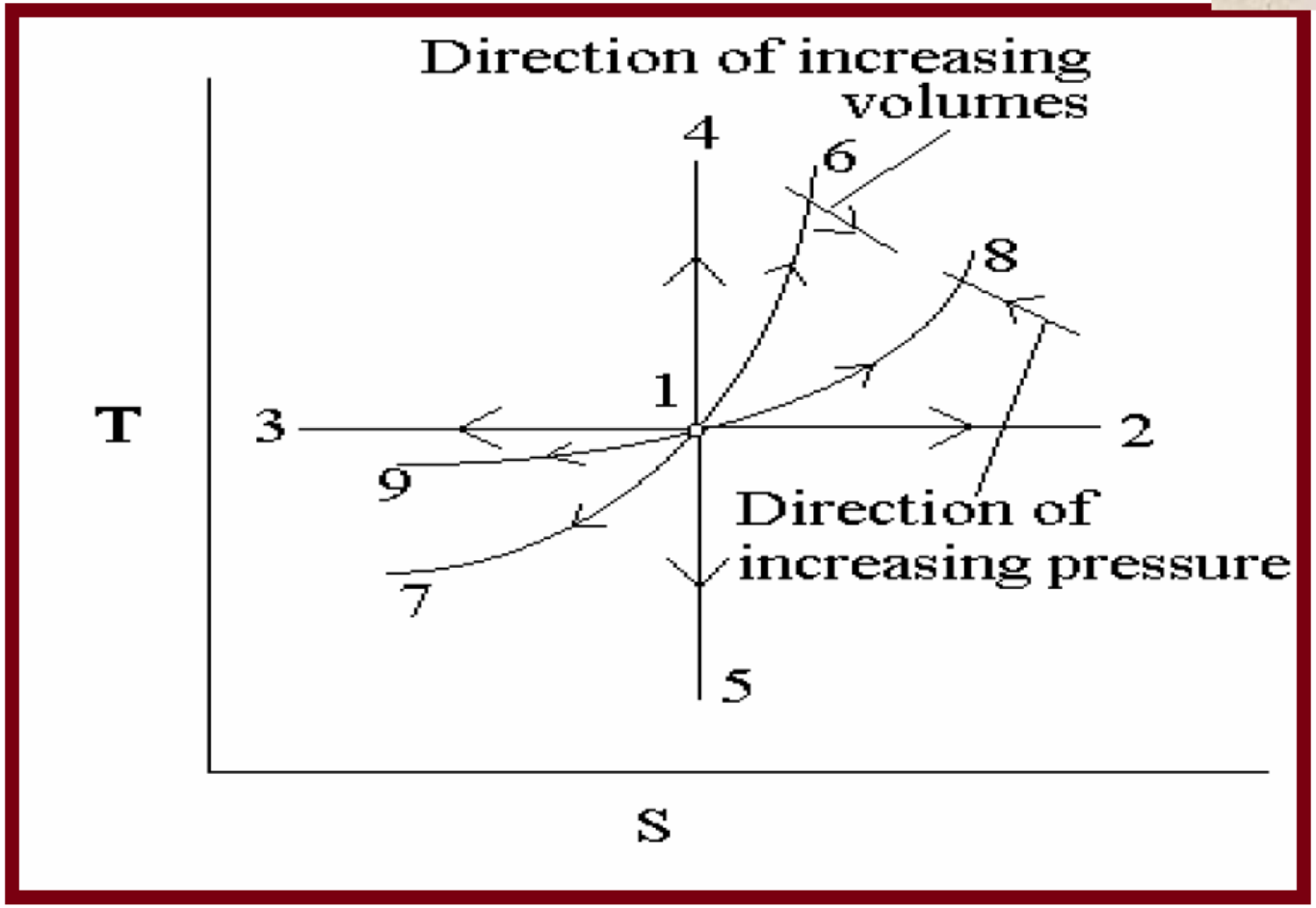
- Recap: Lecture 14: 25th February 2014, 0830-0930 hrs.
  - Entropy change and entropy generation
  - Increase of entropy principle
  - Tds equations
  - Entropy change of liquids, solids and ideal gases
  - Third law of thermodynamics
  - Entropy and energy transfer

