AXIOMATIC EXPOSITION OF EXTENDED THERMODYNAMICS

S.I. Serdyukov

Chemistry Department, Moscow State University, 119992 Moscow, Russia
Electronic address: serdkv@tech.chem.msu.ru

A non-statistical paradigm of the thermodynamics exposition[1,2] can be extended on the uniform systems, given by usual thermodynamic variables and their time derivatives. Such systems are considered within the framework of extended thermodynamics.

A state of a system is characterized by external parameters $\beta = \{\beta_1, \ldots, \beta_{N'}\}$, amounts of constituents $n = \{n_1, \ldots, n_N\}$, time derivatives $\dot{\beta} = \{\dot{\beta}_1, \ldots, \dot{\beta}_{N'}\}$, $\dot{n} = \{\dot{n}_1, \ldots, \dot{n}_N\}$. In the equilibrium state (stable or not stable) $\dot{\beta} = 0$, $\dot{n} = 0$. Generally, at $\dot{\beta} \neq 0$, $\dot{n} \neq 0$ the state is uniform, not equilibrium.

The *First Law*[1] of thermodynamics "asserts that any two states of a system may always be the initial and final states of a weight process. Such a process involves no net effects external to the system except the change in elevation between z_1 and z_2 of a weight, that is, solely a mechanical effect[3]".

The property energy E is implication of the First Law of thermodynamics, and is function of the β, n, not $\dot{\beta}$, $\dot{n}$. A state of a system can be given by variables E, β, n, and $\dot{E}$, $\dot{\beta}$, $\dot{n}$.

The *Second Law* of thermodynamics[1] asserts that among all the states of a system with a given value of the energy E, given values of the external parameters β and the amounts of constituents n, there exists one and only one stable equilibrium state.

Let us introduce reference reservoir R_0 with a set of stable equilibrium states. Further, let us introduce reservoir R with variables E, β, n, and reservoir R' with the same E, β, n and additional variables $\dot{E}$, $\dot{\beta}$, $\dot{n}$.

To define the properties of reservoirs R_0 and R, we consider arbitrary auxiliary system A, arbitrary states A_1 and A_2, and reversible weight process for the composite systems AR_0 and AR in which system A changes state from A_1 to A_2. We can obtain

[1] E.P. Gyftopoulos, G.P. Beretta, *Thermodynamics: Foundations and Applications*, 1991.
[2] G.P. Beretta, *Int. J. of Thermodynamics*, 11 (2008) 39.
[3] E.P. Gyftopoulos, *Physica A*, 307 (2002) 405. 9 (2006) 137.

change in energy $(\Delta E_{R_0})^{\text{sW,rev}}_{\text{A}_1\text{A}_2}$ and $(\Delta E_R)^{\text{sW,rev}}_{\text{A}_1\text{A}_2}$ for the R_0 and R, respectively. Reservoir R$'$ can be interconnected to reservoir R by means of reversible weight process and, consequently, we can obtain change in energy $(\Delta E_{R'})^{\text{sW,rev}}_{\text{A}_1\text{A}_2}$ for the reservoir R$'$.

Using $(\Delta E_{R_0})^{\text{sW,rev}}_{\text{A}_1\text{A}_2}$ and $(\Delta E_{R'})^{\text{sW,rev}}_{\text{A}_1\text{A}_2}$, the generalized temperature $\theta_{R'}$ with respect to temperature T_{R_0} of reference reservoir R_0 can be defined:

$$\theta_{R'} = \left.\frac{(\Delta E_{R'})^{\text{sW,rev}}_{\text{A}_1\text{A}_2}}{(\Delta E_{R_0})^{\text{sW,rev}}_{\text{A}_1\text{A}_2}}\right|_{\beta,n,\dot{E},\dot{\beta},\dot{n}} T_{R_0}.$$

By analogy, for a system with variable values of $\beta_1 = V$ and n and fixed $\{\beta_2, \ldots, \beta_N\}$, we can introduce generalized pressure $\pi_{R'}$

$$\pi_{R'} = -\left.\left(\frac{\Delta E_{R'}}{\Delta V_{R'}}\right)^{\text{sW,rev}}_{\text{A}_1\text{A}_2}\right|_{\beta',n,\dot{E},\dot{\beta},\dot{n}} + \frac{\theta_{R'}}{T_{R_0}}\left[p_{R_0} + \left.\left(\frac{\Delta E_{R_0}}{\Delta V_{R_0}}\right)^{\text{sW,rev}}_{\text{A}_1\text{A}_2}\right|_{\beta',n}\right]$$

and generalized total potential $\tilde{\mu}_{iR'}$

$$\tilde{\mu}_{iR'} = \left.\left(\frac{\Delta E_{R'}}{\Delta n_{iR'}}\right)^{\text{sW,rev}}_{\text{A}_1\text{A}_2}\right|_{\beta,n',\dot{E},\dot{\beta},\dot{n}} - \frac{\theta_{R'}}{T_{R_0}}\left[\mu_{iR_0} - \left.\left(\frac{\Delta E_{R_0}}{\Delta n_{iR_0}}\right)^{\text{sW,rev}}_{\text{A}_1\text{A}_2}\right|_{\beta,n'}\right].$$

