

Melting and Crystallization of Sugars in High-Solids Systems

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ABSTRACT: Crystalline structures of sugars, particularly that of sucrose, depend on crystallization conditions and the presence of impurities. Sugar crystals show melting that often occurs at low temperatures with time- and temperature-dependent characteristics. Melting at low temperatures can be accounted for by the presence of impurities and defects. Sugar crystals also contain noncrystalline regions that may undergo decomposition and subsequent dissolution at the decomposition interface and acceleration of decomposition reactions. Such processes with melting establish a supersaturated condition for the remaining crystals, leading to a time-dependent melting point depression and subsequent melting of the remaining crystals. Decomposition of sugars, as well as dissolution and melting of sugar crystals, are separate phenomena, although they are commonly found to coincide. Decomposition of sugars requires the presence and mobility of molecules for reactions outside the crystal lattice; that is, the molecular mobility of amorphous or melted regions is a prerequisite for decomposition, whereas melting of sugar crystals occurs as a separate thermodynamic process with no chemical change of the molecules.

KEYWORDS: *sugar, sucrose, melting, crystallization, caramelization*

■ INTRODUCTION

Melting refers to the phase transition of a substance from solid to liquid state. The solid state is the crystalline state of a material, although other states may show solid-like properties. For example, glassy materials exhibit a solid structure, but should be classified as solid-like liquids, as their disordered structure does not show any solid–liquid phase transition and

melting point. In thermodynamics, the melting point of a pure substance can be exactly defined as the temperature at which

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the disordered liquid and molecularly ordered solid states of the substance exhibit the same Gibbs energy and coexist in equilibrium. The melting process, however, is not simple, and it begins preferentially at a crystal surface. Lindemann¹ proposed that melting occurred when thermal vibrations exceeded a critical fraction of the interatomic distance, allowing collisions between neighboring atoms. Born² defined melting as loss of elastic shear modulus. In general, melting of a crystal shows the loss of the regular repetition of lattice positions over long sequences in three dimensions, and positional disordering of units is universal in melting.³ Ubbelohde³ pointed out that melting and crystallization, as described by classical thermodynamics, do not require any consideration of the structures of the solid and liquid states. Ubbelohde³ stated that melting is a function of the detailed structure of the crystalline state, and the diversity of crystal chemistry leads to various laws of melting. General rules of melting of organic, molecular crystals are difficult to establish, and those proposed apply only when the molecular and crystal structures of the materials compared are similar.³

Melting and crystallization properties of sucrose have been of significant interest, because of their importance in sugar manufacturing, storage, and applications. Melting of sucrose and chemical changes during heating, often referred to as caramelization, have been of significant interest.^{4,5} Gélis⁴ introduced the words “caramelan”, “caramelen”, and “caramelin”. Caramelan was the first product formed through loss of water from sucrose molecules as a result of dehydration (condensation) and polymerization reactions. Caramelan was brown with bitter flavor and corresponded to about 12% loss in mass as water and was referred to with the formula $C_{12}H_{18}O_9$. Caramelen was darker and differed from caramelan, as it was not soluble in 84% ethanol. It was produced from sucrose with increased, 15%, loss in mass as water, and the higher degree of polymerization gave the formula $C_{36}H_{50}O_{25}$. Caramelin was produced at 22% loss of mass as water. Caramelin was a mix of strongly colored, hot-water-soluble substances with the average formula $C_{96}H_{102}O_{51}$. These amorphous products appeared as complex mixtures and formed in sucrose during heating at 180–190 °C.^{4,5}

In most studies, caramelization reactions followed the appearance of a liquid state as a result of melting of crystals. According to Gélis,⁴ sucrose melted at 160 °C, but could also be changed at that temperature to glucose and anhydrofructose (levulosan), $C_6H_{10}O_5$. Further work showed that a reaction of anhydrofructose and anhydroglucose (glucosan) produced isosaccharosan (anhydrous sucrose).⁶ Von Elbe⁷ reported that caramelan was a mix of colorless components and a dark brown humin. These studies emphasized the complexity of sugar melting that was often associated with the formation of degradation products. The results were dependent on experimental temperature conditions and time. Several other sugars exhibit similarities in thermal behavior to sucrose melting and caramelization.⁸ Typical examples of other sugars showing variations in melting properties and appearance of colored decomposition products include fructose and glucose, which form hydroxymethylfurfural (HMF) in dehydration reactions,⁹ lactose and maltose,⁸ and xylose.¹⁰ Changes of sucrose at melting to monomeric components may enhance thermal degradation. It may also be assumed that degradation and dehydration reactions are involved in melting of most sugars. Industrial caramelization processes, as related to manufacturing of sugar-based caramels, differ significantly

from spontaneous caramelization of sugars during heating. Caramels are produced from a mix of caramel ingredients, as reviewed by Martin¹¹ and Sengar and Sharma.¹²

Crystallization as a physicochemical process and its industrial importance were discussed by Hartel¹³ and Mullin.¹⁴ Although crystallization and melting as thermodynamic processes represent the same but reverse changes in phase, they follow quite different physicochemical principles. Kinetic factors that control crystal growth and the consequent crystal structure have significant effects on the melting properties of the crystals. Several single-crystal X-ray and neutron diffraction studies have revealed the crystal structure and the characteristics of hydrogen bonding in sucrose crystals.^{15–18} The loss of crystalline structure can occur thermally as a result of heating of crystals or by dissolution of crystals in a solvent. Sugars are manufactured using solvent purification and crystallization processes, and the presence of solvent inclusions and impurities, such as salts, monosaccharides, oligosaccharides, and polysaccharides, is typical of sugars.¹⁹

Melting properties of monosaccharides, disaccharides, and oligosaccharides, using thermal analytical measurements, were studied by, for example, Raemy and Schweizer,²⁰ Roos,²¹ and Hurtt et al.²² Beckett et al.²³ carried out a comprehensive study of the effects of salts, other sugars, and solvents on melting of sucrose. These studies on melting of sucrose and other sugars have shown that the melting properties depend on melting temperature and time. Later studies have suggested that sugars do not melt, but the loss of crystalline structure occurs as a result of a kinetic decomposition process,^{24–28} although decomposition prior to loss of crystalline structure is unlikely.²⁹ Melting of sucrose and other sugars occurs in numerous food manufacturing processes, but the lack of a single, well-defined melting temperature for sugar crystals has caused much confusion in interpretation of experimental data on their melting properties. The mechanisms involved in sugar melting include dislocation of molecules from the crystal structure to produce the liquid melt. Decomposition of molecules at their positions in the crystal lattice is required in the absence of melting. Such decomposition of sugar molecules must require loosening of molecular bonding in the crystal and accommodation of any reaction products within the crystal structure around the reaction site. The present review considers crystallization as a process building crystal structures that affect and underpin melting properties of sucrose and other sugars. Melting characteristics of sugars are discussed and analyzed with available data and theories on reactivity and crystal properties that explain melting characteristics, physicochemical processes, and thermal phenomena associated with heating of crystalline sucrose and other sugars.

