THE EXTENSION OF CLASSICAL PHENOMENOLOGICAL THERMODYNAMICS TO OPEN SYSTEMS (THE CHEMICAL POTENTIAL)

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ABSTRACT

The traditional introduction of the chemical potential is through the assumption that the entropy is a differentiable function of U, V and the molar quantities of the chemical components; but entropy and energy functions are defined only for states of closed systems. An alternative introduction is accordingly given here. It meets this difficulty, and is in accordance with recent axiomatizations. An outline of the proposal is given, followed by a critical analysis of the assumptions involved.

Traditional thermodynamics introduces the chemical potential starting from the assumption that the entropy S of an open system can be regarded as a differentiable function of the internal energy U, the volume V and the molar quantities of the different components N_α, N_β, ... However, the definitions of S and U refer to adiabatic linkage, and this presumes closed systems.

Landsberg[1] meets this criticism by the introduction of a "fourth law" which implies that for a certain class of systems (more precisely: for certain sets of states) the entropy is a first order homogeneous function of U, V, N_α, N_β, ... Tisza[2] introduces a phase postulate: a simple system exists potentially in a number of phases, which are spatially homogeneous material extensions, for which a continuous first order homogeneous phase entropy function $S(U, V, N_\alpha, N_\beta,...)$ is defined. Both assume the existence of a function $S(U, V, N_\alpha, N_\beta,...)$ for a precisely defined class of open systems, abandoning an operational definition of entropy and internal energy.

This paper intends to give an alternative, which does not take refuge in an assumption of the above kind, and is in accordance with the operational approach to entropy and internal energy of recent axiomatizations[3-7]: the domains of definition of entropy and energy functions remain restricted to closed systems. The approach is so simple, that it can serve to introduce the chemical potential in undergraduate courses. I will start with an outline, suitable for teaching; afterwards I will justify the assumptions which are involved and in doing so prepare a more formal theory.

Outline of a simple introduction of the chemical potential

Consider a system, which is materially connected with respect to the

component α with a homogeneous pure substance α, through a wall permeable exclusively for the component α. The two systems together, denoted by Z_{12}, are closed. The part systems are denoted by $Z_1^\star$ and $Z_2^\star$; the stars indicate that these systems are open (see *Figure 1*).
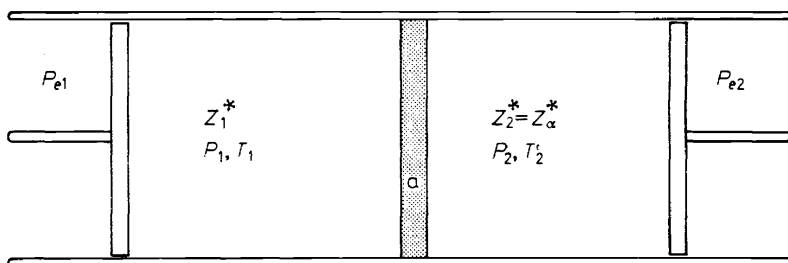

Figure 1. The pressures P_{e1} and P_{e2} of the environment are independently variable; the environment has a unique temperature T_e; a: wall permeable to component α exclusively; all other walls are diathermal, i.e. $T_1 = T_2 = T_e$; the pistons are freely movable, i.e. $P_1 = P_{e1}$, $P_2 = P_{2e}$.

For system Z_{12} an internal energy function U_{12} and an entropy function S_{12} are defined. The volumes V_1 and V_2 of the part systems and U_{12}, or S_{12}, form a complete set of independent variables of the system Z_{12}. (1)
For an infinitesimal quasistatic change of state of system Z_{12}:

$$dU_{12} = T\,dS_{12} - P_1\,dV_1 - P_2\,dV_2 \tag{2}$$

For the homogeneous pure substance $Z_2^\star$ one can write:

$$V_2 = N_\alpha^0 v_\alpha^0 \tag{3}$$

$$v_\alpha^0 = v_\alpha^0(P, T) \tag{4}$$

$$U_2^\star = N_\alpha^0 u_\alpha^0 \tag{5}$$

$$u_\alpha^0 = u_\alpha^0(P, T) \tag{6}$$

$$S_2^\star = N_\alpha^0 s_\alpha^0 \tag{7}$$

$$s_\alpha^0 = s_\alpha^0(u_\alpha^0, v_\alpha^0) = s_\alpha^0(P, T) \tag{8}$$

The functions $U_2^\star$ and $S_2^\star$, with variable N_α^0, are called the "*extended internal energy function*" and the "*extended entropy function*" respectively. The stars indicate that they are not energy functions and entropy functions in the strict sense (i.e. accessibility functions). For constant N_α^0, however, the functions are reduced to energy functions and entropy functions for the closed pure substance α. v_α^0, u_α^0 and s_α^0 are the molar volume, energy and entropy of the pure substance α; the superscript ^{0} indicates that we are concerned with pure substances. Define also:

$$dU_1^\star = dU_{12} - dU_2^\star \tag{9}$$

$$dS_1^\star = dS_{12} - dS_2^\star \tag{10}$$

Suppose that an infinitesimal isothermal quasistatic process of Z_{12} is associated with the transport of a quantity dN_α from Z_2 to Z_1. Then:

$$
\begin{aligned}
dU_1^\star &= dU_{12} - dU_2^\star = T\,dS_{12} - P_1\,dV_1 - P_2\,dV_2 - dU_2^\star \\
&= T\,dS_1^\star + T\,dS_2^\star - P_1\,dV_1 - P_2\,dV_2 - dU_2^\star \\
&= T\,dS_1^\star - P_1\,dV_1 + T\,d(N_\alpha^0 s_\alpha^0) - P_2\,d(N_\alpha^0 v_\alpha^0) - d(N_\alpha^0 u_\alpha^0) \\
&= T\,dS_1^\star - P_1\,dV_1 + N_\alpha^0(T\,ds_\alpha^0 - P_2\,dv_\alpha^0 - du_\alpha^0) \\
&\quad + (Ts_\alpha^0 - P_2 v_\alpha^0 - u_\alpha^0)\,dN_\alpha^0 \\
&= T\,dS_1^\star - P_1\,dV_1 - g_\alpha^0\,dN_\alpha^0
\end{aligned}
\tag{11}
$$

Now *define* the chemical potential of the component α in the system $Z_1^\star$: $\mu_{\alpha 1}$, as the molar Gibbs free energy g_α^0 of the pure substance $Z_2^\star$ in equilibrium under material connection with the system $Z_1^\star$ $\qquad$ (12)

Thus
$$
dU_1^\star = T\,dS_1^\star - P_1\,dV_1 + \mu_{\alpha 1}\,dN_{\alpha 1}
\tag{13}
$$

This outline will conclude by proving that for arbitrary states z_i and z_j: z_i and z_j are in equilibrium under material connection with respect to component α, or abbreviated "in α-equilibrium", if and only if $\mu_\alpha(z_i) = \mu_\alpha(z_j)$ and $T(z_i) = T(z_j)$.

If $\mu_\alpha(z_i) = \mu_\alpha(z_j)$ and $T(z_i) = T(z_j)$, then for states of a pure substance α in equilibrium with z_i and z_j, say z_α' and z_α'' respectively, $g_\alpha^0(z_\alpha') = g_\alpha^0(z_\alpha'')$ and $T(z_\alpha') = T(z_\alpha'') = T(z_i) = T(z_j)$. Now $(\partial g_\alpha^0 / \partial P)_T = v_\alpha^0 > 0$, therefore $P(z_\alpha') = P(z_\alpha'')$ and consequently $z_\alpha' = z_\alpha''$. Thus z_i and z_j are in "α-equilibrium" with the same state, and consequently also in mutual α-equilibrium. If z_i and z_j are in mutual "α-equilibrium" then they are in "α-equilibrium" with the same state of a pure substance α, as a consequence of the transitivity of "α-equilibrium". Therefore $\mu_\alpha(z_i) = \mu_\alpha(z_j)$ and $T(z_i) = T(z_j)$†.

A critical analysis of the outline proposed

The above argument contains a number of terms and statements which, in a more rigorous treatment, need explanation and justification.

