Chapter N° 2:

First law of thermodynamics

Before we get into the first law of thermodynamics, we need to understand the relation between heat and work and the concept of internal energy. Just like mass, energy is always conserved, i.e., it can neither be created nor destroyed, but it can be transformed from one form to another.

Heat

Heat transfer is a thermodynamic process representing the transfer of energy in the form of thermal agitation of the constituent particles. In practice one needs heating elements to do the job, f.i. a flame.

Heat capacity: If a system absorbs an amount of heat ΔQ, its temperature rises proportionally by an amount ΔT :

$$Q = m \, C \, \Delta T$$

Mechanical work

Mechanical work is defined as an energy transfer to the system through the change of an external parameter. Work is the only energy which is transferred to the system through external macroscopic forces.

Example: consider the mechanical work performed on a gas due to an infinitesimal volume change (reversible transformation).
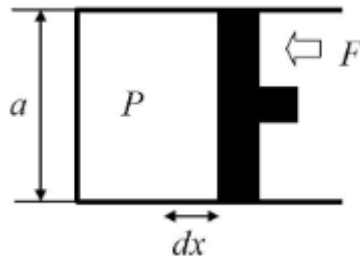
$$dV = adx$$

where a is the active area of the piston. In equilibrium, the external force F is related to pressure P as

$$F = -P \, a$$

For an infinitesimal process, the change of the position of the wall by dx results in performing work δW :

$$\delta W = F \, dx = -P \, dV$$

For a transformation of the system along a finite reversible path in the equation-of-state space (viz for a process with finite change of volume), the total work performed is

$$\Delta W = -\int_{V_1}^{V_2} P dV$$

Note:

• Mechanical work is positive when it is performed on the system.

• δW is not an exact differential, i.e., W (P, V) does not define any state property.

• ΔW depends on the path connecting A (V$_1$) and B (V$_2$).

Reversible and Irreversible Work

In any real experiment, we must have $P_{ext} > P_{gas}$, and any real experiment is necessarily irreversible. In a reversible experiment, we have $P_{ext} = P_{gas} = P$, and the reversible work, w_{rev}, is

$$W_{rev} = \int_{V_1}^{V_2} -P_{ext} dV = \int_{V_1}^{V_2} -P dV$$

For one mole of an ideal gas, we have *P=RT/V*. Since the temperature is constant, the reversible isothermal work becomes

$$W_{rev} = \int_{V_1}^{V_2} -\frac{nRT}{V} dV = -nRT ln\frac{V_2}{V_1}$$

From *Boyle's* Law:

$$W_{rev} = -nRT ln\frac{P_1}{P_2}$$

In contrast, an irreversible expansion corresponds to movement of the piston when $P_{gas} >$ $P_{applied}$ and $\mathbf{P} = \mathbf{P_f}$. Therefore, the work done on the gas is less in the reversible case than it is in the irreversible case. (Both work terms are less than zero. The absolute value of the reversible work is greater than the absolute value of the irreversible work).

$$W_{rev} = \int_{V_1}^{V_2} -P_2 dV = -P_2 \int_{V_1}^{V_2} (V_2 - V_1)$$

First law of the thermodynamic

The internal energy of an isolated system is conserved under any thermodynamical change.

$$U_2 - U_1 = W + Q = \Delta U$$

Δ**U** : internal energy (function of state),

Q: heat added to the system

W : work done on the system.

Enthalpy

When a process occurs at constant pressure, the heat evolved (either released or absorbed) is equal to the change in enthalpy. Enthalpy (*H*) is the sum of the internal energy (*U*) and the product of pressure and volume (*PV*) given by the equation:

$$H=U+PV \quad (1)$$

When a process occurs at constant pressure, the heat evolved (either released or absorbed) is equal to the change in enthalpy. Enthalpy is a state function which depends entirely on the state functions *T*, *P* and *U*. Enthalpy is usually expressed as the change in enthalpy (ΔH) for a process between initial and final states:

$$\Delta H = \Delta U + \Delta PV \quad (2)$$

If temperature and pressure remain constant through the process and the work is limited to pressure-volume work, then the enthalpy change is given by the equation:

$$\Delta H = \Delta U + P\Delta V$$

$$\Delta U = n\, C_V . \Delta T, \quad \Delta H = n\, C_p . \Delta T$$

Relation between C_p and C_v

$$H = U + PV$$
$$H = U + nRT$$
$$\Delta H = \Delta U + nR\Delta T$$
$$C_P \Delta T = C_V \Delta T + nR\Delta T$$
$$C_P = C_V + nR$$
$$C_P - C_V = nR$$

Mayer relation

This relation is called Mayer. this relation It implies that the molar specific heat capacity of an ideal gas at constant pressure is greater than molar specific heat capacity at constant volume. The relation shows that specific heat at constant pressure (C_P) is always greater than specific heat at constant volume (C_V).

