
The First Law of Thermodynamics (FL)

The First Law of Thermodynamics

- Explain and manipulate the first law [Ch 2.4]
- Write the integral and differential forms of the first law
- Describe the physical meaning of each of the terms within both the integral and differential form of the first law
- Identify when the open and closed forms of the first law are applicable
- Determine when each term in the first law is zero or negligible
- Establish whether the ideal gas law is appropriate or if more advanced approaches are necessary (including tabulated data) [Ch 1.8]
- Identify, formulate, and solve simple engineering problems (such as expansion/compression in piston-cylinder systems and power cycles) [Ch 2.7-2.9]
- Describe the molecular basis for internal energy, heat transfer, work, and heat capacity [Ch 2.1-2.2]
- Explain the difference between a reversible and irreversible process [Ch 2.3]
- Distinguish between reversible and irreversible processes [Ch 2.3]
- Explain the utility of enthalpy, flow work, and shaft work [Ch 2.5]
- Calculate enthalpy changes associated with sensible heat, latent heat, and chemical reaction [Ch 2.6]

FL: The First Law of Thermodynamics

The First Law of Thermodynamics

LAW:

The first law of thermodynamics states that the total energy in the universe is constant.

$$\Delta E_{univ} = 0$$

Stated in this way, the most significant implication of this law is that energy can change **forms**, but the total amount must remain constant.

Even so, this statement is not of terribly practical utility, so we can restate the first law in a more useful form as:

LAW:

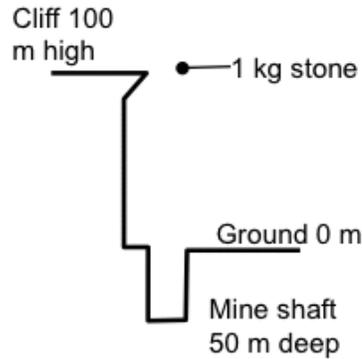
*The first law of thermodynamics can be restated as the total energy **change** of a system must be equal an opposite to the total energy **change** of the surroundings.*

NOTE:

This means that the energy of a system can change forms, but can only change in total amount through interactions with the surroundings.

EXAMPLE:

A 1 kg stone is held on a 100 m high cliff. What is its gravitational potential energy? It is dropped into the mine shaft. What is its potential energy and kinetic energy when it is passing the ground level. What is its potential and kinetic energy when it is about to hit the bottom of the mine shaft. Ignore air friction. What happens to this energy when the stone hits the bottom and comes to rest?



FL: Forms of Energy (Exchange)

Forms of Energy

$$\Delta E_{tot} = \Delta E_k + \Delta E_p + \Delta U$$

DEFINITION:

The **internal energy**, U , of a system is related to the molecular energy contained within the materials of the system.

- Molecular energy of motion:
 - translational -- fluids (gases and liquids) $\rightarrow \frac{RT}{2}$ per degree of freedom
 - rotations -- non-rotationally symmetric fluids $\rightarrow \frac{RT}{2}$ per degree of freedom
 - vibrational/phonon -- solids
- Molecular potential energy:
 - state of aggregation (phase)
 - chemical bonds

NOTE:

For ideal gases u is a function of temperature only. Why?

DEFINITION:

Work is typically thought of as "useful" energy. It is a way that energy is exchanged between system/surroundings. It is a path function. (Mechanical equilibrium)

- PV work: $W = \int F_E dx = -\int_{V_1}^{V_2} P_E dV$
- "shaft work": work transferred via an object that crosses system boundary

DEFINITION:

Heat is a way that energy is exchanged between system/surroundings via thermal energy. It is a path function. (Thermal equilibrium)

- sensible heat: heat that can be "sensed" (i.e., due to a change in temperature)
 - latent heat: heat that is used to change the state of aggregation of a material (i.e., does not change temperature)
-