(a) Every presentation of thermodynamics contains an appeal to the existence of thermal equilibrium, pressure equilibrium, material equilibrium with respect to chemical components α, β (or "α-equilibrium"), etc., with properties which are more or less explicitly defined, e.g. the zeroth law. In a formal approach this implies an assumption concerning the existence of equivalence relations defined on the set of all possible pairs of states of systems to which the relation considered can be applied[3, 7]. Systems are in such an approach sets of (equilibrium) states: $Z_i = \{z_i, z_i', z_i'', \ldots\}$. The pair of states $z_i z_j$ belongs to the "α-equilibrium equivalence relation" or "α-connection" C_{μ_α} iff the systems Z_i and Z_j, in states z_i and z_j respectively are in equilibrium when materially connected with respect to component α (through a semipermeable wall). This is a rule of interpretation. α-Connection is applicable to all systems which contain the component α. In traditional thermodynamics it is always tacitly assumed that α-equilibrium is reflexive,

† NOTE: Kestin[8], and also Vanderslice *et al.*[9], offer a similar approach. In their derivation the system $Z_2^\star$ is, however, an infinitesimal system, and they assume that $ds_\alpha^0 = 0$, $dv_\alpha^0 = 0$ and $du_\alpha^0 = 0$, which can be criticized.

symmetric and transitive. A further property of "α-equilibrium", "β-equilibrium" etc. is that they imply thermal equilibrium or "θ-equilibrium".

(b) Similarly an appeal is made to the existence of different types of isolation, e.g. adiabatic, energetic or material isolations. In a formal theory[3–7], this will be expressed in existence statements of "accessibility relations", which are equivalence relations defined on the cartesian products $Z_i \times Z_i$. In the case of adiabatic isolation and energetic isolation the systems Z_i are closed systems; the pairs $z_i' z_i''$ contained in the adiabatic isolation relation are reversibly adiabatically accessible; the equivalence classes are the classes of states of equal entropy.

"Material isolation with respect to component α' can also be expressed as an equivalence relation on $Z_i^\star \times Z_i^\star$, where $Z_i^\star$ are open systems containing this component, and the equivalence classes are the classes of states of equal material content for component α. The term "component" needs careful definition if chemical reactions can occur[2].

(c) In this paper we presuppose that extensive[7] entropy functions $S_i(z_i)$, internal energy functions $U_i(z_i)$, and deformation coordinate functions, e.g. $V_i(z_i)$, defined on closed systems, and absolute temperature and pressure functions $T(z_i)$ and $P(z_i)$ are available, and that the Gibbs fundamental equation for closed systems: $dU_i = T dS_i - P dV_i$ has been derived. An axiomatization of this fundamental part of thermodynamics on a strictly operational basis is given elsewhere[7]. A further axiomatic development, which leads to the Gibbs fundamental equation for open systems, will now be attempted.

(d) The term "homogeneity of a system" has not so far been defined formally in axiomatizations[2]. A definition requires some preparation: Two states are called "*similar*" if and only if the pair belongs to all applicable connection equivalence relations (i.e. if they are in equilibrium under all possible connections). Thus only states of systems which differ only in extent can be similar. A "*simple system*" is a system $Z^\star$, whose closed parts Z_i, $Z_j \subset Z^\star$, i.e. the equivalence classes of equal material content, are completely specified by $[U_i, V_i]$, $[U_j, V_j]$. A "*homogeneous system*" is a simple system Z^*, such that for closed parts Z_i, $Z_j \subset Z^\star$ the following statement holds: for pairs of similar states z_i', z_j' and z_i'', z_j''

$$\frac{S_i(z_i') \ N \ S_i(z_i'')}{S_j(z_j') - S_j(z_j'')} = \frac{U_i(z_i') - U_j(z_i'')}{U_j(z_j') - U_j(z_j'')} = \frac{V_i(z_i') - V_i(z_i'')}{V_j(z_j') - V_j(z_j'')} = \frac{M_i}{M_j} \tag{14}$$

where M_i and M_j are the masses of the closed systems Z_i and Z_j. If we choose similar states as states of reference for the entropies S_i and S_j and also similar states as states of reference for the internal energies (and possibly for the volumes) then one can write: for all similar states z_i and z_j:

$$\frac{S_i(z_i)}{S_j(z_j)} = \frac{U_i(z_i)}{U_j(z_j)} = \frac{V_i(z_i)}{V_j(z_j)} = \frac{M_i}{M_j} \tag{15}$$

