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# RECIPROCITY RELATIONS. MAXWELL, ONSAGER A THERMOKINETIC APPROACH

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## Abstract

Thermokinetics is the general kinetic theory of physico-chemical phenomena. Though its basic conception is very old, the thermodynamic theory has been developed only in the last two decades. The scope of Thermokinetics extends to equilibria (dynamics of equilibria), to near-equilibrium (Onsagerian Irreversible Thermodynamics) and far from equilibrium processes (chemical reactions). The kinetic treatment results in new interpretations for old concepts, such as rate coefficients, symmetry relations, cross effects, etc. The proper selection of variables leads to a symmetric and unified system of static and dynamic properties and relationships. As Maxwell's experimentally confirmed reciprocities (MRR) confirmed the existence of the entropy, in a similar way, the empirical dynamic reciprocities (DRR) lead to the 'Entropy dissipation Function ($D_S$)' and vice versa, DRR can be proved, similarly to MRR, as the reciprocity of the second derivative matrix of $D_S$. Onsager's ORR is regarded as a special case of DRR. Problems about other proofs are listed in brief.

*Keywords:* thermostatics, thermokinetics, reciprocity relations, Maxwell, Onsager.

## 1. Introduction

### Beauty in Description of Nature

The old Greeks believed in that Nature is built up of simple, symmetrical elements: (regular polyhedra), its description must be as simple and symmetrical as geometry and mathematics, reflecting its beauty in structure [1].

To Leonardo da Vinci is attributed the saying:

'When a construction is not beautiful then it cannot be good'

Copernicus and Kepler searched a more simple and beautiful interpretation of the motions of the system of Earth, Sun and planets: the heliocentric model. Mechanics arrived at a stage of evolution when its fundamental relations exhibit a perfect beauty. Well known are Hamilton's canonical equations, Einstein's space-time relativistic relations, the Schrödinger equation and unified relationships of elementary particles and interactions. The

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beauty is accompanied with symmetries, general validity, unified description, simplicity, possibility of making general calculus in a wide range of applications.

J.W.Gibbs wrote (motto of Tisza's 'Generalized Thermodynamics' [2]):

'One of the principal objects of theoretical research in any department of knowledge is to find the point of view from which the subject appéars in its greatest simplicity'.

In developing theoretical models it was always an important question: which of the variables are to be selected, which points of view, which coordinates fit best the nature of the material system. This, in most cases, may differ from the point of view of experimental observations (example: the characterization of the heat conductance of an anisotropic, e.g., triclinic crystal needs six independent parameters in the Cartesian coordinates but only three in the oblique-angled eigen-system. The entropy, chemical potential, heat or diffusional mass flow etc., are in most cases not directly measurable).

Experience proves that the two main 'points of view' differ in that

a. Textbooks of the 'observer-applier' type deal with the interaction of the material world and man, from the point of view of the latter. Descriptions lead to complicated (ugly) relations (see: Earth-centric astronomy, thermodynamic books written for engineers dealing with heat and work, engines, perpetuum mobile, temperature defined by thermometer, entropy by calorimeter, I., II., III. Law, equations of state of non-ideal gases). Quoting Truesdell [3]: they are '... loaded with words like piston, boiler, condenser, heat bath, reservoir, ideal engine, perfect gas, quasi-static, cyclic, nearly in equilibrium, isolated...'
b. The 'exact' treatise deals with the Nature in itself and not with the observer. (Astronomy dealing with solar system. Gibbsian, Onsagerian thermodynamics and 'thermokinetics'. Unified general laws, symmetric and definite matrices, simple and descriptive equations of state). The aim is simplicity, ease of understanding, exact definitions and beauty of the system of relationships.

The 'exact' thermodynamics, thanks to Gibbs, Onsager, Prigogine, Callen and others, arrived at some high level of beauty.

But.

Not all were satisfied perfectly by the thermodynamics as it appeared in most textbooks. Truesdell wrote (loc.cit. [3]): 'The difference between mechanics and thermodynamics is that thermodynamics never grow up'.

Though the target of the critics is first of all the 'observer-centric' technical thermodynamics, some beuty-breaks, disharmonies burden the latter one as well. One may ask: 'isn't thermodynamics finished yet? The answer is firm: Yes, not'. The search for a more proper representation is to be continued, some necessary corrections need to be made, false notes are to be corrected.

