

Sugars and other sweeteners are often the main components of a confection. Besides making them sweet, they also provide bulk to the candy. However, the physico-chemical properties of the sweeteners do more than just provide bulk. The physical characteristics of a candy, which include consistency, chewy or stretchy characteristics, melt-in-the-mouth behavior, flavor release, and many other properties, are dependent on the nature of the sweetener. For example, sucrose by itself can be turned into candies with completely different characteristics – rock candy and cotton candy – simply by how it is processed. Rock candy, a crystalline form of sucrose, has very little color or flavor and takes a long time to dissolve in the mouth. Cotton candy, on the other hand, is a glassy form of sucrose that has colors and flavors distributed throughout the candy and dissolves almost instantaneously when placed in the mouth. To make high quality candies, it is important that the confectioner understand the properties of sugars that lead to these completely different characteristics.

2.1 Sweetness

The sweetness of sugars is related to their chemical structure and its interaction with taste receptors on the tongue. A detailed discussion of the chemistry of sweetness is beyond the scope of this book, especially since this is still an active

area of research; see Fernstrom et al. (2012) for a recent review of mechanisms of sweetness.

Because a wide range of sweeteners may be used in confections, a comparison of the relative sweetness of the different sweeteners is needed. Numerous sensory comparisons of the sweet taste sensations of different sweeteners have been put forth. One method compares the threshold value needed for the subject to detect and identify the taste sensation of the substance under study. The threshold values for glucose, sucrose and fructose are 0.7%, 0.3% and 0.2%, respectively. At these low concentrations, fructose has a greater sweet sensation than either sucrose or glucose.

In the isosweet technique, the concentration of the substance under study determines which is equal in taste sensation to a certain concentration of sucrose. For example, concentrations of 15.5% or 48.1% glucose are required to equal the sweet taste sensation of 10% and 40% sucrose, respectively. Thus, at 10% sucrose concentration, glucose is only 65% ($10/15.5 \times 100$) as sweet, while at 40% sucrose concentration, glucose is 85% ($40/48.1 \times 100$) as sweet. At higher concentration of sugars, the differences in degree of sweet taste sensation become less pronounced.

A third method for comparing sweetness is the relative sweetness scale, where a 10% sucrose concentration is given a sweetness value of 1 (or 100). The relative sweetness of any other sweetener is then based on the relative concentration of

Table 2.1 Relative sweetness of sugars and other sweeteners (various sources)

Sweetener	Relative sweetness ^a
Fructose	1.3–1.5
Invert sugar	1.1–1.25
Sucrose	1.0
Xylitol	1.0
Maltitol	0.8–0.9
Maltitol syrup	0.7–0.8
Glucose	0.7
Glucose syrup (60 DE)	0.65
Sorbitol	0.5–0.6
Mannitol	0.5–0.6
Isomalt	0.5
Glucose syrup (43 DE)	0.45
Lactitol	0.4
Glucose syrup (36 DE)	0.3
Maltose	0.3–0.5
Maltodextrin	0.1–0.3
Lactose	0.15–0.25
Polydextrose	0

^aBased on sweetness relative to 10% sucrose solution (given a value of 1)

that sugar that gives the equivalent sweet taste sensation. Table 2.1 summarizes relative sweetness values for some of the important sweeteners used in confections.

2.2 Viscosity

Viscosity of a fluid may be defined as the fluid's ability to move under shear, as when it is pumped, stirred, boiled, sprayed or swallowed, for example. For a low viscosity fluid, like water, only a relatively small force is needed to induce flow, whereas higher viscosity fluids require more force to generate the same extent of flow. In this sense, viscosity is an important term for process engineers in designing pumping systems and equipment. The size of a pump needed to transport invert sugar (low viscosity) is significantly less for an equivalent flow rate of low DE glucose syrup. As another example, the viscosity of engrossing syrup is a critical factor for sugar panning operators to ensure proper syrup coverage on candy pieces tumbling in the pan. If viscosity

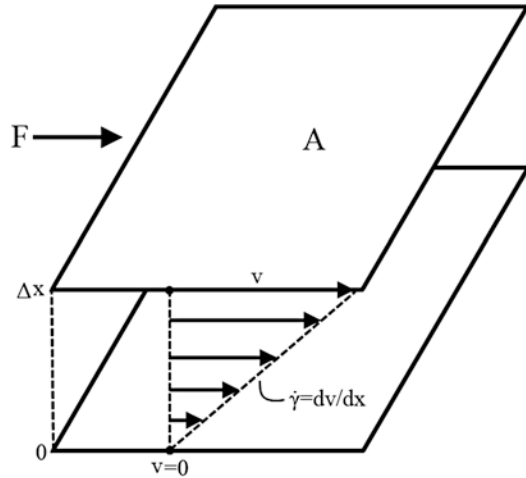


Figure 2.1 Shear flow between two flat plates (area A). The *top* plate is moving at velocity, v , while the *bottom* plate is stationary ($v = 0$)

of the engrossing syrup is too high, the pieces tumbling in the pan will not be adequately covered, whereas thin engrossing syrup leaves a residue on the inside of the pan rather than coating the pieces. Furthermore, viscosity also has important ramifications in the sensory qualities of confections. Typically, more viscous syrups are considered to be thicker and have higher consistency (mouthfeel). For these reasons, a good understanding of viscosity and what factors affect viscosity is one of the most important concepts for a confectioner. A good source for more details on viscosity, and the entire field of fluid rheology, can be found in Steffe (1996).

Technically, viscosity for simple liquids (like water or sugar solutions) may be defined as the proportionality factor between the applied shearing force and the velocity gradient in the fluid caused by that shearing force. Imagine a fluid between two parallel plates of area A separated by distance x , as shown schematically in Figure 2.1. When a force, F , is applied to the top plate, it moves with a velocity, v , depending on the nature of the fluid (how the molecules respond to that applied force). If the bottom plate is stationary and there is no slip (fluid velocity at the bottom wall is 0), then the applied force creates a velocity gradient, dv/dx , from v at the moving plate to 0 at the bottom plate. The relationship

between the applied force, or shear stress σ , and the velocity gradient, or shear rate $\dot{\gamma}$, is given mathematically as:

$$\sigma = F/A = \mu\dot{\gamma} = \mu\left(\frac{dv}{dx}\right) \quad (2.1)$$

where, the proportionality constant, μ , is the viscosity of the fluid between the plates. In practical terms, fluids with a higher viscosity require a greater amount of force to move at a certain speed.

When sugars are dissolved in water, the resulting syrups follow the general rule given by Equation 2.1. Fluids that behave according to Equation 2.1, where the shear stress is directly proportional to the applied shear rate, are called Newtonian fluids. A plot of shear stress versus shear rate gives a straight line, with the slope of the line being the Newtonian viscosity. The main characteristic that makes a Newtonian fluid is that the viscosity is the same regardless of how much shear is applied (how fast it is stirred or pumped). That is, shear stress increases in a direct proportion to the shear rate. Almost all sugar solutions, including glucose syrups, are Newtonian fluids. Oils (liquid fats) also belong to the Newtonian fluid category. Fluids are non-Newtonian when the apparent viscosity depends on the rate of shearing (see Section 15.5.3 for more details). For fluids with certain types of thickening agents (proteins, gums, etc.) and fluids with particulate matter, as found in fondant (aqueous) and chocolate (lipid-based), more complex relationships between shear rate and viscosity apply. Equation 2.1 no longer holds and more complex equations are necessary (see Section 15.5.3).

From a physical standpoint, viscosity is related to the ability of molecules to move past each other during shearing (mixing, pouring, pumping, swallowing, etc.). Factors that affect the ability of molecules to move relative to each other also affect viscosity. For Newtonian sugar solutions, the value of viscosity is dependent on the molecular weight of the sugar, the concentration and temperature. In general, high molecular weight sugars at high concentrations and low temperatures have high viscosity. Larger molecules generally have

more difficulty moving past each other during shearing and therefore, exhibit higher viscosity. For example, lower DE glucose syrups with higher average molecular weight are significantly more viscous than the higher DE glucose syrups. Invert sugar, made up of two monosaccharides, has a very low viscosity. For comparison of the effects of molecular size, the viscosity of invert sugar and sucrose at 20 °C are shown in Figure 2.2. At equivalent weight concentrations, the viscosity of invert sugar is significantly less than that of sucrose due to the lower molecular weight.

The number of molecules present in solution, expressed as concentration, also impacts viscosity. The more molecules there are, higher concentration, the more likely those molecules are to impact each other and so the viscosity is higher. Viscosities of sucrose solutions at different concentrations are shown in Figure 2.3. Finally, when temperature increases, the kinetic energy of each molecule increases, which allows the molecules to move past each more readily, resulting in lower viscosity, also shown in Figure 2.3.

Glucose syrups, with a range of saccharide composition, behave as Newtonian fluids with a viscosity dependent on DE, as seen in Figure 2.4. Glucose syrups from different manufacturers, although they have the same DE, may have different viscosity due to the different saccharide distribution (and average molecular weight). However, the increase in viscosity with a decrease in DE of a glucose syrup can clearly be seen. This is evidenced by the relative ease of flow of 63 DE glucose syrup compared to 42 DE glucose syrup. Mageean et al. (1991) summarize viscosity data for a wide range of confectionery sweeteners.

2.3 Heat of Solution

When a sugar crystal dissolves in water, heat is evolved or absorbed depending on the nature of the process. Heat evolution is associated with the sugar molecules going from solid state to liquid state. The lattice enthalpy is the change in enthalpy as the sugar (and water when crystal hydrates exist) molecules dissociate from the crystal lattice. Solute-solute (endothermic,

Figure 2.2 Comparison of viscosity of sucrose and invert sugar at 20 °C (Data from Mageean et al. 1991)

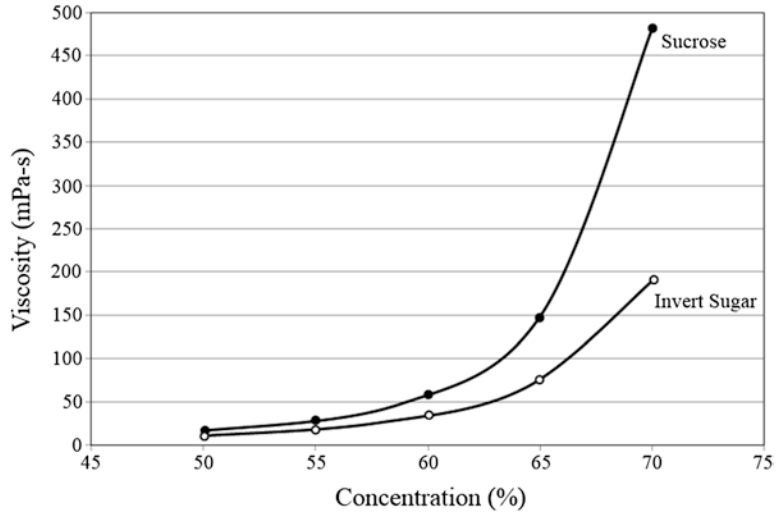


Figure 2.3 Dependence of sucrose viscosity on concentration and temperature (Data from Mageean et al. 1991)

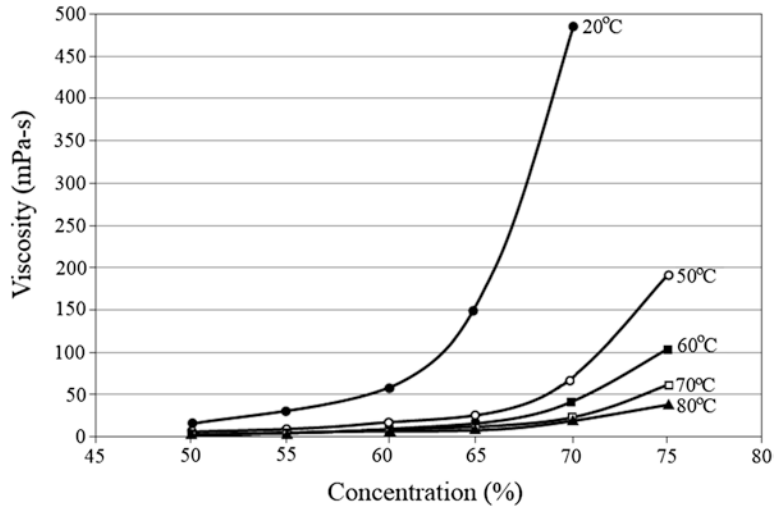


Figure 2.4 Dependence of glucose syrup viscosity (at 80% dry substance) on temperature (Data from Mageean et al. 1991)

