# CONCEPTUAL PROBLEMS OF MODERN IRREVERSIBLE THERMODYNAMICS

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## Contents

## 1.  Introduction[1–3,11,14]

Macroscopic thermodynamics of equilibrium referred to as classical thermodynamics is concerned with macroscopic states of matter, with experimentally observable properties and with energetics of systems exchanging heat, work and/or matter with the surroundings. It rests on two fundamental laws: the balance of energy and the so-called second principle. The latter introduces two new concepts, absolute temperature and entropy, and states that entropy never decreases in an isolated system. Classical thermodynamics does not enquire into the mechanism of the phenomena and thus is unconcerned with molecular structure of the systems under investigation. It is a theoretically well founded theory and in the practice a very successful method.

Classical thermodynamics is restricted to equilibrium situations. It is correct for equilibrium systems, for reversible (equilibrium) processes and for processes between equilibrium states. Absolute temperature and entropy are defined rigorously and unambiguously only in equilibrium. Outside equilibrium, entropy enters the theory through an inequality only and it is not uniquely defined. The relationships in classical thermodynamics between state variables (e.g. the Gibbs equation) lose their validity in nonequilibrium. The range of application of classical thermodynamics is therefore very narrow. It is in particular unable to describe situations far from equilibrium and the behaviour of continuous systems or of complicated materials (materials with memory, nonuniform systems, etc.). Their treatment falls under the head of thermodynamics of irreversible processes which originally tried to overcome these difficulties in two ways: either the existence of absolute temperature and of entropy outside equilibrium was simply assumed or different hypotheses, for example the local equilibrium, were used.

Unlike classical thermodynamics, which is one universal theory, thermodynamics of irreversible processes presents several faces. We shall review besides classical irreversible thermodynamics only the most important macroscopic theories, the extended irreversible thermodynamics and the ratio- nal thermodynamics. Some other theories, such as the so-called entropy-free thermodynamics or the theory of hidden variables, will not be discussed as they are of a rather special nature.

In addition to the phenomenological macroscopic theories there exist also microscopic theories of irreversible thermodynamics. They facilitate a deeper insight and their importance will in our opinion still grow in the future. We mention the methods based on the kinetic theory of gases and on the fluctuation theories, and in particular the more general methods and theories rooted in nonequilibrium statistical mechanics. For example, the linear response theory based on the fluctuation-dissipation theorem which relates the phenomenological parameters to the nature of microscopic dynamics and fluctuations. These theories lie beyond the scope of this treatise, however, and they will not be analyzed here.

## 2.  Classical irreversible thermodynamics[4–8,10]

Classical irreversible thermodynamics (CIT) as developed by Onsager, Prigogine (Nobel prize for chemistry in 1968 and 1977) and many others, forms the base for all the later formulations of irreversible thermodynamics. It has to be emphasized that it is based on the concept of local equilibrium. This fundamental hypothesis assumes that the system can be split mentally into cells which are sufficiently large to be treated as macroscopic thermodynamic subsystems but, at the same time, sufficiently small that equilibrium is very close to being realized in each cell. The hypothesis thus postulates that the local and instantaneous relations between the thermal and mechanical properties of a physical system are the same as for a uniform system at equilibrium. This implies that all the variables of equilibrium thermodynamics remain significant and that all the relationships of classical thermodynamics between state variables remain valid outside equilibrium provided that they are stated locally at each instant of time. That means particularly that entropy outside equilibrium depends on the same variables as at equilibrium and that the Gibbs equation is here correct.

The central concept of CIT is the rate at which entropy is produced during an irreversible process. It has been since the origin of irreversible thermodynamics related experimentally to the well-known empirical laws like Fourier's, Fick's or Ohm's. The rate of local entropy production $\sigma$ follows from the general balance equation of entropy

$$\frac{\partial(\rho s)}{\partial t} = -\nabla.(\mathbf{J}_s + \rho s \mathbf{v}) + \sigma \qquad (1)$$

with

$$\sigma \geq 0 \qquad (2)$$

Here $\rho$ is the mass density, $s$ is the local specific entropy, $\mathbf{J}_s$ is the local entropy flux and $\mathbf{v}$ is the velocity field. $\nabla$ means

the nabla operator and it is worth noticing that the flux $\mathbf{J}_s$ contains two terms: the first is connected with heat conduction and the second arises from the diffusion. Relation (2) is in agreement with the second law of thermodynamics. The basic distinction is here between reversible and irreversible processes, since only the irreversible ones contribute to entropy production.

