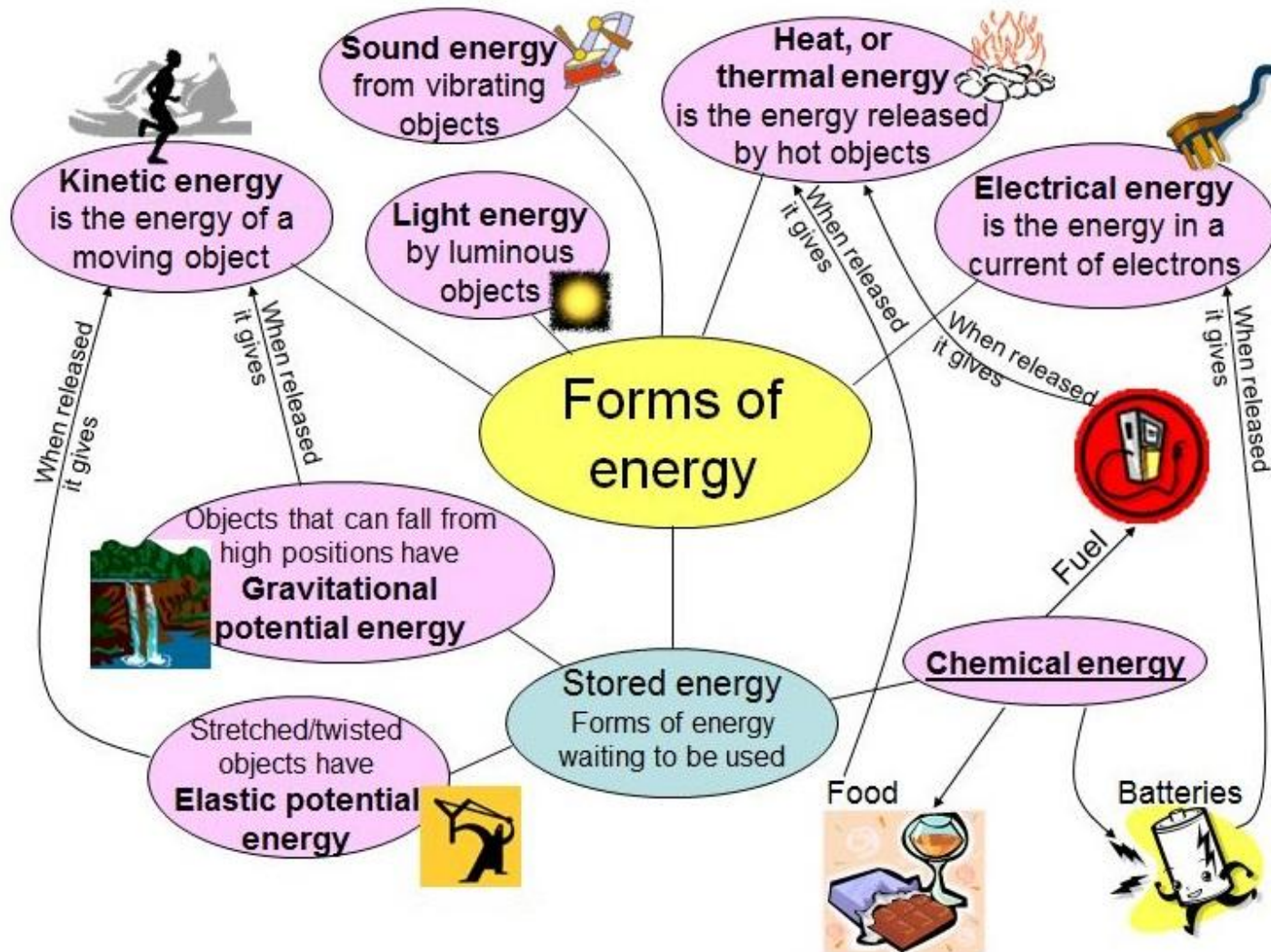


# THERMODYNAMICS

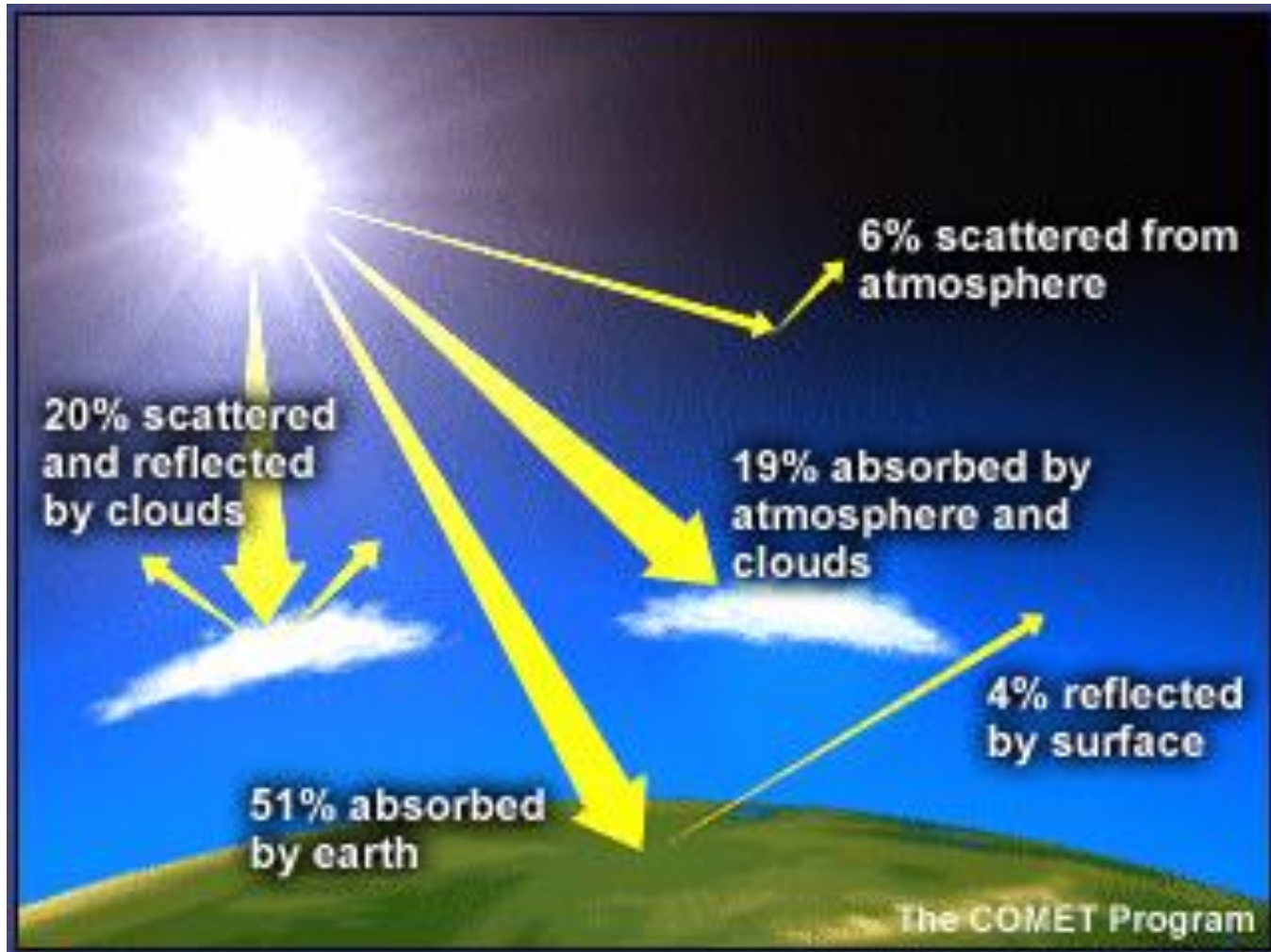
## ENERGY IN NATURE



# THERMODYNAMICS

## ENERGY IN NATURE

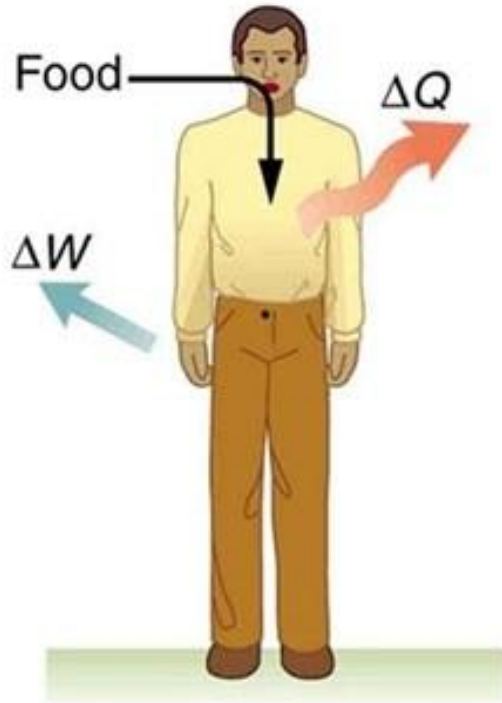
Common energy source for life on Earth – Sun radiation