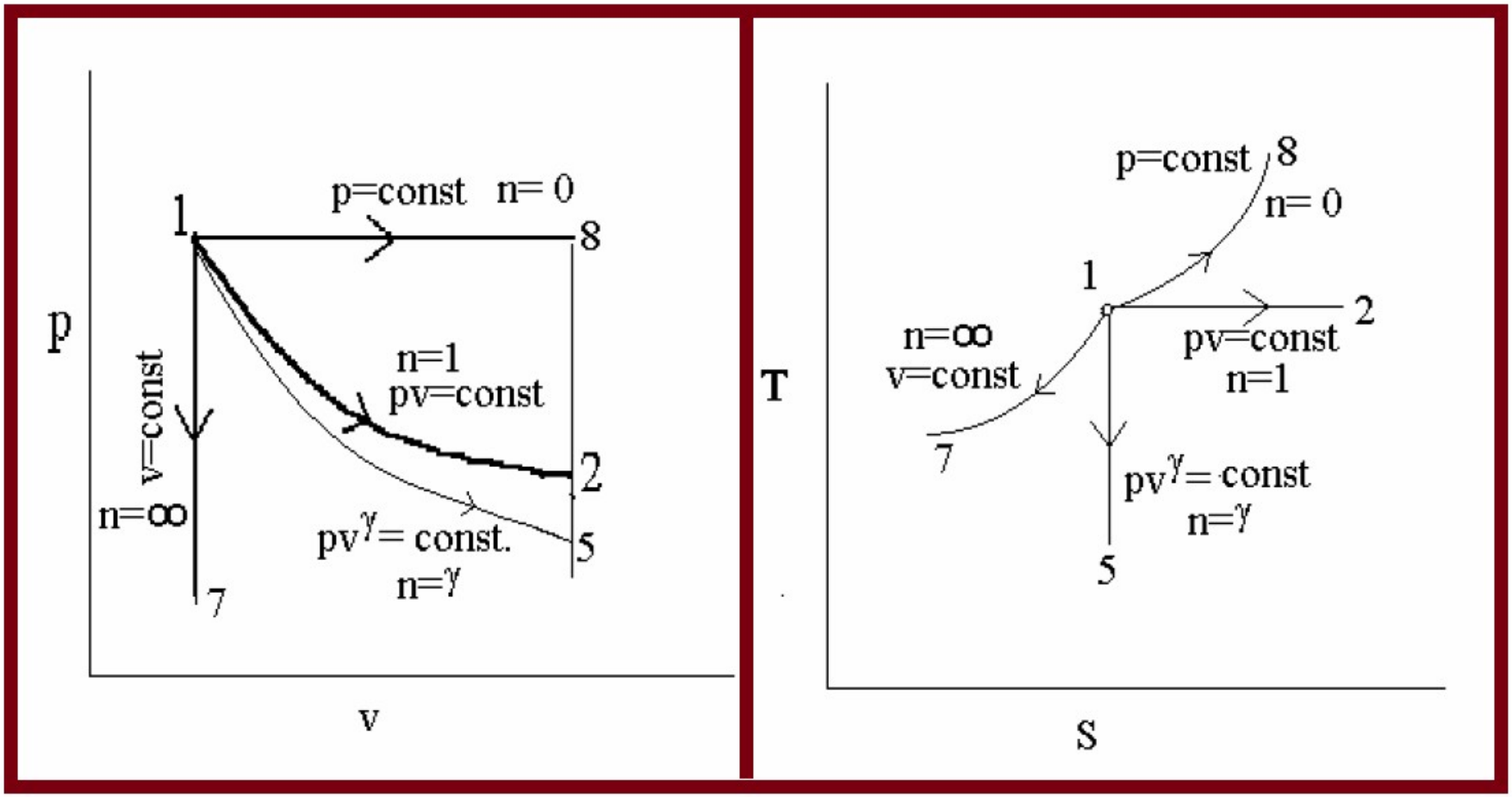


7--6 Const V line

9-1-8 Const. P line

	s	T	p	v
1-2 Isothermal expansion	↑	—	↓	↑
1-3 Isothermal compression	↓	—	↑	↓
1.4 Isentropic compression	—	↑	↑	↓
1-5 Isentropic expansion	—	↓	↓	↑
1-6 Isochoric heating	↑	↑	↑	—
1-7 Isochoric cooling	↓	↓	↓	—
1-8 Isobaric heating/expansion	↑	↑	—	↑
1-9 Isobaric cooling/compression	↓	↓	—	↓

Comparison Between P-v and T-s Planes



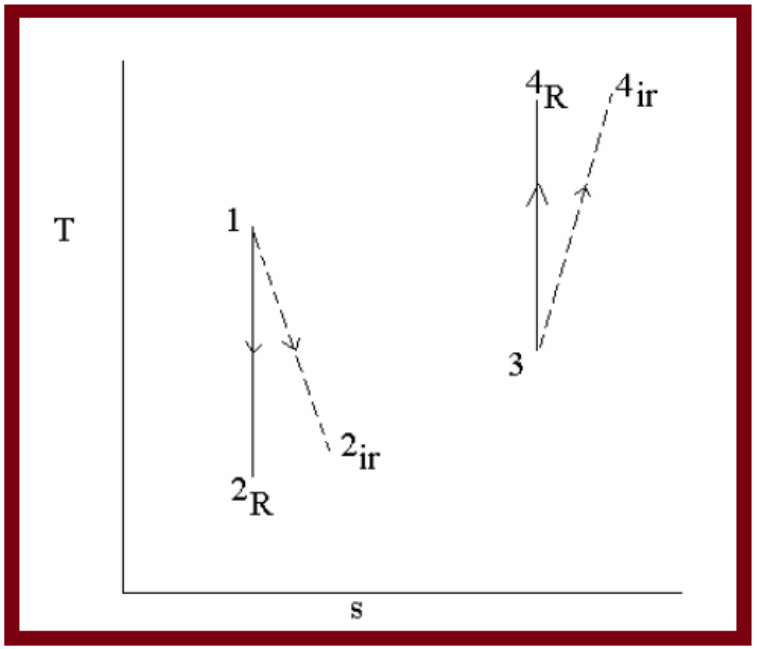
Moral 1

$(S_1\text{-}S_2)_{irreversible} > (S_1\text{-}S_2)_{reversible}$

An irreversible process generates more entropy than a reversible process.

Moral 2:

If process B is adiabatic but irreversible $S_1\text{-}S_2 > 0$ or $S_1 > S_2$



Exergy

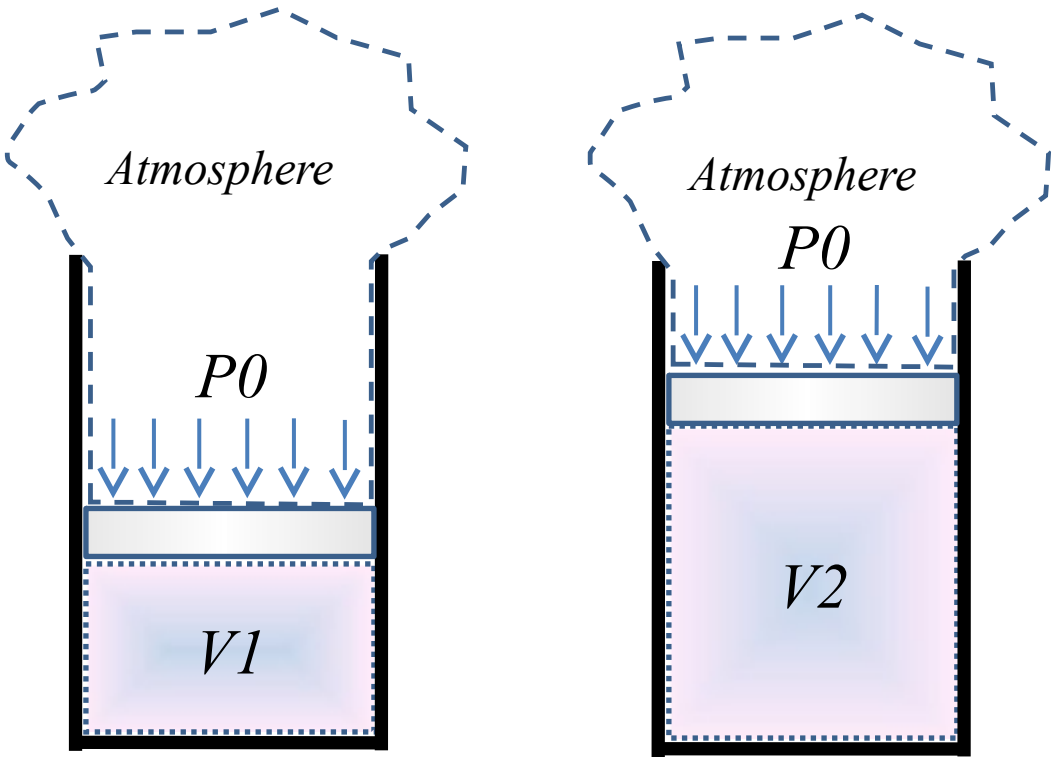
- Exergy associated with KE and PE:
  - KE and PE are forms of mechanical energy that can be completely converted to work.
  - Therefore the exergy associated with KE and PE will be equal to the magnitude of KE and PE regardless of the temperature and pressure.

$$xKE=V2/2$$

$$xPE=gz$$

- However, the internal energy, u, and enthalpy, h, of a system are not entirely available for work.

Surroundings work and useful work



Surroundings work, $W_{surr} = P_0(V_2 - V_1)$

Useful work, $W_u = W - W_{surr} = W - P_0(V_2 - V_1)$

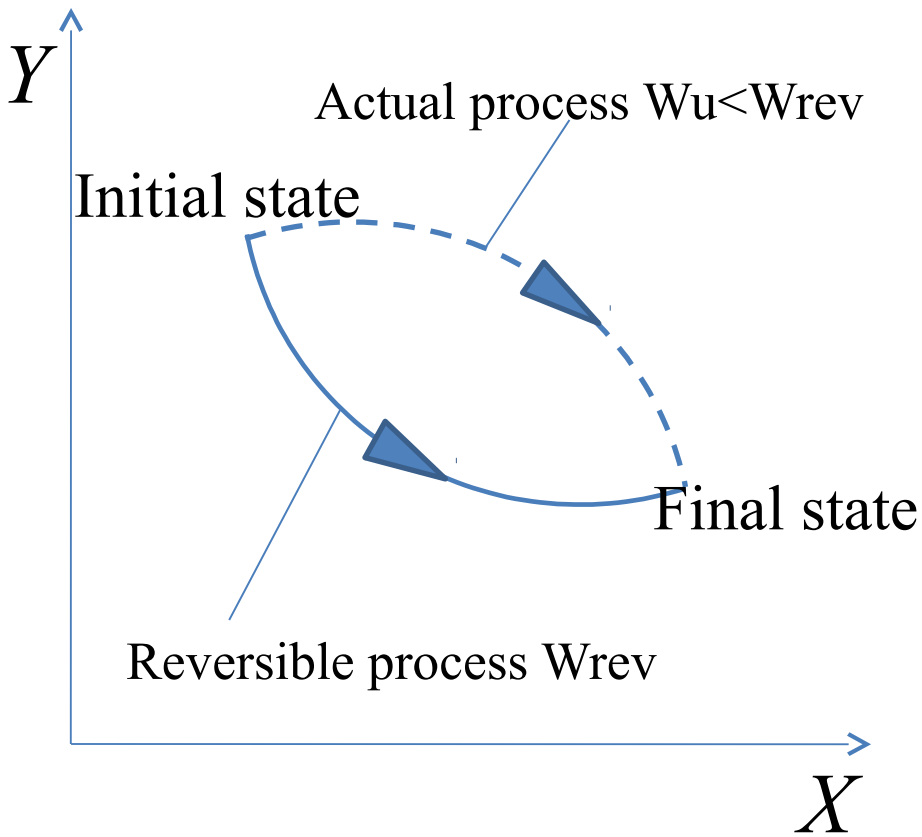
Surroundings work and useful work

- *Wsurr* represents a loss during expansion process and gain during compression.
- The work done by or against the atmospheric pressure has significance only for systems that involve moving boundary work.
- It has no significance for cyclic devices and systems whose boundaries remain fixed during a process such as rigid tanks and steady-flow devices.

Reversible work and irreversibility

- Reversible work, Wrev: the maximum amount of useful work that can be produced as a system undergoes a process between the specified initial and final states.
- When the final state is the dead state, the reversible work equals exergy.
- For processes that require work, reversible work represents the minimum amount of work necessary to carry out that process.

Reversible work and irreversibility



Irreversibility= Reversible work – Useful work

$$I = Wrev - Wu$$

- Difference between the reversible work *Wrev the useful work Wu* is due to the irreversibilities: Irreversibility, I
- The irreversibility is equivalent to the *exergy destroyed.*
- For a totally reversible process, the actual and reversible work terms are identical, and thus the irreversibility is zero
- Totally reversible processes generate no entropy.
- Irreversibility represents the energy that could have been converted to work but was not.