■ THERMODYNAMICS OF MELTING

Thermodynamic principles are often applied to define equilibrium states of materials. A single substance, such as a sugar, can theoretically exist in three equilibrium states, that is, solid, liquid, and gaseous states. The material at any particular thermodynamic condition has a characteristic value for its internal energy (U), enthalpy (H), and entropy (S). These state quantities are dependent on the interrelated state variables, pressure (P), temperature (T), and volume (V). The internal energy is defined as the sum of all energy of the system, such as a sucrose crystal, whereas changes in internal energy (dU) can be quantified by the total quantities of heat (q) and work (w) exchanged with surroundings (eq 1).

$$U = q + w \quad (1)$$

A central principle of thermodynamics is that state variables are interrelated, that is, if there is a change in P , T , or V , there must be a change in at least one of the other state variables. Accordingly, changes in thermodynamic quantities may occur at a constant P , T , or V . Most melting processes take place at atmospheric conditions, and for simplicity, the present consideration assumes sugar melting at an approximately constant pressure. A constant-pressure process assumes a change in energy content of a system to occur as a result of heat transfer between the system and its surroundings, as well as work done on the surroundings by the system, corresponding to a required change in volume. The total heat transfer between the system and its surroundings can then be defined as enthalpy (H) (eq 2).

$$H = U + PV \quad (2)$$

The enthalpy changes of systems at atmospheric conditions can be derived from measurements of differences in heat contents at various states of the material. Such measurements are typically made using calorimetric analyses.

Equations 1 and 2 represent the zeroth and first laws of thermodynamics, respectively. The second law of thermodynamics defines entropy (S), which considers the direction of heat flow (Q) and the level of disorder or conservation of energy (eq 3).

$$S = \frac{Q}{T} \quad (3)$$

The definition of entropy can be used to relate energy changes with surroundings to internal energy (eq 4) and enthalpy (eq 5).

$$dU = TdS - PdV \quad (4)$$

$$dH = TdS + PdV \quad (5)$$

The Gibbs free energy (G) is a quantity that defines the energy that a system can use for mechanical work other than pressure–volume work and heat; that is, at a constant pressure and temperature, the Gibbs energy is the energy of the system which is not converted to heat (eq 6).

$$dG = dH - TdS \quad (6)$$

The probability of a thermodynamic change in a system can be assessed using Gibbs energy as a criterion. Reactions that result in a decrease in Gibbs energy are spontaneous, whereas an increase in Gibbs energy identifies a forced reaction. Systems exhibiting the same Gibbs energies may coexist in equilibrium. As shown in Figure 1, thermodynamic melting at a constant temperature and pressure of a substance occurs at the temperature at which the two phases, liquid and solid, exhibit the same Gibbs energies. Differential thermal analysis (DTA) systems use the constant temperature of a phase change for melting point determination. Thermodynamic melting of a substance causes a temperature difference between a sample and reference, which can be used to derive the melting point.

Simple thermodynamic consideration of melting can be applied to melting point determination. Melting point determination is commonly used in the analysis of purity of crystalline materials. As described in Figure 1, chemically pure crystals often melt at a characteristic melting point, whereas impurities or defects in crystals alter melting characteristics and lower the melting point.

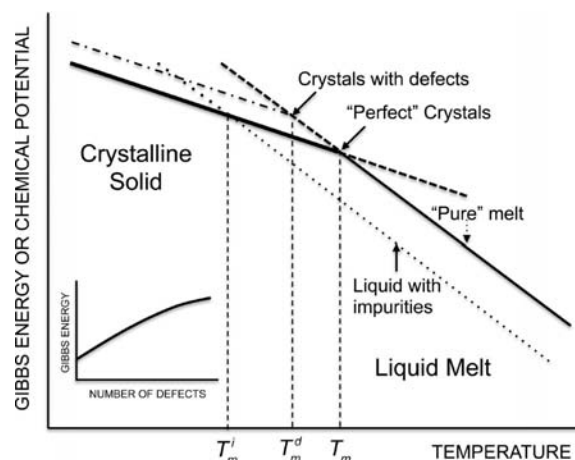


Figure 1. Gibbs energy and chemical potential of a melting system. At the melting temperature of pure molecular crystals (T_m), the solid and liquid states have the same Gibbs energies. A liquid with impurities exhibits a lower Gibbs energy and a respective lower melting temperature of the crystals (T_m^i) (melting point depression). Crystals with defects have a higher Gibbs energy than “ideal” crystals, and their melting can occur at a lower temperature (T_m^d). The stable form always has the lowest Gibbs energy. In a dynamic heating process, crystals with impurities and defects melt at a lower temperature, and they may also show chemical degradation with a consequent increase in impurities and defects. In sugar melting, these processes advance degradation that can show temperature- and time-dependent acceleration of melting and degradation.

FACTORS AFFECTING MELTING

The melting point of a crystalline substance is a characteristic value of the substance. The basic thermodynamic criteria for melting are simplistic and describe melting properties of highly pure, ideal crystals. The theories of melting based on those of Lindemann¹ and Born² provide more information on the molecular processes and mechanical changes, respectively, taking place during melting. Lindemann¹ assumed that all atoms vibrate with the same frequency, and melting occurs when vibrations exceed a critical value. Although this rule lacks a physical basis, it applies well to simple crystals, but is less accurate for melting of complex crystals. According to Lawson,³⁰ melting involves both the crystal and liquid phases and must consider vibrations in the liquid, which are often ignored in melting theories. Likewise, the product phase must be considered in a decomposition reaction. A well-known problem in the determination of melting points of sugars, including fructose, glucose, and sucrose as the most common examples, is their decomposition at temperatures close to the melting point.³¹ For example, the melting point of sucrose is affected by the presence of impurities, water, and small amounts of noncrystalline (amorphous) sucrose. Despite the known difficulties in the determination of melting points of sugars, a generally agreed upon temperature for melting of sucrose at 186 °C has been reported.³¹

Although theories of melting are lacking, it must be recognized that the bonding between particles in crystals is broken to establish a liquid state with a high translational mobility of molecules. Factors affecting melting properties of crystals reflect the relative strength of bonding of individual molecules and include defects in crystal structure, the presence of impurities, and the presence of a solvent (Figure 1). Sugars are hydrophilic organic molecules and difficult to crystallize as

pure single crystals. Kumaresan and Babu³² used palm juice to crystallize single sucrose crystals from aqueous solutions. The crystals were of good quality but showed cracks, which may be avoided in crystallization from nonaqueous solutions. These crystals, in thermogravimetric analysis (TGA) and DTA studies, showed melting followed by decomposition. However, even in melting of single crystals, the melting process may vary across the crystal lattice, depending on local defects and impurities. Kumaresan and Babu³² found a DTA melting peak of a single crystal of sucrose at 189 °C. Spectroscopic analysis of the crystals confirmed the absence of impurities.