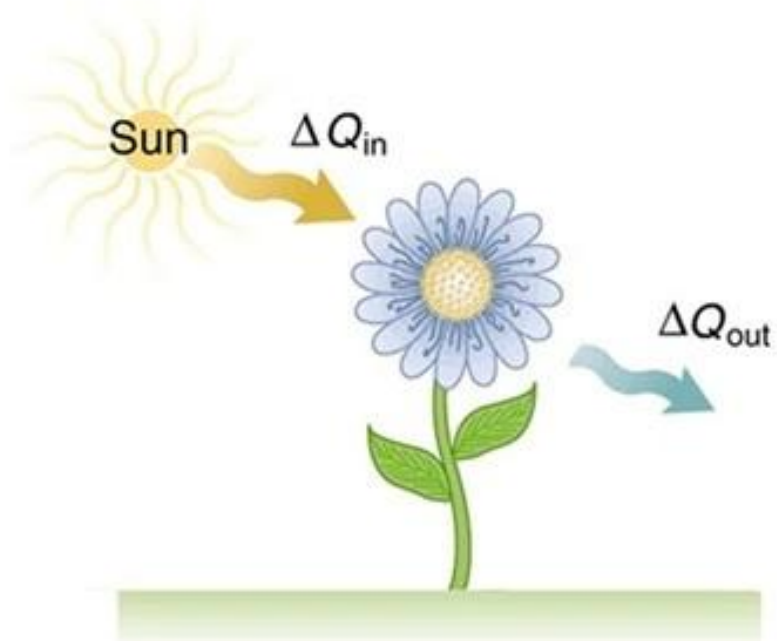
# THERMODYNAMICS

## ENERGY TRANSFER IN NATURE

Main form of energy inside all natural systems – internal energy  $U$



$$\Delta U = \text{food energy} - \Delta Q - \Delta W$$



$$\Delta U = \Delta Q_{in} - \Delta Q_{out}$$

Internal energy in combination with heat transfer(s) and mechanical work(s) done - base for phenomenological thermodynamics laws.

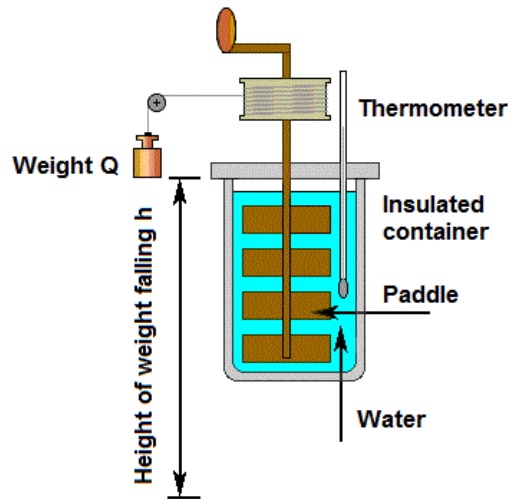
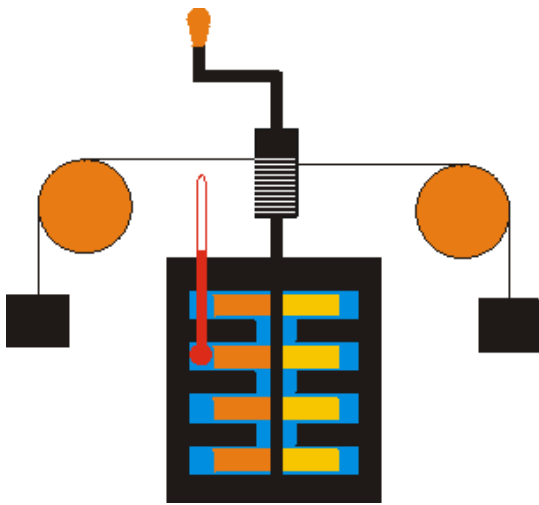
# THERMODYNAMICS

## ENERGY EXCHANGE IN NATURE

Common energy transfer – mechanical to thermal

### - Joule experiment (1845)

heating of water during mixing of water inside an isolated container by paddle wheel - increasing of T of water on the cost of decreasing of potential energy



$$Q \cdot \Delta h = c_w \cdot m_w \cdot \Delta T$$

$$\Delta T = \frac{Q \cdot \Delta h}{c_w \cdot m_w}$$

### - fast crumble of fruits inside blender

heating of fruits during mixing - increasing of T of crumbled fruits

### - mutual friction of bodies (hands)

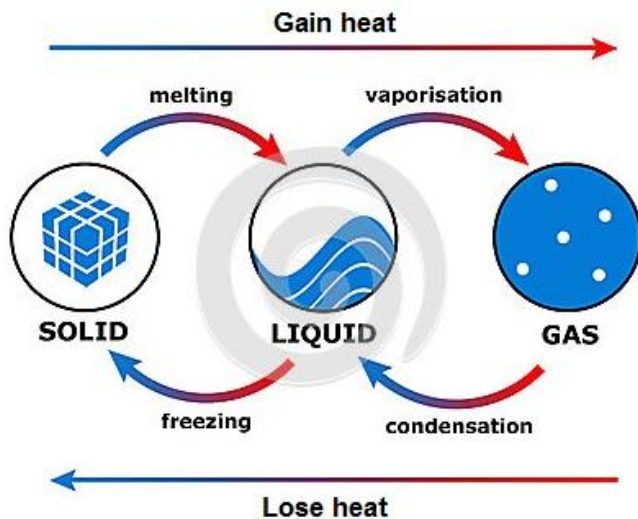
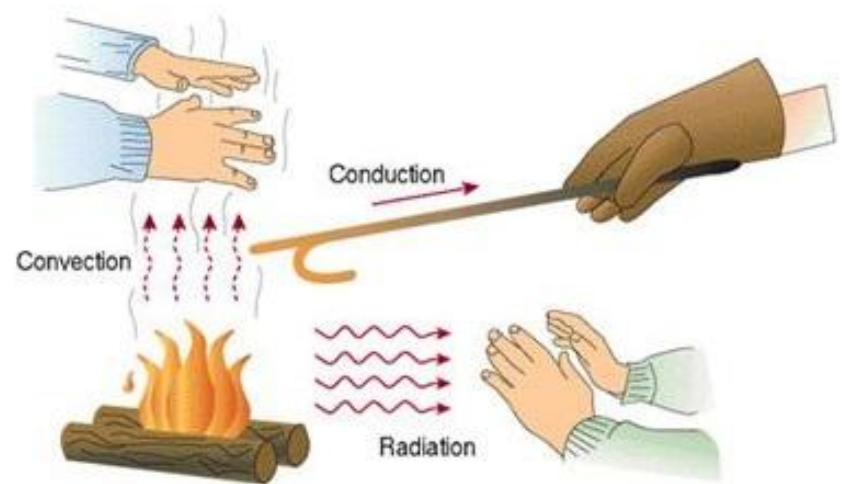
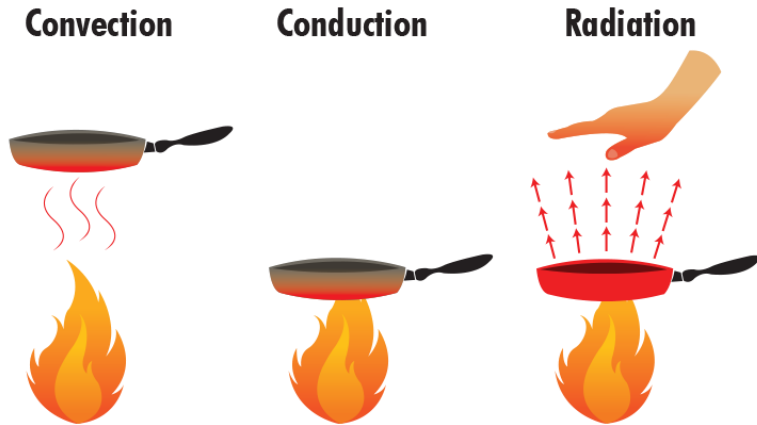
heating of abraded surfaces - increasing of their T



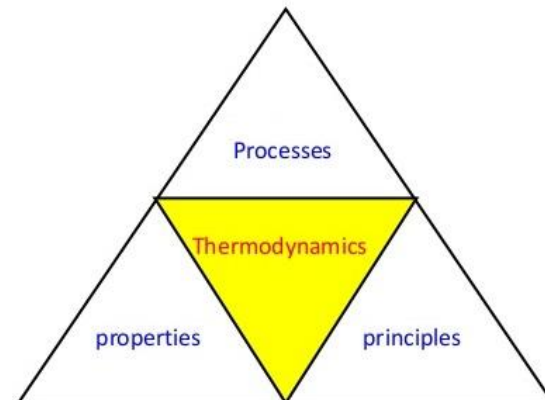
# THERMODYNAMICS

## ENERGY EXCHANGE IN NATURE

### Common thermal related effects



### Thermodynamics Triangle



# THERMODYNAMICS

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## ENERGY IN GAS SYSTEM

Energy of gas as the thermodynamic system - two basic forms:

- **kinetics** - result of translational, rotational and oscillatory motions
- **potential** - result of mutual interactions of particles (real gas)

Primary energy of every thermodynamic system: **internal energy**

$$U = E_k + E_p = \text{const}$$

When internal energy  $U$  is constant - isolated thermodynamic system, i.e. without exchange of energy in contact with surroundings.

