Laws of thermodynamics

0. If the spatial distribution of intensive quantities is homogeneous, than the system is in equilibrium.

I. $\Delta E = Q + W$ thermal and mechanical interactions

$$W = -p\Delta V \qquad \text{(see exceptions)}$$

Further possible interaction

$$W_N = \mu_N \Delta N \qquad \text{or} \qquad W_v = \mu_v \Delta v$$

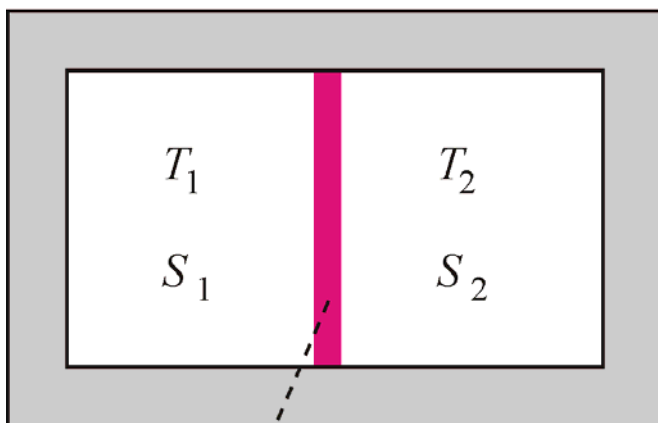Physical meaning of μ, chemical potential (change of energy): Appearance of any new particles increases the kinetic energy of the system, furthermore because of its interaction with the other particles the potential energy also changes.

II. A qualitative statement for the direction of spontaneous processes;   in thermal interactions T equalizes, these processes are irreversible.

For quantitative phrasing we need to introduce the entropy (S); formally, if $\Delta E = Q$ than $Q = T\Delta S$

How does the entropy (S) change during thermalization?

isolated system, $\Delta E = 0$ $\Delta E_1 = -\Delta E_2$

$$\Delta S = \frac{\Delta E_1}{T_1} + \frac{\Delta E_2}{T_2} =$$

$$= \Delta E_1 \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \rightarrow \Delta S \geq 0$$

heat-coducting wall

S non-conserved quantity!

Statistical interpretation of entropy

We could see that the above introduced entropy increases.

Is there any other quantity having the same feature?

Microstate: microscopic parameters of all the particles of the system (e.g. position, velocity) are known.

(all the microstates are equally probable)

Macrostate: distribution of macroscopic parameters (e.g. temperature, pressure, density, energy) is known.

The number of microstates that belong to the same macrostate is called thermodynamic probability: Ω

An example:
The thermodynamic system is the air in the lecture hall

$$\Omega_{AB} = \Omega_A \Omega_B$$

Ω increases during the equalization process, but it isn't additive

$$\ln\Omega_{AB} = \ln\Omega_A + \ln\Omega_B$$

$$S = k \ln\Omega \qquad (\Omega = e^{\frac{S}{k}})$$

III. The entropy of a singlecomponent, crystallizing material is 0 at 0 K temperature.

$$S = k \ln\Omega = k \ln 1 = 0$$

An important example: free expansion of a gas
no work, no heat, but the entropy increases

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Thermodynamic potential functions

Hess's theorem:
transition heat of an overall reaction only depends on the initial and the final states.

Lemma: small change of a product (e.g. xy)
$$\Delta xy \approx x\Delta y + y\Delta x$$

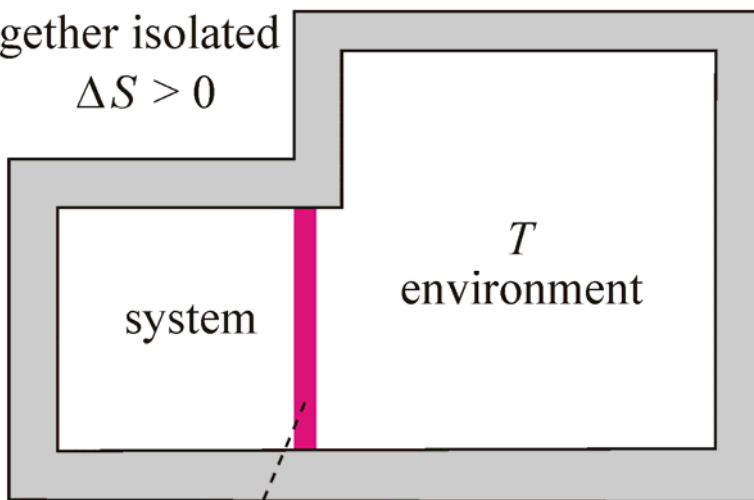Most chemical reactions pass off at constant pressure ($\Delta p = 0$)

$$\Delta E = Q + W \qquad \rightarrow \qquad \Delta E = Q - p\Delta V, \qquad \text{but } p\Delta V = \Delta pV$$

thus $\Delta(E + pV) \equiv \boldsymbol{\Delta H} = Q$ \qquad enthalpy change

Direction of processes in non-isolated systems

system and environment together isolated
$\Delta S > 0$

system

T environment

heat-conducting wall

$$\Delta S = \Delta S_r + \Delta S_k > 0$$

$$\Delta S_k = \frac{-Q}{T}$$

$$\Delta S_r - \frac{Q}{T} > 0$$

$$* T\Delta S_r > Q = \Delta E_r$$

$$0 > \Delta E - T\Delta S, \text{ but } \Delta T = 0$$

$$\Delta(E - TS) \equiv \boldsymbol{\Delta F} < 0$$

Helmholtz free energy change

If p is also constant (moving wall), than $* T\Delta S_r > Q = \Delta E_r + p\Delta V$

$$0 > \Delta E - T\Delta S + p\Delta V, \qquad \text{but } \Delta T = 0 \text{ and } \Delta p = 0$$

$$\Delta(E - TS + pV) = \Delta(H - TS) \equiv \boldsymbol{\Delta G} < 0$$

Gibbs free energy change

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Boltzmann-distribution

Premises: equipartition in thermal equilibrium (T = constant)

Two important parameters:
ε_i the possible energy of particles, n_i occupation number

Further conditions:
$$E = \sum_i n_i \varepsilon_i \qquad\qquad N = \sum_i n_i$$

The ratio of thermodynamic probabilities ($\Omega_2 < \Omega_1$) of two macrostates ($\varepsilon_2 > \varepsilon_1$, $\Delta\varepsilon = \varepsilon_2 - \varepsilon_1$):

$$\frac{p_2}{p_1} = \frac{\Omega_2}{\Omega_1} = \frac{e^{\frac{S_2}{k}}}{e^{\frac{S_1}{k}}} = e^{\frac{S_2 - S_1}{k}}$$

Decrease of entropy (the higher the energy of a state, the less probable its occupation is):

$$\Delta S = -\frac{\Delta\varepsilon}{T}$$

$$\frac{n_2}{n_1} = e^{-\frac{\Delta\varepsilon}{kT}} = e^{-\frac{\Delta E}{RT}} \qquad\qquad (kN_A = R)$$

E.g. barometric formula, rates of chemical reactions

$T_1 < T_2 < T_3$