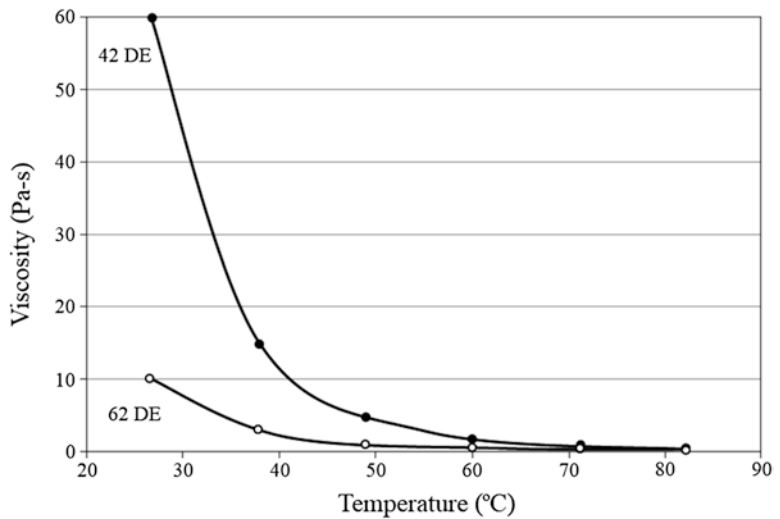


Table 2.2 Heats of solution (at 25 °C) for various crystalline sweeteners. By convention, a positive heat of solution indicates an endothermic (cooling) process

Sweetener	Molecular weight	Heat of solution (J/g)
Sucrose	342	18
Glucose anhydrous	182	60.6
Glucose monohydrate	182	105
Isomalt	344	39.3
Lactitol (monohydrate)	362	58.2
Maltitol	344	56.1
Sorbitol	182	111
Mannitol	182	121
Xylitol	152	153
Erythritol	122	180

Sources: Fritzsche (1995), Embuscado and Patil (2001), and Pancoast and Junk (1980)

removes heat from the environment) and, where pertinent, solvent-solvent (exothermic, adds heat to the environment) attractions must be broken in order for the crystal to dissolve. Once sugar molecules are dissociated from the lattice, there is an enthalpy term associated with solvation (or water hydration) of the sugar molecules (solute-solvent attraction), as they become part of the solution phase. This term is also exothermic, meaning heat is evolved into the solution. Finally, there is an enthalpy associated with dilution of the sugar molecules to the final concentration. By convention, the heat of solution for an endothermic process (cooling; removes heat) is positive while that for an exothermic process (warming; adds heat) is negative. Based on these energy principles, some crystals when dissolved in water cause the temperature to decrease (endothermic) while others cause temperature to increase (exothermic). For the most part, the sweeteners used in confections all give a cooling effect upon dissolution. Table 2.2 shows standard heats of solution for different confectionery ingredients. Many polyol crystals have a substantial cooling effect, which leads to some of the specific eating characteristics of sugar-free confections.

Sugar solids dissolving in water or saliva undergo complex changes as the molecules make the transition from a solid state to a diluted liquid state (Cammenga and Zielasko 1996). When a

crystal dissolves, the endothermic change in lattice energy (latent heat) dominates the heat effect. However, when an amorphous glassy solid dissolves, there is no endothermic lattice energy, only an exothermic enthalpy of solvation (water hydration around the newly released sugar molecule). This means that when a piece of glassy hard candy dissolves in the mouth, there is a slight heating effect (not a cooling effect). Reiser et al. (1995) quotes a value of -16.9 kJ/mol for the heat of solution of a sucrose glass, whereas Knecht (1990) gives a value of -3.5 kcal/mol (8.4 kJ/mol). Cammenga and Zielasko (1996) found a heat of solution of -12.4 kJ/mol for dissolution of isomalt glass in water.

Note that when a concentrated sugar (or polyol) solution is diluted by addition of water (or saliva), this change in concentration, or dilution, is accompanied by an enthalpy change. This correlates to the third enthalpy term discussed above and is sometimes called heat of dilution. In most sugars and polyols, the heat of dilution is relatively small compared to the heat of solution (crystal dissolving). In sucrose, heat of dilution is generally about 1% of heat of solution (Reiser et al. 1995).

2.4 Specific Optical Rotation

When polarized light, or light vibrating in only one direction, passes through a sugar solution, the angle of polarization of that light is rotated depending on the type and concentration of the dissolved sugar. In the past, this property was used to measure the concentration of dissolved sugar with a polarimeter, although with better concentration measurement methods, the polarimeter method is rarely used any more.

A solution of glucose rotates a plane of polarized light to the right (clockwise), or in the *dextro*-rotary direction. It is this property of glucose that has led to it being called dextrose. Fructose, on the other hand, rotates light to the left, or in the *levo*-rotary direction (counter clockwise), which is why fructose is sometimes called levulose. Most of the sugars of concern in confectionery syrups, including sucrose, maltose and

Table 2.3 Specific optical rotation (Light source: D-line of Na) of various sugars at 20% concentration

Sweetener	Temperature (°C)	Optical rotation (degrees/dm)
Sucrose	20	+65.2
α -D-glucose	20	+53.0
Fructose	25	-91.4
Invert sugar	20	-20.4

Estimated from Mageean et al. (1991)

lactose, rotate light to the right. Since glucose, maltose and higher molecular weight glucose polymers all rotate polarized light to the right, glucose syrups have the same property.

The type of sugar, its concentration, temperature, and the wavelength and path length of light passing through the sugar solution all affect the measured optical rotation. Specific optical rotation is defined as the angle of rotation of polarized light of specified wavelength (the D line of sodium at 589.3 nm) passing a distance of 10 cm through a solution at 20 °C, as given by Equation 2.2.

$$[\alpha]_{\lambda}^T = \frac{\alpha}{l * c} \quad (2.2)$$

Here, α is optical rotation, l is the path length of light, and c is concentration. Specific optical rotation of various sugars at 20% is given in Table 2.3.

Under standardized conditions, fructose rotates light farther to the left (-91.4°) than glucose rotates light to the right (+53.0°), so that invert sugar, the equimolar combination of glucose and fructose, has a slight left-handed optical rotation (-20.4°). Sucrose has a positive optical rotation (+65.2°). When it is hydrolyzed to form invert sugar, the equimolar mixture of glucose and fructose, the optical rotation switches from positive to negative. It is this “inversion” of the optical rotation from right to left that historically gave rise to name “invert sugar” upon complete hydrolysis of sucrose.

2.5 Refractive Index

Another optical property of solutions is refractive index. When you look at an object immersed in a pool of water, you know that the object is not

really where it appears to be. As light passes from air into an aqueous solution, its direction is changed, or refracted, depending on the optical properties of the solution. This well-known change in path of a light beam when it goes from air into water is due to the difference in speed of light in the two materials. Refractive index of a material is generally given as the ratio of the speed of light in air (or technically, in vacuum) to the speed of light in the material. The refractive index of water at 20 °C is 1.3329 (relative to air, which is generally considered to have a refractive index of 1.0000 using sodium light as the source). In contrast, the refractive index for a saturated sugar solution (67 wt %) at 20 °C is 1.4581.

Each type of sugar exhibits a slightly different effect on refractive index, depending on its molecular properties. For pure sucrose, the change in refractive index with different concentration is shown in Figure 2.5. Based on this correlation, the measurement of refractive index can be used to quantify the concentration of sucrose in aqueous solution. That is, the exact concentration of a pure sucrose solution can be determined by measuring its refractive index. The concentration (from Figure 2.5) that corresponds to a measured refractive index is the concentration of the unknown solution. However, since refractive index changes with temperature, it should always be measured at a standard temperature of 20 °C (68 °F).

Also shown in Figure 2.5 is the effect of invert sugar on refractive index of solution. Fructose and glucose molecules have a slightly different refracting power than sucrose and thus, a different standard curve (from that of sucrose) must be used to calibrate the measurement of refractive index with concentration. There is a slightly different curve for each sugar and mixture of sugars. Figure 2.6 shows the refractive index curves for several different glucose syrups. Since glucose syrups can vary quite widely in saccharide composition, depending on manufacturer, process, and target DE, each glucose syrup will have a unique refractive index profile. The Corn Refiners Association, Inc. of the United States provides tabulated data for various glucose syrups, along with corrections for differences in DE and ash content (Corn Refiners Association 1990).

Figure 2.5 Refractive index of sucrose and invert sugar solutions at 20 °C (Data from Pancoast and Junk 1980)

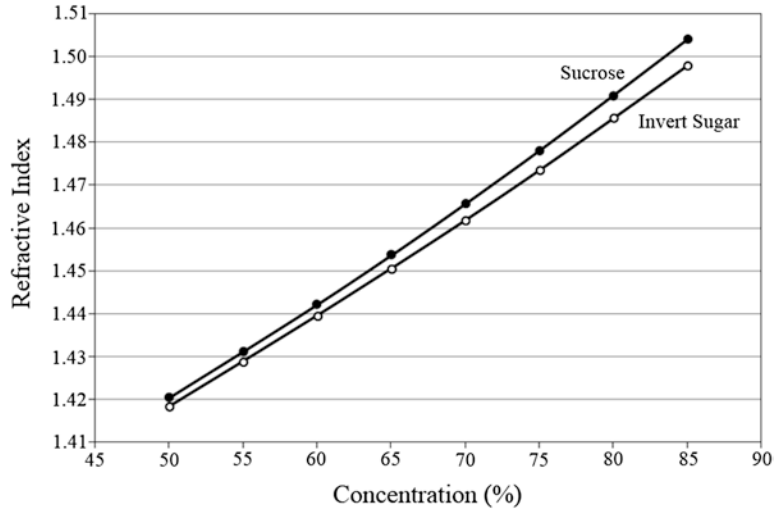
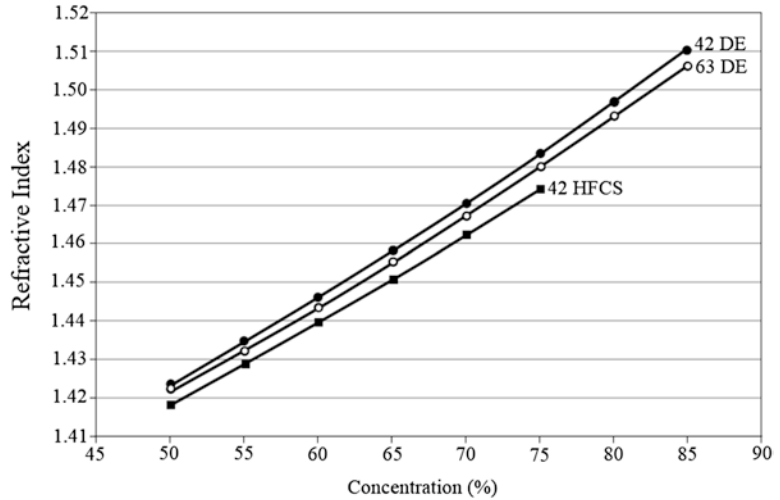


Figure 2.6 Refractive index curves at 20 °C for several glucose syrups: 42 DE (acid converted), 63 DE (dual converted) and 42 HFCS (high fructose corn syrup) (Data from Pancoast and Junk 1980)



Refractive index is measured with a refractometer, which is essentially a prism with a goniometer for measuring the angle of refraction of a beam of light as it passes through the solution. A small dab of sugar solution is placed on the prism and light is passed through the solution under controlled conditions. Refractive index is measured as the angle of refraction of the light between sugar solution and prism.