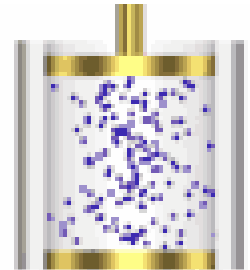
Complete description of every thermodynamic system via:

- **parameters of state:**

pressure  $p$ , volume  $V$ , temperature  $T$ , mass  $m$

- **functions of state and/or process:**

internal energy  $U$ , heat of process (transition)  $Q$ , mechanical work  $W$ , enthalpy  $H$  and entropy  $S$



**Such approach: domain of phenomenological thermodynamics**

# THERMODYNAMICS

## COMPLETE THERMODYNAMIC PROCESS

- Any change of gas internal energy  $U$  as a result (mostly together) of:
- heat energy consumed (or gave up) by system (exchange of heat energy  $Q$  with surroundings by heating or cooling)
  - mechanical work  $W$  performed by gas for the surroundings (against external force  $F$ ) or done on gas system by external force  $F$

Commonly accepted nonlinear changes of energetic quantities - in mathematical analysis infinitesimal changes should be considered like

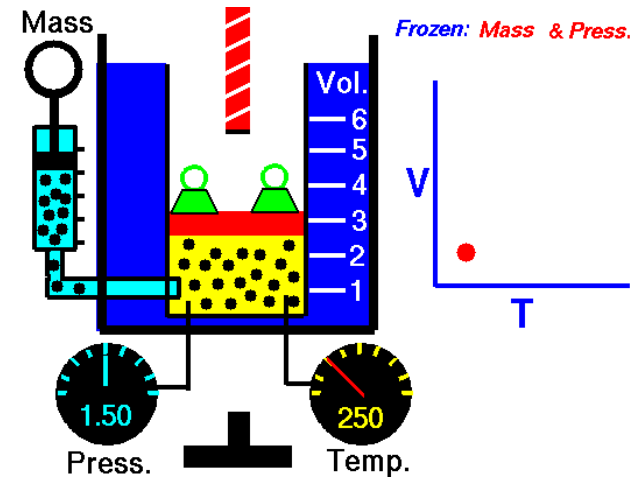
$$dU = \delta Q + \delta W$$

where:

$dU$  - complete differential (as function of state)

$\delta Q$  and  $\delta W$  - incomplete differential functions of process

- principle of conservation energy in isolated thermodynamic systems - **First law of thermodynamics (Claussius - 1850)**



# THERMODYNAMICS

## FIRST LAW OF THERMODYNAMICS



First primary function: **internal energy**

For deal gas - sum of kinetic energy of all molecules  $N$

For  $n = 1$  mole

$$U = N_A \cdot \bar{E}_k = \frac{3}{2} N_A \cdot k \cdot T = \frac{3}{2} R \cdot T$$

For an isochoric process ( $V = \text{const}$ ) – no variation of volume -  $dV = 0$

Mechanical work done in an isochoric process

$$dW = p dV = 0 \quad \text{thus} \quad dU = dQ + dW = dQ + p \cdot dV = dQ$$

Finally

$$dU = C_V \cdot dT = \frac{i}{2} R \cdot dT$$

where:  $C_V$  - heat capacity at constant volume

Every change of internal energy is only determined by the variation of temperature  $dT$  and is not dependent on type of thermodynamic process

- **internal energy plays a role of function of state**



# THERMODYNAMICS

## FIRST LAW OF THERMODYNAMICS

Second primary function - **mechanical work of pressure**

Infinitely small value of mechanical work done by external force  $F$  after shift of piston of section  $S$  by distance  $dx$

$$dW = F \cdot dx = p \cdot A \cdot dx = p \cdot dV$$

(-) under influence of external force ( $dV < 0$ )

(+) when gas performs mechanical work ( $dV > 0$ )

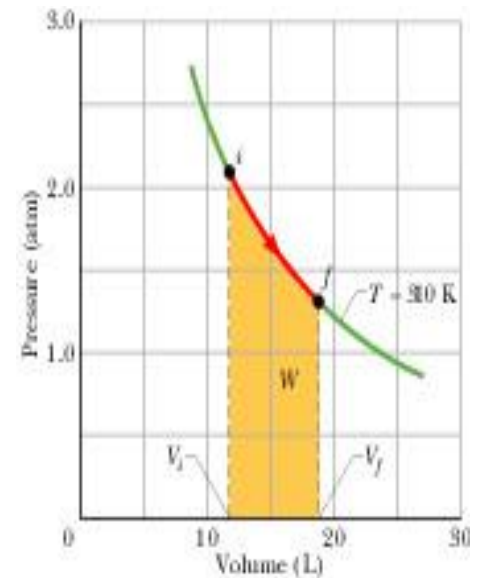
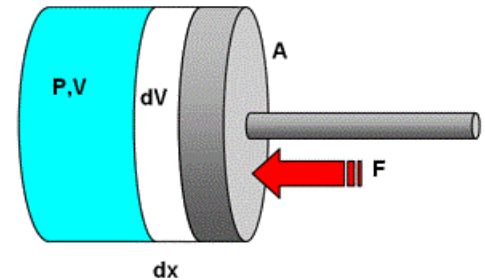
Finite value of mechanical work

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

Thus, complete for of I thermodynamics principle

$$dU = dQ - pdV$$

In general, mechanical work depends on type of thermodynamic process and energy transfer - mechanical work, as well as heat energy of transition (consumed or gave up by system) - **functions of process.**



# THERMODYNAMICS

## FIRST LAW OF THERMODYNAMICS AND GAS TRANSITIONS

- **ISOCHORIC PROCESS**

Thermodynamic system: closed gas vessel

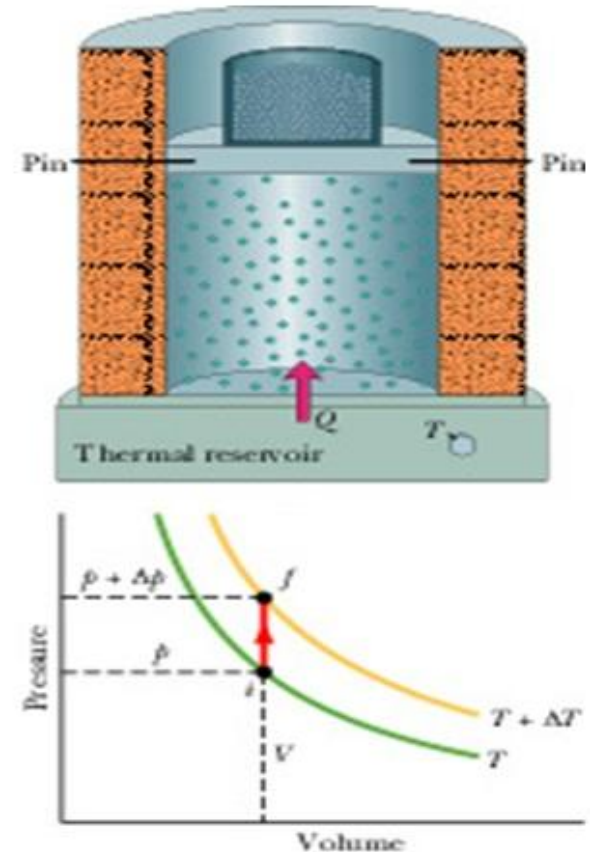
$V = \text{const}$ , thus  $dV = 0$

Mechanical work of pressure  $dW=0$

### I thermodynamics principle

$$dU = dQ = C_V \cdot dT = \frac{i}{2} R \cdot dT$$

Heat energy delivered (picked up) in (from) gas system causes increase (decrease) of its internal energy.



# THERMODYNAMICS

## FIRST LAW OF THERMODYNAMICS AND GAS TRANSITIONS

### • ISOTHERMIC PROCESS

Thermodynamic system: closed gas vessel  
on thermostat

$T = \text{const}$ , thus  $dT = 0$

### First law of thermodynamics

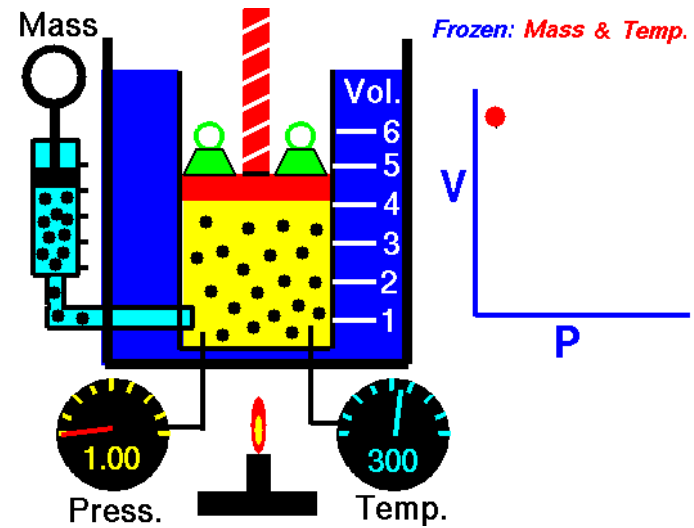
$$dU = dQ + dW = 0 \quad \text{thus} \quad dQ = dW = p dV$$

Heat energy delivered (picked up) exchanges on mechanical work of gas - compression/expansion – variation of gas volume as result of mechanical work done by external forces

$$W_{12} = \int_1^2 dW = \int_1^2 p \cdot dV = R \cdot T \int_1^2 \frac{dV}{V} = R \cdot T \ln \frac{V_1}{V_2}$$

Two possibilities:

- at compression ( $dV < 0$ ) - mechanical work done (+) by external force
- at expansion ( $dV > 0$ ) - mechanical work performed (-) on expence of delivered heat energy.



