

# Thermal & Statistical Physics

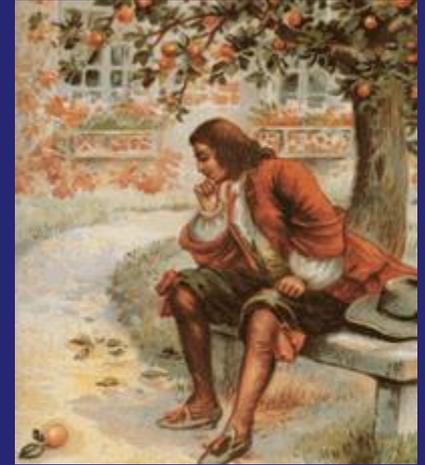
*Thermal & Statistical Physics*  
**PHYS 343**

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# LECTURE 12



*Heat Capacity*

*Heat Engines*

*Entropy*

*2<sup>nd</sup> Law*

*3<sup>rd</sup> Law*

# Heat capacity

- A body has a capacity for heat. The smaller the temperature change in a body caused by the transfer of a given quantity of heat, the greater its capacity.
- A heat capacity:  $C \equiv \frac{dQ}{dT}$ 
  - a process-dependent quantity rather than a state function.
- Two heat capacities,  $C_V$  and  $C_P$ , are in common use for homogeneous fluids; both as state functions, defined unambiguously in relation to other state functions.

# Heat capacities at ...

At constant volume •

$$C_v = \left( \frac{\partial E}{\partial T} \right)_v$$
$$\Delta E = \int_{T_1}^{T_2} C_v dT \quad (\text{const } v)$$

- $C_v$  is a state function and is independent of the process.

At constant pressure •

$$C_p \equiv \left( \frac{\partial H}{\partial T} \right)_p$$
$$\Delta H = \int_{T_1}^{T_2} C_p dT \quad (\text{const } P)$$

- $C_p$  is a state function and is independent of the process.

# Specific Heat Capacities...

$$Q = n c \Delta T$$

$c$  : molar specific heat capacity in units of  $J/(\text{mol}\cdot\text{K})$

$n$  : number of moles

$$\Delta T = T_f - T_i$$

$$Q = \Delta E + W$$

$$Q_{\text{constant pressure}} = \frac{3}{2}nR(T_f - T_i) + nR(T_f - T_i) = \frac{5}{2}nR(T_f - T_i)$$

$$Q_{\text{constant volume}} = \frac{3}{2}nR(T_f - T_i) + 0$$

# Specific Heat Capacities

The molar specific heat capacities can now be determined

*Constant pressure  
for a monatomic  
ideal gas*

$$C_P = \frac{Q_{\text{constant pressure}}}{n(T_f - T_i)} = \frac{5}{2}R$$

*Constant volume  
for a monatomic  
ideal gas*

$$C_V = \frac{Q_{\text{constant volume}}}{n(T_f - T_i)} = \frac{3}{2}R$$

The ratio specific heats is  $\gamma$  of the

*Monatomic  
ideal gas*

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3}$$

**Example :** Calculate the internal-energy and enthalpy changes that occur when air is changed from an initial state of 40°F and 10 atm, where its molar volume is 36.49 ft<sup>3</sup>/lb-mole, to a final state of 140°F and 1 atm. Assume for air that  $PV/T$  is constant and that  $C_V = 5$  and  $C_P = 7$  Btu/lb-mol.F.

Independent of paths! —————> Two-step process:

- (1) cooled at constant volume to the final pressure;
- (2) heated at constant pressure to the final temperature.

