Thermodynamic aspects of transport processes

Thermodiffusion:
one end of a U-shaped pipe with Na_2SO_4-salt solution was heated with hot steam, and the other end was cooled with ice. Due to the temperature difference, dissolved salt migrated from the warmer section of the pipe to the colder section. (Ludwig–Soret-effect)
The law that describes this phenomenon is:

$$J_v = -L_T \frac{\Delta T}{\Delta x} .$$

We can see that this equation is very similar to Fick's first law, so the coefficient L_T corresponds in some sense to the diffusion coefficient.

Heat conduction
If the net particle flux is zero, means the same number of particles cross the wall from left to right as right to left, but the temperature-difference between the two sides is maintained, we are faced with another phenomenon (Fourier).

$$J_E = -\lambda \frac{\Delta T}{\Delta x} .$$

Thermodynamic system
This can be a gas of a given volume, a bacterium, a lymphocyte, an animal or a human, but it can also be a part of the body, like the heart, or even the Earth as a whole.
Any other substance in interaction with the examined system is called the **environment**.

type	matter exchange	energy-exchange
isolated	–	–
closed	–	+
open	+	+

Extensive and intensive quantities

Quantities that behave like volume when dividing the system into sub-systems ($V_{total} = V_1 + V_2$) are called **extensive** quantities.

Energy (E), mass (m), charge (Q), and number of particles (N) are all like this. (They are proportional to the "size" of the system.)

We call our system **homogenous**, if any division of the system, by any of the extensive quantities can be written up as

$$\frac{x_{total}}{V_{total}} = \frac{x_{subsystem}}{V_{subsystem}} .$$

In homogenous thermodynamic systems there are quantities, which value remains the same after division into sub-systems. These are **intensive** quantities.

Pressure (p) and temperature (T) are all like this. (They are independent of the "size" of the system.)

Uniform description of transport processes

Every transport process is caused by an inhomogeneity. The inhomogeneity can be determined by measuring the **differences in intensive quantities**. Transport takes place to decrease these differences between sub-systems. It can only be achieved by a **flux of some extensive quantities**.

The formal similarity among the laws of transport processes, reveal a more general rule, known as the **Onsager-relation**:

$$J = LX , \text{ where}$$

$J = \dfrac{\Delta x_{extensive}}{A \Delta t}$ **flux-density** of the flowing extensive quantity

$X = \dfrac{-\Delta y_{intensive}}{\Delta x}$ **thermodynamic force** exerted by the gradient of the corresponding intensive quantity

L is the so-called **conductivity coefficient**. (if $X = 0$, **equilibrium**)

Laws of thermodynamics

A condition for equilibrium was that intensive quantities associated with the different interactions are uniform throughout the system. This is the **zeroth law of thermodynamics**.

First law of thermodynamics (energy-conservation)
The change in the internal energy (ΔE) of the system is equal to the sum of the transfer of heat (Q_E) to the system and the work being done on the system (W):

$$\Delta E = Q_E + W$$

The **internal energy** consists of the kinetic and interactional (structural) energy and it does not include the kinetic and potential energies of the macroscopic system as a whole.

Originally, we only took account of mechanical interaction when calculating the work being done on the system, thus it has a very simple form:

$$W = -p\Delta V \;.$$

The work done by other forces (electric, material etc.):

$$W_Q = \varphi\Delta Q \;,\; W_\nu = \mu\Delta\nu \;,$$

where φ and Q note the electric potential and the charge, μ is the chemical potential, ν is the number of moles.

Since the ionic charge of ν moles of ions of z valency is $Q = zF\nu$ (F is the Faraday-constant, $F = N_A q_e$), the work terms of the two interactions can be fused:

$$W_{\nu Q} = \mu\Delta\nu + \varphi\Delta(zF\nu) = (\mu + zF\varphi)\Delta\nu = \mu_e\Delta\nu$$

where μ_e the so-called **electro-chemical potential**.

