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CHEMICAL THERMODYNAMICS AND THERMOCHEMISTR

System with Variable Energy, Volume and Number of Particles: Evaluation of Partition Function and Thermodynamic Quantities[1]

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Abstract—Partition function and thermodynamic parameters of the system open with respect to energy E, volume V and number of particles N, whereas temperature T, chemical potential μ and pressure P were kept constant, were considered by the procedure proposed by Gibbs. The mean values of variable energy, volume and number of particles were obtained by universal expression for such values. The entropy was determined by its general statistical definition. The thermodynamic potential and other thermodynamic quantities were also turned out naturally.

Keywords: System with variable energy, volume and number of particles, partition function, thermodynamic quantities, entropy.

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INTRODUCTION

The aim of this paper is to derive the partition function and thermodynamic quantities for a system that exchanges energy E, volume V and number of particles N with the reservoir, the system which we shall call henceforth totally open system. The analysed system is in thermal, chemical and mechanical equilibrium with the environment. That means to take temperature T, chemical potential μ and pressure P constant. In the literature available to the authors, the consideration of such system from statistical thermodynamic point of view is not found, whereas the analogue analysis of a system open with respect to energy, energy and volume, or, energy and number of particles is widespread [1–30].

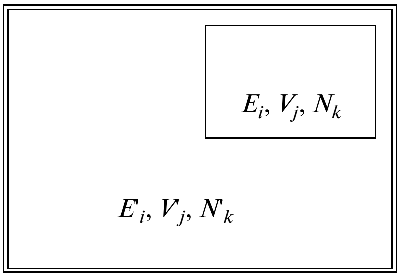
RESULTS

The Partition Function of an Imaginary Totally Open System

To define the expression for the partition function of the system, we shall start from the expression for the probability that the analyzed system has the energy E_i, the volume V_j, and the number of particles N_k, $W(E_i, V_j, N_k)$. This system is in equilibrium with the reservoir with the energy E_i', the volume V_j' and the number of particles N_k'. The total energy of the reservoir and the system E^0, the total volume V^0 and the total number of particles N^0 are constant (figure):

$$\begin{aligned} E^0 &= E_i + E_i' = \text{const}, \\ V^0 &= V_j + V_j' = \text{const}, \\ N^0 &= N_k + N_k'. \end{aligned} \tag{1}$$

In other words, the whole system (reservoir + considered system) is isolated from the surrounding and in a state of mutual equilibrium. Therefore, if $g(E_i, V_j, N_k)$ is the number of different states of the considered system with energy E_i, the volume V_j, and the number of particles N_k, and $g(E_i', V_j', N_k')$ is the number of different states of the reservoir with the energy E_i', the volume V_j' and the number of particles N_k', the proba-



The system in the thermodynamic equilibrium with the reservoir.

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bility $W(E_i, V_j, N_k)$ is directly proportional to their product:

$$W(E_i, V_j, N_k) = Ag(E'_i, V'_j, N'_k)g(E_i, V_j, N_k). \qquad (2)$$

The system is much smaller than the reservoir, its energy, volume and the number of particles contained in it is small in comparison with the energy volume and number of particles in the reservoir:

$$E_i > E'_i, \quad V_j > V'_j, \quad \text{and} \quad N_k > N'_k. \qquad (3)$$

Hence, we can expand the function $\ln g(E'_i, V'_j, N'_k)$ in a Taylor series in a neighbourhood of the point ($E'_i = E^0 - E_i \approx E^0$, $V'_j = V^0 - V_j \approx V^0$, $N'_k = N^0 - N_k \approx N^0$) and lock up ourselves to the linear terms of the expansion. In the obtained expression:

$$\begin{aligned}\ln g(E'_i, V'_j, N'_k) &\approx \ln g(E^0, V^0, N^0) - E_i\frac{\partial \ln g(E^0, V^0, N^0)}{\partial E^0}\\ &- V_j\frac{\partial \ln g(E^0, V^0, N^0)}{\partial V^0} - N_k\frac{\partial \ln g(E^0, V^0, N^0)}{\partial N^0} = \alpha;\end{aligned} \qquad (4)$$