# THERMODYNAMICS

## FIRST LAW OF THERMODYNAMICS AND GAS TRANSITIONS

### • ISOBARIC PROCESS

Thermodynamic system: gas vessel with motionless piston

$p = \text{const}$

### First law of thermodynamics

$$dU = dQ + dW = C_p \cdot dT - p \cdot dV = C_V \cdot dT$$

Delivered heat energy:

- causes increase of internal energy
- uses for mechanical work for gas expansion

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

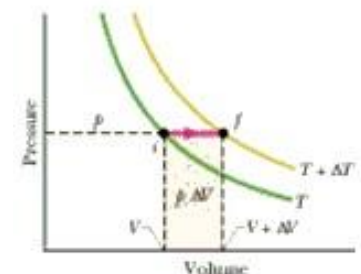
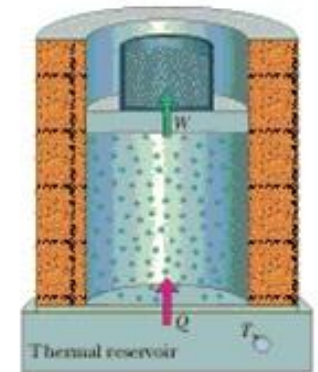
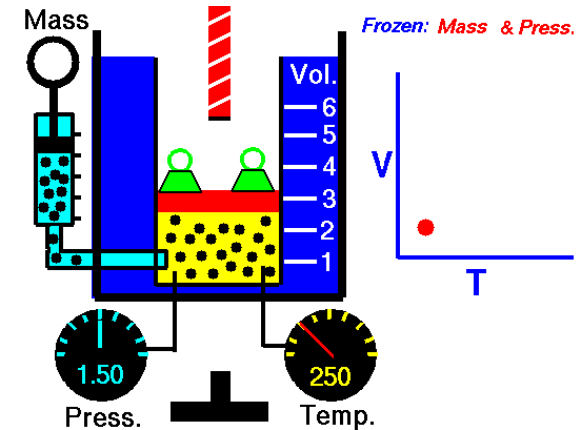
After differentiation of equation of state of ideal gas

$$p \cdot dV = R \cdot dT$$

Finally

$$C_V \cdot dT = C_p \cdot dT - p \cdot dV = C_p \cdot dT - R \cdot dT$$

where:  $C_p$  - heat capacity at constant pressure.



# THERMODYNAMICS

## FIRST LAW OF THERMODYNAMICS AND GAS TRANSITIONS

A complete first law of thermodynamics

$$C_p \cdot dT = C_V \cdot dT + p \cdot dV = C_V \cdot dT + R \cdot dT = (C_V + R) \cdot dT$$

After transformation heat capacity at constant pressure

$$C_p = C_V + R = \frac{i}{2}R + R = \frac{i+2}{2}R$$

A heat capacity ratio

$$\frac{C_p}{C_V} = \kappa = \frac{i+2}{2}$$

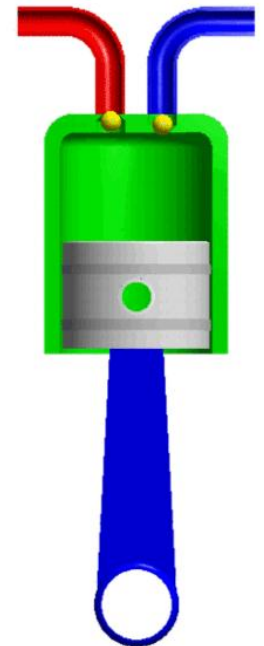
Depends on number of degree of freedom  $i$

Finally,

**First law of thermodynamics for isobaric process**

$$dQ = dU + p \cdot dV = d(U + pV) = dH$$

where  $dH$  - variation of **enthalpy as amount of exchanged heat energy**



# THERMODYNAMICS

## FIRST LAW OF THERMODYNAMICS AND GAS TRANSITIONS

### • ADIABATIC PROCESS

Thermodynamic system: isolated gas vessel

No heat exchange with surroundings -  $dQ = 0$

All parameters of states like  $p, V, T \neq \text{const}$

Thus

$$dU = dW = C_V \cdot dT$$

Two possibilities:

- gas performs mechanical work on expence of internal energy change

- mechanical work by external force causes increase of internal energy

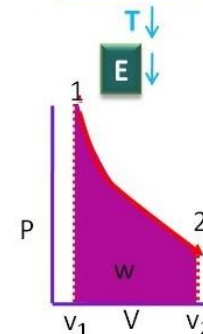
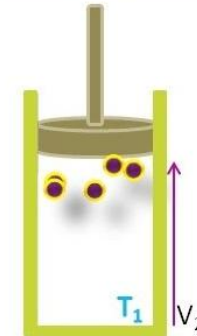
Gas pressure for  $n = 1$  mole of gas  $p = \frac{R \cdot T}{V}$

**First law of thermodynamics**  $C_V \cdot dT = p \cdot dV = R \cdot T \frac{dV}{V}$

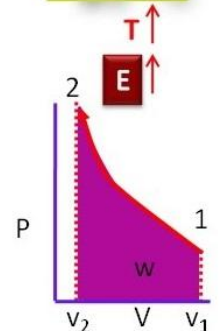
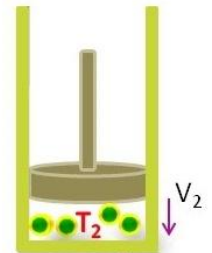
After transformation (ordering of the variables)

$$\frac{R}{C_V} \frac{dV}{V} = \frac{C_p - C_V}{C_V} \frac{dV}{V} = (\kappa - 1) \frac{dV}{V} = \frac{dT}{T}$$

Adiabatic expansion



Adiabatic compression



# THERMODYNAMICS

## FIRST LAW OF THERMODYNAMICS AND GAS TRANSITIONS

### • ADIABATIC PROCESS

After double-sided integration  $(\kappa - 1) \int_1^2 \frac{dV}{V} = \int_1^2 \frac{dT}{T}$

one can obtain  $(\kappa - 1) \ln \frac{V_2}{V_1} = \ln \frac{T_2}{T_1}$

Thus  $T_2 \cdot V_2^{\kappa-1} = T_1 \cdot V_1^{\kappa-1} = T \cdot V^{\kappa-1} = \text{const}$

After final transformation using Poisson equations for adiabatic process

$$\frac{p^{\kappa-1}}{T^{\kappa}} = \text{const} \quad \text{or} \quad p \cdot V^{\kappa} = \text{const}$$

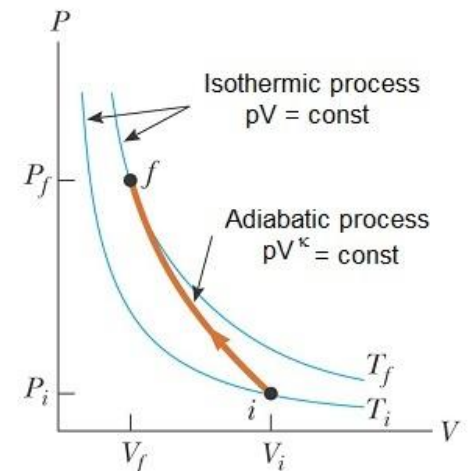
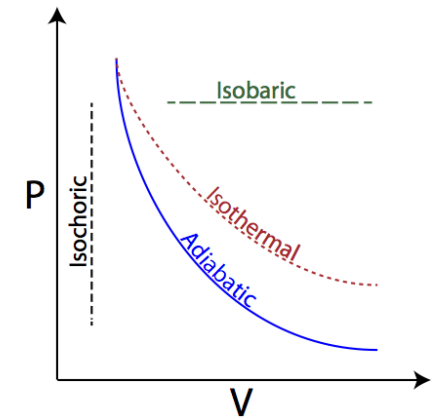
Using equation of state of ideal gas - another forms

$$dU = C_V \cdot dT = p \cdot dV = dW$$

In adiabatic expansion gas performs mechanical work on expense of decrease of internal energy

### Common effects:

- heat exchange in atmosphere
- thermodynamics cycles



# THERMODYNAMICS

## HEAT EXCHANGE IN ATMOSPHERE

Air pressure above Earth surface almost adiabatical decrease of result of small thermal conductivity