Reversible work and irreversibility

- Irreversibility, I, can be expressed as

$$I = W_{rev,out} - W_{u,out}$$

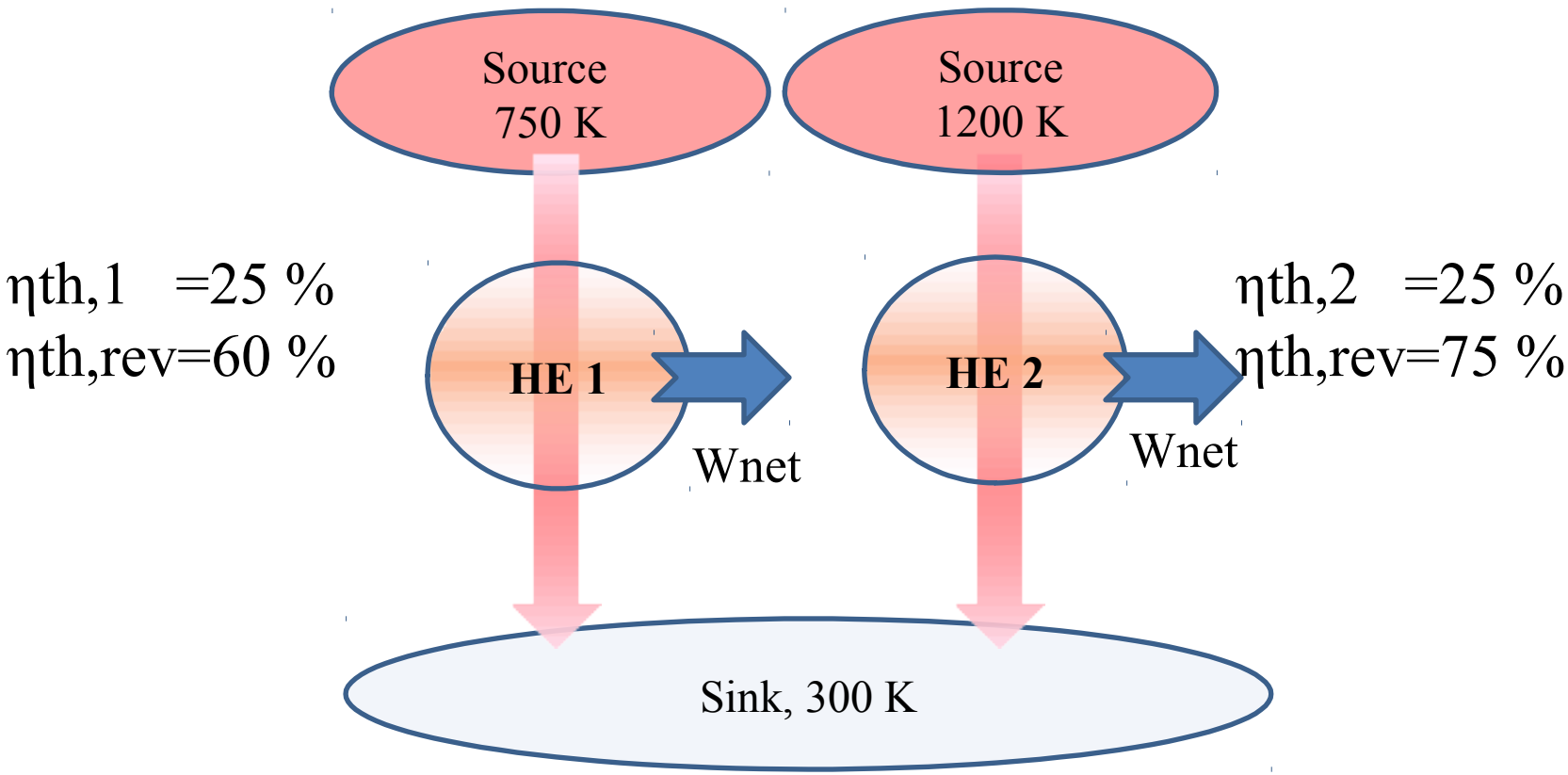
Or, $$I = W_{u,in} - W_{rev,in}$$

- Irreversibility is a positive quantity for all actual (irreversible) processes
  - since $W_{rev} \geq W_u$ for work producing devices and $W_{rev} \leq W_u$ for work-consuming devices.

Second law efficiency

- Thermal efficiency, COPR/HP based on the first law: first law efficiency
- Makes no reference to the best possible performance.
- The ratio of the actual thermal efficiency to the maximum possible (reversible) thermal efficiency under the same conditions: Second law efficiency, η_{II}

Second law efficiency



Second law efficiency

- The second law efficiency is expressed in different forms depending upon the type of device under consideration.

For heat engines, $\eta_{II} = \dfrac{\eta_{th}}{\eta_{th,rev}}$

For work producing devices, $\eta_{II} = \dfrac{W_u}{W_{rev}}$

For work consuming devices, $\eta_{II} = \dfrac{W_{rev}}{W_u}$

For refrigerators and heat pumps, $\eta_{II} = \dfrac{COP}{COP_{rev}}$

Second law efficiency

- In general,

  η_{II}= Exergy recovered/Exergy supplied

  = 1- Exergy destroyed/Exergy supplied
- Second-law efficiency is a measure of the performance of a device relative to its performance under reversible conditions.
- Hence, second-law efficiency of all reversible devices is 100 percent.