$$T_1 = 40 + 459.67 = 499.67 \text{ R}$$

$$T_2 = 140 + 459.67 = 599.67 \text{ R}$$

Constant volume

$$T' = T_1 \frac{P_1}{P_2} = 49.97 \text{ R}$$

$$\Delta U = C_V \Delta T = -2248.5 \text{ Btu}$$

$$\Delta H = \Delta U + \Delta(PV) = -3141.6 \text{ Btu}$$

Intermediate state

Constant pressure

$$V_2 = V_1 \frac{P_1 T_2}{P_2 T_1} = 437.93 \text{ ft}^3$$

$$\Delta H = C_P \Delta T = 3847.9 \text{ Btu}$$

$$\Delta U = \Delta H - P \Delta V = 2756.2 \text{ Btu}$$

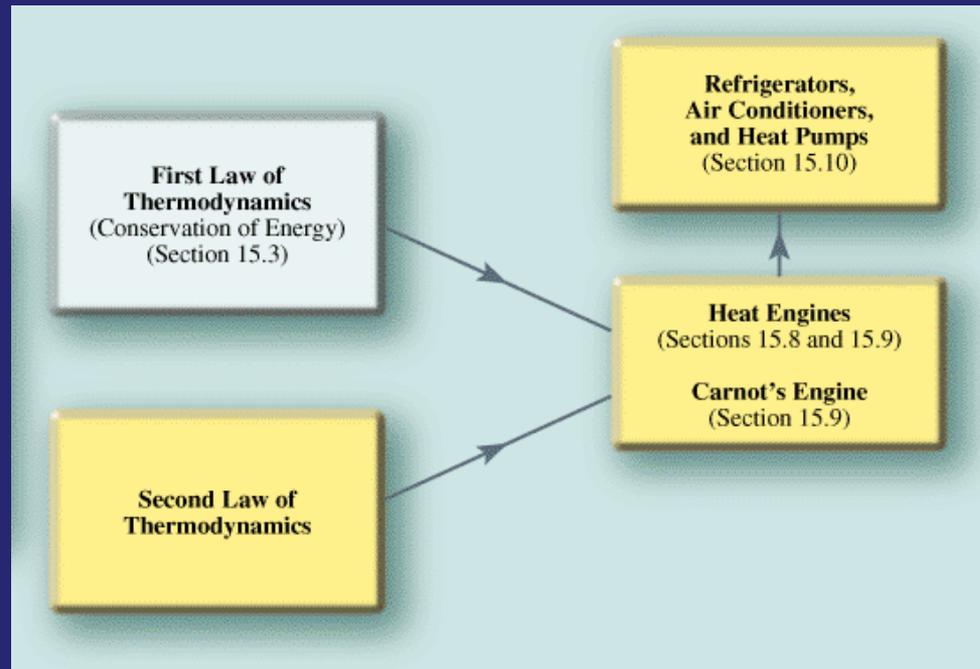
$$\Delta H = \Delta H_1 + \Delta H_2 = 507.7 \text{ Btu}$$

$$\Delta U = \Delta U_1 + \Delta U_2 = 706.3 \text{ Btu}$$

# *Second Law of Thermodynamic*

## THE SECOND LAW OF THERMODYNAMICS: THE HEAT FLOW STATEMENT:

Heat flows spontaneously from a substance at a higher temperature to a substance at a lower temperature and does not flow spontaneously in the reverse direction.

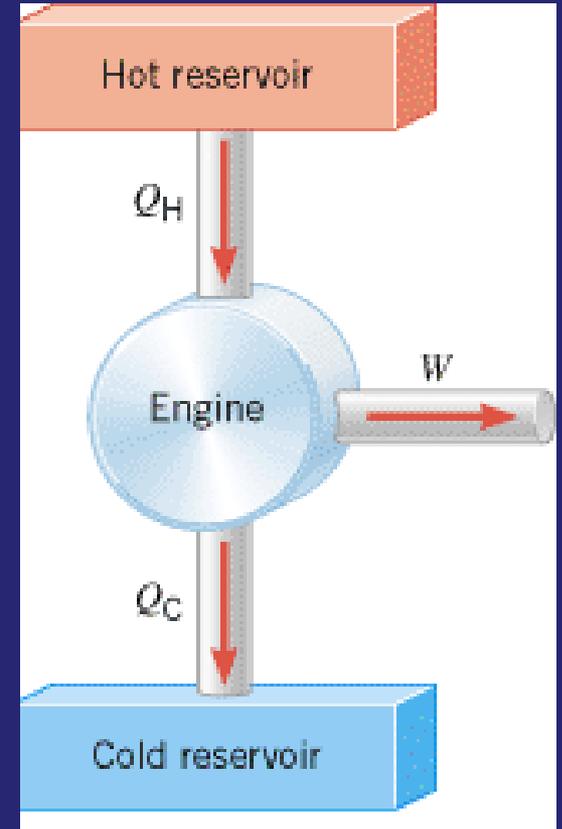


# *Heat Engine*

- *A device that is able to convert thermal energy to mechanical energy.*
- *An internal combustion engine.*

