The Gibbs-Duhem Equation and Equilibrium of Matter in External Fields and Temperature Gradients. Towards a Rational Thermodynamics. III

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The possibility of homogeneous integration of the internal energy (Ĥ) is considered in connection with a discussion of the proper form of the Gibbs-Duhem equation in thermodynamic systems. It is found that the Gibbs-Duhem equation solely involves variations in “internal” Brensted-potentials (negative pressure, temperature, chemical potentials, polarising electric or magnetic fields or interfacial tensions) and not variations in “external” Brensted-potentials (electric or gravitational potentials). Equilibrium conditions and overall force balances are established for isothermal systems.

A subdivision of the internal energy (Ĥ) of a system into Gibbsonian internal energy (Ĥ), potential energy (PE) and macroscopic kinetic energy (KE) is considered. The signs of the corresponding time derivatives are seen as important clues to the nature of various types of energy transformations.

Attempts to use equilibrium thermodynamics to describe the partial equilibrium of matter in temperature fields are doomed to failure, since it can be shown on a purely phenomenological basis that “entropies of transport” have nothing to do with partial molar entropies.

The previous papers in the present series have been concerned with the relation between Brenstedian and Gibbsonian energetics and the definition and properties of the exergy and with the connection between exergy loss and entropy production. In this paper we shall take up certain fundamental questions regarding the proper form of the Gibbs-Duhem equation in thermodynamic systems submitted to external fields, a subject which has often led to confusion in the past. We shall make the important distinction between internal Brensted-potentials (e.g., −p,T,μi) giving rise to Gibbsonian internal energy (Ĥ) and external potentials (electric and gravitational potentials) giving rise to potential energy (PE). The appropriate equilibrium conditions for matter in isothermal fields are discussed and it is proposed that the sign of the time derivatives dĤ/dt and dPE/dt together with the sign of the time derivative of the macroscopic kinetic energy (KE) give important information about the physical nature behind the energy transformations taking place in a system.

In the so-called “quasi-thermostatic” methods, equilibrium thermodynamics is used for describing the partial equilibrium of matter in temperature gradients. We shall see that such methods fail to yield a description of the Soret-effect where a composition gradient evolves as a consequence of a difference in temperature. A lot of further evidence is given which shows that “entropies of transport” are purely dynamical quantities which have nothing to do with partial molar entropies. Therefore an entirely new principle of non-equilibrium thermodynamics is called for in order to describe, e.g., the Thomson relation between thermo-electromotoric force and Peltier-entropy transfer.

INTERNAL ENERGY AND GIBBS-DUHEM EQUATION

In the first paper in this series we defined the general internal energy of a thermodynamic system to be
\[ E = \sum_i \int_0^{K_1} P_i dK_i \]  

(1)

If the system is not discrete, but continuous, we may consider a small, fixed region in Cartesian space \( \delta \Omega \) with an energy given by

\[ \delta E = \sum_i \int_0^{\delta K_i} P_i \delta K_i \]  

(2)

In general, the values of the potentials at a certain position \((x,y,z)\) will be functions of the concentrations \(c_K\) of the quantities at \((x,y,z)\) or functionals of the concentration distributions. For example, the electric potential \(\psi\) is linked to the charge density \((\rho_q)\) and the absolute permittivity through the Poisson equation

\[ \nabla^2 \psi = -\frac{\rho_q}{\varepsilon} \]  

(3)

(for application of this equation in problems of electrokinetics and electrolyte diffusion see Refs. 3 and 4). The solution to (3) for a given charge distribution is

\[ \psi(x,y,z) = \frac{1}{4\pi \varepsilon} \int_{\Omega} \frac{\rho_q(x',y',z') \, dx'dy'dz'}{\sqrt{(x-x')^2 + (y-y')^2 + (z-z')^2}} \]  

(4)

showing that \(\psi\) is a functional of \(c_q(x,y,z)\).

