

# Introduction to Physics I

**Laws of thermodynamics**

Carnot cycle

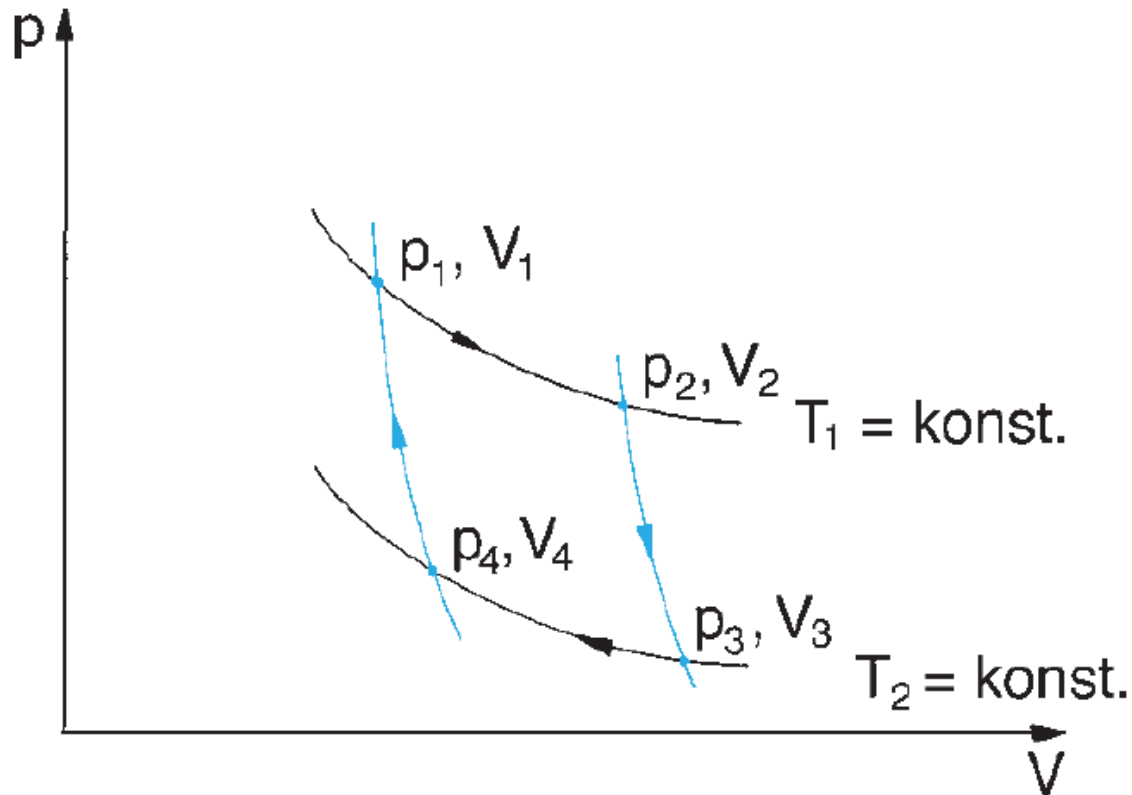
2<sup>nd</sup> law of thermodynamics

energy balance

heat machines

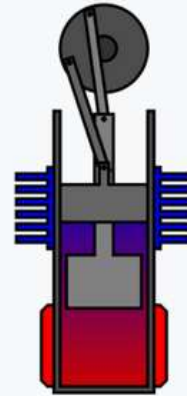
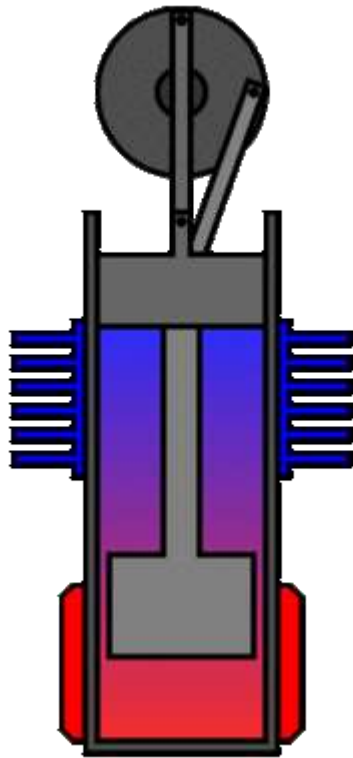
# reversible heat-work transformation