FL: Forms of the First Law

Forms of the First Law of Thermodynamics

- Integral form of the first law (closed system):

$$\Delta U + \Delta E_k + \Delta E_p = W + Q$$

$$\Delta u + \Delta e_k + \Delta e_p = w + q$$

- Differential form of the first law (closed system):

$$dU + dE_k + dE_p = \delta W + \delta Q$$

$$du + de_k + de_p = \delta w + \delta q$$

$$\frac{dU}{dt} + \frac{dE_k}{dt} + \frac{dE_p}{dt} = \dot{W} + \dot{Q}$$

$$\frac{du}{dt} + \frac{de_k}{dt} + \frac{de_p}{dt} = \dot{w} + \dot{q}$$

OUTCOME:

Write the integral and differential forms of the first law

OUTCOME:

Describe the physical meaning of each of the terms within both the integral and differential form of the first law

OUTCOME:

Determine when each term in the first law is zero or negligible

NOTE:

We will often ignore changes in potential and kinetic energy. Why?

EXAMPLE:

If we assume that the stone from the previous example problem lands in a puddle of water (10kg) at the bottom of the mine shaft, and that the energy lost by the stone is completely used to heat the water. What is the final temperature of the water if it started at 20°C?

FL: Reversible and Irreversible Processes

Reversible and Irreversible Processes

DEFINITION:

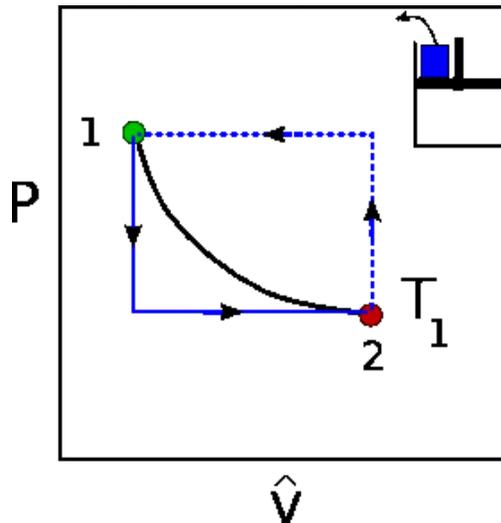
A **reversible process** is one which can be "undone" without affecting the surroundings. Alternatively, it is a process that can reverse direction at any point due to an infinitesimal change in external conditions (driving force).

NOTE:

A reversible process is an ideal one that yields the maximum possible work attainable.

EXAMPLE:

Consider the following isothermal expansions/compressions of an ideal gas. Calculate the work for each step when the total mass of the blocks is 1020kg, the area of the piston surface is 0.1 m², the initial height of the piston is 0.4m and the amount of gas present is 1 mol.



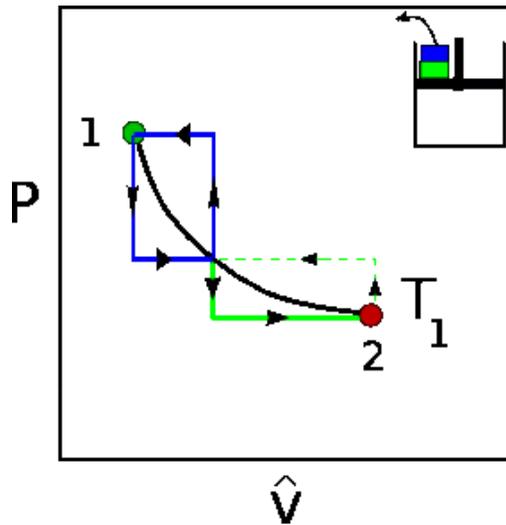
$$\Delta U + \Delta E_k + \Delta E_p = Q + W$$

$$W = -Q$$

$$W = -Q = -\int P_E dV = -P_E \Delta V$$

NOTE:

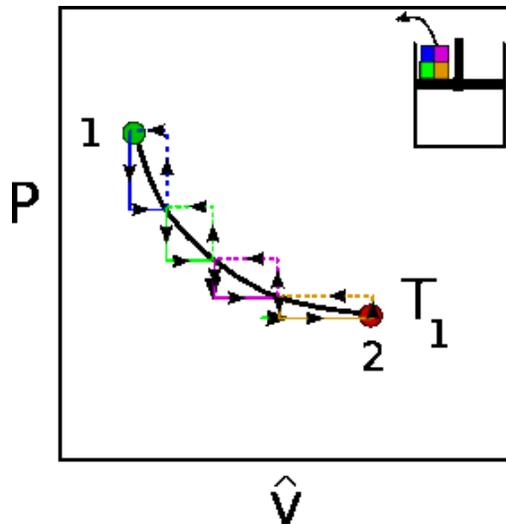
P_E is larger for the compression than for the expansion! The work obtained from the expansion is less than that required for the compression.



$$W = -Q = -\int P_E dV = -(P_E \Delta V)_{1 \rightarrow i} - (P_E \Delta V)_{i \rightarrow 2}$$

NOTE:

The difference between $(P_E \Delta V)_{i \rightarrow 1(2)}$ and $(P_E \Delta V)_{1(2) \rightarrow i}$ (the forward vs the reverse) is smaller than for the 1 step process. The difference in the work obtained/required is also smaller.



$$W = -Q = -\int P_E dV = -(P_E \Delta V)_{1 \rightarrow i_1} - (P_E \Delta V)_{i_1 \rightarrow i_2} - (P_E \Delta V)_{i_2 \rightarrow i_3} - (P_E \Delta V)_{i_3 \rightarrow 2}$$

NOTE:

Again, the difference decreases further for the multi-step process. If the step gets even smaller, the external pressure at each step eventually becomes essentially equal to the internal pressure at each step ($P_E \rightarrow P$).

$$W = -Q = -\int P_E dV = -\int P dV = -\int nRT \frac{dV}{V} = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

OUTCOME:

Explain the difference between a reversible and irreversible process.

NOTE:

Because a reversible process is the ideal/limiting case, we will use it as the reference point for efficiency calculations.

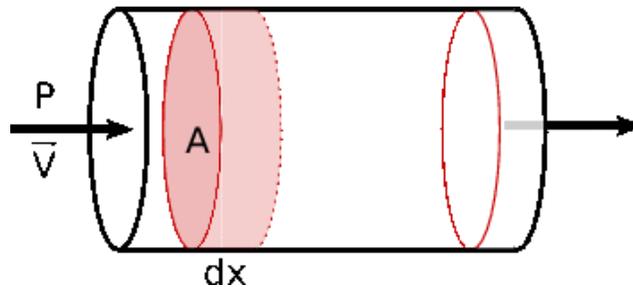
FL: Enthalpy and the open form of the First Law

Introducing Enthalpy and the open form of the First Law

$$\frac{dU}{dt} + \frac{dE_k}{dt} + \frac{dE_p}{dt} = \dot{W} + \dot{Q} + \text{"flow of energy with material"}$$

$$\frac{du}{dt} + \frac{de_k}{dt} + \frac{de_p}{dt} = \dot{w} + \dot{q} + \text{"flow of energy with material (per unit material)"}$$

Start with the work terms ...



$$\dot{W} = \frac{\delta W}{dt} = \frac{-d(PV)}{dt} = -P \frac{dV}{dt} = -P A \frac{dx}{dt} = -P A \vec{V} = P \dot{m} v$$

NOTE:

Here we are making use of the fact that $A\vec{V}$ is equal to the volumetric flow rate, so that dividing it by the specific volume (which we call \hat{V} in the scribble notes, but v here) gives us the mass flow rate so

$$\frac{A\vec{V}}{v} = \dot{m}$$

$$\dot{w} = \frac{\dot{W}}{\dot{m}} = P v$$

NOTE:

This relation holds for all input streams and output streams (with a change in sign).

IMPORTANT:

The way that energy "flows with material" is via that material's internal, kinetic, and/or potential energy (per unit material).