Refractometers read refractive index, which is directly related to the sugar concentration but the measured values depend on the types of sugars present in solution. However, refractometers used in the candy industry are typically calibrated to

read sucrose concentration (weight % basis). That is, the refractive index is converted to a scale based on the equivalent concentration of sucrose based on the correlation in Figure 2.5. For a pure sucrose solution, the refractometer reading of concentration is accurate and reflects the true sucrose concentration. However, since each sugar reads a slightly different refractive index for a given concentration, the refractive index reading from a mixed sugar solution does not give the exact concentration of that sugar mixture in solution. To note this discrepancy between pure sucrose and complex sugar mixtures, the concentration reading from a refractometer is called

degrees Brix ($^{\circ}$ Brix) rather than true concentration. That is, a pure sucrose solution with a concentration of 67% (weight basis) should read 67° Brix on the refractometer scale – the true concentration and $^{\circ}$ Brix give the same reading. If that pure sucrose solution is cooked to higher temperature so that some inversion of the sucrose takes place, the refractometer reading will be influenced by the presence of the glucose and fructose so that a $^{\circ}$ Brix reading of 90 no longer means that the sucrose concentration in that solution is 90%. A portion of the reading comes from the invert sugar, which has a different standard curve than sucrose (Figure 2.5).

The addition of glucose syrup to confectionery syrup leads to even more deviation between true concentration and $^{\circ}$ Brix. Correction factors for refractive index that allow determination of true concentration from $^{\circ}$ Brix are tabulated in various references (Pancoast and Junk 1980). The principle for correcting refractometer readings for binary blends of two sugars (denoted with different subscripts as 1 and 2) is given by Pancoast and Junk (1980) as:

$$n_D^{20} = \frac{\left(\frac{P_1 n_1}{S_1}\right) + \left(\frac{P_2 n_2}{S_2}\right)}{\left(\frac{P_1}{S_1} + \frac{P_2}{S_2}\right)} \quad (2.3)$$

where, n_D^{20} is refractive index (at 20 $^{\circ}$ C for the D line of sodium light), P_1 and P_2 are percentages of the two sugar syrups being blended together, n_1 and n_2 are refractive indexes of each of the sugars being blended, and S_1 and S_2 are the dissolved solids (in percent) of each of the sugars.

For example, an equal mixture ($P_1 = P_2 = 50\%$) of saturated sucrose ($S_1 = 66.7\%$ with $n_1 = 1.4581$) with a 42 DE glucose syrup ($S_2 = 80\%$ and $n_2 = 1.49745$) is calculated from Equation 2.3 to have a refractive index of 1.47602. According to Table 2.4, the observed $^{\circ}$ Brix from a refractometer reading for the above mixture would be 74.0%. This reading would be in error due to the greater contribution of glucose syrup to the refractive index and thus, the actual dissolved solids concentration of the mixture would be less. The corrected dry solids content of this blended syrup would actually be 72.74%, so the correc-

Table 2.4 Comparison of solids content of sucrose and 42 DE glucose syrup mixtures based on refractometer measurement

Sucrose solids (%)	Glucose syrup solids (%)	Solids content as measured ^a (%)	Actual solids content (%)
100	0	66.50	66.50
90	10	67.93	67.66
80	20	69.39	68.86
70	30	70.89	70.11
60	40	72.42	71.40
50	50	74.00	72.74
40	60	75.62	74.13
30	70	77.29	75.57
20	80	79.00	77.08
10	90	80.75	78.64
0	100	82.57	80.27

From Pancoast and Junk (1980)

^aBrix – refractometer reading as if all dissolved solids were sucrose

tion factor would be -1.26% . Similar tables are available for mixtures of sucrose solutions with glucose syrups of different DE, high fructose corn syrup, dextrose solution, and invert sugar (see Pancoast and Junk 1980 for more details).

Since the differences in solids content when using $^{\circ}$ Brix are generally small, within a percent or two at most, most confectioners choose to ignore these differences. Typically, as long as the product meets the desired specifications (hardness, etc.), the refractive index read as $^{\circ}$ Brix provides an adequate quality control tool in most circumstances.

2.6 Density/Specific Gravity

Density, or weight per unit volume, is an important property of sugar solutions since it provides a measure of how much sugar is dissolved in water. Because the molecular weight of sugar is so much greater than that of water, high concentration sugar syrups have higher density than water. Often, specific gravity, or the relative density of sugar syrup to water, is used to correlate against concentration. Since density of a material depends on the temperature at which it is measured, specific gravity must be specified at a

Figure 2.7 Density of various sugar solutions at 20°C (Data from Mageean et al. 1991)

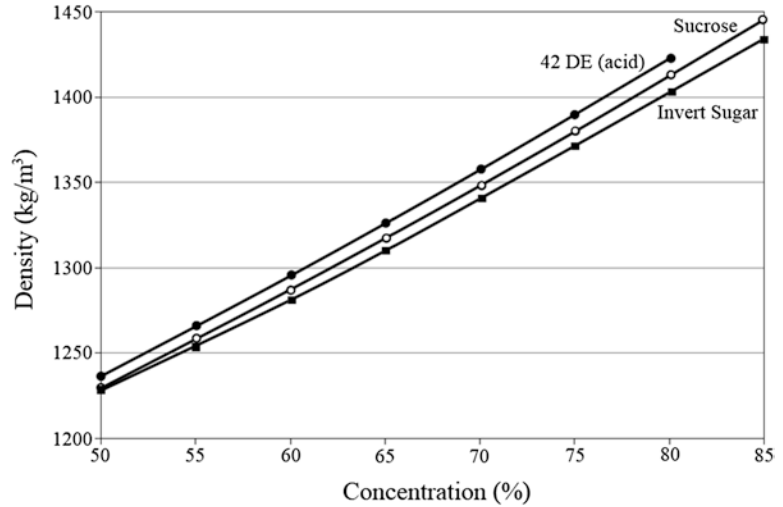
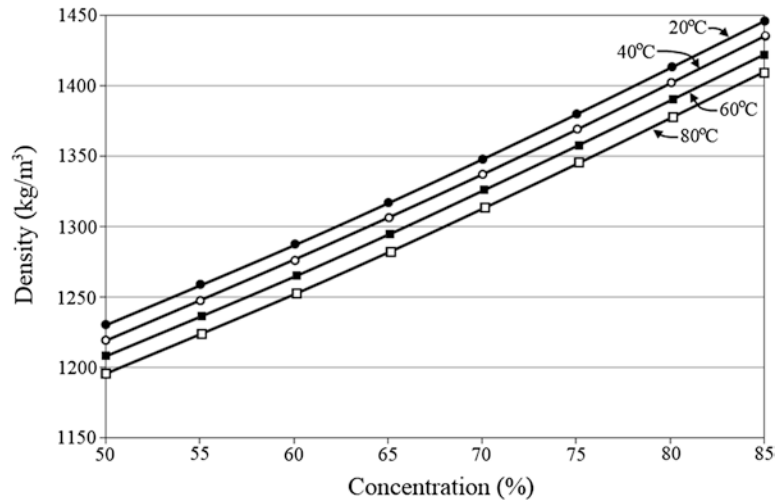


Figure 2.8 Effect of temperature on density of sucrose solutions (Data from Mageean et al. 1991)



certain temperature. It is most common to find specific gravity tables for sugar solutions where the density of sugar solution at 20 °C is referenced to the density of water at 4 °C, the temperature of maximum density for water (often taken as 1.000 g/mL although it is slightly lower than this). Figure 2.7 shows that density of sugar solutions increases as a function of concentration and that higher molecular weight sugars give solutions with higher density. Figure 2.8 shows the dependence of density of sucrose solutions on temperature. As expected, the density of sugar solutions decreases slightly as temperature increases. Data for specific gravity of a wide

range of sugar solutions are tabulated in Pancoast and Junk (1980).

Specific gravity, or density, has in the past been typically measured by use of a hydrometer. A hydrometer is a floating glass tube with a weight in the bottom (i.e., mercury, lead shot) that is calibrated to read specific gravity along the stem. It is placed into the liquid and the level that the hydrometer sinks into the fluid is noted on the glass stem. Different hydrometers are used for fluids of different specific gravity. Electronic hydrometers, with continuous read-outs, now replace glass hydrometers in many applications. Continuous, in-line fluid density measurement is

now common in many industries. Many in-line density meters are based on introduction of a vibrating element in the flow stream. The damping of the vibration is proportional to density. Alternatively, changes in ultrasonic vibrations can be used to measure density in-line as well.

The specific gravity of glucose (corn) syrups has long been of interest to the confectioner. The specific gravity of glucose syrups depends on both the saccharide composition and the water content. Typically, density, or specific gravity, of glucose syrups has been specified in units of degrees Baumé (°Bé), defined as (Pancoast and Junk 1980):

$$^{\circ}\text{Bé} = m - \frac{m}{\text{SG}_{15.6^{\circ}\text{C}}} \quad (2.4)$$

Here, m is a modulus (usually taken to be 145 – the ratio of the total volume of water displaced by the hydrometer to the volume displaced by the unit scale length of the hydrometer stem), and $\text{SG}_{15.6}$ is the true specific gravity at 15.6 °C (60 °F). According to Pancoast and Junk (1980), the corn refining industry reports “commercial Baumé” by adding 1 to the measured value at 15.6 °C (60 °F) in order to estimate the value at 37.8 °C (100 °F). The Corn Refiners Association bulletin E-8, the standard method for measurement of Baumé, indicates that measurements are made at 60 °C (140 °F) with an appropriate hydrometer (streamlines type, 145 modulus, standardized at 60 °F). The Baumé is then calculated as:

$$\text{Baumé} = \text{Obs. } ^{\circ}\text{Bé at } 60^{\circ}\text{C (140}^{\circ}\text{F)} + 1.00^{\circ}\text{Bé} + \text{Correction} \quad (2.5)$$

The correction factor is required to correct for the difference in temperature of reading, 60 °C (140 °F) and temperature of hydrometer standardization, 15.56 °C (60 °F). The correction factor corrects for the relative thermal expansion of the hydrometer (glass) and the particular liquid.

More accurate (and simpler) determination of °Bé is accomplished by measuring refractive index to obtain total solids followed by calculation of °Bé from tables that correlate total solids

with specific gravity. The Corn Refiners Association (Washington, DC) offers a software program (RI-DS) for correlating refractive index and dry substance based on the composition profile of a glucose syrup. That is, the relative weight of each saccharide (monosaccharides, disaccharide, trisaccharide and above) is input into the program. The output includes refractive index, dissolved solids, °Brix and commercial Baumé.

2.7 Boiling Point Elevation

One of the most important concepts in confectionery manufacture is the relationship between boiling temperature and final water content of the confection. The well-known boiling point elevation relationship is used to control the water content of a candy through control of the cook temperature (final boiling point).

The boiling point is directly related to the amount of water vapor in the air above the sugar syrup. The amount of water vapor that air can hold (given as water vapor pressure) increases with an increase in temperature (Table 2.5). It is this relationship between vapor pressure and temperature that defines the boiling point. Specifically, when the vapor pressure above a surface of water reaches the pressure of the ambient environment (atmospheric pressure), the water begins to boil. For normal atmospheric pressure (1 atmosphere = 14.7 psi absolute = 760 mm Hg = 29.92 in Hg = 101.3 kPa), the temperature where the saturation vapor pressure reaches atmospheric pressure occurs at 100 °C (212 °F). When atmospheric pressure changes, due to normal meteorological events (e.g., high or low pressure systems), the temperature at which water boils changes. Table 2.6 shows the relationship between atmospheric pressure and boiling temperature of water. When atmospheric pressure decreases below the standard value (101.3 kPa), the boiling temperature decreases; when pressure is greater than normal atmospheric pressure, the boiling temperature increases. Since water content of candy syrups is determined by cooking to a specified temperature, slight changes in atmospheric pressure can lead to changes in

Table 2.5 Temperature dependence of vapor pressure of pure water

Temperature (°C)	Vapor pressure (kPa)	Temperature (°C)	Vapor pressure (kPa)
20	2.34	65	25.00
25	3.17	70	31.16
30	4.24	75	38.54
35	5.62	80	47.34
40	7.38	85	57.81
45	9.58	90	70.09
50	12.33	95	84.51
55	15.74	100	101.32 ^a
60	19.92		

Data from Handbook of Chemistry and Physics (1978)

^aNormal atmospheric pressure

Table 2.6 Pressure dependence of boiling point of water

Pressure (kPa)	Boiling temperature (°C)	Pressure (kPa)	Boiling temperature (°C)
93.32	97.71	101.32 ^a	100.00
94.66	98.11	102.66	100.37
95.99	98.49	103.99	100.73
97.32	98.88	105.32	101.09
98.66	99.26	106.66	101.44
99.99	99.63		

Data from Handbook of Chemistry and Physics (1978)

^aNormal atmospheric pressure

final water content of the candy. Even the reduced atmospheric pressure at high elevations can cause changes in moisture content of a cooked candy.