## Carnot cycle

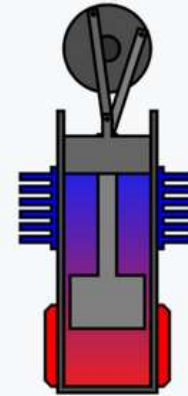


**Abb. 12.1**  $p$ - $V$ -Diagramm des Carnot'schen Kreisprozesses.

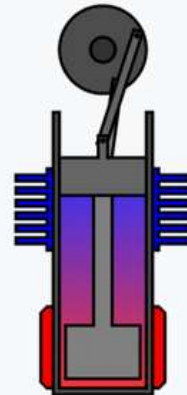
# Stirling engine



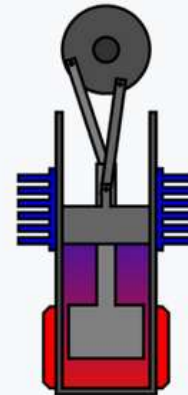
1. Power piston (dark grey) has compressed the gas, the displacer piston (light grey) has moved so that most of the gas is adjacent to the hot heat exchanger.



2. The heated gas increases in pressure and pushes the power piston to the farthest limit of the **power stroke**.

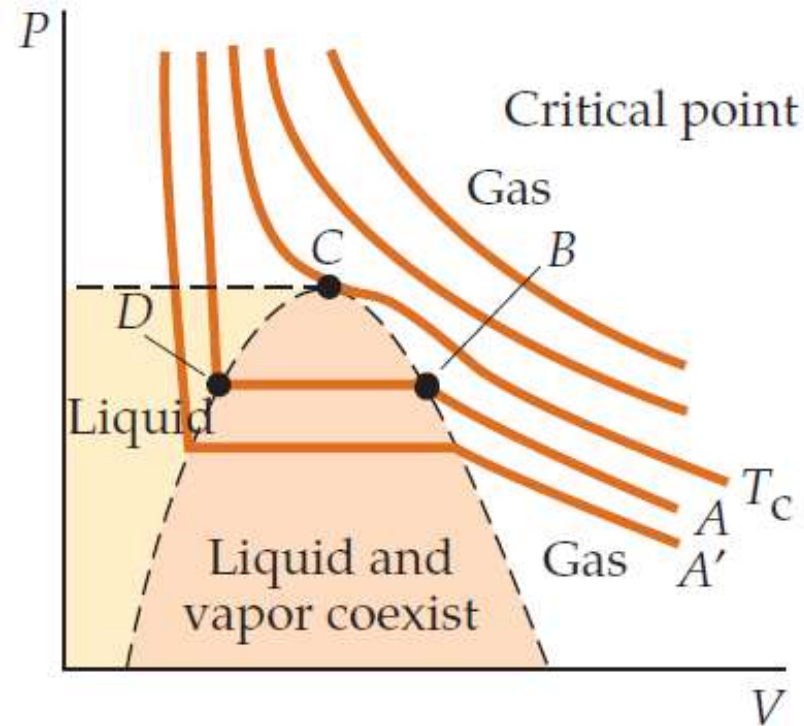
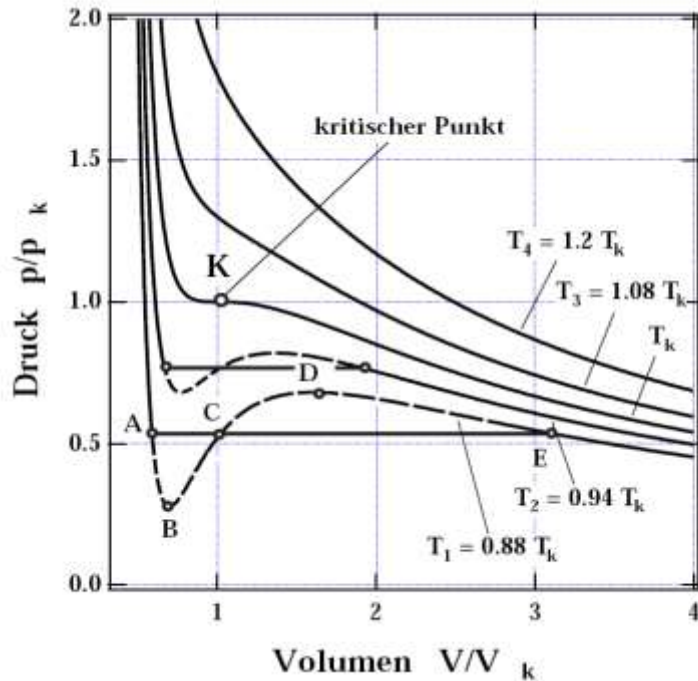