Some instances of disharmony found in thermodynamics are

a. Gibbs' fundamental equations.
b. Einstein's model for the equilibrium of matter and radiation.
c. Limited validity of the Law of Microscopic Reversibility.
d. Onsager's kinetics: why is it restricted to linear relations?
e. Difficulties at the proof of the Reciprocal Relations.
f. Non-ideal systems : why are not valid the ideal equations of state?

The answers can be given in terms of the kinetic theory, the

**Thermokinetics**

## 2. Gibbs, the Fundamental Equations, Density- and Potential-Space

The fundamental equations, written for a global system exhibit some asymmetry :

GIBBS

$$dS = (1/T) \cdot dU + \sum_k (-\mu_k/T) \cdot dN_k + (P/T) \cdot dV \,, \tag{1}$$

EULER

$$S = (1/T) \cdot U + \sum_k (-\mu_k/T) \cdot N_k + (P/T) \cdot V \,, \tag{2}$$

GIBBS–DUHEM

$$0 = U \cdot d(1/T) + \sum_k N_k \cdot d(-\mu_k/T) + V \cdot d(P/T) \,. \tag{3}$$

Two of the three relationships are independent, thus the number of variables is greater than necessary by one. This may cause some problems. For example, the second derivative matrix of the entropy is singular, its inverse cannot be calculated. The Legendre-transformed form of the entropy is zero.

The so called '**local**' system is more convenient. A local system is a small area of given volume without any physical walls (open system ). The Gibbs space is then spanned by the densities (in other word, the concentrations), defined as

$$C_i \equiv \lim_{V \to 0} (E_i/V) \,. \tag{4}$$

By definition, the density of the volume is $C_V = 1$ and $dV = 0$. For local systems, consequently, the superfluous variable, the volume disappears (densities do not depend on the volume). Taking $dV = 0$ and dividing by $V$:

GIBBS

$$d(S/V) = (1/T)\cdot d(U/V) + \sum_k (-\mu_k/T)\cdot dC_k = dW^C, \quad (5)$$

EULER

$$(S/V - P/T) = (1/T)\cdot (U/V) + \sum_k (-\mu_k/T)\cdot C_k \equiv W, \quad (6)$$

GIBBS–DUHEM

$$-d(P/T) = (U/V)\cdot d(1/T) + \sum_k C_k d(-\mu_k/T) = dW^F. \quad (7)$$

As seen, $P/T$ is a Legendre-transformed of $S/V$. As $S/V$ is the principal quantity of the **density-space**, $P/T$ is the same for the **potential-space** both connecting potentials and densities. $W$ is used mostly in statistical studies, called as 'KRAMERS potential' [4].

Denoting the *independent* sets of $C$'s and $F$'s by $C_i$ and $F_i$

$$dW = d(\sum_i C_i\cdot F_i) = \sum_i F_i\cdot dC_i + \sum_i C_i\cdot dF_i =$$

$$= d(S/V) + d(-P/T) = d^C W + d^F W \quad (8)$$

$$F_i = \left(\frac{\partial(S/V)}{\partial C_i}\right);\quad C_i = \left(\frac{-\partial(P/T)}{\partial F_i}\right). \quad (9)$$

Both $S/V$ and $P/T$ have nonsingular second derivative matrices. Experiments confirm that in many instances $P/T$ may deserve more attention than S!

(In mechanics, the kinetic energy, function of the conservative momenta, is the parallel of the entropy density, and the velocity of the $F_i$').

## 3. Thermokinetics. Rate Equations

### 3.1. Absolute and Net Rates

Thermodynamic systems consist of a great number of similar elements (e.g., particles). Processes are carried by the motions of the particles. Thermodynamic motions differ from those of mechanics in that any process is accompanied by its reverse. As it was put in words by FOWLER (1924) [5]: **'any one process of exchange acting in a particular direction must be invariably companied by an analogous reverse process'**. Consequently