Melting of crystals needs to take into account the possibility of the presence of a liquid phase around crystals. On the other hand, solid particles in a liquid or melt produce surface effects that contribute to crystallization properties by decreasing the freezing point. The solid particles in crystals produce grain boundaries (defects) with lower melting temperatures. Surface effects also dominate freezing of liquids in capillaries. The surface effect on the vapor pressure (p) in capillaries is defined by the Kelvin equation (eq 7), where p_0 is the vapor pressure in the chemically pure saturated state, σ is the surface tension at the liquid–gas (LG) interface, r is the radius, ρ is the density, and R is the gas constant. This is particularly important in understanding properties of water in foods, but similarly in understanding the freezing and melting properties of all substances that would show altered freezing and melting properties at curved surfaces.

$$-\ln \frac{p}{p_0} = \frac{2\sigma_{LG}}{r\rho RT} \quad (7)$$

Impurities in sugar crystals may appear as liquid inclusions, such as solvent residues and liquid substances. The effect of impurities on the freezing point, in systems in which the impurity is soluble in the liquid phase of a crystallizing liquid, has been traditionally described by Raoult's law. The application of Raoult's law assumes that the impurity is not soluble in the crystalline solid, for example, low concentrations of sugars in water. The freezing-point depression in eq 8, where H_m is the heat of melting, T_m is the melting point of the pure substance, and N is the mole fraction of the substance, refers to the temperature at which the last crystals melt in a heating process (T_f , the highest temperature at which the Gibbs energy of the liquid and solid states is the same, as shown by T_m^i in Figure 1), but the first crystals melt at the eutectic temperature or around the glass transition temperature of a noncrystalline solute–solvent phase.

$$H_m \left(\frac{1}{T_f} - \frac{1}{T_m} \right) = R \ln N \quad (8)$$

In the crystalline state, we may assume an increase in the chemical potential of the sugar molecules in the presence of defects, for example, dislocations of molecules in the crystal lattice (Figure 1). The presence of impurities and solvents, including water, with crystals results in a multicomponent system, and melting must occur over a temperature range (Figure 2).

Several metals may exhibit surface melting, that is, formation of a liquid film on crystal surfaces below the melting point.³³ Superheating of metal crystals, under conditions not allowing surface melting, to temperatures above the melting point has also been reported.³⁴ Melting and crystallization are reverse processes that occur theoretically under the same thermody-

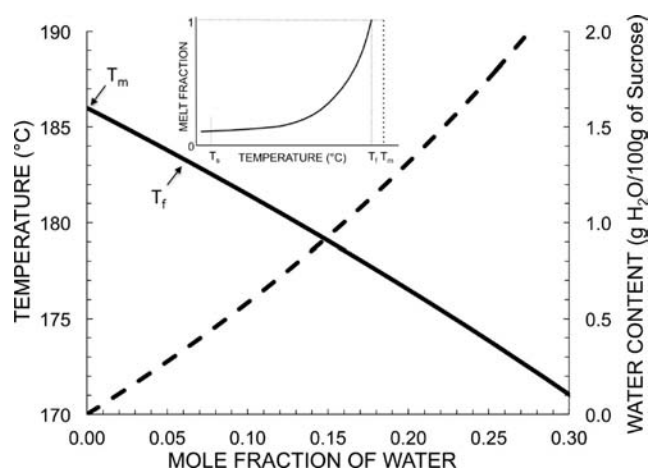


Figure 2. Melting point (T_m) depression of sucrose in the presence of water (or some other impurity), according to Raoult's law. The dashed curve shows water content, when the mole fraction refers to that of water as impurity. The melting temperature (T_f) is that at which the last crystals melt, whereas the liquid phase (melt fraction shown in the inset) appears at substantially lower temperatures above the eutectic or glass transition temperature (T_g).

namic conditions. Crystallization of a melt, however, does not occur at the melting temperature, unless a sufficient driving force for nucleation and growth of the nuclei into crystals is established. Under normal atmospheric conditions, a sufficient supercooling of a crystallizing material is required. Crystallization processes are well-established in the chemical and process engineering areas.^{14,35}

■ SUCROSE CRYSTAL

Sucrose is the most common, traditional sweet ingredient of foods. Sucrose in large quantities at a purity level of >99.9% is obtained from sugar beet and sugar cane through extraction and crystallization processes.^{19,36,37} Sucrose molecules in crystals form two intramolecular hydrogen bonds^{16,17,38} that also appear in aqueous solutions at increasing levels of concentration.³⁹ The sucrose molecule has eight hydroxyl groups that may form hydrogen bonds, although one of the hydroxyl groups is excluded from hydrogen bonding in crystals.^{16,19}

As described by Mullin,¹⁴ crystalline solids can be specified according to interparticle bonding of atoms or molecules in the solid state. The main types of bonding in crystals include ionic, covalent, molecular, and metallic bonding, with characteristic forces holding the particles (structural units) in place in the crystal lattice. Examples of these four groups include sodium chloride (electrostatic forces), diamond (shared electrons between atoms), organic compounds (π -bonds and hydrogen bonds), and metals (shared outer electrons). In melting processes, these bonds need to be broken by heat or transfer of a sufficient quantity of other forms of energy to result in long-range positional disorder.

The molecular structure of sucrose has evolved from the glycosylation studies of Fisher.⁴⁰ The intramolecular and intermolecular bonding properties of organic molecules are important in the description of the molecular arrangement in crystallization. Sucrose forms anhydrous crystals from aqueous solutions, with predominant development of (100) faces.¹⁵ Sucrose crystals are classified as monoclinic sphenoidal $SP2_1$ crystals. The crystal belongs to the monoclinic family, with one two-fold axis of rotation and one mirror plane. Sucrose crystal

characteristics are given in Table 1. The packing of the molecules in the crystal is governed by hydrogen bond

Table 1. Properties of Sucrose Crystals¹⁷

crystal property	parameter value
space group	$P2_1$
a	10.8633 (5) Å
b	8.7050 (4) Å
c	7.7585 (4) Å
β	102.945 (6)°
cell volume	715.04 Å ³
Z	2
d (calcd)	1.590 kg m ⁻³
d (exptl)	1.58 kg m ⁻³

formation between the hydroxyl groups, mainly of the furanose residues. The contacts between the glucose residues are more of the van der Waals type.¹⁵ A single sucrose crystal, as presented by Smythe,⁴¹ is shown in Figure 3. The axis of

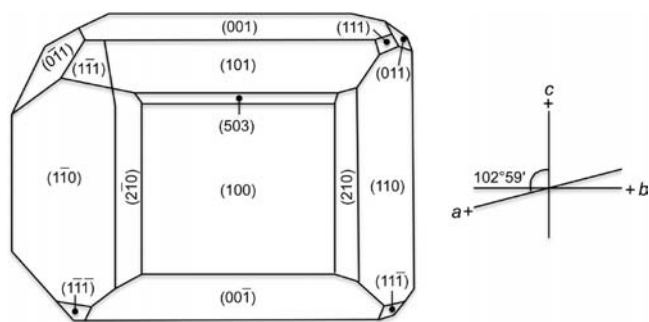


Figure 3. Sucrose crystal (redrawn from Smythe⁴¹).

symmetry coincides with the crystallographic b -axis and is asymmetrical in length; that is, the left end of the b -axis, the left pole, differs from the opposite end, the right pole.

