

The dictates and the range of applicability of the laws of thermodynamics for developing an irreversible thermodynamical framework†

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Abstract . The sensing of thermal, mechanical and chemical interactions is a crucial demand for developing an irreversible thermodynamical framework which as has been revealed herein is inherent in the laws of thermodynamics. This requirement elegantly conforms well both with the assertion of Bridgman (1969) about the realm of 'universe of operations' of thermodynamics and Eddington's (1931) law of Nature based on 'time's arrow' which is inherent in irreversible processes. Though the laws of thermodynamics conspicuously remain silent about the chemical interactions but it has been shown that they surface out in the course of the development of an irreversible thermodynamical framework. Moreover, it gets revealed that the thermodynamic irreversibility is all about the imbalances in chemical interactions.

Keywords Irreversible thermodynamics, time's arrow and irreversibility, nature of thermodynamics

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1. Introduction

Since past couple of years, it is being stressed upon that an irreversible thermodynamical framework needs to be developed with a base of the laws of thermodynamics [1–10]. Indeed, there cannot be two opinions about this assertion. We may recall that these laws are the generalizations of the observations by the mankind of the multitude of facets of the macroscopic processes and so far no contradictory evidences have been found. However, a rigorous understanding of these laws from the point of view of developing an irreversible thermodynamical framework some how remained as not accomplished in its totality. This does not mean that the thermodynamic literature is devoid of the attempts based on the use of the second law of thermodynamics *via* Clausius' inequality and the Boltzmann H-theorem. Nevertheless, in spite of the best efforts made till now (see for example the references [1–7, 11–13]) the lines of approaches adopted starting from Clausius' inequality

and Boltzmann integro-differential equation [14] which produces the Boltzmann H-theorem, a statistical mechanical counter-part of the second law of thermodynamics, there is no sign of getting them culminated into an unambiguous thermodynamical framework for irreversible processes. Therefore, we have made efforts to identify and remove the existing stumbling blocks in this field which in turn revealed that so far certain vital features of the laws of thermodynamics remained unharnessed perhaps because of a lack of their proper comprehension and understanding and/or because of not being able to assimilate their proper perception. In this paper, we are reporting the details of our efforts and deductions thereof which does show that what Bridgman [15,16] and Eddington [17] have stressed upon several decades ago has not been properly taken care of. In doing so, we obtain a clear insight of the domain of the operation of thermodynamics of irreversible processes and that of the role played by chemical interactions therein.

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2. The laws of thermodynamics

For developing a thermodynamical framework, the zeroth, first and second laws of thermodynamics are needed to be properly understood. It is to be noted that each one of them describes an impossibility, namely :

the zeroth law of thermodynamics :

“it is impossible that heat will flow from one body to another both having same temperature and are brought in a diathermal contact.”

the first law of thermodynamics :

“it is impossible to increase or decrease the internal energy of a system in the absence of its thermal and mechanical interactions with surroundings.”

(impossibility of a perpetual motion of the first kind)

the second law of thermodynamics :

“it is impossible for a device to continuously absorb heat in its cyclic operation.”

(impossibility of a perpetual motion of the second kind).

Each one of the above three statements (laws) refers to a closed system and in each one of them, the thermal interaction of the system with its surroundings plays a key role. Only the first law of thermodynamics recognizes and brings in the thermodynamic fold, the mechanical interactions of a system (closed) with its surroundings (of course, on the lines of Bridgman [16] we include gravitational, magnetic, electrical *etc.* interactions in the fold of mechanical interactions) and the chemical interactions remain submerged within these laws.

3. Sensing of thermal, mechanical and chemical interactions

Thus, when one is led to consider the interactions (thermal, mechanical and chemical) of a system, the first requirement to be adhered with is that of its size. Bridgman [15,16] has described that there is a plateau region with respect to the size of the measuring gadget. If the size of the gadget is comparable to that of the system or less than say $10^{15} - 10^9$ cm³ [10,18] the fluctuations will be dominant even if the sensitivity of the measuring gadget is not high. Bridgman has not explicitly spelled-out but this conclusion conforms well with equilibrium as well as nonequilibrium states of a system. The second requirement is that of the time periods of these interactions. Of course, in the case of equilibrium, one can afford to wait for sufficiently long time periods to register a reading and hence it is felt that there is no rigorous requirement of the time scales allowed in this case. Of course, as cautioned by Bridgman [16] one should not go to such a long time scales of sporadic atomic disintegrations which have proceeded to their characteristic equilibrium they may have.