For the total internal energy in the region \(\Omega\) occupied by our system, we have

\[ E = \int_{\Omega} \rho_q d\Omega = \int_{\Omega} \frac{\delta E}{\delta \Omega} d\Omega = \int_{\Omega} \left[ \sum_i \int_0^{c_K} P_i dK_i \right] d\Omega \]  

(5)

where \(c_E\) is the concentration of internal energy. The last expression is obtained using (2) and the definition of concentration of a given quantity \(K\)

\[ c_K = \frac{\delta K}{\delta \Omega} \]  

(6)

In case of the quantity being the volume \((K = V)\) we have to be aware of not to interchange the meanings of the element of fixed volume in Cartesian space \(\delta \Omega\) and the element of transported Bredsted-volume \(\delta V\). Filling up, e.g., a jar with water at constant \(p\) means that the concentration of Bredsted-volume added to the water goes from 0 to 1. From eqn. (5) we obtain

\[ c_E = \sum \int_0^{c_K} P dK \]  

(7)

and

\[ dc_E = \sum P dK \]  

(8)

If \(-\) and only if \(-\) it is possible to find an integration path for the internal energy where the potentials remain unaltered we have

\[ c_E = \sum P \int_0^{c_K} dK = \sum P c_K \]  

(9)

By differentiation of (9) and comparison with (8) we get the general form of Gibbs-Duhem's equation

\[ \sum c_K \delta P = 0 \]  

(10)

Now, in the thermodynamic phases considered by Gibbs (Ref. 29, pp. 55-349) the effect of gravity and electric fields were not considered in any great detail (see pp. 144-150 and pp. 331-333, however). Such a phase characterized by \((V,S,n_i)\) and \((-p, T, \mu_i)\) may be built up isothermally and isobarically and with fixed chemical potentials by adding volume, entropy and moles of different components in the same constant proportions as in the final phase, since the composition will not change during the process of loading. Here we have neglected the contribution to internal energy from the interfacial tension at the boundaries of the considered phase. Thus, we have for the Gibbs-Duhem equation in that particular case

\[ -\delta p + c_S \delta T + \sum c_i \delta \mu_i = 0 \]  

(11)

We may even enlarge our list of quantities with the dielectric polarisation \(\mathcal{G}\) and magnetisation \(\mathcal{H}\), if they can be added at constant conjugated potentials, i.e. constant polarising fields \(\mathcal{G}\) and \(\mathcal{H}\). This will be the case, when the molar polarisation and magnetisation are unique functions of \(\mathcal{G}\) and \(\mathcal{H}\) at constant \(p, T\) and composition (e.g. a Langevin type of relationship \(\delta\)). In such cases we have the Gibbs-Duhem equation

\[ V \delta p - S \delta T + \sum n_i \delta \mu_i + \mathcal{G} \delta \mathcal{S} + \mathcal{H} \delta \mathcal{H} = 0 \]  

(12)

which may be given in terms of concentrations, if desired. Many multi-phase systems may also
be built up at constant potentials. Now we have as further quantities *internal* interfacial
area with associated excess surface concentrations and surface entropy, but these surface
quantities may often be added in constant proportions to the bulk quantities in such a
way that the interfacial tensions (σ) and the surface chemical potentials remain constant.
In that way we obtain general Gibbs-Duhem equations such as
\[
\sum_{\alpha} (V^\alpha \delta p^\alpha - S^\alpha \delta T^\alpha + \sum_{i} n_i^\alpha \delta \mu_i^\alpha) + \sum_{\alpha\beta} \left( A^{\alpha\beta} \delta \sigma^{\alpha\beta} - \delta S^{\alpha\beta} \delta T^{\alpha\beta} + \sum_{i} \Gamma_i^{\alpha\beta} A^{\alpha\beta} \delta \mu_i^{\alpha\beta} \right) = 0 \quad (13)
\]
Summation over Greek indices represents summation over phases and double Greek indices
over interfaces between phases. Since each bulk phase satisfies separately its own Gibbs-Duhem
eqn. (11) we have for the αβ-interface
\[
A^{\alpha\beta} \delta \sigma^{\alpha\beta} - \delta S^{\alpha\beta} \delta T^{\alpha\beta} + \sum_{i} \Gamma_i^{\alpha\beta} A^{\alpha\beta} \delta \mu_i^{\alpha\beta} = 0 \quad (14)
\]
where \( S^{\alpha\beta} \) is the excess interfacial entropy and \( \Gamma_i^{\alpha\beta} \) the excess interfacial concentration of the
i\( \)th component. Important relations are derived from eqn. (14), e.g. the Gibbs adsorption
equation for determining interfacial excess concentrations of surfactants experimentally
from interfacial tension/concentration relationships.\(^9\)

