

4. FIRST LAW OF THERMODYNAMICS

PROPERTIES OF GAS MIXTURES:

Change in Properties for Thermodynamic Cycle is zero.	E.g. $\oint dV = 0, \oint dP = 0, \oint dT = 0$
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STATEMENT OF FIRST LAW (FOR CYCLE):

When System is undergoing cycle, net heat transfer is equal to net-work transfer.	$\oint Q = \oint W$ & $Q_{net} = W_{net}$
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This is valid for reversible and irreversible cycles.

FIRST LAW (FOR A NON-FLOW PROCESS):

For Cycle, $\oint Q - W = 0 = \oint dE$, Where $E = \text{Energy}$	For Process, Non-Flow Energy Eq. $\Rightarrow dE = Q - W$
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This is valid for reversible and irreversible cycles.

Non-Flow Energy Eq. (N.F.E.E.) For Closed System and Reversible Process.	$dE = Q - PdV [\because W = PdV]$
N.F.E.E. For isolated System, <i>Energy E = Constant</i>	$dE = 0,$

TYPE OF ENERGY				
TRANSIT ENERGY		STORED ENERGY		
HEAT	WORK	MICROSCOPIC	MACROSCOPIC	
		Small or Molecular Level	Large or Bulk	
		INTERNAL	KE: Due to Velocity	PE: Due to Elevation

INTERNAL ENERGY: It's energy associated with molecules. It includes,

Translational K.E.	Rotational K.E.	Vibrational K.E.
INTERNAL ENERGY (U)		INTERNAL ENERGY ($u = U/m$)
It's Extensive Property.		It's intensive property (Independent of mass)

TOTAL ENERGY OF SYSTEM (E): $E = \text{Macroscopic} + \text{Microscopic}$

$dE = dU$	Here, $d(K.E.)$ & $d(P.E.) \cong 0$
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FIRST LAW (AFTER NEGLECTING K.E. & P.E.):

For Reversible and Irreversible process: $dU = Q - W$	For Reversible process: $dU = Q - PdV [\because W = PdV]$
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JOULE'S LAW: "For an ideal Gas internal energy is function of temperature only" ($u = f(T)$)

For Supply Q : T & u increases.	For Rejecting Q : T & u decreases.	For $Q = 0$: T & u remains constant.
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ENTHALPY (H)	SPECIFIC ENTHALPY (h)
$H \text{ (in KJ)} = U + PV$	$h \text{ (in KJ/Kg)} = u + Pv$
Where, U = Total internal Energy (KJ) P = Pressure (KPa) V = Total Volume (m^3)	Where, u = Specific internal Energy (KJ/Kg) P = Pressure (KPa) v = Total Volume (m^3/Kg)
It's Extensive Property.	It's intensive property (Independent of mass)

SPECIFIC HEAT AT CONSTANT VOLUME C_V	SPECIFIC HEAT AT CONSTANT PRESSURE C_P
$C_V = \left[\frac{\partial u}{\partial T} \right]_V$ (For Ideal & Real Gas)	$C_P = \left[\frac{\partial h}{\partial T} \right]_P$ (For Ideal & Real Gas)
For ideal Gas, $C_V = du/dT$ & $C_V = f(T)$	For ideal Gas, $C_P = dh/dT$ & $C_P = f(T)$
$dU \text{ (in KJ)} = m C_V dT$ $du \text{ (in KJ/kg)} = C_V dT$	$dH \text{ (in KJ)} = m C_P dT$ $dh \text{ (in KJ/kg)} = C_P dT$
Molar Specific Heat at Constant Volume: $\bar{C}_V \text{ (in KJ/Kmol K)} = C_V M$	Molar Specific Heat at Constant Pressure: $\bar{C}_P \text{ (in KJ/Kmol K)} = C_P M$
Molar Internal Energy Change: $d\bar{U} \text{ (in KJ)} = n \bar{C}_V dT$	Molar Enthalpy Change: $d\bar{H} \text{ (in KJ)} = n \bar{C}_P dT$

"For an ideal Gas Enthalpy is function of temperature only" ($h = f(T)$ because $u = f(T)$ & $Pv = RT$)

For Increase T : h increases.	For Decrease T : h Decreases.	For $T = 0$: h remains constant.
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IDEAL GAS RELATION: From h (in KJ/Kg) $= u + Pv$ & $Pv = RT$