However, when it is a case of nonequilibrium and the system is evolving irreversibly, we need to be pretty specific. Bridgman [15,16] has described the requirement of a time period needed for registering a reading and he asserts that one needs to be well within the corresponding plateau region. In this connection, it is pertinent to recall that according to Bridgman [16], the ‘universe of operations’ of thermodynamics is determined by the ‘instrumental operations of laboratory’ otherwise one would simply end into a ‘paper and pencil operation’. As the act of registering a reading of a macroscopic property, in general, is a ‘typical irreversible process’, the above discussed two fundamental requirements get elegantly translated into the minimum size of a system allowed in thermodynamics and the ability of a system to respond in a minimum time period to the conditions imposed on it by its interacting surroundings *i.e.* by which the corresponding irreversible processes get initiated.

The said response of a system therefore, depends on how fast it interacts thermally and mechanically with its surroundings. In other words, what is the minimum time period in which a system senses thermal and/or mechanical (due to contact forces) interactions and as a consequence of it there gets initiated an irreversible process. The answer to this query conveys us the following two messages namely :

1. “thermodynamics recognizes only those processes which proceed at a rate slower or approaching to that of the sensing of the said interactions.”
2. “as the occurrence of fluctuations does not require an interaction of the system with its surroundings the fluctuational processes do not fall within the fold of thermodynamics.”

4. The constraints of time’s arrow

Another natural index, fundamental for the development of thermodynamics of irreversible processes, is that of time’s arrow. As described by Eddington [17] “the great thing about time is that it goes on and on”, *i.e.* it has its arrow directed towards future. As stated above, the irreversible processes (that is having time’s arrow) have their origin in the sensing by the system of thermal and mechanical interactions with its surroundings and that of internal chemical interactions. Therefore, ‘the minimum length of time’s arrow’ allowed in thermodynamics, is obviously much more than that of the time period of fluctuations. Of course, in the fluctuational processes the time is still there and retains its ordinary properties, but has lost its arrow. Thus, it should be clear to the reader that why fluctuational processes remain out side of the ‘universe of operations’ of thermodynamics as stated in the preceding section.

Indeed a 'one is to one' correspondence between thermodynamics of irreversible processes and time's arrow has been identified by Eddington [17] (it is amusing that this he has done much earlier than a formal thermodynamical framework for irreversible processes was developed in the fourth decade of the past century). His first assertion reads as,

... the law of monotonic increase of entropy for adiabatically closed systems is the pointer of the "arrow of time" ...

then he identifies a very powerful law of Nature and in his own words it reads in the following ways, namely :

1. time's arrow is the property of entropy alone.
2. nothing in the statistics of an assemblage can distinguish a direction of time when entropy fails to distinguish one.
3. ... other statistical characters besides entropy might perhaps be used to discriminate time's arrow, they can only succeed when it succeeds and they fail when it fails.

In respect of the above statements (the law of Nature), Eddington [17] has also stated that it does not seem to be rigorously deducible from the second law of thermodynamics, and presumably must be regarded as an additional secondary law. However, we have recently deduced the above statements [19] using the Chapman-Enskog method of kinetic theory [14] and the second law of thermodynamics. Moreover, the above statements of the said law of Nature culminates into the following secondary law [19,20], namely :

"For a process to be an irreversible one, it must be accompanied by the production of entropy".

5. The dictates inherent in the laws of thermodynamics

Let us now illustrate that the above described requirements are indeed inherent in the laws of thermodynamics. For this purpose one needs to understand that the guiding principle herein is that all processes and the mathematical descriptions which correspond to the time scales shorter than the minimum length of time's arrow of irreversible processes, remain excluded from the purview of thermodynamics. With this understanding, let us discuss the following question in the context of irreversible thermodynamics starting with the zeroth law of thermodynamics and look for its answer.