Our objective is now to explicitly calculate the local rate of entropy production in terms of the "force" that drives an irreversible process and of the response to this force, the "flux". Since the local-equilibrium hypothesis allows us to write Gibbs equation locally for any time, the suitable starting point is this equation in terms of time derivatives,

$$T\dot{s} = \dot{u} + p\dot{v} - \sum_k \mu_k \dot{c}_k \qquad (3)$$

Here the lowercast letters *s*, *u*, and *v* indicate extensive quantities per unit mass, $\mu_k$ is the chemical potential of the constituent *k* and $c_k$ the mass fraction of *k*. Replace $\dot{u}$, $\dot{v}$, and $\dot{c}_k$ by the appropriate balance equations, and after rearrangements one obtains for σ an expression which contains six different effects: the first is related to heat conduction, the second to matter flow (diffusion), the third and fourth to mechanical dissipation (viscosity), the fifth to chemical reaction and the sixth to electrical currents.

We shall not write out this complicated equation (see Chapter 3), but emphasize rather the following important result: all the terms it contains have the character of a sum of the products of thermodynamic fluxes $J_k$ (for example heat flux, diffusion, chemical reaction) and of conjugated generalized forces $X_k$ (gradients of temperature, gradients of chemical potential, affinities). Thus the basic formula for the rate of entropy production of the irreversible process can be written in the simple form,

$$\sigma = \sum_k J_k X_k \qquad (4)$$

That means, the rate of production of entropy is the sum of products of each flux with the associated force. Evidently, all $J_k$ and $X_k$ vanish at equilibrium.

The existence of a non-negative entropy production is one of the main points underlying CIT. The further is the existence of linear constitutive laws. They postulate that the fluxes $J_i$ and the generalized forces $X_j$ are related linearly:

$$J_i = \sum_j L_{ij} X_j \qquad (5)$$

Equations (5) are called phenomenological equations and the coefficients $L_{ij}$ phenomenological (kinetic) coefficients. This scheme automatically includes the empirical laws mentioned above. Experimental evidence and theoretical considerations in statistical mechanics have confirmed that a wide class of processes can be described by means of linear relations between fluxes and forces. This is true in particular for transport processes.

The phenomenological coefficients are subject to the rule of selectivity limiting the possibility of interference between irreversible processes of different tensorial character and they are dominated by the Onsager reciprocal relations which state that

$$L_{ij} = L_{ji} \qquad (6)$$

It is, when the flow $J_i$ corresponding to the irreversible process *i* is influenced by the force $X_j$ of the irreversible process *j*, then the flow $J_j$ is also influenced by the force $X_i$ through the same coefficient.

The Onsager relations belong to the most significant results of CIT. They were originally based only on experiments, but they are motivated today usually on a molecular base and were shown to be a consequence of the time-reversal invariance of the microscopic dynamics. The validity of these relations has been challenged on the microscopic level, but they are generally accepted to be correct at the macroscopic level. Experimental tests showed that they are a particularly powerful tool for linear processes and for studying coupled phenomena, like thermodiffusion, thermoelectric and thermomagnetic effects.

CIT is the most successful method of irreversible thermodynamics and it turned out to be very useful in many practical situations. Its current tasks are the linear transport phenomena, the coupled phenomena, the mixtures and chemical kinetics. It must be conceded however that the theories underlying it are not general and are of an approximative character. They are correct only near equilibrium and the hypothesis of local equilibrium is only consistent with local and instantaneous relations between fluxes and forces. There are also several limitations on the microscopic level, but they will not be discussed here. Efforts have been made to enlarge the range of applications of CIT and they led to the formulations of the following new theories.

