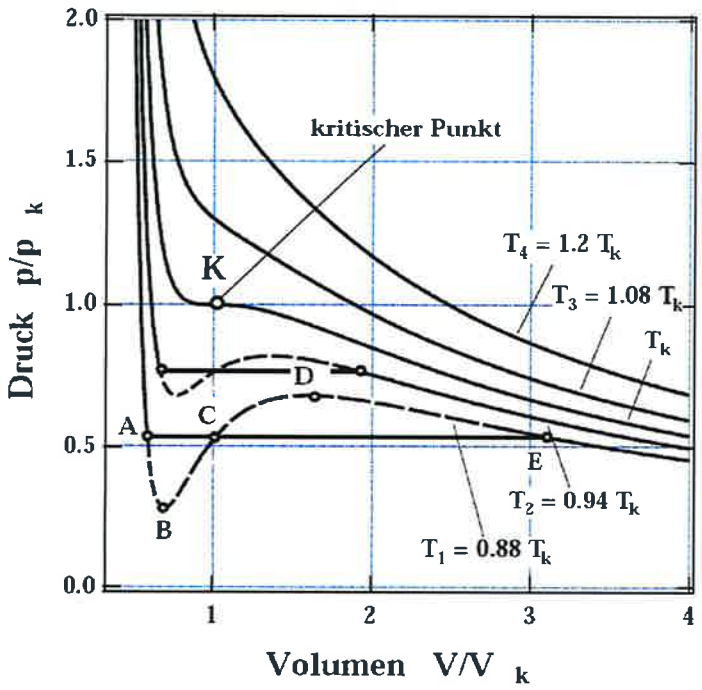
real gas law: van der Waals



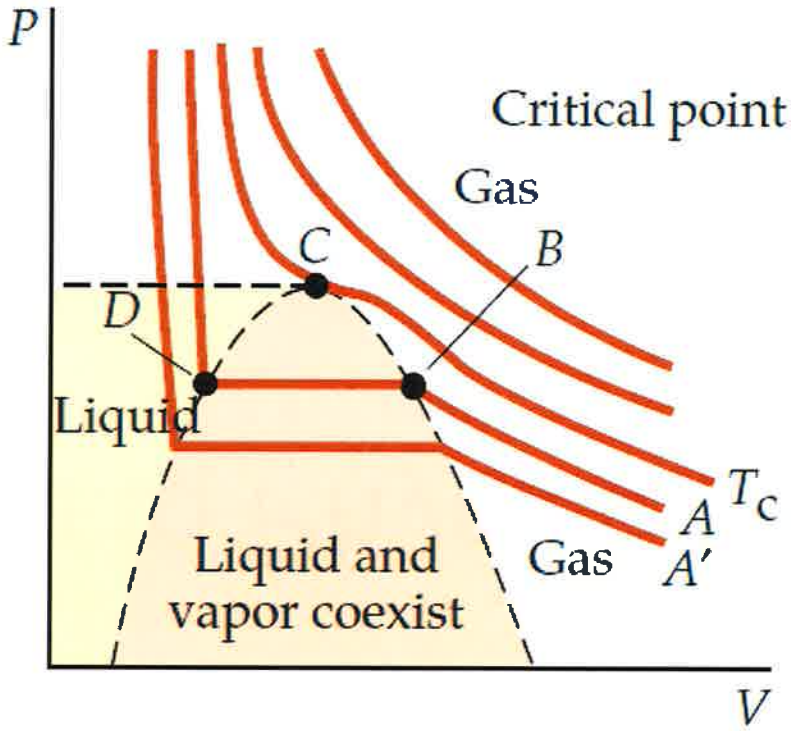
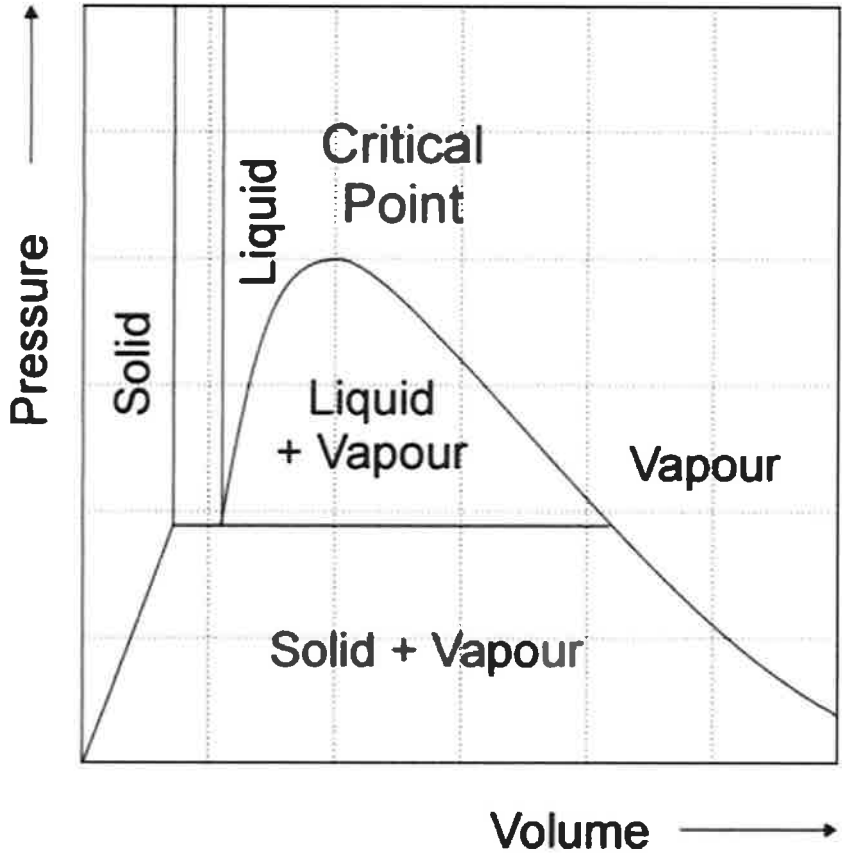


