

2.5

Reversible



Irreversible

In all thermodynamic processes, the changes that occur in the environment must be considered in conjunction with the changes that occur in the thermodynamic system

System

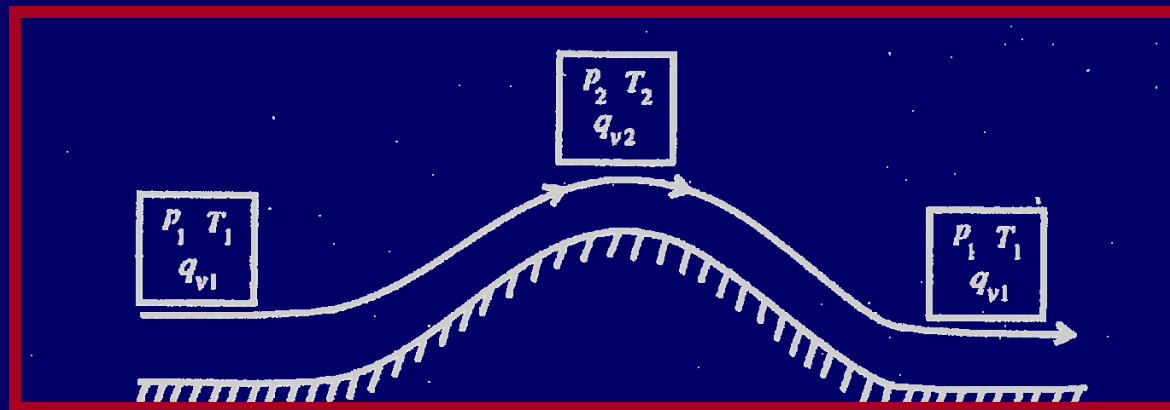
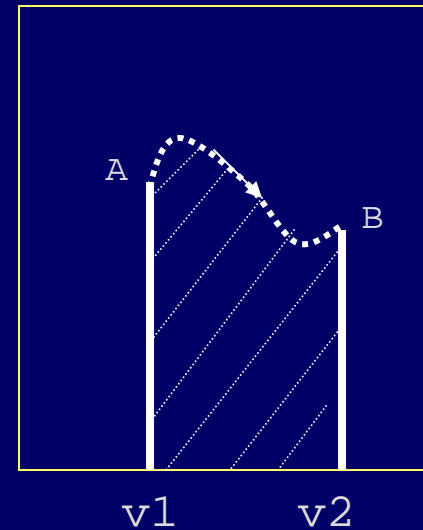
environment

## Reversible

The system is in an equilibrium state throughout the process

The system passes at an infinitesimal rate through a continuous succession of balance states that are infinitesimally different from each other

★ The process can be reversed and the system and its environment will return to the initial state