Hydrogen bonding in sucrose crystals was described by Brown and Levy.¹⁶ Packing of the sucrose molecules is determined mainly by hydrogen bonds involving the hydroxyl groups of the molecules.⁴¹ There are seven hydrogen bonds per asymmetric unit, of which two are intramolecular and five intermolecular. Sucrose molecules in a crystal show hydrogen bonding that involves all oxygen atoms, and the crystalline structure has the characteristic of a large number of weak hydrogen bonds.³⁸ The two intramolecular hydrogen bonds occur between O-1f-H...O-2g and O-6f-H...O-5g of the fructofuranose (f) and glucopyranose (g) residues (Figure 4). An unusual, four-center hydrogen bonding involves O-4g-H that forms two intermolecular hydrogen bonds to (i) fructofuranose ring O-2f and (ii) glucopyranose O-6g and one intramolecular hydrogen bond to O-3g. There is also one unusual triangle in a two-center bond from O-6g-H to O-3g-H.³⁸ The packing of sucrose molecules is dense,³⁸ and each molecule is surrounded by 6 pairs of 12 neighboring molecules. The strongest layer is formed by a combination of two-fold screw symmetry and translational symmetry. The two-fold screw axis is parallel to the b -axis, with strong interaction of the molecules through hydrogen bonds and van der Waals interactions. This element serves as a structural model in crystal growth.³⁸ The development of a sucrose crystal with a characteristic number of 15 faces determines the appearance of

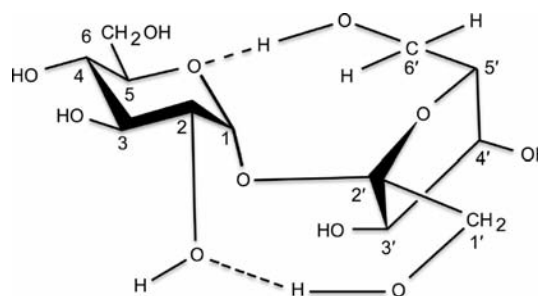


Figure 4. Two internal hydrogen bonds forming in sucrose at high concentrations in water and in crystallization (redrawn from Mathlouthi³⁹).

the crystal. The presence of impurities modifies the growth rate of various faces, the crystal habit, and causes abnormalities in faces.¹⁹ The growth of faces with impurities may favor their presence, or there may be a competition in arrangement of impurities with sucrose molecules diffusing from the mother liquid.

■ IRREGULARITIES IN CRYSTALS

The sizes of sucrose crystals may vary considerably, although crystals generally grow to clearly visible sizes. Most crystals are not perfect, and even the most organized crystals show defects and impurities.^{3,14} The most important lattice imperfections are (i) point (zero-dimensional), (ii) line (one-dimensional), and (iii) surface (two-dimensional) defects. Point defects are vacancies and interstitials. Line defects include edge and screw dislocations that occur, during crystal growth, as a result of surface and internal stresses. Surface defects are imperfections that occur as a result of mechanical and thermal stresses during crystal growth or of irregular growth. The morphology of a crystal is determined by the growth rates of the different crystallographic faces.¹⁴ Microscopy images of typical, commercial but chemically pure fructose, glucose, and sucrose are shown in Figure 5.

Industrial sucrose crystallization processes were developed to manufacture highly purified, refined sucrose crystals of uniform sizes. The sizes produced may depend on intended applications of the products. Less purified, brown-colored products are also produced. It may be assumed, however, that although refined sucrose crystals have a high chemical purity, no crystallization processes can provide perfect, uniform, and defect-free crystals. Even a single crystal carefully made in a laboratory may show some cracking.³²

Impurities inside the crystal lattice are referred to as inclusions. These are typical of all crystals, including those with well-defined structures, such as diamonds. The inclusions can be solid, liquid, or gaseous impurities. Sucrose crystals are relatively large, which increases the probability of inclusions. Some high molecular mass, colored components may bond to sucrose molecules, and small quantities of mother liquid can be encapsulated inside crystals. A washing step in sugar manufacturing aims at decreasing impurities, but their removal leaves cavities on the crystal surfaces. The presence of such cavities, in crystals produced in the presence of dextrans as impurities, was demonstrated by Khaddour et al.⁴² using atomic force microscopy.

In sucrose crystallization, several phenomena affecting crystal structure and chemical purity have been reported:¹⁹

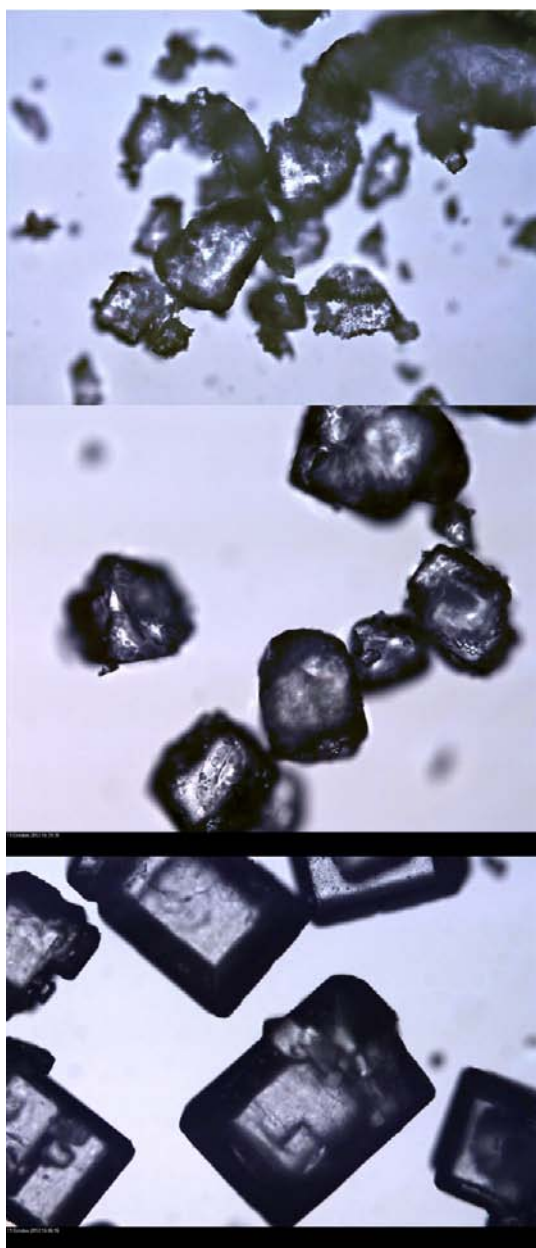


Figure 5. Microscopy images of fructose 20 \times (top), glucose 40 \times (middle), and sucrose 10 \times (bottom). Images represent random samples of analytical grade materials (Sigma-Aldrich, St. Louis, MO, USA). The variation in crystal size, number of defects, and aggregation is substantial.

Twin Formation. Twin crystals are formed by rotation and may give (i) crystals with left poles toward each other, (ii) crystals with right poles grown together, and (iii) single crystals growing together along the a face. An important factor that can significantly affect crystal melting is that joints of the two crystals can accommodate mother liquor. The mother liquid entrapped in joints between crystals is not removed in the washing step of the refining process.¹⁹

Conglomerates. Conglomerates are crystals that have randomly grown together. These may show different appearances, as several crystals have fused together during crystal growth.

The formation of twins and conglomerates increases crystal sizes and decreases refined sucrose quality. High super-

saturation levels in the crystallization process promote formation of twins and conglomerates. Conglomerate formation is also affected by seed characteristics, stirring, and the time of crystallization.