## 3.   Extended irreversible thermodynamics[9,10]

Extended irreversible thermodynamics (EIT) is the last variant of irreversible thermodynamics. Its principal objective is to go beyond the local equilibrium hypothesis by generalizing the classical theory. EIT is not a universal theory, but assumes many faces. The generalized macroscopic formulation which represents the core of the whole theory, is corroborated from a microscopic point of view by the kinetic theory, nonequilibrium information theory and other formulations of nonequilibrium statistical mechanics. In addition, an axiomatic version of EIT has been proposed which is formulated along the line of thought of rational thermodynamics (see Chap. 4) and borrows some methods and concepts of it. In this article we shall sketch out only the generalized macroscopic version and we shall follow mostly the method of Lebon.

Macroscopic EIT enlarges the CIT and this is achieved in two ways:
1.  The theory introduces besides the classical thermodynamic variables, such as density, concentration, temperature, as new independent variables some nonequilibrium quantities taking the form of the heat flux, the viscous pressure

tensor, the flux of matter, the flux of electric current, etc. These "complementary" variables are then treated on the same level as the usual classical variables.

2. To compensate for the lack of evolution equations, supplementary rate equations for the dissipative fluxes are introduced, in addition to the usual balance equations of mass, momentum and energy. These rate equations are compatible with the second law of thermodynamics. Whereas the evolution equations for the classical variables are given by the usual balance laws, no general criteria exist concerning the evolution equations of the dissipative fluxes. A natural way to obtain them from a macroscopic base is then to generalize CIT.

We outline now the formalism. The central role plays here the entropy. We assume that the system depends locally not only on the classical variables, but also on the dissipative fluxes which we regard as independent variables. It is worth noting that these fluxes, and also generalized forces, in equations of EIT are not necessarily scalar quantities but they represent vectorial and tensorial quantities as well. For simplicity, we restrict ourselves in the next discussion to a pure Stokesian fluid, where only heat flux $\mathbf{q}$ and bulk viscous pressure $p^v$ are taken as supplementary independent variables, and for this special case we have for the generalized entropy the relation

$$s = s(u, v, \mathbf{q}, p^v) \qquad (7)$$

Here $u$ and $v$ have their usual meaning and the specific entropy $s$ is an additive and positive quantity. From the differential form of eq. (*7*) we arrive to the generalized Gibbs equation (in Lebon's notation)

$$\mathrm{d}s = T^{-1}\mathrm{d}u + T^{-1}p\mathrm{d}v - T^{-1}v(\alpha_{10}\mathbf{q} \cdot \mathrm{d}\mathbf{q} + \alpha_{00}p^v\mathrm{d}p^v) \qquad (8)$$

which is the central thermodynamic result of EIT for the case of a Stokesian fluid. We note that eq. (*8*) is useless unless we have identified the parameter $\alpha$ in physical terms. This is done with help of the evolution equations of the fluxes.

The theory of EIT yields farther an expression for the generalized entropy flux and in particular for the entropy production which has the structure of a bilinear form similar to eq. (*4*) in CIT, but contains additional terms depending on the time and space derivatives of the fluxes. The nonequilibrium absolute temperature and the nonequilibrium thermodynamic pressure are introduced and in terms of them the nonequilibrium equations of state are derived. Of special interest are the supplementary rate equations for the dissipative fluxes which compensate for the lack of evolution equations. They are original but contain unfortunately besides the $\alpha$ coefficients several new coefficients which must be identified on physical grounds.

EIT provides a link between thermodynamics and dynamics of fluxes, and it is especially useful in describing systems with relatively long relaxation times, e.g. solids at low temperatures, superfluids, some viscoelastic fluids, etc. The statements behind it are confirmed by the kinetic theory of gases and by statistical mechanics.

It may be asked what are the reasons for choosing the fluxes rather than the gradients of the classical variables as new independent quantities. This question has been answered

by Lebon as follows. The fluxes are associated with well defined microscopic operators and they are advantageous for slow and steady state phenomena. By expressing entropy in terms of the fluxes the classical theory of fluctuations can be easily generalized.

The formalism of EIT has been the subject of some criticisms. In particular:

– Every dissipative flux is considered as a quantity characterized by a single evolution equation. However, this is in practice not always the case.

