

CH2303 Chemical Engineering Thermodynamics I

Unit – II

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First Law of Thermodynamics

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Contents

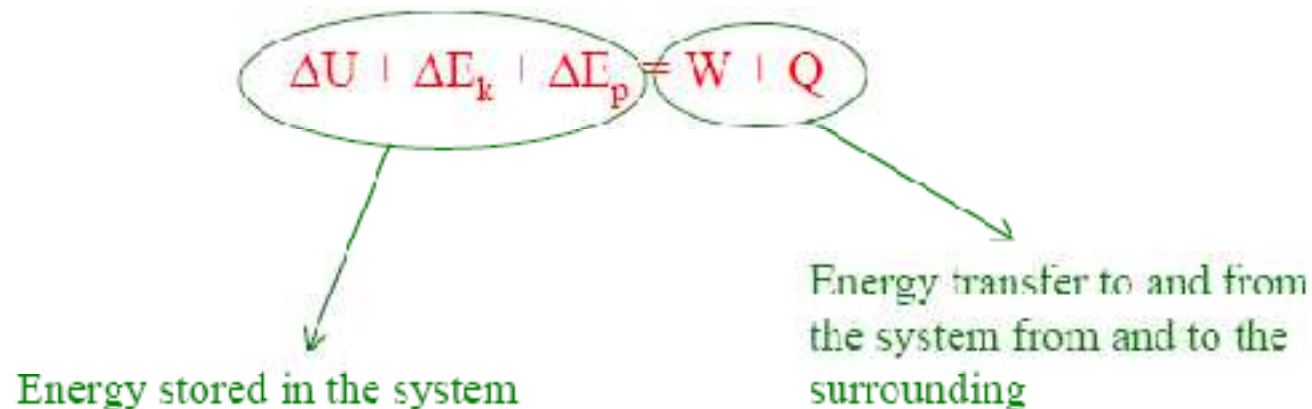
- Statements of first law for the non flow and flow systems, enthalpy and heat capacity

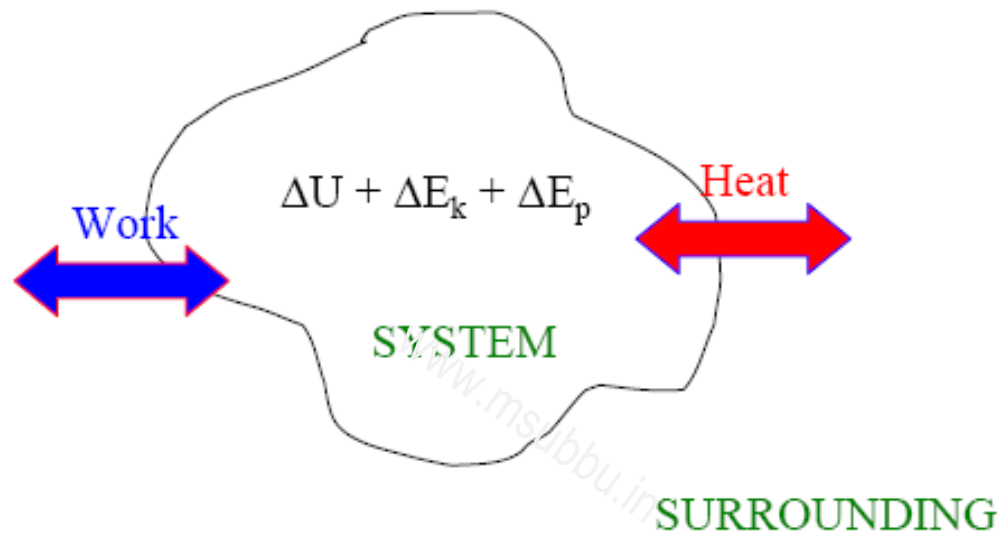
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First Law of Thermodynamics

- It's the law of conservation of energy
- *Change in total energy of the system is compensated by an equal and opposite change in the total energy of the surroundings.*

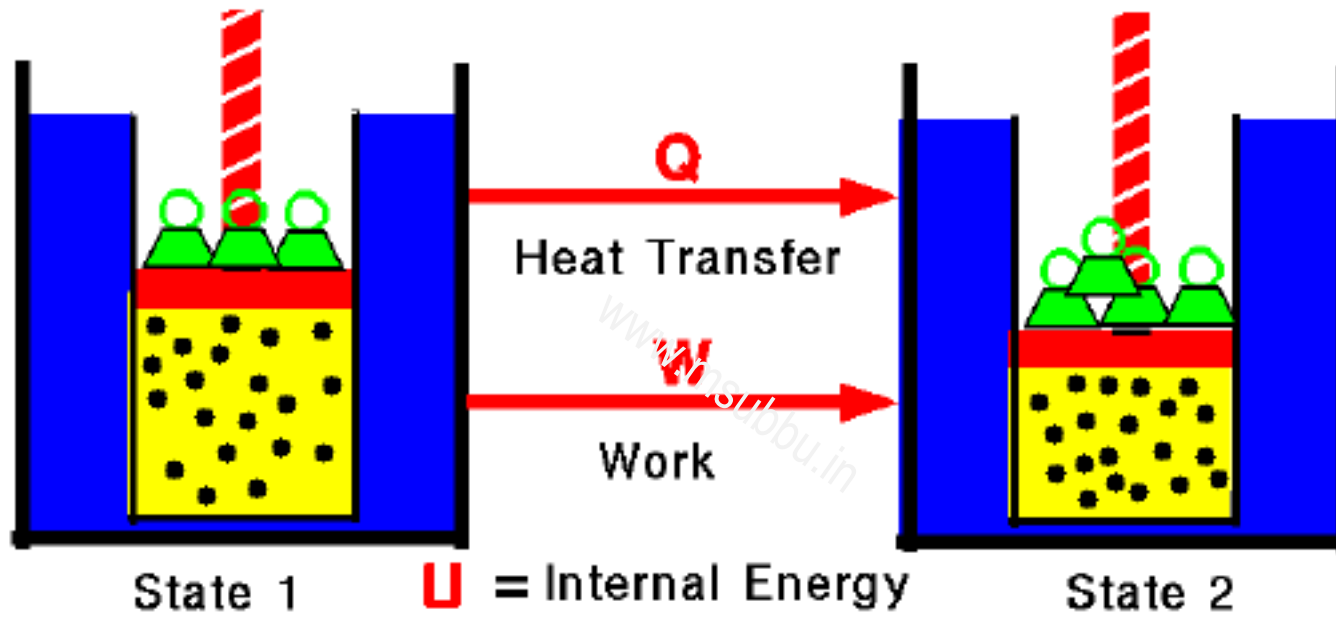
For a closed system:





In many applications of the first law, the system undergoes no change in external potential or kinetic energy, but only changes in internal energy. For these non-flow processes, the first law becomes:

$$\Delta U = Q + W$$



State 1

U = Internal Energy

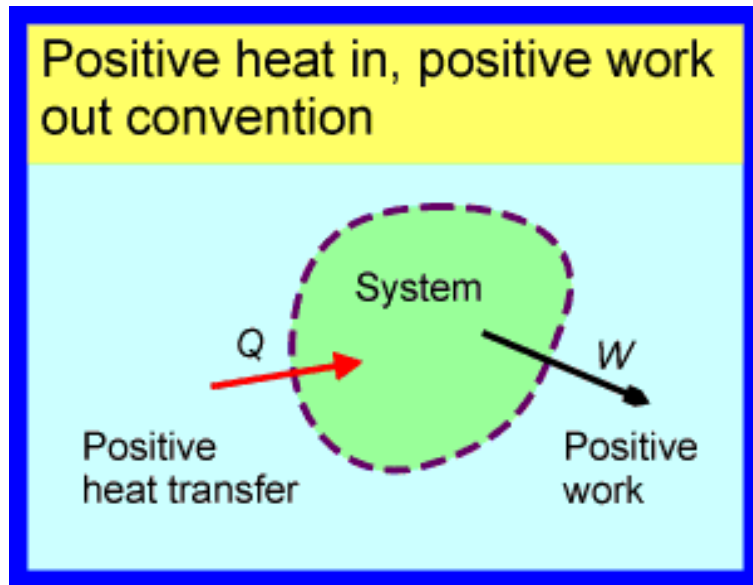
State 2

$$U_2 - U_1 = Q + W$$

Sign conventions for heat and work

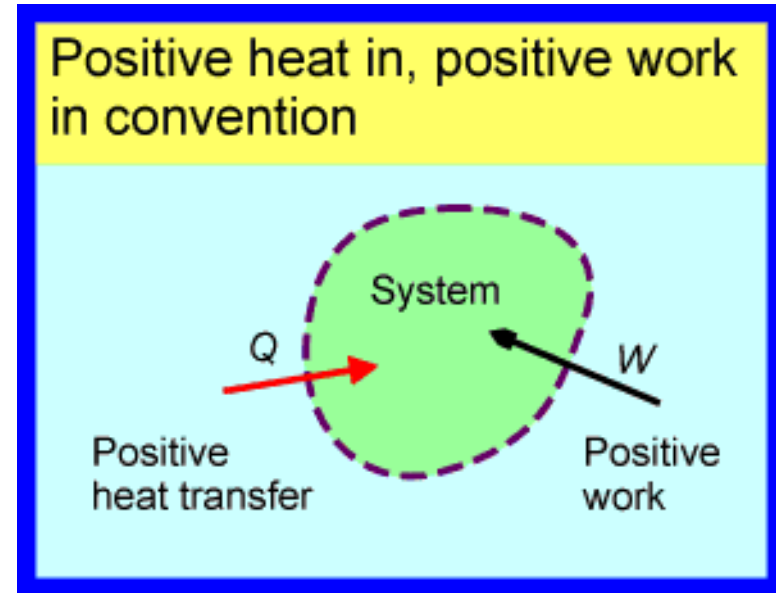
There are two sign conventions in common use.

