ENTROPY AND TEMPERATURE
TWO SIMPLE THERMODYNAMIC MODELS

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Summary

It is demonstrated by calculation on two models that already in such simple cases, the most important thermal properties can be interpreted. It could be shown what negative temperature means and what entropy and heat capacity of such systems are. On considering three possible states, equilibrium and non-equilibrium states could be compared. It was shown, by a kinetic method, how equilibrium is reached, why entropy is a maximum at equilibrium, and why it does increase if there is no equilibrium. It was demonstrated the simplest elemental system which can have a temperature, and shown why a non-equilibrium system did not have a definite temperature. Finally, it has been shown how the different averages (entropy, internal energy, free energy) can be visualized by $\ln x_i - E_i$ plots.

Introduction

A thermodynamic system is a macroscopic body consisting of a great number of indistinguishable elements (e.g. molecules). These elements can have different states which can vary either continuously or discontinuously. These different states mean different energies within one degree of freedom (such as of translational, rotational or vibrational type).

A property of the macroscopic body is either the sum of the appropriate properties of its elements (as e.g. mass), or some type of an average of them (e.g. temperature, entropy, etc.).

Special states of thermodynamic systems are the equilibrium states. If a body is completely isolated from outside changes, it reaches equilibrium relatively quickly.

The macroscopic observation, characterization of the states of systems generally requires the assumption of an equilibrium state. Temperature can be unambiguously measured, e.g., if at least the part of the system in contact with the thermometer is in thermal ("local") equilibrium (i.e. it has a definite temperature) and this temperature is equal to the temperature of the thermometer.

A non-equilibrium state can also be imagined, where no temperature can be defined at all, as numerous temperatures exist simultaneously in the same place.

As it is known, thermodynamic equilibrium can be characterized in various ways:

a) Thermostatic definition: in a closed system, entropy is a maximum at equilibrium.
b) Thermodynamic definition: at equilibrium the forces vanish, the appropriate "potentials" (e.g. temperature) equilibrate.
c) Kinetic definition: The rates of internal ordering processes (relaxation) vanish, a steady state is achieved.

Statistical mechanics studies equilibrium in a different way. In statistical mechanics, the main questions are [1].

a) What is the numerical distribution of the elements in the different states and at equilibrium?
b) What relationships exist between the different *averages* and the quantities measurable macroscopically (e.g. entropy, temperature).?
c) What is the kinetics of internal relaxation processes, what fluctuations around the equilibrium are possible?

Theories based on statistics generally postulate that the actual state of all molecules is never known in a macroscopic system, neither is their real distribution: this would really exceed the possibilities of observation. What we actually know is only a probability. (E.g. we do not know what we shall throw with a dice, but we know exactly that the probability for throwing e.g. 2 is 1/6.)

Thus e.g. the molar entropy (S) can be defined as

$$S = k \cdot \ln W \tag{1}$$

(here $\underline{k}$ is the Boltzmann constant, W is the overall thermodynamic probability of the system). Or, if p_i means the probability of residence in the i-th microstate, then

$$S = -R \sum_i p_i \ln p_i \tag{2}$$

We do not know anything about the real momentary distribution, i.e. what fraction of the molecules is in the i-th state (x_i)

$$x_i = \frac{n_i}{\sum_i n_i} \tag{3}$$

However, we know that in an unperturbed state for molecules of a considerable number

$$x_i \rightarrow p_i$$

The situation is different if the methods of statistics are applied for mathematical models. In the case of models, there are no constraints for cognizability, we provide all the necessary information. We can design a thermodynamic model by providing the state of every x_i. In this case, there is no need for working with probabilities. By analog to (2), we can define an entropy which, naturally, will not be completely identical with that defined in terms of probabilities, but it will behave very similarly, the two kinds of entropy are identical. For equilibrium systems,

$$S = -R \sum_i x_i \ln x_i \tag{4}$$

This entropy is the average of ln x_i's. This entropy is determined exclusively by the distribution, and can be interpreted for every distribution (i.e. not only for equilibrium systems) [5]. (As we shall see later, this is not true for the temperature!)