– There exist still other "additional" variables and variety of evolution equations for the fluxes as well.

– Entropy is regarded as an analytical function of the fluxes, but this is not an essential assumption and non-analytical developments have been proposed.

– EIT is no longer compatible with the concept of local equilibrium (for example the memory for temperature), the status of entropy and the validity of the Gibbs equation in nonequilibrium are therefore controversial (see Chapter 4).

## 4. Rational thermodynamics[9–14]

This theory is not a current thermodynamic theory but nonlinear thermomechanics of continuous media and it is drastically different from CIT. However, since it is very general, it takes the classical method for its linear approximation. It is a phenomenological and macroscopic theory which ignores the molecular structure and it is also a mathematical theory. Its structure is clear and logical, and the formulation of the results is exact and free from ambiguities.

The concept of local equilibrium is abandoned and for the characterization of a system the new concept of memory is introduced. The behaviour of the system is thus determined not only by the present value of the variables but also by the whole history of their past value. Main objective of rational thermodynamics is to provide a method for deriving constitutive equations which serve for a most faithful description of actual physical processes. It operates with a certain number of axiomes and this point has been often criticized in the sense that "it uses a set of a priori postulates and constitutive functionals for defining a thermodynamic body" (S. Lengyel, 1984). Finally, rational thermodynamics is not one universal theory but rather a working programme.

The method of rational thermodynamics resembles to that of mechanics:

1. Selection of quantities describing the system (primitive concepts and concepts defined in terms of them).
2. General laws or balances valid for all the sphere under investigation (e.g. the first and the second law, balance laws of mass, momentum and energy).
3. Construction of constitutive equations (it is a sort of generalized equations of state formulated in an abstract form).
4. Application of constitutive postulates, which are used for a general formulation of constitutive relations.

The searched solution of the task under consideration consists in the insertion of constitutive equations in general laws or balances ad 2. It leads to differential equations which must be solved hereupon.

The constitutive postulates are for rational thermodyna-

mics characteristic, they serve mainly to restrictions of constitutive equations and help to find their ultimate forms. In particular, the constitutive equations must meet these postulates which are usually called "principles", but some of them are only useful rules. Of special interest for thermodynamics is the principle of admissibility, called also the entropy principle, which opened a way to construct rational thermodynamics. We mention further the principle of equipresence (concerns the presence of variables in constitutives), the principle of objectivity (frame independence), the principle of local action (influence of neighbourhood), the principle of memory (heredity) and the principle of symmetry. The above axioms are general enough to be applied to all constitutive equations.

We now outline the method of rational thermodynamics on the example of the celebrated theory of Šilhavý which will be presented in simplified terms.

The theory first introduces a new concept called the heat distribution which informs us how much heat was exchanged at each empirical temperature and it is of importance in the framework of the second law. Second, four postulates concerning the properties of the thermodynamic system under investigation are claimed and two more for the universe. The postulates for the system which is in the theory considered as a closed one, concern the work, the heat distribution and the processes taking place in the system, and the postulates for the universe formulate its closeness and completeness, respectively.

The core of the formalism are the very original and clever definitions of the first and the second laws of thermodynamics. Since they are formulated exclusively in terms of the primitive notions of heat, work, empirical temperature and in terms of cyclic processes, their experimental verification is at least in principle possible.

The first law is postulated as assertions about the nonexistence of perpetual motion of the first kind: In any cyclic process the system can perform work $w$ if and only if it absorbs heat $q$:

$$w < 0 \Leftrightarrow q > 0 \qquad (9)$$

The second law is formulated as the postulate of the impossibility of the perpetual motion of the second kind: In a cyclic real or ideal process the system can absorb heat only if it emits some heat, i.e.,

$$q^+ > 0 \Rightarrow q^- > 0 \qquad (10)$$

where $q^+$ is the heat absorbed and $q^-$ the heat emitted during the process.

