy balance for a closed system

- For n moles of a homogeneous fluid contained in a closed system the energy balance is:

$$d(nU) = dQ + dW \quad \text{or} \quad d(nU) = dQ - P d(nV)$$

For a mechanically reversible, closed-system process $dW = -P d(nV)$

Constant Volume Process

If a process occurs at constant total volume, the work is zero, thus the energy balance will reduced to

$$d(nU) = dQ \quad \text{or} \quad Q = n \Delta U$$

Thus the heat transferred in a mechanically reversible, constant-volume, closed system process equals the internal-energy change of the system.

Constant Pressure Process

- The general energy balance for closed system

$$dQ = d(nU) + P d(nV)$$

- For a constant pressure change of state

$$dQ = d(nU) + d(n P V) = d[n(U + PV)]$$

$U + PV$ group suggest a convenience thermodynamic property of interest called **enthalpy H**.

$$H = U + PV$$

- The proceeding energy balance can be written as

$$dQ = d n H \text{ ~~} dQ \text{ } \text{ or } Q = n \Delta H~~$$

Thus the heat transferred in a mechanically reversible, constant-pressure, closed system process equals the enthalpy change of the system.

The concept of enthalpy

- For system open to mass, one additional flow of energy must be included, which arises from the fact that as an element of fluid moves, it does work on the fluid ahead of it.
- Each of these work term are $P\Delta V$ type and occurs only to the system open to mass flow.
- Most processes in nature take place at constant pressure as compared to constant volume
- So if the volume is not constant during a process, some provision must be made to accommodate this change in volume, i.e. some energy must be spent on this (increasing or decreasing volume)

The concept of enthalpy

- Enthalpy is defined as the total energy content in a system
- Enthalpy has same units as that of internal energy or work and is denoted by H or h

$$H = U + PV \text{ or } h = u + Pv$$

- It is a property like internal energy
- Enthalpy per unit mass is specific enthalpy
- Being an intensive state function, enthalpy can be calculated as function of temperature and pressure for future use in calculation of Q and W for any process involving these substance.

The concept of Heat Capacity

- We know that it takes different amounts of energy to raise the temperature of identical masses of different substances by 1 degree
- For example 4.5 kJ are needed to raise the temperature of 1 kg of iron from 20 to 30 °C whereas it takes 9 times this energy (41.8 kJ to be exact) to raise the temperature of 1 kg of water by the same amount
- Why is this so? This needs to be understood
- This is because different substances have different energy storing capabilities

The concept of heat capacity

- It is thus desirable to have a tool that enables us to compare the energy storage capabilities of various substances. Such a tool is heat capacity, (on unit mass basis called specific heat).

It is defined as the energy required to raise the temperature of a unit mass of a substance by one degree

- Denoting Heat capacity by C and specific heat by c , we have by definition

$$C = \delta Q / dT \text{ or } c = \delta q / dT$$

- The SI unit of specific heat (c) is kJ/kg.K
- Since heat transfer is a path function, specific heat is a process dependent quantity

Specific heat at constant volume and pressure

- In general however this energy would depend on how the process is executed
- **Specific heat at constant volume (C_v):** It is viewed as the energy required to raise the temperature of a unit mass of a substance by one degree as the volume is maintained constant
- **Specific heat at constant pressure (C_p):** The energy required to raise the temperature of a unit mass of a substance by one degree at constant pressure is the specific heat at constant pressure
- The specific heat at constant pressure will always be greater than that at constant volume because at constant pressure the system can change volume and energy for this expansion must be supplied