3. The displacer piston now moves, shunting the gas to the cold end of the cylinder.



4. The cooled gas is now compressed by the flywheel momentum. This takes less energy, since its pressure drops when it is cooled.

# real gas law: van der Waals



**FIGURE 20-5** Isotherms on the  $PV$  diagram for a substance. For temperatures above the critical temperature  $T_c$ , the substance remains a gas at all pressures. Except for the region where the liquid and vapor coexist, these curves are described quite well by the van der Waals equation. The pressure for the horizontal portions of the curves in the shaded region is the vapor pressure which is the pressure at which the vapor and liquid are in equilibrium. In the region shaded yellow, to the left of the region shaded pink, the substance is a liquid and is nearly incompressible.

# real gas law - van der Waals equation of state

~~12/11/18~~  
12/11/18

• at high pressure  $P$  or low temperature  $T$ : breakdown of ideal gas law

and  $P \cdot V = n \cdot R \cdot T$  requires corrections

$$\left( P + \frac{a \cdot n^2}{V^2} \right) \cdot (V - b \cdot n) = n \cdot R \cdot T \quad n \text{ moles of gas}$$

van der Waals eq. of state

Corrections because 1) molecules have a finite (non zero) volume  $b$  for one mole of gas

2) force  $F$  between gas molecules:

•  $F$  attracts gas molecule approaching wall container  
( $\rightarrow$  remember how we calculated  $\bar{P}$ )

$F \propto \frac{n}{V}$ , density of molecules pulling back

• nb of molecules hitting container-wall per unit time  $\propto \frac{n}{V}$

hence correction to pressure  $P \propto \left( \frac{n}{V} \right)^2$

constant  $a$ : small for inert gases (Ar, N<sub>2</sub>) (low reactivity)

$\left( \frac{a \cdot n^2}{V^2}, b \cdot n \right)$  small for large  $V$   
 $\rightarrow$  ideal gas law

slide  
phase diag.

• isotherms  shape!  $\rightarrow$   $\exists$  critical point  $T_c$

• v.d Waals eq. describes isotherms outside shaded region where liquid & vapor coexist  $\rightarrow$  2 different states gas & liquid

$\Rightarrow$  gas can condense when  $P \& V \downarrow$

- phase diag PV, PT, PVT
- condensation cloud behind aircraft

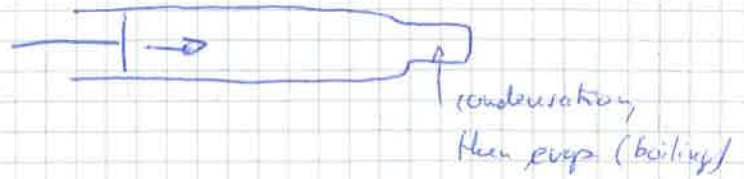
exp c/c

exp real gases: move<sup>u</sup> on phase diagram

i) Druck - Kondensation

trifluoromethan/  
propene

$C_6H_{10}$



ii) CO<sub>2</sub> tubes

careful,  
not down!