From the postulate (*9*) and those about the thermodynamic system and the universe follow these logical consequences: The existence of the mechanical equivalent of heat, $J$, of a state function called the internal energy, $U$, and of the balance of energy

$$\Delta U = Jq + w \qquad (11)$$

One takes usually $J = 1$ and $U$ is determined within an additive constant (it is unique). The balance (*11*) is not bound to any concrete model and is therefore applicable to an arbitrary system (material).

From the formulation of the second law (*10*) and the postulates about the system and the universe follow the following consequences: The existence of the absolute temperature, $T$, of the Clausius inequality for any cyclic process and the state function entropy, $S$, for each process of the universe such that for every process the entropic inequality

$$\Delta S \ge \int \frac{\mathrm{d}Q}{T} \qquad (12)$$

is valid. Here d$Q$ is the heat exchanged during the processes at the absolute temperature $T$. Unlike $U$, entropy is not unique in the sense that more entropies satisfying (*12*) and differing by a function of state may be constructed. On the other hand, it is indeed constant within an additive constant in the special case in which the initial and the final states of $S$ are known and fixed, e.g. in reversible processes. Relation (*12*) is not restricted to any concrete model and is thus applicable to an arbitrary system.

The proof of these results is made geometrically, but it is tedious and will not be shown here.

It can be concluded that the results of the Šilhavý's method show the practicability of basic thermodynamic laws and of the quantities they contain (absolute temperature, entropy, entropic inequality) also in general thermodynamic systems and processes. It means also in nonequilibrium situations, and they enlarge the classical results very much. These excellent results mean a fundamental contribution to the whole modem thermodynamics.

The theory of Šilhavý is applicable in the whole classical thermodynamics and in the majority of irreversible thermodynamics, mainly in irreversible transport phenomena, in the mixtures and in chemical kinetics. Its principal deficiency is that its range of application is limited to closed systems and to cases with a single empirical temperature. Thus, it is for example not applicable to diffusing mixtures or to plasma.

**Note:**

It is of interest that the postulate of linearity of CIT follows from the general theory of rational thermodynamics. On the other hand, the Onsager reciprocal relations follow only after some additional assumptions about the constitutive equations.

## 5.   Concluding remarks

Classical (linear) irreversible thermodynamics is based on the fundamental hypothesis of local equilibrium. The validity of the results of equilibrium thermodynamics is thus anticipated at the outset. The classical method turned out to be very useful in many practical situations, but the theories underlying it are not general and they are of an approximative character. The method is inadequate to treat situations far from equilibrium or systems with complicated inner structures (e.g. bodies with memory).

Extended irreversible thermodynamics is no longer based on the local-equilibrium hypothesis but it generalizes and enlarges the classical theory. It introduces besides the classical thermodynamic variables the dissipative fluxes as new inde-

pendent variables. To compensate for the lack of evolution equations, supplementary rate equations for the dissipative fluxes are introduced. The central thermodynamic result is the generalized Gibbs equation. The statements behind this theory are confirmed by the kinetic theory of gases and by statistical mechanics.

Rational thermodynamics presents a very rigorous mathematical formalism and it abandons the hypothesis of local equilibrium. It is a phenomenological and macroscopic theory which ignores the molecular structure and assumes that materials have a memory. Its main objective is to derive constitutive equations which must meet a certain number of a priori postulates.

The theory of Šilhavý demonstrates the practicability of the methods of equilibrium thermodynamics in nonequilibrium for closed systems with a single empirical temperature. This method enlarges the results of classical thermodynamics essentially in these points: it proves the existence of absolute temperature and of entropy also in nonequilibrium and derives the energy balance and the entropy inequality for an arbitrary system. Entropy is unique within an additive constant because the Gibbs equation (i.e. local equilibrium) is valid.

The present note is devoted to the phenomenological and macroscopic aspects and the promising microscopic approaches lie therefore outside the scope of this paper.

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**I. Vavruch** *(CH-1723 Marly, Switzerland):* **Conceptual Problems of Modern Irreversible Thermodynamics**

This article deals with the general ideas of irreversible thermodynamics. First the classic theory is discussed, next extended irreversible thermodynamics and rational thermodynamics are treated. To limit the enormous extent of the subject, only macroscopic aspects are examined.