$C_p - C_v = R$	$C_p/C_v = \gamma$	$C_v = R/(\gamma - 1)$	$C_v = \gamma R/(\gamma - 1)$
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MOLAR IDEAL GAS RELATION:

$\bar{C}_p - \bar{C}_v = \bar{R}$	$\bar{C}_p/\bar{C}_v = \gamma$	$\bar{C}_v = \bar{R}/(\gamma - 1)$	$\bar{C}_v = \gamma \bar{R}/(\gamma - 1)$
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- For Ideal Gas " γ " Depends only on molecular structure.
- For Ideal Gas Specific Heats (C_p & C_v) depends on molecular weights and molecular structure.

$C_v = \gamma \bar{R}/M(\gamma - 1)$	$C_v = \bar{R}/M(\gamma - 1)$
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HEAT TRANSFER EQUATIONS IN NON-FLOW PROCESS:

PROCESS	EQUATIONS ($dU = Q - W$)	FOR IDEAL GAS,
Isochoric Process	$Q = dU (\because W = 0)$	$dU = mC_v dT$
Isobaric Process (Reversible)	$Q = dH (\because P = \text{Constant})$	dH (in KJ) $= mC_p dT$
Isothermal Process	$Q = W (\because T = \text{Constant} \& U = f(T))$	$W = c \ln(V_2/V_1)$
Adiabatic Process ($Q = 0$)	$dU = -W$, It indicates Work done by/on the system is due to change in U.	
Polytropic Process	$Q_{poly} = W_{poly} \left[\frac{\gamma - n}{\gamma - 1} \right]$, where $W_{poly} = \frac{P_1 V_1 - P_2 V_2}{n - 1}$	$PV = mRT$ & dU Eq. $C_v = R/(\gamma - 1)$

POLYTROPIC SPECIFIC HEAT (C_n):	$C_n = C_v \left[\frac{n - \gamma}{n - 1} \right]$
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DERIVATION OF $PV^\gamma = C$ FOR REVERSIBLE ADIABATIC PROCESS:

$dU = Q - W$ & $H = U + PV$ Here For the process, $Q = 0$ (Adiabatic) & $W = PdV$ (Reversible)	By Derivation of enthalpy we will obtain form both equations, $PV^\gamma = C$
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γ VALUES FOR VARIOUS GASES:

From the physics: $u = (n/2)RT$ Here, $C_v = (n/2)R (\because C_v = du/dT)$ From the enthalpy equation, $C_p = (n/2 + 1)R (\because C_p = dh/dT \& \text{physics eq.})$	Here, u = Internal Energy (in KJ/Kg), R = Characteristic Gas Constant (in $KJ/kg K$), T = Absolute temperature (in K), n = Degrees of freedom, $\gamma = 1 + 2/n$
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Type of Gas	Translational DOF	Rotational DOF	Total DOF	C_v	C_p	γ
Mono-Atomic Gas (He, Ar)	3	0	3	$(3/2)R$	$(5/2)R$	1.67
Di-Atomic (O_2, N_2)	3	2	5	$(5/2)R$	$(7/2)R$	1.4
Poly Atomic (CO_2, CH_4)	3	3	6	$3R$	$4R$	1.33

APPLICATION OF FIRST LAW:

FREE EXPANSION PROCESS: Expansion of gas against vacuum. $dU = 0$, $U = \text{Constant}$	Note: 1. Insulated chamber. $Q = 0$. 2. No Resistance from vacuum. $W = 0$.
IDEAL GAS FREE EXPANSION: It's irreversible isothermal Process. The temperature is initially dropping after again reaches to the initial temp.	$P_1 V_1 = P_2 V_2$ ($\because PV = mRT, u \& h = f(T)$ for ideal gas)

PERPETUAL MOTION MACHINE OF FIRST KIND (PMM-I):

There is a machine which is producing work continuously without taking any input energy. It's impossible because it violates first law of thermodynamics.	Perpetual = Continuous
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CHANGE IN INTERNAL ENERGY OF SOLID AND LIQUIDS:

For solid and liquids, $W = 0 (\because dV = 0)$.	Hence, $Q = dU = mCdT$
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SPECIFIC HEAT & CHARACTERISTIC GAS CONSTANT FOR GAS MIXTURE:

