First Law of Thermodynamics

Dr Guohong Tian

g.tian@surrey.ac.uk

Content

- First Law and its corollary
- Definition of energy and its forms, conservation of energy
- c_v and c_p, the equations, and their eligibility
- Enthalpy and its definition
- Isobaric, isochoric and isothermal processes; polytropic and isentropic processes
- Steady Flow Energy Equation
- External (shaft) work
- Nozzle and diffuser; turbine and compressor; throttle; and heat exchanger

The First Law

When a system is taken through a cycle, the cyclic integral of the heat is proportional to the cyclic integral of the work.

$$\sum Q - \sum W = 0$$

In integral form

$$\oint dQ - \oint dW = 0$$

Note: in some references you may find the first law is written in the form of $\oint \delta Q + \oint \delta W = 0$. This sign conversion is totally arbitrary and in this case, the work is defined as $dW = -pdV$.
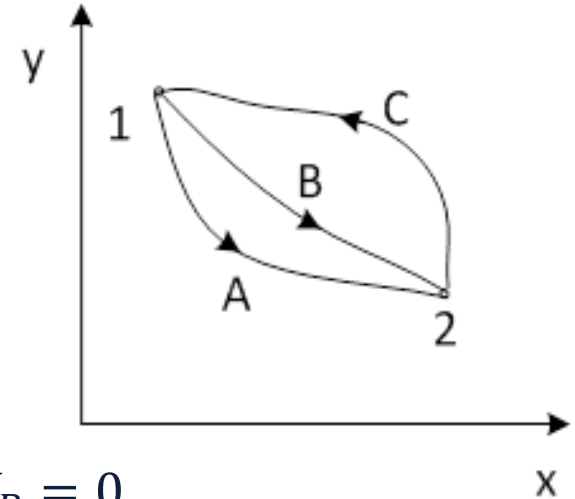
System energy

Corollary of the First Law:

If we consider two cycles AC and BC

AC: $\int_1^2 dQ_A + \int_2^1 dQ_C - \int_1^2 dW_A - \int_2^1 dW_C = 0$

BC: $\int_1^2 dQ_B + \int_2^1 dQ_C - \int_1^2 dW_B - \int_2^1 dW_C = 0$

Subtracting the second from the first

$$\int_1^2 dQ_A - \int_1^2 dQ_B - \int_1^2 dW_A + \int_1^2 dW_B = 0$$

Rearrange:

$$\int_1^2 (dQ - dW)_A = \int_1^2 (dQ - dW)_B$$

Implies: quantity (Q-W) depends only on the initial and final states

We define Energy: E=Q-W

Or $dE = \delta Q - \delta W$

Energy forms conservation of energy

Potential Energy: PE = mg(z − z$_0$)

Kinetic Energy: KE = mc^2

    or rotating body: KE = I ω^2

Internal Energy: U = f(T)

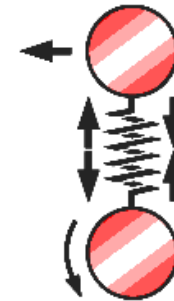$$E = U + \left(\frac{1}{2}mc^2\right) + (mgZ) + etc.\,(electrica$$

SENSIBLE AND LATENT ENERGY

CHEMICAL ENERGY …..)

Or $dE = dU + d(KE) + d(PE) = dU +$

First Law:

$$Q - W = E_2 - E_1 = (U_2 + mc^2{}_2 + m_g$$

NUCLEAR ENERGY

Or in specific form:

$$q - w = \Delta(u + \frac{1}{2}c^2 + gz)$$
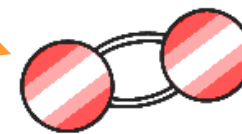
Conservation of energy and first type perpetual machine
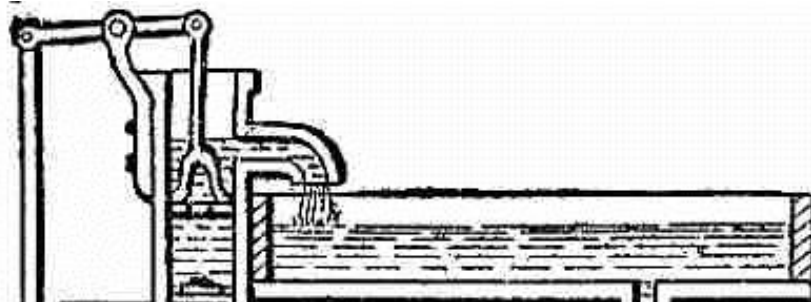
Conservation of energy: the net change of the energy of the control mass is always equal to the net transfer of energy across the boundary as heat and work.
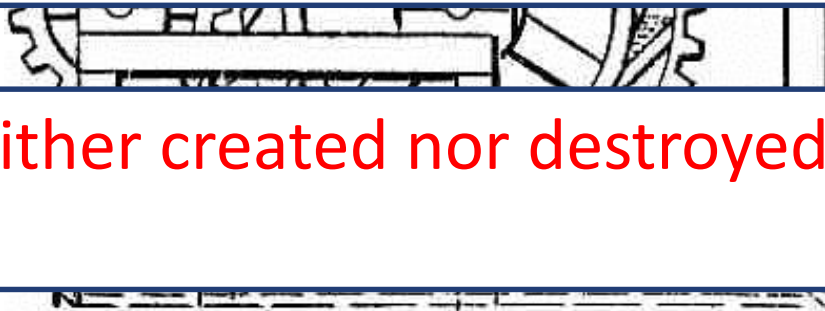
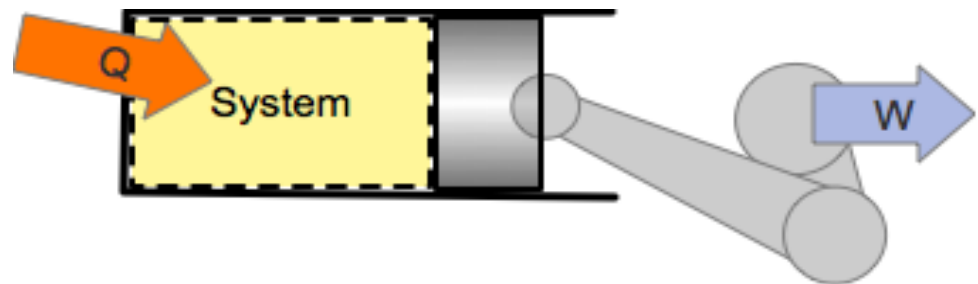Energy is neither created nor destroyed, it only changes form.