Sucrose crystals, in refined sucrose from various sources (beet and cane), crystallize fairly similarly, as the impurities are present at low concentrations. Impurities affect the relative growth rates of the faces of a sucrose crystal and cause a concomitant effect on sucrose crystal shape.⁴¹ A stereospecific adsorption of impurities at kink sites on the growing crystal surfaces was noted. Mathlouthi⁴³ pointed out that a thin layer of amorphous sugar is often present at the surface of crystalline sugar. Amorphous regions of sugars on sugar crystals may be considered as impurities, and the number of amorphous regions may be expected to increase in the presence of foreign molecules at growing sugar crystals. Agglomeration of crystals increases significantly with increasing crystal size.⁴⁴

Crystals of sucrose from raw sugar beet and cane processing differ morphologically.¹⁹ One difference is found in the c/b ratio of the crystal's elongation along the c - and b -axes. Crystallization from the beet process gives $c/b < 1$, and crystallization from the cane process gives $c/b > 1$. These differences result from the differences in impurities present. Elongation along the b -axis is caused by impurities in sugar beets (high in raffinose), and impurities in sugar cane (high in mono-, oligo-, and polysaccharides) cause elongation along the c -axis.^{19,45} Interestingly, under unusual steric conditions, glucose and fructose units are present at crystal surfaces. Normally, the main pairs of faces on the sucrose crystal follow planes between adjacent sucrose molecules, such that the skeleton of the molecule, the furanose and pyranose rings, is not intersected by these planes, but the hydroxyl groups are exposed at each face.⁴¹ At low levels of impurities, particularly raffinose, a poisoning phenomenon is observed, whereas a high level of impurities causes competition effects, for example, by monosaccharides. Sucrose crystals in the presence of raffinose grow along the b -axis to a needle-like appearance.⁴⁶ Monosaccharides cause the appearance of rare faces and D-shaped crystals.^{19,47} Cane processing may also involve high levels of polysaccharides, particularly dextrans, which promote the growth of long crystals along the c -axis. Glucose mainly slows the growth rate of the left-pole faces, whereas fructose cannot stop growth of any form but reduces growth kinetics⁴⁸ (Figure 6). Both monosaccharides result in kink poisoning in sucrose crystals. A sufficient number of glucose molecules can disrupt the crystal lattice and slow the development of (110) faces. A pair of fructose molecules, one in fructopyranose form

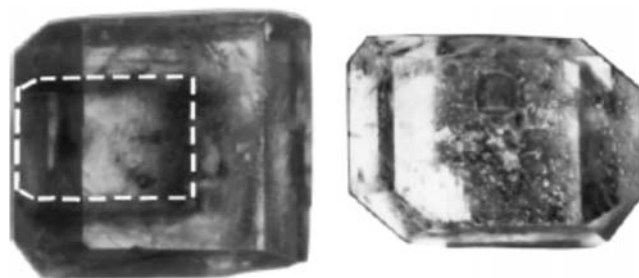


Figure 6. Images of sucrose crystals formed in the presence of 150 g glucose/100 g H₂O (left) and 150 g fructose/100 g H₂O (right). Glucose stopped the growth of (110) forms. Fructose reduced strongly the (011) and (111) forms.⁴⁸

and one in fructofuranose form, can replace sucrose molecules in the same kink, but the (011) growth rate becomes reduced. These findings⁴⁸ quite clearly demonstrated the presence of glucose and fructose molecules in sucrose crystals, which typically grow in the presence of some quantity of fructose and glucose.⁴⁹

Faria et al.⁴⁴ conducted a comprehensive quality analysis of sucrose crystals. The effects of typical impurities in sucrose crystals – dextrans, raffinose, glucose, and sodium carbonate – on crystal morphology and agglomeration were assessed using imaging analysis. Dextrans were reported to increase the viscosity of solutions and decrease crystallization rate, but crystal elongation was less than expected. Raffinose was found to cause a strong inhibition of sucrose crystallization and formation of a large number of small crystals. Crystals produced in the presence of raffinose showed elongation along the *b*-axis. Glucose, which was present in all sucrose solutions, inhibited nucleation and crystal growth, and caused a spread of crystal size distribution. Sodium carbonate, which is used in refining to remove impurities, was the strongest inhibitor of sucrose crystallization. Dextrans lowered the interfacial free energy of sucrose crystal growth, which increased the linear crystal growth rate.⁴² The surface points accommodating dextran molecules were assumed to show higher chemical potential and therefore reduced growth rate. Such surface points in a melting process would be expected to show a higher mobility and a lower temperature for the release of sucrose molecules from the crystal lattice.

■ THERMAL ANALYSIS

Differential scanning calorimetry (DSC) and DTA, in various modifications of the instruments, such as modulated DSC (MDSC) and hyperheating DSC, have often been used to determine melting properties of organic substances, including sugars. Melting and decomposition profiles of sugars have also been studied using thermogravimetry (TG). Several studies of carbohydrates have reported thermal properties and glass transition temperatures (T_g) for sugar melts.^{21,50,51} Kumaresan and Babu³² used single crystals, for which melting and three subsequent decomposition processes derived from TG data were identified. The decomposition steps showed loss of mass as a result of loss of water, carbon monoxide, and carbon dioxide, as well as hydrogen. The loss of water was dominant in the first decomposition step, which notably occurred well above the melting endotherm of the single crystal.

Degradation reactions of sugars, associated with their melting, affect crystallization properties of the melts, as well as their glass transition temperatures. Studies on melting and caramelization of sucrose have shown the appearance of water as a product of the complex chemical reactions.¹¹ Water in sugar melts decreases the T_g , as a result of water plasticization.^{21,50} The appearance of water in sugar melting can, in glass transition measurements, result in lower T_g than would be true for the anhydrous materials.⁵¹ Sucrose degradation also produces fructose and glucose molecules that most likely plasticize sucrose and lower the T_g of the melt.⁵² Fructose and glucose have lower melting points than sucrose, and they are potential solvents for crystalline sucrose.⁵² The large variation of sucrose T_g from 52 °C⁵³ to 74 °C⁵⁴ has been explained by the use of onset and midpoint values of the T_g range and by residual water, as well as by thermal history effects on the glass transition.^{50,51,55,56}

Vanhal and Blond⁵¹ used DSC to melt approximately 4 mg samples of sucrose crystals by (i) heating to temperatures of 190–235 °C at 10 °C/min, (ii) using heating rates of 5–40 °C/min to a final temperature of 200 °C, and (iii) heating to 190 °C at 10 °C/min, followed by isothermal holding at 190 °C for 5 or 10 min. All samples after melting were rapidly cooled at 40 °C/min and then analyzed for fructose, glucose, and sucrose contents. The melting peak maximum temperature was found at 190 °C, in agreement with Roos.²¹ The peak temperature in DSC measurements, however, was dependent on the heating rate, as well as on the size of the sample.²² The T_g decreased for final heating temperatures over the range of 190–215 °C, but increased for higher final temperatures.⁵¹ High-performance liquid chromatography analyses showed that, at the final heating temperature of 190 °C, only sucrose was present, suggesting minimal decomposition during sucrose melting at that temperature. Heating to temperatures above 215 °C resulted in the disappearance of sucrose, whereas the fructose and glucose contents showed a maximum at 215 °C. Polymerization products were present at increasing concentrations at the higher temperatures. These findings⁵¹ confirmed the degradation of sucrose to fructose and glucose upon melting, as well as the dehydration reactions leading to polymerization and an increased T_g . Sucrose decomposition and polymerization reactions were time-dependent, as less sucrose converted to fructose and glucose when the heating rate was increased. Sucrose degradation also increased with the length of the heat treatment. These findings were in agreement with earlier studies^{57,58} that reported degradation of sucrose to fructose and glucose with further dehydration and polymerization reactions. Fructose concentrations were lower than glucose concentrations, as even at 135 °C, fructose degraded more rapidly than did glucose. Sucrose degradation studies showed that when a noncrystalline state of sucrose appeared, molecular mobility was possible, resulting in rapid sucrose degradation.⁵¹ This conclusion was clearly supported by the fact that temperature (melting) was a more important factor controlling sucrose degradation than was the length of heating (time).