$C_{p\text{mix}} = mf_1 C_{p1} + mf_2 C_{p2} + \dots$	$C_{v\text{mix}} = mf_1 C_{v1} + mf_2 C_{v2} + \dots$	
$R_{\text{mix}} = mf_1 R_1 + mf_2 R_2 + \dots$	$h_{\text{mix}} = mf_1 h_1 + mf_2 h_2 + \dots$	$u_{\text{mix}} = mf_1 u_1 + mf_2 u_2 + \dots$

DALTON'S LAW OF PARTIAL PRESSURE:

Ideal Gas (At T, V, P_1) + Ideal Gas (At T, V, P_2) + \dots = Ideal Gas (At $T, V, P_1 + P_2 + \dots$)

RELATION BETWEEN MOLE FRACTION & PRESSURE FRACTION FROM DALTON'S LAW:

$$x = \frac{n_i}{n_{mix}} = \frac{P_i}{P_{mix}} (\because \text{Dalton's condition \& } PV = nRT)$$

HEAT TRANSFER TO THE GAS MIXTURES:

Isochoric Process	$Q = dU_{mix} = dU_1 + dU_2 + \dots = m_{mix} C_{V,mix} dT_{mix}$ $= m_1 C_{V,1} dT_1 + m_2 C_{V,2} dT_2 + \dots$ $\therefore Q = (m_1 C_{V,1} + m_2 C_{V,2}) dT (\because dT_1 = dT_2 = dT)$ Where, $C_{V,1} = R_1/(\gamma - 1)$ & $C_{V,2} = R_2/(\gamma - 1)$	$m_{mix} = m_1 + m_2 + \dots$ $dT_{mix} = (T_f - T_i)_{mix} = dT$ $C_{V,mix} = m f_1 C_{V,1} + m f_2 C_{V,2} + \dots$
Isobaric Process	$Q = dH_{mix} = dH_1 + dH_2 + \dots = m_{mix} C_{P,mix} dT_{mix}$ $= m_1 C_{P,1} dT_1 + m_2 C_{P,2} dT_2 + \dots$ $\therefore Q = (m_1 C_{P,1} + m_2 C_{P,2}) (T_f - T_i)_{mix}$	$\therefore dT_1 = dT_2 = dT = (T_f - T_i)_{mix}$
Adiabatic Mixing of Ideal Gas in Rigid Tank	$dU_{mix} = 0 = dU_1 + dU_2 + \dots = m_{mix} C_{V,mix} dT_{mix}$ $(\because Q = W = 0)$ $\therefore m_1 C_{V,1} dT_1 + m_2 C_{V,2} dT_2 + \dots = 0$ $\therefore m_1 C_{V,1} (T_f - T_1) + m_2 C_{V,2} (T_f - T_2) = 0$ Where, $C_{V,1} = R_1/(\gamma - 1)$ & $C_{V,2} = R_2/(\gamma - 1)$	$T_1 = \text{Initial Temp of Gas 1,}$ $T_2 = \text{Initial Temp of Gas 2,}$ $T_f = \text{Final Temp of Gas mixture,}$ $(T_{fin} - T_{ini})_i = dT_i$

VANDER WALL'S EQUATION: It's Actual/ Real Gas Equation.

For Actual Gas, we can't ignore intermolecular force and volume of gas, $\left[P + \frac{a}{V^2} \right] (V - b) = mRT$ Where, $a/V^2 = \text{Inter molecular Forces, } b = \text{Volume of Molecules.}$	For Ideal Gas: 1. Intermolecular Force $\cong 0$ 2. Volume of Gas Molecules $\cong 0$ Ideal Gas Eq.: $PV = mRT$
Units: If $P(\text{In Pa}) \Leftrightarrow a/V^2(\text{In Pa})$ If $V(\text{In } m^3) \Leftrightarrow b(\text{In } m^3)$	

FIRST LAW FOR OPEN SYSTEM:

OPEN SYSTEM: Mass & Energy Transfer Allowed.	CONTROL VOLUME: It's Volume of open system.
CONTROL SURFACE: Imaginary surface separates open system and surroundings.	
STEADY FLOW PROCESS: Fluid properties don't change with respect to time at a given location.	
Mass Balance: $m_1 = m_2$ Energy Balance: $E_1 = E_2$ Energy & Mass inside always remains constant.	
CONTINUITY EQUATION:	$\dot{m}(\text{in kg/s}) = \rho AV$ $(\rho AV)_1 = (\rho AV)_2$ For Incompressible fluid, $(AV)_1 = (AV)_2$ $\left(\frac{AV}{v}\right)_1 = \left(\frac{AV}{v}\right)_2$

FLOW WORK: The work associated with flowing fluid. $W_{flow}(\text{in KJ}) = PV$ & $W_{flow}(\text{in KJ/kg}) = Pv$.

