

EQUATION OF STATE

In general, a relation between three thermodynamic properties, typically P, V, T .

Ideal gas: idealization where we neglect interactions among molecules (except for their role in establishing equilibrium).

$$PV = N k_B T$$

pressure volume # of molecules temperature in kelvins

Boltzmann's constant
 $k_B \approx 1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$

Alternative form of the Equation of State (EoS) :

$$N = \frac{M}{m}$$

total mass

mass of a molecule

$$V = \frac{M}{\rho} = Mv$$

density

specific volume
(= volume per unit mass)

$$PV = Nk_B T \Rightarrow P \cancel{M} v = \frac{M}{m} k_B T$$

constant characteristic of given gas
gas constant R

$$P = \rho R T \Leftrightarrow P v = R T$$

EXAMPLE : air under standard conditions

$$P = 100 \text{ kPa}$$

$$T = 273.15 \text{ K}$$

$$R \approx 287 \text{ J/kg}\cdot\text{K}$$

$$\left. \begin{array}{l} P = 100 \text{ kPa} \\ T = 273.15 \text{ K} \\ R \approx 287 \text{ J/kg}\cdot\text{K} \end{array} \right\} \rightarrow \rho = \frac{P}{RT} \approx \underline{\underline{1.28 \text{ kg/m}^3}}$$

INTERNAL ENERGY

For ideal gases, all internal energy is stored in the motion of the individual molecules : translational motion, rotations, vibrations.

Important consequence : average internal energy per molecule only depends on temperature, not volume (or density).

$$U(V, T) = M u(T)$$

↑
specific
internal energy

EXAMPLE : monoatomic gases (He, Ne, Ar, ...)

only translational kinetic energy :

$$U = \frac{3}{2} N k_B T = \frac{3}{2} \frac{M}{m} k_B T$$

⇓

$$u(T) = \frac{3}{2} \frac{k_B}{m} T \quad \Rightarrow \quad u(T) = \frac{3}{2} RT$$

CONSTANT-VOLUME SPECIFIC HEAT

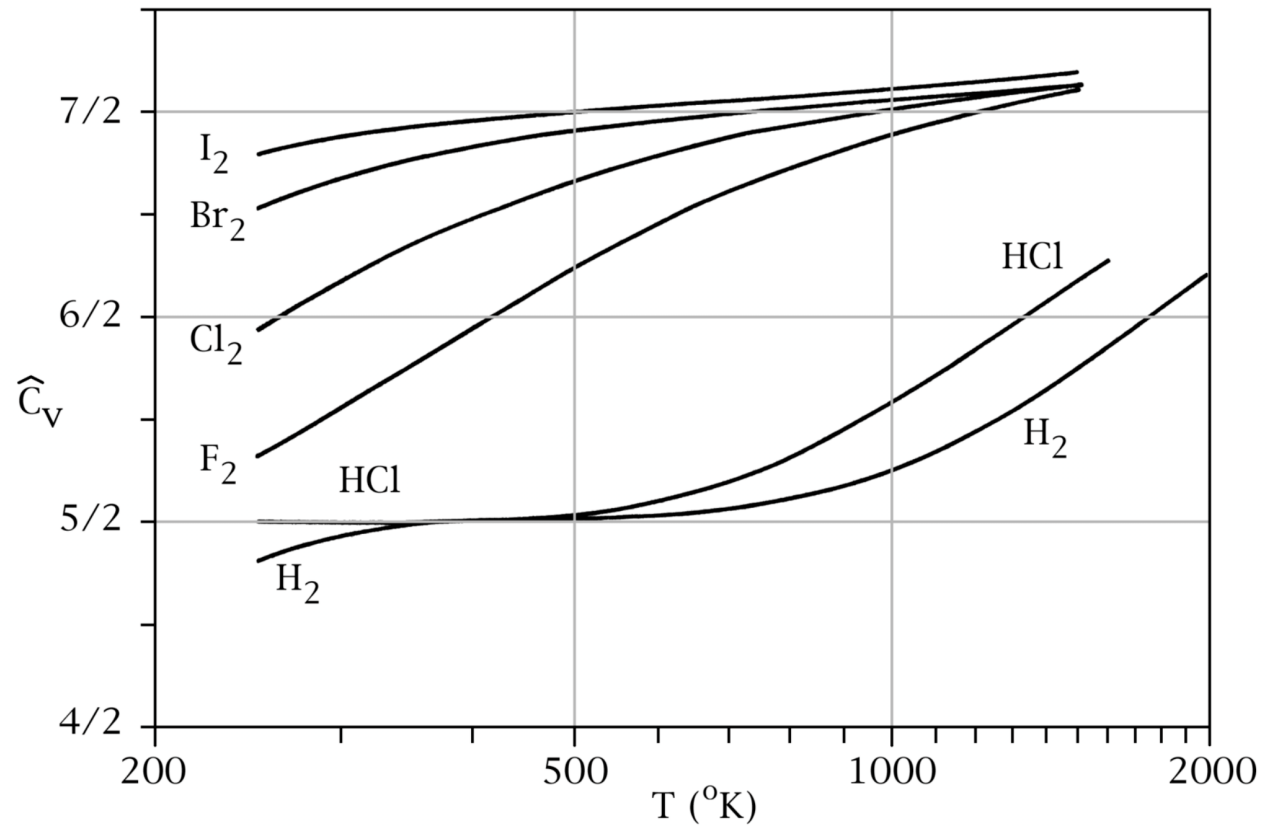
Material constant measuring the capacity of the gas to store internal energy