Similarly, the system always has an internal energy (U), which is the sum of the energies of the elements:

$$U = \sum_i x_i E_i \tag{5}$$

In the models whose thermodynamic behavior is studied the following parameters are kept constant:

— energy levels (in real systems this is equivalent to a constant volume),

— the total number of particles (constant mass). These models have only one degree of freedom.

Model system with two states

This is the simplest model possible: it has only one ground state (1) and one excited (2) state. As will be shown, already in this simple case we can define not only the internal energy and entropy, but also the temperature and heat capacity. The numbers of particles are n_1 and n_2, energies of the levels are E_1 and E_2. For the sake of simplicity, let $E_1 = 0$ and $E_2 = E$. Variables are: internal energy (U) and the distribution between the two states, i.e. the entropy changes, too.

Distributions are characterized by:

$$x_1 = \frac{n_1}{n_1 + n_2} \qquad \text{and} \qquad x_2 = \frac{n_2}{n_1 + n_2},$$

According to (4), entropy is defined as:

$$S = -R(x_1 \ln x_1 + x_2 \ln x_2)$$

and the internal energy as:

$$U = Ex_2$$

Other thermal quantities are derived from these in the usual way as in thermodynamics in general [3]

$$1/T = \partial S/\partial U = R/E \ln x_1/x_2 \tag{6}$$

$$T = \partial U/\partial S = E/R\,(\ln x_1/x_2)^{-1} \tag{7}$$

$$-1/\mathrm{T}^2 \mathrm{C}_v = \partial^2 \mathrm{S}/\partial \mathrm{U}^2 = -\mathrm{R}/\mathrm{E}^2 \frac{1}{x_1 x_2} \tag{8a}$$

$$C_v = R x_1 x_2 \left(\ln \frac{x_1}{x_2}\right)^2 \tag{8b}$$

Calculation results summarized in Table 1 should be studied in two regions separately:

Table 1

$x_1 + x_2 = 1$

x_2	$x_1 \ln x_1 + x_2 \ln x_2$	$\ln \frac{x_1}{x_2}$	$\left(\ln \frac{x_1}{x_2}\right)^{-1}$	$\frac{1}{x_1 \cdot x_2}$	$x_1 x_2 \left(\ln \frac{x_1}{x_2}\right)^2$
0	0	$+\infty$	0	$+\infty$	0
0.001	0.00791	6.9067	0.1447	1001	0.0476
0.01	0.0560	4.5951	0.2176	101.0	0.2090
0.02	0.0980	3.8918	0.2569	51.02	0.2968
0.03	0.1347	3.4761	0.2877	34.36	0.3517
0.04	0.1679	3.1780	0.3146	26.04	0.3879
0.05	0.1985	2.9444	0.3396	21.05	0.4119
0.06	0.2270	2.7515	0.3634	17.73	0.4270
0.07	0.2536	2.5867	0.3866	15.36	0.4356
0.08	0.2788	2.4423	0.4094	13.59	0.4390
0.09	0.3025	2.3136	0.4322	12.21	0.4384
0.1	0.3251	2.1972	0.4551	11.11	0.4345
0.2	0.5004	1.3863	0.7213	6.25	0.3075
0.3	0.6109	0.8473	1.1802	4.76	0.1508
0.4	0.6730	0.4055	2.4663	4.17	0.0394
0.5	0.6931	0	∞	4.00	0
0.6	0.6730	-0.4055	-2.4663	4.17	0.0394
0.7	0.6109	-0.8473	-1.1802	4.76	0.1508
0.8	0.5004	-1.3863	-0.7213	6.25	0.3075
0.9	0.3251	-2.1972	-0.4551	11.11	0.4345
1	0	$-\infty$	0	∞	0
$\sim U$	$\sim S$	$\sim 1/T$	$\sim T$	$\sim -\left(\frac{\partial^2 S}{\partial U^2}\right)$	$\sim C_V$

(A) $0<x_2<0.08$: a relatively weakly excited system. It does not differ strongly from those systems where the levels are not limited to two. If there were other states, they would be populated only very scarcely.

Data from Table 1 falling into this region are shown in Fig. 1.