- Differential form of the first law (open system, temporary):

$$\begin{aligned} \frac{dU}{dt} + \frac{dE_k}{dt} + \frac{dE_p}{dt} &= \\ \sum_{in} [\dot{m}(u + e_k + e_p)]_{in} - \sum_{out} [\dot{m}(u + e_k + e_p)]_{out} &+ \\ \dot{Q} + [\dot{W}_{shaft} + \sum_{in} (\dot{m}Pv)_{in} - \sum_{out} (-\dot{m}Pv)_{out}] & \\ \frac{du}{dt} + \frac{de_k}{dt} + \frac{de_p}{dt} &= \\ \sum_{in} (u + e_k + e_p)_{in} - \sum_{out} (u + e_k + e_p)_{out} &+ \\ \dot{q} + [\dot{w}_{shaft} + \sum_{in} (Pv)_{in} - \sum_{out} (-Pv)_{out}] & \end{aligned}$$

DEFINITION:

The **enthalpy** is defined as follows:

$$h \equiv u + Pv$$

- Differential form of the first law (open system, real):

$$\frac{dU}{dt} + \frac{dE_k}{dt} + \frac{dE_p}{dt} = \sum_{in} [\dot{m}(h + e_k + e_p)]_{in} - \sum_{out} [\dot{m}(h + e_k + e_p)]_{out} + \dot{Q} + \dot{W}_{shaft}$$

$$\frac{du}{dt} + \frac{de_k}{dt} + \frac{de_p}{dt} = \sum_{in} (h + e_k + e_p)_{in} - \sum_{out} (h + e_k + e_p)_{out} + \dot{q} + \dot{w}_{shaft}$$

NOTE:

Flow work often cannot be "recovered" as useful.

OUTCOME:

Explain the utility of enthalpy, flow work, and shaft work

NOTE:

For an ideal gas, enthalpy is also only a function of T:

$$h = u + Pv = u + RT$$

Note:

A common form of the open first law is for a steady state process that includes 1 inlet and 1 outlet, which reduces to:

$$\Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p = \dot{Q} + \dot{W}_s$$

Note:

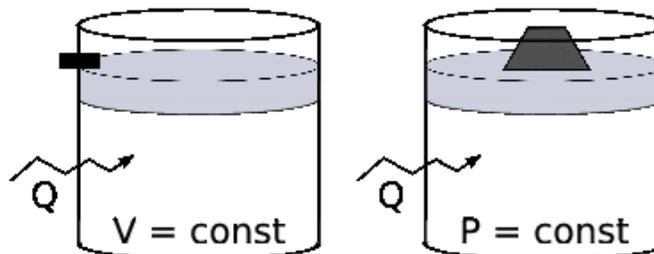
Here Δ refers to $[0_{out} - 0_{in}]$, rather than final-initial (as with closed systems).

FL: Heat Capacities and Latent Heat

"Heat Capacity"

Consider two closed systems to which you add heat ...

$$\Delta u + \Delta e_k + \Delta e_p = w + q$$



- For the constant volume process:

$$\Delta e_k = \Delta e_p = w = 0$$

$$\Delta u = q$$

- For the constant pressure process:

$$\Delta e_k = \Delta e_p = 0$$

$$\Delta u = q + w = q - P \Delta v$$

$$\Delta h = \Delta u + P \Delta v = q$$

For convenience the "other" intensive property is chosen to be temperature ... why?

DEFINITION:

The heat capacity at constant volume is defined as:

$$c_v \equiv \left(\frac{\partial u}{\partial T} \right)_v$$

DEFINITION:

The heat capacity at constant pressure is defined as:

$$c_p \equiv \left(\frac{\partial h}{\partial T} \right)_p$$

IMPORTANT:

For solids and liquids: $c_v \approx c_p$ why?

For ideal gases: $c_p = c_v + R$ why?

For real gases: $c_p > c_v$

NOTE:

Heat capacities are state functions (depend on T!).

TEST YOURSELF:

Verify if the "cold water diet" would work. Some joker proposed that drinking 0.5kg of ice-cold water at each meal would be an effective diet method. Determine the internal energy change this would cause. What if you used ice cubes instead of water?