FIGURE 20-5 Isotherms on the *PV* diagram for a substance. For temperatures above the critical temperature T_c, the substance remains a gas at all pressures. Except for the region where the liquid and vapor coexist, these curves are described quite well by the van der Waals equation. The pressure for 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.

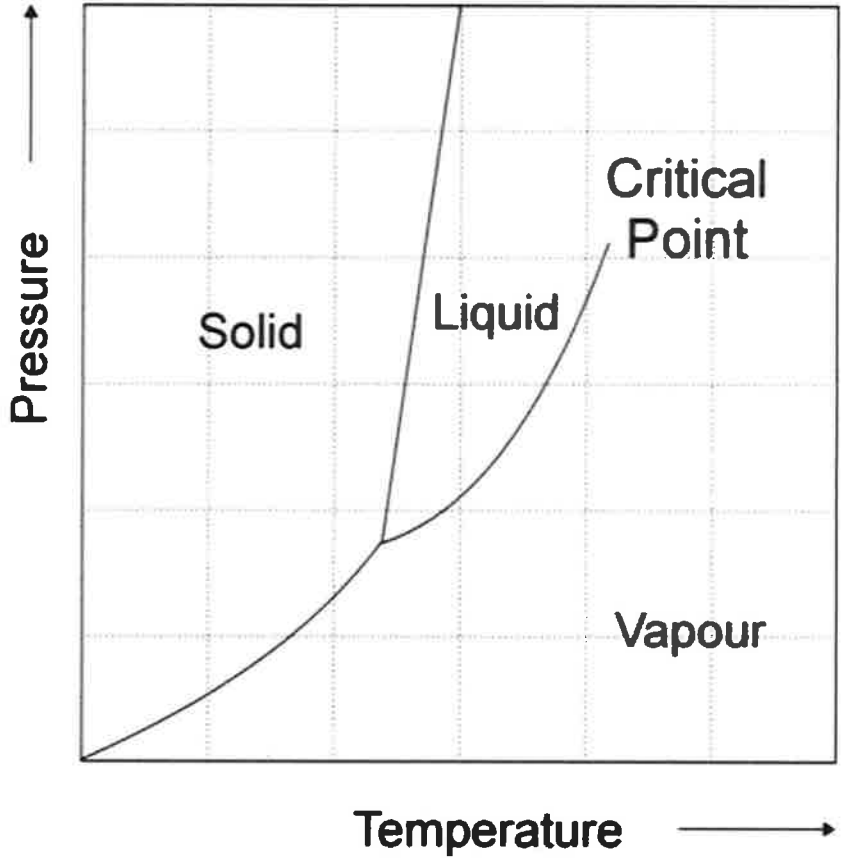
..pler

real gas law: van der Waals

PV diagram



PT diagram



real gas law: van der Waals

Cloud forming behind an aircraft as it breaks the sound barrier. As the aircraft moves through the air, an area of low pressure forms behind it. When the pressure of this air parcel falls below the vapor pressure of gaseous water, the water in the air condenses to form the cloud. Different atmospheric conditions cause the phenomenon to occur at different aircraft speeds. *(U.S. Department of Defense/Photo Researchers, Inc.)*