Passing now to systems involving *external* fields (electric or gravitational) one might be
tempted to generalise the Gibbs-Duhem equation to involve all variations in potentials.

It is therefore a most intriguing question whether or not the expression
\[
-\nabla P + c_5 \nabla T + \sum c_i \nabla \psi + c_M \nabla \phi \quad (15)
\]
equals to zero in continuous media subjected to external gravitational or electric fields (for
simplicity we now exclude any dielectric and magnetic polarization). La Mer, Foss and Reiss
have claimed such a general Gibbs-Duhem equation to be fulfilled.\(^8\) However, in a paper
(edited by J. Koefoed after the death of Brunsted) Brunsted has presented\(^8\) a subtle discussion
of this matter, which does not confirm the conclusion of La Mer, Foss and Reiss. His arguments become somewhat obscured by
the fact that he considers only a single chemical component in equilibrium in a gravitational
field, however. Therefore, here we treat the general case of multi-component equilibrium
in gravitational and electric fields.

It is easily seen that if the expression (15) is equal to zero and the charge density \( c_\psi \) or the electric field strength \( -\nabla \psi \) is equal to zero, there can be no pressure gradients in an isothermal system subjected to gravity forces when the gradients in electro-gravi-chemical potentials vanish
\[
\nabla \tilde{\mu}_i = \nabla (\mu_i + z_i F \phi + M \phi) = 0 \quad (16)
\]
Eqn. (16) is the expression for isothermal equilibrium of matter in gravitational and
electric fields, and the same equation is quoted by La Mer, Foss and Reiss. Actually it is just
the work principle of Brunsted applied on the virtual displacement of one mol of component
i in Cartesian space. We know, however, that there certainly are pressure gradients in grava-

\[\text{Fig. 1. Different modes of charging a gravity field with matter.}\]

tional systems at equilibrium (hydrostatic pressure), and this can only mean that the “general” Gibbs-Duhem equation is not correct.

Since the proofs of the various Gibbs-Duhem equations rely only on the possibility of homogeneous integration of the internal energy into the expression given by eqn. (9), one might wonder, why it is not possible to choose an integration path, where all potentials remain constant, when we change our system with the various quantities. The difficulty is illustrated in Fig. 1. For simplicity we consider a discrete system with two containers mounted at different heights in a gravity field. One can choose either to supply Brønsted-volume, entropy and moles of the components together with the molecular masses at fixed temperature and pressure at each position, or to supply the moles, the masses and the entropy at equal volumes of the containers. In the first case the volumes in the containers change during the process of filling up the containers and thereby the center of gravity, i.e. φ, changes in each case, whereas T, p, and the chemical potentials remain constant. In the second case the φ’s are constant, but p and the μ’s will vary if dT is chosen to be zero. Thus, it is not possible to choose an integration path with φ, ψ, T, p, and the μ’s being simultaneously constants. Therefore, a Gibbs-Duhem equation can only be established for potentials and quantities involved in the traditional (Gibbsian) internal energy which we may designate by the usual symbol U. We have

\[
c_V = -p + Tc_S + \sum \mu_i c_i \quad (17a)
\]

\[-\nabla p + c_S \nabla T + \sum c_i \nabla \mu_i = 0 \quad (17b)
\]

In isothermal external fields \(\nabla T = 0\), and when this is introduced in the Gibbs-Duhem eqn. (17b) together with the equilibrium conditions (16) for each component, we obtain the overall force balance on an element of volume

\[-\nabla p = c_M \nabla \phi + c_V \nabla \psi \quad (18)
\]