$$c_v(T) = \frac{du(T)}{dT}$$

EXAMPLE : monoatomic gases

$$u(T) = \frac{3}{2}RT \Rightarrow c_v(T) = \frac{3}{2}R$$

Here $c_v(T)$ is a temperature-independent constant!

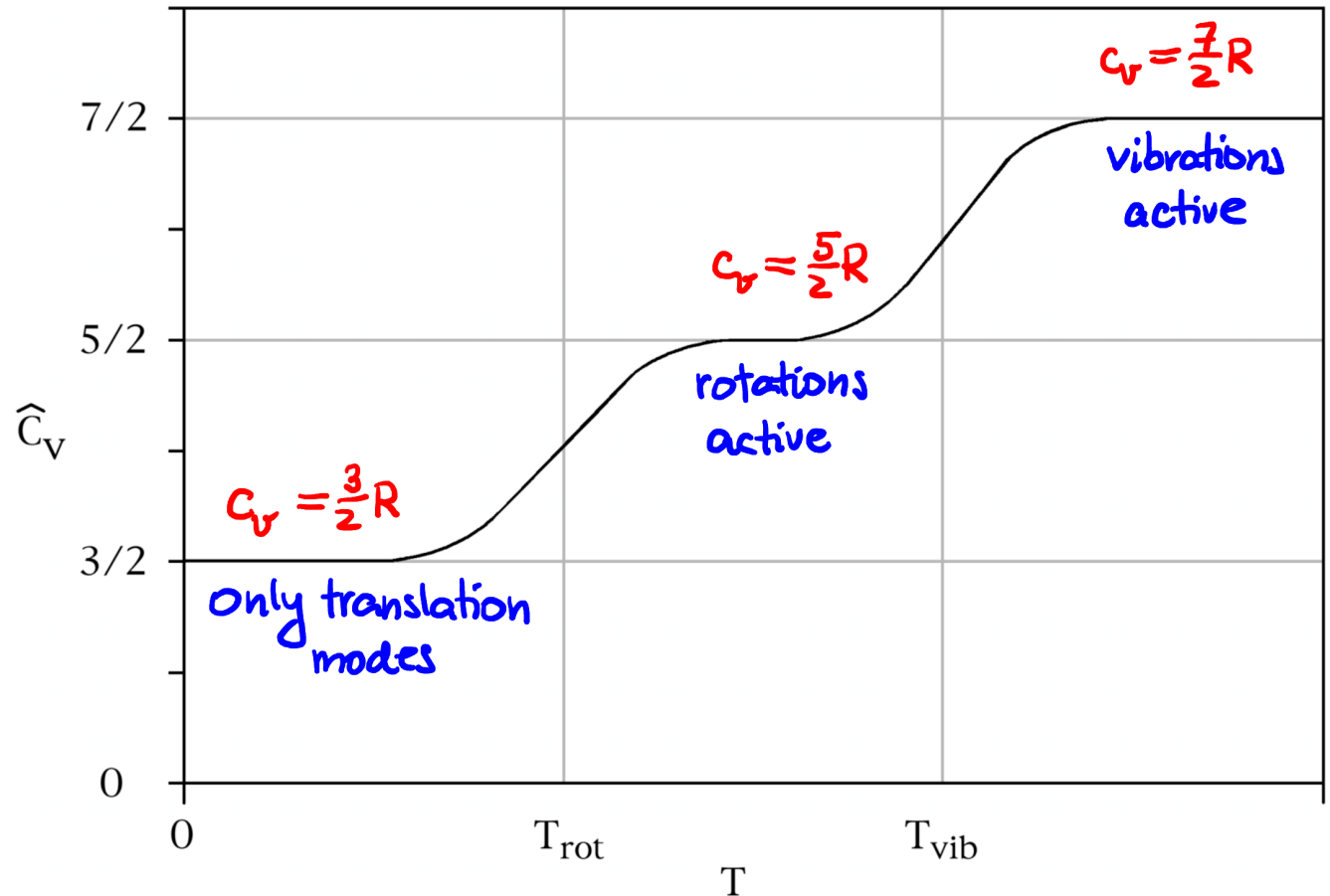


Simple model for gases with diatomic molecules : $c_v = \frac{n}{2}R$ where n is the number of "active degrees of freedom" (3 for translations, 2 for rotations, 2 for vibrations).

EXAMPLE : nitrogen N_2

$$R \approx 296.8 \text{ J/kg}\cdot\text{K}$$

T [K]	c_v/R
100	2.50
300	2.50
500	2.56
700	2.70
900	2.86
1100	3.00



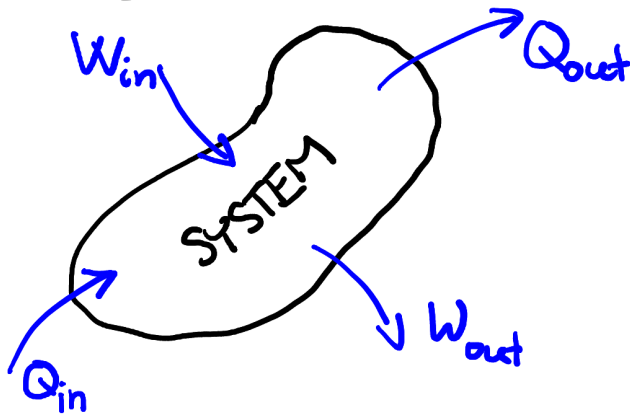
FIRST LAW OF THERMODYNAMICS

Nothing but energy conservation : for a closed system, change in the system's energy = energy supplied from outside minus energy released to the environment.

$$\Delta E = E_{in} - E_{out}$$

For thermodynamic systems at rest, ΔE amounts to change in internal energy.

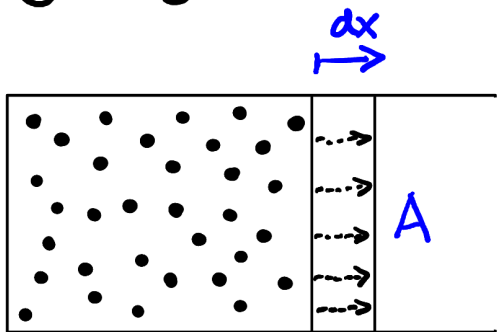
Energy transfer between the system and the environment : ● work
● heat



$$\Delta U = \underbrace{(Q_{in} - Q_{out})}_{\text{net heat absorbed}} + \underbrace{(W_{in} - W_{out})}_{\text{net work received}}$$

VOLUME WORK

Work done by a gas (ideal or not) during expansion :