reversible heat-work transformation
Carnot cycle

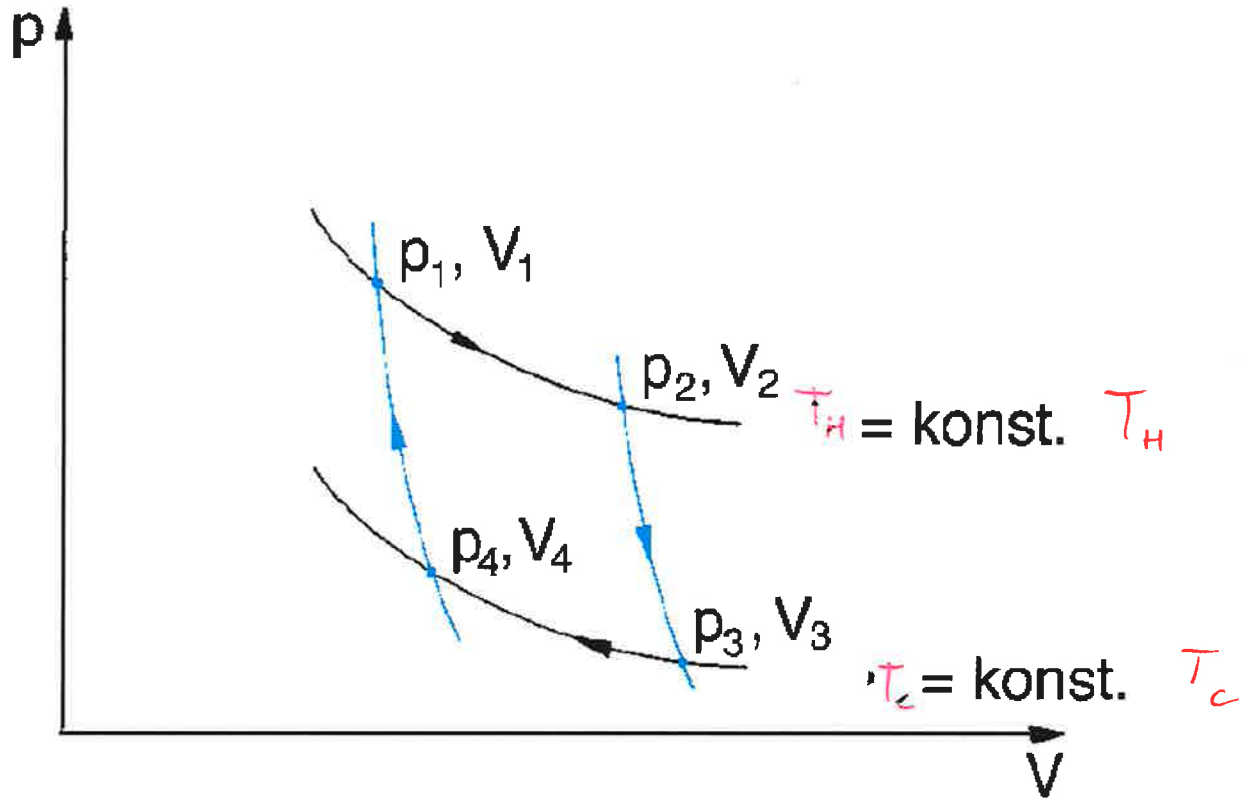


Abb. 12.1 *p-V*-Diagramm des Carnot'schen Kreisprozesses.

L26

real gas law - van der Waals equation of state

- at high pressure P or low temperature T breakdown of ideal gas law

and $PV = nRT$ requires corrections

$$\left(P + \frac{a \cdot n^2}{V^2}\right) \cdot \left(V - b\,n\right) = n \cdot R \cdot T$$

n mole 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 (→ remember how we calculated P)

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

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

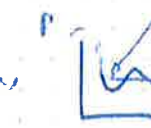
Hence correction to pressure P $\propto \left(\frac{n}{V}\right)^2$

Constant a : small for inert gases (Ar, N_2) (low reactivity)

($\frac{a n^2}{V^2}$, $b\,n$ small for large V

→ ideal gas law)

slide phase diag.