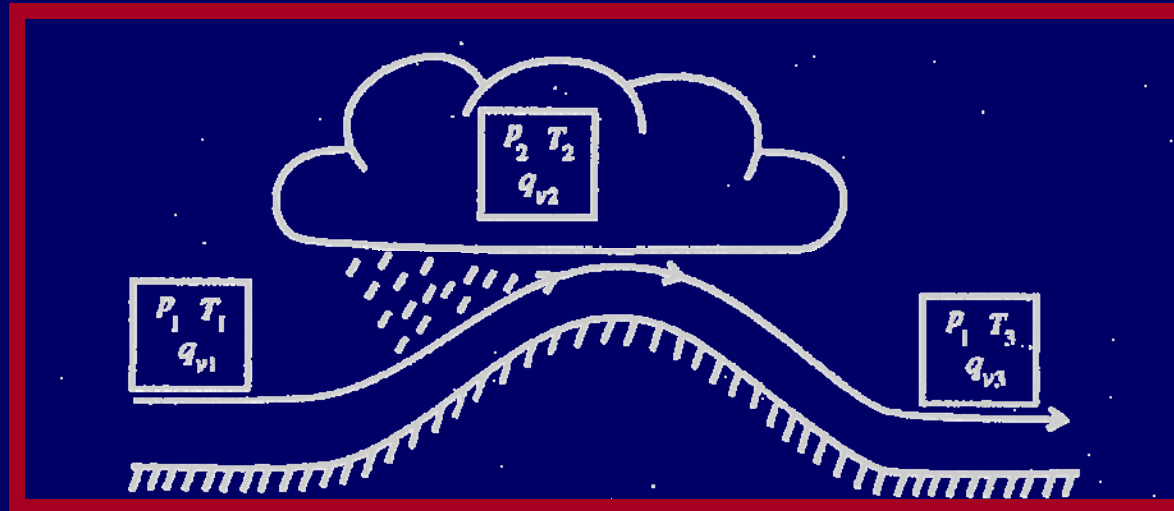


*adiabatic process*

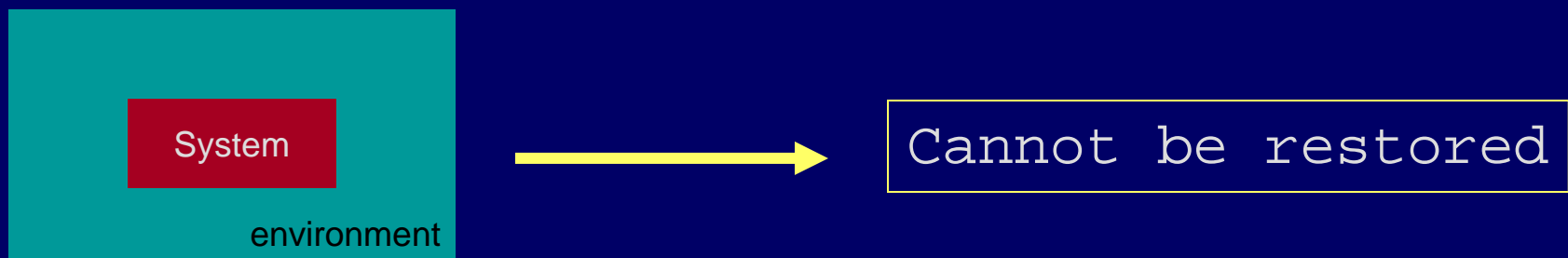
$$dq = 0$$

# Irreversible

If the system is restore to its initial state, the environment will have change



The term irreversible does not mean that the system cannot return to its original state