Hurttta et al.²² studied the melting behavior of fructose, glucose, and sucrose, using DSC and TG. They referred to anomalous melting as the process by which the recrystallized melt was different from the original form, there was a change in conformation of molecules during melting, or melting was associated with decomposition reactions. They noted that a mix of crystals could vary in their melting properties, and a melting range rather than a melting temperature could be found. This could be interpreted as a melting process during which crystals of various sizes and impurities melt individually, giving no consistent results in repeated melting experiments.

■ REACTIVITY OF SOLIDS

Understanding sugar melting requires a brief review of solid-state chemistry and reactions. Topochemical reactions occur in conditions under which the properties of reaction products are determined by constraints set by the three-dimensional periodic surroundings of the reactant(s).⁵⁹ Solids, including crystals, participate in several reactions, such as reactions with gases (e.g., oxidation), as well as thermal and photochemical reactions. Solid-state chemistry recognizes reactions in five categories, which result in products differing chemically from the solid reactant: (i) solids as reactants producing different reaction products (decomposition and polymerization reac-

tions); (ii) solids reacting with gases, for example, oxidation; (iii) solids reacting with solids; (iv) solids reacting with liquids; and (v) reactions of solid surfaces.⁶⁰

Rothenberg et al.⁶¹ studied reactions of two solid reactants, which were referred to as (i) solid-phase synthesis that involved molecules in a fluid phase reacting with a solid substrate, such as polymer-supported peptide syntheses; (ii) solvent-free synthesis (any reaction with no solvent); and (iii) solid-state synthesis or solid–solid reactions that involved two solid reactants to produce a solid product in the absence of any liquid or gaseous phases. Many solid–solid reactions are carried out using grinding of crystalline reactants. Grinding produces amorphous substances that become reactive liquids. For example, an aldol condensation could produce α,β -unsaturated ketones from two carbonyl compounds (aldehyde–ketone or ketone–ketone) in the presence of a strong base, and the existence of a liquid phase (melt) was a prerequisite for the reaction.⁶¹ The same authors also found that oxidative coupling of naphthols to binaphthols showed very slow reaction rates at room temperature, whereas heating of coground reactants to 50 °C produced a liquid phase that gave a rapid rate for the reaction. A number of other examples of solid–solid reactions showed that the reactions are not true solid–solid reactions, but the systems exhibit a clear appearance of a liquid phase prior to the reaction. In solids, only molecules at particle surfaces would be able to react, as orientation of the molecules in solids is fixed, and the energy to disrupt the crystal lattice is considerable.⁶¹ A liquid phase was required to provide sufficient mobility to the reactant molecules for productive collisions.

Chemical processes can occur within a crystal lattice and produce different products from those produced in the liquid state. Single-phase and heterophase solid-state chemical kinetics of thermally induced methyl transfer in tetraglycine methyl ester is one example.⁶² There was a significant effect of disorder on the chemical reactivity of tetraglycine methyl ester, as a result of milling of the solid.⁶³ Point defects contribute significantly to reactivity of other than organic solids.⁶⁰ The more important factors affecting reactivity of organic solids are line defects and planar defects. In the absence of defects, molecular packing mainly controls solid-state reactivity (topochemical reactions). Examples of such reactions include several polymerization reactions that can be induced by heat, irradiation, X-rays, and ultraviolet light. The reactions follow nucleation–growth processes that often involve inclusion complexes and other defects as nucleation sites.⁶⁰ Decomposition of inorganic solids, as well as solid-state reactions in organic substances, occur by nucleation, and thermal decomposition is sensitive to pretreatment of crystals, because of dislocations of particles. Pretreatments may include simple scratching, various forms of irradiation, such as UV, X-ray, or γ radiation, or bombardment with neutrons or protons.⁶⁰

Photodimerization reactions belong to those occurring in crystals as solid–solid transformations. Photodimerization involves double bonds in reactant molecules. Molecules at surfaces and at dislocations of crystals have a higher chemical potential and provide reaction sites for thermal reactions.⁶⁴ Photodimerization reactions, of which dimerization of cinnamic acid is a classic example, are topochemically controlled; that is, their occurrence and rate depend on molecular packing. Such reactions require that double bonds are parallel, with the distance between reacting atoms being $<4.2 \text{ \AA}$.^{64,65} Abnormalities of crystal structures at dislocations permit dimerization,⁶⁴ and there is a progressive change in reactant and product

concentrations.⁶⁵ Careful analysis of crystal structures determined for various stages of phototransformations has shown that reactant and product molecules do not assume fixed positions in crystals.⁶⁵ Accordingly, the reactions do not occur in molecules before absorption of sufficient energy from photons to release molecules from the crystal lattice. There are additional stresses to which reactant molecules are exposed as a result of volumetric changes with increasing product quantity as the reaction proceeds. The product molecules also remain initially separate from positions in pure product crystals.⁶⁵ Although sucrose molecules during melting may not show photochemical reactions, it is interesting to note that, also in photochemical reactions, molecules are released from the crystal lattice prior to the reaction, that is, photons are required at the reaction site to release molecules.

Solid-state decomposition of unreleased sucrose molecules in crystals is an unlikely event. Sucrose molecules have no double or triple bonds that could be reactive sites in a solid-state process, particularly in photochemical reactions. Possible reactions of crystalline sucrose include oxidation or reactions with other gases, where thermal losses of molecules from crystals or reactions at surfaces are required. During heating and melting of sucrose crystals, sucrose is the only possible reactant. Solid–solid reactions in pure sucrose crystals may not occur, but thermal dehydration reactions remain a possibility. Thermal decomposition of sucrose and other sugars is a well-known phenomenon. Thermal decomposition of sucrose initiates as a first-order, intramolecular displacement reaction that produces D-glucose and a fructose derivative.⁵⁷ This reaction is followed by formation of trisaccharides and polymeric materials in dehydration reactions.

■ AMORPHOUS SUCROSE

Amorphous sucrose and other sugars are typical components of dehydrated foods and many pharmaceuticals. Properties of the amorphous solids differ significantly from those of crystalline solids. The stability of amorphous sugars is highly dependent on water sorption, mainly because of water plasticization and crystallization of amorphous structures. Several studies have reported methods to detect crystallinity in amorphous materials. Crystallinity of sucrose at a 0.2% level in an amorphous preparation could be measured by synchrotron X-ray powder diffractometry,⁶⁶ whereas Lappalainen et al.⁶⁷ detected amorphous sucrose at a 0.062% level and determined a limit for quantification at 0.207%. These studies derived the amorphous sucrose content from crystalline and amorphous X-ray diffraction intensities and the change in specific heat (ΔC_p) over the glass transition, respectively.