The Gibbsian internal energy \(U\) will only be a part of the general internal energy \(E\) of a thermodynamic system defined by eqn. (1). Especially we notice — by comparison with the table of quantities and conjugated potentials given in the first paper in this series — that we have neither included electric charge and heavy mass, nor inertial mass and the conjugated “velocity potential” \(v^2/2\) where \(v\) is the velocity of the local center of mass. The corresponding contribution to the integral (5) give rise to potential energy

\[
P_E = \int_\Omega c_P E d\Omega = \int_\Omega \left\{ \int_0^{c_M} \int_0^{c_M} \phi dc_M \right\} d\Omega
\]

(19)

and macroscopic kinetic energy (e.g. hydrodynamic motion)

\[
K_E = \int_\Omega \left\{ \frac{1}{2} c_M \right\} d\Omega = \int_\Omega \left\{ \int_0^{c_M} \nu d(c_M\nu) \right\} d\Omega
\]

(20)

The last integral in eqn. (20) corresponds to a bipartition of the “kinetic work” which is often more convenient than \(P = v^2/2\) and \(K = M\).

Here \(K = M\nu\), i.e. the linear momentum is chosen as a “vectorial quantity”. The conjugated “vectorial potential” becomes then the velocity itself. The total internal energy is now the sum of the Gibbsian energy, the potential energy and the kinetic energy

\[
E = U + P_E + K_E
\]

(21)

In an isolated thermodynamic system \(dE/dt = 0\), but that does not mean, obviously, that the three time derivatives are separately zero. On the contrary, the signs of \(dU/dt\), \(dP_E/dt\) and \(dK_E/dt\) are important clues to the understanding of the nature of the physical processes going on in the system. Some examples would be illuminating:

1. \(dU = dP_E = dK_E = 0\). Internal, irreversible processes such as “heat” conduction, diffusion processes and chemical reactions.
2. \(dU > 0\), \(dP_E < 0\), \(dK_E = 0\). “Joule heating” of an electrical resistance.
3. \(dU < 0\), \(dP_E > 0\), \(dK_E = 0\). Thermoelectric phenomena where electrons (or “positive holes”) are taken against the gradient of their electrochemical potential by a flux of entropy.
4. \(dU > 0\), \(dP_E = 0\), \(dK_E < 0\). Viscous dissipation of hydrodynamic motion.
5. \(dU = 0\), \(dP_E \pm 0\), \(dK_E = 0\). Frictionless Bernoulli (Euler) motion of an incompressible fluid.
6. \(dU < 0\), \(dP_E = 0\), \(dK_E > 0\). Formation of spontaneous convection cells (“dissipative struc-
tures” in the terminology of Glansdorff and Prigogine\textsuperscript{19} at liquid-liquid boundaries due to chemical reactions on the interface\textsuperscript{11–13} or due to mass transfer.\textsuperscript{14–17}

EQUILIBRIUM OF MATTER IN TEMPERATURE GRADIENTS

If we also have gradients of temperature it becomes necessary to modify some of the statements in the previous section concerning the equilibrium of matter. The equilibrium is now a partial equilibrium, since the system \textit{in toto} is not in equilibrium because of the unbalanced flow of entropy (see Ref. 2). However, we may imagine that this entropy has no influence on the quasi-equilibrium condition for component \( i \). Instead of (16) we now write

\[ \nabla \mu_i + \mathbf{S}_i \nabla T + c_i F \nabla \phi + M_i \nabla \phi = 0 \]  

(22)

according to Brensted’s work principle, since we move partial molar entropy \( (\mathbf{S}) \) with one mol of component \( i \) as well as charge \( c_i F \) and mass \( M_i \). In the isothermal case this transport is neutral and need not be included in the work principle. Weighting each of the eqns. (22) with \( c_i \) and summing we obtain

\[ \sum c_i \nabla \mu_i + c_S \nabla T + c_q \nabla \phi + c_M \nabla \phi = 0 \]  

(23)

and introducing the Gibbs-Duhem eqn. (17b) we recover the overall force balance on an element of volume (18).