The composition of an aqueous solution influences the boiling point of water through the colligative effect. Solute molecules influence the interactions among water molecules depending on the number of solute molecules and their size, as expressed by molality. This impacts the colligative properties, including boiling point and freezing point temperatures, water activity and osmotic pressure. Addition of smaller molecules affects these properties to a greater extent than addition of the same number of larger molecules. When equivalent weights of either glucose or sucrose are added to a sugar solution, there is a greater change in the colligative properties with the glucose solution than the sucrose solution due

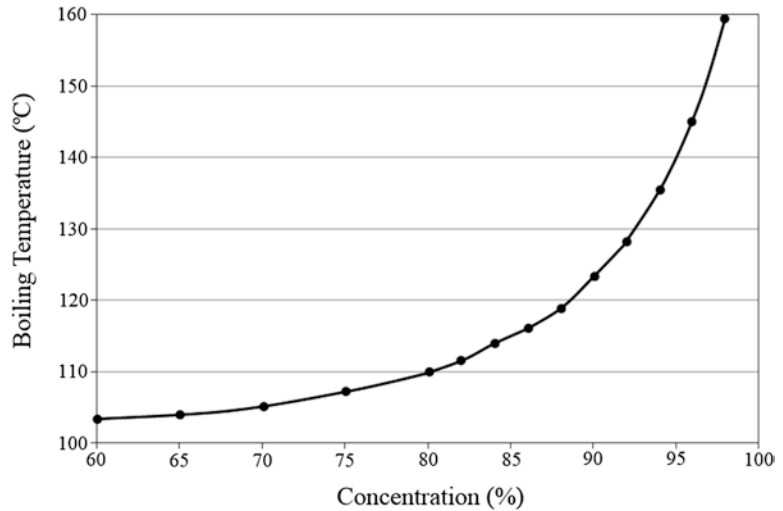
to smaller size of glucose molecules (higher number of moles for a given weight addition).

The interactions between solute and water molecules cause a decrease in the vapor pressure above the solution, which leads to an increase in the boiling point temperature (a boiling point elevation). The reduction in vapor pressure above a sugar solution means it must be heated to a higher temperature in order for the vapor pressure to be equal to the atmospheric pressure, the condition necessary for boiling to occur. Salts generally demonstrate an even greater effect on boiling point elevation than sugars owing to their lower molecular weight (higher molality at a given weight concentration).

When a sucrose solution is heated, it will first start to boil at the temperature associated with the boiling point for the given concentration and atmospheric pressure. For example, from Figure 2.9, the boiling point temperature for a sucrose solution saturated at room temperature (67%) is about 104.3 °C (220 °F). When that syrup begins to boil, water molecules are lost to the air and the solution becomes more concentrated. This higher concentration means that the boiling point temperature is now higher, according to Figure 2.9. Thus, as the sucrose solution continues to boil, both its concentration and boiling temperature increase according to the relationship shown in Figure 2.9. It is this relationship that allows the candy maker to know the concentration of sugar in a cooking syrup by simply measuring temperature. This is an important concept for confectioners since each candy must be cooked to the proper temperature to ensure the proper final water content in the product. However, it is important that the proper boiling point elevation curve is used for the specific sugar mixtures found in the candy formulation.

A significant body of literature exists giving boiling point elevations for various sugar solutions (see, for example, Pancoast and Junk 1980; Mageean et al. 1991; Starzak and Peacock 1998; Starzak and Mathlouthi 2006). However, there is considerable variation in the reported literature on boiling point elevation due to the difficulty in accurately measuring water content for different boiling temperatures. In part, this variation in the

Figure 2.9 Effects of sucrose concentration on boiling point elevation of aqueous solutions (Data from Norrish 1967)



literature results from measurement difficulties and in part, it results from changes in the sugar syrup during heating. Once a sugar syrup has been cooked to the desired temperature, it must be cooled before water content can be measured. However, water is still evaporating from the syrup as it is cooling; therefore, unless great care is taken, the water content associated with a certain cook temperature generally underestimates the true water content since some of the moisture loss actually occurred during cooling. In addition, inversion of sucrose into fructose and glucose (with higher boiling point elevation) and decomposition of sugars (i.e., fructose) during cooking to high temperatures also introduces errors into boiling point measurements, especially at elevated temperatures (low moisture content). For these reasons, data provided in the literature must be used with caution.

Norrish (1967) evaluated boiling point elevation data for sugar solutions. Figure 2.9 shows the effects of pure sucrose on boiling point temperature of aqueous solutions at atmospheric pressure based on this study. Boiling point temperature increases from 100 °C (212 °F) with no sucrose to about 140.3 °C (284.5 °F) when sucrose reaches a concentration of 95% (by weight). When only 2% water remains (98% solids content), the boiling point temperature of a pure sucrose solution should be about 159.5 °C (319.1 °F). To document the

disparity of data available in the literature, Cakebread (1972) states that the boiling point temperature for a 98% sucrose solution should be 137.7 °C (279.9 °F). This is over 20 °C less than the value from Jones (1959). For more details, this disparity in boiling point elevation (and other colligative properties) is discussed further in Starzak and Mathlouthi (2006) and Hartel et al. (2011).

Data in the literature for boiling point temperatures of other sugars of interest in confections are also inconsistent for the reasons noted above. Thus, all such data must be used with extreme caution. However, to demonstrate the influence of average molecular weight on boiling point elevation, Figure 2.10 shows data from the same study comparing glucose, sucrose, and 42 DE glucose syrup (Mageean et al. 1991). As average molecular weight increases, the boiling point temperature also increases, as expected based on colligative principles.

Figure 2.9 applies when atmospheric pressure is 101.3 kPa (760 mm Hg). Higher or lower pressures cause the boiling point temperature to change accordingly, with higher boiling temperatures at higher pressure and lower boiling temperatures under vacuum operation. Figure 2.11 shows the change in boiling point temperature of sucrose solutions for pressures slightly different than standard ambient pressure. Atmospheric pressure varies slightly due to natural weather

Figure 2.10

Comparison of boiling point temperatures for glucose, sucrose and 42 DE corn syrup (With permission Hartel et al. 2011)

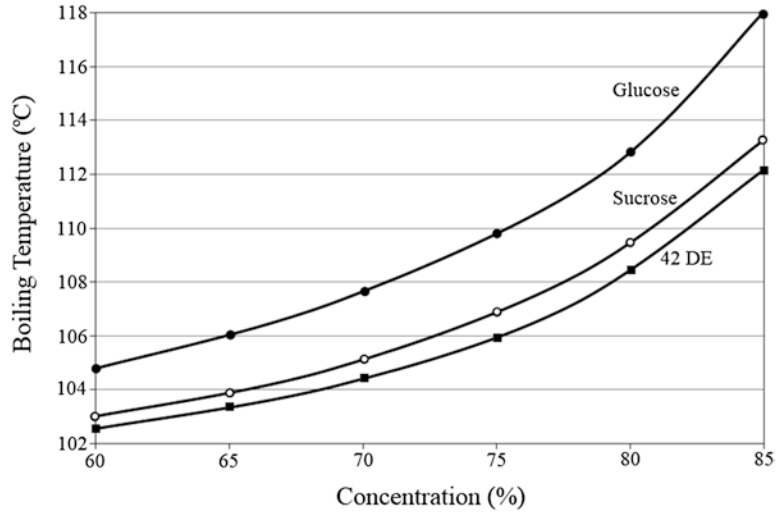
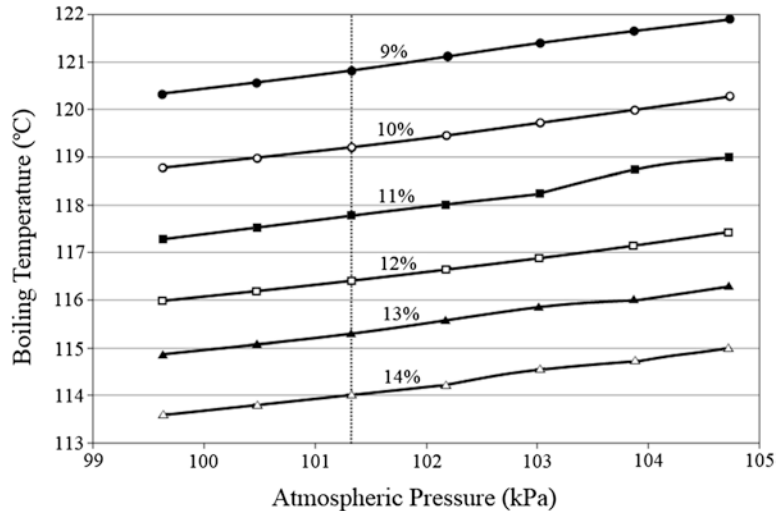


Figure 2.11 Effects of atmospheric pressure on boiling point temperature of pure sucrose solutions with water content from 9% to 14%. The vertical line represents normal atmospheric pressure (Data from Jeffery 2004)



phenomena (high or low pressure systems). A fluctuation of 3 kPa (22.5 mm Hg), from 99.8 kPa (748.75 mm Hg) to 102.8 kPa (771.25 mm Hg), well within normal daily variations in barometric pressure, would change the water content of a sugar syrup by approximately 0.5% if the same cook temperature was used. That is, a formulation cooked on a low pressure day could potentially have about 0.5% less water than the same formulation cooked on a high pressure day. Such a change in water content can potentially cause significant differences in texture, quality and shelf life of the confection,

although most confectioners are not concerned with the effects of varying barometric pressure.

A similar effect on boiling point is observed with changes in altitude. Since atmospheric pressure decreases with increasing altitude, a manufacturing facility located at high elevation would have to compensate in cook temperature to mimic a product cooked at a facility at low elevation. In general, for each 304.8 m (1,000 ft) increase in altitude, there is an equivalent decrease in boiling point of about 1.1 °C (2 °F) (Stansell 1992). This can lead to an increase in water content on the order of 0.5%, again potentially leading to

significant changes in texture and quality of a confection.

In commercial confectionery manufacturing, it is common to cook sugar syrups under vacuum¹ to reduce the effects of degradation reactions, including inversion and browning. Boiling point temperatures are significantly lowered by vacuum operation since a reduction in pressure means a lower vapor pressure is needed for boiling to occur. For example, boiling to 135 °C (275 °F) under a vacuum of 9.9 kPa absolute pressure (27" Hg of vacuum) is about equivalent to boiling to 150 °C (302 °F) at atmospheric pressure, both conditions resulting in a water content of about 3%.