Knowledge of the amorphous content of a crystalline material is crucial, as it also quantifies the amount of a liquid phase in crystals. The presence of an amorphous phase in sugar crystals is well-known, as it relates to the presence of solvent residues (inclusions) that are likely to contain dissolved sugars and impurities. Saleki-Gerhardt et al.⁶⁸ used sucrose as a model to assess crystallinity in milled crystals and mixtures of amorphous and crystalline sucrose, using powder X-ray diffraction and water sorption. Powder X-ray diffraction could quantify amorphous material at concentrations above 5–10%, but water sorption studies could detect disorder at levels below 1%. The study by Lappalainen et al.⁶⁷ included experiments on the effect of sucrose grinding on the content of amorphous sucrose within the material. Their study showed that grinding of sucrose crystals, using a ball mill for 2.5 min at high grinding

intensity, increased the amorphous sugar content significantly. If this information is considered in the context of handling, transportation, and storage of crystalline sugars, one may conclude that some amorphous material must appear commonly on crystal surfaces of commercial sugars. Vippagunta et al.⁶⁹ identified exposure of crystals during pharmaceuticals processing to stresses such as temperature, pressure, relative humidity, and comminution, which are typical of drying, milling, granulation, and compression. Such stresses result in defects in crystal lattices. Defects occurring at crystal surfaces can migrate, transform, and change in number and nature, often leading to polymorphic changes, of which a polymorphic transition of aspartame hemihydrate during ball-milling or heating for 30 min at 160 °C has been reported.⁶⁹ Brittain⁷⁰ reviewed effects of mechanical processing and treatments of pharmaceutical materials and concluded that the energy associated with any handling step could result in undesirable changes in solid-state characteristics.

Lactose is a common food and pharmaceutical material that is a reducing sugar and exists in anomeric α -lactose and β -lactose forms. Grinding of α -lactose monohydrate, α -lactose anhydrate, and β -lactose anhydrate at room temperature produced an amorphous phase.⁷¹ The amorphous lactose was hygroscopic and sensitive to water sorption at various humidities. Anomerization of lactose in α -lactose monohydrate was dependent on crystallinity, whereas anomerization in α - and β -lactose anhydrate systems was dependent on sorbed water. These results showed that anomerization required a liquid phase, and water plasticization of the amorphous lactose formed in grinding of lactose anhydrates was required to provide sufficient mobility for the lactose molecules to undergo anomerization.

The importance of traces of amorphous substances to the stability of pharmaceutical materials shows their high impact on the behavior of organic crystals. Nevertheless, the relatively high accuracy of several methods to quantify amorphous contents in crystalline solids aside,⁷² amorphous sites and defects in crystals affecting melting characteristics are properties of individual crystals. In melting of a population of sugar crystals, a high variation in the melting behavior of individual crystals is expected.

■ DECOMPOSITION AND MELTING

Thomas and Williams⁷³ pointed out that the nature of lattice defects was well-known for ionic and covalent structures of inorganic solids, but imperfections in organic molecular structures were poorly understood. Conversely, numerous phenomena occurring in organic crystals were explained on the basis of dislocation theory. Thomas and Williams⁷³ carried out a comprehensive study of the role of dislocations in sucrose properties and decomposition using microscopy. Sucrose crystals (5–10 mm linear dimension) were carefully grown over several days from saturated solution at 40 °C. The fresh (100) surfaces of crystals with uniform morphology and showing no pockets of occluded water were cleaved for microscopy. The crystals showed alignments of dislocations resulting from cleavage, crystal growth, mechanical damage, or extended alignment at subgrain boundaries. Etching by 1:1 ethanol–water produced etch pits that developed at dislocations on the crystal surfaces.

Decomposition and caramelization reactions of sugars may occur at temperatures below the melting point. Some decomposition may be achieved by irradiation treatments but,

more importantly, by heating. Thomas and Williams⁷³ used heat treatments lasting several hours at 120 °C in a vacuum. They reported that relatively large quantities of water appeared at crystal surfaces during heating. These water droplets were found at zones of higher imperfections of the sucrose crystals. There was a strong indication that occluded water was retained in the vicinity of dislocation cores, and the water in sucrose (0.01–0.4%) was located along dislocation cores. Heating for 6 h, as shown in Figure 7, produced decomposition “volcanoes”

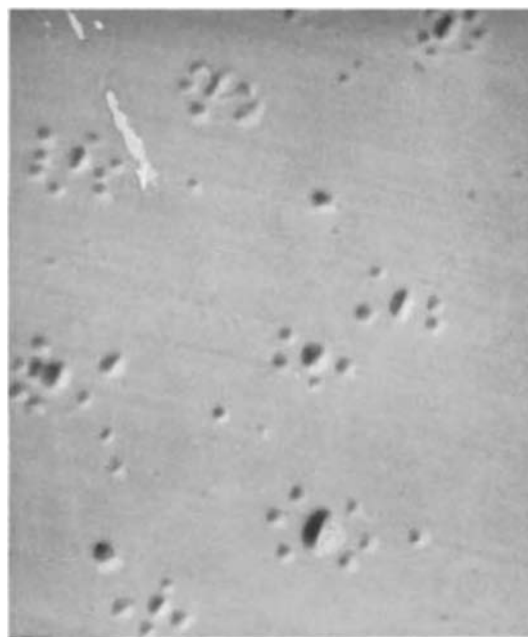


Figure 7. Decomposition “volcanoes” on the cleaved face of a sucrose crystal after heating for 6 h at 120 °C under vacuum.⁷³

and suggested that preferential decomposition took place at dislocations. These volcanoes produced satellites, which could be taken as an indication of higher reactivity or autocatalysis at the dislocations. Separated halves, however, did not mirror volcanoes or decomposition on the separated faces, because the dislocations moved through the lattice prior to decomposition.

Decomposition, solid-state reactions, and melting of sugars are separate processes that may coincide during heating of sugars. Studies of sugars as single samples of crystals, using thermal analytical techniques, cannot distinguish such separate phenomena in a single thermogram of a heating scan. Studies involving DSC and TG measurements have referred to anomalous melting, although anomerization, decomposition, and melting have been identified as a multiphased phenomenon.²² Lee et al.²⁴ concluded that decomposition was a kinetic process that caused the loss of crystalline structure of fructose, glucose, and sucrose. They referred to sugar melting as apparent melting, to distinguish the kinetic process from a thermodynamic melting process that was measured by MDSC, which divides thermal processes into reversing and non-reversing transformations. For example, melting at a thermodynamic melting temperature can be a reversing phenomenon, whereas a decomposition reaction is a nonreversing, kinetic process. Lee et al.²⁴ compared mannitol melting with the melting of fructose, glucose, and sucrose. Mannitol melting appeared as a sharp melting endotherm, different from those for sugars that exhibited time-dependent melting.

Taking into account the data on sugar crystal characteristics⁴⁸ and various phenomena associated with sugar melting,²² we conclude that melting and other thermodynamic processes, such as melting point depression and variation in chemical potential of molecules, must contribute to the thermal melting of sugars.²⁹ The melting process is accompanied by kinetic decomposition reactions, in addition to the kinetic changes in liquid sugar content resulting from defects in crystals, and the presence of solvents, including water, and for sucrose, the component sugars, fructose and glucose.²⁹ Such temperature-dependent, interrelated compositional and solid–liquid transformations and reactions cannot be simply referred to as kinetic decomposition, instead of melting. Indeed, the presence of molecules outside crystal structures is required for reactions,²⁹ as described for solid-state reactions, including anomerization of sugars. It may also be noted that polyols (sugar alcohols), including mannitol, do not exhibit reducing groups or thermal dehydration reactions similar to those of sugars.