STEADY FLOW ENERGY EQUATION:

$E = K.E. + P.E. + U + F.E$ $E = \frac{1}{2}mv^2 + mgz + U + PV = \frac{1}{2}mv^2 + mgz + H$ $e = \frac{v^2}{2} + gz + u + Pv = \frac{v^2}{2} + gz + h$	Supplied heat = Q , Work Done by the System = $W_{CV} = W_{system}$, $w_{CV}(\text{in KJ/kg}) = W/m$ $q(\text{in KJ/kg}) = Q/m$ $SFEE: \left(\frac{v^2}{2} + gz + h\right)_1 + q = \left(\frac{v^2}{2} + gz + h\right)_2 + w_{CV}$
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1. S.F.E.E. is valid for reversible and irreversible process.

Units of S.F.E.E.:

In J/kg	$\left(\frac{v^2}{2} + gz + h\right)_1 + q = \left(\frac{v^2}{2} + gz + h\right)_2 + w_{CV}$	$v = \text{Velocity (m/s)}$ $z = \text{Elevation (m)}$	$g = (m/s^2)$
In KJ/s or KW	$\dot{m}_1 \left(\frac{v^2}{2000} + \frac{gz}{1000} + h\right)_1 + \dot{Q} = \dot{m}_2 \left(\frac{v^2}{2000} + \frac{gz}{1000} + h\right)_2 + \dot{W}_{CV}$	$\dot{m}_1 = \dot{m}_2 = \dot{m}$ $\dot{Q} = \dot{m}_1 q$	$\dot{W}_{CV} = \dot{m}_2 w_{CV}$

EXAMPLES OF STEADY FLOW/OPEN SYSTEM PROCESS:

TURBINE: $h_1 = h_2 + w_T$ $w_T = h_1 - h_2$ Here, $h_1 > h_2$ (Expansion Process) $\Leftrightarrow w_T > 0$ \therefore It's Work Producing Device.	NOTE: 1. KE & PE are negligible compared to Enthalpy. $KE \& PE \cong 0$ 2. Turbine is insulated. $q \cong 0$.
IC ENGINE: $h_1 + q = h_2 + w_{IC}$ $w_{IC} = h_1 + q - h_2$ Here, $h_1 > h_2 \Leftrightarrow w_{IC} > 0$ \therefore It's Work Producing Device.	NOTE: 1. KE & PE are negligible compared to Enthalpy. $KE \& PE \cong 0$ If IC Engine is insulated. $q \cong 0$. $w_{IC} = h_1 - h_2$

ROTARY/ RECIPROCATING COMPRESSOR:		NOTE: 1. KE & PE change are negligible compared to Enthalpy. $KE \& PE \cong 0$ 2. Compressor is insulated. $q \cong 0$.
$h_1 + q = h_2 + w_c$	$w_c = h_1 + q - h_2$	
Here, $h_1 < h_2$ (Compression Process) $\Leftrightarrow w_c < 0$ \therefore It's Work Consuming Device.		

FLOW WORK	CONTROL VOLUME WORK
Work done by control volume is zero.	Work done by control volume is not equal to zero.
It just works required to flow of liquid.	It's the work done by the system it includes flow work.

NON-WORK DEVICES:

DEVICES	NOTES
PIPELINE: $h_1 + q = h_2$ Special Case of Pipeline: Electric heater is inserted inside pipeline. $w_{CV} = -w_{Electric}$	1. $w_{CV} = 0$ (Pipeline is not doing any work) 2. $D_1 = D_2 \Rightarrow v_1 = v_2$ (Cross section area is same) 3. $Z_1 = Z_2$ (Pipeline is horizontal)
NOZZLE: $h_1 = \frac{v_2^2}{2} + h_2$	1. $w_{CV} = 0$ (Nozzle is not doing any work) 2. $D_1 \gg D_2 \Rightarrow v_1 \ll v_2$ (Cross section area isn't same) 3. $Z_1 = Z_2$ (Nozzle is horizontal) 4. Nozzle is insulated. $q \cong 0$.
DIFFUSER: $h_1 + \frac{v_1^2}{2} = h_2$	1. $w_{CV} = 0$ (Diffuser is not doing any work) 2. $D_1 \ll D_2 \Rightarrow v_1 \gg v_2$ (Cross section area isn't same) 3. $Z_1 = Z_2$ (Diffuser is horizontal) 4. Diffuser is insulated. $q \cong 0$.