5.1. The zeroth law and the generalized zeroth law of thermodynamics :

The traditional zeroth law of thermodynamics (see for example reference [21]) deals with the question of thermal equilibrium when bodies are in equilibrium with each other and the generalized zeroth law of thermodynamics [8] takes

care of the thermal equilibration between bodies not in equilibrium. The former version of the zeroth law legitimizes the temperature function in equilibrium and the latter version in nonequilibrium. Let us pose the question, that --- "what is the minimum time period in which two bodies brought into a diathermal contact will sense that they have the same (or different) temperature"? The obvious answer is that $\tau_{th} \gg \tau_{fluc}$ where τ_{th} is the minimum time required for the diathermal contact and τ_{fluc} is the fluctuational time scale. This is so because neither the energy (heat) transfer between bodies in the time intervals $\sim \tau_{fluc}$ is governed by the difference in temperature nor if the bodies have same temperature it will forbid the heat transfer between them during τ_{fluc} when they are in a diathermal contact, but this transfer of energy corresponds to the process of fluctuation.

5.2 The first law of thermodynamics :

Let us first recall its mathematical statement, namely :

$$dU = dQ + dW. \quad (1)$$

Once the zeroth law has prescribed a minimum time period for sensing of the thermal interaction (in the thermodynamic sense), then dQ of eq. (1) needs to be the one measured on the time scale of τ_{th} and hence dW of eq. (1) needs to be measured on the time scale $\tau_{mech} \sim \tau_{th}$ (of course, dQ as well as dW retain their exact meaning even during the fluctuational time period as described in the preceding paragraph but then time's arrow is non-existent therein). That is, in thermodynamics, there is this very precise meaning of the time period which is required by the system to sense the thermal and mechanical interactions of its surroundings.

In this connection, it is pertinent to state that U of eq. (1) is primarily obtained for a nonequilibrium state which conspicuously remained non-stressed in the thermodynamic literature. To understand this, let us recall the mathematical statement of Joule's law of mechanical equivalent of heat [21], namely :

$$\oint_{irr} dW = -J \oint_{irr} dQ \Rightarrow \oint_{irr} (dQ + dW) = 0 \quad (J = 1) \quad (2)$$

which produces eq. (1) as the third cyclic integral of eq. (2) vanishes, and hence U so obtained pertains to the nonequilibrium states comprising the said cycle.

5.3. The second law of thermodynamics :

Let us first recall the Clausius inequality, namely :

$$\oint \frac{dQ}{T_R} < 0, \quad (3)$$

where T_R is the temperature of the heat reservoir which exchanges $-dQ$ amount of heat with the system, and its

most general version [9], which takes care of the situations in which the system simultaneously interacts with several heat reservoirs of different temperatures at different positions of its bounding surface, namely :

$$\oint_{in A} \frac{Q(A,t)}{T(A,t)} \cdot dAdt < 0. \quad (4)$$

Again the net gain or loss, commensurate with the minimum length of time's arrow allowed in thermodynamics, by the system of dQ and the generation of heat flux, Q , are determined only if one waits for a much more longer time than the fluctuational time scale. In eq. (4), A is the total bounding surface area of the system, \mathcal{A} is the surface area coordinate, $d\mathcal{A}$ is the tiny surface area vector, T is the temperature provided by the generalized zeroth law of thermodynamics [8] and t is time.

Thus, when a thermodynamical framework (for equilibrium as well as for irreversible processes) is developed using the laws of thermodynamics, the above described restrictions on the size of the system and the time scales allowed remain inherently involved therein. Indeed, in the case of equilibrium it is not necessary to wait for a very long duration of time for registering a reading of a thermodynamic property of the system. The minimum time required for this purpose depends on the efficiency of the gadget used but it necessarily has to be equal to or more than τ_{th} . Therefore, it is easy to appreciate that one cannot indiscriminately use a thermodynamical framework.

In the words of Bridgman [16], the above deduction reads as — "the universe of operations of thermodynamics is itself a sub-group of all the operations which we can now perform, including operations of all scales of magnitude".

It is now required to illustrate how an irreversible thermodynamical framework commensurate with the above revelations should be developed. This is exemplified in the following section by considering a simple case of irreversibility only on account of a chemical reaction at a finite rate. In doing so the chemical interactions surface out which needs an appropriate quantification.

6. Chemical interactions

In the preceding discussion it has been made clear that the minimum time required for sensing of thermal and mechanical interactions is indeed inherent in the laws of thermodynamics and in their mathematical expressions. However, therein chemical interactions as such remain submerged. Therefore, how this latter interaction surfaces out in the thermodynamical framework has been described below.