**any 'net' process rates ($J_i$) are differences**

of 'forward' ($j_i^{\rightarrow}$) and 'backward' ($j_i^{\leftarrow}$) '**absolute**' process rates:

$$\mathbf{J_i = j_i^{\rightarrow} - j_i^{\leftarrow}} \tag{10}$$

Examples: chemical reaction 'from left to right' and 'from right to left'(arrows $\longrightarrow$ and $\longleftarrow$), evaporation and vapour condensation, in gases the flux of particles in directions $+X$ and $-X$ and the anodic and cathodic exchange current at electrode surfaces. Onsagerian 'irreversible thermodynamics' (IT) always deals with 'net' fluxes ($J_i$). IT, consequently, have lost any contact with thermostatics. In equilibria net fluxes (and the forces) always vanish, the rate equations degenerate to $0 = 0$. The kinetic theory (Thermokinetics), in contrast, deals with absolute rates, studies therefore not only irreversible processes but dynamics of equilibria as well. (It cannot be called irreversible theory ). $j_i$ absolute rates ( as the potentials ) do not vanish but equilibrate in equilibria. Knowing the rate relations between $j_i$ and $F_i$, one knows all from the relations of $J_i$ and $X_i$, their differences . Onsager's IT is, consequently, a part of the general kinetic theory as its linear limiting case. It is hard to understand that, since Onsager, in process thermodynamics the absolute rates have been quite forgotten.

$$\begin{tikzcd}
\text{Net fluxes} & J_i \arrow[d] & = & j_i^{\rightarrow} \arrow[d] & - & j_i^{\leftarrow} \arrow[d] & \text{Absolute fluxes} \\
 & \text{linear} \arrow[d] & & {} \arrow[d] & \text{non-linear} & {} \arrow[d] & \text{rate relations} \\
\text{Forces} & X_i & = & F_i'' & - & F_i' & \text{Potentials} \\
 & \text{(Onsager, IT)} & & & \text{(Thermokinetics)} & &
\end{tikzcd}$$

### *3.2. The Two Important Types of Rate Equations*

#### *3.2.1. The Kinetic Mass-Action Law (MA)*

The law was declared by GULDBERG and WAAGE (1872) [6]. In brief, MA asserts: **the rate of a process is proportional to the number density of the participants**. The factor of proportionality is called the *rate constant of the process* ($k$).

$$\mathbf{j(C_n)}\ . \tag{11}$$

This is the absolute rate in terms of the densities (density-space).

The law, though it was not declared, was employed since the first half of the 19th century, first of all, for chemical processes. Boltzmann, Maxwell,

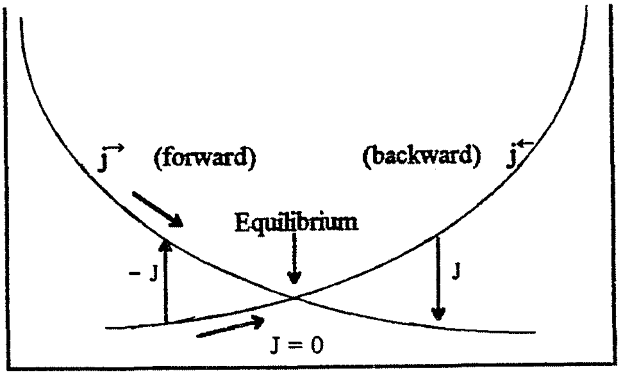


*Fig. 1.* Absolute and net process rates

Einstein, Tolman, Onsager and many others up to now, all calculated with rate equations of the MA type. The physical content of the law seems clear and self-evident. However, in some instances problems arose, calculations with MA are responsible for a series of problems. It really works well only for elementary (atomic) processes, and for ideal mixtures. The time-reversal symmetry law, the Microscopic Reversibility is therefore restricted to microscopic processes, Onsager coped hardly with MA type equations. The processes in non-ideal systems are described only in a very complicated way, the activities cannot be avoided threatening its original meaning. The exclusive use of MA equations is responsible for the fact that a kinetic thermodynamic theory could not be developed for a very long time.

### *3.2.2. The Potential-Action Type Rate Equations (PA)*

In PA type relationships the absolute process rates ($j$) are expressed

$$\textit{in terms of the potentials} \quad \mathbf{j}_i(\mathbf{F}_1 \ldots, \mathbf{F}_n)\,, \tag{12}$$

where the variables $F_i$ form the set of independent potentials (potential-space). (12) reminds us of the Onsagerian 'ohmic' rate equations (net fluxes in terms of the forces). This representation exhibits more favourable properties.

First, rate equations of different types of processes have a unified, general form [7].

Secondly, it leads to the time-reversal symmetry law [8], [9] of general importance.