Apart from, we can introduce intensive values $\Lambda_{R'}$, $\Xi_{R'}$ and $\Gamma_{iR'}$ corresponding to $\dot{E}_{R'}$, $\dot{V}_{R'}$, and $\dot{n}_{iR'}$, respectively:

$$\Lambda_{R'} = -\left.\left(\frac{\Delta E_{R'}}{\Delta \dot{E}_{R'}}\right)^{\text{sW,rev}}_{\text{A}_1\text{A}_2}\right|_{\beta,n,\dot{\beta},\dot{n}}, \qquad \Xi_{R'} = -\left.\left(\frac{\Delta E_{R'}}{\Delta \dot{V}_{R'}}\right)^{\text{sW,rev}}_{\text{A}_1\text{A}_2}\right|_{\beta,n,\dot{E},\dot{\beta}',\dot{n}},$$

$$\text{and} \qquad \Gamma_{iR'} = -\left.\left(\frac{\Delta E_{R'}}{\Delta \dot{n}_{iR'}}\right)^{\text{sW,rev}}_{\text{A}_1\text{A}_2}\right|_{\beta,n,\dot{E},\dot{\beta},\dot{n}'}.$$

According the theorems of the first and second laws there are exists property entropy, with the value denoted by S. For a system with variable values of $\beta_1 = V$ and n and fixed $\{\beta_2, \ldots, \beta_N\}$, the entropy diffrence can be defined as

$$S_2 - S_1 = \frac{1}{\theta'_R}[(E_2 - E_1) - (\mathcal{E}_2^{R'} - \mathcal{E}_1^{R'}) + \pi_{R'}(V_2 - V_1) - \sum \tilde{\mu}_{iR'}(n_{i2} - n_{i1}) +$$
$$+\Lambda_{R'}(\dot{E}_2 - \dot{E}_1) + \Xi_{R'}(\dot{V}_2 - \dot{V}_1) - \sum \Gamma_{iR'}(\dot{n}_{i2} - \dot{n}_{i1})],$$

where $\mathcal{E}^{R'}$ is the generalized available energy.

The entropy of the system is given by the fundamental relation, that is a function of the form

$$S = S(E, \beta, n; \dot{E}, \dot{\beta}, \dot{n}).$$

For a system with $\beta = \{V\}$ and $E = U$ (U is the internal energy), we have

$$S = S(U, V, n; \dot{U}, \dot{V}, \dot{n})$$

and $\theta = 1/(\partial S/\partial U)_{V,n;\dot{U},\dot{V},\dot{n}}$ is the generalized temperature, $\pi = \theta(\partial S/\partial V)_{U,n;\dot{U},\dot{V},\dot{n}}$ is the generalized pressure, $\tilde{\mu}_i = -\theta(\partial S/\partial n_i)_{U,V,n';\dot{U},\dot{V},\dot{n}}$ is the generalized chemical potential of the ith constituent,

$$\Lambda = \theta\left(\frac{\partial S}{\partial \dot{U}}\right)_{U,V,n;\dot{V},\dot{n}}, \qquad \Xi = \theta\left(\frac{\partial S}{\partial \dot{V}}\right)_{U,V,n;\dot{U},\dot{n}}, \qquad \Gamma_i = -\theta\left(\frac{\partial S}{\partial \dot{n}_i}\right)_{U,V,n;\dot{U},\dot{V},\dot{n}'}$$

are a new intensive quantities. The first differential for S is

$$\theta dS = dU + \pi dV - \sum_i \tilde{\mu}_i dn_i + \Lambda d\dot{U} + \Xi d\dot{V} - \sum_i \Gamma_i d\dot{n}_i.$$

To construct a thermodynamic formalism for the nonuniform system, instead of the local equilibrium hypothesis, we propose a *local uniformity hypothesis*: the system that is nonuniform as a whole will be regarded as uniform at each point. This means that the nonuniform system should be described in terms of the same variables u, v $(= 1/\rho)$, c_i $(= n_i/\sum n_i)$, $\dot{u}$, $\dot{v}$, and $\dot{c}_i$. Then, instead of last relation, we obtain a similar relation in the form

$$\theta ds = du + \pi dv - \sum_i \tilde{\mu}_i dc_i + \Lambda d\dot{u} + \Xi d\dot{v} - \sum_i \Gamma_i d\dot{c}_i.$$

Only in the particular case where entropy density is function of $\dot{u} + p\dot{v}$,

$$s = s(u, v, c_1, \ldots, c_N; \dot{u} + p\dot{v}, \dot{c}_1, \ldots, \dot{c}_N),$$

the formalism of extended irreversible thermodynamics is considered[4].

[4]S.I. Serdyukov, *Phys. Lett. A*, 316 (2003) 177; 324 (2004) 262. S.I. Serdyukov, *C. R. Physique*, 8 (2007) 93.