

Generalised Gibbs-Duhem Equations and Quasi-thermodynamic Methods

TORBEN SMITH SØRENSEN

Fysisk-Kemisk Institut, Technical University of Denmark, DK-2800 Lyngby, Denmark

Matter in gravitational and electric fields. In my third paper in the series "Towards a Rational Thermodynamics"¹ I pointed out that a straightforward generalisation of the Gibbs-Duhem equation to include the effect of external fields – such as proposed by La Mer, Foss and Reiss² – leads to contradictions with well-established facts, e.g. that pressure gradients exist at equilibrium in gravitational fields. In a short communication³ by Torben Knudsen my propositions are criticised. He argues that the "generalised" Gibbs-Duhem equation should rather be (in the case of only a single component present)

$$d\mu - VdP + VdP + Md\phi = 0 \quad (1)$$

where the first $-VdP$ term is the "normal" Gibbs-Duhem term due to local equilibrium or – in Brønsted's terminology – the work principle, applied to infinitesimally diverging systems. The second $+VdP$ term should then be a work term due to the change in position of the volume element (V) as a whole in the pressure gradient regarded as an "external field".

To me Knudsen's arguments seem to be of an *ad hoc* nature. It is very confusing to operate with two sorts of pressures: an internal and an external. It is very confusing – and inconsistent with usual lines of thought in physics and irreversible thermodynamics – to speak about pressure as an external field. In the momentum balance equation the action of external fields shows up as a source term [see, e.g., Ref. 4, eqn. (1.31)], since momentum is introduced into the volume element from distant momentum-reservoirs through the action of the external fields. On the contrary, pressure may be considered as a flux of momentum from neighbouring volume elements. Although pressure gradients are sometimes consequences of the action of external fields, they do not generically belong to the class of external fields. Finally, trying to follow the arguments of Knudsen, it is difficult to understand why the "internal" pressure should contribute the term $-VdP$ to the Gibbs-Duhem equation, while the "external" pressure contributes with $+VdP$. A clear cut Brønstedian process of building up the system is lacking in Knudsen's communication.

It was exactly such a procedure for building up the system which I devised in my paper (see Ref. 1,

Fig. 1) to explain why a homogeneous integration of the total internal energy (Gibbs' internal energy + potential energy) is not possible – and similarly not a "generalisation" of the Gibbs-Duhem equation. However, there is one important comment in Knudsen's paper regarding this point: It is indeed possible to build up a system in a one-dimensional gravitational field by adding quantities in fixed proportions without changing any of the potentials. One just has to add quantities in a direction perpendicular to the field. Thus, with *this* interpretation of the differentials (dK) a homogeneous integration of the complete internal energy to $E = \Sigma PK$ is possible and a generalised Gibbs-Duhem equation of the form

$$SdT - VdP + \Sigma n_i d\tilde{\mu}_i = 0 \quad (2)$$

can be derived. It might have been this interpretation of the generalised G.D. equation which La Mer, Foss and Reiss had in mind, but then it is confusing that they speak about eqn. (2) in connection with discussion of the equilibrium conditions ($d\tilde{\mu}_i = 0$) in the direction of the field.

A similar example where a generalisation of Gibbs-Duhem's equation is possible – and highly useful – is given by the case of an electric double layer at a liquid-liquid interface. We consider the system as composed of bulk phase I with surface layer α and bulk phase II with surface layer β . The two dividing surfaces and the interfacial surface are selected so that phases I and II are electroneutral and the positive surface charge of α corresponds to the negative surface charge of β . By building up the system in the directions of the interface we derive the following generalised Gibbs-Duhem equation (T and P taken as constants for brevity)

$$\Sigma_I n_i^I d\tilde{\mu}_i^I + \Sigma_{II} n_i^{II} d\tilde{\mu}_i^{II} + A \Sigma_{\alpha} \Gamma_i^{\alpha} d\tilde{\mu}_i^{\alpha} + \Sigma_{\beta} \Gamma_i^{\beta} d\tilde{\mu}_i^{\beta} + Ad\sigma = 0 \quad (3)$$

where A is the interfacial area of the final system, Γ_i are surface excess concentrations and σ is the interfacial tension. Since we have electroneutrality in the bulk solutions we have separately for each bulk solution

$$\Sigma n_i d\tilde{\mu}_i = \Sigma n_i d\mu_i + (\Sigma z_i F n_i) d\psi = \Sigma n_i d\mu_i = 0 \quad (4)$$