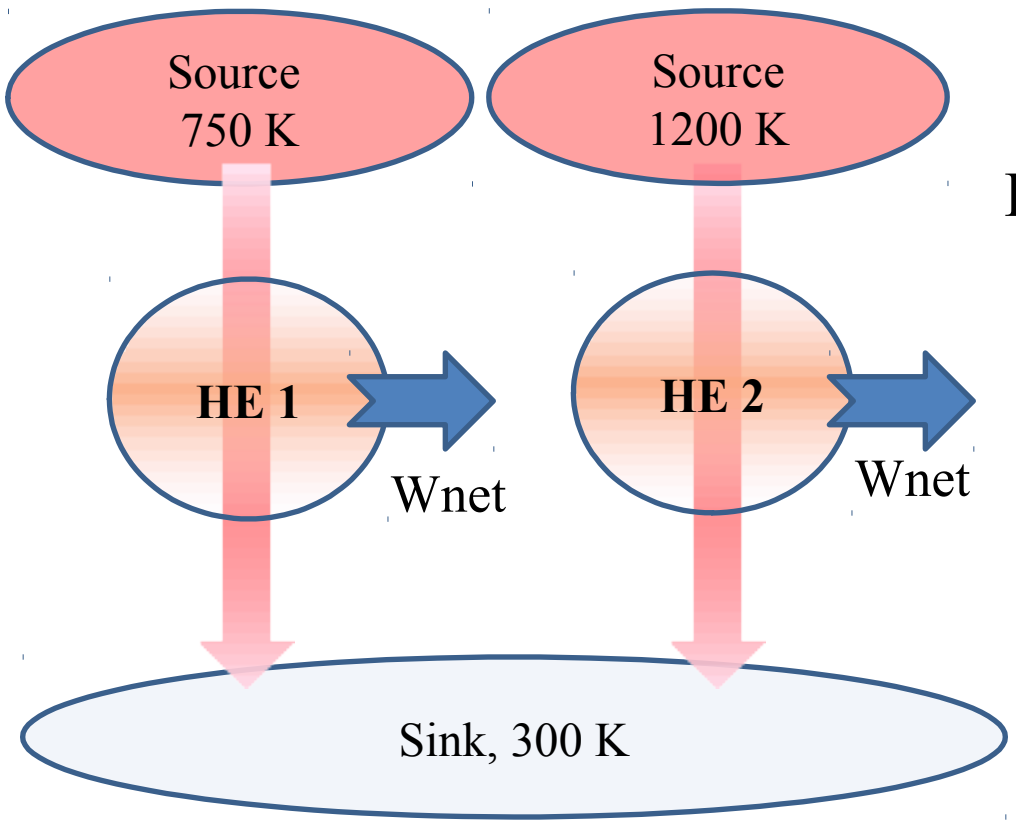
Second law efficiency

- For a heat engine,
  - The exergy supplied is the decrease in the exergy of the heat transferred to the engine
  - Exergy transferred to the engine is the difference between the exergy of the heat supplied and the exergy of the heat rejected.
  - The exergy of the heat rejected at the temperature of the surroundings is zero.
  - The net work output is the recovered exergy.

Second law efficiency

- For a refrigerator of heat pump,
  - The exergy supplied is the work input, Since the work supplied to a cyclic device is entirely available.
  - Recovered exergy is the exergy of the heat transferred to the high temperature reservoir for a heat pump.
  - Recovered exergy is the exergy of the heat transferred from low temperature reservoir for a refrigerator.
  - For a heat exchanger with two unmixed fluid streams, normally the exergy supplied is the decrease in the exergy of the high temperature fluid stream and exergy recovered is the increase in the exergy of the lower temperature fluid stream.

Second law efficiency



HE 1

$\eta_{th,1} = 25\ \%$

$\eta_{th,rev} = 60\ \%$

$\eta_{II,1} = 25/60 = 0.417$

HE 2

$\eta_{th,2} = 25\ \%$

$\eta_{th,rev} = 75\ \%$

$\eta_{II,2} = 25/75 = 0.333$

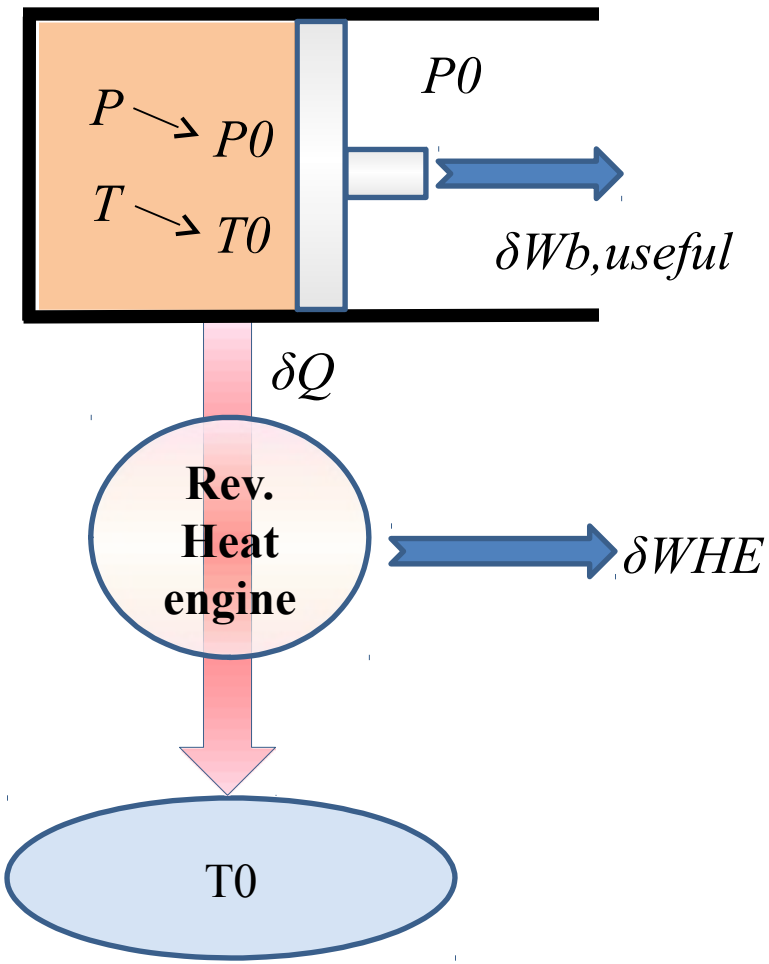
Exergy change of a system

- The value of exergy (unlike energy) depends on the state of the environment as well as the state of the system.
- The exergy of a system that is in equilibrium with its surroundings is zero.
- This state of the system is referred to as a "dead state".

Exergy of a closed system

- To derive an expression for exergy change of a closed system, we consider a piston-cylinder assembly.
- The system undergoes a differential change of state.
- Heat transfer from the system occurs through a reversible heat engine (to avoid any irreversibilities).
- The total work done = Work done (PdV) + the work done by the reversible heat engine.