The complex sum of changes in enthalpy or heat flow found in variations of DSC or MDSC measurements provides no data on the separate thermodynamic processes and subsequent chemical changes. As found for all materials, molecular mobility is a prerequisite for reactions and allocation of reaction products in solids. In crystals, some molecules must be or become released from crystal lattices prior to chemical reactions, including anomerization and decomposition of sugars. Beckett et al.²³ studied the origin of a premelting endotherm at approximately 150 °C, in DSC traces, typical of some commercial sucrose crystals, whereas the main melting endotherm occurred at 190 °C. They found that the lower temperature endotherm was absent when sucrose was crystallized in the presence of KCl, NaCl, or K₂SO₄. Beckett et al.²³ concluded that the lower temperature endotherm could relate to crystallization conditions and appeared when excess water was available during sucrose crystallization. Lee and Chang⁷⁴ carried out a comprehensive study of sucrose crystallization from 1:1 methanol–water (MRS), furfuryl alcohol–water (FARS), and tetrahydrofurfuryl alcohol–water (TARS) at 60 °C, aiming at producing crystals in 5–7 days with significant melting at 150 °C, and to investigate whether sucrose polymorphism was responsible for the occurrence of the endotherm at 150 °C. Lee and Chang⁷⁴ used various methods for the identification of the crystal properties at various temperatures. On the basis of single-crystal X-ray diffraction, powder X-ray diffraction, Fourier transform infrared (FTIR), scanning electron microscopy (SEM), electron spectroscopy for thermal analysis (ESCA), water content, and electrolytes analyses, Lee and Chang⁷⁴ concluded that FARS crystals formed under a higher viscosity condition consisted of sucrose molecules with different degrees of conformational disorders about the –CH₂–OH groups at C-6' and C-6. This led to misalignment of the hydrogen bond between the hydroxyl groups and the glucopyranose ring. Such misalignment was found to result in the lowering of the melting temperature, in agreement with disfiguration of crystal habits. Powder X-ray diffraction at various temperatures confirmed melting of the parent commercial sucrose at 180 °C, but the FARS crystals showed melting around 160 °C. FARS crystals were also found to show a higher solubility than that of the parent commercial crystals. The conformational disorders in sucrose took place to various degrees, depending on crystallization viscosity, rate of solvent evaporation, and mixing, resulting in crystals with a wide range of melting temperatures.

Lee et al.²⁴ noted the appearance of two endotherms, in studies of sucrose melting, and the enhancement of decomposition reactions by impurities in sugar crystals, and they suggested that the endotherms were due to decomposition and not melting. Lee et al.²⁴ paid significant attention to the specific heat of sugars during heating, which was derived from the reversing heat capacity (C_p) obtained from MDSC measurements. The change in C_p for sugars occurred over a broad temperature range, whereas that for indium and mannitol was sharp, showing the change from solid to liquid corresponding to the difference in C_p of the two phases. The increase in C_p for the sugars occurred differently over a temperature range and more gradually after complete loss of crystalline structure. This was taken as an indication of a kinetic process causing loss of crystalline structure, instead of melting, as the sugars were also not found to melt–recrystallize in temperature modulation. Indeed, as expected, decomposition products could accelerate melting and subsequent decomposition, with progressive inhibition of recrystallization.²⁴ Although Lee et al.²⁴ concluded that decomposition was a kinetic process that caused the loss of crystalline structure in sugars, their study actually simply confirmed that decomposition, as a time-dependent or kinetic process, often coincides with sugar melting. Magon and Pyda also reported heating rate dependence of α -D-glucose⁷⁵ and D-(–)fructose⁷⁶ melting and the associated decomposition. The melting region was strongly affected by melting, anomerization, and degradation. However, there was no indication of the loss of crystalline structure prior to melting that was followed by degradation and other changes. Lee et al.²⁴ neither proved that sugars do not melt, and melting of sugars is commonly found by all methods that can indicate a crystalline solid-to-liquid transformation, including the compositional study of Lee et al.²⁵ Furthermore, noncrystalline molecules exist in sugar crystals, and dislocations are needed for crystal growth,⁷⁷ allowing their decomposition reactions to occur at temperatures below the melting point.²⁹ In other words, decomposition is not required for the loss of crystalline structure in sugars, but melting is required to produce a sugar melt.²⁹ It must be noted that Lee et al.²⁵ also found sugar melts as the predominant products of the loss of crystalline structure, rather than the decomposition products, which would have been the case if loss of crystalline structure occurred by decomposition. The biggest problem with the conclusion of Lee et al.,^{24–27} that sugars decompose instead of melting, was that the effects of melting point depression, impurities, including decomposition products of sugars, and lattice defects on the thermodynamic properties of sugars were ignored.²⁹ Their hypothesis of chemical transformation (sucrose degradation) in the crystalline lattice of sucrose, explained by using data for chemical degradation and loss of crystal structure at temperatures of 122–138 °C, cannot be supported by the assumptions of solid-state reactions (i.e., chemical transformation of molecules within the crystal lattice). A rigorous thermodynamic study of sugar melting would find the melting point depression and its effects on the apparent heat capacity, as well as the effects of reaction and solubilization heats on the total heat flow.²⁹ Much of such processes would be dependent on time and temperature and would be kinetic in nature.²⁹

Typical melting scans of sucrose obtained by DSC, as well as TG data, show no loss of water in dynamic measurements, until decomposition occurs at temperatures well above 200 °C.⁷⁴ Decomposition of sucrose occurred during long heating times

at temperatures as low as 120 °C and also showed dehydration.^{25,73} Monosaccharides, fructose and glucose, are reducing sugars that produce hydroxymethylfurfural in dehydration reactions. The formation of HMF from the more reactive fructose occurs more rapidly than from glucose, which is more susceptible to forming oligosaccharides.⁷⁸ These monosaccharides, along with water produced in dehydration reactions, act also as solvents for sucrose crystals.⁵² We conclude that multicrystalline sucrose preparations contain noncrystalline regions, and sucrose molecules in these liquid regions degrade, producing multiple degradation products. Some of these degradation products, including fructose and HMF, have low melting points, thus providing additional liquid media for further dissolution (and degradation) of sucrose. The reactivity of monosaccharides, compared to corresponding polyols, is high and may be used to explain the decomposition and melting differences of these compounds. For example, xylitol and maltitol show sharp melting endotherms, whereas both fructose and glucose exhibit time-dependent melting characteristics.^{75,76} Moreover, it is important to note that hydrate crystals of sugars, such as trehalose,^{79,80} show different melting behavior from anhydrous crystals.

Sugars crystallize as molecular crystals with relatively high melting temperatures. Crystallization of sugars normally takes place from an aqueous solution, but the crystalline structures and melting properties depend on the origin of the sugars, crystallization conditions, and solvents. Formation of perfect single crystals of sugars is unlikely. The chemical reactivity of sugars is high and results in dehydration and polymerization reactions in sugar melts. Thermal decomposition in sugar crystals, around solvent inclusions, impurities, and lattice defects, may occur during a long heat treatment below the melting point of sugar crystals. Such processes establish a supersaturated condition for the remaining crystals, leading to a time-dependent melting point depression and subsequent melting of the remaining crystals. Decomposition of sugars and melting of sugar crystals are separate phenomena, although they are commonly found to coincide. Decomposition of sugars requires mobility of molecules for reactions outside the crystal lattice; that is, molecular mobility is a prerequisite for decomposition, whereas melting of sugar crystals occurs as a separate thermodynamic process.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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