1



$$\Delta U = Q - W$$

2

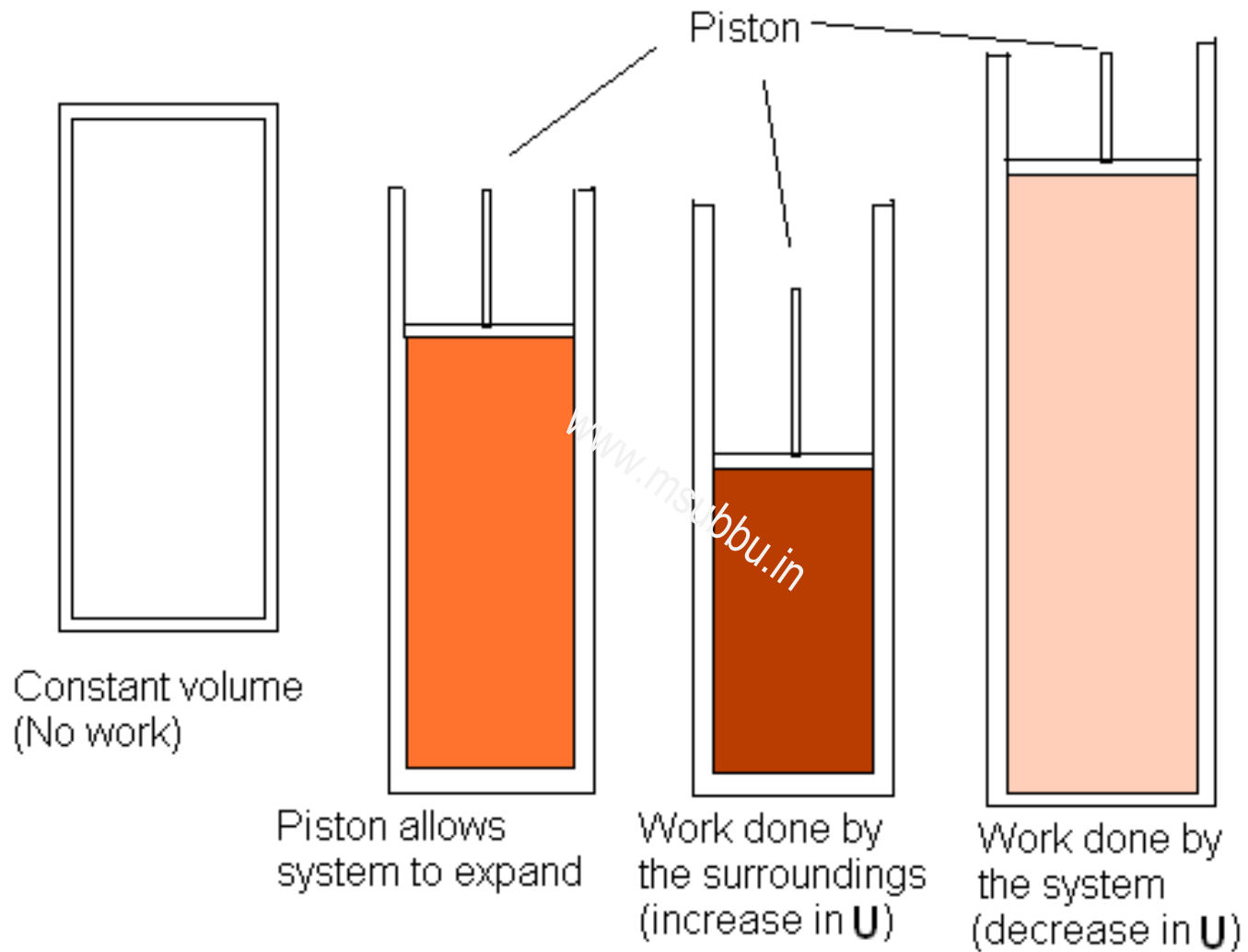


$$\Delta U = Q + W$$

We use the above convention

Sign conventions for heat and work (contd.)

- The first is still the most common in the English-speaking world and probably dates back to the introduction of steam engines. In that era, engineers were particularly interested in heat engines for pumping water or driving machinery. The desired output was work and the required input was heat. It made sense to describe both as positive quantities.
- The second sign convention, which I favour, is the most common in the non-English-speaking world. According to this convention heat and work are both taken as positive when their direction is into the system of interest.
- In my opinion the second convention is the most consistent, as all transfers or interactions at the boundary can be treated in the same way: they are taken as positive when inwards and negative when outwards. **We will use the second convention.**



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Enthalpy

Enthalpy denoted as H is defined as below:

$$H = U + PV$$

Differentiating,

$$dH = dU + PdV + VdP$$

Substituting for dU from

$$\begin{aligned} dU &= dQ + dW \\ &= dQ - PdV \end{aligned}$$

Therefore,

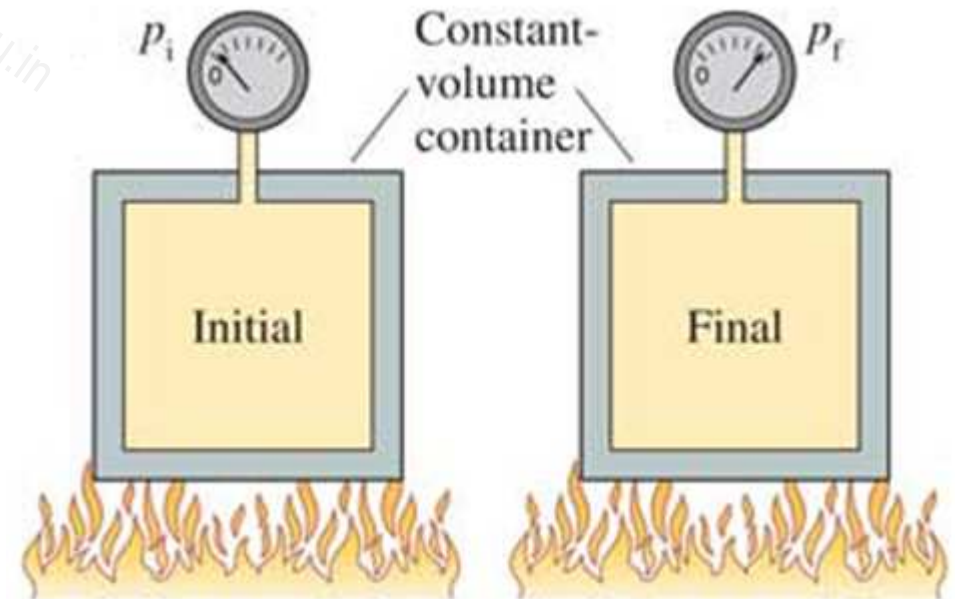
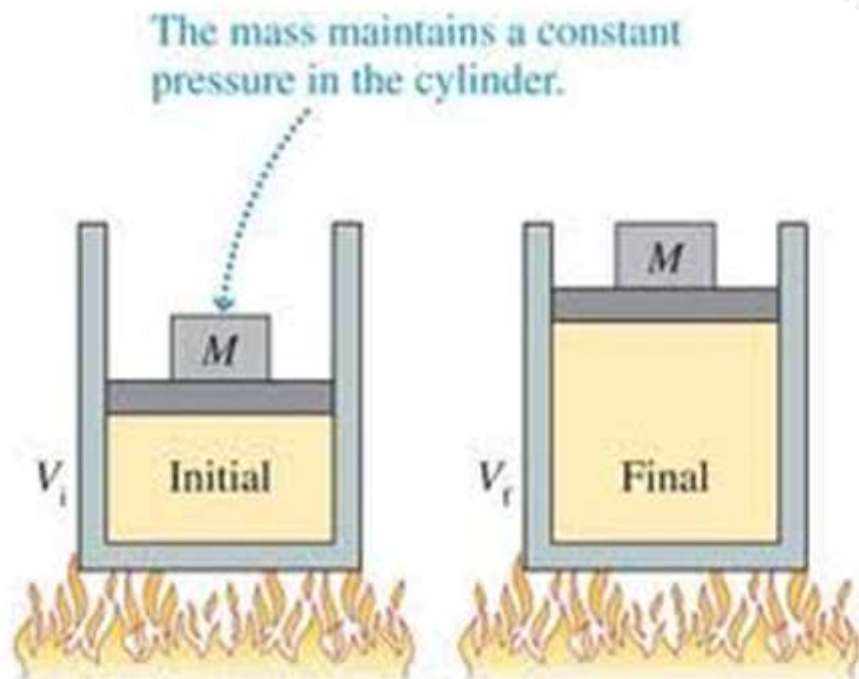
$$\begin{aligned} dH &= dQ - PdV + PdV + VdP \\ &= dQ + VdP \end{aligned}$$