This justifies the introduction of specific entropies, internal energies and volumes for homogeneous systems, and in the case of pure substances, defined below, the introduction of the molar quantities:

$$s_\alpha^0 \equiv \frac{S_{\alpha i}}{N_{\alpha i}^0} \tag{16}$$

$$u_\alpha^0 \equiv \frac{U_{\alpha i}}{N_{\alpha i}^0} \tag{17}$$

$$v_\alpha^0 \equiv \frac{V_{\alpha i}}{N_{\alpha i}^0} \tag{18}$$

An immediate consequence of homogeneity is that the intensities form a complete set of independent variables for closed parts. If not, then similar states z_i' and z_i'' would exist, such that $U_i(z_i') \neq U_i(z_i'')$ or $V_i(z_i') \neq V_i(z_i'')$. But this contradicts

$$\frac{U_i(z_i')}{U_i(z_i'')} = \frac{V_i(z_i')}{V_i(z_i'')} = \frac{M_i}{M_i} = 1 \tag{19}$$

(e) A "*pure substance*" can be defined as a system to which only one material connection is applicable. An alternative definition can perhaps be as follows: A "*pure substance*" is a simple system such that for closed parts:

$$S_i = N_{1i}s_1(P, T) + N_{2i}s_2(P, T) + \dots \tag{20}$$

$$U_i = N_{1i}u_1(P, T) + N_{2i}u_2(P, T) + \dots \tag{21}$$

$$V_i = N_{1i}v_1(P, T) + N_{2i}v_2(P, T) + \dots \tag{22}$$

and

$$N_{1i} + N_{2i} + \dots = N_i \tag{23}$$

It is essential that there exist two or more functions $s_1, s_2, \dots$, and $u_1, u_2, \dots$ and $v_1, v_2, \dots$ for certain P, T domains and that S_i, U_i and V_i are linear combinations of these functions, which are completely specified by P and T. The functions are called "*molar entropies, energies, volumes of the phases* $1, 2, \dots$", and $N_{1i}, N_{2i}, \dots$ are called the "*molar content of the phases* $1, 2, \dots$".

(f) Finally the assumption is made that a closed system Z, which is divided into simple parts $Z_1^\star$ and $Z_2^\star$ through a semipermeable wall, has a complete set of independent variables $[U, V_1, V_2]$. The precise status of this assumption is not yet clear. It is possible to consider this assumption as a definition of "semipermeable wall". "Semipermeability" has to be understood as non-permeability with respect to at least one component of the system. The limiting case is non-permeability with respect to all components; the wall is then only diathermal. The attraction of this procedure is that the existence of a semipermeable wall in a given system is decided by means of completely external criteria: there is no need to look inside the system. The ideal of phenomenological thermodynamics to consider the system as a black box, can thus be maintained. The objection that the part volumes V_1 and V_2 imply a look inside the system can be met: what matters are the volume differences ΔV_1 and ΔV_2 and these can be measured without knowledge of the part volume.

The formal introduction of the chemical potential runs as follows: Consider a system Z, which is divided through a semipermeable wall into

simple parts $Z_1^\star$ and $Z_2^\star$, the latter being a pure substance α. Let the system undergo an infinitesimal, quasistatic, isothermal change $(\mathrm{d}U,\ \mathrm{d}V_1,\ \mathrm{d}V_2)$. Suppose that with this change a change $\mathrm{d}N_\alpha^0$ in the variable N_α^0 of the pure substance $Z_2^\star$ is associated. We shall say, again in "black box language", that $Z_1^\star$ undergoes a change $\mathrm{d}N_{\alpha 1} = -\mathrm{d}N_\alpha^0$. Then

$$\mathrm{d}U_1^\star = \mathrm{d}U - \mathrm{d}U_2^\star = \ldots = T\mathrm{d}S_1^\star - P\mathrm{d}V_1 + \mu_\alpha \mathrm{d}N_{\alpha 1}.$$

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