

Connor wool takes up heat: Gas coo

Copper wool takes up heat: Gas cools

#### Hot air motor as heat pump

Lower room: Heat will be detracted and added to upper room



### **5.8.Thermodynamic Work**

Gas (P,V,T),(P,V,T) are state variables 1,2,3,4 are equilibrium states Considered are quasistatic processes:

Change of P,T,V ',very slow, very small" Prozess is reversibel!

e.g: Sand: + grain of sand

Piston down

- Sandkörnchen

**Piston back** 





Irreversible processes:

Work performed:

air

$$W = W(P, V, T)$$

e.g: Chemicel reaktions, perfume  $\rightarrow$ 

#### 5.9.Carnot -cycle

(The most efficient heat cycle)

#### Exchange of heat possible or interrupted!





$$\begin{array}{|c|c|}\hline P \bullet V = R \bullet T & T \bullet V^{\gamma - 1} = \text{constant} \\ \hline U = c_V \bullet T & \Delta Q = \Delta U + \Delta W \end{array}$$

1:  $W_1$  positive,  $\Delta U = 0 \Rightarrow \Delta Q_{T_2} = W_1$ 2:  $\Delta Q = 0, W_2$  positive,  $\Rightarrow \Delta U = W_2 = c_V \cdot (T_2 - T_1)$ 3:  $\Delta U = 0 \Rightarrow W_3 = \Delta Q_{T_1} \prec 0$ 

4: 
$$\Delta Q = 0 \Rightarrow W_4 = \Delta U = c_V \quad (T_1 - T_2)$$
  
Overall:  $W = \Delta Q_{T_2}(\succ 0) + \Delta Q_{T_1}(\prec 0)$ 

Efficiency of CARNOT- machine

$$W_{1} = \int^{1} P \cdot dV \quad \text{with} \quad P = \frac{N \cdot k \cdot T}{V}$$
$$= N \cdot k \cdot T_{2} \cdot \int^{1} \frac{dV}{V} = N \cdot k \cdot T_{2} \cdot \ln \frac{V_{2}}{V_{1}};$$
$$V_{2}(\text{ Volume after cycle from 1 etc.})$$

analogical:  $W_3 = N \cdot k \cdot T_1 \cdot \ln \frac{V_4}{V_3};$ 



For adiabatical prozesses applies:

$$T_{2} \cdot V_{2}^{\gamma-1} = T_{1} \cdot V_{3}^{\gamma-1}$$

$$T_{1} \cdot V_{4}^{\gamma-1} = T_{2} \cdot V_{1}^{\gamma-1}$$

$$\Rightarrow \frac{V_{3}}{V_{4}} = \frac{V_{2}}{V_{1}} \Rightarrow$$

$$\frac{W_{1}}{W_{3}} = \frac{\Delta Q_{T_{2}}}{\Delta Q_{T_{1}}} = -\frac{T_{2}}{T_{1}}$$

$$\frac{\Delta Q_{T_{2}}}{T_{2}} = -\frac{\Delta Q_{T_{1}}}{T_{1}} \Rightarrow$$

$$\frac{\Delta Q_{T_2}}{T_2} = -\frac{\Delta Q_{T_1}}{T_1} \Rightarrow \qquad W = \Delta Q_{T_2} (1 - \frac{T_1}{T_2})$$

$$(1 - \frac{T_1}{T_2}) = \eta \Rightarrow \eta = \frac{\Delta T}{T}$$
Result: Only a part of  $Q_{T_2}$ 

can be inverted to work!

Kelvin(1824-1907)

#### 5.10. Second fundamental law of thermodynamics R. Clausius (1822-1888) :

Not all energy conserving prozesses are possible

# Heat, without work performed, flows always from higher to lower temperature! Clausius introduced the term entropy S. with $dQ = T \cdot dS$ or $dS = \frac{dQ}{T}$ $\Delta S = S_{end} - S_{beginning} = \int_{beginning}^{end} \frac{dQ}{T} \qquad \Delta S_{CARNOT} = 0 : \text{Reversible!}$ because (s.above): $\frac{\Delta Q_{T_2}}{T_2} = -\frac{\Delta Q_{T_1}}{T_1}$ Irreversible prozesses lead to $\Delta S \succ 0$ Clausius: 1. Energy of the world is constant

2. The entropy of the world pursuit to a maximum !'

## 5.11. Entropy and probability (Boltzmann)

Example:

 $N = N_1 + N_2$ 

N particles in I and II

Probability

 $N_1$  in I and  $N_2$  II

e.g.: N=8

One possibility 8 in I 8 posibilties 1 in I, 7 in II



Uniform distribution: i.e: 4 in I 4 in II



The more P, the smaller  $N_1 - N_2$ P at most:  $N_1 = N_2 = \frac{N}{2}$ in general: At  $N = 10^{23}$ All other states are improbable!

Possibilities for realisation P

$$P = \frac{N!}{N_1! \cdot N_2!}$$

Irreversible growth of S leads to growing molecular disorder.

Connection between P and S



 $N_1 = N_2$  in the example above, forms the endpoint of an irreversible development!

# Entropy grows into direction of future, not past, arrow of time!

**5.12. Third fundamental law of thermodynamics** 

The thermodynamical state of equilibrium at absolute point sero is a state of maximal order, which only one realisation process *P*=1 !