The thermodynamic properties calculated show the general behavior of thermodynamic systems:

Entropy:
- it is always positive,
- its curvature as a function of internal energy is negative,
- it increases monotonically with internal energy (see Fig. 1/a),

The first derivative, the reciprocal temperature:
- is always positive,
- it decreases monotonically with increasing internal energy (i.e. the temperature increases monotonically) (Fig. 1/b).

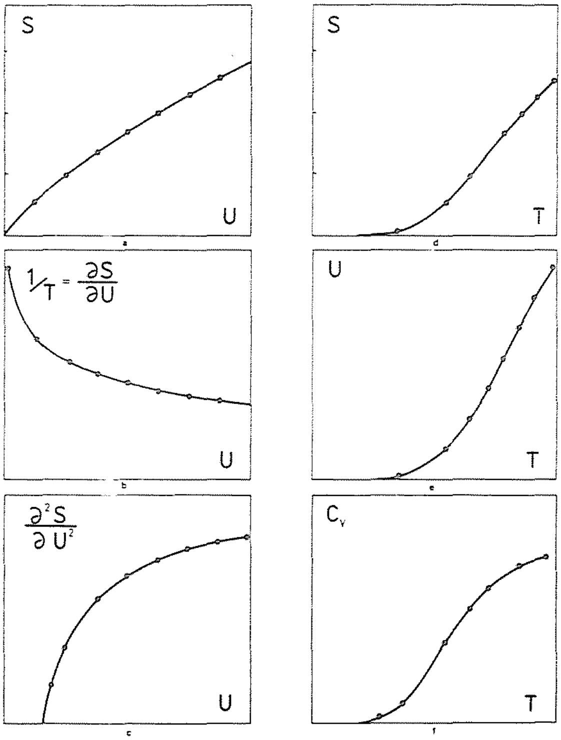

Fig. 1. Calculated quantities with a two-state model.
The entropy (a), the reciprocal temperature (b) and $\partial^2 S/\partial U^2$ (c) as functions of the internal energy. The entropy (d), the internal energy (e) and the heat capacity (f) as functions of the temperature

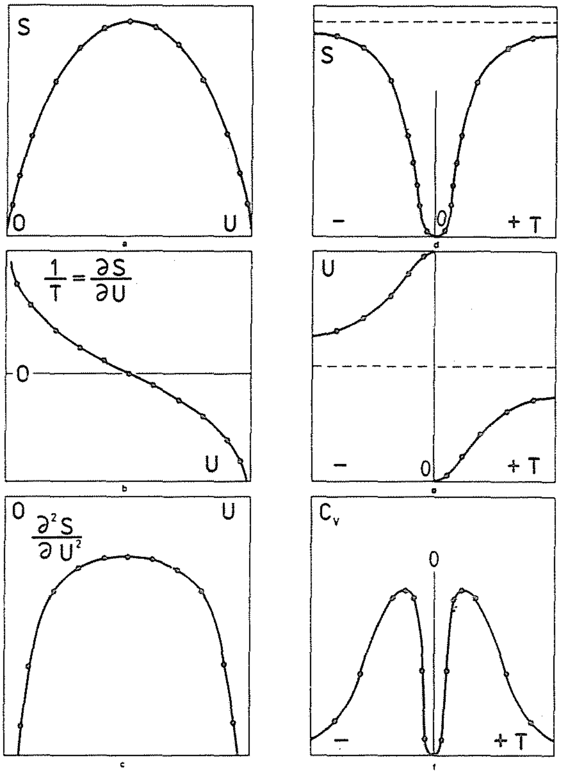

Fig. 2. Calculated quantities with a "limited energy assumption".
The entropy (a), the reciprocal temperature (b) and $\partial^2 S/\partial U^2$ (c) as functions of the internal energy. The entropy (d), the internal energy (e) and the heat capacity (f) as funtions of the temperature

The second derivative:

- — its value is always negative (stability),
- — at $U=0$ its value is infinite and it increases monotonically up to 0 with increasing energy, its curvature as a function of U is negative (convex) (Fig. 1/c).