- 3 tubes,  $V = \text{const}$  during  $\Delta T$   
different quantities of gas  
middle tube: at critical point

vary  $T$  to "explore" phase diagram

3) Critical opalescence

optical phenomena close to critical point

contains  $V = \text{const}$ ,  $SF_6$  gas  $\rightarrow$  critical temperature  $T_c$

1908: Leon von Soret-Schulzki's observations

1910: A. Einstein quantitative treatment of density fluctuations

Rayleigh scattering of light due to density fluctuations!

a)  $T \uparrow$ , full evaporation; limit gas-liquid disappears

b)  $T \downarrow$ , start condensation: no transparency!

density fluctuations  $\rightarrow$  light scattering

Note: opalescence remains when large fluctuations are visible

$\rightarrow$  small scale fluctuations (and) still present

# the laws of thermodynamics

o reminder: 1st law of thermodynamics

$U = E_{int}$   
 internal energy of gas (kinetic energy, energy stored in bonds between atoms in molecule, electrical energy - Phys II)

$$dU = dQ_{in} + dW_{on}$$

change in internal energy of gas      heat absorbed by system      work done on system

conservation of energy

o total energy conserved (1st law): energy transformed (e.g. work in temperature)

consider this experiment: block/table system



friction work on block, (motion) friction,  $U_{system}$  (internal energy)

- a) thermal equil.
- b) heating of system
- c) stop motion, cooling, back to equil.

1st law: initial & final state identical

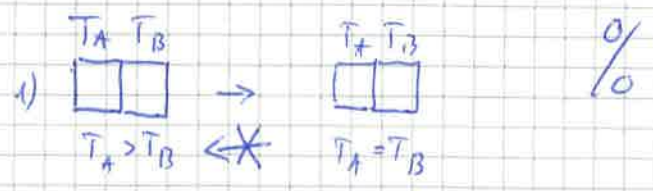
$\Rightarrow$  energy  $\Delta Q$  transferred to environment = work done on system

reverse the process of setting in movement the block on the table to cool off the system (convert int. energy/heat into work) never takes place!

(would be ok with 1st law, though)

$\Rightarrow$  reversible & irreversible processes

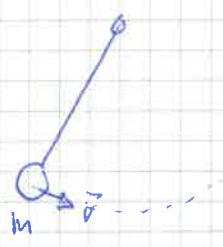
examples (irreversible)



a process whose only net result is to absorb heat from a cold reservoir and release the same amount of heat to a hot reservoir is impossible

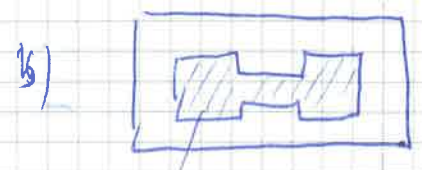
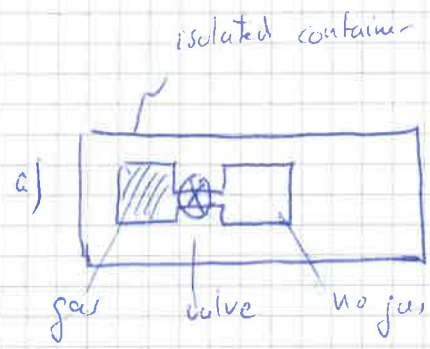
2nd law of thermodynamics (Clausius formulation)

example  
(reversible)



pendulum (no friction)  
reversible transformation  
of kinetic energy in potential  
energy

example  
(irreversible)



irreversible expansion  
of gas in full volume



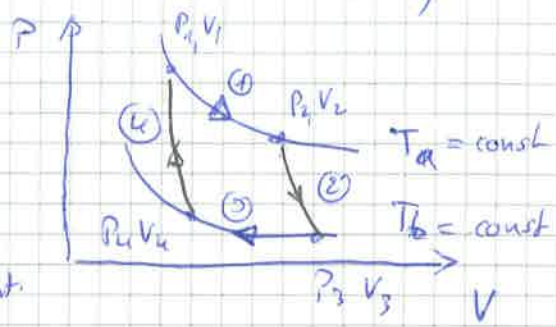
a particular, reversible process of heat transforming in work

Carnot cycle or Carnot engine

ideal (max efficiency) model for heat engine, (transforming heat in mechanical work)

(slide)