- isotherms 

shape ! → ∃ critical point T_c

- Vd Waal, eq describes isotherms outside shaded region where liquid & vapor coexist → 2 different states gas liquid

=> gas can condensate when P & V ↘

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

exp 9/c

the laws of thermodynamics

- reminder: 1st law of thermodynamics

$$\Delta E_{int} = Q_{in} + W_{on}$$

or

$$\Delta E_{int} = Q_{in} - W_{by}$$

ΔE_{int}: change in internal energy of gas

Q_{in}: heat absorbed by system

W_{on}: work done on system

W_{by}: work by system

conservation of energy

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

- total energy conserved (1st law) energy transformed (eg. work in temperature)

consider the experiment: block/table system

a) thermal equil

b) heating of system: friction → work on block (motion) → U_{system} ↗ (int energy)

c) stop motion, cooling back to equil

1st law: initial & final state identical

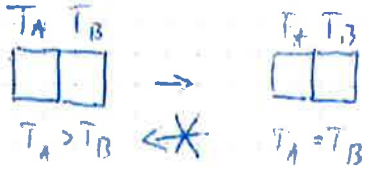
⇒ energy ΔQ transferred to environment = work done on system

the reverse 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)

⇒ ∃ reversible & irreversible processes

example: (irreversible)

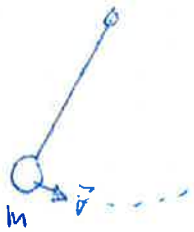


0/0

‖ 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

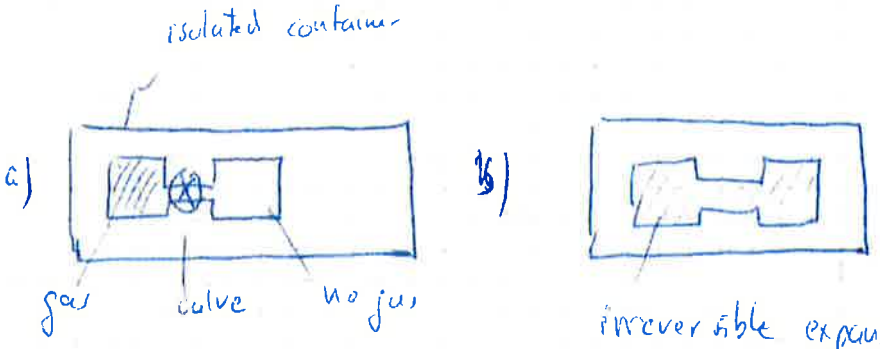
2nd law of thermodynamics (Clausius formulation)

example
(reversible)



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

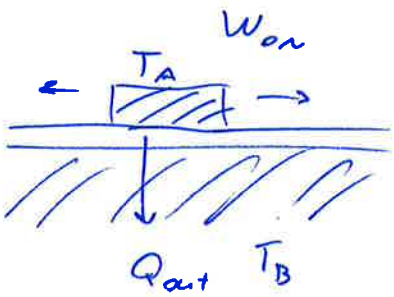
example
(irreversible)



irreversible expansion
of gas in full volume

$$\Delta E_{int} = Q_{in} + W_{on}$$

$$\Delta E_{int} = Q_{in} - W_{by}$$



① $T_A = T_B$, Equil.

② W_{on} , no time to exchange heat

↳ $Q_{out} = Q_{in} = 0$

$\therefore \Delta E_{int_2} = W_{on} \rightarrow T_A > T_B$

↗ out of Equil.

③ After time, goes back to Equil.