Non-flow energy equation

General energy form

$$q - w = \Delta(u + \frac{1}{2}c^2 + gz)$$

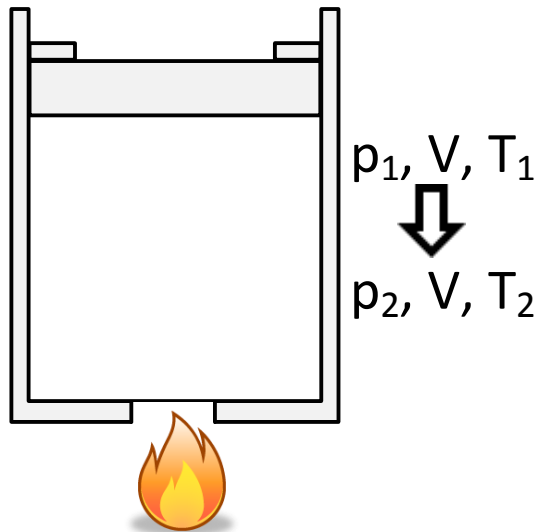For NON-FLOW process this is approximated by

$$q - w = u_2 - u_1$$

P.E. and K.E are neglected as they are small in comparison with the change in internal energy.
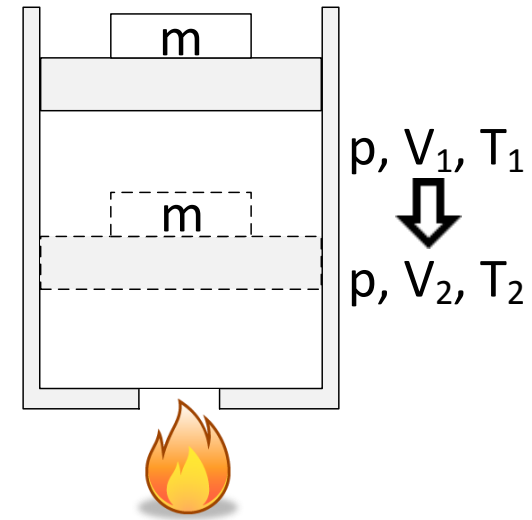
Specific heat capacities

Specific heat (**capacity**) is the energy supplied to raise the unit mass of the substance one unit of temperature

p_1, V, T_1
⇩
p_2, V, T_2

p, V_1, T_1
⇩
p, V_2, T_2

$$c_V = \frac{1}{m}\left[\frac{\Delta Q}{\Delta T}\right]_V = \left[\frac{\Delta q}{\Delta T}\right]_V$$

$$c_p = \frac{1}{m}\left[\frac{\Delta Q}{\Delta T}\right]_p = \left[\frac{\Delta q}{\Delta T}\right]_p$$

Specific heat capacity at constant volume

Specific heat capacity at constant pressure

Constant volume specific heat

From the First Law

$$du = dq - dw = dq - pdv$$

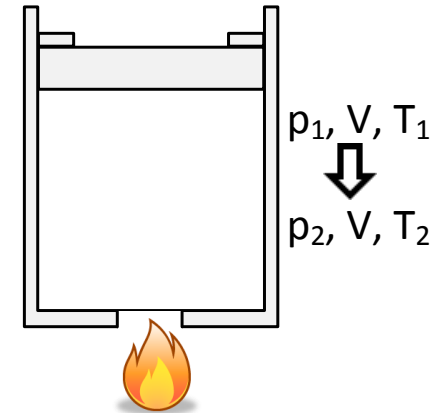As constant volume: $dv = 0$

p₁, V, T₁

p₂, V, T₂

Therefore:

$$c_V = \left[\frac{\Delta q}{\Delta T}\right]_V = \left[\frac{\partial u}{\partial T}\right]_V$$

Because $u = f(T, v)$

For general change:

$$du = \boxed{\left[\frac{\partial u}{\partial T}\right]_V} dT + \left[\frac{\partial u}{\partial V}\right]_T dV = \boxed{c_V} dT + \left[\frac{\partial u}{\partial V}\right]_T dV$$

$$c_V = \frac{1}{m}\left[\frac{\Delta Q}{\Delta T}\right]_V = \left[\frac{\Delta q}{\Delta T}\right]_V$$