Exponential decrease of gas pressure on  $h$

$$dp = \rho \cdot g \cdot dh = \frac{M \cdot p}{R \cdot T} g \cdot dh$$

Using one of the Poisson's equations

$$T \cdot V^{\kappa-1} = \text{const}$$

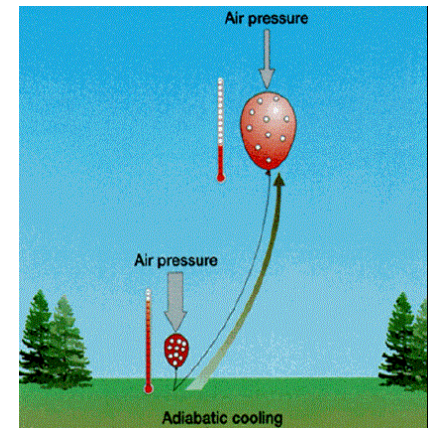
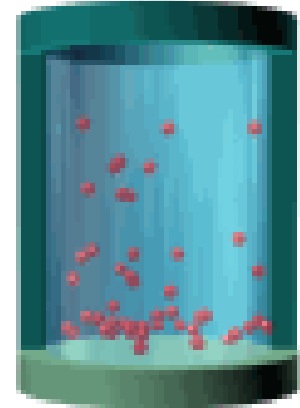
and equation of state of ideal gas for  $n = 1$  mole one can obtain

$$\frac{T}{p^{\frac{\kappa-1}{\kappa}}} = \text{const}$$

After finding logarithm for both sides and their differentiation

$$\frac{dT}{T} = -\frac{\kappa-1}{\kappa} \frac{dp}{p} \quad \text{or} \quad \frac{dT}{dh} = \frac{\kappa-1}{\kappa} \frac{g \cdot M}{R} = K = 10 [K / km]$$

Decrease of temperature in air atmosphere by 10 [K] with increasing of height over sea level by 1 [km] – very good correlation with natural data





# THERMODYNAMICS

## THERMODYNAMIC CYCLES

In any thermodynamic process mechanical work done by pressure

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

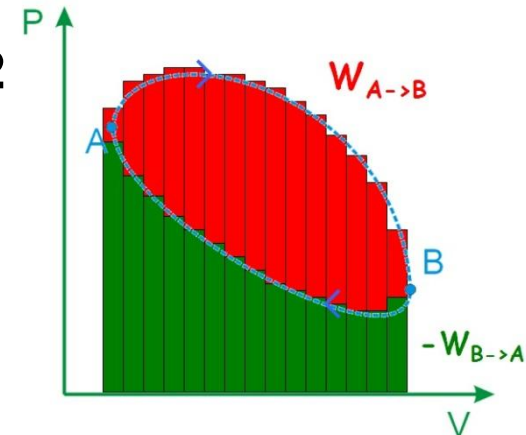
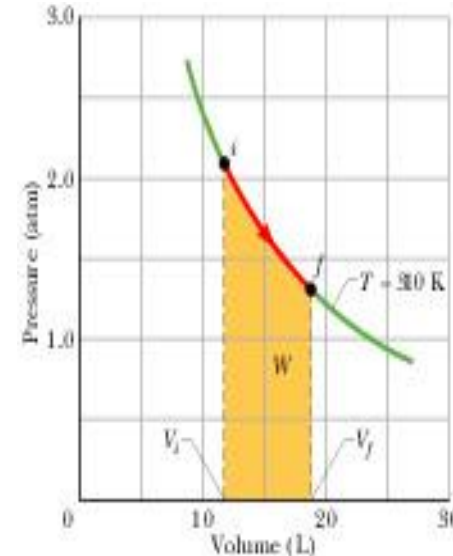
corresponds to area under p-V curve for proper process

In the cyclic process (closed path) net mechanical work done by pressure in one cycle

$$W_{cp} = \oint dW = \oint p dV = \int_A^B p \cdot dV + \int_B^A p \cdot dV = \int_A^B p \cdot dV - \int_B^A p \cdot dV = 0$$

path1
path2
path1
path2

corresponds to area within closed cycle on p-V diagram



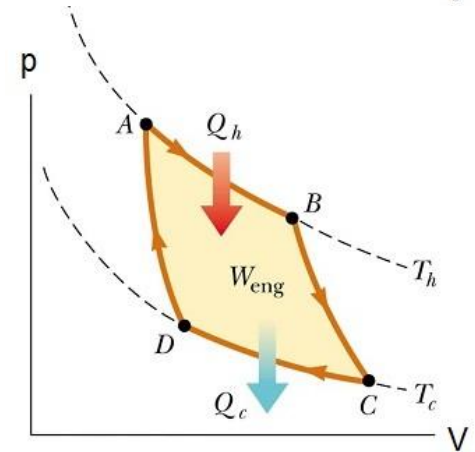
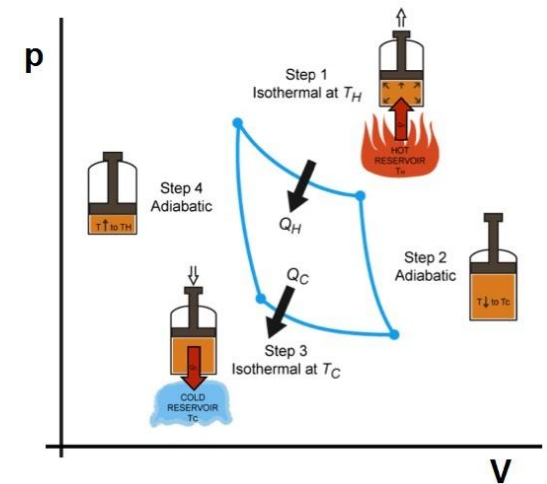
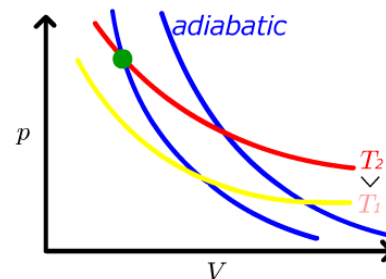
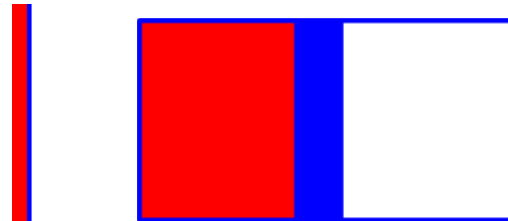
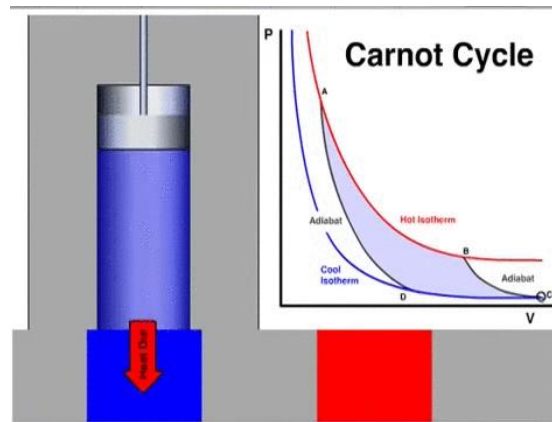
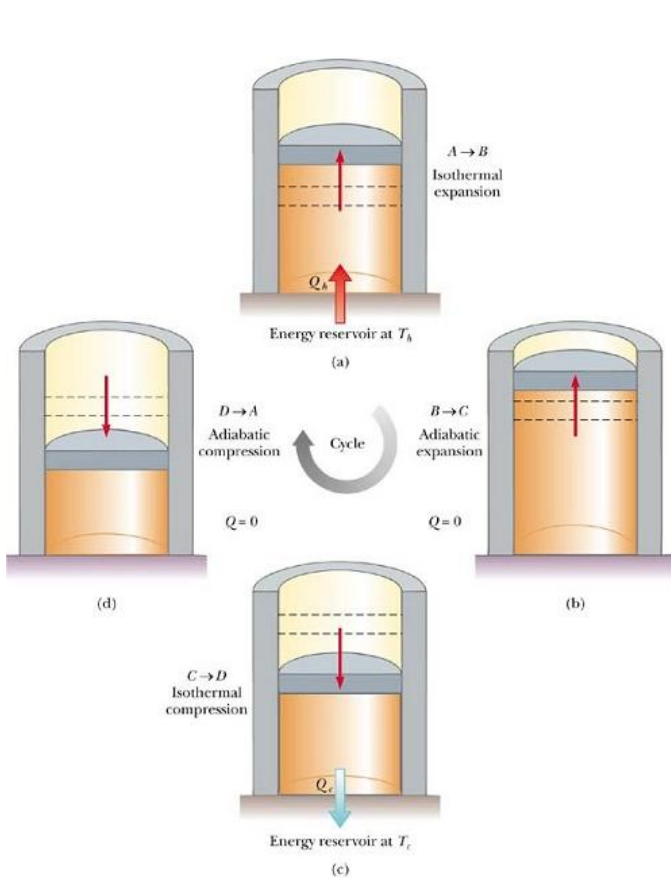
# THERMODYNAMICS