we can introduce indefinite multipliers α, β and γ:

$$\begin{aligned}\partial \ln g(E^0, V^0, N^0)/\partial E^0 &= \beta,\\ \partial \ln g(E^0, V^0, N^0)/\partial V^0 &= \gamma,\\ \partial \ln g(E^0, V^0, N^0)/\partial N^0 &= \alpha\end{aligned} \qquad (5)$$

and easily obtain $W(E_i, V_j, N_k)$ in the form:

$$\begin{aligned}W(E_i, V_j, N_k) &= Ag(E_i, V_j, N_k)g(E^0, V^0, N^0)\\ &\times \exp(-\beta E_i - \gamma V_j - \alpha N_k).\end{aligned} \qquad (6)$$

Since, each partial derivative of any quantity with respect to one parameter implies that all other parameters of which the quantity depends on are constant, we can drop the indication what is constant in expressions (4) and (5), for brevity. The value of the constant A can be determined from the normalization condition:

$$\sum_i\sum_j\sum_k W(E_i, V_j, N_k) = 1. \qquad (7)$$

The probability distribution of the states of a system with variable energy, volume and number of particles can finally be written in the form:

$$\begin{aligned}&W(E_i, V_j, N_k)\\ &= \frac{g(E_i, V_j, N_k)\exp(-\beta E_i - \gamma V_j - \alpha N_k)}{\sum_i\sum_j\sum_k g(E_i, V_j, N_k)\exp(-\beta E_i - \gamma V_j - \alpha N_k)}.\end{aligned} \qquad (8)$$

Taking into account physical meaning of the indefinite multipliers α, β and γ (Appendix) the probability that the system has the energy E_i, the volume V_j, and the number of particles N_k is:

$$\begin{aligned}&W(E_i, V_j, N_k)\\ &= \frac{g(E_i, V_j, N_k)\exp\left(\frac{\mu N_k - E_i - PV_j}{k_B T}\right)}{\sum_i\sum_j\sum_k g(E_i, V_j, N_k)\exp\left(\frac{\mu N_k - E_i - PV_j}{k_B T}\right)}.\end{aligned} \qquad (9)$$

Here, the number of different states with same energy, volume and number of particles $g(E_i, N_k, V_j)$ is the well known degeneracy or the statistical weight of this system [6]. The expression in the denominator (9) is the corresponding partition function or statistical sum, i.e. the total number of different states of the system under consideration:

$$\begin{aligned}&\Pi(T, P, \mu)\\ &= \sum_i\sum_j\sum_k g(E_i, V_j, N_k)\exp\left(\frac{\mu N_k - E_i - PV_j}{k_B T}\right).\end{aligned} \qquad (10)$$

The summation in the denominator goes over all the states accessible to the system. However, the probability to find a system in all states with the energy E_i, the volume V_j, and the number of particles N_k differs from the probability that the system will be in one state with energy E_i, the volume V_j, and the number of particles N_k for the statistical wait g.

Thermodynamic Functions

The evaluation of thermodynamic quantities for totally open system has been done in analogy with the deriving of corresponding expressions for the thermodynamic quantities of other types of systems that are common in literature which exchange less than three quantities with the environment: isolated, closed, open and isothermal-isobaric system.

@Mean values of energy, volume and number of particles.@ Knowing the probability distribution $W(E_i, V_j, N_k)$ we can find the mean values of energy, volume and number of particles by definition for mean values of any quantity. Thus,

$$\begin{aligned}\bar{E} &= \sum_i\sum_j\sum_k E_i W(E_i, V_j, N_k)\\ &= \frac{1}{\Pi}\sum_i\sum_j\sum_k E_i g\exp\left(\frac{\mu N_k - E_i - PV_j}{k_B T}\right),\end{aligned} \qquad (11)$$

$$\begin{aligned}\bar{V} &= \sum_i\sum_j\sum_k V_j W(E_i, V_j, N_k)\\ &= \frac{1}{\Pi}\sum_i\sum_j\sum_k V_j g\exp\left(\frac{\mu N_k - E_i - PV_j}{k_B T}\right),\end{aligned} \qquad (12)$$

$$\begin{aligned}\bar{N} &= \sum_i\sum_j\sum_k N_k W(E_i, V_j, N_k) \\ &= \frac{1}{\Pi}\sum_i\sum_j\sum_k N_k g \exp\left(\frac{\mu N_k - E_i - PV_j}{k_\mathrm{B}T}\right).\end{aligned} \tag{13}$$