By Gay-Lussac's experiment

$$\left[\frac{\partial u}{\partial V}\right]_T = 0$$

Therefore

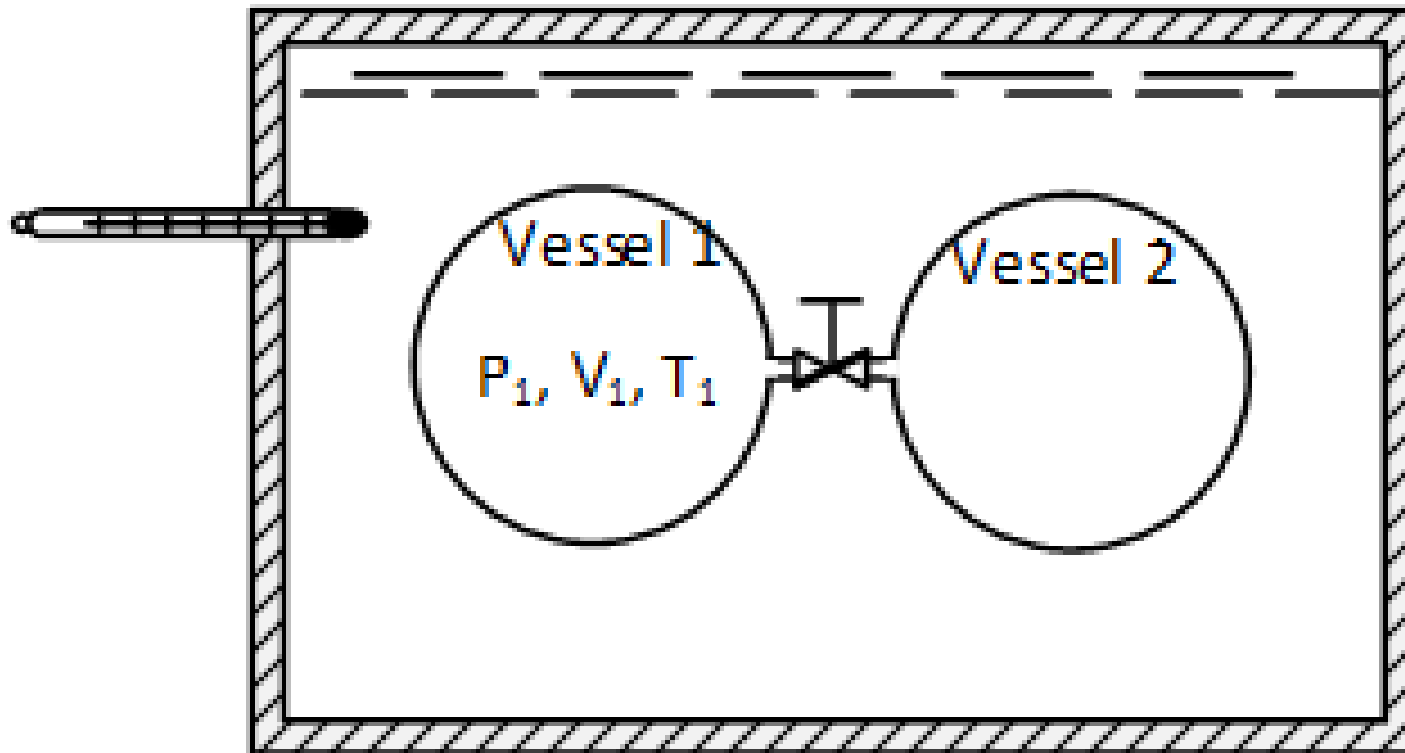$$du = \left[\frac{\partial u}{\partial T}\right]_V dT = c_V dT$$

Or for constant c_V $u_2 - u_1 = c_V(T_2 - T_1)$

Only for ideal gases!

AKA Joule's experiment

$$\left[\frac{\partial u}{\partial V}\right]_T = 0$$

Enthalpy and Constant pressure specific heat

We define **Enthalpy**, h or H by

$$h = u + p.v \qquad \text{or} \qquad H = U + p.V$$

$$U = Q - W$$
$$du = dq - p\,dv$$

Hence
$$dh = du + p.dv + v.dp$$

Substitute to the First Law:
$$dq = dh - v.dp$$

Constant pressure specific heat:
$$c_p = \frac{1}{m}\left[\frac{\Delta Q}{\Delta T}\right]_p = \left[\frac{\Delta q}{\Delta T}\right]_p$$

Due to constant pressure
$$dp = 0 \qquad \text{hence } dq = dh$$

Hence:
$$c_p = \left[\frac{dh}{dT}\right]_p$$

In a general change
$$dh = \left[\frac{\partial h}{\partial T}\right]_p dT + \left[\frac{\partial h}{\partial p}\right]_T dp$$

Constant pressure specific heat

For **ideal gases**, u is a function of T only, and also $pv = RT$ is a function of T only

$h = u + pv$ is a function of T only, hence $\left[\dfrac{\partial h}{\partial p}\right]_T = 0$

Thus $\qquad\qquad\qquad\qquad dh = c_p dT$

For gases with constant c_p $\qquad\qquad \Delta h = h_2 - h_1 = c_p(T_2 - T_1)$

For **an ideal gas**, $\qquad\qquad\qquad h = u + p.v = u + RT$

$\dfrac{dh}{dT} = \dfrac{du}{dT} + R \qquad \longrightarrow \qquad c_p = c_V + R \qquad$ or $\qquad c_p - c_V = R$