PV graph



2 isotherms (1), (3)  
2 adiabatic (2), (4) processes

(1) isothermal expansion of gas

$T = \text{const} \Rightarrow \Delta U = 0$   
no increase of int. energy

$-\Delta W_1 = \Delta Q_1$   
work produced by system (- sign)      heat exchanged with environment (reservoir)

$$-\Delta W_1 = \int_1^2 P \cdot dV = \int_1^2 nRT_a \cdot \frac{dV}{V} = nRT_a \cdot \ln\left(\frac{V_2}{V_1}\right)$$

$P = \frac{n \cdot R \cdot T}{V}$

(2) adiabatic expansion of gas

$\Delta Q = 0$ ,       $-\Delta W_2 = \Delta U = \Delta E_{int} = C_v(T_a - T_b)$

.. heat capacity  $C_v$

(3) isothermal compression  $T = \text{const}$

$\Delta W_3 = \int_3^4 P \cdot dV = n \cdot R \cdot T_b \cdot \ln\left(\frac{V_4}{V_3}\right) = -\Delta Q_3$   
work on gas

(4) adiabatic compression  $\Delta Q = 0$

$\Delta W_4 = C_v \cdot (T_a - T_b)$ ,       $\Delta W_4 = -\Delta W_2$

Total work produced by gas,  $\Delta W = \sum \Delta W_i$

$$-\Delta W = -\Delta W_1 + \Delta W_2 + \Delta W_3 + \Delta W_4$$

$$= nRT_a \cdot \ln\left(\frac{V_2}{V_1}\right) + nRT_b \cdot \ln\left(\frac{V_4}{V_3}\right)$$

for an adiabatic process:  $T \cdot V^{\gamma-1} = \text{const}$  ( $\gamma = \frac{C_p}{C_v}$ )

thus  $T_a \cdot V_2^{\gamma-1} = T_b \cdot V_3^{\gamma-1}$

and  $T_b \cdot V_4^{\gamma-1} = T_a \cdot V_1^{\gamma-1}$

divide:  $\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1}$

and  $\frac{V_2}{V_1} = \frac{V_3}{V_4}$

For the work:

$$-\Delta W = n \cdot R \cdot \left( T_a \ln \frac{V_2}{V_1} + T_b \ln \frac{V_4}{V_3} \right) = n \cdot R \cdot (T_a - T_b) \cdot \ln \frac{V_2}{V_1}$$

$\underbrace{\ln \frac{V_4}{V_3}}_{-\ln \frac{V_2}{V_1}}$

$\parallel -\Delta W = n \cdot R \cdot (T_a - T_b) \cdot \ln \frac{V_2}{V_1}$

total work produced during Carnot cycle

During this cycle energy is exchanged with the warm  $(T_a)$  and cold  $(T_b)$  reservoirs:

$\Delta Q_1$  is taken from hot reservoir  $(T_a)$

$\Delta Q_3$  is injected in cold reservoir  $(T_b)$

efficiency of cycle

$$\eta = \frac{-\Delta W}{\Delta Q_1} = \frac{\text{work produced by system}}{\text{heat taken from hot reservoir}}$$

$$\eta = \frac{nR(T_a - T_b) \cdot \ln(V_2/V_1)}{nR T_a \ln(V_2/V_1)} = \frac{T_a - T_b}{T_a}$$

$\parallel \eta = 1 - \frac{T_b}{T_a}$

max efficiency of a heat engine/machine ( $\Delta Q_3$  never  $\neq 0$ !)

## 2nd law of thermodynamics:

L25 4

a heat engine working in a cycle cannot produce only the effect of absorbing heat from a single reservoir and performing an equivalent amount of work

(possible for a noncyclic process)

• To address the reversibility question of a thermodynamic process, we introduce a new quantity, the entropy  $S$  (measure for the disorder of a system)

• heat exchange during Carnot cycle (reversible process):

heat ~~absorbed~~ <sup>taken</sup> from <sup>hot</sup> reservoir ( $T_a$ ):  $\Delta Q_1 = nRT_a \ln \frac{V_2}{V_1}$   
heat released in cold reservoir ( $T_b$ ):  $-\Delta Q_3 = nRT_b \ln \frac{V_4}{V_3}$

$$\frac{\Delta Q_1}{T} = n \cdot R \cdot \ln \frac{V_2}{V_1}$$

$$-\frac{\Delta Q_3}{T_b} = n \cdot R \ln \frac{V_4}{V_3} = -n \cdot R \ln \frac{V_2}{V_1} = \frac{\Delta Q_1}{T_a} \quad !$$