# *Requirements*

- *High temperature source*
- *Low temperature sink*



# Heat Engines

Uses heat to perform work

- Hot reservoir provides heat
- Part of the heat is used to do work
- remaining heat is rejected to a cold reservoir

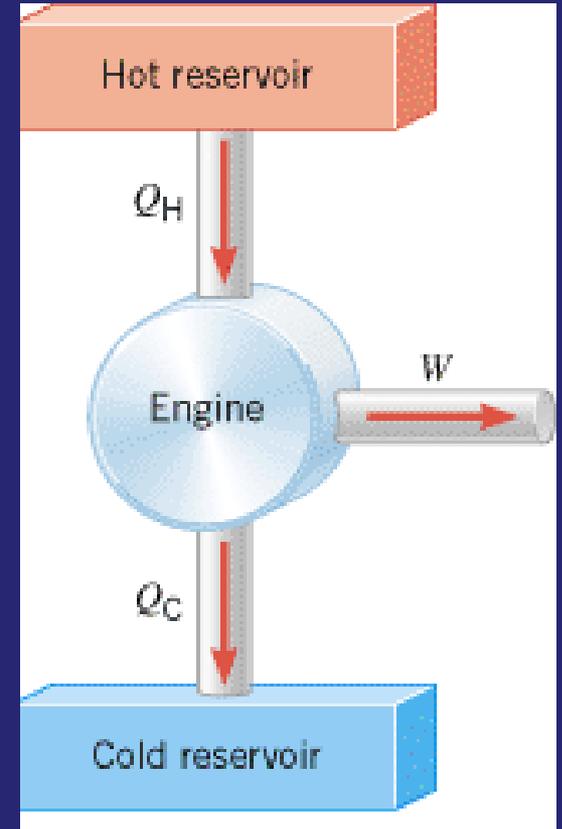
**Efficiency = Work done / input heat =  $W / Q_H$**

Should obey the principle of conservation of energy:

$$Q_H = W + Q_C$$

$$e_{ff} = W / Q_H$$

$$e_{ff} = (Q_H - Q_C) / Q_H$$



# Efficiency

$$Eff = 1 - \frac{Q_C}{Q_H}$$



# *The Carnot Cycle ....*

- The most efficient type of heat engine
- Developed by Sadi Carnot
- Piston works between heat source and heat sink
- Four processes
- It is only theoretical...it does not exist.

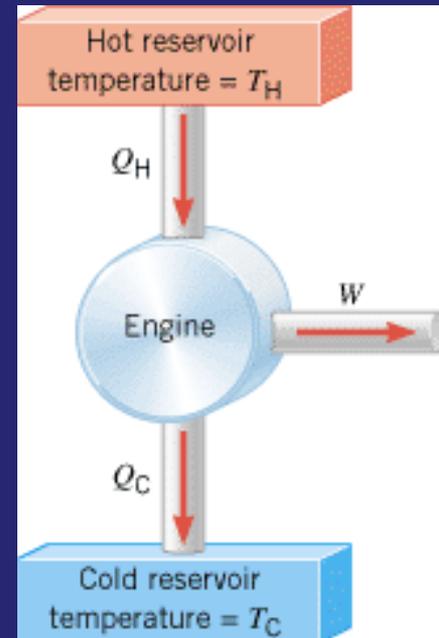
# Carnot's Principle

## Sadi Carnot (1796-1832)

*A reversible process is one in which both the system and its environment can be returned to exactly the states they were in before the process occurred.*

No irreversible engine operating between two reservoirs at constant temperatures can have a greater efficiency than a reversible engine operating between the same temperatures. Furthermore, all reversible engines operating between the same temperatures have the same efficiency.

$$\text{Efficiency of a Carnot engine} = e_{\text{Carnot}} = 1 - \frac{T_C}{T_H}$$