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

Meyer's formula

Heat capacities

For gases

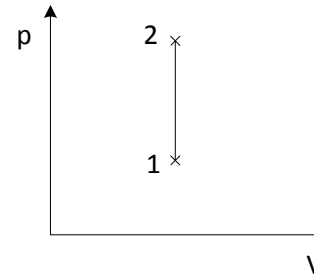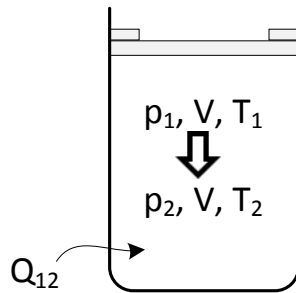|	c_V	c_p	Note
By definition	$c_V = \left[\dfrac{\mathrm{d}q}{\mathrm{d}T}\right]_V$	$c_p = \left[\dfrac{\mathrm{d}q}{\mathrm{d}T}\right]_p$	For specific processes (constant V or constant p), but any substance
By derivation	$c_V = \dfrac{du}{dt}$	$c_p = \dfrac{dh}{dt}$	For any processes (not just constant V or constant p), but ideal gases only

For liquids and solid

$$c_V \approx c_p \approx c$$

$$dh \approx du \approx cdT$$

Isochoric (constant volume) process

Work done during the process:

$$W_{12} = \int_1^2 pdV = 0$$

Heat transfer during the process

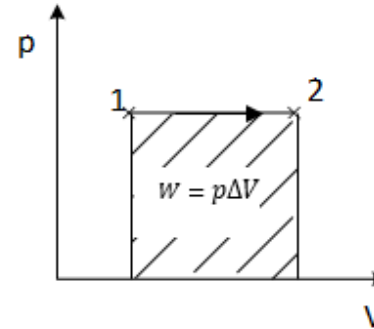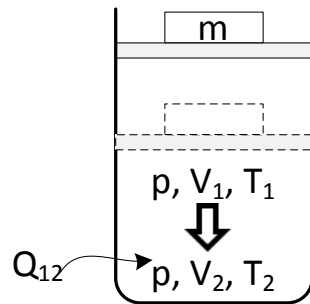$$dQ = dU = mc_V dT$$

For gases with constant c_v

$$Q_{12} = \Delta U_{12} = mc_V(T_2 - T_1)$$

Isobaric (constant pressure) process

Work done in process:

$$W_{12} = \int_1^2 p\,dV = p(V_2 - V_1)$$

Heat transfer in process:

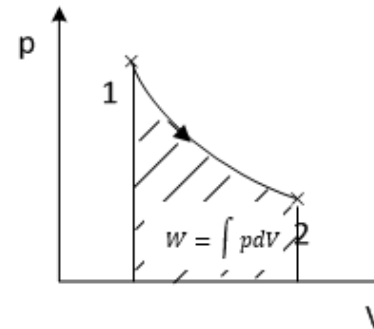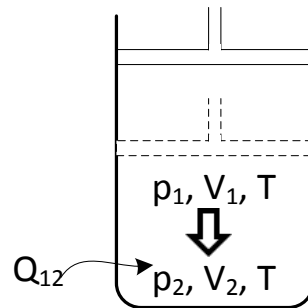$$dQ = m c_p dT$$

For gases with constant c_p

$$Q_{12} = m c_p (T_2 - T_1)$$

For any gases, from the First Law

$$Q_{12} = U_2 - U_1 + p(V_2 - V_1) = (U_2 + pV_2) - (U_1 + pV_1) = H_2 - H_1 = m(h_2 - h_1)$$

Isothermal (constant temperature) process

Work done during the process:

$$W_{12} = \int_1^2 p\,dV$$

For an **ideal gas**:
$$p_1 V_1 = p_2 V_2 = mRT$$

$$W_{12} = \int_1^2 \frac{mRT}{V}\,dV = mRT \int_1^2 \frac{1}{V}\,dV = p_1 V_1 \ln(V_2/V_1)$$

Heat transfer during the process

$$\Delta U = mc_V \Delta T = 0$$

Heat transfer

$$Q_{12} = W_{12} + \Delta U = W_{12} + 0 = p_1 V_1 \ln(V_2/V_1)$$

Polytropic process

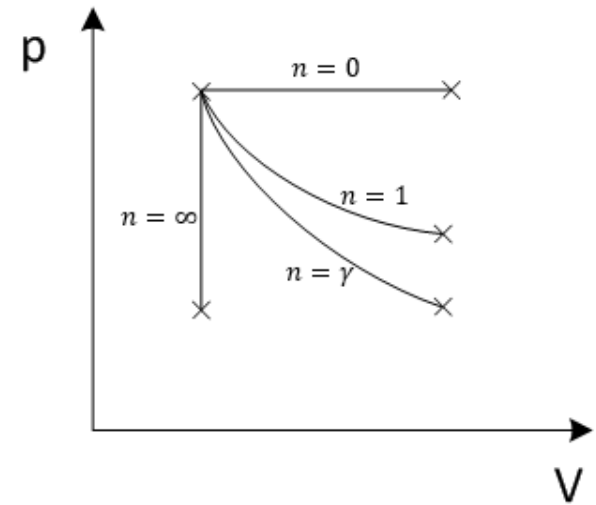Many real processes follow relationships of the form

$pV^n = constant$ or $pv^n = constant$

for $1 \leq n \leq \gamma$ (γ is the ratio of sp heats $\gamma = \frac{c_p}{c_V}$)

For an **ideal gas**, alternative ways of expressing the Polytropic relationship from $pV^n = C$:

$TV^{(n-1)} = C$ or $pT^{-n/(n-1)} = C$

Work done in process

$$W_{12} = \int_1^2 p\,dV = C \int_1^2 \frac{1}{V^n}\,dV = \frac{C}{1-n}\left[\frac{1}{V^{n-1}}\right]_1^2 = \frac{1}{1-n}\left[\frac{p_2 V_2{}^n}{V_2{}^{n-1}} - \frac{p_1 V_1{}^n}{V_1{}^{n-1}}\right] = \frac{p_2 V_2 - p_1 V_1}{1-n}$$

Internal energy change: $\Delta U = mc_V(T_2 - T_1)$

Heat transfer: $Q_{12} = \Delta U + W_{12}$

Reversible adiabatic (Isentropic) process

An **adiabatic** process is one in which no heat crosses the system boundary.

