Preface

After a quick glance at it, one is liable to pass the judgment that thermodynamics appears to be an old subject in science. Yet it is hardly true, since, when closely examined, it is still a developing subject. It is regarded by many in science as an old subject because its basic principles were enunciated almost 160 years ago and the theory of reversible processes was basically completed in the hands of J. W. Gibbs within the span of 25 years from the time when the thermodynamic laws were stated by Clausius and Kelvin. It thus appears that there is nothing new to add to the subject. Nevertheless, the general theory of thermodynamic processes that include irreversible processes has been in an arrested state of evolution and has remained incomplete until L. Onsager, J. Meixner, and I. Prigogine formulated a theory of linear irreversible processes. This theory is still incomplete because irreversible processes about which the second law of thermodynamics is basically concerned have not received a fully satisfactory theoretical treatment. Fuller treatments of the subject are given serious attention in recent years. Therefore thermodynamics in the generalized sense is still worth serious study, if possible, from the viewpoint more general than that taken in the traditional approach to the subject and, in particular, equilibrium thermodynamics where only reversible processes are studied.

Since reversible processes are the idealized limits of irreversible processes observed in nature, the thermodynamics of reversible processes, namely, equilibrium thermodynamics, must be the limiting form of a more general theory of thermodynamic processes, and as such, it is worth having a fresh examination in what manner it is a limiting theory. We examine some basic aspects of equilibrium thermodynamics under such a motivation in this textbook, which also contains traditional treatments of various topics taught in courses in thermodynamics at an advanced undergraduate level and graduate level. The treatments given to the second law of thermodynamics and related topics, such as equilibrium conditions and stability of equilibrium in this work are different from those in conventional textbooks on equilibrium thermodynamics. In fact these are extended versions of those found in conventional textbooks. Examples of application of the extended treatment of the second law is discussed in the last chapter to show how one might apply the concepts to study irreversible processes far from equilibrium.

The materials on the conventional topics of thermodynamics in this book, excluding those related to the second law, have been taught by B.C.E. over many years in the courses of thermodynamics at McGill University. The treatments given to the second law of thermodynamics and related topics in this book, being new and more recent fruits of labor on the part of M.A.-G. have not been exposed to the classes in the past. However, we believe that they should be an integral part of a course on equilibrium thermodynamics. The reason is that not only the new results of research add to the science of thermodynamics, the mathematical representation of the second law of thermodynamics that adequately covers irreversible processes, and provides clarifications of various related topics about which the conventional treatment of the subjects leaves us uncomfortable, but also the equilibrium thermodynamics of reversible processes emerges as the limiting case of a more general theory of thermodynamic processes as it should be. Furthermore, the generalized mathematical representation of the second law of thermodynamics removes some nagging conceptual features that arise from the fact that the entropy was originally defined for reversible processes only. Yet one still thinks of the entropy as if it is a nonequilibrium quantity, when it comes to systems in the vicinity of an equilibrium state, as in the case of equilibrium conditions and stability of equilibrium states. Therefore, when equilibrium thermodynamics is considered from the generalized theory, namely, generalized thermodynamics, we can form more harmonized viewpoints towards the subject and contemplate formulation of a more comprehensive theory of thermodynamic processes, reversible or irreversible. In this potential lies our desire to examine equilibrium thermodynamics from an angle different from the traditional viewpoint. The examples discussed in the last chapter, albeit brief, illustrate the utility of the concept of calortropy in study of irreversible processes. The reader interested in more involved discussions on irreversible phenomena and hydrodynamics in the nonlinear regime is referred to monographs dealing with the subjects. Such monographs are available at present. It is the hope of the authors that this work will act as a stepping stone towards a more complete theory of irreversible phenomena.

B.C.E. & M.A.-G.
September 2009