2.8 Solubility

An important aspect of sugars, salts, polyols and other confectionery ingredients is their ability to dissolve in water. When sugar crystals are added to water, the crystals dissolve until the dissolved molecules reach a maximum concentration, called the solubility or saturation concentration. The saturation concentration depends on the type of solute and the temperature of the solution. All sweeteners used in confections have what is known as a regular solubility curve, where the maximum concentration in solution increases as temperature goes up. In contrast, some salt molecules have an inverse solubility, where the maximum concentration in solution decreases as temperature increases. Such molecules, like calcium and magnesium bicarbonate, cause problems of scaling in hard waters due to this inverse solubility curve. As the temperature

¹ Specification of a vacuum is based on an inverse pressure scale and is almost always given in units of inches of mercury (in Hg). That is, rather than increasing from absolute zero pressure, a vacuum scale increases numerically as pressure is reduced below atmospheric pressure. For example, since atmospheric pressure is 29.92 in Hg, a complete (absolute) vacuum would be 29.92 in Hg vacuum, equivalent to zero absolute pressure. A vacuum of 28 in Hg would then be the equivalent of an absolute pressure of $29.92 - 28 = 1.92$ in Hg. Note: atmospheric pressure = 29.92 in Hg = 760 mm Hg = 101.325 kPa = 1.01325 bar = 14.696 psi (pounds per square inch).

of hard water increases, the solubility concentration of these salts decreases until eventually they precipitate out.

When no further dissolution of sugar crystals occurs in solution, the sugar molecules in the liquid state are in thermodynamic equilibrium with the sugar molecules in the remaining crystals. There is no further net change in molecules from crystal to liquid or back again, although as with all equilibrium states, there is a continuous exchange of molecules between the two states (just no net change). Thermodynamically, equilibrium is defined as when the chemical potentials of the molecules in the two states are identical.

To measure solubility of a material in water, there are generally two approaches. The first approach is to add an overabundance of crystalline solids and allow the solution to mix, and crystals to dissolve, until no further changes in solution concentration occur. The maximum concentration attained is the saturation concentration, or solubility. The second approach is to prepare a high concentration solution (above the expected saturation concentration) and add a few seed crystals to initiate crystallization. As the crystals grow, solute molecules are removed from solution and the concentration of solute in the liquid phase decreases until equilibrium is attained. The final concentration of the liquid phase is the saturation concentration. Ideally, if a true equilibrium is attained and there are no kinetic constraints, both methods should give the same value of solubility concentration.

2.8.1 Solubility of Sugars

Sucrose exhibits a normal solubility curve, as shown in Figure 2.12, with saturation concentration increasing as temperature increases. At room temperature, sucrose is saturated at a concentration of about 67%, with that number increasing to over 80% at 90 °C (194 °F). Compared to sucrose, fructose is more soluble and lactose less soluble at all temperatures (Figure 2.13). Glucose, on the other hand has lower solubility than sucrose at temperatures less than about 50 °C (122 °F) and then higher solubility at higher temperatures.

Figure 2.12 Solubility of sucrose as function of temperature (Data from Mageean et al. 1991)

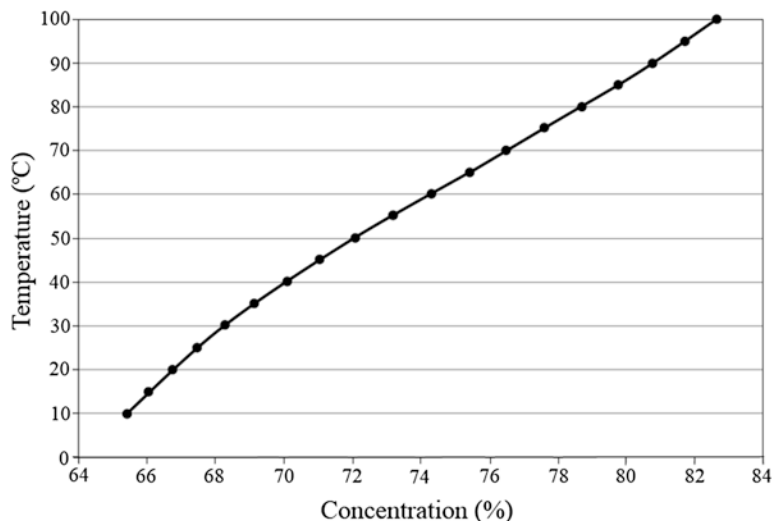
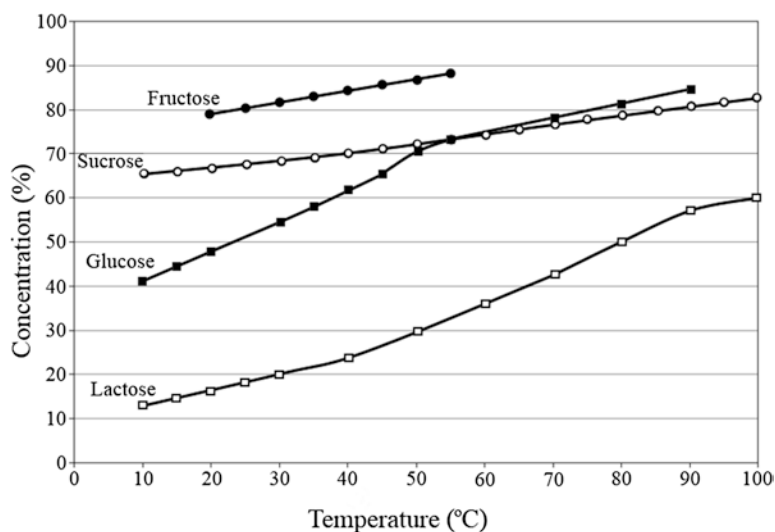


Figure 2.13 Solubility of various sugars (Data from Mageean et al. 1991)



In Figure 2.13, the solubility curves for glucose and lactose are not continuous, with breaks at about 50 °C (122 °F) and 93 °C (199.4 °F), respectively. These breakpoints represent the change from one anomer being the least soluble in solution to another. For example, glucose crystallizes as monohydrate at temperatures below about 50 °C and in an anhydrous form above that temperature. Glucose monohydrate is less soluble than the anhydrous form below 50 °C, so it is most likely to crystallize, whereas above 50 °C, the anhydrous form is the least soluble, so it is most likely to crystallize at elevated temperatures. Likewise, at temperatures less than 93 °C

(199.4 °F), the alpha form of lactose is the least soluble, whereas at temperatures greater than 93 °C, the beta form of lactose is the least soluble. For this reason, to crystallize β lactose from solution requires crystallization temperatures greater than 93 °C.

2.8.2 Solubility of Polyols

Similar to the sugars, polyols show different solubilities in water depending on the molecular structure (and extent of hydrogen bonding with water). Figure 2.14 shows that maltitol is significantly

Figure 2.14 Solubility of isomalt (Data from Palatinit 1996) and maltitol (Data from Cammenga and Zielasko 1996) as function of temperature

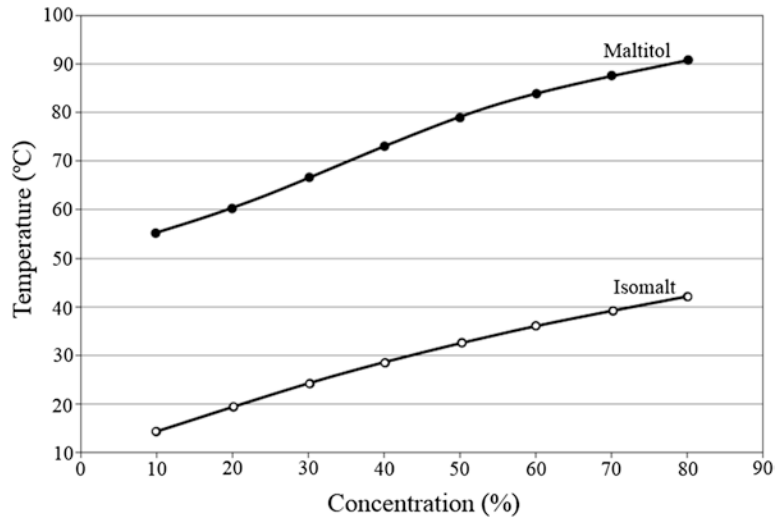
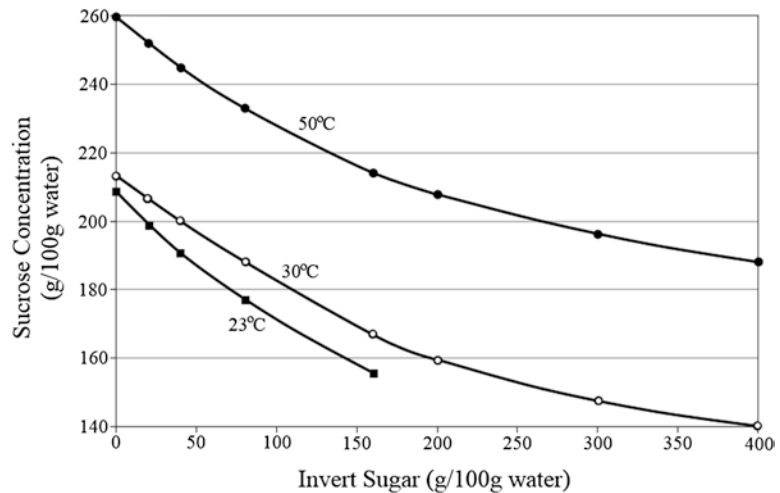


Figure 2.15 Solubility of sucrose in the presence of invert sugar (With permission Hartel et al. 2011)



more soluble than isomalt. The solubility concentration of maltitol at room temperature is about 60%, whereas isomalt is a lot less soluble at 24.5% at room temperature. The solubility concentrations of other polyols at room temperature include: γ sorbitol – 67.5%; mannitol – 18%; xylitol – 63%; lactitol – 55%; and erythritol – 37% (Embuscado and Patil 2001).

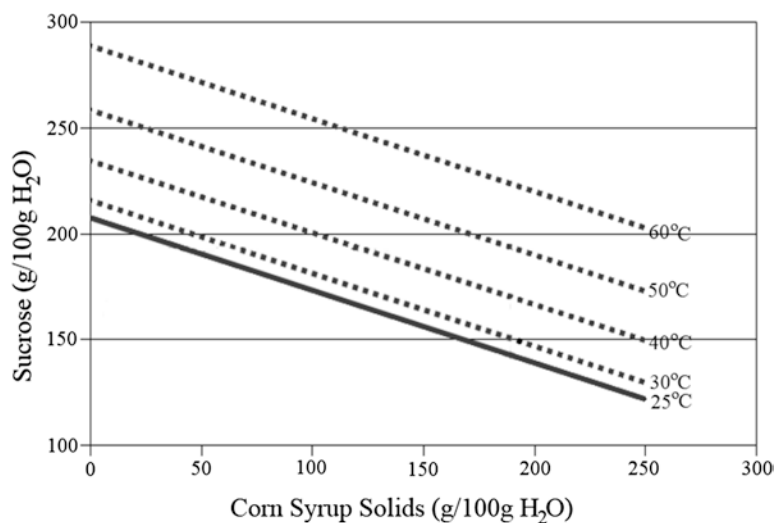
2.8.3 Solubility in Mixed Confectionery Syrups

When more than one sugar is dissolved in water, there is a competition for water molecules and the

solubility concentration of each sugar decreases. For example, when invert sugar is mixed with sucrose, the maximum concentration of sucrose that can be dissolved decreases somewhat due to the presence of the glucose and fructose molecules. The more invert sugar present in solution, the lower the saturation concentration of sucrose at a given temperature, as seen in Figure 2.15. In this case, addition of 50 g invert sugar/100 g water causes about a 10% decrease in sucrose saturation concentration at room temperature, from 208.6 to 188 g sucrose/100 g water.

A similar situation applies for mixtures of sucrose and glucose syrup, where the presence of glucose syrup solids decreases the amount of

Figure 2.16 Effects of glucose syrup solids on sucrose solubility (Jonathon 2004). *Solid line based on data, dashed lines based on projected curves*



sucrose that can be dissolved in water. Figure 2.16 documents the decrease in solubility as the level of glucose syrup solids increases. Despite its importance in confections, very little quantitative data is available to show the effects of different glucose syrup solids (DE, saccharide distribution, etc.) on sucrose solubility. Fortunately, there appear to be minimal differences between the effects of invert sugar (Figure 2.15) and glucose syrup solids (Figure 2.16). In both cases, about 150/100 g water of the impurity give about the same solubility concentration (160 g sucrose/100 g water) at room temperature.