For a reversible adiabatic process, according to definition,

$$Q_{12} = 0$$

Hence work done in process

$$W_{12} = -(U_2 - U_1)$$

From the First Law, for gases with constant specific heat

$$dq - pdv = du = c_V dT$$

For adiabatic processes

$$dq = 0$$

Hence

$$-pdv = c_V dT$$

For an ideal gas

$$pv = RT$$

Substituting

$$-\frac{dv}{v} = \frac{c_V dT}{RT} \quad \text{where} \quad R = c_p - c_V$$

Define heat capacity radio

$$\gamma = \frac{c_p}{c_V}, \quad \text{then } R = c_p - c_V = (\gamma - 1)c_V$$

Substituting

$$-\ln v = \frac{1}{\gamma - 1} \ln T + const.$$

$$(\gamma - 1)\ln v + \ln T = const.$$

$$T v^{\gamma - 1} = const.$$
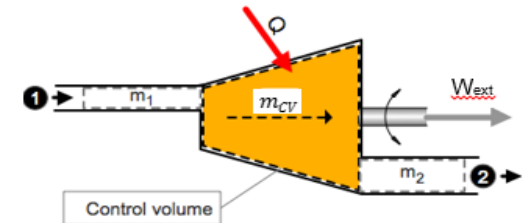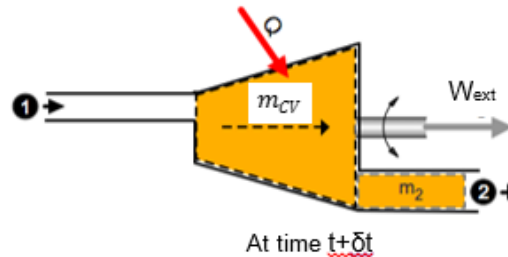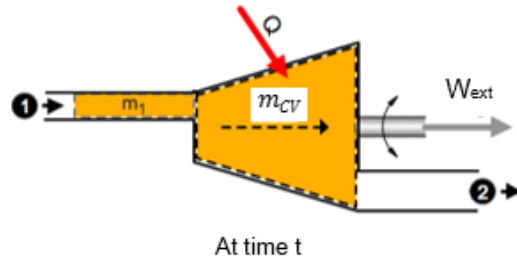
Or from the equation of states

$$pv^\gamma = const.$$

> Adiabatic ≠ Isothermal

For dry air, we can usually use $\gamma = 1.4$

General continuity equation for a constant volume system

General continuity equation for a constant volume system

$$0 = \frac{\partial m_{CV}}{\partial t} + \dot{m}_{out} - \dot{m}_{in}$$

At time t

At time t+δt

Control volume

Boundary work = $\displaystyle\int pdV \cong mpv$

Work ... $\quad W = W_S + m_2 p_2 v_2 - m_1 p_1 v_1$

Energy ... $\quad E_2 - E_1 = (E_{CV2} + m_2 e_2) - (E_{CV1} + m_1 e_1)$

Applied the First Law

$$Q - (W_{ext} + m_2 p_2 v_2 - m_1 p_1 v_1)$$
$$= \left[E_{CV2} + m_2 \left(u_2 + \frac{1}{2} c_2^2 + gz_2 \right) \right] - \left[E_{CV1} + m_1 \left(u_1 + \frac{1}{2} c_1^2 + gz_1 \right) \right]$$

BUT $m_1 = m_2 = m$ and on average $E_{CV2} = E_{CV1}$

$$Q - W_{ext} = m \left[\left(\boxed{p_2 v_2 + u_2} + \frac{1}{2} c_2{}^2 + gz_2 \right) - \left(\boxed{p_1 v_1 + u_1} + \frac{1}{2} c_1{}^2 + gz_1 \right) \right]$$

$$h_2 \qquad\qquad\qquad\qquad h_1$$

SFEE $\qquad \dot{Q} - \dot{W}_{ext} = \dot{m} \left[\left(h_2 + \frac{1}{2} c_2{}^2 + gz_2 \right) - \left(h_1 + \frac{1}{2} c_1{}^2 + gz_1 \right) \right]$

$$\dot{Q} - \dot{W}_{ext} = \dot{m} (h_2 - h_1)$$
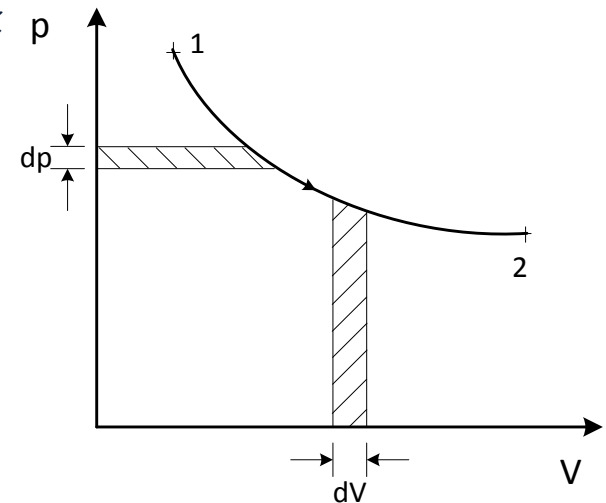
External work