Let us start with the expression for the mean number of particles in terms of the partition function and parameters of the system (T, μ, $P = \mathrm{const}$). It can be easily obtained by differentiating the partition function with respect to chemical potential only:

$$\begin{aligned}\left(\frac{\partial \Pi}{\partial \mu}\right)_{T,P} &= \frac{1}{k_\mathrm{B}T}\sum_i\sum_j\sum_k N_k g \exp\left(\frac{\mu N_k - E_i - PV_j}{k_\mathrm{B}T}\right) \\ &= \frac{\Pi \bar{N}}{k_\mathrm{B}T}.\end{aligned} \tag{14}$$

Thus, the expression for the mean number of particles is:

$$\bar{N} = k_\mathrm{B}T(\partial \ln\Pi/\partial\mu)_{T,P}. \tag{15}$$

The expression for the mean volume of the system in terms of the partition function and the parameters of the system (T, μ, $P = \mathrm{const}$) can be obtained by differentiating the partition function with respect to the pressure:

$$\begin{aligned}\left(\frac{\partial \Pi}{\partial P}\right)_{T,\mu} &= \frac{1}{k_\mathrm{B}T}\sum_i\sum_j\sum_k g \exp\left(\frac{\mu N_k - E_i - PV_j}{k_\mathrm{B}T}\right)(-V_j) \\ &= -\frac{\Pi \bar{V}}{k_\mathrm{B}T},\end{aligned} \tag{16}$$

and the expression for the mean volume of the system is:

$$\bar{V} = -k_\mathrm{B}T\left(\frac{\partial \ln\Pi}{\partial P}\right)_{\mu,T}. \tag{17}$$

The mean energy of this system in terms of the partition function and the parameters of the system (T, μ, $P = \mathrm{const}$) can be obtained by differentiating the partition function with respect to the temperature:

$$\begin{aligned}\left(\frac{\partial \Pi}{\partial T}\right)_{P,\mu} &= -\frac{1}{k_\mathrm{B}T^2}\sum_i\sum_j\sum_k g \exp\left(\frac{\mu N_k - E_i - PV_j}{k_\mathrm{B}T}\right) \\ &\times(\mu N_k - E_i - PV_j) = -\frac{\Pi}{k_\mathrm{B}T^2}(\mu\bar{N} - \bar{E} - P\bar{V}).\end{aligned} \tag{18}$$

Thus, the mean energy of the system is:

$$\bar{E} = \mu\bar{N} - P\bar{V} + k_\mathrm{B}T^2\left(\frac{\partial \ln\Pi}{\partial T}\right)_{\mu,P}. \tag{19}$$

Using the expressions for the mean values of the number of particles (15) and the volume (17) we can easily obtain:

$$\begin{aligned}\bar{E} &= \mu k_\mathrm{B}T\left(\frac{\partial \ln\Pi}{\partial \mu}\right)_{P,T} + Pk_\mathrm{B}T\left(\frac{\partial \ln\Pi}{\partial P}\right)_{\mu,T} \\ &+ k_\mathrm{B}T^2\left(\frac{\partial \ln\Pi}{\partial T}\right)_{\mu,P}.\end{aligned} \tag{20}$$