MULTI STREAMS DEVICES:

DEVICES	NOTES				
HEAT EXCHANGER: Mass Balance: <table border="1" style="margin-left: 20px;"> <tr> <td>$\dot{m}_2 = \dot{m}_4 = \dot{m}_{Hot}$</td><td>$\dot{m}_1 = \dot{m}_3 = \dot{m}_{Cold}$</td></tr> <tr> <td colspan="2">$\dot{m}_1 + \dot{m}_2 = \dot{m}_3 + \dot{m}_4$</td></tr> </table> By SFEE (in KW), $\dot{m}_{Hot}(h_2 - h_4) = \dot{m}_{Cold}(h_3 - h_1)$ $\dot{m}_{Hot}(h_2 - h_4) = \dot{m}_{Cold}(h_3 - h_1) + \dot{Q}$ $\dot{Q}_{loss \text{ by the hot fluid}} = \dot{Q}_{gained \text{ by the cold fluid}} + \dot{Q}_{loss}$	$\dot{m}_2 = \dot{m}_4 = \dot{m}_{Hot}$	$\dot{m}_1 = \dot{m}_3 = \dot{m}_{Cold}$	$\dot{m}_1 + \dot{m}_2 = \dot{m}_3 + \dot{m}_4$		1. $w_{CV} = \dot{W}_{CV} = 0$ (HE is not doing any work) 2. HE is insulated. $\dot{Q} \cong 0$. 3. KE & PE are negligible compared to Enthalpy. $KE \& PE \cong 0$
$\dot{m}_2 = \dot{m}_4 = \dot{m}_{Hot}$	$\dot{m}_1 = \dot{m}_3 = \dot{m}_{Cold}$				
$\dot{m}_1 + \dot{m}_2 = \dot{m}_3 + \dot{m}_4$					
	4. If we consider heat loss = \dot{Q}_{loss}				

FLOW WORK IN EVACUATED BOTTLE:

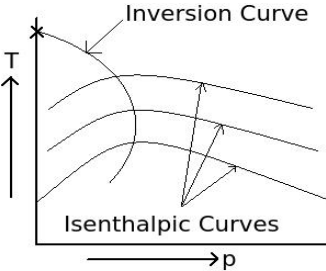
$W_{flow} = PV$	1. This is not expansion case.
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THROTTLING PROCESS: It's flow of fluid through a small passage.

At Partially opening of valve, By Applying S.F.E.E., $h_1 = h_2 = h = \text{Constant}$ Hence, It's Isenthalpic process. Here, pressure decreases. (according to Bernoulli's equation)	1. KE & PE change are negligible compared to Enthalpy. $KE \& PE \cong 0$ 2. Throttling heat transfer $q \cong 0$. (\because Area for $q = 0$) In throat, Pressure decrease, Area decrease, Velocity increase.
NOZZLE	THROTTLING
C/s Area Gradually decreases.	Drastically C/s area decreases. It's irreversible process (Due to molecular friction at sudden reducing C/s).

Throttling is irreversible adiabatic ($\because q \cong 0$) process.

JOULE-THOMSON:

COEFFICIENT (μ): It's defined as ratio of change in temperature to the change in pressure at constant enthalpy. $\mu = \left[\frac{dT}{dP} \right]_{h=c}$	EXPERIMENT: Throttling valve and section both sides.		
	Initially Valve is fully open	At partially closing successively	
	At A: h_1, P_1, T_1	At B: h_i, P_i, T_i	
	PLOTTED GRAPH: T-P Diagram. OBSERVATION: Pressure decreases with increasing in temp. and reaches maximum. If Further Pressure decreases, temp. decreases.		
ISENTHALPIC CURVE: Enthalpy remains constant.		INVERSION CURVE: $\mu = 0$ (Slop of T-P dia. = 0) line.	

