Short Communications

Brønstedian Energetics and the Gibbs-Duhem Equation

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In his third paper in Acta Chemica Scandinavica about energetics,[1] Torben Smith Sørensen discusses the Gibbs-Duhem equation and its bearing on non-equilibrium thermodynamics. The first part of Sørensens paper is concerned with the possible extension of the Gibbs-Duhem equation to include external forces. Sørensen concludes that the straightforward addition of a term representing the effect of the external field yields an equation not verified by experiment. In the opinion of the present author the apparent impossibility of a straightforward extension of the Gibbs-Duhem equation to include the effect of external fields is due to an incorrect treatment of the role played by the pressure. When allowing for external forces in the Gibbs-Duhem equation, the external force nature of the pressure should be recognized.

Continuing to systems with temperature gradients Sørensen correctly states that, the equation: $d\mu_1 + \bar{S}_1 dT = 0$, is unable to predict a Soret effect for a two-component system. This is not remarkable, since it was never intended to do so. The relevant equation for two-component systems reads:

$$d\mu_1 + \bar{S}_1 dT - \frac{\partial \mu_1}{\partial X} dX = 0 \qquad (1)$$

X being the mol fraction.

One-component systems in a gravitational field. The reason why the so-called generalized Gibbs-Duhem equation for continous media in a gravitational or other external field has brought about confusion, as stated in Sørensens article, is in my opinion to be found in the failing to recognize the pressure as another external field. External forces acting on the small volume element under consideration are not merely gravitational, but include surface forces from the outside pressure. The reason why this obvious contribution to the external forces is

overlooked is probably due to the pressure already being included in the purely thermodynamic equation:

$$d\mu - VdP = 0 \qquad (2)$$

But the pressure appearing in (2) has a specific thermodynamic significance. It is the pressure inside the volume element, acting when this element changes its volume through a spatial basic process, giving rise to the work term $-VdP$, when the volume V is transported between P and $P+dP$. The external pressure or the outside pressure is "active" when the volume element changes its position in the pressure field, without change of volume. It contributes the term VdP. As the volume element is infinitesimal the two pressures are of course measured at the same point in space, and are phenomenologically identical. The generalized Gibbs-Duhem with the inclusion of all external forces now reads:

$$d\mu - VdP + VdP + Md\phi = 0 \qquad (3)$$

where M is the mass of the volume element and ϕ the gravitational potential. The nominal content of eqn. (3) is of course:

$$d\mu + Md\phi = 0 \qquad (4)$$

which can be taken as the statement of the constancy of the gravi-chemical potential. Eqn. (4) could have been derived by adding the purely mechanical equilibrium condition:

$$VdP + Md\phi = 0 \qquad (5)$$

to the purely thermodynamic one (2).

Another way of arguing would be to consider the build up of the small volume element and keeping all potentials constant during this process. This is perfectly possible, although stated to the contrary in Sørensens article. Infinitesimal contributions of quantities to the system should merely extend this in horizontal directions, thus keeping the gravitational potential constant. Besides the three obvious terms: $N\mu$, $M\phi$ and $-PV$, being the chemical, gravitational and spatial energy terms, the term PV enters into the calculation of the total

energy of the sub-system. This last term stems from the fact that, the sub-system built up in this experiment is "floating" in the rest of the system, and the transport of the sub-system, keeping the volume constant, to levels of zero pressure would contribute the work term PV. Thus the total energy is $N\mu + M\phi$, corresponding to the Gibbs-Duhem equation (4).

Equilibrium of matter in temperature gradients. As stated in the beginning of this note eqn. (1) is the equation to be employed for two-component systems with temperature gradients. Transforming this equation it reads:

$$d\mu_1 + (\bar{S}_1 - \frac{\partial \mu_1}{\partial X}\frac{dX}{dT})dT = 0 \tag{6}$$

The quantity dX/dT is a measure of the Soret effect. Its value depends on the specific components constituting the system. For metalline conductors, considered as two-component systems, composed of positive ions and negative electrons, it must be concluded that $dX/dT = 0$, since the simpler equation $d\tilde{\mu}_1 + \bar{S}_1 dT = 0$, $\tilde{\mu}_1$ is now the electro-chemical potential, can accurately predict the relation between thermo-emf and the Peltier heat.

As dX/dT for any system is a purely dynamical quantity, depending on the specific interactions between phonons and chemical constituents, it takes but little imagination to concieve its directional nature, as for instance in single crystals. Thus there seems only little difficulty in explaining the thermo-emf observed for cells composed of identical single crystals oriented in different directions. $\bar{S}_1$ and $\partial\mu_1/\partial X$ remains of course functions of temperature only, whereas the dynamical quantity dX/dT depends on direction, giving rise to different values of $d\mu_1$ when going in different directions in the single crystal.

Defining now the entropy of transport $\bar{S}_1^*$ by:

$$\bar{S}_1^* = \bar{S}_1 - \frac{\partial \mu_1}{\partial X}\frac{dX}{dT} \tag{7}$$

eqn. (6) will read:

$$d\mu_1 + \bar{S}_1^* dT = 0 \tag{8}$$

which is equivalent to Sørensens eqn. (28).

The author of this note fails to see the entirely "new principle of non-equilibrium thermodynamics", inherent in eqn. (8). It is derivable through the thermodynamic eqn. (1), which is a well-established equation from equilibrium thermodynamics. Its application on non-equilibrium systems is granted by the "local equilibrium" or the Brønsted "work principle for infinitesimally diverging systems".

1. Sørensen, T. S. *Acta Chem. Scand. A 31* (1977) 437.