KFKI-1983-10

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BUDAPEST

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ABSTRACT

A simple method is proposed for obtaining the generally accepted formula of the concentration dependence of entropy in ideal solutions. The derivation, while implying a new definition of ideal mixtures, is independent both of macroscopic material properties and microscopic models.

АННОТАЦИЯ

Предложен простой метод получения общепринятой формулы концентрационной зависимости энтропии в идеальных растворах. Математическое описание, включающее новое определение идеальных растворов, не зависит ни от макроскопических свойств материалов, ни от микроскопических моделей.

KIVONAT

Ideális elegyek koncentrációtól függő entrópiájának levezetésére egyszerü módszert javasolunk. Az eljárás, amely az ideális elegyek egy uj definicióján alapszik, független,mind makroszkópos anyagi tulajdonságoktól, mind mikroszkópos modellektől.

INTRODUCTION

In one of his most important contributions Baxendale[1] showed
how radiation chemical kinetics could give rise to basic ideas in
thermodynamics. Treating the kinetic behaviour of hydrated elec-
trons he succeded in developing a new, physically reasonable zero
point of the electrode potential scale. In keeping rather with
the spirit of this work than with its method, we suggest here a
new derivation for the entropy of mixing as a function of con-
centration, starting out from certain ideas relevant to radiation
chemistry.

Spontaneous mixing has long been regarded as an archetype of
isothermal irreversible processes. Particularly the formation of
ideal mixtures, where neither change in volume nor heat effect ac-
companies mixing, demonstrates clearly that it is not mechanical
work or heat that drives mixing but an increase in entropy.

The difference between the entropy of a mixture and that of
the pure components is called entropy of mixing, ΔS_m which, for
two component ideal mixtures, is usually given as

$$\Delta S_m^{id} = -kn[x \ln x + (1-x)\ln(1-x)] \qquad (1)$$

where k is Boltzmann's constant, n the number of molecules in the
mixture, x and (1-x) are the mole fractions of the components.

Important as the notion and concentration dependence of ΔS_m^{id}
are the deduction of eq.(1), as handed down from Gibbs[2] up till
the present, cannot be regarded as conceptually flawless. Macro-
scopic thermodynamic development rests on the perfect gas equa-
tion of state (e.g. Refs. 3-7). Calculating the mechanical work
done by pure perfect gases when becoming mixed (or what amounts
to the same thing, the work needed for demixing a perfect gas
mixture), one obtains eq.(1). The generalization of this express-

ion for substances other than perfect gases inescapably involves
some approximations. Whereas mixing in the liquid phase is de-
scribed in terms of mixing in the equilibrium vapour phase one
has (a) to <u>define</u> an ideal solution as a system where the fugacity
of each component is proportional to the corresponding mole frac-
tion in the entire concentration range and (b) to <u>neglect</u> either
the volume or the compressibility of the condensed phase[5,8].

Ideal solutions can be defined in an alternative way[9] as sys-
tems in which the chemical potentials of the components are given
by the expression

$$\mu^{id} = \mu_o + RT \ln x \tag{2}$$

This expression leads directly to eq.(1) and, being a definition,
cannot be argued about. It is, however, the same thing as if
eq.(1) were regarded as a definition of the entropy of mixing and
its derivation from more elementary principles were being waived.

The statistical mechanical derivation of the entropy of mix-
ing is based on the change in the number of configurations due to
the presence of two components instead of one (e.g. Refs. 10,11).
The expression for ΔS_m^{id} is then calculated by the Boltzmann rela-
tionship as

$$\Delta S_m^{id} = k \ln \frac{W_{mixture}^{id}}{W_{components}} \tag{3}$$

where $W_{components}$ denotes the total number of configurations in
the pure components and $W_{mixture}^{id}$ that in the ideal mixture. This
calculation can be carried out regorously only if the molecules
of the pure components are distinguishable. This is so with crys-
tals where the molecular sites are fixed hence molecules can be
distinguished by their space coordinates. In this case eq.(3)
leads to eq.(1). With liquid solutions, however, some approxima-
tions like the cage model must be involved[11] in order to justify
the simple combinatorics used for evaluating the RHS of eq.(3).

Recently a mathematical discussion[12,13] was presented on the
"entropy of taking a statistical mixture" to be "distinguished
from the often discussed 'entropy of mixing' which, while related,

is distinct" showing the entropy to increase due to mixing without offering any functional dependence of entropy on concentration.