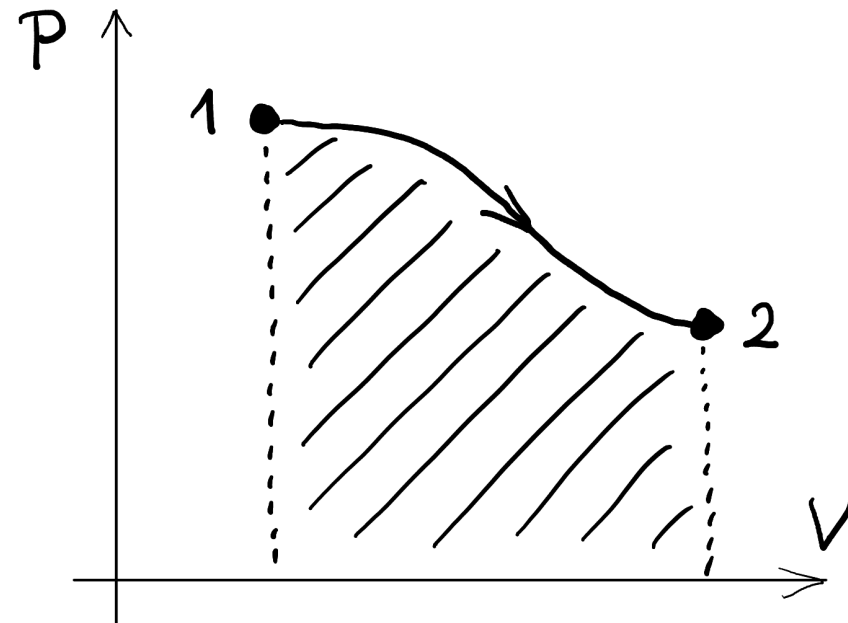
$$dW = F dx = P A dx = P dV$$

↑ assumes that the process is quasi-equilibrium!

General rule for any quasi-equilibrium process :

$$\Delta W_{1 \rightarrow 2} = \int_1^2 P dV$$

The result clearly depends on the process that connects the initial and final states.



BASIC PROCESSES IN IDEAL GASES

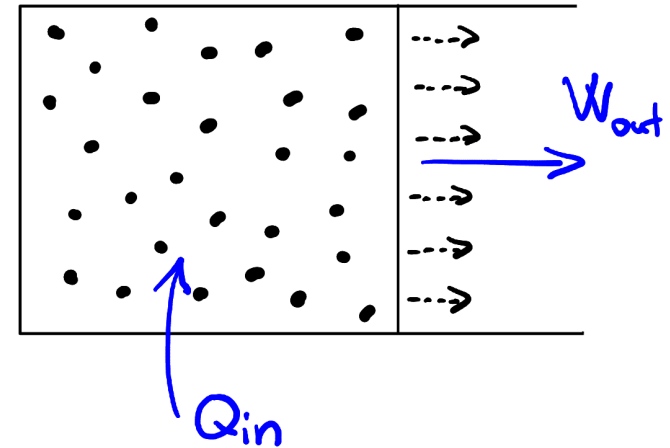
Isothermal expansion/compression

● temperature does not change $\Rightarrow \underline{\underline{\Delta U = 0}}$

● 1st law $\Rightarrow \underline{\underline{Q_{in} = W_{out}}}$

●
$$W_{out} = \int_1^2 P dV = \int_1^2 \frac{Nk_B T}{V} dV = Nk_B T \int_1^2 \frac{dV}{V}$$

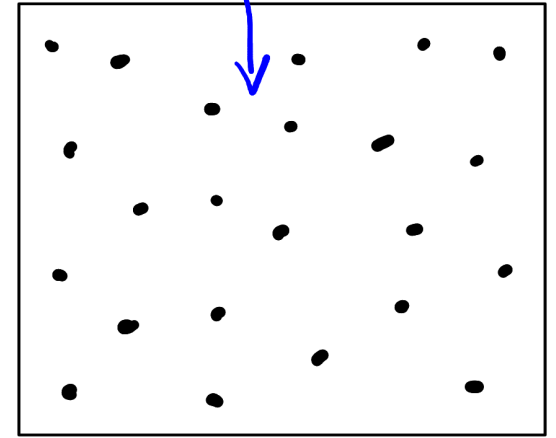
$$Q_{in} = W_{out} = Nk_B T \ln \frac{V_2}{V_1}$$



Applications: usually a poor approximation of real processes, since keeping the temperature constant requires very slow changes, unless we deal with saturated vapor in equilibrium with a liquid phase.