$\frac{V_2}{V_1} = \frac{V_3}{V_4}$

$\Rightarrow$  over a reversible cycle  $\left(\frac{\Delta Q}{T}\right)_{\text{total}}$  is conserved

def: change of entropy  $dS$  of a system as it goes from one state to another in a reversible process

$$\parallel dS = \frac{dQ_{\text{rev}}}{T}$$

$dQ_{\text{rev}}$ : heat absorbed by the system during a reversible process

Cyclic process from state 1 to state 2:

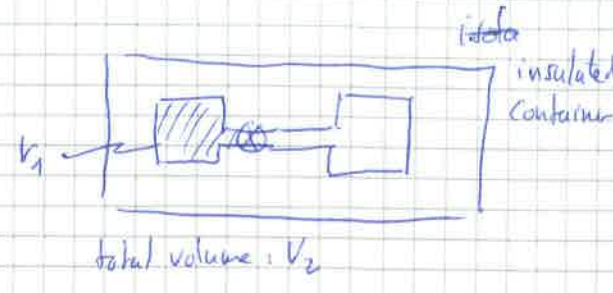
$$\Delta S = \int_1^2 \frac{dQ}{T} + \int_2^1 \frac{dQ}{T} = 0 \quad [S] = J/K$$

for a reversible process  $\left(\Delta S = \oint \frac{dQ}{T} = 0\right)$   
(entropy is a state variable)

reversible / irreversible

The entropy change of a closed system undergoing state changes during a reversible process is zero ( $\Delta S = 0$ ), while it increases for an irreversible process ( $\Delta S > 0$ )

example: a) free expansion of an ideal gas  
 not reversible ( $\Delta Q = 0$ ,  $\Delta W = 0$ )  
 $\Rightarrow U = \text{const}$ )  
 $\Delta S = \int \frac{dQ}{T} \dots ?$   
 cannot be used



b) consider isothermal expansion, reversible process,  $T_2 = T_1$

1st law  $dU = dQ_{rev} + dW_{on}$   
 $C_v \cdot dT = dQ_{rev} - P \cdot dV$   
 $P = \frac{nRT}{V}$   
 $C_v \frac{dT}{T} = \frac{dQ_{rev}}{T} - n \cdot R \cdot \frac{dV}{V}$

and  $dS = \frac{dQ_{rev}}{T} = C_v \frac{dT}{T} + nR \frac{dV}{V}$

Ass  $\rightarrow C_v = \text{const}$  ( $\frac{dQ_{rev}}{T}$  is the differential of the function S)

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dQ_{rev}}{T} = C_v \cdot \ln \frac{T_2}{T_1} + n \cdot R \cdot \ln \frac{V_2}{V_1}$$

entropy change of an ideal gas going from state 1 ( $T_1, V_1$ ) to state 2 ( $T_2, V_2$ )

for  $T_2 = T_1$ :  $\Delta S = nR \cdot \ln \frac{V_2}{V_1}$

c) back to free expansion (drawing above)

$\Delta Q = 0$  so  $\Delta S = 0 \dots ?$  no, because  $\Delta S = \int \frac{dQ_{rev}}{T}$  cannot be used (reversible)

but initial & final states of gas ( $V_1 \rightarrow V_2$ ) are the same for both processes!

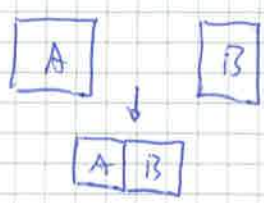
entropy property | entropy change  $\Delta S$  for any process depends only on the initial and final states of the system

here for the isothermal or free expansion, we therefore have

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

and  $\Delta S > 0$  as  $V_2 > V_1$ , the entropy has increased

example: irreversible process: equilibration of T, 2 identical blocks of metal (iron)



$m_A = m_B = 1 \text{ kg}$   
 $c = 452 \text{ J/kgK}$  specific heat  
 $T_A = 200 \text{ K}$   
 $T_B = 400 \text{ K}$