When dealing with electron and hole transport in irradiated liquid mixtures[14,15] we had to determine the probability of small liquid regions occurring which regions, due to fluctuations, consist of the molecules of one component only. The occurrence of such "pure" regions, as is always the case in the theory of fluctuations, is closely connected with entropy changes. Generalizing some of our considerations made in this context, in the present paper we propose a new derivation for eq.(1) which, while based on eq.(3) and on simple statistical rules, involves a definition of ideal mixtures which is thought to be intuitively self-evident.

DERIVATION OF ENTROPY OF MIXING AS A FUNCTION OF CONCENTRATION

Let a mixture consist of n molecules, nx of them being of type A, n(1-x) of them of type B. Without any loss of generality one can always take inequality $x \leq (1-x)$ to prevail.

Now consider the mixture to be transferred molecule by molecule into an empty container. The probability of putting one molecule of A into the empty container is denoted by p. If the mixture is ideal differences in molecular volumes or intermolecular energies play no role in the random selection of molecules hence p is determined solely by the relative number of the component molecules.

Let an ideal mixture be defined by the expression

$$p = x \qquad , \qquad \qquad (4)$$

i.e. the probability of finding one molecule of a given component is equal to its mole fraction. We hope this definition to be graphic enough to be accepted as a reasonable point of departure.

The probability of transferring one molecule of A equals x. The probability of trasferring two molecules of A is, however, smaller than x^2 since the mole fraction of A in the mixture has become smaller after extracting the first A molecule. Generally

speaking the mole fraction becomes smaller and smaller as more and more A molecules have been transferred. After the transference of (i-1) molecules of A the mole fraction of A in the mixture, x_i, is given as

$$x_i = \frac{nx - (i-1)}{n - (i-1)} \qquad (5)$$

This is so because (i-1) molecules of A have been extracted thus one has to decrease by this amount both the initial number of A molecules and the total initial number of molecules in order to find x_i.

The probability of putting one A molecule only into the empty container is $p_1 = x_1 = x$; that of putting two A molecules only is $p_2 = x_1 x_2$ etc. The probability of putting ℓ molecules of A only into the empty container from the mixture is given as

$$p_\ell = \prod_{i=1}^{\ell} x_i = \prod_{i=1}^{\ell} \frac{nx - (i-1)}{n - (i-1)} \; . \qquad (6)$$

Let ℓ be the total number of A molecules in the mixture, $\ell = nx$. Thus the extraction of ℓ molecules of A without any single molecule of B means complete demixing of the ideal mixture. This renders p_ℓ identical with p_{dem}^{id}, the probability of demixing of an ideal mixture.

Now we can evaluate eq.(6). Let if first be rewritten as

$$p_{dem}^{id} = p_\ell = \frac{\dfrac{(nx)!}{(nx-\ell)!}}{\dfrac{n!}{(n-\ell)!}} \; . \qquad (7)$$

Recalling Stirling approximation, inserting ℓ and knowing that $0!=1$ the logarithm of eq.(7) becomes

$$\ln p_{dem}^{id} = n \left[x \ln x + (1-x) \ln (1-x) \right] \qquad (8)$$

This is the probability of demixing of an ideal mixture.

The probability of demixing is equal to the number of configurations in the pure components divided by those in the mixture,

$$p_{dem}^{id} = \frac{W_{components}}{W_{mixture}} \tag{9}$$

Hence, comparing eqs.(3),(8) and (9) one finds

$$\Delta S_m^{id} = -k \ln p_{dem}^{id} = -kn[x \ln x + (1-x)\ln(1-x)] \tag{1'}$$

thus obtaining the entropy of mixing. By this we have proved eq. (1).

DISCUSSION

The community of chemists and physicists has had little doubt regarding the entropy of mixing as expressed by eq.(1). They have been believing that a formula which was found to be correct for perfect gases and for crystals must hold also for intermediate states, whatever the word "intermediate" means in this context. The novelty of the present argument lies in its approach of abandoning both macroscopic material properties and microscopic models thus showing eq.(1) to be generally valid.