Exergy of a closed system



From the first law for the system,

$$-\delta Q - \delta W = dU$$

Here, $\delta W = PdV$

$$= (P - P_0)dV + P_0 dV$$

$$= \delta W_{b,useful} + P_0 dV$$

Exergy of a closed system

For the reversible heat engine,

$$dS = \delta Q / T \quad and \quad \eta_{th} = 1 - T_0 / T$$

Therefore, $\delta W_{HE} = \left(1 - \frac{T_0}{T}\right)\delta Q = \delta Q - \frac{T_0}{T}\delta Q$

$$Here \frac{\partial Q}{T} + \frac{\partial Q_o}{T_o} = 0$$

$$Therefore, \frac{\partial Q}{T} = -T_o dS$$

$$= \delta Q - (-T_0 dS)$$

$$or, \delta Q = \delta W_{HE} - T_0 dS$$

$$\therefore \delta W_{total,useful} = \delta W_{HE} + \delta W_{b,useful} = -dU - P_0 dV + T_0 dS$$

Integrating from given state to the dead state (0),

$$W_{total,useful} = (U - U_0) + P_0(V - V_0) - T_0(S - S_0)$$

Exergy of a closed system

A closed system may possess KE and PE.

Therefore the exergy of a closed system is

$$X = (U - U_0) + P_0(V - V_0) - T_0(S - S_0) + m\frac{V^2}{2} + mgz$$

(Since KE and PE are themselves forms of exergy)

For unit mass,

$$\phi = (u - u_0) + P_0(v - v_0) - T_0(s - s_0) + \frac{V^2}{2} + gz$$

Exergy change of a closed system

Exergy change of a system is the difference between the initial and final exergies of the system.

$$\Delta X = X_2 - X_1 = m(\phi_2 - \phi_1)$$

$$= (U_2 - U_1) + P_0(V_2 - V_1) - T_0(S_2 - S_1) + m\frac{V_2^2 - V_1^2}{2} + mg(z_2 - z_1)$$

Or, per unit mass,

$$\Delta\phi = (u_2 - u_1) + P_0(v_2 - v_1) - T_0(s_2 - s_1) + \frac{V_2^2 - V_1^2}{2} + g(z_2 - z_1)$$

Exergy of a flow system

Exergy change of a flow system will consist of

enthalpy ($h = u + pv$)

$$x_{flowing\,fluid} = x_{non-flowing\,fluid} + x_{flow}$$

$$= (u - u_0) + P_0(v - v_0) - T_0(s - s_0) + \frac{V^2}{2} + gz + (P - P_0)v$$

$$= (u + Pv) - (u_0 + P_0 v_0) - T_0(s - s_0) + \frac{V^2}{2} + gz$$

$$= (h - h_0) - T_0(s - s_0) + \frac{V^2}{2} + gz$$

This is known as the flow exergy, Ψ or ψ (per unit mass)

Exergy change of a flow system

Flow exergy change,

$$\Delta\Psi = (H_2 - H_1) + T_0(S_2 - S_1) + m\frac{V_2^2 - V_1^2}{2} + mg(z_2 - z_1)$$

Flow exergy change per unit mass,

$$\Delta\psi = (h_2 - h_1) + T_0(s_2 - s_1) + \frac{V_2^2 - V_1^2}{2} + g(z_2 - z_1)$$

How do the exergy equations compare with the energy equations for closed systems and flow systems?

Decrease of exergy principle

- The exergy of an isolated system during a process always decreases or, in the limiting case of a reversible process, remains constant.
- Exergy never increases and exergy is destroyed during an actual process.
- From the energy and entropy balances, we can show that:
  $-T_0 S_{gen} = X_2 - X_1 \leq 0$
- Since $T_0 S_{gen} \geq 0$, it follows that for an isolated system $(X_2 - X_1) \leq 0$

Exergy destruction

- Irreversibilities always cause increase in entropy.
- Increase in entropy leads to destruction of exergy.
- Exergy destroyed is proportional to entropy generated.
- For actual processes, exergy destroyed is always a positive quantity.
- Exergy destroyed represents the lost work potential and is also called the irreversibility or lost work.

Exergy destruction

$$Xdestroyed = T0Sgen \geq 0$$

$$X_{destroyed} \begin{cases} > 0 & \text{Irreversible process} \\ = 0 & \text{Reversible process} \\ < 0 & \text{Impossible process} \end{cases}$$

Exergy balance

- The exergy change of a system during a process is equal to the difference between the net exergy transfer through the system boundary and the exergy destroyed within the system boundaries as a result of irreversibilities.