External work (or useful work) is separated from the work done at the boundaries. i.e. flow work $\quad p_2 v_2 - p_1 v_1$

For the flow process $w_{ext} = total\ work - flow\ work$

$$= w + (pv)_1 - (pv)_2$$

$$= \int_1^2 pdv + p_1 v_1 - p_2 v_2$$

$$= -\int_1^2 vdp$$

$$W_{non-flow} = W_{ext} - W_{flow}$$

$$\int pdv \qquad \int vdp$$

Process	Non-flow work done	Steady flow work done	"flow work"
v=const	0	$-v(p_2 - p_1)$	$v(p_2 - p_1)$
p=const	$p(v_2 - v_1)$	0	$p(v_2 - v_1)$
pv^n=const	$\dfrac{p_2 v_2 - p_1 v_1}{1 - n}$	$\dfrac{n(p_2 v_2 - p_1 v_1)}{1 - n}$	$(p_2 v_2 - p_1 v_1)$

From SFEE

$$q - w_{ext} = (h_2 + \frac{1}{2}c_2^2 + gz_2) - (h_1 + \frac{1}{2}c_1^2 + gz_1)$$

If we neglect the heat transfer, external work, internal energy change of the flow (no temperature change), and assume the flow being incompressible (constant density), the equation becomes:

$$h_2 + \frac{1}{2}c_2^2 + gz_2 = h_1 + \frac{1}{2}c_1^2 + gz_1 \qquad \text{q and } w_{ext} \text{ neglected}$$
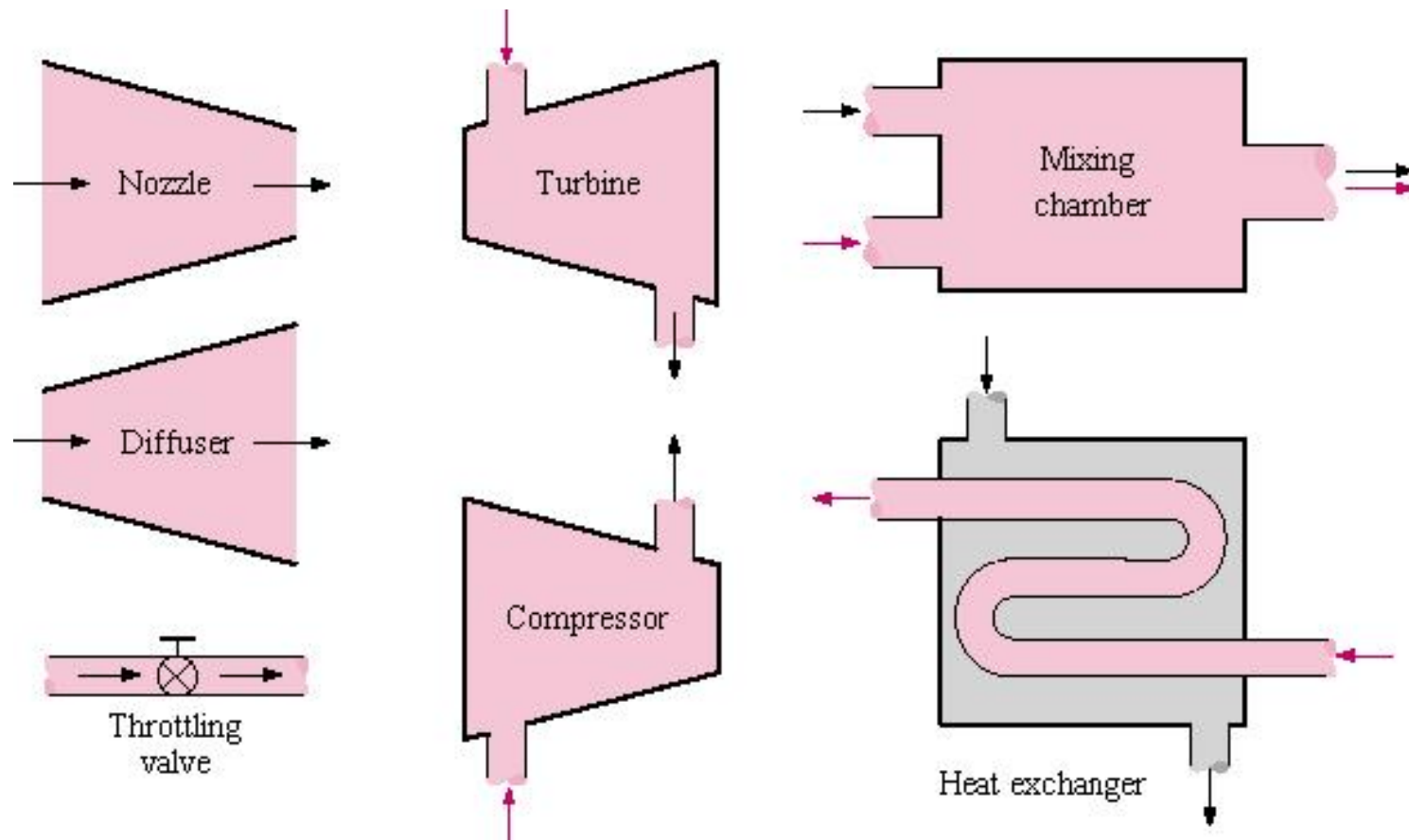
$$p_2 v_2 + \frac{1}{2}c_2^2 + gz_2 = p_1 v_1 + \frac{1}{2}c_1^2 + gz_1 \qquad \text{Internal energy change neglected}$$