Thirdly, they make possible to develop a thermodynamic theory for non-ideal systems [10].

### 3.3. *The Entropy Dissipation Function*

The dynamic parallel of the Kramers potential is the Entropy Dissipation $D_S$) [11]

$$D_S \equiv \sum_i j_i \cdot F_i \,, \tag{13}$$

$j_i$ and $F_i$ form the independent set again. The exact differential of $D_S$ is

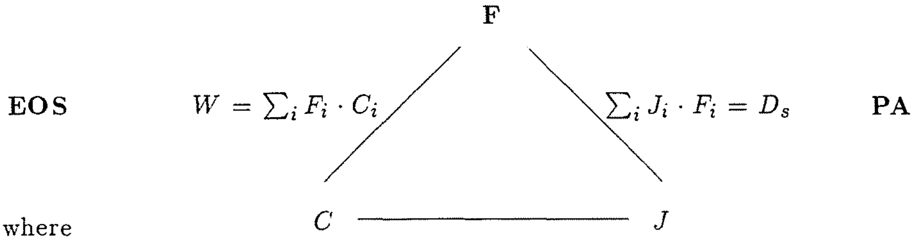
$$dD_S = \sum_i F_i \cdot j_i + \sum_i j_i \cdot dF_i = dD_S^j + dD_S^F \,. \tag{14}$$

Comparison with (8) shows that $D_S^j$ is the parallel of $S/V$ and $D_S^F$ of $P/T$.

The first derivatives are

$$F_i = \left(\frac{\partial D_S^j}{\partial j_i}\right) \;; \quad j_i = \left(\frac{\partial D_S^F}{\partial F_i}\right) . \tag{15}$$

The absolute rates form the third important set of entities in the unified thermodynamic system. The relations may be visualized as follows:



where

EOS means the equations of state at equilibrium
MA means Mass-Action type rate equations and
PA means the Potential-Action type rate equations.

## 4. Reciprocities

### 4.1. *Thermostatics. Maxwell's Reciprocity Relations*

The dependences of the differentials represent the appropriate matrices of the exact differentials of Jacobian form

$$dC_i = \sum_i \Gamma_{ik} \cdot dF_k \,, \tag{16}$$

$$dF_i = \sum_i \Gamma_{ik}^{-1} \cdot dC_k \,. \tag{17}$$

The elements $\Gamma_{ik}$ form a quadratic matrix ('state matrix'). The diagonal elements $\Gamma_{ii}$ and $\Gamma_{kk}$ represent the self-effects. $\Gamma_{ik}$ is responsible for the *cross-effect* between the $i$'th and the $k$'th interaction. $\Gamma$ is the second derivative matrix of $P/T$ and $\Gamma^{-1}$ that of the entropy density. It follows from the elementary theorem of calculus that matrix $\Gamma$ is always symmetrical, consequently, no matter if the EOS are linear or not.

$$\Gamma_{ik} = \left(\frac{\partial C_i}{\partial F_k}\right) = \left(\frac{\partial^2 P/T}{\partial F_i \partial F_k}\right) = \left(\frac{\partial^2 P/T}{\partial F_k \partial F_i}\right) = \left(\frac{\partial C_k}{\partial F_i}\right) = \Gamma_{ki}\,, \tag{18}$$

$$\Gamma_{ik}^{-1} = \left(\frac{\partial F_i}{\partial C_k}\right) = \left(\frac{\partial^2 S/V}{\partial C_i \partial C_k}\right) = \left(\frac{\partial^2 S/V}{\partial C_k \partial C_i}\right) = \left(\frac{\partial F_k}{\partial C_i}\right) = \Gamma_{ki}^{-1}\,. \tag{19}$$

$$\begin{gathered}\Gamma_{ik} - \Gamma_{ki} \\ \text{Maxwell's Reciprocity Relations (MRR)}\end{gathered} \tag{20}$$

This reciprocity is *confirmed by experiments*. Mathematically it is proved by (19). The sufficient condition of the symmetry is that $P/T$ and $S/V$ exist and are continuous functions of the potentials and densities, respectively. (Local equilibrium).