Specific Heat

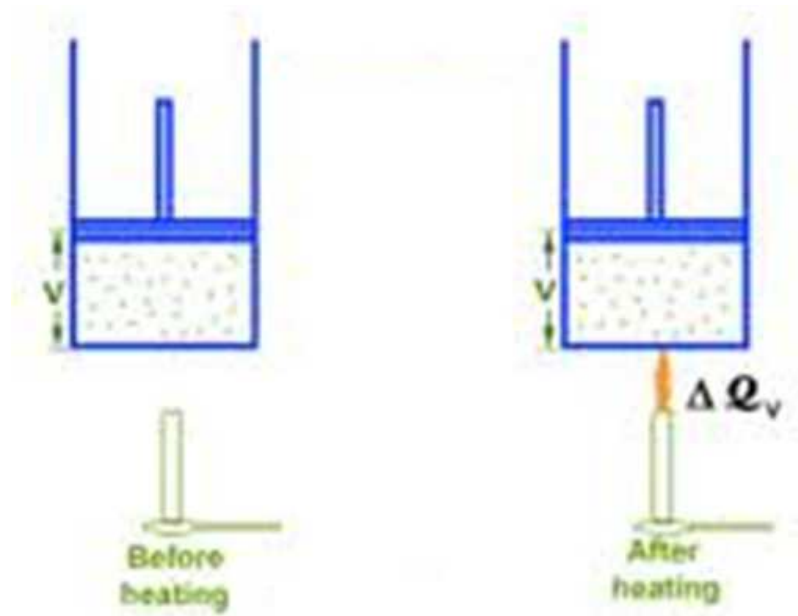
By definition

$$C_P = \left(\frac{dQ}{dT} \right)_P \quad (1)$$

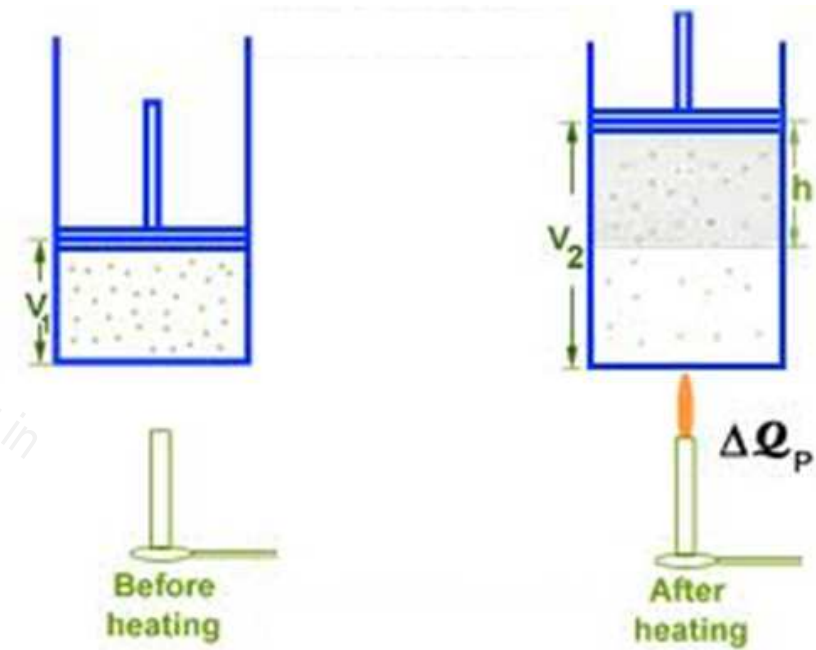
$$C_V = \left(\frac{dQ}{dT} \right)_V \quad (2)$$



Constant Volume Heat Addition

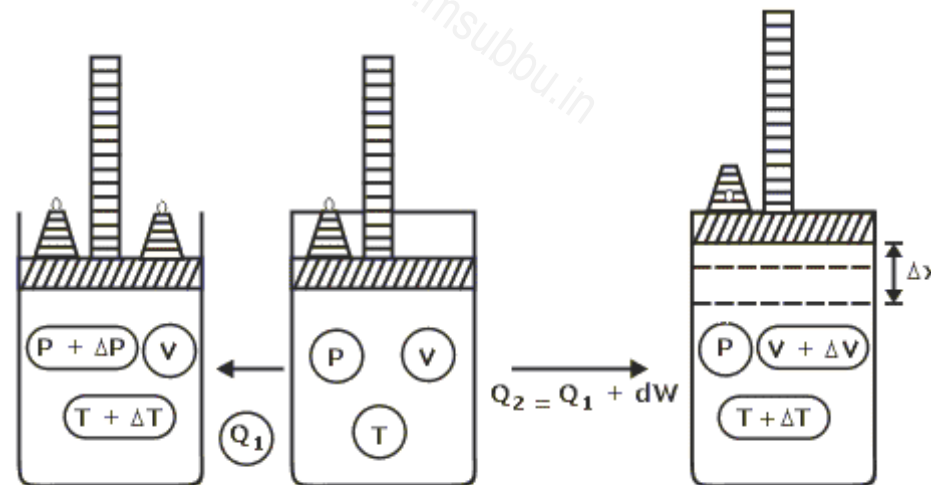


Constant Pressure Heat Addition



C_p and C_v

- We expect that C_p will be bigger than C_v for the simple reason that more heat will need to be added when heating at constant pressure than when heating at constant volume. This is because in the latter case additional energy will be expended on doing work on the atmosphere as the gas expands. It turns out that indeed C_p is bigger than C_v in practice



Relation between C_p and C_v

Figure: <http://www.tutorvista.com/content/physics/physics-iii/heat-and-thermodynamics/mayers-formula.php>

Specific heat capacities at 25 °C and 1 atm

| Substance | Phase | C_p $J/(g \cdot K)$ | $C_{p,m}$ $J/(mol \cdot K)$ | $C_{v,m}$ $J/(mol \cdot K)$ |
|-----------------------------------|----------------|--------------------------|--------------------------------|--------------------------------|
| Air (Sea level, dry, 0 °C) | gas | 1 | 29.07 | 20.76 |
| Air (room conditions) | gas | 1.01 | 29.19 | 20.85 |
| Argon | gas | 0.52 | 20.79 | 12.47 |
| Carbon dioxide (CO ₂) | gas | 0.84 | 36.94 | 28.46 |
| Helium | gas | 5.19 | 20.79 | 12.47 |
| Hydrogen | gas | 14.3 | 28.82 | |
| Nitrogen | gas | 1.04 | 29.12 | 20.8 |
| Neon | gas | 1.03 | 20.79 | 12.47 |
| Oxygen | gas | 0.92 | 29.38 | |
| Water (steam) | gas (100 °C) | 2.08 | 37.47 | 28.03 |
| Water | liquid (25 °C) | 4.18 | 75.33 | 74.53 |
| Water (ice) | solid (-10 °C) | 2.05 | 38.09 | |

Specific heat values: Notice, however, that, because water has a low molecular weight (molar mass), water has the largest *specific heat capacity of any common liquid or solid*. (The specific heat capacities of gaseous H₂ and He are, unsurprisingly, larger still. A kilogram of hydrogen is an enormous number of molecules, so it takes a lot of heat to warm them all up.)

For liquids In general, $C_p - C_v$ is so small in comparison with gases; but there are cases where $C_p - C_v$ is higher than R .

Ref: Norman O. Smith, *J. Chem. Educ.*, 1965, 42 (12), p 654

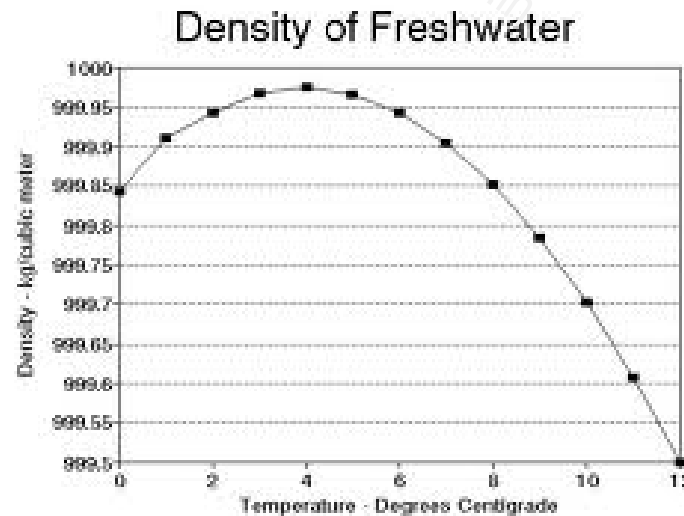
and gases:

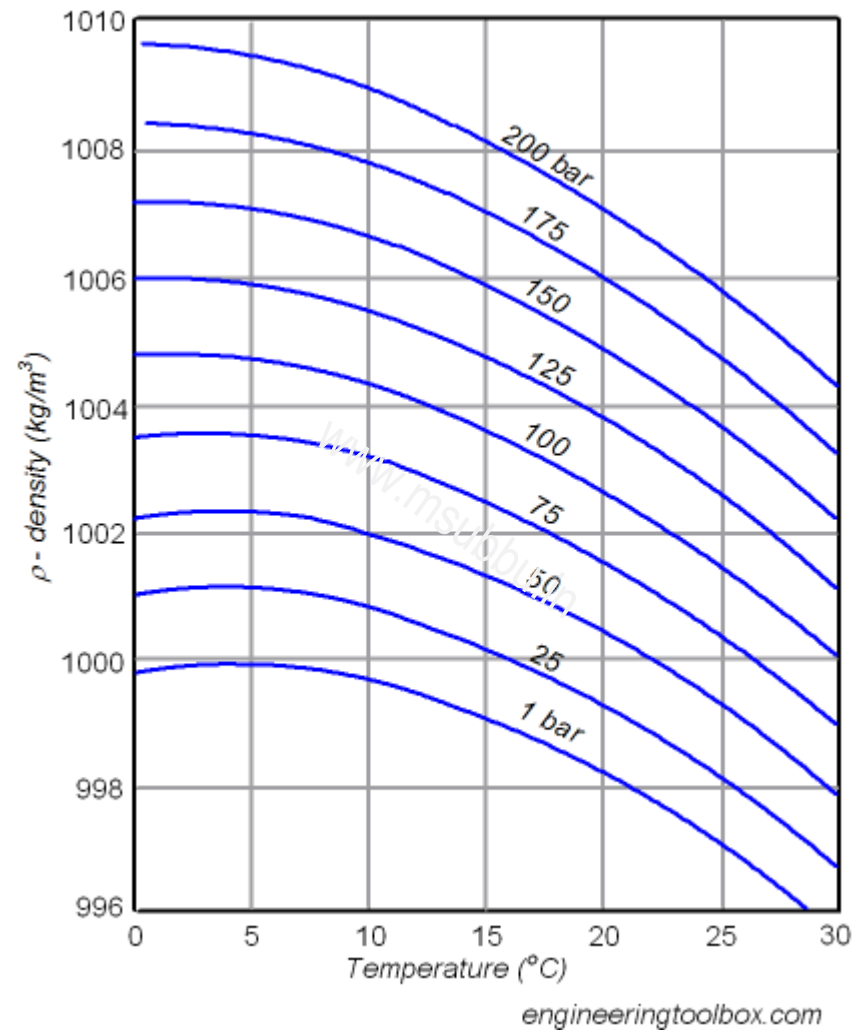


The heat capacity C_p is less than C_v for $H_2O(l)$ near 4°C . Explain this result.

$C_p < C_v$ is valid if V decreases with T at constant P .

This unusual behavior occurs because the density of water increases with temperature in this range of 0 to 4°C . Therefore, work is done by the surroundings on the system as water is heated at constant P between 0°C and 4°C .





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Relation between Specific heats and Energy Properties

First law for closed system

$$dU = dQ + dW$$

For reversible process, $dW = -PdV$. Therefore

$$dU = dQ - PdV$$

For a constant volume process, the above equation reduces to

$$dQ = dU$$

i.e., Amount of heat added during a constant volume process equals the internal energy change.

From the definition of enthalpy, and using first law for a closed system, we can obtain

$$dH = dQ + VdP$$

For a constant pressure process, the above equation reduces to

$$dQ = dH$$

i.e., Amount of heat added during a constant pressure process equals the enthalpy change.



From phase rule, it can be shown that the state of single component single phase system, can be specified by two independent variables of the system. Hence internal energy (U , a state property) can be considered as a function of any two independent variables of the system. Let us consider U as a function of T , and V .

$$U = U(T, V)$$

Differentiating,

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

At constant volume,

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT$$

Dividing by dT at constant V ,

$$\left(\frac{dU}{dT} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$

Using the above, for a closed system involving constant volume change

$$C_V = \left(\frac{dQ}{dT} \right)_V = \left(\frac{dU}{dT} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$

i.e.,

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

U & H for Ideal Gases

For ideal gases, U is a function of T alone. Hence the above equation can be written as,

$$C_V = \frac{dU}{dT}$$

Likewise, by considering H as a function of T and P , it can be proved that,

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

For ideal gases, H is a function of T alone. Hence the above equation can be written as,

$$C_P = \frac{dH}{dT}$$

Relation between C_p and C_v for an ideal gas

From Eqn.(2.4), we have

$$C_P = \frac{dH}{dT}$$

From the definition of H ,

$$H = U + PV$$

For an ideal gas

$$PV = RT$$

Hence, we have

$$\begin{aligned} C_P &= \frac{d(U + PV)}{dT} \\ &= \frac{d(U + RT)}{dT} \\ &= \frac{dU}{dT} + R \end{aligned}$$

Using Eqn.(2.3) in the above, we get

$$C_P = C_V + R$$

i.e.,

$$C_P - C_V = R$$

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Relation between P and V for Reversible Process of an Ideal Gas

From first law of thermodynamics,

$$dU = dQ + dW$$

Rearranging the above, and substituting for dU and dW , as

$$dU = C_V dT$$

and

$$dW = -PdV$$

we get,

$$C_V dT = dQ - PdV$$

For an adiabatic process, $dQ = 0$. Hence the above equation becomes,

$$C_V dT = -PdV \tag{3.1}$$

For an ideal gas, $PV = RT$. i.e.,

$$T = \frac{PV}{R}$$

Differentiating, we get

$$dT = \frac{1}{R} (PdV + VdP)$$

Substituting for dT from this in Eqn.(3.1), we get

$$\frac{C_V}{R} (PdV + VdP) = -PdV$$

Rearranging the above in terms of derivatives of P and V , we get

$$\left(1 + \frac{C_V}{R}\right) PdV = -\frac{C_V}{R} VdP \quad (3.2)$$

From Eqn.(2.5) we have, $C_P - C_V = R$. i.e.,

$$C_V + R = C_P$$

Using this in Eqn.(3.2) and simplifying, we get

$$C_P PdV = -C_V V dP \quad (3.3)$$

The ratio C_P/C_V is defined as γ . i.e.,

$$\frac{C_P}{C_V} = \gamma \quad (3.4)$$

Integrating on both sides, we get

$$\ln P = -\gamma \ln V + C_1$$

where C_1 is an integration constant. Rearranging the above equation, we get

$$\ln P + \ln V^\gamma = C_1$$

i.e.,

$$\ln(PV^\gamma) = C_1$$

Taking exponential on both sides, we get

$$\exp(\ln(PV^\gamma)) = \exp(C_1)$$

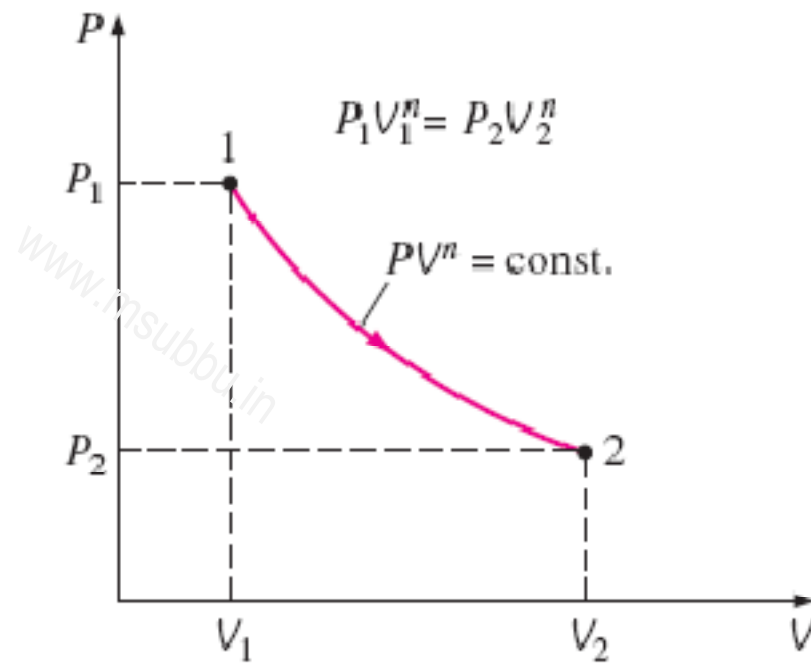
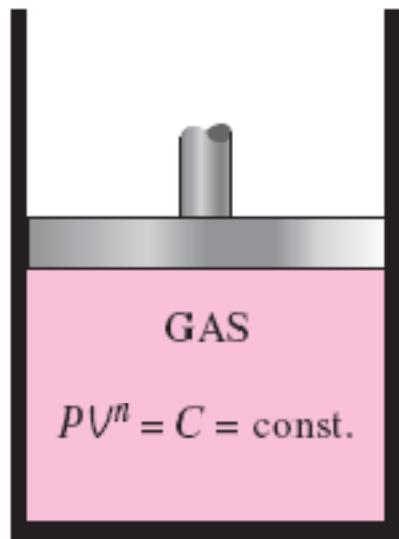
i.e.,