$$p_2 + \frac{1}{2}\rho c_2^2 + \rho g z_2 = p_1 + \frac{1}{2}\rho c_1^2 + \rho g z_1 \qquad \text{Incompressible}$$
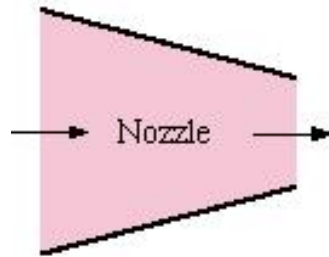
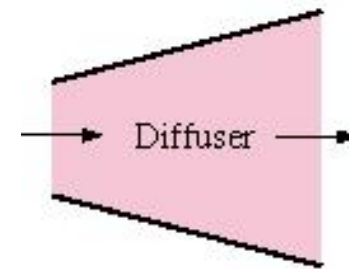$$p + \frac{1}{2}\rho c^2 + \rho g z = constant$$

Looks familiar?

bernoulli equation

UNIVERSITY OF SURREY

Nozzle

Diffuser

SI

v	m/s
a	m/s^2
F	$kg \cdot m \cdot s^{-2}$
w	$kg \cdot m^2 \cdot s^{-2}$
M	$N \cdot m \quad kg \cdot m^2 \cdot s^{-2}$
P	$kg \cdot m^{-1} \cdot s^{-2}$

Apply SFEE

$$q - w_{ext} = (h_2 + \frac{1}{2}c_2^2 + gz_2) - (h_1 + \frac{1}{2}c_1^2 + gz_1)$$

If we neglect the heat transfer and potential energy change, and there is no external work (no parts moving), the equation becomes:

$$\left(h_2 + \frac{1}{2}c_2^2\right) - \left(h_1 + \frac{1}{2}c_1^2\right) = 0$$

Or

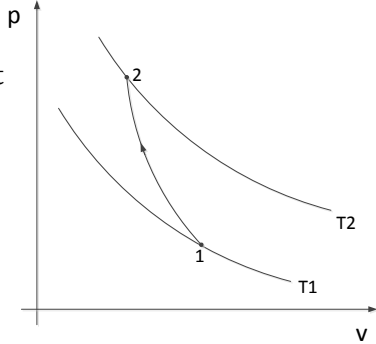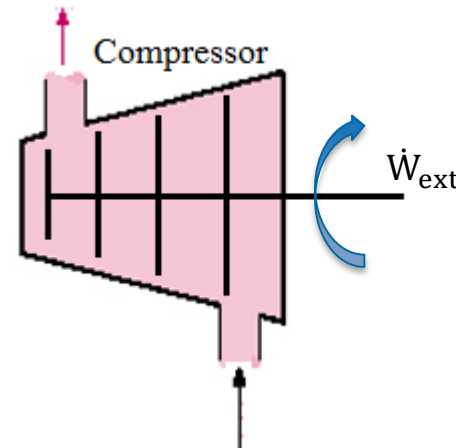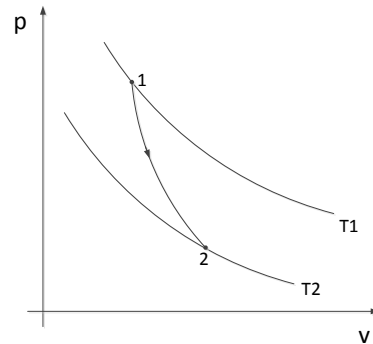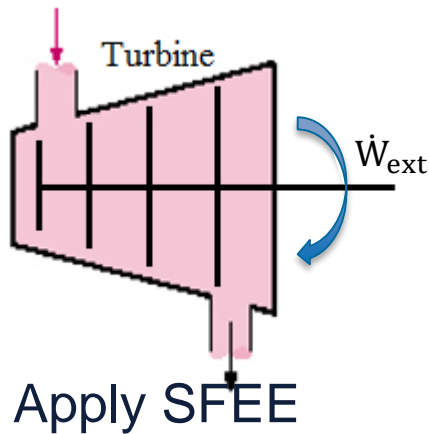$$\Delta h = -\Delta(\frac{1}{2}c^2)$$

For nozzles

$h \downarrow \quad c \uparrow$

For diffusers

$h \uparrow \quad c \downarrow$

Apply SFEE

$$q - w_{ext} = (h_2 + \frac{1}{2}c_2^2 + gz_2) - (h_1 + \frac{1}{2}c_1^2 + gz_1)$$

If we neglect the heat transfer and potential energy change, also neglect the kinetic energy change, the equation becomes:
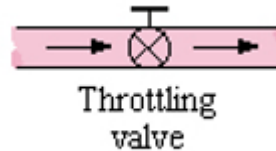
$$-w_{ext} = \Delta h$$

For turbines

$h \downarrow \quad w_{ext} > 0$

For compressors

$h \uparrow \quad w_{ext} < 0$

Be noted, this is for reversible adiabatic processes. Isentropic efficiency will be defined after learned 2nd Law.