### *4.2. The Dynamic Reciprocity Relations*

The partial derivatives connecting $j_i$'s and $F_i$'s form the matrix $\Lambda$

$$dj_i = \sum_i \Lambda_{ik} \cdot dF_k\,, \tag{21}$$

$$dF_i = \sum_i \Lambda_{ik}^{-1} \cdot dj_k\,. \tag{22}$$

$\Lambda_{ik}$ are the second derivative of the Entropy Dissipation. They from symmetric matrix

$$\Lambda_{ik}^{-1} = \left(\frac{\partial F_i}{\partial j_k}\right) = \left(\frac{\partial^2 D_S^j}{\partial j_i \partial j_k}\right) = \left(\frac{\partial^2 D_S^j}{\partial j_k \partial j_i}\right) = \left(\frac{\partial F_k}{\partial j_i}\right) = \Lambda_{ki}^{-1}\,, \tag{23}$$

$$\Lambda_{ik} = \left(\frac{\partial j_i}{\partial F_k}\right) = \left(\frac{\partial^2 D_S^F}{\partial F_i \partial F_k}\right) = \left(\frac{\partial^2 D_S^F}{\partial F_k \partial F_i}\right) = \left(\frac{\partial j_k}{\partial F_i}\right) = \Lambda_{ki}\,. \tag{24}$$

$$\begin{gathered}\Lambda_{ik} - \Lambda_{ki} \\ \text{The Dynamic Reciprocity Relations (DRR)}\end{gathered} \tag{25}$$

(The dynamic equivalent of MRR). The validity of DRR does not depend on the functional form $j(F)$, consequently, *is not confined to linearity.* Summing the two symmetrical relationships we get

$$\begin{tikzcd}
 & & \mathbf{dF} \arrow[dl, dash, "\sum_i dF_i \cdot dC_i \leq 0"', "\Gamma"] \arrow[dr, dash, "\sum_i dj_i \cdot dF_i \leq 0", "\Lambda"'] & & \\
\text{Negative } \delta^2(S/V) & \mathbf{dC} \arrow[rr, dash] & & \mathbf{dj} & \text{Negative } \delta^2\mathbf{D_s}
\end{tikzcd} \tag{26}$$

### *4.3. Onsager's Reciprocity*

Lars Onsager with his two famous papers which appeared in 1931 [12], laid down the foundations of the thermodynamic theory of non-equilibrium ('irreversible') systems. In his work he declared the reciprocity between different processes as a general thermodynamic law. Onsager supposed that, not far from equilibrium, the (net) fluxes ($J_i$) are linear functions of the forces ($X_k$) (the 'Ohm's laws' of thermodynamics)

$$J_i = \sum_k L_{ik} \cdot X_k \, , \tag{27}$$

where $J_i$ is the net rate of the $i$'th process, $X_k$ is the k'th thermodynamic driving force (difference or gradient of $F_k$) $L_{ik}$ is the appropriate rate coefficient.

Onsager's reciprocity principle asserts symmetries for the cross coefficients

$$\mathbf{L_{ik} - L_{ki}} \qquad \text{(Onsager's Reciprocity Relations) (ORR)} \tag{28}$$

Similarly to that of Maxwell, this reciprocity is confirmed by experiments.

(Later H.B.G. CASIMIR [13] has extended the law to more general systems, e.g., to the presence of magnetic field and therefore the cross symmetry law is often called 'Onsager–Casimir Relations'). Onsager has tried to give a general proof of these relations. His approach was based on the law of MR declared not long before, supposing that it was a law of general validity responsible for all dynamic symmetries in thermodynamics. He derived the reciprocities by an argument borrowed from fluctuation-dissipation theory with the assumption that the rate at which a fluctuation in an equilibrium ensemble regresses equals the rate at which the ensemble average of the same quantity will change in a nonequilibrium ensemble. For example, he supposed that the average decay of temperature fluctuations obeys the ordinary laws of heat conduction. (His first example was the heat flow in an anisotropic body). From a fluctuation-dissipation law called by him the law of microscopic reversibility he derived the symmetry relation for this phenomenon. This proof was not convincing for all. MEIXNER wrote (1973): [14] (p.55.) 'The Onsager–Casimir reciprocal relations yield more information than the fluctuation-dissipation theorem combined with microscopic reversibility. Rather, this is a separate and independent statement'.

Onsager was, in searching a general proof for (28), in a very difficult position.

First, use of net and not *absolute* fluxes restricted all statements to linear rate relations.

Secondly, the Microscopic Reversibility concerns only absolute reverse rate pairs of a *single* process and cannot do anything with cross effect of *different* processes.