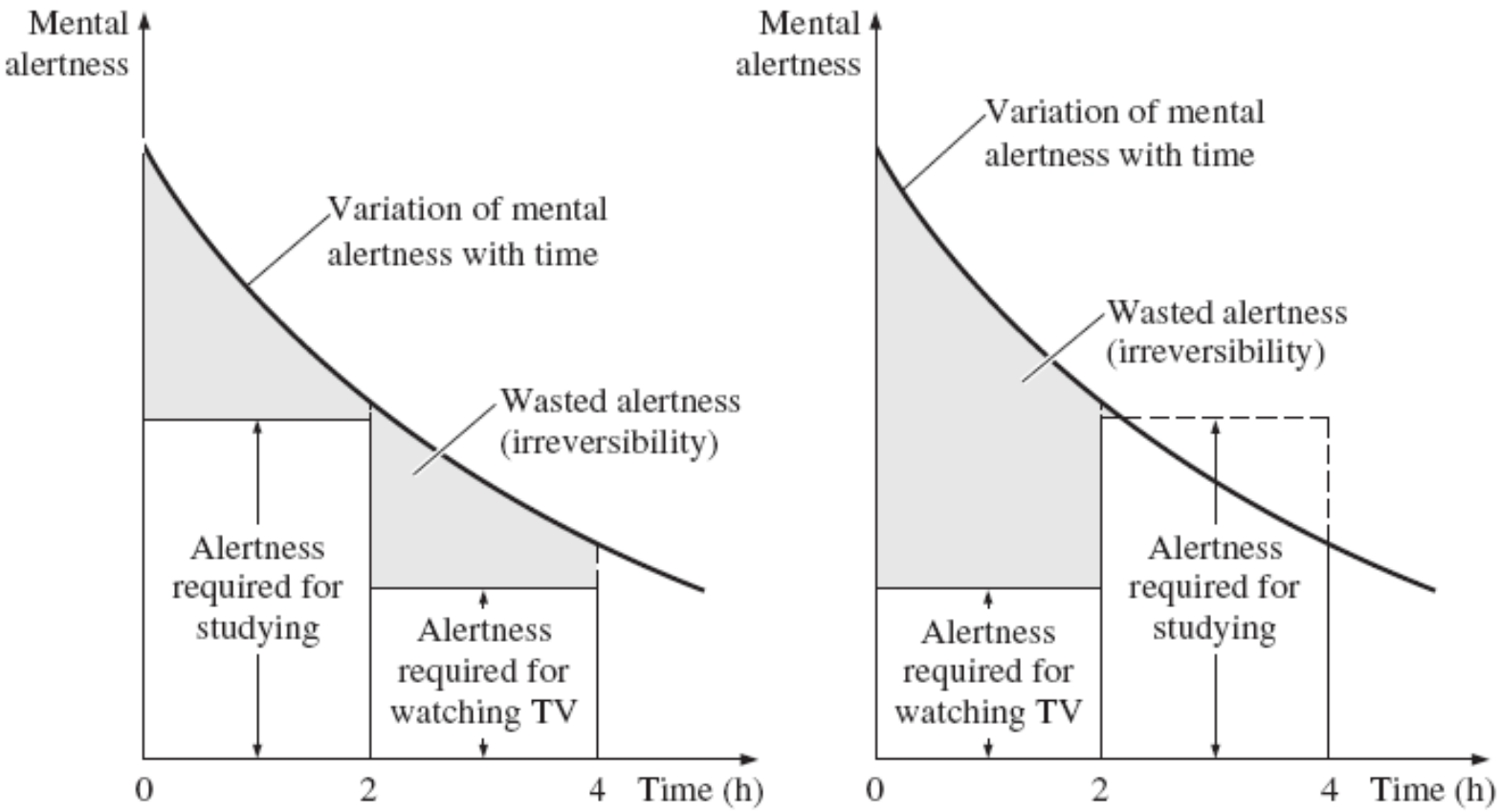
$$X_{in} - X_{out} - X_{destroyed} = \Delta X_{system}$$

Net exergy transfer by heat and mass | Exergy generation | Change in exergy

This can also be expressed in the rate form as,

$$\dot{X}_{in} - \dot{X}_{out} - \dot{X}_{destroyed} = \Delta \dot{X}_{system}$$

Rate of net exergy transfer by heat and mass | Rate of exergy generation | Rate of change in exergy



(*a*) Studying first (*b*) Watching a movie first

The irreversibility associated with a student studying and watching a movie on television, each for two hours.

1.2 Helmholtz energy (Helmholtz function)

There are a number of ways of obtaining an expression for Helmholtz energy, but the one based on the Clausius derivation of entropy gives the most insight.

In the previous section, the criteria for equilibrium were discussed and these were derived in terms of $\Delta S)_E$. The variation of entropy is not always easy to visualise, and it would be more useful if the criteria could be derived in a more tangible form related to other properties of the system under consideration. Consider the arrangements in Figs 1.3(a) and (b). Figure 1.3(a) shows a System A, which is a general system of constant composition in which the work output, δW, can be either shaft or displacement work, or a combination of both. Figure 1.3(b) is a more specific example in which the work output is displacement work, $p\ \delta V$; the system in Fig 1.3(b) is easier to understand.