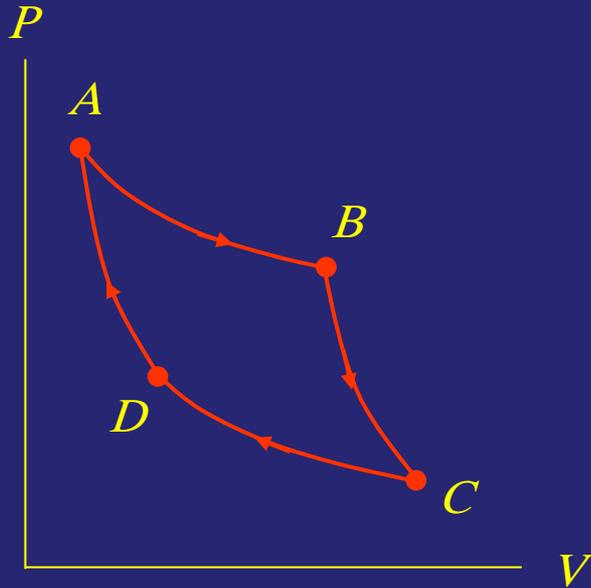


## *The Carnot Cycle....*

### *The Four Processes*

- Isothermal expansion
- Adiabatic expansion
- Isothermal compression
- Adiabatic compression

# The Carnot Cycle



Efficiency of Carnot engine:

$AB$  : reversible isothermal at temperature  $T_1$

$BC$ : reversible adiabatic

$CD$  : reversible isothermal at temperature  $T_2 < T_1$

$DA$  : reversible adiabatic

$$\Delta U_{ABCD} = 0 \Rightarrow q_{AB} + q_{CD} = -w > 0$$

(the system does work)

$$\eta = \frac{|w|}{q_{AB}} = 1 - \frac{|q_{CD}|}{q_{AB}}$$

$$\eta = 1 - \frac{T_2}{T_1} < 1 \quad (\text{unless } T_2 = 0)$$

One can never utilize all the thermal energy given to the engine by converting it into mechanical work.

# Efficiency of Carnot engine

$$\eta = 1 - \frac{T_2}{T_1} < 1 \quad (\text{unless } T_2 = 0)$$

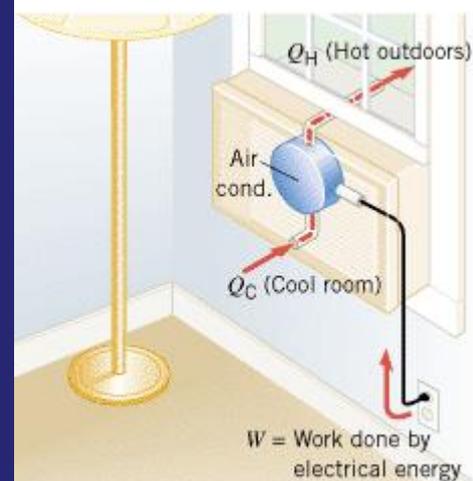
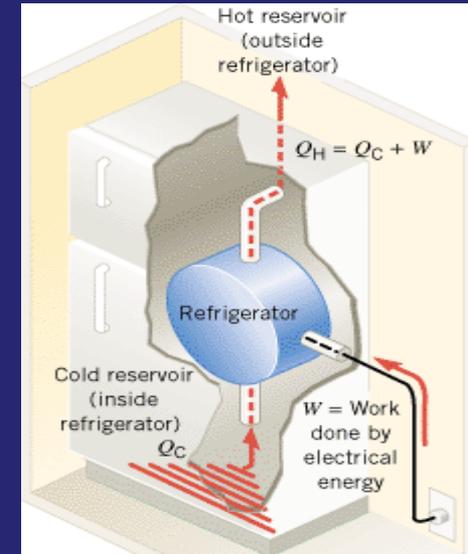
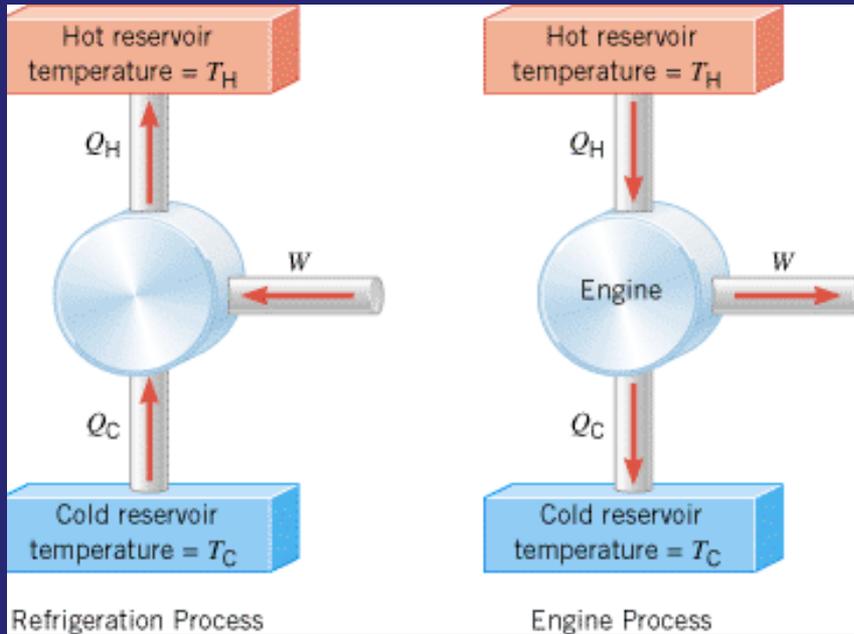
## *The Carnot Cycle....*