This behavior is characteristic for every stable thermodynamic system. In Figs 1/d, e and f, S, U, and C_v are plotted in their better known form of temperature dependence. It should be noted that every curve start with zero slope at the temperature of the absolute zero.

(B) $0.1<x_2<1$, region of "limited energy". In this case, due to higher excitation, the effect of the constraint that no higher levels are allowed, is noticeable. The internal energy of such a system is constrained from above:

$$0 \leq U \leq E$$

If to such a system energy is transferred, a state is achieved in which the population of the ground and excited levels is identical. In this state, the reciprocal temperature is zero, which means

$$T=\infty$$

If the number of excited particles is increased by further energy transfer, inverse population is created, which, according to our definition of the temperature, means a negative temperature (Fig. 2/b):

$$T<0$$

Such systems exist also in nature: in lasers, inverse population is created during pumping, i.e. the temperature of this degree of freedom is negative. The situation is similar for particles of 1/2 spin in a magnetic field. Here, two different states are possible (parallel or antiparallel to the direction of the magnetic field), these represent different energies. In this case an inverse population can also be created.

The behavior of basic thermal properties in several cases are the same in the positive and negative temperature regions, but there are also differences.

Entropy:

- — is always positive,
- — its curvature as a function of U is always negative (convex) but
- — it does not increase monotonically with the internal energy, it decreases in the negative temperature region, and reaches zero again at the limiting energy.

Reciprocal temperature:

- — it decreases monotonically with increasing U also in this case, but its domain is

$$+\infty > 1/T > -\infty$$

Consequently, $1/T$ passes continuously from the positive to the negative temperature region (Fig. 2/b).

Accordingly, the temperature increases from $U=0$, $T=0$, it reaches infinity at a finite U

$$U=0.5\,E \qquad T=\infty\,,$$

then it increases from $T=-\infty$, and at $U=E$ $T=0$ (Fig. 2/e).

Thus, negative temperatures can be realized by passing the infinite temperature and not by passing $T=0$. The absolute zero cannot be either reached or crossed.

The second derivative containing the constant-volume heat capacity is always negative, (stability criterion) but it does not increase monotonically (Fig. 2/c)

$$U=0, \quad T=0. \qquad (-T^2C_v)^{-1}=-\infty\,,$$

i.e. it starts from $-\infty$ ("limiting stability"), then passes through a maximum at $T=\infty$ ("minimum stability"), and decreases again (negative temperature), after that nearing $-\infty$ again, and reaches it at $U=E$.

The constant-volume heat capacity, C_v shows a characteristic shape as the function of temperature (Fig. 2/f).

A system with only two states is an oversimplified model: the energy determines the distribution unambiguously. As a consequence, the relationship between S and U is always unequivocal. Their derivative, the temperature, could always be defined unambiguously, the system always "had a temperature". Accordingly, here we could not deal with the distribution, entropy and temperature of the equilibrium and non-equilibrium states.

These problems can be discussed in a somewhat more general, but not yet too complicated model system.

Model system with three states

This model makes possible to study such systems, in which, under complete isolation, more internal configurations coexist. The canonical distribution reached at the end, can be characterized in many ways. The usual procedure described in text-books is: to select the most probable distribution from all possible (or, what is equivalent to this, the one with the highest entropy). This is essentially variational calculus, and understanding is made difficult by the fact that students are not familiar with it (it is true mainly for chemistry students). Equilibrium can also be characterized by the equalizing of certain intensity parameters: in the case of thermal equilibrium by equalizing temperature.

However, this method cannot be used as it is not clear what temperature or temperatures exist in a non-relaxed body. The phenomenological interpretation of temperature can only be applied for relaxed systems.

In our model we use the third, most descriptive kinetic method. We will examine what energy exchange processes, manifesting themselves in the variation of the distribution, are possible, what their rates are, what the direction of spontaneous changes in the distribution are, and at what distribution does the rate decrease to zero, reaching thereby the steady state. At the same time, it is also proved that this steady state is the state of maximum entropy. The conclusion concerning the temperature is the most interesting: it is demonstrated that in a non-relaxed system more temperatures exist simultaneously. These temperatures approach each other during the relaxation process, and at equilibrium, the partial temperatures become identical. This is the state in which the system has a single, definite temperature.