Isochoric processes

- volume is by definition constant \Rightarrow $W_{out} = 0$
- any process where the gas is kept in a closed rigid container
- 1st law \Rightarrow $\Delta U = Q_{in}$
- the resulting change in temperature is parameterized by the specific heat



$$\left. \begin{array}{l} dU = dQ_{in} \\ \parallel \quad \parallel \\ M du \quad M c_v dT \end{array} \right\} \Leftrightarrow du(T) = c_v(T) dT$$

Isobaric processes

- pressure is by definition constant \Rightarrow $W_{out} = P(V_2 - V_1)$

- 1st law $\Rightarrow dQ_{in} = dU + dW_{out} = dU + PdV$

$$Q_{in} = (U_2 + PV_2) - (U_1 + PV_1)$$

Heat transfer in an isobaric process does not measure the change in U ,

but rather the change in the **enthalpy** $H = U + PV$

- specific heat at constant pressure : $c_p(T) = \frac{dh(T)}{dT}$

Relation between specific heats of ideal gases :

$$c_p = \frac{du}{dT} + \frac{d(Pv)}{dT} = c_v + \frac{d(RT)}{dT} \quad \Rightarrow \quad c_p(T) = c_v(T) + R$$

Adiabatic expansion/compression

- by definition involves no heat exchange

- 1st law $\Rightarrow 0 = dq_{in} = du + P dv = c_v dT + P dv$

$$0 = \overset{c_p}{(c_v + R)} P dv + c_v v dP \quad \leftarrow \dots \dots d\left(\frac{Pv}{R}\right) = \frac{1}{R}(P dv + v dP)$$

$$0 = \frac{dP}{P} + \frac{c_p}{c_v} \frac{dv}{v}$$

adiabatic index $\gamma = c_p/c_v$

Assuming that the specific heats are temperature-independent (reasonable in small temperature ranges!), this integrates to $Pv^\gamma = \text{const.}$

Alternative forms of the equation for adiabatic processes :

$$TV^{\gamma-1} = \text{const.}$$

$$P^{1-\gamma} T^{\gamma} = \text{const.}$$

Back to 1st law : $0 = Q_{in} = \Delta U + W_{out}$ where

$$W_{out} = \int_1^2 P dV = \int_1^2 \frac{c}{V^{\gamma}} dV \quad \leftarrow \text{constant} = \frac{c}{1-\gamma} [V^{1-\gamma}]_1^2 = \frac{1}{1-\gamma} \left(V_2 \frac{c}{V_2^{\gamma}} - V_1 \frac{c}{V_1^{\gamma}} \right)$$

Final result :
$$\Delta U = -W_{out} = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

MIXTURES OF GASES

Mixtures of ideal gases satisfy **Dalton's law** :

$$P_{\text{total}} = P_1 + P_2 + P_3 + \dots$$



partial pressures of the components

Assume mixture of gases with mass fractions c_i

$$P_i V = N_i k_B T = \frac{M_i}{m_i} k_B T = c_i M \frac{k_B}{m_i} T \Rightarrow P_i v = c_i \frac{k_B}{m_i} T$$

Sum over all components to get

$$P_{\text{total}} v = \left(\sum_i c_i \frac{k_B}{m_i} \right) T$$

$$R = \sum_i c_i \frac{k_B}{m_i} = \sum_i c_i R_i$$

EXAMPLE : composition of air

- 75.5% nitrogen
- 23.2% oxygen
- 1.3% argon
- 0.06% carbon dioxide
- ...

RELATIVE HUMIDITY

The amount of water vapor in the air is limited by the saturation pressure of water at the given temperature.