Thirdly, the law of Microscopic Reversibility can be applied only to microscopic, atomic processes.

Fourthly, in deriving the relations of rate equations Onsager could use only rate equations of the $j(C)$ type, consequently, the calculations were complicated.

The problem can be solved:

Because ORR is a special linear version of DRR from the reciprocity DRR follows the reciprocity ORR.

Remember that in thermodynamics operation '*d*' may have more physical meanings.

A few of them may be:

a. Small difference (deviation from equilibrium):

$$dC \cong \Delta C \ , \quad dF \cong \Delta F = X \ , \quad dj \cong Dj = -J \tag{29}$$

b. Gradients or divergences $\nabla C$ or $\nabla J$
c. Time rate of change $dC/dt$
d. For chemical reactions, '*d*' is to be replaced by the stoichiometric matrix.

Near equilibrium

$$-dj_i \cong J_i = \sum_k L_{ik} \cdot X_k \cong \sum_k L_{ik} \cdot dF_k = -\sum_k \Lambda_{ik} \cdot dF_k \ . \tag{30}$$

Consequently, the symmetry of $\Lambda$ is equivalent to the symmetry of

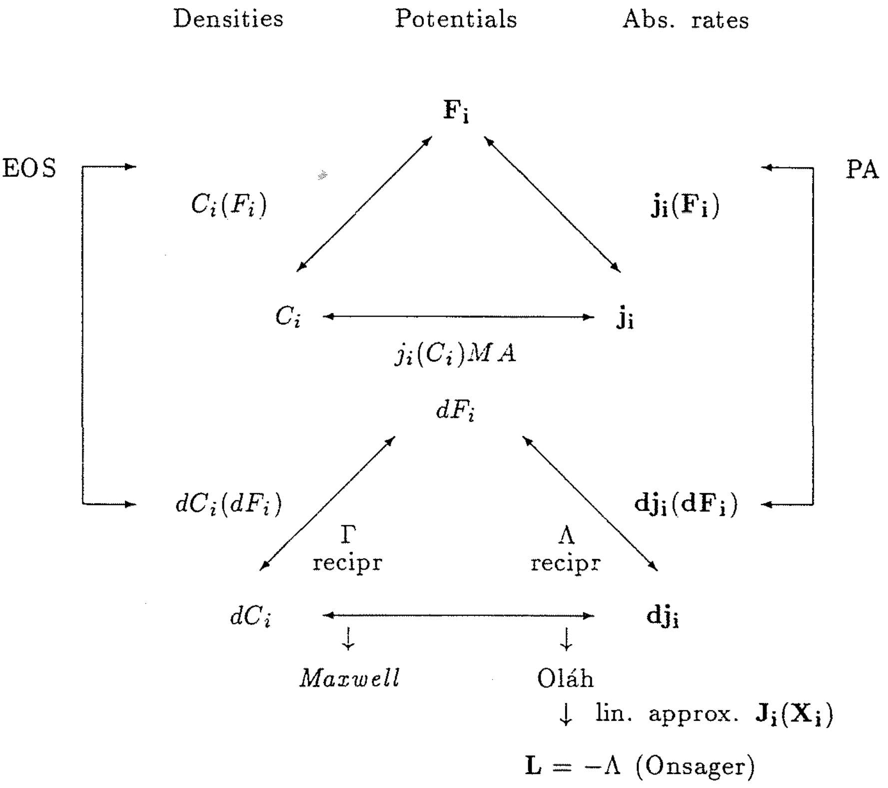
$$\mathbf{L}_{\mathbf{ik}} = -\mathbf{\Lambda}_{\mathbf{ik}} = -\mathbf{\Lambda}_{\mathbf{ki}} = \mathbf{L}_{\mathbf{ki}} \tag{31}$$

quod erat demonstrandum.

## 5. Summary

The derivation can be summarized as follows

| Thermostatics | Thermokinetics |
|---|---|
| $W = \sum_i C_i \cdot F_i =$<br>$= \sum_i F_i \cdot dC_i + \sum_i C_i \cdot dF_i =$<br>$= d(S/V) + d(-P/T)$ | $D_s = \sum_i j_i \cdot F_i =$<br>$= \sum_i j_i \cdot dF_i + \sum_i F_i \cdot dj_i$<br>$= dD_s^F + dD_s^j$ |



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