Our model system with three states is a closed system, which means that

1) The energy levels are fixed:

$$E_1 = 0$$
$$E_2 = E, \quad \text{and}$$
$$E_3 = 2E$$

(This assumption of fixed energy levels generally means a fixed volume.)

2) The total number of particles is fixed:

$$n_1 + n_2 + n_3 = 333$$

3) The total energy is fixed:

$$U = n_1 \cdot 0 + n_2 \cdot E + n_3 \cdot 2E = 36E$$

On using these assumptions, the possible distributions can be ordered in a linear series, as is shown in Table 2, the initial distribution being 297/36/0, and the last (limiting) one 315/0/18.

Table 2

Distribution			$w/kn^2 =$	$S/R =$	$0.434 \cdot \ln \frac{x_1}{x_2}$	$0.434 \cdot \ln \frac{x_2}{x_3}$	$\frac{1}{2} \cdot 0.434 \cdot \ln \frac{x_1}{x_3}$
n_1	n_2	n_3	$= x_1 x_3 - x_2^2$	$= -\sum x_i \ln x_i$			
297	36	0	-0.01169	0.3425	0.9164	$+\infty$	$+\infty$
298	34	1	-0.00773	0.3498	0.9427	1.5315	1.2371
299	32	2	-0.00384	0.3525	0.9705	1.2041	1.0873
300	30	3	0.0	0.3553	1.0	1.0	1.0
301	28	4	$+0.00379$	0.3526	1.0314	0.8451	0.9382
302	26	5	$+0.00752$	0.3507	1.0650	0.7160	0.8905
303	24	6	$+0.01120$	0.3478	1.1012	0.6020	0.8516
304	22	7	$+0.01482$	0.3439	1.1404	0.4973	0.8188
	⋮						
308	14	11	$+0.31806$	0.3181	1.3617	0.1047	0.7236
309	12	12	$+0.03214$	0.3089	1.4108	0.0	0.7054
310	10	13	$+0.03544$	0.2985	1.4914	-0.1139	0.6888
	⋮						
315	0	18	$+0.05113$	0.2103	$+\infty$	$-\infty$	0.6215

The stoichiometric and rate equations of energy exchange (relaxation) can be formulated similarly to those of chemical reactions:

$$A_1 + A_3 \rightleftharpoons 2A_2 \tag{9}$$

$$w = \vec{k} \cdot n_1 \cdot n_3 - \overleftarrow{k} \cdot n_2^2 \tag{10}$$

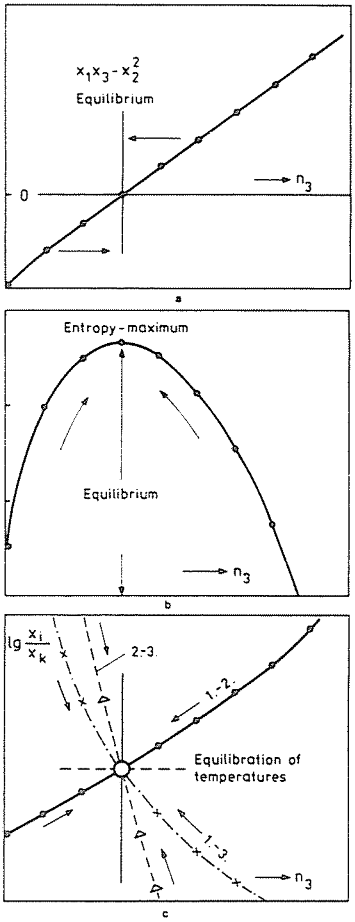

Fig. 3. Equilibrium and non-equilibrium
a) Rate of equilibration process at various configurations.
b) Entropy values at various configurations.
c) Equalization of the three internal temperatures

The principle of microscopic reversibility valid in general for microscopic processes provides the following relationship for such energy exchanges:

$$\vec{k}=\overleftarrow{k}=k \tag{11}$$

thus

$$w=k\cdot n^2(x_1x_3-x_2^2) \tag{12}$$

Let us first calculate the product difference in brackets, then the rate for all possible distributions. These quantities are shown in column 2 of Table 2, and in Fig. 3/a plotted as functions of n_3.