## CLOSED CARNOT CYCLE

First important practical closed cyclic process - **Carnot cycle**

Four successive stages of an ideal gas



# THERMODYNAMICS

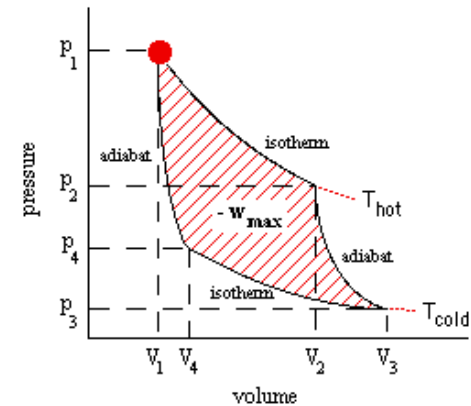
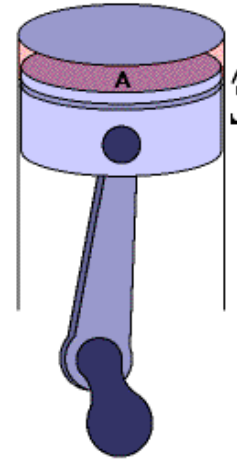
## CARNOT CYCLE

Heat energy absorbed by gas from higher temperature reservoir - expense of mechanical work done in isothermal expansion at temperature  $T_h$

$$|Q_h| = k \cdot T_h \cdot \ln \frac{V_B}{V_A}$$

Heat energy deposited at lower temperature  $T_c$

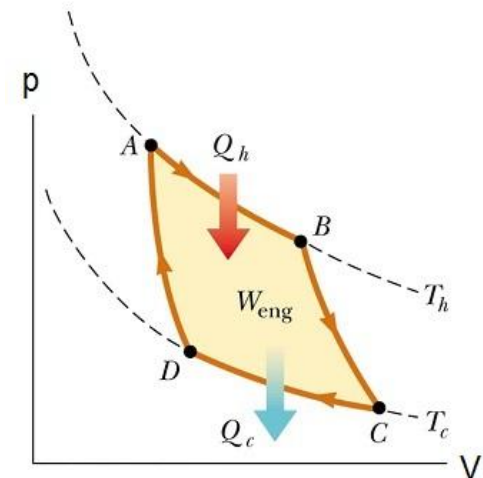
$$|Q_c| = k \cdot T_c \cdot \ln \frac{V_C}{V_D}$$



Equations of state for two adiabatic processes:

process B - C 
$$T_h \cdot V_B^{\kappa-1} = T_c \cdot V_C^{\kappa-1}$$

process D - A 
$$T_c \cdot V_D^{\kappa-1} = T_h \cdot V_A^{\kappa-1}$$



# THERMODYNAMICS

## CARNOT CYCLE

After transformation

$$\left(\frac{V_D}{V_A}\right)^{\kappa-1} = \frac{T_h}{T_c} = \left(\frac{V_C}{V_B}\right)^{\kappa-1}$$

then

$$\frac{V_D}{V_A} = \frac{V_C}{V_B}$$

and

$$\frac{V_B}{V_A} = \frac{V_C}{V_D}$$

thus

$$\left|\frac{Q_h}{Q_c}\right| = \frac{k \cdot T_h \cdot \ln \frac{V_B}{V_A}}{k \cdot T_c \cdot \ln \frac{V_C}{V_D}} = \frac{T_h}{T_c}$$

and

$$\left|\frac{Q_h}{T_h}\right| = \left|\frac{Q_c}{T_c}\right|$$

- general characteristics of all reversible cycles.

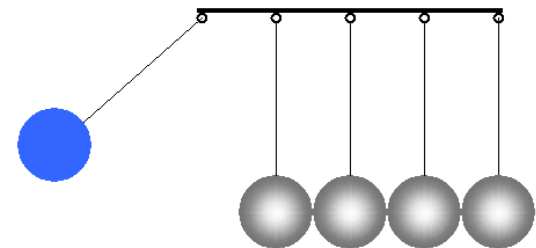
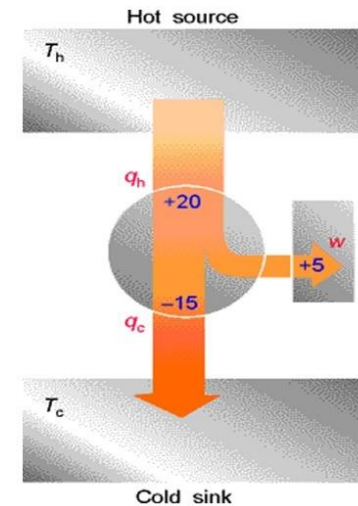
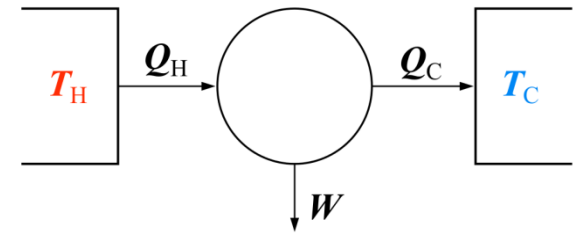
Additional transformation

$$\left|\frac{Q_h - Q_c}{Q_h}\right| = \left|\frac{T_h - T_c}{T_h}\right| = \eta < 1$$

General behaviour of all reversible cycles – efficiency always  $< 1!$

**ideal motion without loss of energy is impossible - 1 type perpetum mobile**

- model device (system) once started working without any external energy; true in mechanics- Newton's pendulum vibrations



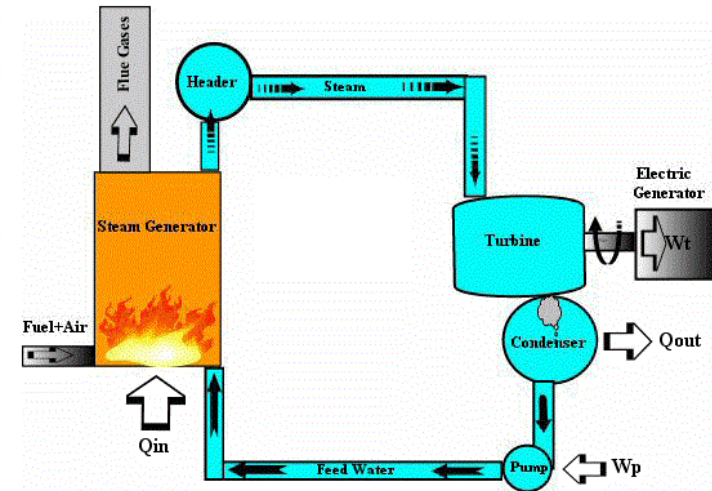
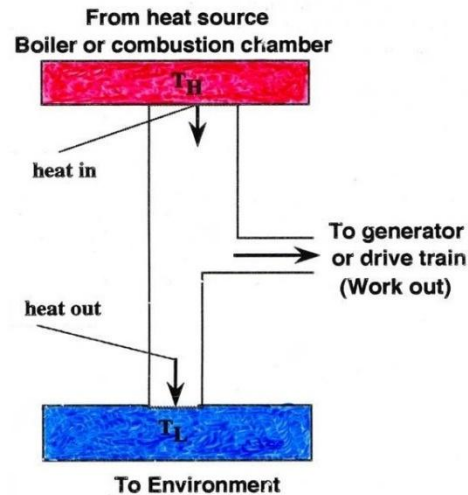
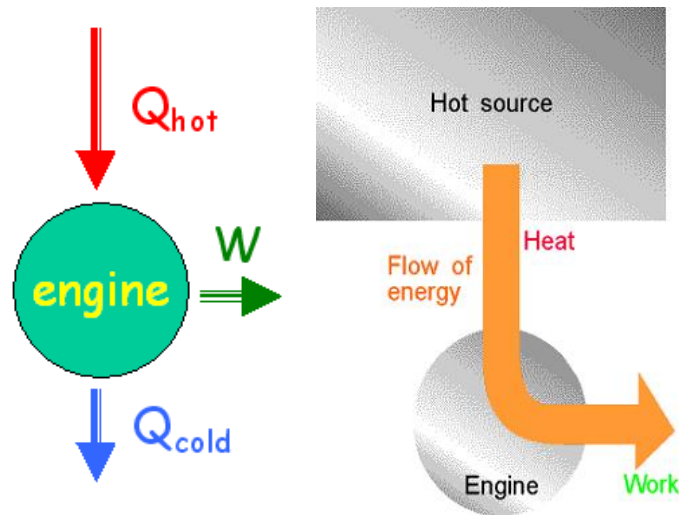
Most common application of Carnot cycle: **heat engine and heat pump**

# THERMODYNAMICS

## HEAT ENGINE

### IDEA:

net mechanical work  $W$  is done by the system: heat energy  $Q_{hot}$  is taken from the heat source (**heating**) at temperature  $T_H$  and then deposited as  $Q_{cold}$  in the low temperature reservoir (**cooling**) at temperature  $T_C$