- Takes in heat from heat reservoir without changing temperature
- Does work on its environment
- Drops heat into heat sink
- The environment does work on it
- This is a cyclic process

## *The Carnot Cycle ....*

- $Q_H$  = heat taken in from heat source
- $Q_C$  = heat removed to heat sink
- $W$  = Work done
- $T_H$  = temperature of heat source
- $T_C$  = temperature of heat sink

# Refrigerators, Air conditioners and Heat Pumps



*Refrigerator or  
air conditioner*

Coefficient of  
performance =  $\frac{Q_C}{W}$

# Entropy

In general, irreversible processes cause us to lose some, but not necessarily all, of the ability to perform work. This partial loss can be expressed in terms of a concept called *entropy*.

To introduce the idea of entropy we recall the relation  $Q_C/Q_H = T_C/T_H$  that applies to a Carnot engine. This equation can be rearranged as  $Q_C/T_C = Q_H/T_H$ , which focuses attention on the heat  $Q$  divided by the Kelvin temperature  $T$ . The quantity  $Q/T$  is called the change in the entropy  $\Delta S$ :

$$\Delta S = \left( \frac{Q}{T} \right)_R$$

Change in entropy of Carnot's engine

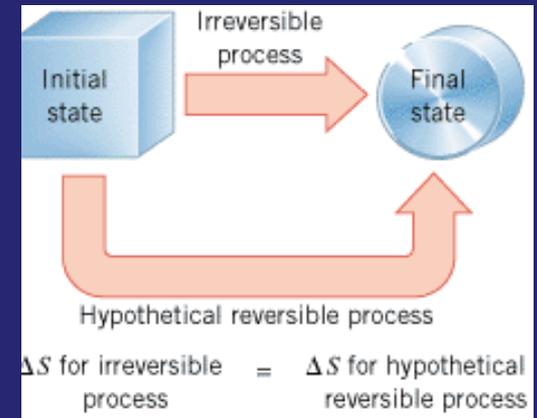
$$\Delta S_C + \Delta S_H = \frac{Q_C}{T_C} - \frac{Q_H}{T_H} = 0$$

Reversible process does not alter the total entropy of the universe (2<sup>nd</sup> Law in terms of entropy).