Specific heat at constant volume

From definition of specific heat

$$c_v = (\delta q / dT)_v = (1/m)(\delta Q / dT)_v$$

Since $P dV = 0$, $\delta Q = dU$ (from First Law)

$$c_v = (\delta u / dT)_v = (1/m)(dU / dT)_v$$

This is nothing but the change in internal energy with temperature

Specific heat at constant pressure

From definition of specific heat

$$c_p = (\delta q / dT)_p = (1/m)(\delta Q / dT)_p$$

Since $\delta Q = dH$ (for constant pressure reversible process)

$$c_p = (\delta h / dT)_p = (1/m)(dH/dT)_p$$

This is nothing but the change in enthalpy with temperature

Specific heat at constant volume and pressure

- Unlike c , c_p and c_v are state functions and hence are properties
- The expressions for both contain thermodynamic properties and can be written as

$$c_p = f(h, T, P) \text{ and } c_v = f(u, T, v)$$

- The difference between c_p and c_v is not very large
- Both c_p and c_v are temperature dependent
- For a given mass, specific heat values will be different if temperature changes from 300 – 301 K as compared to a change of temperature from 1000 – 1001 K
- For solids and liquids specific volume is small and its changes insignificant. There is only one specific heat.
Thus $\delta q = dh = du = c dT$

Mass and Energy Balances for Open Systems

- The laws of mass and energy conservation apply to all processes, to open as well as to closed systems
- Measures of flow
 - Mass flowrate, \dot{m}
 - Molar flowrate, \dot{n}
 - Volumetric flowrate, q
 - Velocity, u

} measure of quantity per unit time
- Interrelations

$\dot{m} = M\dot{n}$	and	$q = uA$
$\dot{m} = uA\rho$	and	$\dot{n} = uA\rho_m$

where M = molar mass, A = cross sectional area for flow, ρ = density, ρ_m = molar density and u = velocity.

The general balance

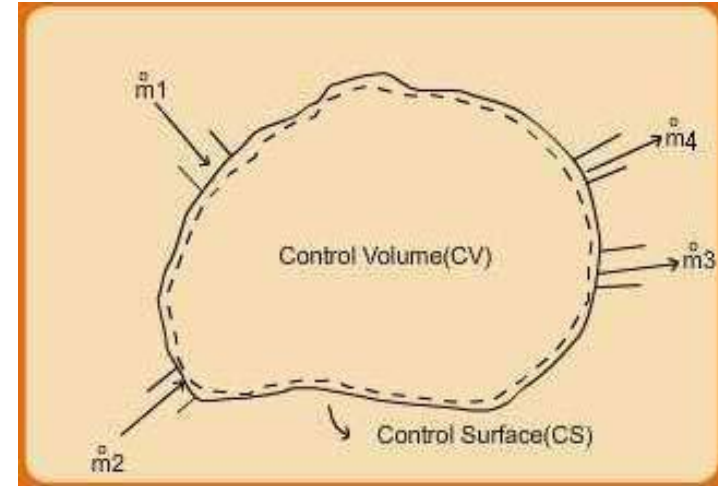
- Each year 50,000 people move into a city; 20,000 move out; 22,000 are born and 10,000 die. Write a balance on the population on the city...

A balance on the conserved quantity in a system, may be written in general way:

$$\begin{array}{ccccccc} \text{Input} & & \text{generation} & & \text{Output} & & \text{consumption} & & \text{Accumulation} \\ \text{(enters} & & \text{(produced} & & \text{(leaves} & & \text{(consumed} & & \text{(Buildup} \\ \text{through} & + & \text{within} & - & \text{through} & - & \text{within} & = & \text{Within} \\ \text{system} & & \text{system)} & & \text{system} & & \text{system)} & & \text{system)} \\ \text{boundary)} & & & & \text{boundaries)} & & & & \end{array}$$

Mass balance for open system

- The conservation law to an open system is applied to fixed region in space (control volume) with a defined boundary (control surface)
- Mass can flow across the boundary of the control volume
- Consider an open system with which has multiple inlets (1, 2) and outlets (3, 4)