6.1. The case of equilibrium and reversibility :

In the case of equilibrium a simple version of eq. (1) is

$$dU = dQ_{rev} - pdV \quad (5)$$

and eq. (3) reads as

$$\oint \frac{dQ}{T} = 0, \quad (6)$$

where now T is the temperature of the system which is identical with that of the heat reservoir, namely T_R . As the cyclic integral of eq. (6) vanishes its integrand is obtained as an exact differential and hence the Clausius entropy, S , for an equilibrium state is obtained as

$$dS = \frac{dQ_{rev}}{T} \quad (7)$$

On combining eqs. (5) and (7), one obtains the Clausius differential relation [21], namely :

$$dU = TdS - pdV. \quad (8)$$

Neither eq. (5) nor eq. (7) asserts that no chemical conversion will take place within the system when it (a multicomponent and if chemically reactive one) is carried reversibly [6,22,23]. Hence, though chemical interactions very much exist within the system but do not get surfaced out in the above thermodynamical framework. This is so because there exists no imbalance in the existing chemical interactions within the system.

6.2 The case of nonequilibrium and irreversibility :

In the case of nonequilibrium the chemical interactions surface out in the corresponding thermodynamical framework. This happens because now there exists an imbalance in chemical interactions. This we illustrate below by considering the case of irreversibility in spatially uniform systems. It is to be noted that this is the case of a closed system having irreversibility only on account of a chemical reaction at a finite rate. In this case, eq. (3) reads as

$$\oint \frac{dQ}{T} < 0. \quad (9)$$

Now on following Eu's method [2,5,9], let us define the Clausius uncompensation function N as

$$N = -\oint \frac{1}{T} \frac{dQ}{dt} dt > 0. \quad (10)$$

Indeed, it is important to keep in mind that the magnitude of dt of eq. (10) and of all equations to follow hereafter is equal to that of τ_{th} . Next, we treat N as an independent quantity which gives

$$N = -\oint \frac{dN}{dt} dt > 0. \quad (11)$$

From eq. (11), we get the following dictates of the second law of thermodynamics, namely :

$$\frac{dN}{dt} > 0, \quad dN > 0. \quad (12)$$

Now combining eqs. (10) and (11), the result is

$$\oint \left[\frac{1}{T} \frac{dQ}{dt} + \frac{dN}{dt} \right] dt = 0. \quad (13)$$

Thus, the vanishing of the cyclic integral of eq. (13) establishes the time-dependent entropy function $S(t)$ as

$$\frac{dS}{dt} = \frac{1}{T} \frac{dQ}{dt} + \frac{dN}{dt}. \quad (14)$$

Now in the present case, eq. (1) reads as

$$\frac{dU}{dt} - \frac{dQ}{dt} - p \frac{dV}{dt}. \quad (15)$$

Substitution of eq. (14) into eq. (15) gives

$$\frac{dU}{dt} = T \frac{dS}{dt} - p \frac{dV}{dt} - T \frac{dN}{dt}. \quad (16)$$

The last term on the right hand side of eq. (16) originates from the existence of irreversibility which in the present case, is due to the occurrence of a chemical reaction at a finite rate. As in chemical reactions, the composition of the system changes, hence the existing chemical interactions must be the root cause of the appearance of dN/dt in the above description. The details of grasping of this fact is as follows. Rearranging eq. (16), we get

$$-T \frac{dN}{dt} = \frac{d(U + pV - TS)}{dt} - V \frac{dp}{dt} + S \frac{dT}{dt} \quad (17)$$

It is amusing to note that the term $(U + pV - TS)$ on the right hand side of eq. (17) has appeared on its own, which is none else than the Gibbs function G i.e.,

$$G = U + pV - TS \quad (18)$$

and hence eq. (17) reads as

$$-T \frac{dN}{dt} = \frac{dG}{dt} + S \frac{dT}{dt} - V \frac{dp}{dt}. \quad (19)$$

Thus, we find that the first two terms on the right hand side of eq. (16) and the last two terms on the right hand side of eq. (19) appear on account of thermal and mechanical interactions of the system and hence the last term on the right hand side of eq. (16) and the first term on the right hand side of eq. (19) must be that due to the existing chemical interactions within the system. Therefore, it is concluded that in eq. (19) the function G appears only on account of the existing chemical interactions. In the present case, the chemical interaction determining extensive parameters are the mole numbers of the

components n_k 's, and the corresponding intensive parameters obviously get termed as the chemical potentials μ_k 's. Hence, in the present case, the Gibbs function gets expressed as

$$G = \sum_k n_k \mu_k. \quad (20)$$

The substitution of eq. (20) into eq. (19) gives

$$-T \frac{dN}{dt} = \sum_k \mu_k \frac{dn_k}{dt} + \sum_k n_k \frac{d\mu_k}{dt} + S \frac{dT}{dt} - V \frac{dp}{dt}. \quad (21)$$