Throttling
valve

Apply SFEE

$$q - w_{ext} = (h_2 + \frac{1}{2}c_2^2 + gz_2) - (h_1 + \frac{1}{2}c_1^2 + gz_1)$$

If we neglect the heat transfer and potential energy change, also there is no external work (no moving parts), if the fluid is incompressible (constant density), due to continuity, $c_1 = c_2$, therefore
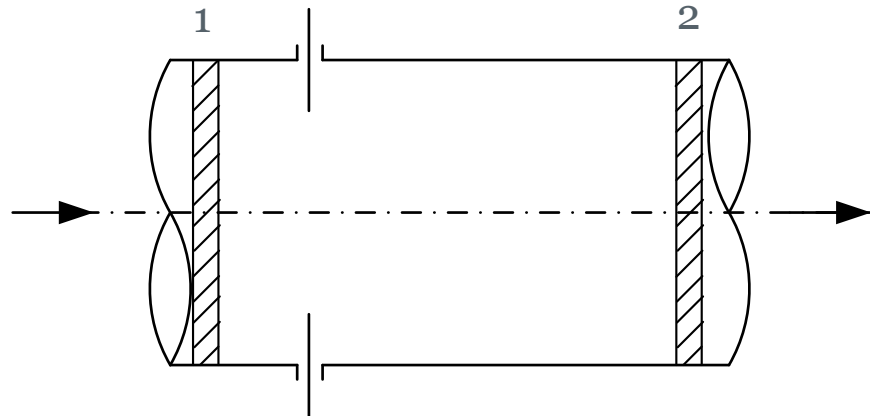
$$h_1 = h_2$$

The only effect through a throttle is pressure will reduce.

why neglect pressure only

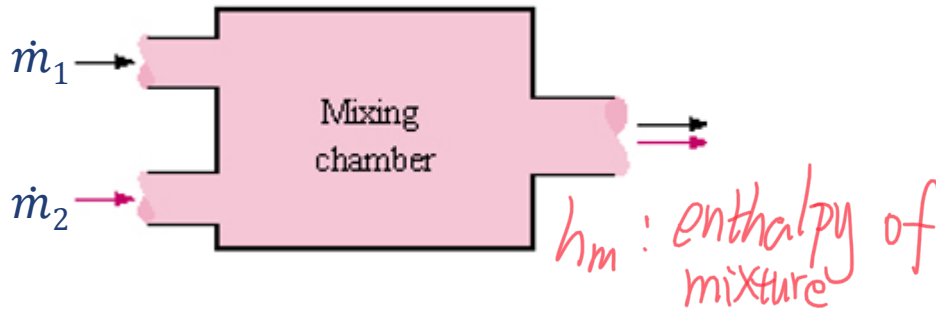This equation applies to all the fluid flow situation

$$\dot{m}v = \dot{V} = Ac \quad \text{or} \quad \dot{m} = \rho Ac$$

$$\dot{m}_1 = \rho_1 A_1 c_1 = \dot{m}_2 = \rho_2 A_2 c_2$$

This equation applies when pipe area changes or when specific volume changes.

But for throttles, area up and down stream is considered constant, if density doesn't change, velocity will have to be constant for steady flow.

h_m : enthalpy of mixture

Direct contact heat exchanger
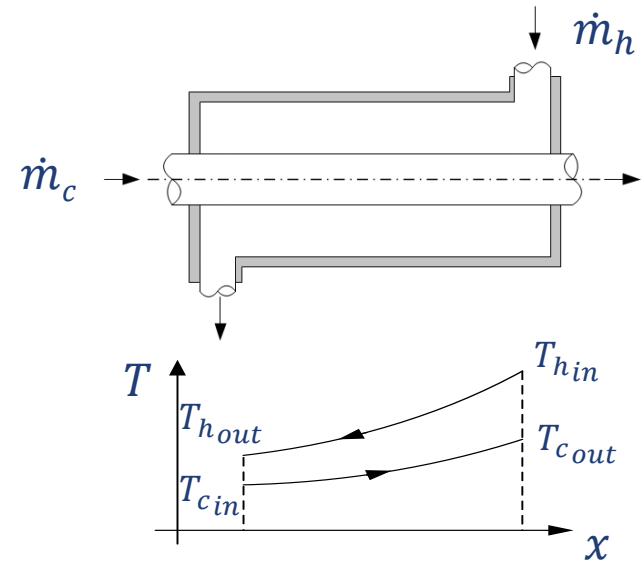
$$\dot{m}_1 h_c \ _+ \ \dot{m}_2 h_h \ = \ (\dot{m}_1 + \dot{m}_2) h_m \ - \ \dot{Q}_L$$

$\dot{Q}_L$: heat leakage   leakage

In the case of water/water mixing, if neglect heat leakage, the equation can be simplified to:

$$\dot{m}_1 T_c \ _+ \ \dot{m}_2 T_h = \ (\dot{m}_1 + \dot{m}_2) T_m$$

Try to derive the above equation yourself!

Apply SFEE for the streams separately

Cold: $\dot{Q}_c = \dot{m}_c \left(h_{c_{out}} - h_{c_{in}} \right)$

Hot: $\dot{Q}_h = \dot{m}_h \left(h_{h_{out}} - h_{h_{in}} \right)$

Neglect leakage:

$$\dot{Q}_c = -\dot{Q}_h$$

Without phase change, for the same fluid, simplified to:

$$\dot{m}_c \left(T_{c_{out}} - T_{c_{in}} \right) = \dot{m}_h \left(T_{h_{out}} - T_{h_{in}} \right)$$

$T_{c\ out}$: temperature of cold substance out

- First Law and its corollary (understanding)

- Definition of energy and its forms, conservation of energy (understanding)

- c_v and c_p, the equations, and their eligibility (understanding)

- Enthalpy and its definition (understanding)

- Isobaric, isochoric and isothermal processes; polytropic and isentropic processes (understanding and calculation)

- Steady Flow Energy Equation (understanding and calculation)

- External (shaft) work(understanding and calculation)

- Nozzle and diffuser; turbine and compressor; throttle; and heat exchanger (understanding and calculation)