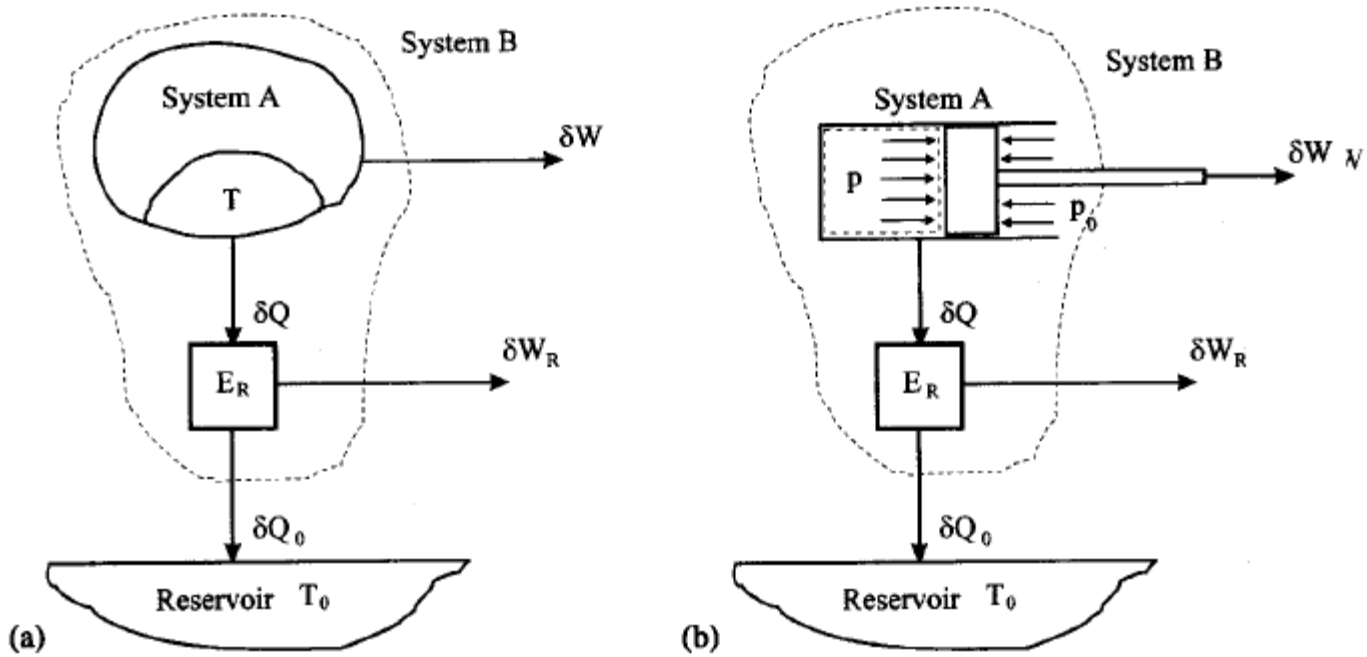


Fig. 1.3 Maximum work achievable from a system

In both arrangements, System A is a closed system (i.e. there are no mass transfers), which delivers an infinitesimal quantity of heat δQ in a ***reversible manner*** to the heat engine E_R. The heat engine then rejects a quantity of heat δQ_0 to a reservoir, e.g. the atmosphere, at temperature T_0.

Let dE, dV and dS denote the changes in internal energy, volume and entropy of the system, which is of constant, invariant composition. For a specified change of state these quantities, which are changes in properties, would be independent of the process or work done. Applying the First Law of Thermodynamics to System A gives

$$\delta W = -dE + \delta Q \tag{1.6}$$

If the heat engine (E_R) and System A are considered to constitute another system, System B, then, applying the First Law of Thermodynamics to System B gives

$$\delta W_{net} = \delta W + \delta W_R = -dE + \delta Q_0 \tag{1.7}$$

where $\delta W + \delta W_R$ = net work done by the heat engine and System A. Since the heat engine is internally reversible, and the entropy flow on either side is equal, then

$$\frac{\delta Q_0}{T_0} = \frac{\delta Q}{T} \tag{1.8}$$

and the change in entropy of System A during this process, because it is reversible, is $dS = \delta Q_R/T$. Hence

$$\left.\begin{aligned}\delta W_{net} &= -dE + T_0\,dS \\ &= -d(E - T_0 S)\end{aligned}\right\}\text{because } T_0 = \text{constant} \tag{1.9}$$

The expression $E - T_0S$ is called the *Helmholtz energy* or *Helmholtz function*. In the absence of motion and gravitational effects the energy, E, may be replaced by the intrinsic internal energy, U, giving

$$\delta W_{net} = -d(U - T_0S) \tag{1.10}$$

The significance of δW_{net} will now be examined. The changes executed were considered to be reversible and δW_{net} was the net work obtained from System B (i.e. System A + heat engine E_R). Thus, δW_{net} must be the maximum quantity of work that can be obtained from the combined system. The expression for δW is called the change in the Helmholtz energy, where the Helmholtz energy is defined as

$$F = U - TS \tag{1.11}$$

Helmholtz energy is a property which has the units of energy, and indicates the maximum work that can be obtained from a system. It can be seen that this is less than the internal energy, U, and it will be shown that the product TS is a measure of the unavailable energy.

1.3 Gibbs energy (Gibbs function)

In the previous section the maximum work that can be obtained from System B, comprising System A and heat engine E_R, was derived. It was also stipulated that System A could change its volume by δV, and while it is doing this it must perform work on the atmosphere equivalent to $p_0\,\delta V$, where p_0 is the pressure of the atmosphere. This work detracts from the work previously calculated and gives the *maximum useful work*, δW_u, as

$$\delta W_u = \delta W_{net} - p_0\,\mathrm{d}V \tag{1.12}$$

if the system is in pressure equilibrium with surroundings.

$$\begin{aligned}\delta W_u &= -\mathrm{d}(E - T_0 S) - p_0\,\mathrm{d}V \\ &= -\mathrm{d}(E + p_0 V - T_0 S)\end{aligned}$$

because p_0 = constant. Hence

$$\delta W_u = -\mathrm{d}(H - TS) \tag{1.13}$$

The quantity $H - TS$ is called the *Gibbs energy*, *Gibbs potential*, or the *Gibbs function*, G. Hence

$$G = H - TS \tag{1.14}$$

Gibbs energy is a property which has the units of energy, and indicates the maximum useful work that can be obtained from a system. It can be seen that this is less than the enthalpy, H, and it will be shown that the product TS is a measure of the unavailable energy.

$$dU = T\,dS - p\,dV + \sum \mu_i\,dn_i$$
$$dH = T\,dS + V\,dp + \sum m_i\,dn_i$$
$$dF = -S\,dT - p\,dV + \sum \mu_i\,dn_i$$
$$dG = -S\,dT + V\,dp + \sum \mu_i\,dn_i$$

1.4.1 HELMHOLTZ ENERGY

(i) The change in Helmholtz energy is the maximum work that can be obtained from a closed system undergoing a reversible process whilst remaining in temperature equilibrium with its surroundings.

(ii) A decrease in Helmholtz energy corresponds to an increase in entropy, hence the minimum value of the function signifies the equilibrium condition.

(iii) A decrease in entropy corresponds to an increase in F; hence the criterion $dF)_T > 0$ is that for stability. This criterion corresponds to work being done on the system.

(iv) For a constant volume system in which $W = 0$, $dF = 0$.

(v) For reversible processes, $F_1 = F_2$; for all other processes there is a decrease in Helmholtz energy.

(vi) *The minimum value of Helmholtz energy corresponds to the equilibrium condition.*

1.4.2 GIBBS ENERGY

(i) The change in Gibbs energy is the maximum useful work that can be obtained from a system undergoing a reversible process whilst remaining in pressure and temperature equilibrium with its surroundings.

(ii) The equilibrium condition for the constraints of constant pressure and temperature can be defined as:

(1) $\mathrm{d}G)_{p,T} < 0$ spontaneous change

(2) $\mathrm{d}G)_{p,T} = 0$ equilibrium

(3) $\Delta G)_{p,T} > 0$ criterion of stability.

(iii) *The minimum value of Gibbs energy corresponds to the equilibrium condition.*