SIGNIFICANCE OF (μ): Joule-Thomson coefficient represents slope of isenthalpic line on T-P diagram.

LHS of Inversion Curve: $\mu = +ve$ (Cooling)	RHS of Inversion Curve: $\mu = -ve$ (Heating)	On of Inversion Curve: $\mu = 0$ Temperature remains constant.
Temperature during throttling of Gas may increase, decrease or may remain constant.		

OPEN SYSTEM WORK TRANSFER:

N. F. E. E.	S. F. E. E.
$Q = dU + W$ & $q = du + w$	$q = dh + w = du + d(Pv) + w$ (Only Flow Work is Added)

OPEN SYSTEM REVERSIBLE WORK TRANSFER:

Take Example of IC engine and consider it as both Open system and closed system as reversible process, By ignoring K.E., P.E. in S.F.E.E., $h_1 + q = h_2 + w_{C.V.} \Leftrightarrow q = dh + w_{C.V.}$ $q = du + d(Pv) + w_{C.V.} = du + Pdv + vdP + w_{C.V.}$	From N.F.E.E., $q = du + Pdv + w$ (\because Reversible Process) By Equating both q equation we can get, $q = - \int v dP$
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- The Area under the curve when projected to pressure axis represents open system reversible work transfer.

$$W_{Open\ System} = PV\ Diagram\ Area\ projected\ on\ P$$

WORK TRANSFER IN VARIOUS FLOW PROCESS:

Isochoric Process	$w = -v(P_2 - P_1)$	($\because v = constant$)
Isobaric Process	$w = 0$	($\because dP = 0$)
Iso Thermal Process	$w = Pv \ln(P_1/P_2) = Pv \ln(v_2/v_1)$	($\because P_1 v_1 = P_2 v_2$)
Adiabatic Process	$w = \gamma \left[\frac{P_1 v_1 - P_2 v_2}{\gamma - 1} \right] = \gamma w_{Closed\ adiabatic}$	($\because Pv^\gamma = Constant$)
Polytropic Process	$w = n \left[\frac{P_1 v_1 - P_2 v_2}{n - 1} \right] = n w_{Closed\ Poly.}$	
Isothermal Open System		Isothermal Close System
$W_{Open\ System} = PV\ Diagram\ Area\ projected\ on\ P$		$W_{Close\ System} = PV\ Diagram\ Area\ projected\ on\ V$
$W_{Open\ System} = W_{Close\ System}$ ($\because PV$ is rectangular hyperbola for isothermal process)		

UNSTEADY FLOW PROCESS:

UNSTEADY FLOW:

Fluid properties change with respect to time at a given location. So, mass and energy get stored in the control volume.

NOTATIONS:

m_i = Inlet Mass	m_e = Exit Mass	m_1 = Initial Mass in the C.V.	m_2 = Final Mass in the C.V.
E_i = Inlet Energy	E_e = Exit Energy	E_1 = Initial Energy in the C.V.	E_2 = Final Energy in the C.V.

MASS BALANCE: $\frac{dm_i}{dt} - \frac{dm_e}{dt} = \left(\frac{dm}{dt} \right)_{C.V.}$	ENERGY BALANCE: $\frac{dE_i}{dt} - \frac{dE_e}{dt} = \left(\frac{dE}{dt} \right)_{C.V.}$
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Here, for the process if C.V. is consuming heat and developing work,

$E_i = \frac{1}{2} m_i v_i^2 + m_i g z_i + H_i + Q$ By neglecting K.E. & P.E., $E_i = m_i h_i + Q$	$E_e = \frac{1}{2} m_e v_e^2 + m_e g z_e + H_e + W_{C.V.}$ By neglecting K.E. & P.E., $E_e = m_e h_e + W_{C.V.}$
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Here,

$\left(\frac{dE}{dt} \right)_{C.V.} = \left(\frac{dU}{dt} \right)_{C.V.} = \frac{d(m_i h_i + Q)}{dt} - \frac{d(m_e h_e + W_{C.V.})}{dt}$	Here, h_i & h_e don't change w. r. t. time, $\therefore \dot{U}_{C.V.} = h_i \dot{m}_i - h_e \dot{m}_e + \dot{Q} - \dot{W}_{C.V.}$
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EXAMPLES OF UNSTEADY FLOW PROCESS:

CHARGING OF TANK/ TANK FILLING PROCESS	DISCHARGING OF TANK
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