(In the discussion of transport processes across membranes, we will encounter this quantity many times, as the intensive quantity of ionic fluxes.)

Second law of thermodynamics

Only those processes proceed in isolated systems where intensive quantities that characterize interactions are to be equilibrated.

The characteristic extensive quantity associated with thermal interaction is called as **entropy** and denoted by S.

$$Q_E = T\Delta S$$

Let's investigate the change of entropy in a spontaneous thermalization process.

E_1 and E_2 are the internal energies of the subsystems
$$(T_1 \neq T_2).$$
The first law of thermodynamics for the subsystems, which consists of only one term in this case:

$$\Delta E_1 = T_1\Delta S_1, \quad \Delta E_2 = T_2\Delta S_2.$$

isolated system, $\Delta E = 0$

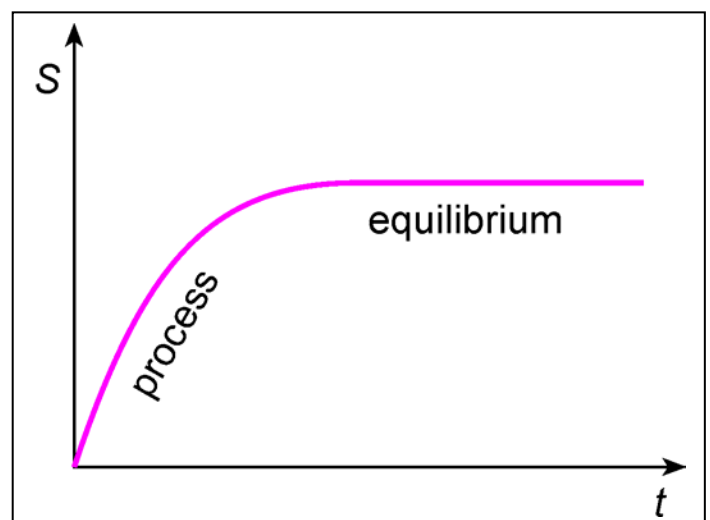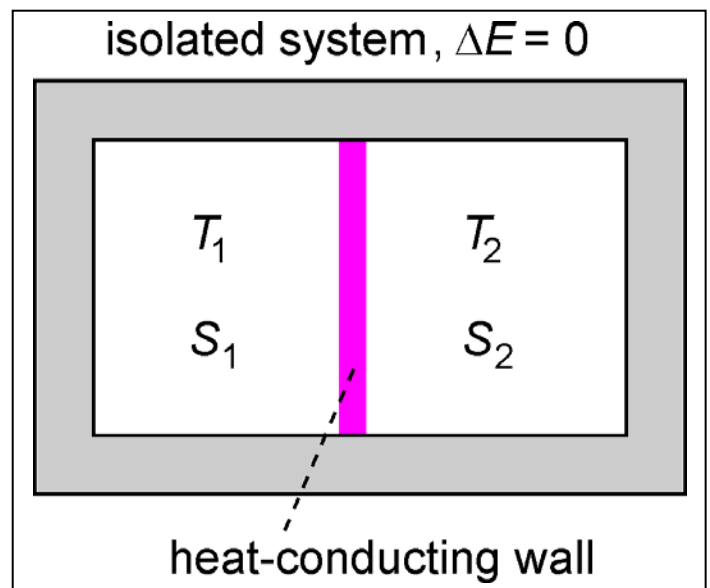T_1 $\quad$ T_2

S_1 $\quad$ S_2

heat-conducting wall

Regarding the fact, that entropy is an extensive quantity and $\Delta E_1 = -\Delta E_2$:

$$\Delta S = \Delta S_1 + \Delta S_2 = \frac{\Delta E_1}{T_1} + \frac{\Delta E_2}{T_2} = \Delta E_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

If $T_1 > T_2$ initially, then the first subsystem cools in the process, thus its internal energy is decreased, i.e. $\Delta E_1 < 0$, but in this case $(1/T_1 - 1/T_2) < 0$. Oppositely…Consequently, **the entropy of an isolated system always increases during the process of thermalization**. Entropy does not conserve.