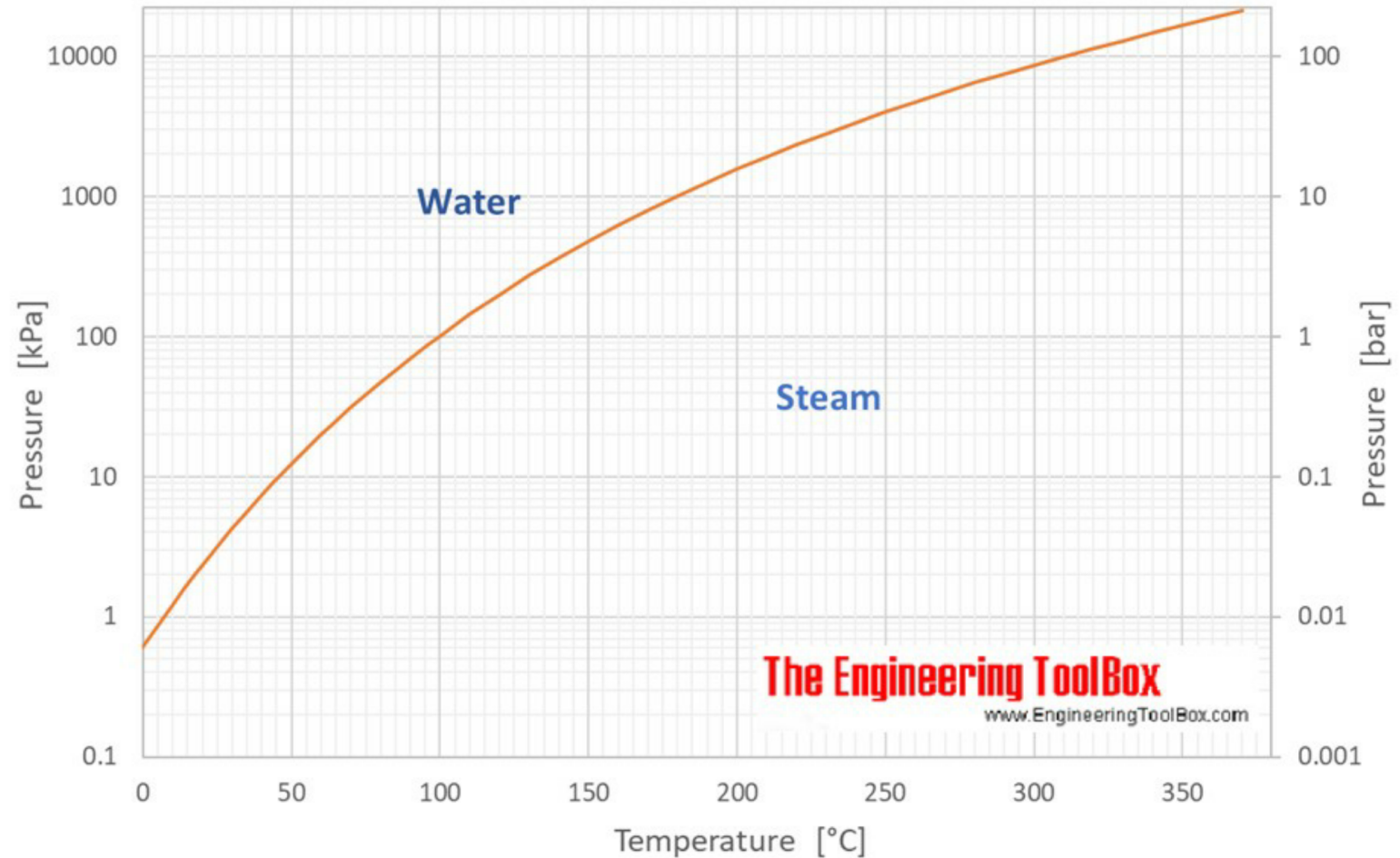
relative humidity

partial pressure of water vapor in the air

$$\varphi = \frac{p}{p_{sat}}$$

saturation pressure at the same temperature

Water saturation pressure



CLAUSIUS-CLAPEYRON EQUATION

The saturation pressure (\Rightarrow humidity) depends sensitively on the temperature!

$$\frac{dP_{\text{sat}}}{dT_{\text{sat}}} = \frac{L}{T_{\text{sat}}(v_g - v_f)}$$

L ← latent heat of evaporation

specific volume of the saturated vapor/liquid

Assuming that v_f can be neglected (☺) and that L is a constant independent on the temperature (☺), the equation can be integrated using the ideal gas

EqM to express $v_g = \frac{RT_{\text{sat}}}{P_{\text{sat}}} \longrightarrow P_{\text{sat}} \exp\left(\frac{L}{RT_{\text{sat}}}\right) = \text{const.}$

IRREVERSIBILITY

Most of what we have done so far was an application of energy conservation (1st law).

But that is clearly not all of thermodynamics :

- Some processes allowed by energy conservation do not occur in nature.
- Natural processes are more or less irreversible.
- Why does everything evolve towards equilibrium?

The key insight is to treat thermodynamical systems as statistical ensembles of many molecules:

- Natural evolution towards states that are statistically more probable.
- Equilibrium is the most probable state under given conditions.