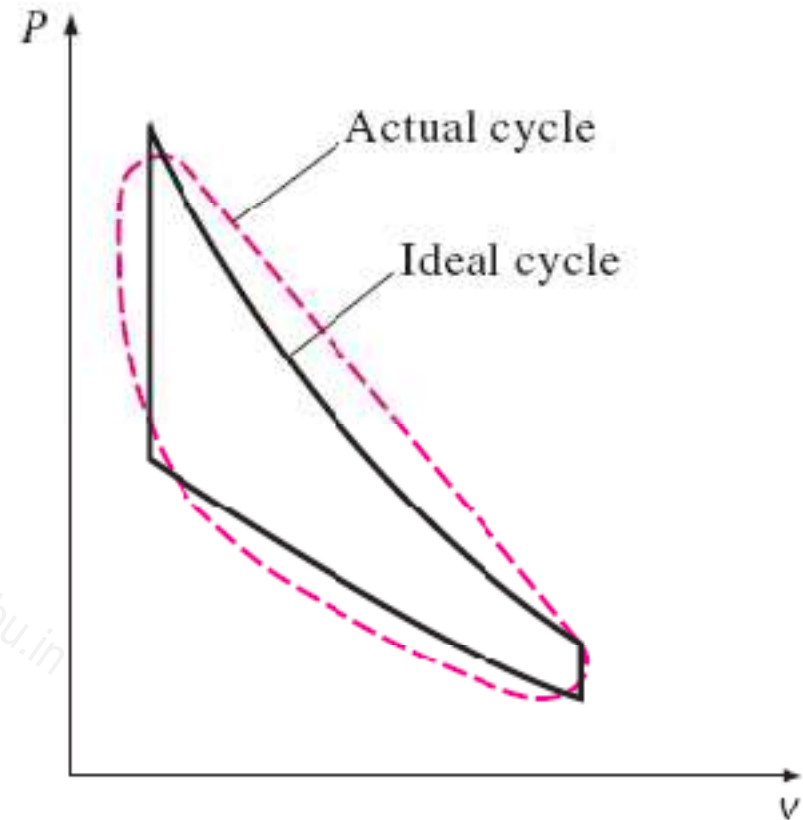
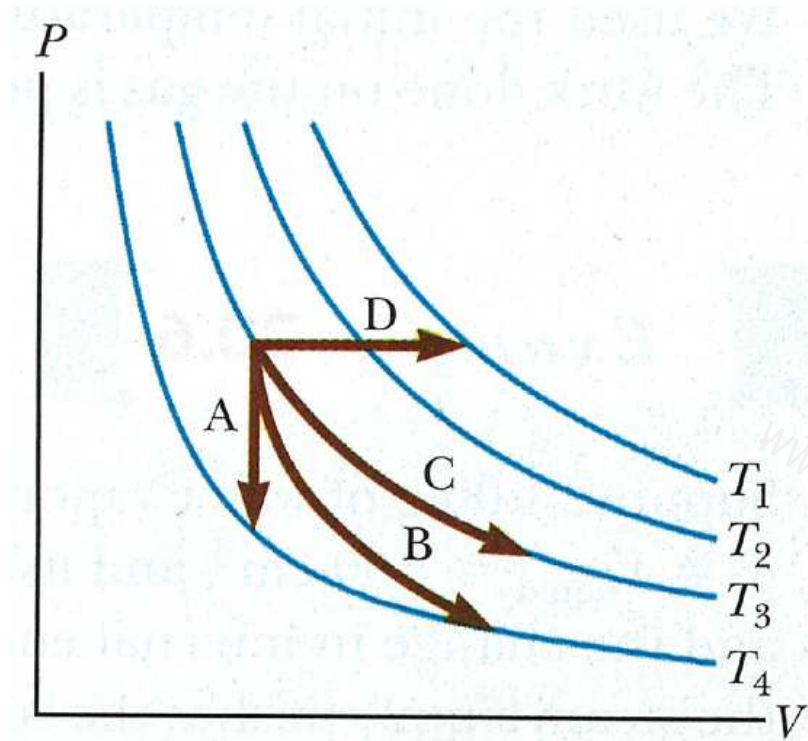
$$PV^\gamma = \text{constant} \quad (3.5)$$



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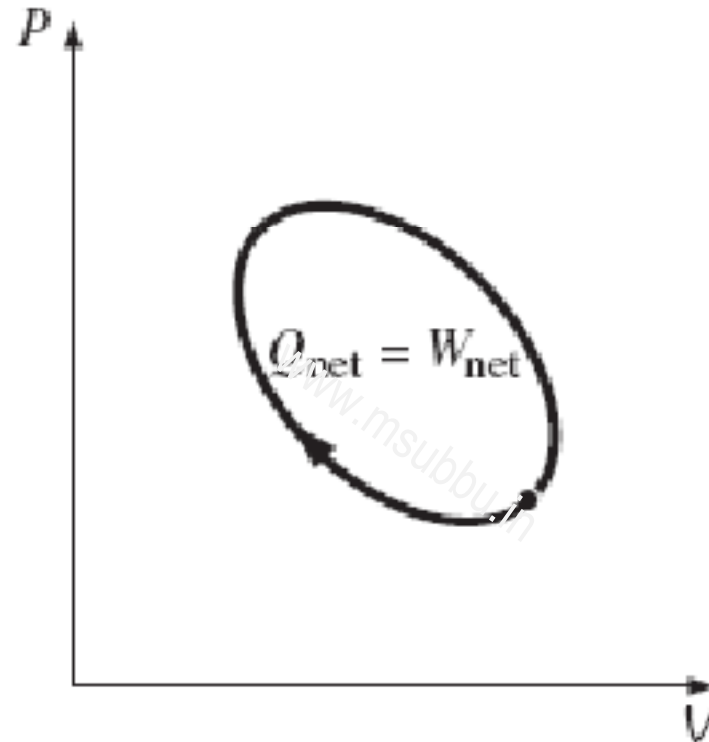




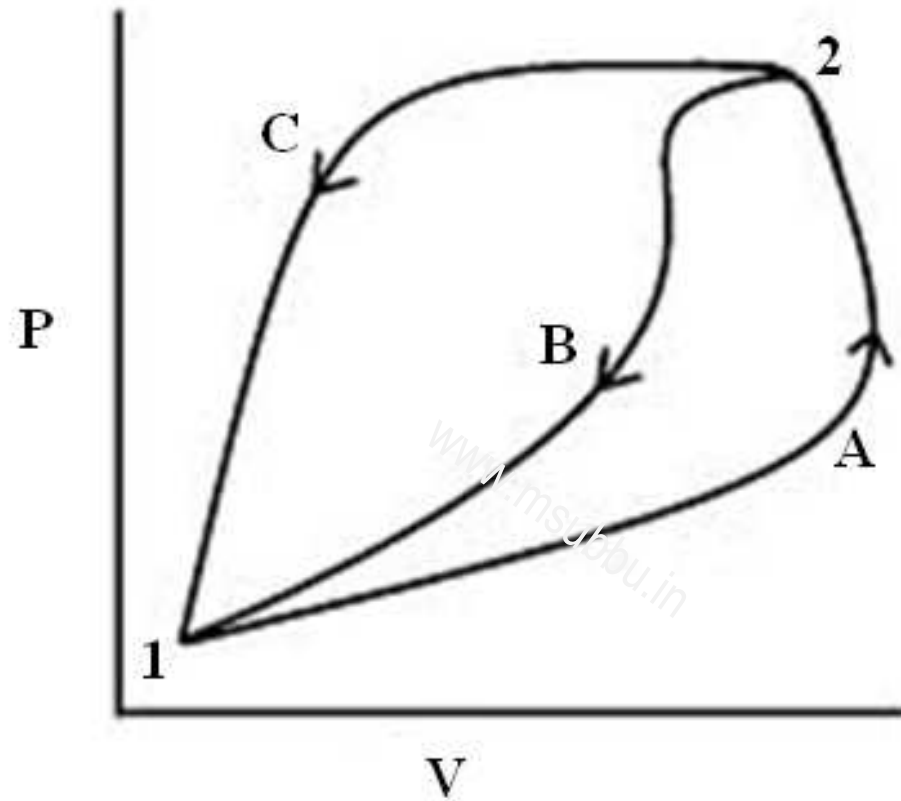


The analysis of many complex processes can be reduced to a manageable level by utilizing some idealizations.