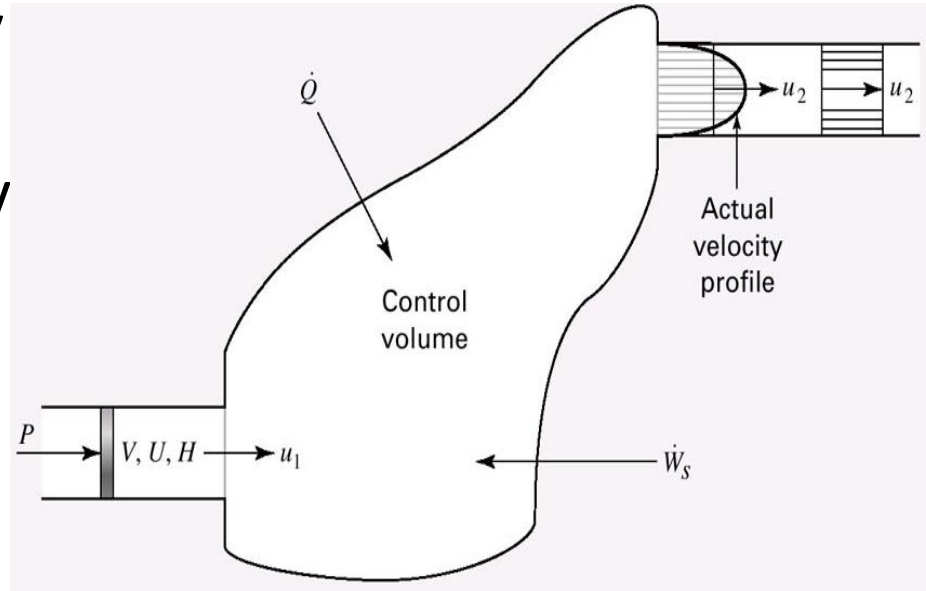
$$\frac{dm_{cv}}{dt} + \Delta(\dot{m})_{fs} = 0$$

where the second term for the control volume is

$$\Delta(\dot{m})_{fs} = \dot{m}_4 + \dot{m}_3 - \dot{m}_2 - \dot{m}_1$$

The general energy balance

- The rate of change of energy within the control volume equals the net rate of energy transfer into the control volume
- Each unit mass of a stream carries with it a total energy of $U + u^2 / 2 + zg$
- The rate of energy accumulation within the control volume includes this quantity in addition to the heat transfer rate Q and work rate (refer 2.12 for detailed derivation)



$$\frac{d(mU)_{cv}}{dt} + \Delta \left[(H + u^2 / 2 + zg) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}$$

Illustration

The heating of a home to increase its temperature must be modeled as an open system, because expansion of the household air at constant pressure results in leakage of air to the outdoors. Assuming that the molar properties of air leaving the home are the same as those of the air in the home, show that energy and mole balances yield the following differential equation:

$$\dot{Q} = -PV \frac{dn}{dt} + n \frac{dU}{dt}$$

$$\frac{dn_{cv}}{dt} + \Delta(\dot{n})_{fs} = 0$$

$$\frac{d(nU)_{cv}}{dt} + \Delta[(H + u^2 / 2 + zg)\dot{n}]_{fs} = \dot{Q} + \dot{W}$$

Energy balance for steady-state flow processes

- For steady state processes, the accumulation term

$d(mU)_{CV} / dt$ is zero

- This means that the mass of the system within CV is constant
- No change occur with time in the properties of the fluid within the CV nor at its entrance and exits

$$\Delta \left[\left\{ H + \frac{u^2}{2} + zg \right\} \dot{m} \right]_{fs} = \dot{Q} + \dot{W}$$

- Division by \dot{m} gives $\Delta H + \frac{\Delta u^2}{2} + g\Delta Z = Q + W_s$

Illustration

Water flows through a horizontal coil heated from the outside by high-temperature flue gases. As it passes through the coil the water changes state from liquid at 200 kPa and 80°C to vapor at 100 kPa and 125 °C. Its entering velocity is 3 m/s and exit velocity is 200 m/s. Determine the heat transferred through the coil per unit mass of water. Enthalpies of the inlet and outlet streams are (Inlet: 334.9 kJ/kg ; Outlet: 2726.5 kJ/kg)

- **Solution:** For ss process

$$\Delta H + \frac{\Delta u^2}{2} + g\Delta Z = Q + W_s$$

Here no significant change in potential energy, no shaft work

$$Q := H_2 - H_1 + \frac{u_2^2 - u_1^2}{2}$$

Calorimetry

- Calorimetry: The technique of measuring heat
- Calorimeter: The instrument containing the system with which heat is exchanged
- Three widely used types among many types
 - Bomb calorimeter (Closed vessel of fixed volume $Q = \Delta U$, measure heat of combustion, Calorific Value)
 - Mixing calorimeter (heat of mixing at constant pressure $Q = \Delta H$)
 - Flow calorimeter ($Q = \Delta H$, measure enthalpy of phase change) * Refer book for detailed description

Instruments are so designed that there are no work, PE, KE effects.