$\rightarrow T_A = T_B$, $\Delta E_{int} = 0$

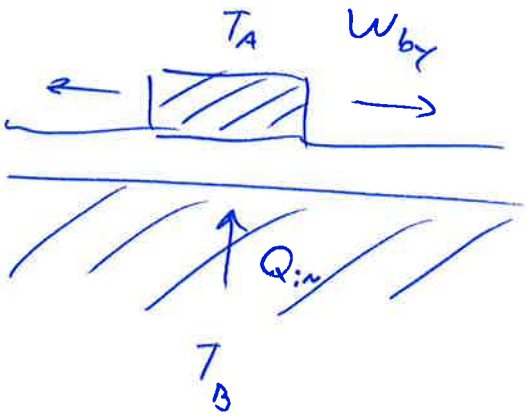
$\Delta E_{int_3} = -W_{on}$

$Q_{in} = -W_{on}$

$Q_{out} = W_{on}$

Work to Heat ✓

Opposite Process:



① $T_A = T_B$

② Heat flows into system

↳ $\Delta E_{int\,2} = Q_{in}$

↳ $T_A > T_B$

↗ out of Equil

③ Heat transforms into work as system equilibrates

$T_A = T_B$, $\Delta E_{int} = 0$

$\Delta E_{int\,3} = -Q_{in}$

$W_{on} = -Q_{in}$

$W_{by} = Q_{in}$

Heat to Work ✗

↳ impossible to convert heat entirely into work!

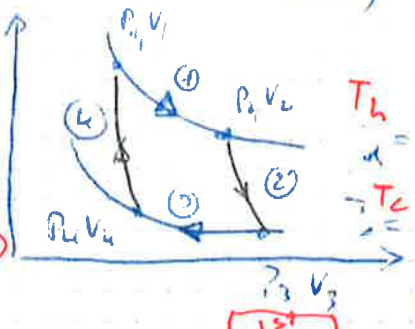
a particular reversible process of heat transforming in work

Carnot' cycle or Carnot engine

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

slide

PV graph



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

(1) isothermal expansion of gas

T = const → $T = T_h$; $\Delta E_{int} = 0$ no increase of int. energy

$W_{by1} = Q_{in1}$

work produced by system (+ sign) ; heat exchanged with environment (reservoir)

1st Law

$\Delta E_{int} = Q_{in} + W_{on}$

$\Delta E_{int} = Q_{in} - W_{by}$

$$W_{by1} = \int_1^2 P\,dV = \int_1^2 nRT_h \frac{dV}{V} = nRT_h \ln\left(\frac{V_2}{V_1}\right) = Q_{in1}$$

positive (area under curve)

$P = \frac{nRT}{V}$

(2) adiabatic expansion of gas

$-W_{by2} = \Delta E_{int2}$

$Q_{in2} = 0$

heat capacity C_v

$-W_{by2} = C_v (T_h - T_c)$

$W_{by2} = -C_v (T_h - T_c)$

(3) isothermal compression T = const, $T = T_c$

$$W_{by3} = \int_3^4 P\,dV = nRT_c \ln\left(\frac{V_4}{V_3}\right) = \dots = Q_{in3}$$

negative (area under curve)

(4) adiabatic compression $Q_{in4} = 0$

$-W_{by4} = \Delta E_{int4}$

$-W_{by4} = C_v (T_c - T_h)$

$W_{by4} = C_v (T_h - T_c)$

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

$W_{by,total} = \sum_i W_{by\,i}$

$$W_{by,total} = nRT_h \ln\left(\frac{V_2}{V_1}\right) + nRT_c \ln\left(\frac{V_4}{V_3}\right) + W_{by2} + W_{by4}$$

for an adiabatic process: $T \cdot V^{\gamma-1} = \text{const}$ / $\gamma = \frac{c_p}{c_v}$ /

thus $T_h V_2^{\gamma-1} = T_c V_3^{\gamma-1}$

and $T_h V_4^{\gamma-1} = T_c V_1^{\gamma-1}$

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:

$$W_{by,total} = n \cdot R \cdot \left(T_h \ln \frac{V_2}{V_1} + T_c \ln \frac{V_4}{V_3} \right) = n R (T_h - T_c) \cdot \ln \frac{V_2}{V_1}$$

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

$$\| W_{by,total} = n \cdot R \cdot (T_h - T_c) \cdot \ln \frac{V_2}{V_1}$$

total work produced during Carnot cycle

During this cycle energy is exchanged with the warm (T_h) and cold (T_c) reservoirs:

$Q_{in1} > 0$ is taken from hot reservoir (T_h)

$Q_{in3} < 0$ is injected in cold reservoir (T_c)

efficiency of cycle

$$\eta = \frac{W_{by,total}}{Q_{in1}} = \frac{\text{work produced by system}}{\text{heat taken from hot reservoir}}$$

$$\eta = \frac{n R (T_h - T_c) \cdot \ln(V_2/V_1)}{n R T_h \ln(V_2/V_1)} = \dots$$

$$\| \eta = 1 - \frac{T_c}{T_h}$$

max efficiency of a heat engine / machine

$T_c > T_h$ ( )