Entropy. Using the general definition of entropy given by Gibbs [6]:

$$\begin{aligned}S &= -k\sum_i\sum_j\sum_k W(E_i, V_j, N_k)\ln W(E_i, V_j, N_k) \\ &= -k_\mathrm{B}\langle \ln W\rangle,\end{aligned} \tag{21}$$

and the probability that system will be in a state with the energy E_i, the volume V_j, and the number of particles N_k:

$$W(E_i, V_j, N_k) = \exp\left(\frac{\mu N_k - E_i - PV_j}{k_\mathrm{B}T}\right)/\Pi, \tag{22}$$

we can easily obtain expression:

$$\begin{aligned}S &= -k_\mathrm{B}\sum_i\sum_j\sum_k W(E_i, V_j, N_k) \\ &\times\left(\frac{\mu N_k}{k_\mathrm{B}T} - \frac{E_i}{k_\mathrm{B}T} - \frac{PV_j}{k_\mathrm{B}T} - \ln\Pi\right),\end{aligned} \tag{23}$$

which directly gives the relation:

$$S = -\frac{\mu\bar{N}}{T} + \frac{\bar{E}}{T} + \frac{P\bar{V}}{T} + k_\mathrm{B}\ln\Pi. \tag{24}$$

Thermodynamic potential. From the last equation we can see that

$$\bar{E} - TS = \mu\bar{N} - P\bar{V} - k_\mathrm{B}T\ln\Pi. \tag{25}$$

The expression $\bar{E} - TS$ is equal to the Helmolz free energy A. The total differential of the Helmholtz free energy A:

$$dA = \mu d\bar{N} + \bar{N}d\mu - Pd\bar{V} - \bar{V}dP - k_\mathrm{B}d(T\ln\Pi) \tag{26}$$

can be compared with the corresponding thermodynamic expression where $V = \bar{V}$ and $N = \bar{N}$:

$$dA = -SdT - Pd\bar{V} + \mu d\bar{N} \tag{27}$$

resulting in:

$$-k_\mathrm{B}d(T\ln\Pi) = -SdT + \bar{V}dP - \bar{N}d\mu. \tag{28}$$

In general, the thermodynamic potential is defined as $X = -k_\mathrm{B}T\ln Y$, where Y is the partition function of any considered system. In this case, $X = -k_\mathrm{B}T\ln\Pi$ such that:

$$dX = -SdT + \bar{V}dP - \bar{N}d\mu. \tag{29}$$

The partition functions, thermodynamic potential and thermodynamic functions derived under different conditions