Despite the reduction in the amount of sucrose that can be dissolved to saturation in the presence of invert sugar or glucose syrup solids, the overall concentration of the mixed solution actually increases. That is, the total amount of dissolved sugars (including sucrose, invert and glucose solids) increases when different sugars are mixed together, as seen for mixtures of sucrose and glucose syrup solids in Figure 2.17. In this figure, as the percentage of glucose syrup solids in the mixture (on a solids basis) increases, the total amount of dissolved sugars, which includes sucrose and glucose syrup solids, increases. In this case, a 50:50 mixture of sucrose and glucose solids contains about 12% more dissolved solids than sucrose alone at saturation. The significance in this phenomenon is the increase in viscosity of this mixture and the reduction in water activity

(making it more stable to microbial problems and drying out on storage).

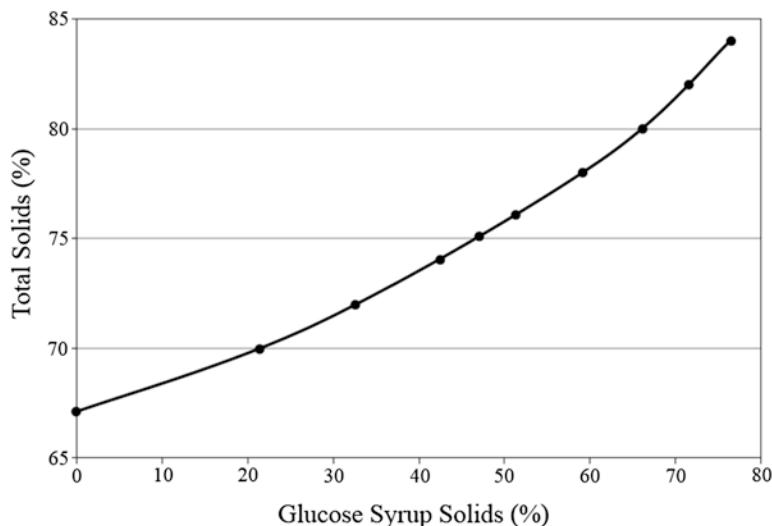
Typically, the effects of other confectionery ingredients, besides other sugars, on the solubility concentration of sucrose are considered to be minimal. Ingredients such as hydrocolloids (starch, gelatin, pectin), fat, colors, flavors, etc., generally have little to no effect on the solubility of sugars. Some dairy ingredients, especially concentrated milk and whey products with high lactose content, can have a significant effect on the solubility of sucrose in water. For example, both glucose syrup and lactose present in a caramel formulation will act as doctoring agents to influence solubility and moderate sucrose crystallization.

When lactose levels are high, greater than the solubility of 16% in water at room temperature, then lactose becomes the sugar most likely to grain. In fact, in caramels made with high levels of milk or whey ingredients, lactose may be more of a problem for graining than sucrose due to its very low solubility (see Chapter 10 for more discussion on crystallization in caramel and fudge).

2.9 Glass Transition Temperature

The glass transition may be defined as the point where a fluid becomes sufficiently viscous to have the solid-like properties characteristic of a glass (or vice-versa, the temperature at which the

Figure 2.17 Total solids concentration for mixtures of sucrose and glucose syrup (42 DE) saturated with respect to sucrose. X-axis represents percent of glucose solids present on a solids basis (Data from Mageean et al. 1991)



viscosity of glass is reduced sufficiently to become fluid-like). Typically, viscosity values at this transition are around 10^{12} to 10^{14} Pa-s. The glass transition is usually taken as the mid-point temperature of the transition, which may extend over a wide range of temperatures (10 °C or more) depending on the composition of the material.

The glass transition temperature depends on the type of molecules forming the glass, the presence of solvent (water), and the addition of humectants (glycerol). In general, it is widely accepted that T_g increases approximately as the molecular weight of the glass-forming substance increases, although there are numerous exceptions to this rule. Table 2.7 compiles T_g values for various dry sweeteners (0% water) of importance to the confectionery industry. In general, monosaccharides have lower T_g than the disaccharides, but within each category, there is a range of T_g . For disaccharides, T_g varies from 65 to 70 °C (149–158 °F) for sucrose to 101 °C (213.8 °F) for lactose. The molecular nature of the sweetener determines T_g , not just their molecular weight.

Mixtures of sweeteners take on T_g values that fall between the values for the components in the mixture. For example, mixtures of sucrose and glucose syrup solids have T_g values that fall somewhere between that of pure sucrose and the glucose syrup being used, as seen in Table 2.8 for two types of glucose syrup solids. Mixtures of 42

Table 2.7 Glass transition temperatures for various sweeteners (in completely dry form) used in confections

Compound	T_g (°C)
Fructose	5–10
Glucose	31
Lactose	101
Maltose	87
Sucrose	62–70
Raffinose	70
Sorbitol	–9
Xylitol	–29
Maltitol	39
Isomalt	63.6
42 DE corn syrup solids	79
20 DE corn syrup solids	139
Polydextrose	90.8
Hydrogenated starch hydrolysate ^a (MW 504)	54.6
Hydrogenated starch hydrolysate ^a (MW 644)	75.0

With permission from Ergun et al. (2010)

^aMaltitol syrups

DE glucose syrup solids with sucrose do not change the T_g of the mixture significantly until nearly half of the mixture is glucose syrup solids. The much higher molecular weight 20 DE syrup solids, with significantly higher T_g than sucrose, cause a substantial increase in T_g of the mixture even at relatively low levels. In contrast, mixtures of sucrose with high DE glucose syrup solids and/or invert sugar solids can cause a significant reduction in T_g of the mixture. For example,

Table 2.8 Glass transition temperatures (onset of calorimeter scan) for dry corn syrup – sucrose mixtures (less than 1% moisture)

Addition level (%) ^a	20 DE ^b	42 DE ^b
0	63.9 ± 1.4	63.9 ± 1.4
10	66.8 ± 0.4	64.1 ± 2.2
20	65.8 ± 2.6	66.9 ± 0.7
50	73.6 ± 3.0	69.1 ± 2.0
75	91.6 ± 1.3	70.9 ± 1.6
100	139.3 ± 0.8	79.0 ± 2.9

From Gabarra (1996)

^aAddition on a dry solids basis (g corn syrup solids/100 g total solids)

^bDE dextrose equivalent

invert sugar solids, an equimolar blend of glucose and fructose, would have a T_g about midway between each of the components, or about 17.5–20 °C (halfway between the values of 5–10 °C for fructose and 30 °C for glucose). Mixtures of sucrose with invert sugar solids would cause a significant reduction in T_g of the mixture. This reduced T_g will have significant effects on texture and shelf life (see Chapter 8 for a discussion on T_g and hard candy qualities).

The amount of water present in a confection has a huge impact on T_g , with even low levels (a few percent) of water causing a substantial (nearly 10 °C) decrease in T_g , as seen in Table 2.9. Slight changes in water content of a candy can have significant effects on T_g , thereby affecting texture and shelf life. Note that a sucrose solution with about 5.5% water has a T_g about room temperature, meaning that sucrose solutions with higher water content would have T_g less than room temperature and never attain the glassy state. Addition of 42 DE glucose syrup solids to the sucrose solution would raise T_g slightly (according to Table 2.8), meaning that the mixture with 5.5% moisture might now have T_g slightly above room temperature. To reiterate, the combination of sweeteners and water content determine T_g of the mixture. These values can be estimated based on composition but are best measured for the specific confection in question (Hartel et al. 2011).

The glass transition temperature, T_g , is important in many confectionery products since it is an indicator of texture and shelf stability. Confections

Table 2.9 Effect of water content on glass transition temperature (T_g) of sucrose

Water content (%)	T_g (°C)
0	69
1	61
2	50
3	42
4	35
5	29

From Ergun et al. (2010)

with T_g above ambient temperature are in the glassy state, where molecular mobility is very low and the molecules are so tightly packed that they are no longer free to move about (either rotationally or translationally). Hard candy, brittles and some caramels fall into this category. These candies are relatively stable as long as they are maintained at conditions where T_g is greater than storage temperature and they are protected from moisture uptake (which lowers T_g). Confections with T_g below ambient temperature (not in the glassy state) have fluid-like characteristics dependent on how far T_g is below ambient temperature. For example, soft fluid confections (syrups, etc.) would have T_g well below 0 °C while firm, chewy candies (chewy nougat, taffy, etc.) have higher T_g (Ergun et al. 2010). As a general rule, candies with a higher T_g are harder and more brittle than those with lower T_g . In fact, the upper limit of T_g for the hardest sugar glass candies is probably between 50 and 60 °C (122 and 140 °F), although this has never been studied carefully. At such high T_g values, a sugar glass becomes sufficiently brittle that they are dangerous, where shards are sharp enough to pierce skin.

Detailed characteristics of the state of sugar in various confections are provided in Section 2.11 and in subsequent chapters on candy categories.

2.10 Crystallization Propensity

Controlling sugar crystallization is one of the most critical aspects of controlling texture, appearance, and overall quality of many confections. Thus, an understanding of the principles of crystallization as applied to confections is necessary. In general,

there are three steps of importance to controlling crystallization: generating supersaturation, forming nuclei, and growth of those nuclei until phase equilibrium is attained. These principles apply for all sweeteners in confections, whether sucrose, glucose, lactose or polyols.

Once a sweetener solution has become supersaturated, the likelihood that it will crystallize depends on numerous parameters. These include the driving force (or supersaturation), the propensity of the specific molecule to crystallize, and the presence of inhibitors (doctoring agents). The driving force for crystallization is the difference between the actual concentration of the sweetener and the saturation concentration. In general, the larger that concentration driving force, the faster crystallization occurs (at least until the glass transition is approached). However, kinetic barriers may exist that retard or inhibit crystal formation. The primary kinetic barriers that impede crystallization of sugars in confections are (1) the reduced molecular mobility near and into the glassy state and (2) the inhibitory effects of doctoring agents commonly used to moderate crystallization in confections (Hartel et al. 2011).

When crystallization occurs, several steps are involved. First, nuclei must be formed from the supersaturated solution as liquid molecules organize into a crystalline (lattice) state. Once crystals have formed, they continue to grow as long as there is an available thermodynamic driving force. That is, as long as the sweetener concentration remains above the solubility concentration for the system (temperature and additives), crystals continue to grow. Since sugar molecules are being removed from the solution phase as crystals grow, the sugar concentration in the liquid phase decreases as crystallization proceeds until the endpoint at phase equilibrium when the solution concentration reaches the solubility concentration at that temperature. The rate of desupersaturation depends on the rate of nucleation and growth. Finally, once the maximal amount of crystals has been reached, there is a possibility of further changes in the crystal size distribution due to thermodynamic ripening mechanisms. That is, changes in the crystal size distribution can occur over time under certain

conditions even though the total amount of crystals does not change.

2.10.1 Generating Supersaturation

In principle, there are three different methods to generate a supersaturated sugar solution: (1) removing water to concentrate the sugars, (2) cooling a concentrated sugar solution until concentration exceeds solubility at that temperature, and (3) adding a second solvent (an anti-solvent for sugar, like alcohol) in which the sugar is not soluble so that the sugar concentration in the mixed solvent is greater than the solubility concentration. To create a supersaturated solution in confections to promote graining, the solubility concentration must be exceeded in the process. This is usually accomplished through a combination of concentration (water removal) and cooling. In all cases, the effect is to increase the difference between the actual sugar concentration in solution and the saturation concentration.

Most confectionery processes involve cooking a dissolved sugar syrup to remove water and concentrate the sugars. As noted in previous sections, boiling a sucrose solution to remove water results in a continual increase in sucrose concentration at the same time the temperature rises due to the boiling point elevation effect. Interestingly, cooking a sucrose solution eventually results in a concentration above the solubility concentration. That is, as a sugar syrup is cooked, it goes from being undersaturated (crystals dissolve) to supersaturated (crystals can form) when the boiling point curve crosses the solubility. As seen in Figure 2.18 for pure sucrose solutions, this transition occurs at a temperature of about 112 °C (233.6 °F), when the concentration has reached about 85%. These values are slightly different when glucose syrups are added to the sugar mixture in confections due to their effects on both boiling point elevation (Section. 2.7) and sugar solubility (Section 2.8).