Using eqn. (22) to describe equilibrium of conducting electrons in a temperature gradient in a metallic conductor, we have

\[ d\mu_e - F d\phi + \mathbf{S}_\phi dT = d\mu_e + \mathbf{S}_e dT = 0 \]  

(24)

Making a junction between two different conductors – (1) and (2) – with the junction elevated to the temperature \( T + \Delta T \), we obtain for the thermo-electromotric force between the two ends of temperature \( T \)

\[ \text{emf}(1 \rightarrow 2) = -\frac{1}{F} \left[ \mathbf{S}_e (1) - \mathbf{S}_e (2) \right] \int_{T}^{T+\Delta T} dT \]

(25)

since the electrochemical potentials of the electron in the two metals are equal at the hot junction. Under the assumption of constant partial molar entropy of the electron we obtain approximately

\[ \text{emf}(1 \rightarrow 2) \simeq -\frac{1}{F} \left[ \mathbf{S}_e (1) - \mathbf{S}_e (2) \right] \Delta T \]  

(26)

On the other hand, in an experiment where positive current \( I_q (C/s) \) is directed from conductor 1 to conductor 2 and the junctions are kept at constant temperatures \( T \) and \( T + dT \) by means of thermostats, we will have transfer of the following Peltier-entropy per unit time to the “hot” thermostat

\[ \frac{dS_{\text{Peltier}}}{dt} = \frac{I_q}{F} (\mathbf{S}_e (2) - \mathbf{S}_e (1)) \]  

(27)

(due to conservation of entropy at the hot junction, the difference between the entropy carried along with the electrons has to be compensated by an entropy exchange with the hot thermostat). Thus, the present “quasi-thermostatic” theory predicts correctly the required relationship between thermo-emf and Peltier heat found by Thomson,\textsuperscript{14,15} since the partial molar entropy of the electron is common for the two experiments.

Thomson himself expressed doubt, however, whether it was correct to use equilibrium thermodynamics to describe virtual displacements of the electron in cases with a “heat” flow. Niels Bohr was probably one of the first to hint that the reversibility of the microscopic Hamiltonian equations of motion was the real physical reason behind Thomson’s relations (see Ref. 20, pp. 22, 71 – 75). As is well known, the symmetry to time reversal of time correlation functions of fluctuations in different physical variables was later made a cornerstone in Lars Onsager’s proof of the reciprocal relations between transport coefficients,\textsuperscript{21} on which proof the later developed framework of irreversible thermodynamics is resting.\textsuperscript{22}

It is also possible on a \textit{phenomenological} basis, however, to prove that the quasi-equilibrium condition (22) cannot be correct. For example, Koefoed\textsuperscript{23} has once pointed to the fact that experimentally one sometimes finds a definite thermo-emf between two identical single crystals with different orientation. But the partial molar entropy of the electron in a crystal cannot be dependent of orientation, and the emf

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should be 0 following (26), if (22) were correct. As another example we may take the thermodiffusion effect discovered by Ludwig and Soret. It is an experimental fact that substances in solution in a column with a temperature gradient has a tendency to concentrate somewhat in one end of the column (predominantly the cooler). When we consider a two component system, and thermodiffusion equilibrium has been reached, we have for an uncharged solute (1) according to (22) in a one dimensional T-profile

$$d\mu_1 + \overline{S}_1 dT = 0$$

For systems with no pressure gradients we have

$$d\mu_i = -\overline{S}_i dT + (\partial\mu_i/\partial X) dX$$

where $X$ is the mol fraction of component 1, since there is only a single composition variable in a two component system. Combining the two equations we obtain

$$(\partial\mu_i/\partial X)_{T,\rho} dX = 0$$

which means that $dX = 0$. Thus, assumption of the equilibrium condition (22) for equilibrium of matter under non-isothermal conditions will exclude the possibility of any Soret-effect. We have to replace (22) by eqn. (28)

$$\nabla \mu_i + \overline{S}_i^* \nabla T + \zeta_i P \nabla \psi + M_i \nabla \phi = 0$$