Cyclic Process



ΔU and ΔH depends are state functions and depend only on initial and final states, not on the path of the process



Q and W depend on the path of the process

Q & W for idealized processes undergone by an ideal gas

For an ideal gas, $\Delta U = C_V \Delta T$ $\Delta H = C_p \Delta T$ $C_p - C_V = R$

- Constant Volume Process (const. V)
 $W = 0, Q = C_V \Delta T$
- Constant Pressure Process (const. P)
 $W = -P \Delta V$ $Q = C_p \Delta T$
- Isothermal Process (const. T)
 $\Delta U = 0, Q = -W, W = RT \ln(V_1/V_2) = RT \ln(P_2/P_1)$
- Reversible Adiabatic Process ($Q = 0; PV^\gamma = \text{const.}, W = \Delta U$)
 $W = (P_2V_2 - P_1V_1) / (\gamma - 1) = R(T_2 - T_1) / (\gamma - 1)$
- Polytropic Process ($PV^n = \text{const.}$)
 $W = (P_2V_2 - P_1V_1) / (n - 1) = R(T_2 - T_1) / (n - 1)$
 $Q = \Delta U - W$

Isothermal Process

As temperature is constant, $\Delta U = 0$. This gives, $Q = -W$

$$W = - \int P dV$$

For an ideal gas,

$$P = \frac{RT}{V}$$

Substituting this in the above equation, we get

$$W = - \int RT \frac{dV}{V}$$

Integrating between the initial state (1) to the final state (2), we get,

$$W = RT \ln \frac{V_1}{V_2}$$

Since, $V_1/V_2 = P_2/P_1$ for an ideal gas at constant temperature, the above equation can also be written as

$$W = RT \ln \frac{P_2}{P_1}$$

Adiabatic Process

By definition

$$W = - \int P dV = - \int_{V_1}^{V_2} P dV \quad (3.6)$$

For the adiabatic process, pressure and volume are related by the expression $PV^\gamma = \text{constant}$. i.e.,

$$PV^\gamma = P_1 V_1^\gamma = P_2 V_2^\gamma = \text{constant} = C_1 \quad (3.7)$$

Substituting for P from Eqn.(3.7) in Eqn.(3.6), we get

$$W = - \int_{V_1}^{V_2} \frac{C_1}{V^\gamma} dV$$

i.e.,

$$W = - \frac{C_1}{-\gamma + 1} \left[V_2^{-\gamma+1} - V_1^{-\gamma+1} \right]$$

Using Eqn.(3.7) in the above, we get

$$W = \frac{1}{\gamma - 1} \left[(P_2 V_2^\gamma) V_2^{1-\gamma} - (P_1 V_1^\gamma) V_1^{1-\gamma} \right]$$

Simplifying, we get

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} \quad (3.8)$$

From ideal gas law, $P_2 V_2 = RT_2$; and $P_1 V_1 = RT_1$. Therefore, the above expression can also be written as

$$W = \frac{R(T_2 - T_1)}{\gamma - 1} \quad (3.9)$$



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Example: **1**

Constant Volume Heating, Constant Pressure Cooling

Air is compressed from 2 atm absolute and 28°C to 6 atm absolute and 28°C by heating at constant volume followed by cooling at constant pressure. Calculate the heat and work requirements and ΔU and ΔH of the air. C_v of air = 0.718 kJ/kg.°C

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Example: 2

Constant Pressure Heating, Constant Volume Cooling

A 28 liter rigid container is open to the atmosphere, and heat is added to the bottom of the container until the air temperature inside reaches 450°C. The container is then quickly sealed, removed from the heating source, and allowed to cool to room temperature of 25°C. How much heat is lost during the cooling process? (C_p of air = 1.005 kJ.kg⁻¹.°C⁻¹)

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Example: **3**

Isothermal Expansion

2 liter of nitrogen originally at $T_1 = 0^\circ\text{C}$ and $P_1 = 5 \text{ atm}$, isothermally expands until the final pressure is $P_2 = 1 \text{ atm}$. How much heat flows into this system during the expansion?
($C_V = 2.5R$)

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Example: 4

Adiabatic Compression, Constant Volume Cooling

220 kg of CO₂ gas at 27°C and 1 atm is compressed adiabatically to 1/5th of its volume. It is then cooled to its original temperature at constant volume. Find Q, ΔU and W for each step and for the entire process. (γ of CO₂ = 1.3)

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Example: **5**

Polytropic Process

Nitrogen expands in a cylinder from 690 kPa and 260°C to 210 kPa and 40°C. Assuming ideal gas behavior, calculate the work done on the face of the piston per kg of nitrogen. Assume pressure and volume are related by $PV^\delta = \text{constant}$, where δ is a suitable exponent. Also calculate Q and ΔU of the process. (C_p of nitrogen = $1.038 \text{ kJ.kg}^{-1}.\text{°C}^{-1}$)

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Exercise: **1**

Cyclic Process - Adiabatic, Isobaric, Isothermal steps

An ideal gas undergoes the following reversible processes:

(a) From an initial state of 343 K and 1 bar it is compressed adiabatically to 423 K.

(b) It is then cooled to 343 K at constant pressure.

(c) Finally, it is expanded to its original state isothermally.

Calculate ΔU , ΔH , W and Q for each step as well as for the entire cycle. Assume $C_v = (3/2)R$.

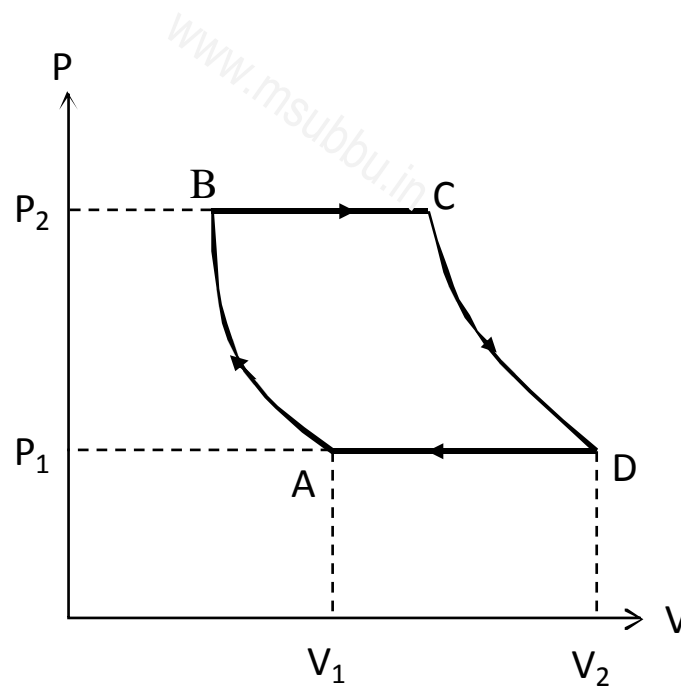
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Exercise: 2

Expression for Net work of a cyclic process:

An ideal gas is carried through a thermodynamic cycle consisting of two isobaric and two isothermal processes, as shown in the figure. Show that the net work done in the entire cycle is given by the equation:

$$W_{\text{net}} = P_1(V_1 - V_2) \ln(P_2/P_1)$$



Exercise: 3

Cyclic Process

A thermodynamic system undergoes a cycle composed of a series of three processes for which $Q_1 = +10$ kJ, $Q_2 = +30$ kJ, and $Q_3 = -5$ kJ. For the first process, $\Delta U = +20$ kJ, and for the third process, $\Delta U = -20$ kJ. What is the work in the second process, and the net work output of the cycle?

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Exercise: 4

Reversible Process described by a PV relation

A particular substance undergoes, expanding from an initial state of 20 bar to a final state of 8 bar. The path for the process is described by the equation:

$$P = (0.036/V) - 4$$

where P is in bar, and V is in m³. If ΔU for the change of state is -1400 J, determine W, Q, and ΔH .

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Exercise: 5

Work of Balloon Expansion

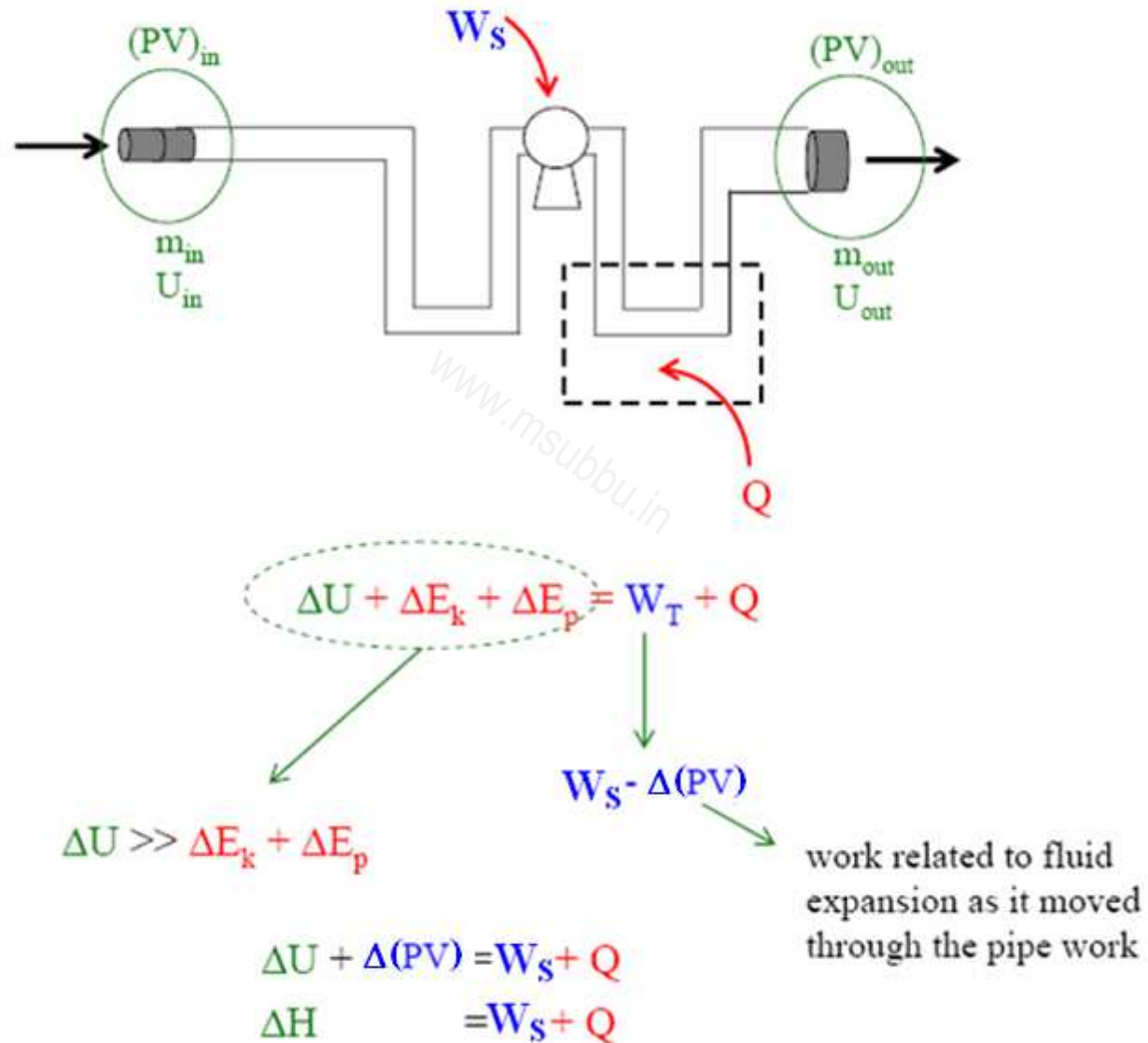
A spherical balloon contains air at $P_1 = 150$ kPa. It has an initial diameter of $D_1 = 0.3$ m. The balloon is heated until its diameter is $D_2 = 0.4$ m. It is known that the pressure in the balloon is proportional to its diameter. Calculate the work of expansion.