Isolated system, Microcanonical ensemble	
$g(E,V,N)$ $S=k\ln g$ $dS=\frac{1}{T}dE+\frac{P}{T}dV-\frac{\mu}{T}dN$	$\frac{1}{T}=\left(\frac{\partial S}{\partial E}\right)_{N,V}=k\left(\frac{\partial\ln g}{\partial E}\right)_{N,V}=k\beta$ $\frac{P}{T}=\left(\frac{\partial S}{\partial V}\right)_{N,E}=k\left(\frac{\partial\ln g}{\partial V}\right)_{N,E}=k\gamma$ $\frac{\mu}{T}=-\left(\frac{\partial S}{\partial N}\right)_{E,V}=-k\left(\frac{\partial\ln g}{\partial N}\right)_{E,V}=-k\alpha$
Closed system, open system with respect to *E*, canonical ensemble	
$Z(T,V,N)$ $Z=\sum_i g(E_i)e^{-E_i/kT}$ $A=-kT\ln Z$ $dA=-SdT-PdV-\mu Nd$	$S=-\left(\frac{\partial A}{\partial T}\right)_{V,N}=k\ln Z+kT\left(\frac{\partial\ln Z}{\partial T}\right)_{V,N}$ $P=-\left(\frac{\partial A}{\partial V}\right)_{T,N}=kT\left(\frac{\partial\ln Z}{\partial V}\right)_{T,N}$ $\mu=\left(\frac{\partial A}{\partial N}\right)_{V,T}=-kT\left(\frac{\partial\ln Z}{\partial N}\right)_{V,T}$
Open system with respect to *E* and *N*, grand canonical ensemble	
$\Xi(T,V,\mu)$ $\Xi=\sum_i\sum_k g(E_i,N_k)\exp(\mu N_k-E_i/kT)$ $\Phi=-PV=-kT\ln\Xi$ $d\Phi=-SdT-PdV-Nd\mu$	$S=-\left(\frac{\partial\phi}{\partial T}\right)_{V,\mu}=k\ln\Xi+kT\left(\frac{\partial\ln\Xi}{\partial T}\right)_{V,\mu}$ $P=-\left(\frac{\partial\phi}{\partial V}\right)_{T,\mu}=kT\left(\frac{\partial\ln\Xi}{\partial V}\right)_{T,\mu}=kT\frac{\ln\Xi}{V}$ $N=-\left(\frac{\partial\phi}{\partial\mu}\right)_{V,T}=kT\left(\frac{\partial\ln\Xi}{\partial\mu}\right)_{V,T}$
Open system with respect to *E* and *V*, isothermal-isobaric canonical ensemble	
$\Delta(T,P,N)$ $\Delta=\sum_i\sum_j g(E_i,V_j)e^{\frac{-E_i-PV_j}{kT}}$ $G=-kT\ln\Delta$ $dG=-SdT+VdP+\mu dN$	$S=-\left(\frac{\partial G}{\partial T}\right)_{N,P}=k\ln\Delta+kT\left(\frac{\partial\ln\Delta}{\partial T}\right)_{N,P}$ $V=\left(\frac{\partial G}{\partial P}\right)_{T,N}=-kT\left(\frac{\partial\ln\Delta}{\partial P}\right)_{T,N}$ $\mu=\left(\frac{\partial G}{\partial N}\right)_{T,P}=-kT\left(\frac{\partial\ln\Xi}{\partial N}\right)_{T,P}$
Open system with respect to *E*, *V* and *N*	
$\Pi(T,P,\mu)$ $\Pi=\sum_i\sum_j\sum_k g(E_i,N_k,V_j)\exp(\mu N_k-E_i-PV_j/kT)$ $X=-kT\ln\Pi$ $dX=-SdT+VdP-Nd\mu$	$S=-\left(\frac{\partial X}{\partial T}\right)_{\mu,P}=k\ln\Pi+kT\left(\frac{\partial\ln\Pi}{\partial T}\right)_{\mu,P}$ $V=\left(\frac{\partial X}{\partial P}\right)_{T,\mu}=-kT\left(\frac{\partial\ln\Pi}{\partial P}\right)_{T,\mu}$ $N=-\left(\frac{\partial X}{\partial\mu}\right)_{T,P}=kT\left(\frac{\partial\ln\Pi}{\partial\mu}\right)_{T,P}$

From the last expression directly follows:

$$S=-\left(\frac{\partial X}{\partial T}\right)_{\mu,P}=-\frac{\partial}{\partial T}(-k_{\mathrm{B}}T\ln\Pi)=k_{\mathrm{B}}\ln\Pi+k_{\mathrm{B}}T\left(\frac{\partial\ln\Pi}{\partial T}\right)_{\mu,P},\quad(30)$$

$$\bar{V}=\left(\frac{\partial X}{\partial P}\right)_{T,\mu}=\frac{\partial}{\partial P}(-k_{\mathrm{B}}T\ln\Pi)=k_{\mathrm{B}}T\left(\frac{\partial\ln\Pi}{\partial P}\right)_{T,\mu},\quad(31)$$

$$\bar{N} = \left(\frac{\partial X}{\partial \mu}\right)_{T,P} = -\frac{\partial}{\partial \mu}(-k_B T \ln \Pi) \\ = k_B T\left(\frac{\partial \ln \Pi}{\partial \mu}\right)_{T,P}. \tag{32}$$

