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Universal inaccessibility principle

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Abstract. The universal inaccessibility principle (UIP) which was previously used in developing the generalized phenomenological irreversible thermodynamic theory (GPITT) is discussed at length. UIP provides both the thermodynamic temperature and the corresponding entropy function for a local nonequilibrium state without involving any physical device. The Carathéodory principle is obtained as a particular case of the equilibrium part of UIP. The system with negative temperatures are also covered by UIP. It is revealed that the use of UIP is implied in the De Donderian thermodynamic description of irreversibility due to chemical reactions and also in the classical irreversible thermodynamic description of Onsager–Prigogine–Meixner–de Groot. The reversible adiabatic paths of a chemically reactive closed system remain perfectly isentropic even if concomitantly a chemical conversion takes place within the system.

Keywords. Thermodynamics; irreversible thermodynamics; thermodynamic processes; thermodynamic properties and entropy.

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1. Introduction

A new irreversible thermodynamic formalism, viz. the generalized phenomenological irreversible thermodynamic theory (GPITT) [1–6] has been developed. This theory reveals that every irreversible thermodynamic formalism is necessarily governed by the validity of Gibbs–Duhem equation (GDE). Hence, according to GPITT all nonequilibrium thermodynamic situations belong to GDE-regulated regime. The breakdown of GDE means the crumbling down of irreversible thermodynamics itself. For example, GPITT derives (does not assume) the traditional local level version of the Gibbs relation, namely:

$$\frac{\mathrm{d}s}{\mathrm{d}t} = T^{-1}\frac{\mathrm{d}u}{\mathrm{d}t} + pT^{-1}\frac{\mathrm{d}v}{\mathrm{d}t} - T^{-1}\sum_k \mu_k \frac{\mathrm{d}c_k}{\mathrm{d}t} \tag{1.1}$$

under the condition that its corresponding GDE, namely

$$s\frac{\mathrm{d}T}{\mathrm{d}t} - v\frac{\mathrm{d}p}{\mathrm{d}t} + \sum_k c_k \frac{\mathrm{d}\mu_k}{\mathrm{d}t} = 0 \tag{1.2}$$

Dedicated to Dr G V Bakore on the occasion of his 5th death anniversary