example

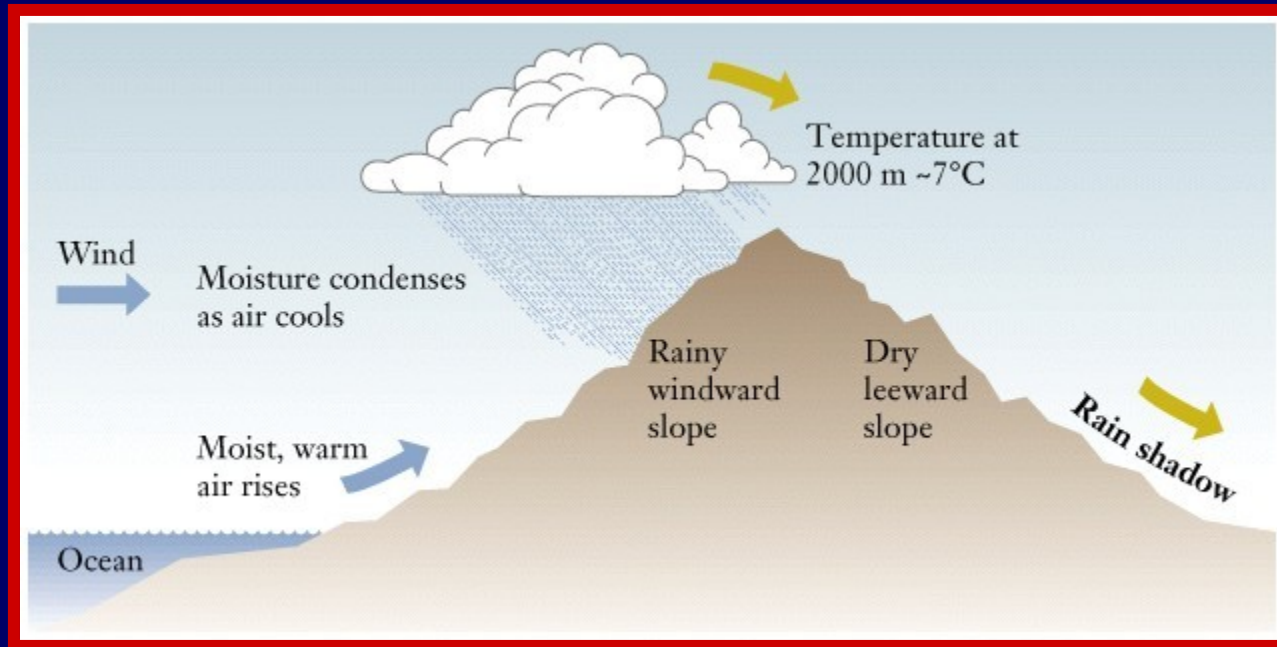
precipitation

If the rain falls to the ground

The total water content of the atmosphere

Temperature of the atmosphere

Irreversibly



$$pv = RT$$

$$dh = c_p dT$$

First law in  
enthalpy form  
for a reversible  
process

$$dh = dq + vdp$$

$$c_p dT = dq + vdp$$

$$dq = c_p dT - vdp$$

$$v = \frac{RT}{p}$$

$$dq = c_p dT - \frac{RT}{p} dp$$

$$\frac{dq}{T} = \frac{c_p dT}{T} - \frac{R}{p} dp$$

$$\frac{dq}{T} = c_p d(\ln T) - R d(\ln p)$$

$$\frac{dq}{T}$$

Exact differential

$$\oint \left( \frac{dq}{T} \right)_{rev} = 0$$

Only for a  
reversible  
process

# Entropy

$\eta$

$$d\eta = \left( \frac{dq}{T} \right)_{rev}$$

Change in entropy from one state to the other

defined associated with a reversible process

Exactly the same for an irreversible process

state variable

$$\oint \left( \frac{dq}{T} \right)_{rev} = 0$$

but

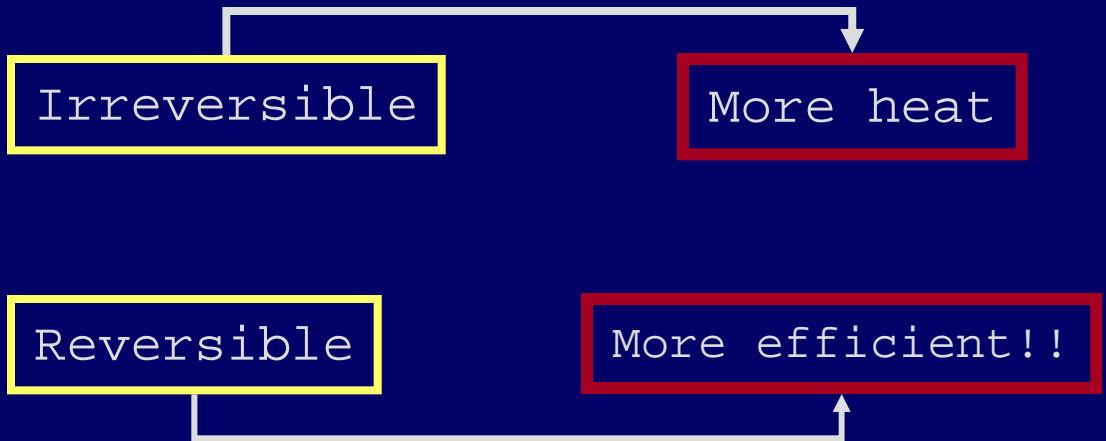
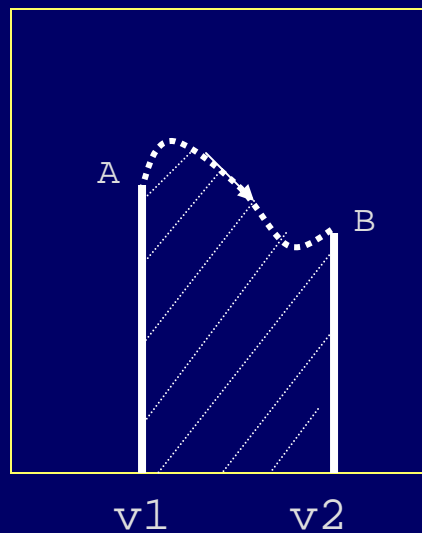
$$\int \left( \frac{dq}{T} \right)$$