A Flow Calorimeter for Enthalpy Measurement

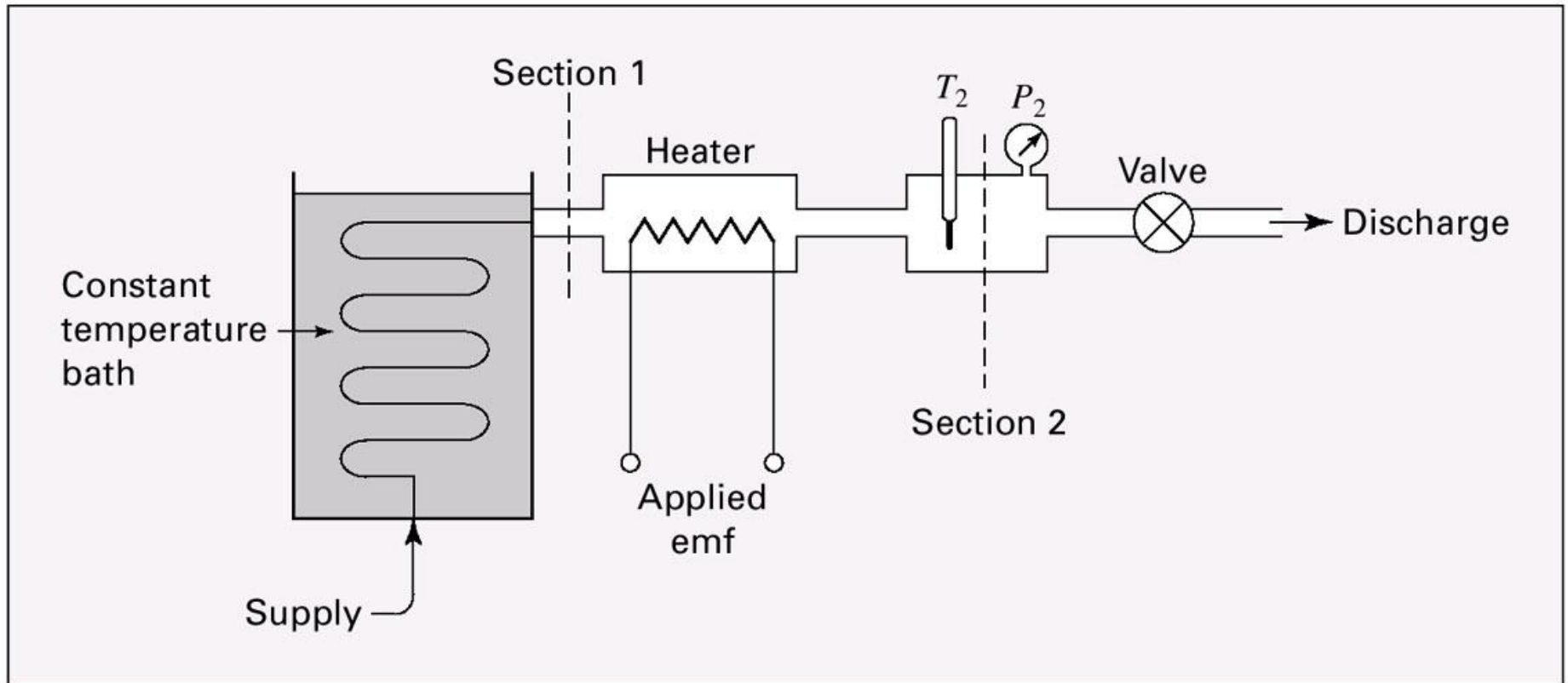


Figure 2.7: Flow calorimeter.