Cooling of the concentrated sugar syrup after reaching the desired cook temperature increases the supersaturation since the solubility concentration decreases as temperature decreases (see

Figure 2.18 State diagram for sucrose (With permission Hartel et al. 2011)

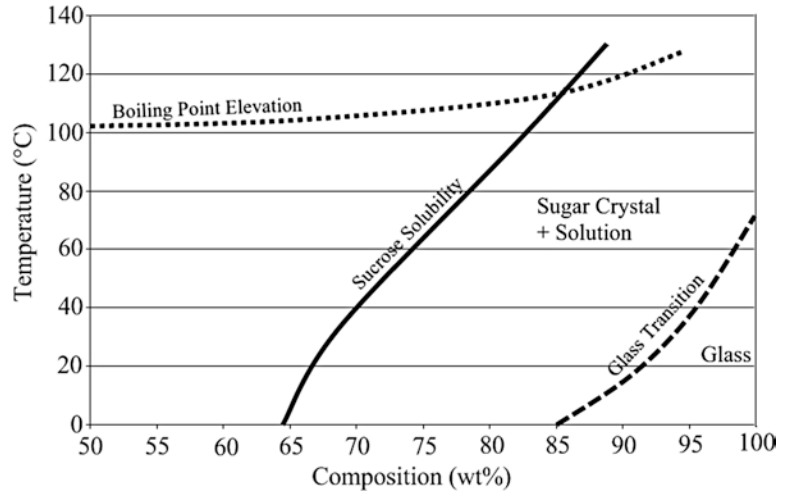


Figure 2.12). Even though the sugar content of the candy batch does not change during cooling (unless some additional evaporation takes place), the supersaturation driving for crystallization increases because of the reduced solubility as temperature decreases.

Thus, during manufacture of many, if not most, confections, there is a period of time where the batch is likely to be supersaturated and will crystallize if conditions are appropriate. In confections where crystals are desired, both formulation factors and processing conditions are selected to promote graining, whereas in confections in which graining is to be avoided, formulation and processing conditions must be selected that minimize the potential for crystal formation (Hartel et al. 2011).

2.10.2 Crystallization

Crystallization involves two steps: nucleation and growth. Controlling crystallization of sweeteners in confections requires an understanding of each step of the process to obtain the desired crystalline content. Further, the competition between nucleation and growth for available supersaturation defines the final dispersion of crystals, whether there are fewer larger particles or numerous small crystals. Ultimately, the confectioner must be able control both formulation and manufacturing conditions to obtain the

desired crystalline structure in the product for the desired textural and sensory properties.

2.10.2.1 Nucleation

Once a solution has become supersaturated, there is a driving force for the sugar molecules to come together to form a crystal nucleus. In all practical confectionery applications, some sort of particle or surface catalyzes nucleation, meaning that the first tiny bits of crystals, or embryos, form on the rough surfaces of microscopic particles (e.g., dust) or the walls of the vessel holding the solution. It is thought that interactions at these catalytic surfaces cause the molecules of the crystallizing species to organize in such a way that formation of the crystal lattice structure is enhanced. This process is often called heterogeneous nucleation since it involves an external component during nucleus formation (in contrast to homogeneous nucleation, which occurs in the absence of any external surface).

In principle, a sufficient number of molecules are needed to form a molecular cluster of sufficient size to become a stable nucleus. Homogeneous nucleation requires a larger number of molecules to form a stable cluster compared to heterogeneous nucleation since the surface present in the latter contributes some of the energy necessary to overcome the barrier to nucleus formation.

From thermodynamic considerations, two competing energy terms are relevant as a nucleus

forms. For one, energy is needed to form a solution-crystal interface with a surface tension governed by the nature of the molecules. This energy term is proportional to the surface area of the nucleus being formed. For the other, energy is released when the molecules complete the phase transition, with energy being given up in the exothermic crystallization step (also known as the heat of crystallization). This energy term is proportional to mass (or volume) of the nucleus being formed. In the classical nucleation theory, these two energy terms are combined to yield measures of the energy barrier needed to overcome for nucleation to occur and the critical size of the nucleus at which point it becomes stable. The critical size of a molecular cluster that will form a stable nucleus is related to the molecular volume, the surface tension of the crystal-solution interface, the temperature, and the supersaturation. Smaller critical sizes are seen at higher supersaturations. For heterogeneous nucleation, the interaction between surface and crystallizing molecules also reduces the number of molecules needed to form a stable nucleus, thus catalyzing nucleation compared to the absence of that surface.

For further details on nucleation, see Hartel (2001) and Mullin (2001).

2.10.2.2 Growth

After a nucleus is formed, it starts to grow immediately and continues to do so as long as it is surrounded by a supersaturated solution. There are several steps that must occur before a sweetener molecule in solution contributes to crystal growth by becoming a unit in the crystal lattice. First, the sweetener molecule must move from the bulk solution to the crystal interface, either by convective motion or diffusion through the bulk. This mass transfer step is influenced by sweetener type (molecular weight) and concentration, temperature, viscosity (generally controlled by concentration and temperature), and agitation or stirring rate. At the interface between crystal lattice and solution, the sweetener molecule may need to be desolvated (lose any waters of hydration not carried into the lattice) before it begins the process of diffusing along the surface to find

an appropriate site for incorporation into the lattice.

In a batch crystallization system, as may occur in a batch of fondant or fudge, once the crystals form during the nucleation step, the crystals grow and cause a decrease in the concentration of sugar in the remaining liquid phase. That is, the molecules that go into increasing the mass of crystals during growth leave the remaining liquid phase depleted in sugar. This decrease in solution concentration, or desupersaturation, continues until the solution concentration reaches the solubility point where it is saturated with sugar at that temperature (Figure 2.12 for pure sugar or Figure 2.16 for invert sugar/glucose syrup).

Further details on crystal growth can be found in Hartel (2001) and Mullin (2001).

2.10.2.3 Crystallization Rate

When a supersaturated solution crystallizes, both nucleation and growth take place. At first, nucleation dominates the process, especially when supersaturations are high, although growth starts almost immediately after the first nuclei are formed. Later in the crystallization process, when supersaturations have been decreased, growth becomes predominant. Nucleation may cease completely while the final supersaturation is relieved in crystal growth, up to the point where the solution reaches the saturation point at the solubility line (no remaining supersaturation). When the processes are combined like this, it is appropriate to talk about crystallization rate as the combined rate of the two steps.

The rate at which a sweetener crystallizes is influenced by the inherent chemical properties of the molecule, the presence of doctoring agents (inhibitors), and external operating conditions. The proper combination of these conditions allows control of graining to either prevent crystallization or to produce the desired crystalline phase (number, size, distribution, etc.).

The rate at which a sweetener crystallizes depends on numerous factors, including (1) the molecular nature, (2) the solubility concentration, (3) the effects of doctoring agents, and (4) the molecular mobility. In general, each sugar has its own inherent rate of crystallization, probably

depending on the molecular interactions in the solution phase. The solubility concentration and its dependence on temperature also affect the rate of crystallization of a sweetener in a confectionery application. Materials with a high solubility, like fructose, generally do not crystallize very rapidly because it is difficult to generate high supersaturations without going to such high solids contents that molecular mobility is curtailed. In contrast, sweeteners with low solubility concentrations, like lactose, generally crystallize more readily because it is easy to generate high supersaturations.

Although most cooked confectionery sugar masses are supersaturated after cooking and cooling, and are thus prone to crystallizing, there is often a period of time in the supersaturated state before graining actually occurs. This time depends to some extent on the nature of the sweetener, or how easily the liquid molecules come together and rearrange into a crystal lattice. In other words, once a sugar syrup becomes supersaturated, the molecules require some time to organize and form into the crystal lattice, to nucleate. Some sweeteners, like mannitol and maltitol, are very easy to crystallize, whereas other sweeteners, like fructose, crystallize only very slowly. This is in part related to the nature of the molecules in solution and how it associates with other molecules (both of the same kind as well as of different kinds of molecules) (Bensouissi et al. 2010), but is also related to the relative supersaturations that can be developed in processing (temperature and concentration).

When a sweetener crystallizes, there is a phase change, liquid to solid that is accompanied by a release of latent heat. The kinetic energy inherent in liquid molecules is released as heat as they become more constrained in the crystal lattice. The amount of heat released depends on the type of sugar. Sucrose is reported to give off 2.5 kcal/mol at 25 °C and 8 kcal/mol at 60 °C (Knecht 1990). As long as this heat generation is removed quickly from the vicinity of the forming crystal, it has little effect on further crystallization. If, however, substantial crystal formation occurs over a very short time in an enclosed space (as can happen during crystallization of fondant),

latent heat generation can cause the local temperature to increase, which in turn affects crystallization rate. For the most part, with the exception of fondant crystallization, the release of latent heat during sugar crystallization has minimal effect in confections.

Doctoring agents are added to confections to moderate crystallization of the primary sweetener. Glucose syrup and invert sugar play this role in sucrose-based confections. The same principle applies for the use of hydrogenated starch hydrolysate (see Section 1.1.2.14) to moderate sugar alcohol (i.e., maltitol, isomalt) crystallization in sugar-free applications. Doctoring agents may moderate crystallization in two ways. First, they may alter the solubility concentration of the sweetener and thereby, change the driving force for crystallization. But more importantly, they serve to interrupt the ability of sugar molecules to come together to form crystals. This inhibition arises primarily from the physical ability of the doctoring agent to impede the movement of the sugar molecules (especially at high viscosity), but may also result in part from chemical interactions (e.g., hydrogen bonding) between the different molecules.

In cases where rapid graining is desired to produce numerous small crystals, as in fondant and hard-panned sugar shells, it is important to minimize the presence of materials that inhibit crystallization. In fondant, the smallest amount of doctoring agent is used that will still give the desired texture. In this case, between 10% and 15% glucose syrup usually gives the desired fondant properties. The engrossing syrup for hard-panned candies should contain less than 1% glucose syrup or invert sugar to allow rapid and massive crystallization as each sugar layer is applied and dried. Although small amounts of glucose syrup can give a more pliable sugar shell, higher levels of glucose syrup do not provide the desired brittle shell by acting as a crystallization inhibitor.

On the other hand, in confections where graining is undesired, higher levels of doctoring agents are typically used. To avoid graining in hard candy and other amorphous sugar products, sufficient levels of inhibitors are needed.

Formulations containing as much as 50–60% glucose syrup, or more, may be needed in these confections. Crystallization rate is also impaired at conditions near the glass transition, due primarily to the lack of sufficient molecular mobility. If the molecules cannot move from place to place or rotate freely, they are unable to organize themselves into a crystal lattice and will not crystallize despite the large supersaturation.

By combining the principles of crystallization promotion and crystallization inhibition, a diagram of crystallization propensity (combined nucleation and growth) can be drawn for processing conditions (temperature and solution concentration). When a sugar solution of set concentration is cooled quickly from the cooking stage to a specific temperature and allowed to crystallize, there are several regions that characterize different aspects of crystallization. Figure 2.19 schematically shows these crystallization zones. When the hot sugar syrup is cooled just below the solubility point, crystallization rate is slow and sporadic. There is significant variability in crystallization onset in this region owing to the inconsistency of nucleation sites that promote formation of the first crystals at these relatively low driving forces.

At lower temperatures, approximately midway between the solubility and glass transition points, there is a region where crystallization occurs most consistently and rapidly (seen as the plateau in crystallization rate in Figure 2.19). The supersaturation driving force is sufficient to promote spontaneous and rapid crystallization, especially when accompanied by intense agitation, yet the mobility of the molecules is still sufficiently high to allow easy access into the crystal lattice. When crystallization is controlled within this region, the maximal number of crystals is formed. Because of the large number (and surface area) of crystals formed, each individual crystal remains small (ideally less than 15 μm), leaving the confection with a smooth texture. This is the ideal condition for graining of fondant, as discussed in more detail in Chapter 9.