Reversible  
Irreversible

$$\int \left( \frac{dq}{T} \right)_{rev} > \int \left( \frac{dq}{T} \right)_{irrev}$$

$$\int \left( \frac{dq}{T} \right)_{rev} > \int \left( \frac{dq}{T} \right)_{irrev}$$

To accomplish a given change in entropy (or state)





Entropy changes for an ideal gas

$$\frac{dq}{T} = c_p d(\ln T) - R d(\ln p)$$

Internal energy form

$$c_v dT = dq - p dv$$

$$p = \frac{RT}{v}$$

$$\frac{dq}{T} = c_v d(\ln T) + R d(\ln v)$$

$$d\eta = c_p d(\ln T) - R d(\ln p)$$

$$d\eta = c_v d(\ln T) + R d(\ln v)$$

$$d\eta = c_p d(\ln T) - R d(\ln p)$$

$$d\eta = c_v d(\ln T) + R d(\ln v)$$

Isobaric heating

$$dp = 0$$

$$d\eta = c_p d(\ln T)$$

$$\Delta\eta = \int_{T_1}^{T_2} c_p \frac{dT}{T}$$

$$\Delta\eta = c_p \ln \frac{T_2}{T_1}$$

Isothermal heating

$$dT = 0$$

$$d\eta = -R d(\ln p) = R d(\ln v)$$

$$\Delta\eta = R \ln \left( \frac{p_1}{p_2} \right) = R \ln \left( \frac{v_2}{v_1} \right)$$

## *Physical interpretation..*

measure of the "multiplicity" associated with the state of the objects.

If a given state can be accomplished in many more ways, then it is more probable than one which can be accomplished in only a few ways.

"**throwing dice**",

**7**   **2**

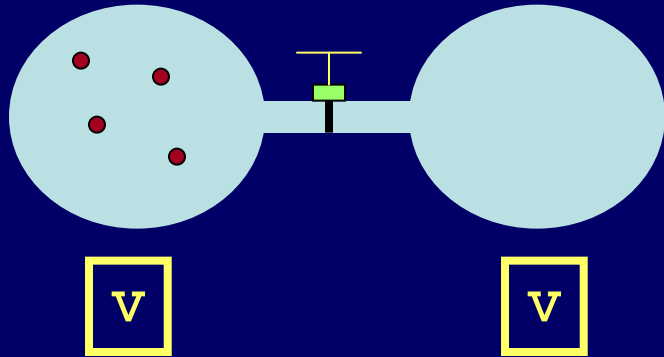
throwing a seven is more probable than a two because you can produce seven in six different ways and there is only one way to produce a two.



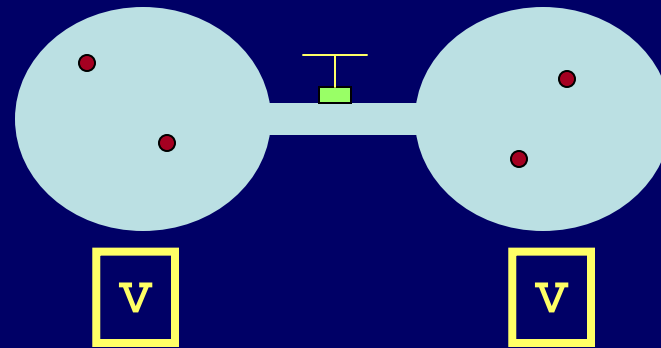
So seven has a higher multiplicity than a two, and we could say that a seven represents higher "disorder" or higher entropy.