This has been achieved by a new definition of the ideal mixture, eq.(4), which while we believe it to be almost self-evident, has turned out to be equivalent with the conventional definition, eq.(2). Their equivalence has been proved solely by recovering eq.(1) using either of the two equations.
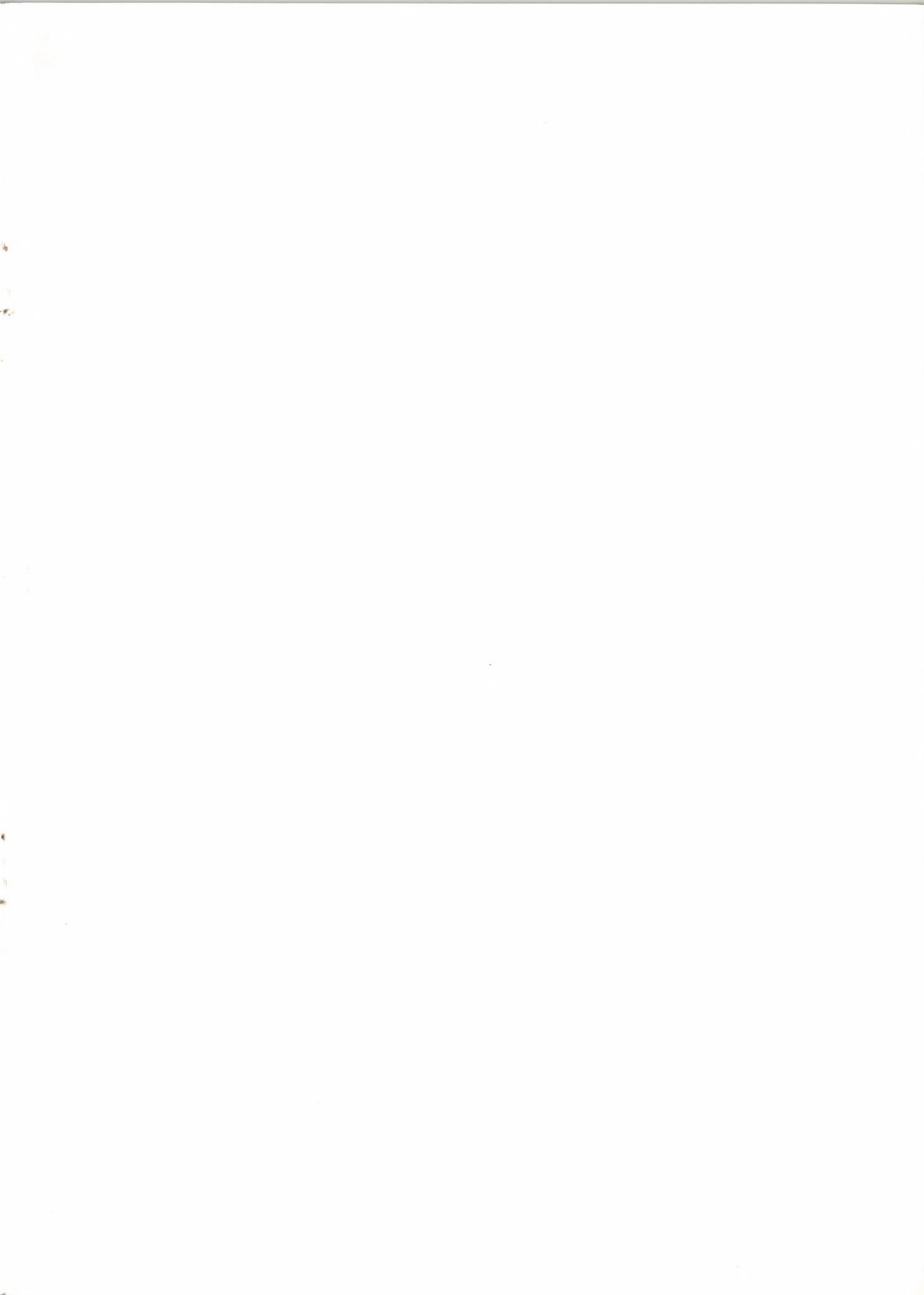
In spite of Boltzmann's statistical mechanical entropy being involved the above treatment is macroscopic in nature. It is related much more to the idea of isothermal demixing by semipermeable membrances than to the enumeration of configurations and the determination of most probable distributions. One may recall an idea of Callen[16] in this context: he introduced Boltzmann's entropy expression as an independent postulate in order to describe statistical fluctuations within the framework of macroscopic thermodynamics.

ACKNOWLEDGEMENT

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