ENTROPY

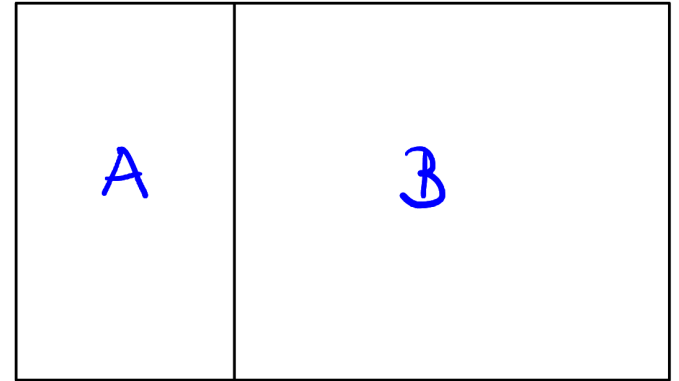
Rough idea : Entropy is a property that measures the **logarithm of probability** to find the system in a given state.

Why logarithm? Makes entropy an extensive property!

$$P_{A \cup B} = P_A P_B$$

\Downarrow

$$\log P_{A \cup B} = \log P_A + \log P_B$$



Thermodynamic definition :

Entropy S is a state property such that in a reversible (quasiequilibrium) process

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

(definition of entropy)

The unidirectional nature of irreversible processes is captured by the **second law of thermodynamics** :

$$dS \geq \frac{dQ_{in}}{T}$$

EXAMPLE : isolated systems do not exchange any heat with their environment.

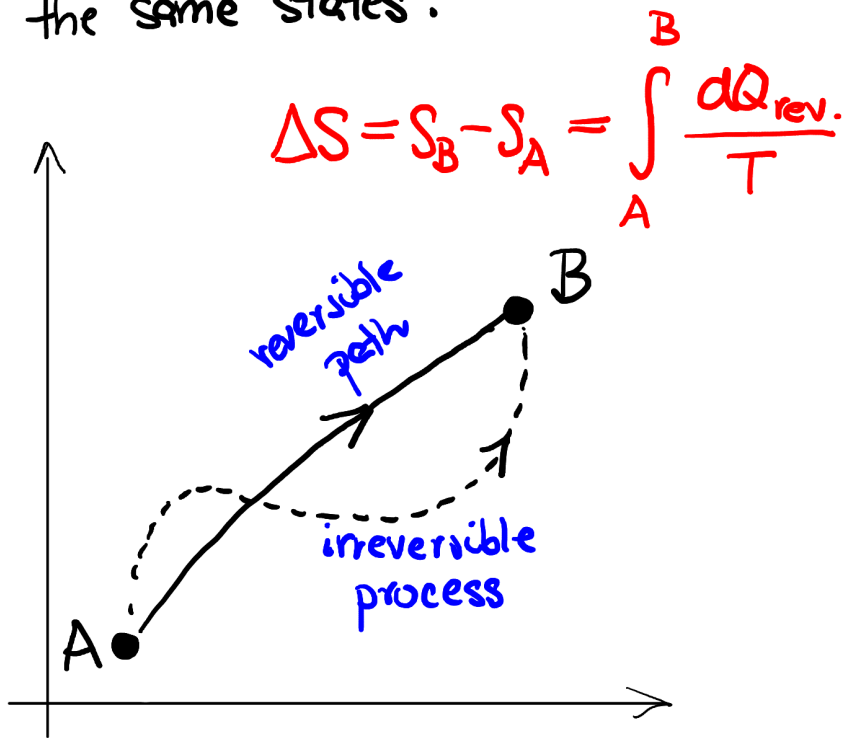
$$dQ_{in} = 0 \Rightarrow dS \geq 0$$

Entropy of an isolated system can never decrease.

ENTROPY AS THERMODYNAMIC PROPERTY

How to actually determine entropy change in an irreversible process?

Using a reversible process connecting the same states?



EXAMPLE : free expansion of an ideal gas from volume V_1 to volume V_2

Temperature does not change in a free expansion.
Use reversible isothermal expansion!

$$\Delta S = \frac{Q_{\text{rev.,in}}}{T} = \frac{W_{\text{rev.,out}}}{T}$$

we have found this before!

$$W_{\text{rev.,out}} = Nk_B T \ln \frac{V_2}{V_1}$$

\Downarrow

$$\Delta S = Nk_B \ln \frac{V_2}{V_1} \Leftrightarrow \underline{\underline{\Delta s = R \ln \frac{V_2}{V_1}}}$$

specific entropy