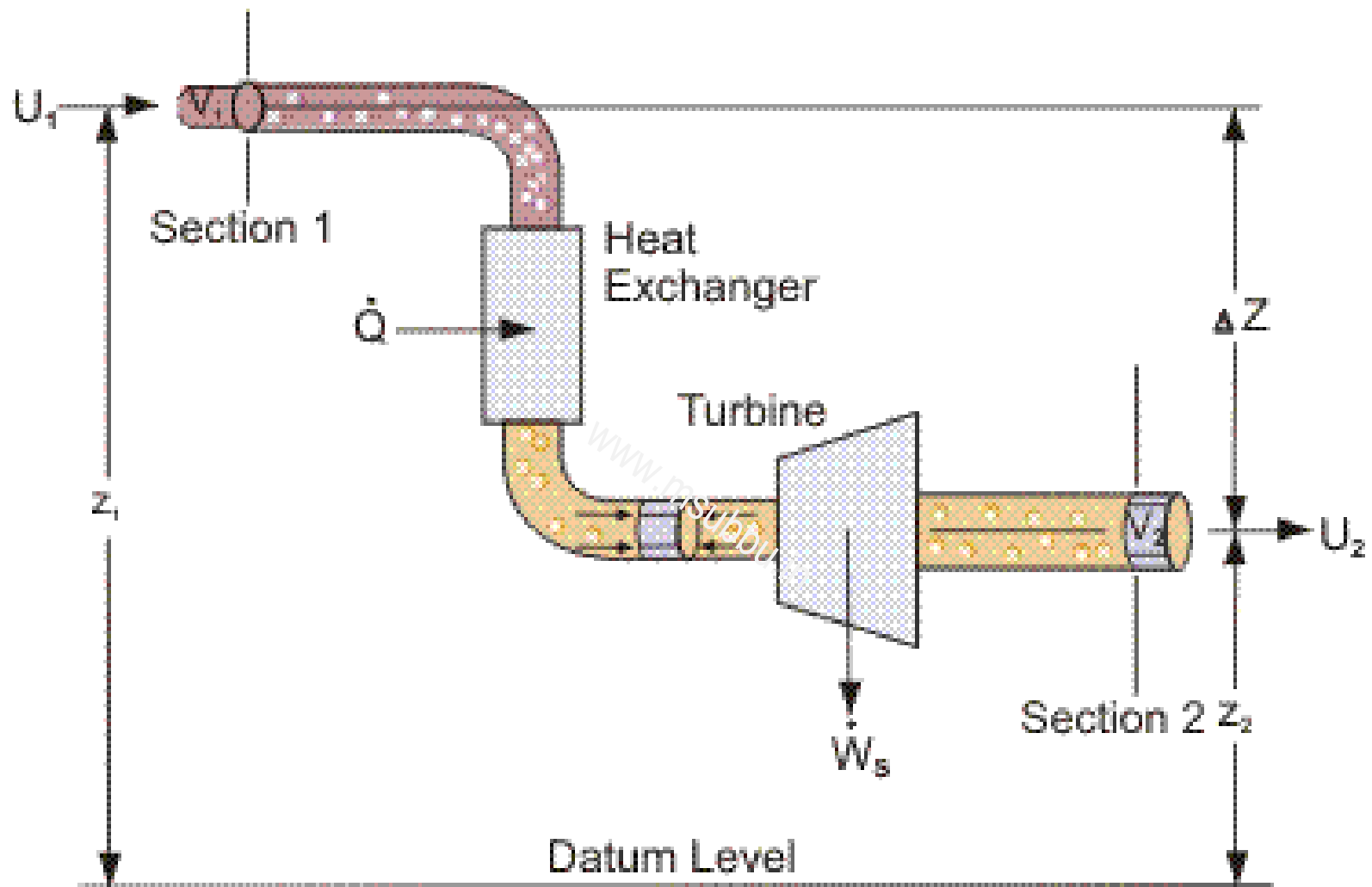
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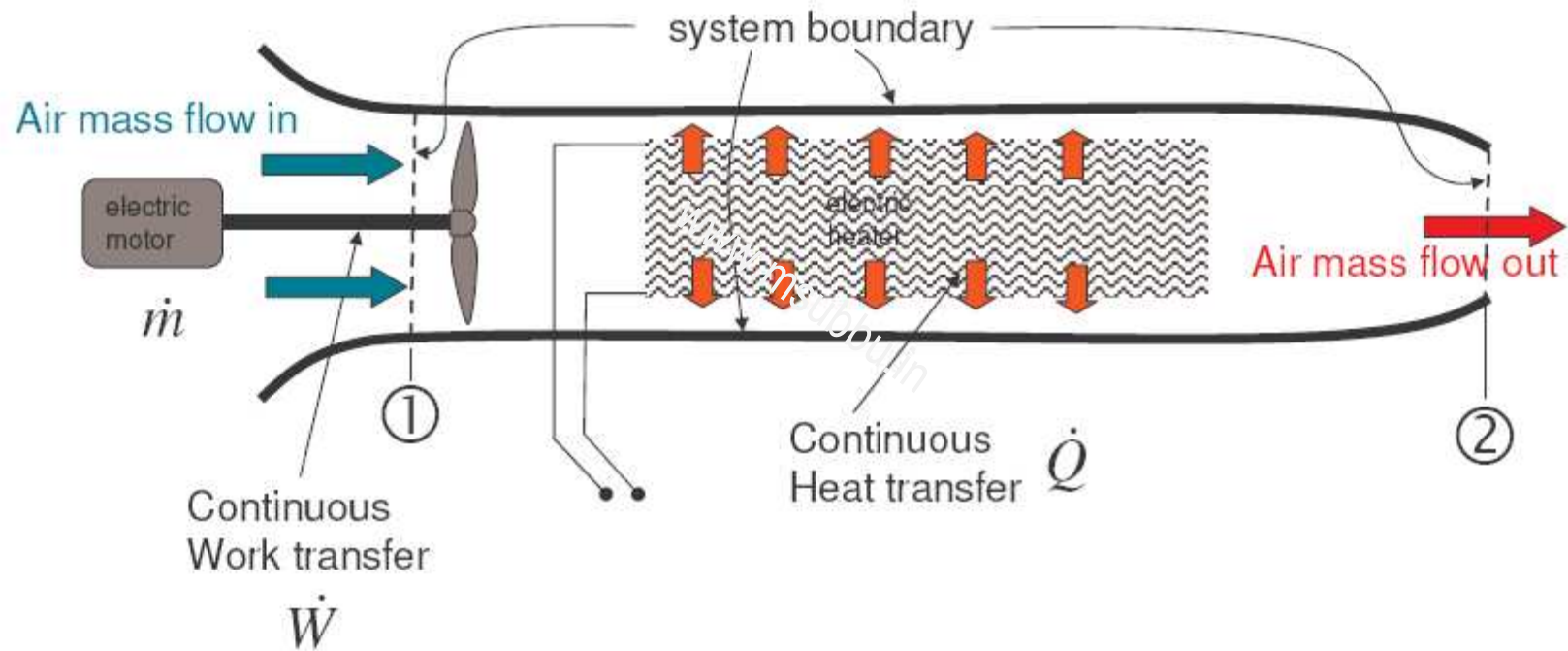