DEFINITION:

*The **latent heat** is the specific enthalpy change associated with a change in state of aggregation (phase).*

NOTE:

The latent heat is often known only at a single temperature, yet this state function is, of course, dependent on temperature. How do we handle that?.

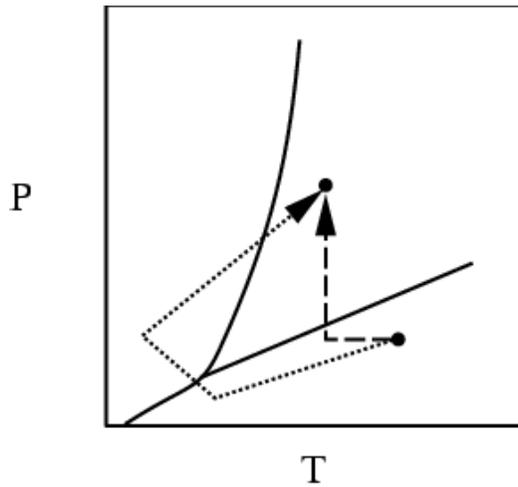
FL: Fictitious Paths

Recall that state functions do not depend on the history of the system (i.e., are independent of path).

Further, recall that fundamental and derived quantities are **not measurable**.

NOTE:

Because we are always interested in changes (Δ 's) in fundamental/derived quantities, we simply choose reference points, and calculate values as differences from those reference points.



NOTE:

In many problems of interest, we will want to use the "real path" of process since we will be interested in determining the path functions (Q and W) as well as possibly U or H . Nevertheless, fictitious paths are useful when we are interested in calculating state functions (only), like U and H .

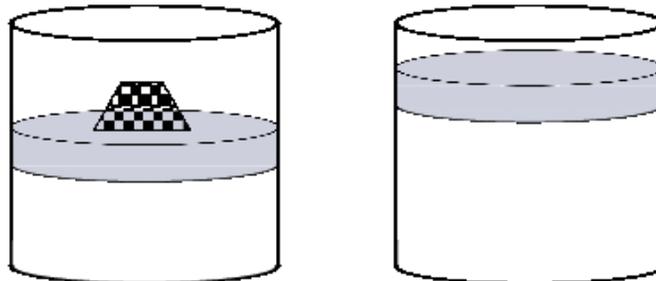
TEST:

Calculate the enthalpy of steam at 200C and 1.5atm relative to a reference state of ice at -10C and 1 atm.

FL: Reversible and Irreversible Processes (take 2)

Adiabatic Reversible Expansion (Compression)

Consider the reversible expansion of an ideal gas where the system is now well-insulated (assume $c_v \neq F(T)$).

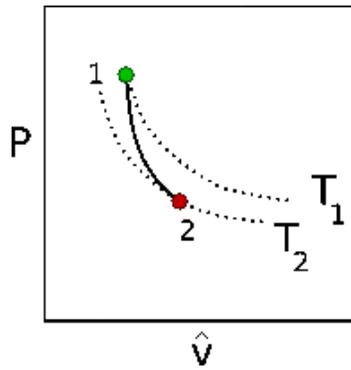


$Q=0$

$$dU + dE_k + dE_p = \delta W + \delta Q$$

$$dU = \delta W + \delta Q$$

$$dU = \delta W$$



$$dU = \delta W$$

$$\int c_v dT = -\int P_E dv$$

Because the process is reversible $P_E \rightarrow P$, and that $d(RT) = d(Pv) = Pdv + vdP$, we can write

$$d(RT) = d(Pv) = Pdv + vdP$$

$$dT = \frac{1}{R}Pdv + \frac{1}{R}vdP$$

which we can plug back in to our original expression, to give

$$\int \frac{c_v}{R} Pdv + \int \frac{c_v}{R} vdP = -\int Pdv$$

$$\int \frac{c_v}{R} vdP = -\int \left(1 + \frac{c_v}{R}\right) Pdv$$

$$\int c_v vdP = -\int (R + c_v) Pdv = -\int c_p Pdv$$

rearranging and integrating gives

$$\int \frac{dP}{P} = -\int \frac{c_p}{c_v} \frac{dv}{v}$$

$$\ln\left(\frac{P_2}{P_1}\right) = -k \ln\left(\frac{v_2}{v_1}\right) = \ln\left(\frac{v_1}{v_2}\right)^k$$