$$c_p - c_v = R$$

$$\gamma = \frac{c_p}{c_v} \Rightarrow c_p = \gamma c_v$$
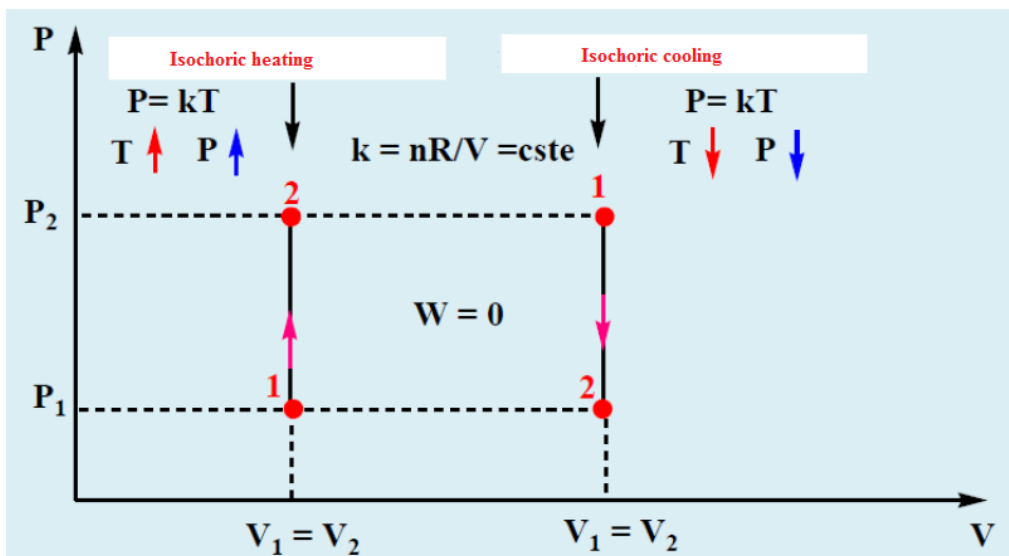
$$c_p - c_v = \gamma c_v - c_v = R$$

$$c_v(\gamma - 1) = R$$

$$c_v = \frac{R}{\gamma - 1}$$

$$c_p = \frac{\gamma R}{\gamma - 1}$$
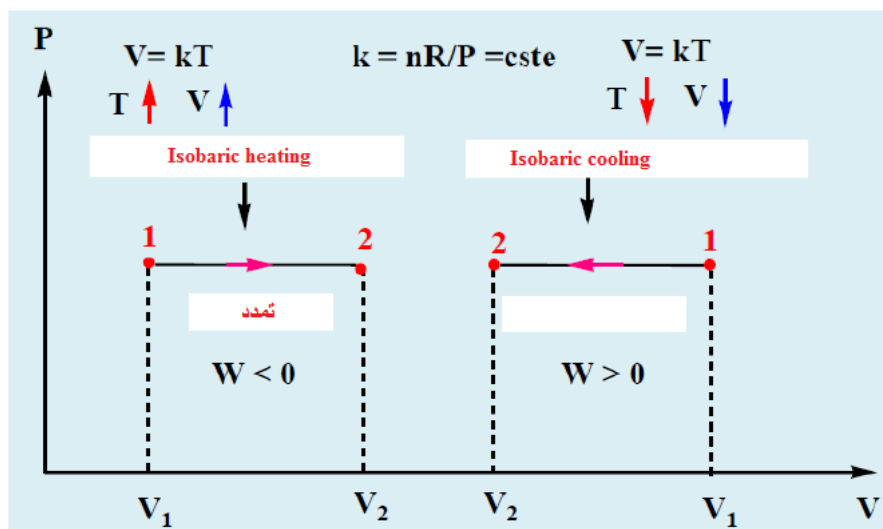
Thermodynamic processes