(28)

where $\overline{S}_i^*$ is the molar "entropy of transport". In anisotropic media we must even take $\overline{S}_i^*$ to be dependent on the chosen direction in space. Since the Gibbs-Duhem eqn. (17b) and the over-all balance of forces (18) still have to be fulfilled, eqn. (23) must still be correct. Weighting each of the eqns. (28) with the concentration $c_i$ and summing, we notice that the following restriction for the entropies of transport has to be respected

$$\sum c_i \overline{S}_i^* = c_S$$

(29)

With the new equilibrium condition (28) we have for the Soret-effect in a two component solution

$$\frac{dX}{dT}_{\text{Soret}} = \frac{\overline{S}_1 - \overline{S}_i^*}{(\partial\mu_i/\partial X)_{T,\rho}}$$

(30)

But the entropy of transport is now a purely dynamical quantity without any basis in equilibrium thermodynamics. There is no guarantee that $\overline{S}_i^*$ will be identical under different experimental conditions. Therefore, the relation between thermo-emf and Peltier-effect must be due to an entirely new principle on non-equilibrium thermodynamics, which may be called "the fourth law of thermodynamics" (expressed for example in Onsager's reciprocal relations).

The measurements of Denbigh and Raumann of the thermo-osmotic pressure differences over rubber membranes exerted by $H_2$ and $CO_2$ constitute still another proof that entropies of transport have nothing to do with partial molar entropies. Using (28) for the description of the quasi-equilibrium of the gas dissolved in the rubber membrane we obtain under the assumption of approximately constant $\overline{S}^*$ for the gas through the membrane (small $\Delta T$ and $\Delta p$)

$$\Delta \mu_{\text{gas in membrane}} + \overline{S}^* \Delta T \cong 0$$

(31)

The difference in chemical potential for the gas is taken between localities just inside the two membrane boundaries. Due to local equilibrium the chemical potentials just outside the membrane must be the same. For small $\Delta T$ and $\Delta p$ we have

$$\Delta \mu_{\text{gas}} \cong -\overline{S}_{\text{gas}} \Delta T + \overline{V}_{\text{gas}} \Delta p$$

(32)

and combining (31) and (32) we have for the thermo-osmotic pressure

$$\left(\frac{\Delta P}{\Delta T}\right)_{\text{thermo-osmosis}} \cong \frac{\overline{S}_{\text{gas}} - \overline{S}^*}{\overline{V}_{\text{gas}}}$$

(33)

If $\overline{S}^*$ were simply the partial molar entropy of the gas dissolved in rubber, eqn. (33) would be nothing more than a simple Clapeyron equation for elevation of the vapor pressure due to an elevation of temperature. The measurements of Denbigh and Raumann show, however, that not only is $\overline{S}^*$ entirely different from the partial molar entropy of the gases dissolved in rubber, but the suspected "entropy of vaporisation" $\overline{S}_{\text{gas}} - \overline{S}^*$ calculated from thermo-osmotic data has even different signs for the gases $H_2$ and $CO_2$.

CONCLUSION

Different types of Gibbs-Duhem equations have been investigated. Of particular importance is the statement that electrical and

gravitational potential variations in space must not be included in the Gibbs-Duhem equation.

A division of internal energy of a general thermodynamic system $E$ into Gibbsian internal energy $U$, potential energy $PE$ and macroscopic kinetic energy $KE$ is made. The signs of $dU/dt$, $dPE/dt$ and $dKE/dt$ constitute important clues to the physical mechanisms involved in the energy transformations.

The quasi-thermostatic methods of calculation of equilibrium of matter in temperature fields are not correct even on a phenomenological basis. The entropy of transport has nothing to do with the partial molar entropy. It is a purely dynamical quantity, and quantitative relationships between different experiments such as thermo-emf and Peltier-effect are due to an entirely new principle of non-equilibrium thermodynamics, as earlier shown by statistical arguments by Bohr and Onsager. A phenomenological treatment of transport-processes containing Onsager's reciprocal relations as a special case will be presented in a forthcoming paper.

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