$$\ln(P_1 v_1^k) = \ln(P_2 v_2^k)$$

$$(Pv^k) = \text{constant}$$

$$(PV^k) = (\text{different})\text{constant}$$

Plugging this result back into the expression for W (i.e., $W = -\int P_E dV = -\int PdV$)

$$W = -\int PdV = -\int (\text{different})\text{constant} V^{-k} dV$$

$$W = \frac{(\text{different})\text{constant}}{k-1} \left[\frac{1}{V^{k-1}} - \frac{1}{V_1^{k-1}} \right]$$

$$W = \frac{1}{k-1} [P_2 V_2 - P_1 V_1]$$

$$W = \frac{nR}{k-1} [T_2 - T_1]$$

NOTE:

To obtain this result we assumed that c_v (and c_p) were not functions of T .

EXERCISE:

How does the internal energy change differ for the compression?

FL: Enthalpy of reaction

Enthalpy of reaction

At the molecular level enthalpy is released/absorbed during a reaction because the energy from the original bonds is released as the bonds are broken and then the new

bonds absorb some energy. Depending on whether the reactants or products are more stable determines whether the net result is a positive or negative "release" of energy.

- implicitly chose "atoms" as reference points
- convention: choose "elements in their natural state" at 298K, 1 atm

DEFINITION:

The **heat of formation** is the enthalpy difference between a molecule and its component elements in their natural state at 298K and 1 atm.

NOTE:

The formation of our molecules of interest simply becomes one of the steps in our fictitious paths now.

OUTCOME:

Calculate enthalpy changes associated with sensible heat, latent heat, and chemical reaction

TEST YOURSELF:

Calculate the adiabatic flame temperature of a Bunsen burner. Assume that CH_4 starts at 25C, is burned with a stoichiometric amount of oxygen, and is burned completely (that is, it produces CO_2 rather than CO).

FL: Engineering equipment

Engineering equipment

DEFINITION:

A **nozzle/diffuser** is a device that converts between kinetic energy and internal energy. This is accomplished by having a change in the cross-sectional area. (Nozzles decreases A_{cs} so that $U \rightarrow E_k$. A diffuser increases A_{cs} so that $E_k \rightarrow U$).

DEFINITION:

A **turbine/pump** uses a shaft to either extract/input work from/into a system.

DEFINITION:

A **heat exchanger** is a device that changes the internal energy of a fluid by inputting/removing heat.

DEFINITION:

A **throttle** is a device that decreases the pressure of a fluid by restricting the flow (typically with an inclusion of some sort).

OUTCOME:

Identify, formulate, and solve simple engineering problems (such as expansion/compression and power cycles)

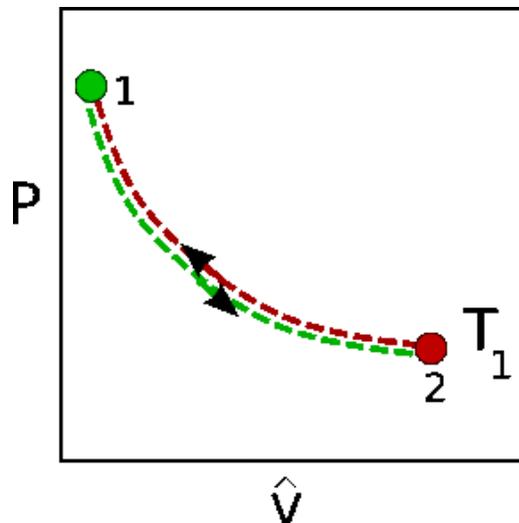
TEST:

Simplify the appropriate version of the first law for each of these devices.