First law for steady flow open system

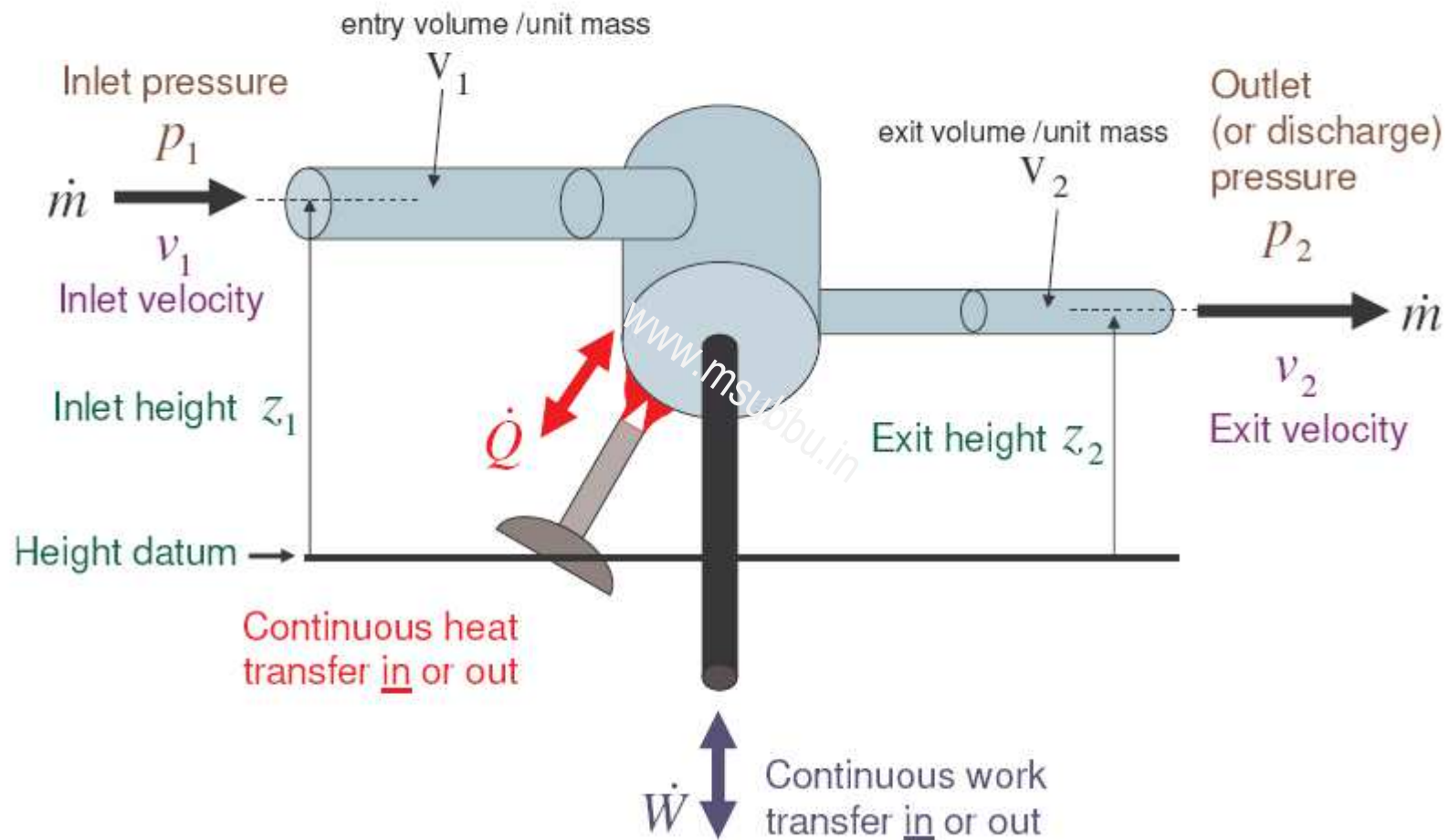




1. A room air heater or hair dryer



The Generalised Steady Flow system



If we have an open system, with mass continuously entering and leaving - three other forms of energy are carried in to or out of the system by virtue of the mass entering or leaving: they are:

$$\text{Kinetic Energy} = \frac{1}{2} mv^2$$

$$\text{Potential Energy} = mgz$$

and the energy required to 'force' mass in to (and out of) the system against the system's (and surroundings') pressure.

$$\text{work / kg} = \text{pressure} \times \text{specific volume (in or out)} = pv$$

$$\therefore \text{for mass } m, \quad \text{energy} = mpv$$

It follows that as well as changing the internal energy (U) of the working fluid, its KE, PE and pV energy can also change because of the work and heat transfer in to or out of the system

For mass m entering and leaving the system:

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

$$\text{change in PE} = mg(z_2 - z_1)$$

$$\text{change in } pV = m(p_2v_2 - p_1v_1)$$

$$\text{change in } U = m(u_2 - u_1)$$

$$Q_m + W_m = \frac{1}{2}m(v_2^2 - v_1^2) + mg(z_2 - z_1) + m(p_2v_2 - p_1v_1) + m(u_2 - u_1)$$

dividing each term by time to obtain rates of energy transfer and mass flow:

$$\dot{Q} + \dot{W} = \dot{m} \left[\frac{1}{2}(v_2^2 - v_1^2) + g(z_2 - z_1) + (p_2v_2 - p_1v_1) + (u_2 - u_1) \right]$$

$$\text{or } \dot{Q} + \dot{W} = \dot{m} \left[\frac{1}{2}(v_2^2 - v_1^2) + g(z_2 - z_1) + \underline{(p_2v_2 + u_2)} - \underline{(p_1v_1 + u_1)} \right]$$

Because a fluid will always have a temperature and pressure at entry and exit – we combine the last two terms - to obtain the ‘composite’ property ‘enthalpy’: (which we defined earlier under the section on Properties of Fluids)

$$h = pv + u$$

we can write the equation very compactly as:

$$\dot{Q} + \dot{W} = \dot{m} \Delta \left[\frac{1}{2} v^2 + gz + h \right]$$

This is known as the steady flow energy equation (SFEE)

Δ means the ‘difference in’ and is always ‘final’-‘initial’ or ‘exit’-‘entry’

$$\dot{Q} + \dot{W} = \dot{m} \left[\left(\frac{v_2^2 - v_1^2}{2} \right) + g(z_2 - z_1) + (h_2 - h_1) \right]$$

In **Thermodynamics** because we are often using gases which are relatively low density fluids, and because the inlet and outlet velocities and heights are often similar we can often simplify the SFEE to:

$$\dot{Q} + \dot{W} = \dot{m} \Delta h$$

or

$$\dot{Q} + \dot{W} = \dot{m} (h_2 - h_1)$$

This is known as the simplified steady flow energy equation (SSFEE).

In **Fluid Dynamics** because we are often using liquids which are relatively high density fluids, and are often not transferring heat to or from the liquid or changing its internal energy content we can often simplify the SFEE to:

$$\dot{W} = \dot{m} \Delta \left[\frac{1}{2} v^2 + gz + pv \right]$$

Example: 1

Steady flow Compressor's Inlet Pipe Diameter

A steady flow adiabatic compressor is used to compress argon from 100 kPa and 27°C to a pressure of 1.2 MPa. The work required is 400 kW. If the inlet flow velocity is 10 m/s, calculate the diameter of the inlet flow line.

($C_p = 1.005 \text{ kJ/kg}\cdot^\circ\text{C}$.)

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Example: 2

Work of Turbine

Air flows through a turbine in a quasi-static adiabatic process from 350 kPa and 550°C to 100 kPa. The inlet velocity is 30 m/s and the outlet velocity is 300 m/s. Calculate the work output of the turbine per kilogram of air. ($C_p = 1.005 \text{ kJ/kg}\cdot^\circ\text{C}$.)

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Example: 3

Diffuser-Nozzle's Outlet Conditions

Air at 20 kPa and -35°C enters a diffuser-nozzle section at 280 m/s. The air goes through a quasi-static adiabatic process until its velocity is reduced to 30 m/s. Calculate the final temperature and pressure ($C_p = 1.005 \text{ kJ/kg}\cdot^{\circ}\text{C}$.)

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Example: 4

Flow Area of a Channel

The velocity of a stream of air is to be slowed by passing it through a flow channel which allows it to go from 50 kPa, -10°C , and 700 m/s to 150 m/s. The process may be assumed to be quasi-static and adiabatic. Calculate the entrance and exit flow areas for a mass flow rate of 1.2 kg/s. ($C_p = 1.005$ kJ/kg. $^{\circ}\text{C}$.)

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Example: 5

Work Required for Pumping of Water

Calculate the work required to pump 40 litre/min of water from 170 kPa and 40°C to 7.5 MPa in an adiabatic process.

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Exercise: 1

Nozzle Exit Velocity

Gases produced during the combustion of a fuel-air mixture, enter a nozzle at 200 kPa, 150°C and 20 m/s and leave the nozzle at 100 kPa and 100°C. The exit area of the nozzle is 0.03 m². Assume that these gases behave like an ideal gas with $C_p = 1.15$ kJ/kg·K and $\gamma = 1.3$, and that the flow of gases through the nozzle is steady and adiabatic. Determine (i) the exit velocity and (ii) the mass flow rate of the gases.