$$\Delta S_{\text{universe}} = 0$$

Entropy : Degree of disorder

Entropy and Arrow of time



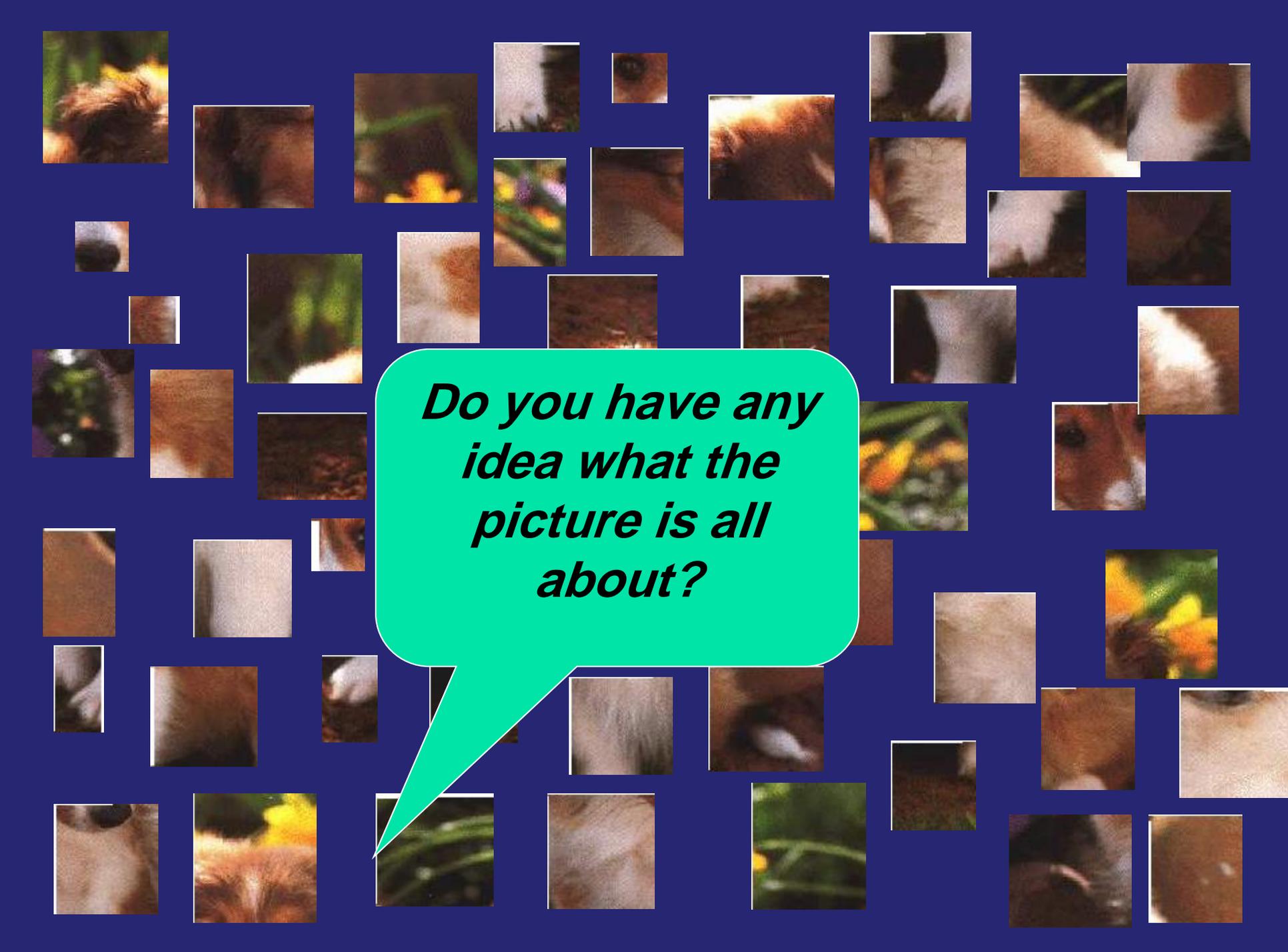
# *Third Law of Thermodynamics*

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THE SECOND LAW OF THERMODYNAMICS STATED IN TERMS OF ENTROPY

The total entropy of the universe does not change when a reversible process occurs

THE THIRD LAW OF THERMODYNAMICS It is not possible to lower the temperature of any system to absolute zero ( $T = 0$  K) in a finite number of steps.



*Do you have any  
idea what the  
picture is all  
about?*