Note the direction of the spontaneous process: if $\underline{w}$ is negative, n_1 and n_3 decrease. (arrow down) if $\underline{w}$ is positive, n_1 and n_3 increase (arrow up). This means that the distribution approaches spontaneously a favored distribution, which is the steady state corresponding to $w=0$ (and, as the system is closed, at the same time it is the *equilibrium* distribution, as well). It is apparent that in this case, the number of particles shows an *exponential* distribution.

Thus

$$x_i = \frac{n_i}{\sum_i n_i} = \frac{10^{-E_i/E}}{\sum 10^{-E_i/E}} \tag{13}$$

The value of the denominator is:

$$Z = \Sigma 10^{-E_i/E} = 10^0 + 10^{-1} + 10^{-2} = 1.11$$

(This quantity will be discussed later)*

The change of *entropy* is discussed on the basis of the above. From the definition of entropy it is clear that to every distribution a definite entropy value can be assigned, though this relation is not reversible: the same entropy can belong to more distributions. The quantities $-\sum_i x_i \ln x_i$ proportional to entropy are seen in column 3 of Table 2, and illustrated in Fig. 3/b as a function of n_3. It is obvious that where $w=0$, i.e. at equilibrium, entropy is a *maximum* relative to entropies belonging to the same energy, mass and volume but in non-equilibrium states. (See: second law of thermodynamics, entropy maximum in closed systems.)

The study that follows concerns the idea of *temperature*. Columns 4 and 5 in Table 2 contain the quantities $\lg x_1 - \lg x_2$ and $\lg x_2 - \lg x_3$, column 6 shows $\frac{\lg x_1 - \lg x_3}{2}$. These quantities are plotted as functions of n_3 in Fig. 3/c. At equilibrium, they neither have zero values, nor extrema but, they equalize. Thus, they should be thermal "potentials" being equalized at equilibrium, which is the temperature.

The thermodynamic temperature has already been interpreted, (it could always be given unambiguously.) In our present modul it is apparent that temperature can only be assigned to a pair of energy levels, and defined as follows:

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* This equilibrium state is not only steady ($w=0$), but also stable: the arrows represent that upon perturbing the equilibrium distribution in either direction, relaxation processes occur, regenerating again the original equilibrium. In this, a significant role is played by the fact that the entropy has a negative curvature, as we shall see later.

$$\frac{1}{T_{ik}} = -R\frac{\ln x_i - \ln x_k}{E_i - E_k} \tag{14}$$

where T_{ik} is the temperature assigned to the i-th and k-th levels. Thus, for three states, three temperatures can be defined, having a correlation between them:

$$T_{12} + T_{23} = 2T_{13} \tag{15}$$

which means that only two of them are independent. At equilibrium, the three temperatures are identical

$$T_{12}^{\text{eq}} = T_{23}^{\text{eq}} = T_{13}^{\text{eq}} = T$$

In this case, the system is characterized by a single temperature.

A non-relaxed system has no unambiguous temperature, or more precisely, it has more temperatures simultaneously.

Far from equilibrium, negative partial temperatures can also exist (inverse population), e.g. for $n_3 \geq 13$ $T_{23} < 0$ (see Fig. 4).

$\ln x_i - E_i$ *plots. Equilibrium thermodynamic averages*

In Fig. 4, the $\ln x_i$ values characteristic for the population of individual energy levels are plotted against E_i values based on the data of columns 4, 5 and 6 in Table 2.

According to eq. (6), the reciprocal temperature is proportional to the (negative) slope of straight lines connecting two points. Till equilibrium is reached, to one distribution belong three straight lines with different slopes, as the three points do not fall on a straight line. During relaxation the three points approach a straight line, the slope of the lines approach each other and finally, at equilibrium, the three points lie on a single straight line, the three temperatures are identical.

