Introduction

Probably the most familiar consequence of heating a crystal of a pure compound is that it melts, without chemical change, at a precise melting point, \( T_m \); the value is a characteristic property of each particular compound. This is not, however, the only possible change that can result from heating, other solids undergo chemical reactions, sublimation, crystallographic transitions, and, in addition, some substances show combinations of these processes, with or without, melting. While undoubted progress has been made in characterizing the phenomenology of the physical and chemical changes mentioned, theory development has been less satisfactory.

Melting

Several alternative representational models for melting can be found in the literature but none has found general acceptance. In an attempt to remove this apparent impasse, the set/liq model for melting [1–4] has been formulated, based on evidence that there is extensive retention of crystal-like order in some melts at the \( T_m \).

Thermal decompositions of solids

Many solids undergo thermal decomposition on heating, crystolysis reactions [5]; this type of chemical change has been intensively studied. The dedicated theory, developed to explain the characteristic behaviour patterns observed, owes much to the kinetic models applied to homogeneous rate processes, though without providing adequate justification for the exten-
sion of theory to heterogeneous reactions. The subject area has developed almost as a distinct discipline and a critical review of the current situation, particularly concerning those aspects that may relate to fusion, forms the greater part of this survey. Some progress has been made in characterizing the kinetics of selected representative crystolysis reactions, and aspects of the reaction mechanisms have been elucidated [5].

Sublimation

The role of equilibration in sublimation kinetics has been discussed by L’vov [6–8] for 50 substances that yield gaseous products only. Greatest progress has been made through studies of the simplest substances: elements, oxides and other binary compounds. A similar primary volatilization step, congruent dissociation of the reactant, is identified [9] as the primary step in a physical approach to formulation of a theory for decompositions of solids. The relationship of this newer model to the alternative older representations appearing in the current literature is discussed below.

Crystallographic transitions

Many crystalline solids transform from one lattice structure to another on heating, without chemical reaction of the constituents, e.g., metals [1]. Changes may proceed by a cooperative (martensitic [4]) transition or by an interface reaction, comparable with those occurring during crystolysis reactions. Little is known about the kinetics and mechanisms of many of these reactions, mentioned here only for completeness: details are not discussed.

Melting with decomposition

On heating, some reactants undergo complex changes, for example, a thermal decomposition may be accompanied by melting, involving the participation of molten intermediates or products. These processes are intentionally omitted from discussion here because it is considered essential first to characterize the chemistry of the simple, contributory steps before making attempts to elucidate the chemistry of more complicated reactions. A problem in the literature is that reactions proceeding through complex, concurrent and/or overlapping consecutive rate processes are not always identified as involving two (or more) distinct rate processes, some of these are described and incorrectly interpreted as a single, simple reaction [10–13]. Elucidation of the mechanisms of complex reactions, including identification of any intermediate compounds participating, measurements of the kinetic parameters, etc., is often experimentally very difficult.

The distinctive types of thermal changes of solids, mentioned above, tend to be considered in different parts of the scientific literature. Melting, sublimation and crystallographic transformations are usually regarded as physical changes, whereas thermal decompositions are undoubtedly chemical reactions. The present comparative analyses are primarily concerned with melting, sublimation and crystolysis reactions because these are the subjects of current theoretical discussions [1–13]. Until recently there appears to have been little overlap of interest and theory development, for these topics, presumably because comparisons of the consequences of heating solids have, hitherto, lacked an acceptable overall theoretical framework. However, if representational models could be developed, capable of contributing to the understanding of the physical or chemical parameters that control each of the different types of change mentioned, this could be expected to advance generally the theory of all thermal properties of solids. (Also the products of these changes, particularly melts [1–4].) Moreover, comparisons of the perceived strengths and weaknesses of theoretical concepts that are applicable to melting and/or sublimation with those that are applied to thermal decompositions may have mutual benefits in advancing understanding of both of these distinctive, but different, types of thermal changes. This aspiration will be addressed in the final section of this review. Before considering these generalities, however, it is appropriate to provide a brief historical survey of theories of solid-state decompositions [5, 14], mainly addressed to readers less familiar with this (almost) specialist and (certainly) distinctive discipline [10–13]. The account is also intended to introduce the terminology used to describe interface reactions and to discuss the kinetic aspects, including mechanisms, of melting in [4].

Melting is a first-order transformation [15], conventionally regarded as a physical change of state because the individual constituents of the solid/melt (atoms, molecules or ions) undergo no chemical change during the (usually) facile and reversible liquefaction/solidification processes. For the simple ionic salts, primarily considered here, the electrostatic interactions that stabilize each crystal can be regarded as primary valence forces. Consequently, any structural changes that accompany melting [1–3] represent modifications to chemical bonding so that fusion can be regarded as including features of a chemical change. It is suggested here, therefore, that aspects of the theory and principles developed to apply to solid-state decompositions [5, 14] may also be applicable to the discussion of fusion given in [4].

Many solids undergo structural transformations, polymorphism, due to temperature dependent variations of the relative stabilities of their alternative pos-