Eq. (21) is a hybrid expression because it has the intensive (μ_k, T, p) and the extensive (n_k 's) parameters as variables. Also the left hand side of eq. (21), as said above, appears only on account of chemical interactions and hence from its right hand side the terms due to thermal and mechanical interactions are needed to be eliminated. Moreover, on the right hand side of eq. (16), we need to have only extensive parameters as variables, which can be guaranteed only if the validity of Gibbs-Duhem equation, namely :

$$\sum_k n_k \frac{d\mu_k}{dt} + S \frac{dT}{dt} - V \frac{dp}{dt} = 0 \quad (22)$$

is assumed and then incorporated. This then reveals that without the validity of Gibbs-Duhem equation, no thermodynamical framework can exist. The missing of this vital demand in the so-called extended irreversible thermodynamics [2,5-7,12,24,25] has unfortunately created a lot of misunderstanding about the concepts of entropy and temperature in nonequilibrium, however, recently it has been resolved (see for example, the references [5,25] and the other ones cited therein). Thus on incorporating eq. (22) in eq. (21), we obtain

$$-T \frac{dN}{dt} = \sum_k \mu_k \frac{dn_k}{dt} < 0. \quad (23)$$

The inequality of eq. (23) stems from the second law of thermodynamics (c.f. eq. (12)).

Now the substitution of eq. (23) into eq. (16) gives

$$\frac{dU}{dt} = T \frac{dS}{dt} - p \frac{dV}{dt} + \sum_k \mu_k \frac{dn_k}{dt} \quad (24)$$

Thus, we see that the chemical interactions determining term (the last one on the right hand side of eq. (24)), surfaces out because of the existence of irreversibility. So, eq. (24) is the Gibbs relation in the time rate form for the closed system undergoing chemical conversions at a finite rate.

Also it is to be noted that the Clausius uncompensation function is solely determined by the chemical interactions (c.f. eq. (23)). This is an amazingly simple but a vital

outcome from the thermodynamic point of view. That is from eqs. (12) and (14), we learn that

$$\frac{dN}{dt} \frac{d_i S}{dt} > 0 \quad (25)$$

which is the rate of entropy production [11] whose expression in the present case is obtained from eq. (23) as

$$\frac{dN}{dt} = \frac{d_i S}{dt} = - \sum_k \frac{\mu_k}{T} \frac{dn_k}{dt} > 0 \quad (26)$$

which is the standard expression [11].

Further, in the present case, as n_k 's vary only on account of chemical conversion and as a single chemical reaction has been assumed to occur, we have from Dalton's law [11]

$$dn_k = \nu_k d\xi, \quad (27)$$

where ξ is the extent of advancement of the chemical reaction and ν_k 's are the stoichiometric coefficients taken positive for products and negative for reactants. Hence, we have

$$\sum_k \mu_k \frac{dn_k}{dt} = \left(\sum_k \mu_k \nu_k \right) \frac{d\xi}{dt} = -\mathcal{A} \frac{d\xi}{dt}, \quad (28)$$

where the chemical affinity \mathcal{A} has its usual expression, namely :

$$\mathcal{A} = - \sum_k \mu_k \nu_k. \quad (29)$$

Hence, eq. (24) transforms to the De Donderian equation [11], namely :

$$\frac{dS}{dt} = \frac{1}{T} \frac{dU}{dt} + \frac{p}{T} \frac{dV}{dt} + \frac{\mathcal{A}}{T} \frac{d\xi}{dt}. \quad (30)$$

As in the event of reversibility, eq. (8) remains valid and hence in the limit of reversibility eq. (30) should get reduced to eq. (8) which means

$$\mathcal{A}^{eq} = - \sum_k \mu_k^{eq} \nu_k = 0. \quad (31)$$

This then clearly shows that eq. (29) quantifies the net imbalance in the chemical interactions and this imbalance vanishes in the case of equilibrium or reversibility which is described by eq. (31). Thus, it gets established that *via* Clausius' inequality we have an access to the chemical interactions and then it further helps in the quantification of the existing extent of imbalance therein.