Isochoric process

$$W = 0$$

$$\Delta U = Q_v = n \int_{T_1}^{T_2} c_v dT$$

$$\Delta H = Q_p = nc_p(T_2 - T_1)$$

$$\Delta H = \gamma \, \Delta U$$

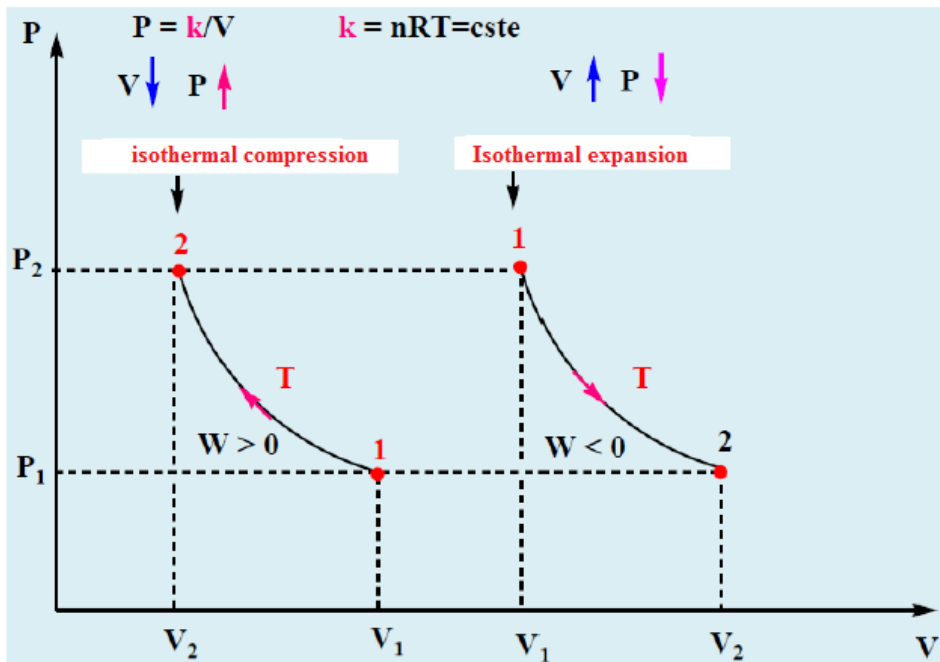**Isobaric process**

$$W = -P(V_2 - V_1) = -nR(T_2 - T_1)$$

$$\Delta U = n \int_{T_1}^{T_2} c_v dT$$

$$\Delta H = Q_p = n \int_{T_1}^{T_2} c_p dT$$

$$\Delta H = Q_p = nc_p(T_2 - T_1)$$

$$\Delta H = \gamma \, \Delta U$$
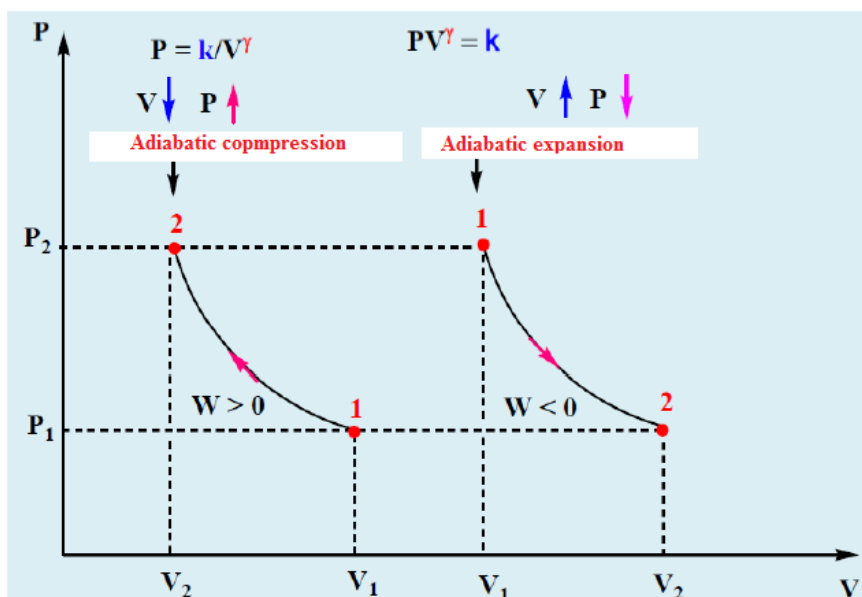
Isothermal process

$P = k/V$ $k = nRT = cste$

$V \downarrow$ $P \uparrow$ $V \uparrow$ $P \downarrow$

isothermal compression   Isothermal expansion

P_2 2   1

T   T

$W > 0$ 1 $W < 0$ 2

P_1

V_2 V_1 V_1 V_2 V

$$W = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2}$$

$$Q = -W$$

$$\Delta U = \Delta H = 0$$

Adiabatic process

$P = k/V^{\gamma}$ $PV^{\gamma} = k$

$V \downarrow$ $P \uparrow$ $V \uparrow$ $P \downarrow$

Adiabatic copmpression   Adiabatic expansion

P_2 2   1

$W > 0$ 1 $W < 0$ 2

P_1

V_2 V_1 V_1 V_2 V

$$W = \Delta U = \frac{1}{\gamma - 1}(P_2V_2 - P_1V_1)$$

$$\Delta U = nc_v(T_2 - T_1)$$

$$\Delta H = Q_p = nc_p(T_2 - T_1)$$

$$Q = 0$$

$$\Delta H = \gamma \Delta U$$

Note :

For monoatomic gases: $\gamma = \frac{5}{3} = 1.66$

For diatomic gases: $\gamma = \frac{7}{5} = 1.4$

For triatomic gases: $\gamma = \frac{9}{7}$

For the cycle:

$\Delta U cycle = \Delta H cycle = 0$

$Q cycle = \Sigma Q = - W cycle$