According to first law of thermodynamics internal energy becomes unchanged, thus

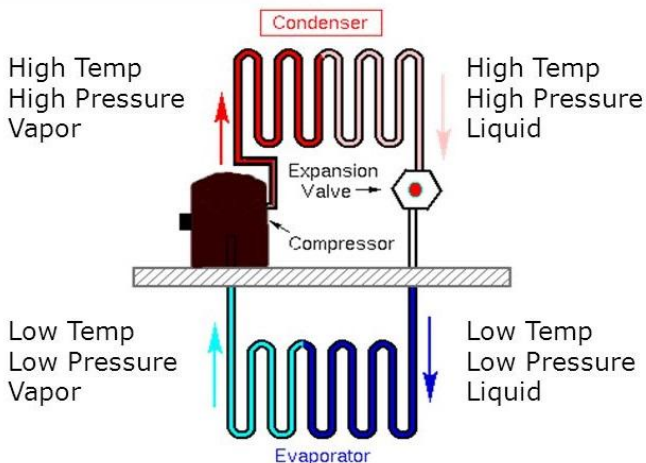
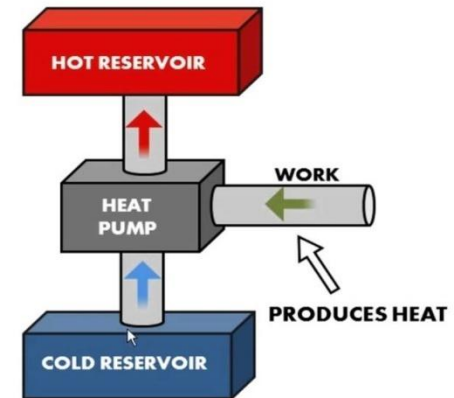
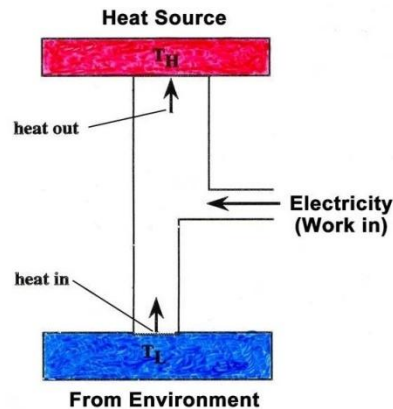
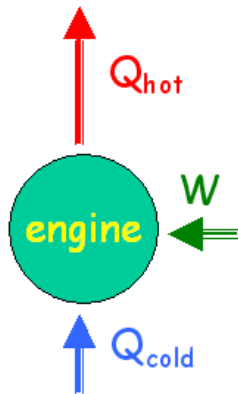
$$W = Q_h - Q_c$$

# THERMODYNAMICS

## HEAT PUMP - REFRIGERATOR

### IDEA:

reversed cyclic process: mechanical work is put into system and then heat energy is taken from low temperature reservoir and then deposited in high-temperature reservoir



# THERMODYNAMICS

## SECOND LAW OF THERMODYNAMICS

Any reversible process can be recognized as comprising of very large thin Carnot cycles  
- for any small cycle

$$\left| \frac{Q_h}{T_h} \right| = \left| \frac{Q_c}{T_c} \right|$$

For complete reversible process  $\sum_i \frac{Q_i}{T_i} = 0$

When  $Q \rightarrow 0$

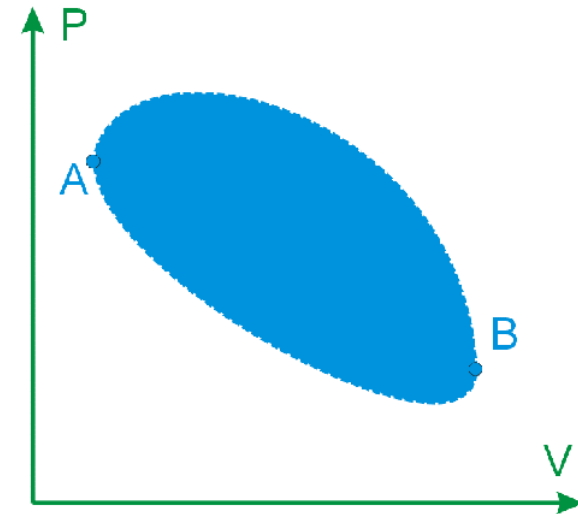
Carnot cycle becomes infinitely small and heat energy variation is independent on path between A and B on  $p$ - $V$

$$\oint \frac{dQ}{T} = 0$$

For irreversible thermodynamic process between two boundary points

$$dS = \int_A^B \frac{dQ}{T}$$

$$\Delta S = \int_A^B \frac{dQ}{T} = S_B - S_A$$



- **Differential and integral second law of thermodynamics, respectively**  
whereas differential first law of thermodynamic  $T \cdot dS = dU + p \cdot dV$

# THERMODYNAMICS

## SECOND LAW OF THERMODYNAMICS

For the exchanged heat energy of arbitrary process

$$dQ = dU + p \cdot dV = d(U + pV) = dH - V \cdot dp = c_p \cdot dT - V \cdot dp$$

Taking into account equation of state  $p \cdot V = R \cdot T$

$$dQ = dH - V \cdot dp = c_p \cdot dT - RT \frac{dp}{p}$$

Dividing by T  $\frac{dQ}{T} = c_p \frac{dT}{T} - R \frac{dp}{p}$

After integration between two boundary states, respectively

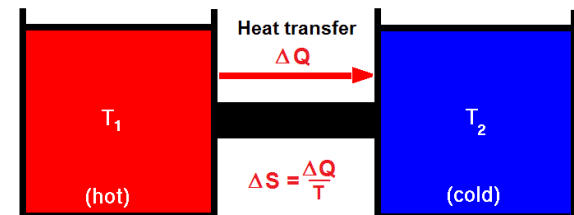
$$\Delta S = S_2 - S_1 = c_p \cdot \ln \frac{T_2}{T_1} - R \cdot \ln \frac{p_2}{p_1}$$

For irreversible process between initial (1) and final (2) states, respectively

$$\Delta S = S_2 - S_1 = S_f - S_i > 0$$

**Second law of thermodynamics - law of entropy (Clausius – 1850)**

Identifies the direction of a process –  
heat can only spontaneously transfer from  
hot object to cold object, **not vice versa**

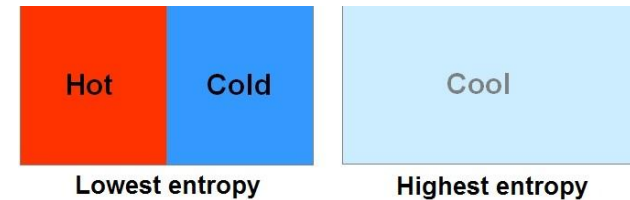
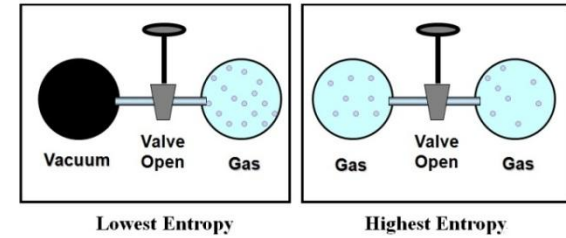
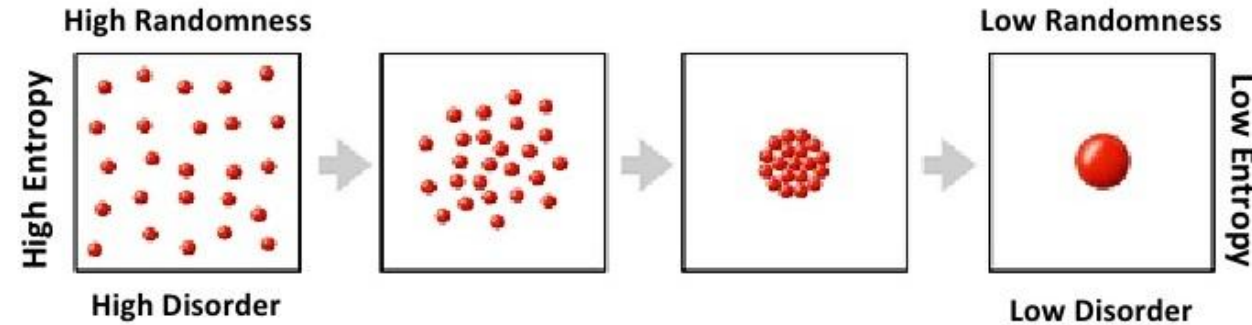




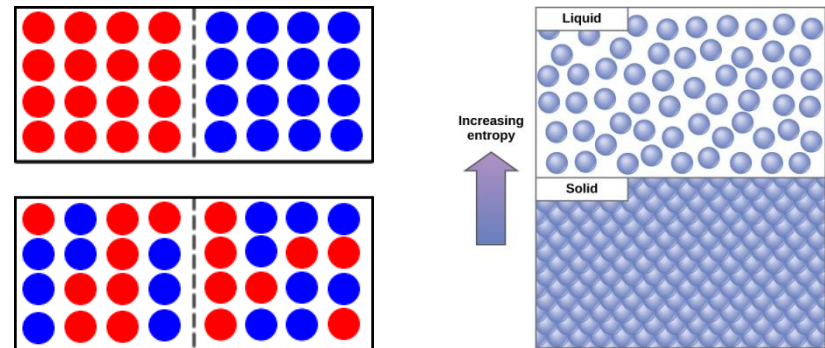
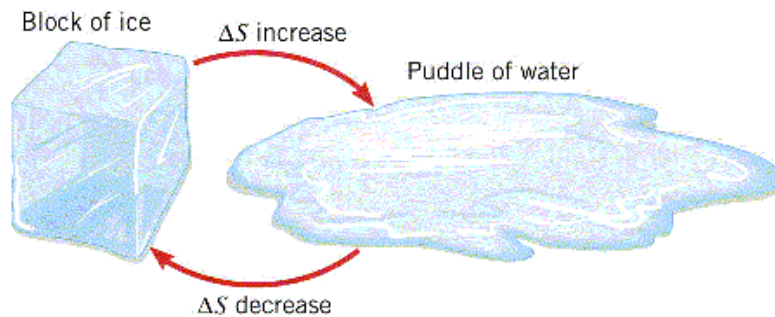
# THERMODYNAMICS