Other thermodynamic functions of the system, as the Helmholtz free energy, the Gibbs free energy, enthalpy and heat capacity, can be expressed simply by substituting the obtained expressions for the entropy, the mean number of particles and the mean volume into the classical thermodynamic expressions. Thus, we get for the Gibbs energy:

$$G = \mu k_B T\left(\frac{\partial \ln \Pi}{\partial \mu}\right)_{P,T} - k_B T \ln \Pi; \tag{33}$$

for the Helmholtz free energy:

$$A = \mu k_B T\left(\frac{\partial \ln \Pi}{\partial \mu}\right)_{P,T} + P k_B T\left(\frac{\partial \ln \Pi}{\partial P}\right)_{\mu,T} \\ - k_B T \ln \Pi; \tag{34}$$

for enthalpy:

$$H = \mu k_B T\left(\frac{\partial \ln \Pi}{\partial \mu}\right)_{P,T} + k_B T^2\left(\frac{\partial \ln \Pi}{\partial T}\right)_{\mu,P}; \tag{35}$$

for isochoric heat capacity:

$$C_V = 2k_B T\left(\frac{\partial \ln \Pi}{\partial T}\right)_{\mu,P} + k_B T^2\left(\frac{\partial \ln \Pi}{\partial T^2}\right)_{\mu,P}; \tag{36}$$

for isobaric heat capacity:

$$C_P = \mu k_B\left(\frac{\partial \ln \Pi}{\partial \mu}\right)_{P,T} + \mu k_B T\left(\frac{\partial^2 \ln \Pi}{\partial \mu \partial T}\right)_{P} \\ + 2k_B T\left(\frac{\partial \ln \Pi}{\partial T}\right)_{\mu,P} + k_B T^2\left(\frac{\partial^2 \ln \Pi}{\partial T^2}\right)_{\mu,P}; \tag{37}$$

and for the difference of the isochoric and isobaric heat capacities:

$$C_P - C_V = \mu k\left(\frac{\partial \ln \Pi}{\partial \mu}\right)_{P,T} + \mu k_B T\left(\frac{\partial^2 \ln \Pi}{\partial \mu \partial T}\right)_{P}. \tag{38}$$

DISCUSSION

The obtained thermodynamic functions are compared with the corresponding ones evaluated when the system is isolated or open with respect to energy, energy and volume, or, energy and number of particles (table). In table are given common names of ensembles, their partition functions with the constant parameters denoted in brackets and expression for corresponding thermodynamic potential as the basic relation for calculation of thermodynamic functions.

All derived thermodynamic quantities are the same functions of the partition function; the only difference is that the partition function has different value for different systems. If the partition function is labelled as Y, the entropy for every system with variable energy is in the following form:

$$S = k_B \ln Y + k_B T\left(\frac{\partial \ln Y}{\partial T}\right)_{\mu,P}. \tag{39}$$

For systems with variable number of particles, the mean number of particles is:

$$\bar{N} = k_B T\left(\frac{\partial \ln Y}{\partial \mu}\right)_{P,T}, \tag{40}$$

while for systems with variable volume, the mean volume is:

$$\bar{V} = -k_B T\left(\frac{\partial \ln Y}{\partial P}\right)_{\mu,T}. \tag{41}$$

CONCLUSION

Thermodynamic quantities of the totally open system in terms of the partition function Π and parameters of the system T, μ and P are derived in analogy with other systems in literature. For this purpose, thermodynamic potential of the form $X = -k_B T \ln \Pi$ is defined. As considered system is open with respect to energy, volume and number of particles, their mean values are also obtained directly by universal expression for such values. Moreover, the entropy is determined by its general statistical definition. Thus, it is shown that the hypothetic system with variable energy, volume and number of particles is the best one for natural evaluation of all thermodynamic quantities.

APPENDIX 1. THE PHYSICAL MEANING OF PARAMETERS A, B AND Γ

There are different manners to find the physical meaning of parameters α, β and γ, that is, to express them in function of well known quantities in classical thermodynamics. With aim to complete the derivation of probability distribution of the states of a system with variable energy, volume and number of particles, we shall briefly present one of them [9].