FL: Thermodynamic Cycles

Thermodynamic Cycles

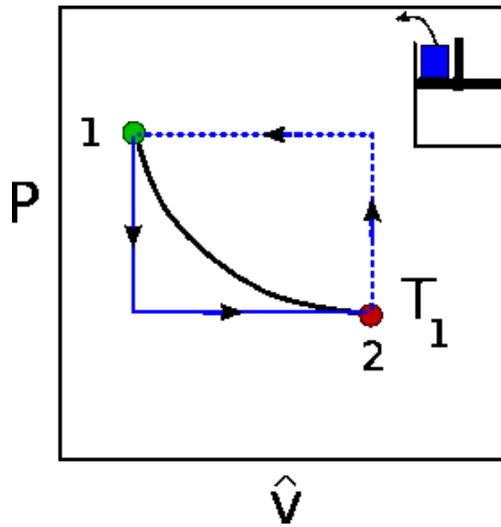
We would like to be able to convert thermal energy to work in order to operate machines of all sorts. Further, we have shown that we can obtain the *maximum* work from a reversible expansion (as opposed to an irreversible one).



NOTE:

- $Q_{exp} = -W_{exp}$
- $Q_{comp} = -W_{comp}$
- $W_{exp} = -W_{comp}!!$ (no net work)

However, we recall that our irreversible process did not cancel out. Why not use that as an "engine"?

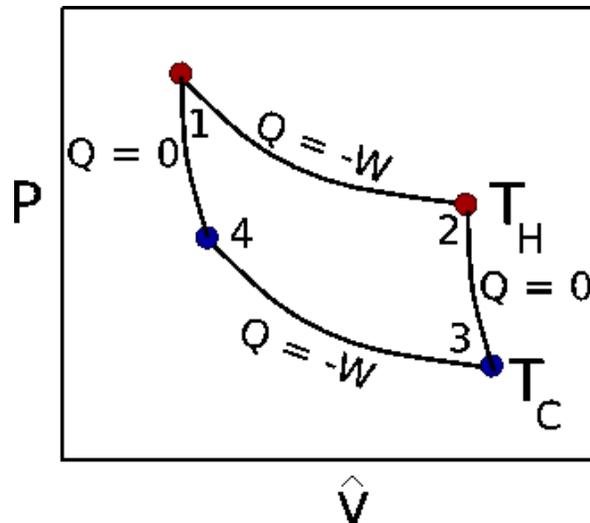


NOTE:

- $-Q_{exp} = W_{exp}$
- $-Q_{comp} = W_{comp}$
- $W_{exp} < -W_{comp}$

DEFINITION:

A **Carnot cycle** is the most efficient engine possible.



$$W_{net} = W_{12} + W_{23} + W_{34} + W_{41}$$

Since the work from 2 → 3 exactly cancels the work from 4 → 1, we get

$$W_{net} = W_{12} + W_{34} = nRT_1 \ln\left(\frac{P_2}{P_1}\right) + nRT_3 \ln\left(\frac{P_4}{P_3}\right)$$

$$Q_{net} = Q_{12} + Q_{34} = Q_H - |Q_C|$$

$$\Delta U_{net} = 0$$

NOTE:

Here we take advantage of the fact that W_{12} and W_{34} have differing signs (since one is work "out" and the other is "in"). Similarly, the signs of Q_{12} and Q_{34} differ, so that the net value is obtained by adding them. When we switch to the Q_H and Q_C notation, we explicitly use the absolute value so that we can emphasize that the net heat flow is

the difference between the amount absorbed from the hot reservoir and that expelled to the cold reservoir.

DEFINITION:

Running a Carnot cycle "forward" is called an engine and has an efficiency of :

$$\eta = \frac{W_{net}}{Q_H}$$

Running a Carnot cycle "backward" is called a refrigeration cycle and has an efficiency of:

$$COP = \frac{Q_C}{W_{net}} \text{ [COP} \equiv \text{"coefficient of performance"}]$$

OUTCOME:

Identify, formulate, and solve simple engineering problems (such as expansion/compression and power cycles)