The next case is that of spatially non-uniform systems for them the starting point is eq. (4), the generalized Clausius' inequality and there follows the steps similar to eqs. (9)–(19) which we have already described in one of our previous papers [26]. However, the relevant part of it will

be considered once again in a forthcoming paper dealing with the manipulations of Boltzmann integro-differential equation [14,18,27] incorporating the above described constraints of thermodynamics which will help us in comprehending and understanding the finer facets of chemical interactions involved in a spatially non-uniform system.

7. Concluding remarks

The aim of this paper was quite limited and hence an host of obvious questions which arises from the discussion presented in this paper has not been spelled out herein. However, in forthcoming papers we will discuss them systematically. For example, the case of chemical interactions is needed to be attended first in its every possible details. This is so because a new facet of it has emerged which needs to be properly understood. Recently, we have already asserted [26] that the existence of physical fluxes (*e.g.* heat, momentum, *etc*) have their origin in the corresponding chemical interactions, which was never revealed in the past. However, once the 'universe of operations' of thermodynamics has been unambiguously understood as discussed above it is now express to throw more light on the said additional facets of chemical interactions for their proper comprehension. This we will be describing with the help of Boltzmann integro-differential equation by imposing on it the constraints of the 'universe of operations' of thermodynamics and it would be shown, in a forthcoming paper, that the physical fluxes basically originate due to the existence of an imbalance in corresponding chemical interaction.

Acknowledgments

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References

- [1] A A Bhalekar *J. Math. Chem* 5 187 (1990)
- [2] B C Eu *Kinetic Theory and Irreversible Thermodynamics* (New York : John Wiley) (1992)
- [3] A A Bhalekar *Proc. Int Symp. ECOS'92* (Zaragoza : Spain) *Am. Soc. Mech. Engg.* 121 (1992)
- [4] B C Eu *Phys. Rev.* E51 768 (1995)
- [5] B C Eu and L S Garcia-Colin *Phys. Rev.* E54 2501 (1996)
- [6] L S Garcia-Colin and A A Bhalekar *Proc. Pakistan Acad. Sci* 34 35 (1997)
- [7] B C Eu *Nonequilibrium Statistical Mechanics : Ensemble Method* (Dordrecht : Kluwer) (1998)
- [8] A A Bhalekar *Indian J. Phys* 74B 153 (2000)
- [9] A A Bhalekar *Asian J Chem.* 12 417 (2000)

- [10] A A Bhalekar *Bull. Calcutta Math Soc* **94** 185 (2002)
- [11] I Prigogine and R Defay *Chemical Thermodynamics* (Transl) D H Everett (London : Longmans Green) (1954)
- [12] See for example : D Jou, J Casas-Vázquez and G Lebon *Extended Irreversible Thermodynamics* (Berlin . Springer-Verlag) (1996) and references cited therein.
- [13] W Muschik *Aspects of Nonequilibrium Thermodynamics* (Singapore : World Scientific) (1990)
- [14] S Chapman and T G Cowling *The Mathematical Theory of Non-Uniform Gases* (Cambridge : Cambridge University Press) (1970)
- [15] P W Bridgman *Proc. Am. Acad Arts Sci* **82** 301 (1953)
- [16] P W Bridgman *The Nature of Thermodynamics* (Gloucester, MA Peter-Smith) (1969)
- [17] A S Eddington *The Nature of the Physical World* (Cambridge Cambridge University Press) (1931)
- [18] P Résibois and M de Leener *Classical Kinetic Theory of Fluids* (New York : John Wiley) (1977)
- [19] A A Bhalekar *Bull Calcutta Math Soc* **92** 463 (2000)
- [20] P Glansdorff and I Prigogine *Thermodynamic Theory of Structure, Stability and Fluctuations* (New York . Wiley) (1971)
- [21] S M Blinder *Advanced Physical Chemistry* (London The Macmillan Company, Collier-Macmillan Limited) (1969)
- [22] A A Bhalekar *Pramana-J. Phys* **50** 281 (1998)
- [23] A A Bhalekar *Asian J Chem.* **12** 433 (2000)
- [24] A A Bhalekar and L S García-Colín *Pramana-J. Phys* **50** 295 (1998)
- [25] A A Bhalekar *Pramana-J. Phys* **53** 331 (1999)
- [26] A A Bhalekar *Bull Calcutta Math Soc.* **94** 209 (2002)
- [27] R L Liboff *Kinetic Theory Classical, Quantum and Relativistic Description* (New Jersey · Prentice-Hall) (1990)