S

process

equilibrium

t

Statistical definition of entropy

Microstate: microscopic parameters (for example position and velocity) of all the elements of the system are known.
Macrostate: distribution of macroscopic parameters (for example temperature, pressure, density etc.).

One macrostate can be realized by a lot of microstates.
The number of microstates that belong to the same macrostate is called **thermodynamic probability**, and its sign is Ω. (Most probable macrostate, $\Omega_{AB} = \Omega_A \Omega_B$, $S_A + S_B = S_{AB}$)

$$S = k \ln \Omega$$

where k is the Boltzmann constant (less probable and more probable states). Entropy, by its nature, never decreases spontaneously.

Third law of thermodynamics
The entropy of a single-component, crystallizing material is 0 at 0 K temperature.

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

Thermodynamic potential functions
Note: (for small changes)
$$\Delta(pV) = (p + \Delta p)(V + \Delta V) - pV$$
$$pV + p\Delta V + V\Delta p + \Delta p \Delta V - pV \approx p\Delta V + V\Delta p$$
If p = const. $\Delta p = 0$ and
$$\Delta(pV) \approx p\Delta V$$

$$\Delta E = Q_E - p\Delta V \Rightarrow \Delta(E + pV) = Q_E = \Delta H$$

Change of enthalpy: **ΔH**
Thus, the fact that enthalpy is a state function is identical with **Hess' law**, which had been formulated much earlier.

Closed system
(isolated as a whole)

$$\Delta S_{\text{total}} = \Delta S_s + \Delta S > 0$$
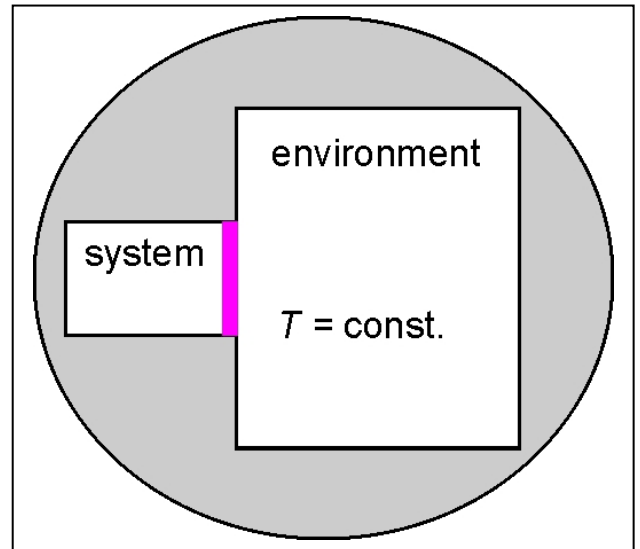
$$\Delta S = -\frac{Q_E}{T}$$

$$T\Delta S_s > Q_E = \Delta E$$

Since T = const. $\Delta T = 0$ thus

$$\Delta(TS) \approx T\Delta S$$

$$0 > \Delta E - T\Delta S_s = \Delta(E - TS) \equiv \Delta F < 0$$

Change of Helmholtz free-energy: ΔF

Closed system with "moving" wall
(isolated as a whole)

$$\Delta S_{\text{total}} = \Delta S_s + \Delta S > 0$$

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

$$T\Delta S_s > Q_E = \Delta E + p\Delta V$$

Since $\Delta T = 0$ and $\Delta p = 0$ thus

$$\Delta(TS) \approx T\Delta S \ ; \Delta(pV) \approx p\Delta V$$

$$0 > \Delta E - T\Delta S_s + p\Delta V = \Delta(E - TS + pV) \equiv \Delta G < 0$$

Change of Gibbs free-energy (free enthalpy): ΔG