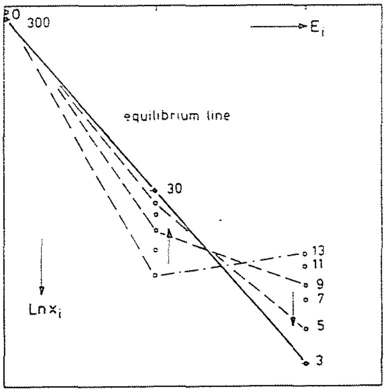

Fig. 4. Plot of the $\ln x_i$ values of the energy levels against E_i values

Table 3

i	E_i	n_i	x_i
1	0.E	300×10^0	$1.11^{-1} \times 10^0$
2	1.E	300×10^1	$1.11^{-1} \times 10^1$
3	2.E	300×10^2	$1.11^{-1} \times 10^2$

By this equilibrium straight line several thermodynamic quantities can be visualized, which correspond to different averages.

The equation of this equilibrium straight line is:

$$\ln x_i = -\ln Z - \frac{E_i}{RT} \tag{16}$$

where

$$Z = \sum e^{-E_i/RT} \tag{17}$$

is the "partition function"

On multiplying (16) by $-x_i$ and summation with respct to $\underline{i}$, and multiplying finally by RT, the following equation is obtained:

$$-RT\sum_i x_i \ln x_i = RT\ln Z + \sum_i x_i E_i \tag{18}$$

$$TS \quad = \quad -A \;+\; U \tag{19}$$

where in (19) the appropriate basic thermodynamic quantities are substituted. In obtaining (18), $\ln Z$ was factored out, and it was considered that $\sum_i x_i = 1$.

In eq. (19) there is a quantity not mentioned so far, this is the "free energy", A.

According to our interpretation, certain averages have been used:

Entropy:

$S = R\sum_i x_i \ln x_i$, average of $\ln x_i$-s.

Internal energy:

$U = \sum_i x_i E_i$, average of E_i-s.

Free energy:

$A = RT\ln Z$, which is a result of a special averaging:

$$A = [D^{-1}B^{-1}CBD] \quad (E_i)$$

where C, B and D symbolize different operations applied for energies E_i in the following sequence:

D: division by $-RT$,
B: construction of an exponential function,
C: summation,
B^{-1}: inverse operation of B (construction of a logarithmic function)
D^{-1}: inverse operation of D (multiplication by $-RT$)

The operator for total averaging is an operation "similar" to operation C.

These averages are shown in Fig. 5 by the application of the straight line $\ln x_i - E_i$.

Based on the above, the effect of temperature can also be deduced:

if the temperature increases:
the slope of the $\ln x_i - E_i$ line *decreases*, the intersection is shifted downwards. As a consequence of this: the internal energy (U) increases, entropy (S) increases, free energy (A) increases.

Summing up the above: we demonstrated by calculation on two thermodynamic model systems that already in such simple cases, the most important thermal properties can be interpreted. They behave similarly to real systems in their basic properties. It could be shown what negative temperature means and what the entropy and heat capacity of such systems are. On considering three possible states, equilibrium and non-equilibrium states could be compared. We have shown, by a kinetic method, how equilibrium is reached, why entropy is a maximum at equilibrium, and why it does increase if there is no equilibrium. By this method we could demonstrate the simplest elemental system which can have a temperature, and show why a non-equilibrium system did not have a definite temperature, and how it did transform into an equilibrium one with a uniform temperature. Finally, it has been shown how the different averages (entropy, internal energy, free energy) can be visualized by $\ln x_i - E_i$ plots.

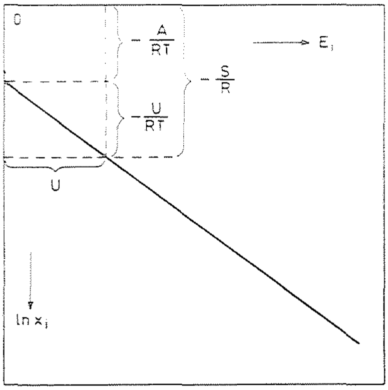

Fig. 5. Interpretation of the thermodynamical quantities U, S, and A on a $\ln x_i - E_i$ diagram

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