2nd law of thermodynamics:

> 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 taken from hot reservoir (T_h) $\quad Q_{in1} = nRT_h \ln V_2/V_1$

heat released in cold reservoir (T_c) $\quad Q_{in3} = nRT_c \cdot \ln V_4/V_3$

$$\frac{Q_{in1}}{T_h} = nR \ln \frac{V_2}{V_1}$$

$$\frac{Q_{in3}}{T_c} = nR \ln \frac{V_4}{V_3} = -nR \ln \frac{V_2}{V_1} = -\frac{Q_{in1}}{T_h} \quad !$$

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

$$\Delta\left(\frac{Q_{in}}{T}\right) = 0$$

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

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

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

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

Cyclic process from state 1 to state 2:

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

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

(entropy is a state variable)

reversible / irreversible

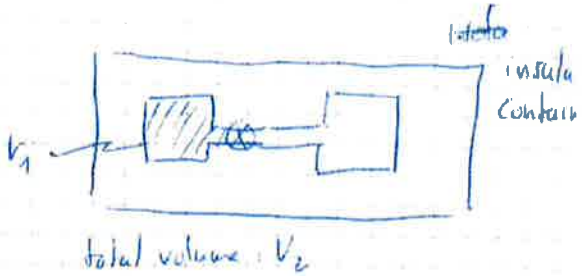
The entropy change of a closed system undergoing state changes during a reversible process is zero ($\Delta S = 0$), while it increases for an irreversible process ($\Delta S > 0$)

example a) free expansion of an ideal gas (not reversible)

($\Delta Q = 0$, $\Delta W = 0$ $\Rightarrow U = \text{const.}$)

$$\Delta S = \int \frac{dQ}{T} \quad ?$$

cannot be used; $= \frac{Q}{T_1}$?



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

1st law $\quad dU = dQ_{rev} + dW_{on}$

$$C_V \cdot dT = dQ_{rev} - p \cdot dV = dQ_{rev} - nRT \frac{dV}{V}$$

($p = \frac{nRT}{V}$)

$$C_V \frac{dT}{T} = \frac{dQ_{rev}}{T} - nR \frac{dV}{V}$$

and

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

Assume $C_V = \text{const.}$ ($\frac{dQ_{rev}}{T}$ is the differential of the function S)

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dQ_{rev}}{T} = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

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

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

c) back to free expansion (following above)

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

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

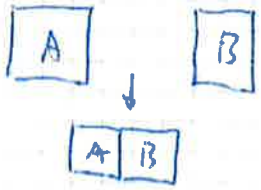
entropy property | entropy change ΔS for any process depend only on the initial and final states of the system

here for the isothermal or free expansion, we therefore have

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

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)



$m_A = m_B = 1\,kg$

$c = 452\ J/kg\,K$ specific heat

$T_A = 200\,K$

$T_B = 400\,K$

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

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

$\Delta T_A = T_{eq} - T_A$, T_{eq} : temp. of equilibrium

$\Delta T_B = T_{eq} - T_B$

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

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

Consider a reversible cooling of metal B to T_{eq} and reversible warming of metal A to T_{eq} (e.g. using a water bath) & calculate ΔS. (same initial & final states!)

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

$\uparrow$ $dQ = mc\,dT$

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

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

$$\equiv 1\,kg\ 452 \frac{J}{kg\,K} (0.405 - 0.288)$$

$$\| \Delta S_{tot} \simeq 53\ J/K > 0$$ 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 $V_2 = V_1$ (of before): V_L V_R, total $2V_L$, $V_L = V_R$

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

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

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

i.e. once every 1024 sec = 17 min
if we look at the gas every second once

- probability, if 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

$$\ln p_N = N \ln \frac{V_2}{V_1} = n N_A \ln \frac{V_2}{V_1}$$

(n: mole)

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

hence

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

entropy can be related to 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, containing a large nb of molecules

- pressure of gas with 10 molecules ? not well defined!
- $N = 50$, $P_N = \left(\frac{1}{2}\right)^{50} \approx 10^{-15}$

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

for 1 mole $\sim 6\,10^{23}$ ..... practically zero