

real gas law - van der Waals equation of state

~~12/11/18~~
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• 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_2)
(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

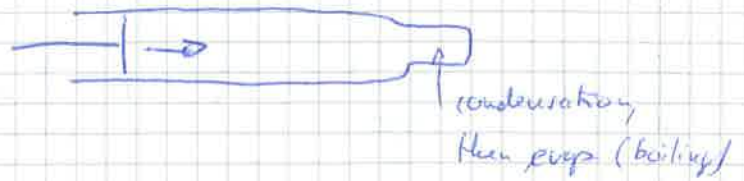
exp $\frac{1}{c}$

exp real gases: move^u on phase diagram

i) Druck - condensation

two bubbles /
propagates

C_6H_{10}



ii) CO_2 tubes

careful,
not down!

- 3 tubes, $V = \text{const}$ during ΔT
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

1902: Russian von Smoluchowski's observation

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 fluct. are visible

\rightarrow small scale fluct. (and) still present

the laws of thermodynamics

o reminder: 1st law of thermodynamics

$$\Delta U = dQ_{in} + dW_{on}$$

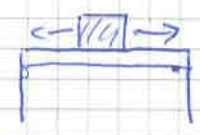
$U = E_{int}$
 internal energy of gas (kinetic energy, energy stored in bonds between atoms in molecule, electrical energy - Phys II)

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

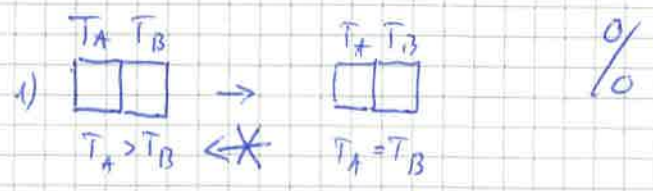
⇒ energy ΔQ transferred to environment = work done on system

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)

⇒ ∃ reversible & irreversible processes

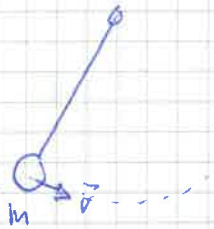
examples (irreversible)



|| 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

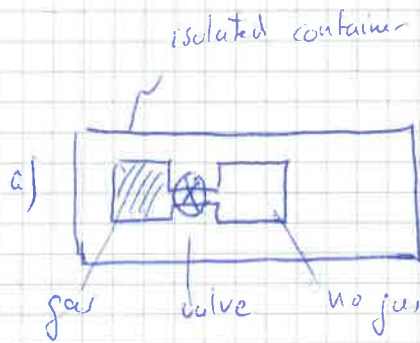
2nd law of thermodynamics (Clausius formulation)

example
(reversible)

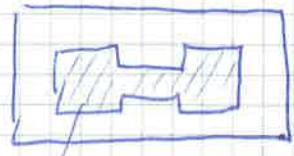


pendulum (no friction)
reversible transformation
of kinetic energy in potential
energy

example
(irreversible)



b)



irreversible expansion
of gas in full volume

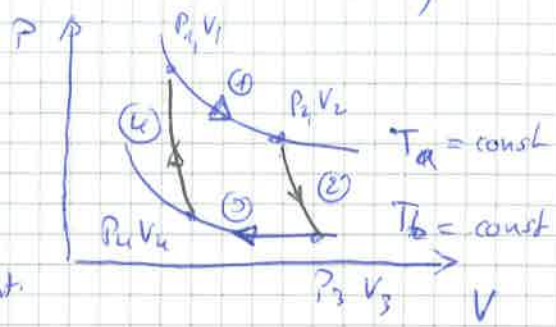
a particular, reversible process of heat transforming in work

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:

- ΔQ_1 is taken from hot reservoir (T_a)
- ΔQ_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 ($\Delta Q_3 \text{ never } \neq 0!$)

2nd law of thermodynamics:

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

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

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

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

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

Cyclic process from state 1 to state 2:

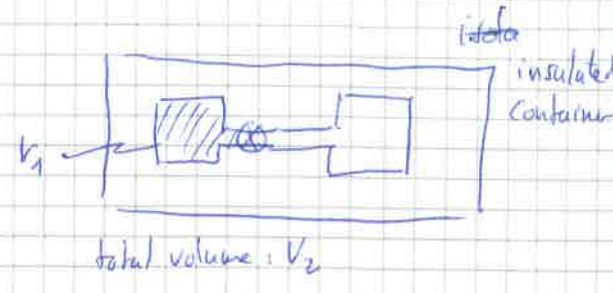
$$\Delta S = \int_1^2 \frac{dQ}{T} + \int_2^1 \frac{dQ}{T} = 0 \quad [S] = J/K$$

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

and $dS = \frac{dQ_{rev}}{T} = C_v \frac{dT}{T} + nR \frac{dV}{V}$
 And $\rightarrow C_v = \text{const}$ ($\frac{dQ_{rev}}{T}$ 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!

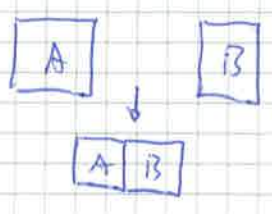
entropy property | entropy change ΔS for any process depends only on the initial and final states of the system

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

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

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

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

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

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

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 ΔS : (same initial & final states)

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

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

$T_{eq} < T_B$

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

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

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


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

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 $2V_L$


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

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_{left} once every 10^{15} seconds \approx 30 million years...

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