## Relationship between entropy and probability

Two isolated bulbs



Volume doubles



Calculate the change in entropy

$$\Delta \eta = Nk \ln \left( \frac{v_{fin}}{v_{init}} \right)$$

$$N = 4 \quad v_{init} = 1 \quad v_{fin} = 2$$

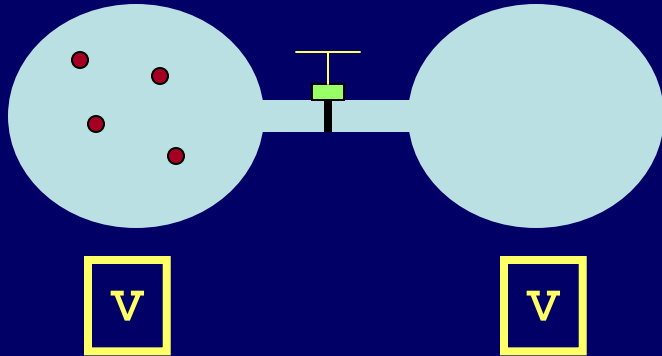
$k$  Boltzmann constant (gas constant per molecule)

$$\Delta \eta = 4k \ln 2$$

$$\Delta \eta = k \ln 2^4$$

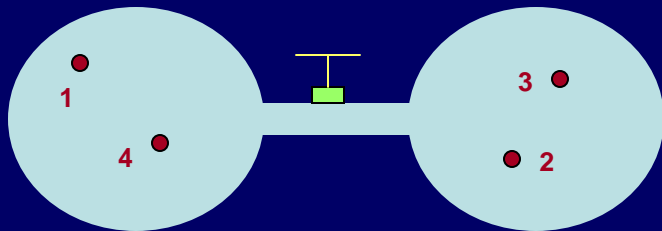
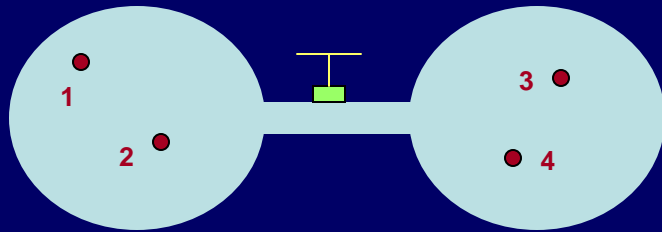
The entropy change is proportional to  $\ln 16$

probabilities



One configuration for the initial state: All four molecules in the left bulb

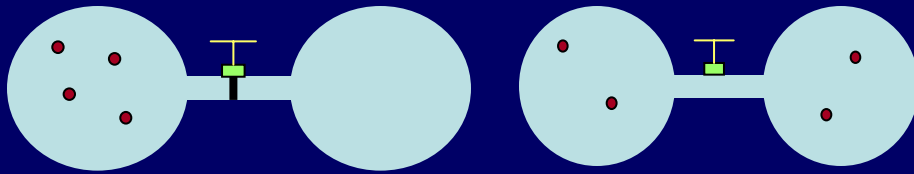
16 ways of arranging the four molecules between the 2 bulbs



# in left bulb	# in right bulb	# of ways to archive configuration, $C$	Probability of the configuration, $P$
0	4	1	1/16
1	3	4	4/16
2	2	6	6/16
3	1	4	4/16
4	0	1	1/16
Total: 16			1

$$\frac{P_{fin}}{P_{init}} = \frac{C_{fin}}{C_{init}} = 16$$

The equilibrium state of the four molecules distributed in two bulbs is more random than four molecules in one bulb



We are less definitive about the location of the molecules in the more "disordered" state

The natural path of all processes is from order to randomness

ENTROPY IN AN ISOLATED SYSTEM WILL TEND TO INCREASE AS THE PROBABILITY SPREADS OUT OVER THE POSSIBLE STATES AND THE SYSTEM APPROACHES EQUILIBRIUM