## SECOND LAW OF THERMODYNAMICS

**ENTROPY** - measure of degree of randomness of energy in a system -  
measure of disorder of matter



During transition from ordered form (solid) to disordered forms (liquid)  
entropy always increases



# THERMODYNAMICS

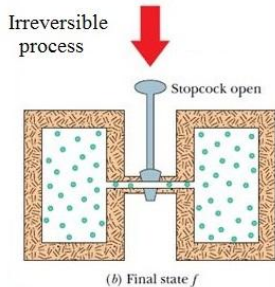
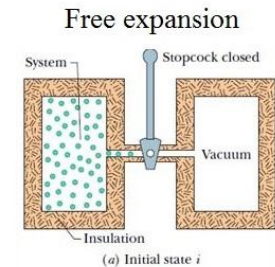
## SECOND LAW OF THERMODYNAMICS

**ENTROPY** - measure of degree of randomness of energy in a system -  
measure of disorder of matter - recognition between the processes

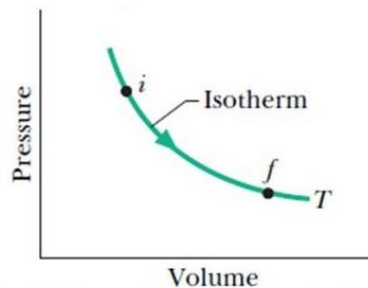
For reversible processes  $S_f = S_i$

For irreversible process  $S_f > S_i$

Free expansion - isothermal process



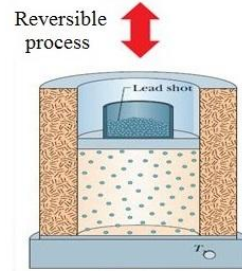
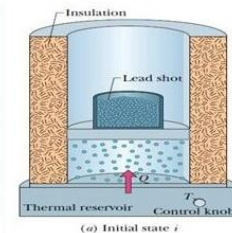
Entropy change of an irreversible process can be found with a reversible one connecting the initial and final states



$$\Delta S = S_f - S_i = \frac{Q}{T}$$

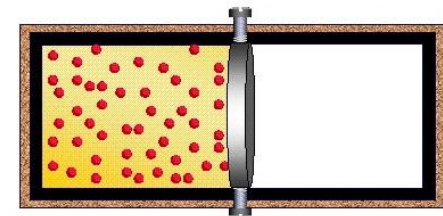
Change of entropy for isothermal process

Isothermal process

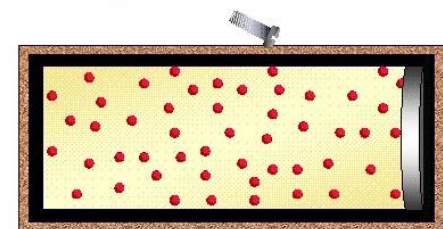


(b) Final state f

Adiabatic expansion



Gas occupies left volume  
right volume is vacuum



Gas expands adiabatically  
and irreversibly  
Energy is constant  
Entropy is maximized

# THERMODYNAMICS

## THIRD LAW OF THERMODYNAMICS

### ENTROPY

For large system statistical-mechanics definition of entropy

Where:

$$S = k \cdot \ln W$$

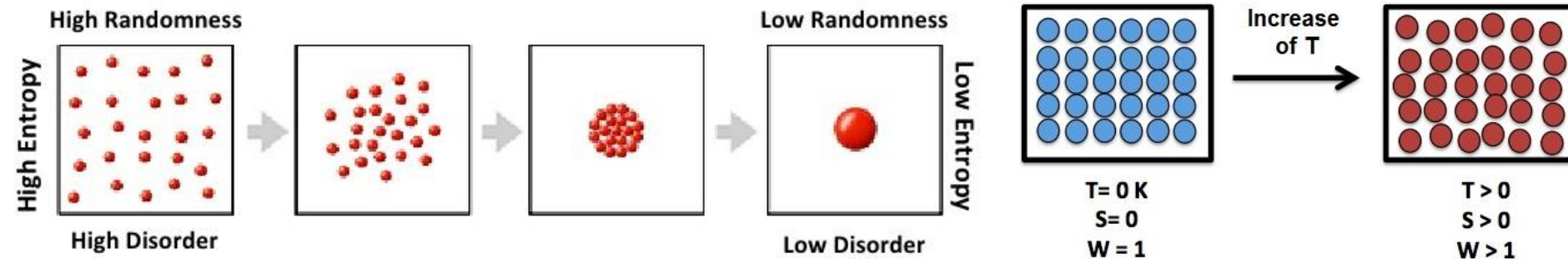
k - Boltzmann constant

W - number of microstates consistent with macroscopic configuration

- Third law of thermodynamics (Lewis, Randall – 1923)

A „perfect” crystal has flawless alignment of all its particles - at absolute zero temperature particles have minimum energy - one microstate - entropy

$$S_{T=0K} = k \cdot \ln 1 = 0$$



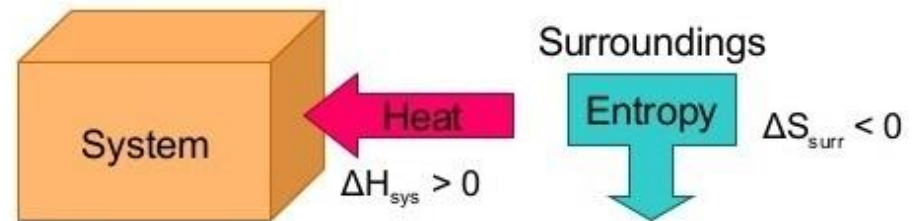
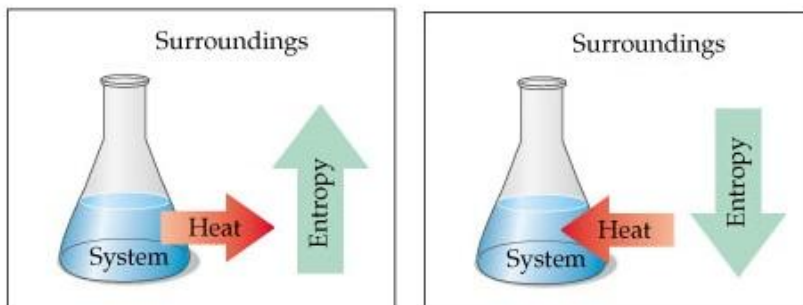
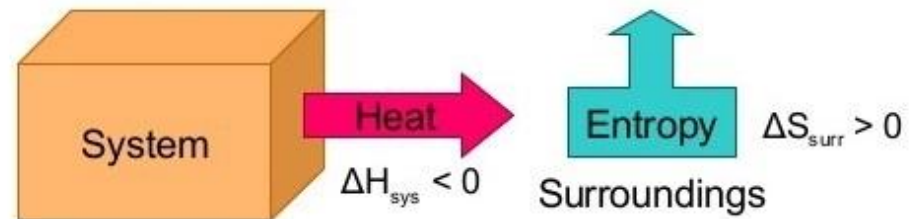
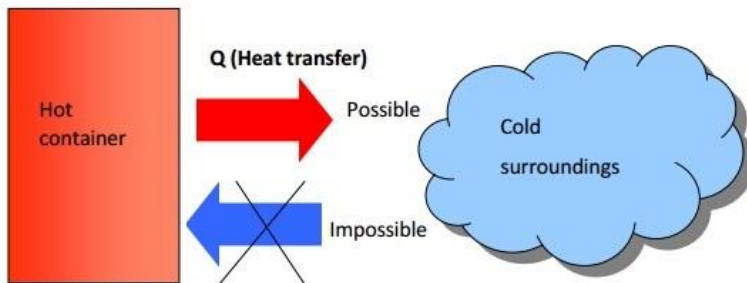
# THERMODYNAMICS

## ENTROPY IN SURROUNDINGS

The total (variation) of entropy of natural systems in surroundings

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

In any spontaneous processes the total entropy is always positive  
- heat transfer from hot container to cold surroundings is only possible



Low T - large entropy change (surroundings)  
High T - small entropy change (surroundings)

# THERMODYNAMICS

## THERMODYNAMICS LAWS - SUMMARY - LIMITATIONS

### Zero Law (Equilibrium principle)

- Two bodies in thermal equilibrium are at same T

### First Law (Energy conservation principle)

Energy is conserved, cannot be created or destroyed; its form can only be converted; however it:

- does not help to predict the certain process is possible or not, and its direction
- does not provide and specify sufficient condition to process take place

### Second Law (Entropy principle)

- Energies can flow equilibrate, their forms changed with loss of usable ones - waste energy cause disorder
- recognition of reversible and irreversible processes

### Third Law (Temperature principle)

„Driving force” for equilibration uniquely defined