Since the partition function of isolated system known as statistical weight or degeneracy $g(E, V, N)$ is a function of energy, volume and number of particles, the total differential of $\ln g$ can be expressed as:

$$d\ln g(E, V, N) = \left(\frac{\partial \ln g(E, V, N)}{\partial E}\right)_{V,N} dE \\ + \left(\frac{\partial \ln g(E, V, N)}{\partial V}\right)_{E,N} dV + \left(\frac{\partial \ln g(E, V, N)}{\partial N}\right)_{E,V} dN \\ = \beta dE + \gamma dV + \alpha dN, \tag{A1}$$

where parameters α, β and γ are equal to the ones defined in equation (5). Therefore, the last expression can be rewritten in the form:

$$dE = \frac{1}{\beta}d\ln g - \frac{\gamma}{\beta}dV - \frac{\alpha}{\beta}dN. \qquad \text{(A2)}$$

and compared to the classical one which correlate dE, dV and dN

$$dE = TdS - PdV + \mu dN. \qquad \text{(A3)}$$

If $S = k_B \ln g$, it follows that the parameters α, β and γ are equal to:

$$\alpha = -\frac{\mu}{k_B T}, \quad \beta = \frac{1}{k_B T}, \quad \text{and} \quad \gamma = \frac{P}{k_B T}. \qquad \text{(A4)}$$

With aim to show that $S = k_B \ln g$, we need to consider a system A^0, made of two subsystems such that $A^0 = A_1 + A_2$, each of which in equilibrium, and apply on them one by one statistical and classical thermodynamic knowledge. From statistical point of view, the number of microstates for the total system $g^0(E_1, E_2)$ is equal to the product of the numbers of microstates for the two initial systems $g_1(E_1)$ and $g_2(E_2)$:

$$g^0(E_1, E_2) = g_1(E_1)g_2(E_2). \qquad \text{(A5)}$$

If they are in a thermal contact exchanging the energy, the equilibrium will be achieved when the number of microstates for the total system is maximal:

$$\partial g^0(E_1)/\partial E_1 = 0. \qquad \text{(A6)}$$

Since $E^0 = E_1 + E_2 = \text{const}$, we can easily obtain the relation:

$$\begin{aligned}\frac{\partial g^0(E_1, E_2)}{\partial E_1} &= \frac{\partial g_1(E_1)}{\partial E_1}g_2(E_2) \\ &+ g_1(E_1)\frac{\partial g_2(E_2)}{\partial E_2}\frac{\partial E_2}{\partial E_1},\end{aligned} \qquad \text{(A7)}$$

which ensues:

$$\partial \ln g_1(E_1)/\partial E_1 = \partial \ln g_2(E_2)/\partial E_2. \qquad \text{(A8)}$$

Taking into account expression:

$$\partial \ln g(E)/\partial E = \beta, \qquad \text{(A9)}$$

we obtain that all subsystems in thermal equilibrium must satisfy the following condition:

$$\beta_1 = \beta_2 = \beta = \text{const}. \qquad \text{(A10)}$$

Furthermore, considering the entropy of the combined subsystem A^0, one comes to the physical meaning of parameter β. Its entropy is the sum of entropies of two subsystems:

$$S^0(E_1, E_2) = S_1(E_1) + S_2(E_2). \qquad \text{(A11)}$$

Since the entropy of the total system is maximal in equilibrium, we obtain:

$$\frac{\partial S_1(E_1)}{\partial E_1} = \frac{\partial S_2(E_2)}{\partial E_2} = \frac{\partial S}{\partial E} = \text{const}. \qquad \text{(A12)}$$

The entropy of the system with a constant volume and number of particles, in classical thermodynamics is:

$$dS = dE/T, \qquad \text{(A13)}$$

such that:

$$(\partial S/\partial E)_{N, V} = 1/T. \qquad \text{(A14)}$$

It follows that the systems are in thermal equilibrium when their temperatures are equal and constant. Since the parameters β have same characteristics for the systems in thermal equilibrium (A10), it follows that there must be direct relation between T and β. Considering (A9) and (A14) it follows that:

$$d\ln g/dS = \beta T. \qquad \text{(A15)}$$

Since both β and T are constants, their product will also be a constant:

$$\beta T = 1/T, \qquad \text{(A16)}$$

where k is the Boltzmann's constant. It follows that the parameter β is equal to:

$$\beta = 1/k_B T. \qquad \text{(A17)}$$

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