1st law of thermo:  $\Delta Q_A + \Delta Q_B = 0$  (energy conservation) A warms up, B cools down

$$m \cdot c \cdot \Delta T_A + m \cdot c \cdot \Delta T_B = 0$$

$\Delta T_A = T_{eq} - T_A$ ,  $T_{eq}$ : temp. after equilibration  
 $\Delta T_B = T_{eq} - T_B$

$$T_{eq} - T_A = -(T_{eq} - T_B)$$

$$T_{eq} = \frac{T_A + T_B}{2} = 300 \text{ K}$$

Consider a reversible cooling of metal B to  $T_{eq}$  and reversible warming of metal A to  $T_{eq}$  (e.g. using a waterbath) & calculate  $\Delta S$ : (same initial & final states)

$$\Delta S_B = \frac{\Delta Q_B}{T} = m \cdot c \cdot \int_{T_B}^{T_{eq}} \frac{dT}{T} = m \cdot c \cdot \ln \frac{T_{eq}}{T_B} < 0$$

$\uparrow$   
 $dQ = m \cdot c \cdot dT$

$T_{eq} < T_B$

and  $\Delta S_A = m \cdot c \cdot \ln \frac{T_{eq}}{T_A} > 0$  as  $T_{eq} > T_A$

$$\Delta S_{total} = m \cdot c \cdot \left( \ln \frac{T_{eq}}{T_A} + \ln \frac{T_{eq}}{T_B} \right)$$

$$\approx 1 \text{ kg} \cdot 452 \frac{\text{J}}{\text{kgK}} \cdot (0.405 - 0.288)$$

$\Delta S_{total} \approx 53 \text{ J/K} > 0$  increase in entropy

# entropy and probability

• entropy: measure of the disorder of a system, related to probability

a state of high order has relatively low probability,  
 " " " low order, " " " high probability.

i.e.: during an irreversible process, a system moves to a state of low prob. to a state of higher prob.; (increase of disorder)

• free expansion of gas  $V_1$  to  $V_2 = 2V_1$  (cf before):  $V_L = V_R$ , total  $2V_L$   
 $V_L = V_R$

$$\Delta S = n \cdot R \cdot \ln \frac{V_2}{V_1} = n \cdot R \cdot \ln 2$$

why irreversible...? why cannot the gas not contract back in  $V_1$ ?  
 it is highly improbable

example: gas with  $N=10$  molecules, prob. to have 10 molecules in  $V_L = ?$

1 molecule :  $p = 1/2$

2 " " :  $p = \frac{1}{2} \cdot \frac{1}{2}$

10 " " :  $p = \left(\frac{1}{2}\right)^{10} = \frac{1}{1024}$

i.e. once every 1024 sec = 17 min

if we look at the gas once every second

• probability of a gas spontaneously contracting from volume  $V_1$  to volume  $V_2 < V_1$ :

probability:  $P_N = \left(\frac{V_2}{V_1}\right)^N$ , prob. to find  $N$  molecules in smaller volume  $V_2$

$$\ln p_N = N \cdot \ln \frac{V_2}{V_1} = \underset{\substack{\uparrow \\ \text{nb. mole}}}{n \cdot N_A} \cdot \ln \frac{V_2}{V_1}$$

entropy change  $\Delta S = n \cdot R \cdot \ln \frac{V_2}{V_1} = n \cdot N_A \cdot k_B \cdot \ln \frac{V_2}{V_1}$

hence

$$\Delta S = k_B \cdot \ln p_N$$

entropy can be related to a probability

that means: the spontaneous contraction of a gas  
is not, strictly speaking, impossible. it has  
a very low probability.

(in a thermodynamic description)

Note: thermodynamics applies to macroscopic systems,  
considering a large nb of molecules

- pressure of gas with 10 molecules ...? not well defined!

-  $N = 50$  ,  $P_{\text{all}} = \left(\frac{1}{2}\right)^{50} \approx 10^{-15}$

looking at the gas once per second, we can expect to see all 50  
molecules in  $V_{\text{left}}$  once every  $10^{15}$  seconds  $\approx$  30 million years...

for 1 mole =  $6 \cdot 10^{23}$  ... practically ... zero