Due to equilibrium between bulk solution and surface, the bulk electrochemical potentials equal the surface electrochemical potentials, and we obtain

$$d\sigma = -\Sigma_{\alpha} \Gamma_i^{\alpha} d\tilde{\mu}_i^{\alpha} - \Sigma_{\beta} \Gamma_i^{\beta} d\tilde{\mu}_i^{\beta} \quad (5)$$

From eqn. (5) it is a simple matter to derive the classical Lippmann equation⁵ of relevance for the study of effects of electrocapillarity at an interface between mercury and an electrolyte solution. The derivation given here is the one usually given (see, e.g., Ref. 6), but unfortunately not very many thermodynamicians pose themselves fundamental questions concerning when and why generalisations of the Gibbs-Duhem equation can be made. The rule which has been found in Ref. 1 and here is straightforward: Whenever a way of building up the system in question can be found, such as by adding the quantities in fixed proportions to the different localities in the system, all the potentials remain constant, we are able to integrate the internal energy to $E = \Sigma PK$ and thereby to obtain a generalised Gibbs-Duhem equation $\Sigma KdP = 0$.

Matter in temperature gradients and the use of quasi-thermostatic arguments. Knudsen's critique of my treatment of the equilibrium of matter in temperature gradients is based upon a misinterpretation of what I have written in Ref. 1. I have never doubted that his eqns. (1) or (6) apply. On the contrary, I used the same equation (Ref. 1, p. 442, 1st column, line 15 from above). But this equation is just a "passive" expression of local equilibrium and therefore useless as an equation of dynamic balance. Just as we have for equilibrium in an electric field at isothermal and isobaric conditions

$$d\tilde{\mu}_i = d\mu_i + z_i F d\psi = 0 \quad (6)$$

together with the obvious equation

$$d\mu_i - \sum_{j=1}^{n-1} (\partial\mu_i / \partial X_j) dX_j = 0, \text{ it would be tempting to use}$$

$$d\tilde{\mu}_i + \bar{S}_i dT = 0 \quad (7)$$

as a general balance equation for matter in temperature gradients. In Ref. 1 I have shown, how it is possible to derive the relation between thermo-emf and Peltier-entropy using eqn. (7). Another variant of this "quasi-thermostatic" method was used already by Thomson in 1854.⁷ The two effects are according to this argumentation related, since the partial molar entropy of the electron appears in both expressions. This method of using equilibrium thermodynamics on non-equilibrium problems is far from unproblematic, however, as understood already by Thomson himself. It is therefore somewhat unfortunate, that Brønsted⁸ used the same kind of arguments at a time where irreversible thermodynamics had reached recognition of the connection between thermo-emf and Peltier-effect as being due to the Onsager reciprocal relations.

Since many chemists still have a "quasi-thermostatic" picture of the world, however, I wanted to point out clearly the inconsistencies connected with the use of eqn. (7). In the case of a single, neutral solute in a temperature gradient, the use of (7) precludes any Soret-effect. Also, the experiments of Denbigh and Raumann on thermo-osmosis with rubber membranes⁹ show clearly that the "entropies of transport" have nothing to do with partial molar entropies. I would not expect either that the entropy of transport of the electron should have anything to do with the partial molar entropy of the electron, but at present I am not aware of any independent method of measuring partial molar entropies of electrons in metallic conductors.

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Received February 17, 1978.