At lower temperatures, below the plateau in crystallization rate, the rate of crystallization

slows down and again becomes more sporadic. As the temperature decreases, the ability of the sugar molecules to migrate and rotate decreases in conjunction with the increase in solution viscosity as the system approaches the glass transition. Note that it is not really the increasing viscosity that “causes” this decrease in crystallization rate, it is the decrease in molecular mobility (which is what causes the higher viscosity). In this temperature region, formation of crystals is severely impeded, particularly as temperature is lowered.

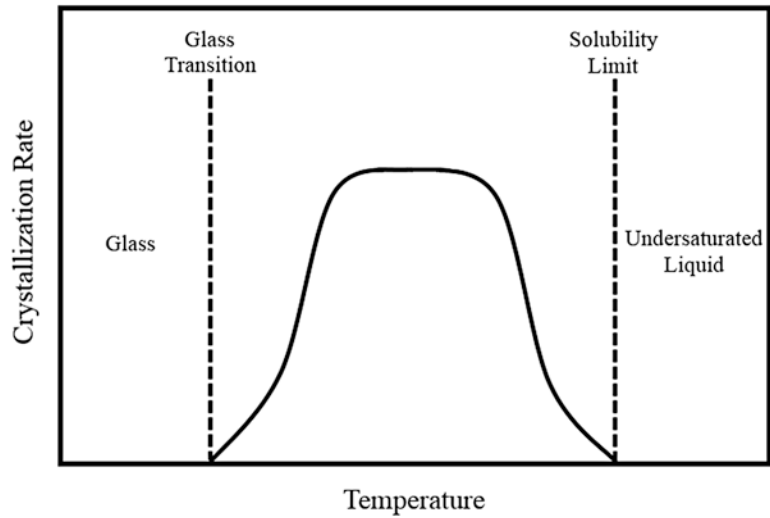
Finally, if the hot candy syrup is cooled quickly through the crystallization zone to the point where temperature falls below the T_g value for that solution (sweetener types and water contents, as discussed in Section 2.9), the glassy state is attained. To avoid crystallization, the solution must be cooled faster than the time required for molecular organization and onset of crystallization. Once the candy mass is cooled below T_g , molecular mobility is so low that crystallization is unlikely to occur over the shelf life of the confection. This is the principle behind forming highly supersaturated products in the glassy state, or hard candies (see Chapter 8).

2.10.3 Seeding

Because of the difficulty in controlling the variable nature of nucleation, there are situations where the nucleation step can be avoided by seeding with the appropriate crystals to grain a batch. Fudge, creams, and nougat are examples of grained confections that might be seeded with crystals rather than crystallized within the process. Fondant is the most common seeding material for confections because of the small sugar crystals, but powdered sugar may be used if careful control of particle size is not critical. Either way, it is important that seeds be added at the appropriate point in the process, namely at the right temperature and water content, to gain the desired effect. Typical amount of seeding material needed to properly grain a confection is 5%.

When fondant is used to seed a batch of fudge or to make cast creams, the fondant must be

Figure 2.19 Regions of crystallization during cooling of a sugar syrup



introduced to the batch at the proper temperature (usually 160–180 °F/71–82 °C). Although warm temperatures are desired to ensure complete dispersion of the fondant into the candy batch, temperatures that are too warm result in dissolution of too many of the fondant crystals. Since the aim is to seed with the optimal number of seed crystals, any dissolution decreases the advantages of seeding. Further, if enough seed crystals dissolve completely away, regions of the confection may then nucleate to relieve the supersaturation. This results in scattered spots (usually whitish in color) randomly distributed throughout the candy.

Table 2.10 Categorization of the states of sugars in sugar-based confections

Category	Examples
Noncrystalline	
Liquid	Syrup candies Gummies and jellies
Amorphous	Ungrained caramel, nougat, and marshmallow Salt water taffy
Glassy	Cotton candy Hard candy Brittles
Crystalline	Rock candy Candy powders Tablets
Partially crystalline	Grained (after dinner) mints Fondants and creams Grained caramel, nougat and marshmallow Fudge Hard and soft panned shell candy

2.11 State of Sugars in Confections

One way to distinguish different confections is in terms of the state of the sweetener. Table 2.10 distinguishes confectionery categories according to whether they are noncrystalline, partially crystalline or mostly crystalline. In liquid confections, the sugars are completely dissolved but viscosity is sufficiently low that the product can be poured. The sugar in amorphous and glassy confections is also completely in solution within the remaining water, but the viscosity is sufficiently high that mobility is limited. In glassy candies, like hard candy and brittles, the viscosity

exceeds 10^{12} Pa-s so that T_g is greater than room temperature. A few candies, namely rock candy, tablets and lozenges, and powdered candies, are mostly crystalline with only minor amounts of other ingredients (colors, flavors, binders, lubricants, etc.). The category of partially-crystalline confections is quite broad and includes fudge, grained nougat and marshmallow, fondants and creams, and sugar-shelled candies. Partially-crystalline confections represent a difficult chal-

lenge for confectioners since the relative contributions of sugars in each state must be carefully controlled to ensure the desired quality and shelf life.

The different states of sugar can be seen on a state diagram, as drawn for pure sucrose in Figure 2.18 (Hartel 2001). Similar diagrams can be developed for other sugars and for mixtures of sugars (as well as for polyols); however, state diagrams for other sweeteners and mixtures are not as common yet as that for sucrose. The state diagram can be used to understand the expected state of sugar during both processing and storage. To effectively use the state diagram to understand the state of sugar in confections, both thermodynamic (equilibrium) and kinetic aspects of crystallization must be understood.

Note that the state diagram in Figure 2.18 overlays equilibrium curves (boiling point elevation, solubility equilibrium of water and sugar) with a nonequilibrium boundary, the glass transition curve, indicating the distinction between glassy and fluid states. The regions delineated by the state diagram provide insight into what state of sugar can be expected at equilibrium, although the kinetic constraints noted earlier (doctoring agents and processing conditions during candy manufacture) also have a significant impact on the final state of sugar found in the candy (Hartel et al. 2011).

At high water content (and any temperature), the dissolved sugar molecules are in liquid form. This occurs when concentration is less than the solubility curve (see Section 2.8). If temperature of a dilute sugar syrup is increased to the boiling point temperature for that concentration, the syrup starts to boil. As boiling continues, the sugar concentration increases, causing a further increase in boiling point temperature. Thus, cooking a sugar syrup causes both temperature and total dissolved sugar concentration to increase according to the boiling point elevation curve (assumes an equilibrium is maintained between solution and vapor – a decent assumption for all but the most rapid cooking processes).

When the concentration of sugar exceeds the solubility curve at a given temperature, crystalli-

zation can occur. As noted previously, sucrose exhibits a unique characteristic where the boiling point elevation curve crosses the solubility curve (see the upper right quadrant of the state diagram in Figure 2.18). This phenomenon means that sucrose crystals can form during cooking under the right conditions (i.e., very slow – usually batch – cooking and limited doctoring agents to inhibit crystallization). A pure sucrose syrup cooked slowly is likely to crystallize even as it continues to boil. It is for this reason – to prevent premature crystallization – that candy makers rinse the inner kettle surface at the syrup line when making batches of grained mints and fondant, which are highly sensitive to graining during cooking.

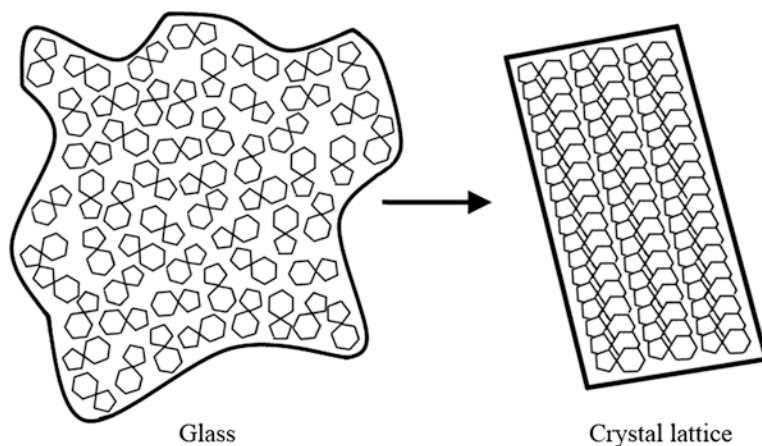
The state diagram can be used to “follow” a candy manufacturing process to help better understand what state the sugar might be expected to take. This approach will be used throughout the various chapters in this book as appropriate.

2.11.1 Crystal or Glass

In a crystal, the sugar molecules are organized in a uniform, repeating lattice structure dependent on the lowest-energy molecular interactions. Crystallization is generally considered an exclusionary process; that is, when a crystal grows slowly, effectively all other molecules besides the sucrose are expelled from the lattice. In contrast to the ordered nature of the crystal lattice, the molecules of a sugar glass are randomly “frozen” together in space due to the rapid cooling of a concentrated solution. Figure 2.20 is a highly schematic attempt to show the difference in molecular arrangement between a crystal and a glass, being highly ordered and random, respectively.

The sugars in the different states have different physical characteristics and this leads to the differences in the characteristics of candy products. A sugar glass (e.g., hard candy) is able to incorporate other molecules (i.e., colors and flavors) since the sugar molecules are only randomly “frozen” together. This allows a hard candy to have colors and flavors uniformly dispersed throughout, and which are released con-

Figure 2.20 Schematic molecular arrangement of sugar molecules in a crystal and a glass



tinuously as the product is consumed. In contrast, the sugar crystal does not allow incorporation of other molecules, except in small amounts, so the majority of the colors and flavors of rock candy are contained on the surfaces of the crystals or in the small gap between individual crystals. Dissolution rates in the mouth are also different between glass and crystal. Since the molecules in the sugar crystal are tightly bonded to their neighbors, it is more difficult for molecules in crystal-line form to dissolve. In glasses, the molecules are easily released from their neighbors due to the random organization and thus, a sugar glass dissolves much more readily in the mouth than a sugar crystal (assuming the same surface area).

Two essentially pure sucrose candies in different states, cotton candy and rock candy, clarify these relationships between making a sugar crystal or a glass. Note that the other sweeteners used in confections behave in a similar manner, albeit with slightly different parameters associated with crystallization and glass formation.

2.11.2 Cotton Candy

When flavored and colored sucrose crystals are melted at temperatures above 190 °C (374 °F), spun into thin fibers (or floss) and cooled rapidly, the result is cotton candy. A favorite at fairs, a cone of cotton candy is a glassy sugar matrix that has been spun into a fine floss and wrapped around a paper stick.

The starting point for cotton candy is essentially fine-granulated table sugar that has been coated with the desired colors and flavors. This powder is poured into the center of a cotton candy machine, often called a spinner. A heater in the center of the unit serves to melt the sugar as it spins, forming a liquid melt of colored and flavored sugar. The liquid sugar melt is forced through small holes on the periphery of the spinner by centrifugal force and a stream of sugar melt exits the spinner. As the liquid melt contacts ambient air, it is cooled very quickly so that the liquid melt immediately turns into a sugar glass in the form of fine strands, or floss. Since T_g for pure sucrose is over 65 °C (149 °F), the rapid cooling results in formation of a glass, rather than recrystallization of the sucrose.

Cotton candy is comprised of a series of fine threads of sugar glass or floss with colors and flavors uniformly dispersed throughout the glassy matrix. This high surface area of a glassy matrix is what allows cotton candy to “melt” in the mouth. Really, cotton candy simply dissolves quite rapidly due to the high surface area. But this same high surface area makes cotton candy highly unstable when exposed to normal air conditions, so that shelf life is short unless sealed tightly in a moisture barrier package. The high surface area provides an opportunity for rapid sorption of water from the environment, which leads to rapid recrystallization since no doctoring agents are added to inhibit crystallization (as would be used in the case of hard candy). Cotton

candy exposed to the atmosphere lasts only a few hours (or less on a really humid day) before it begins to collapse as the sugar recrystallizes. When the sugar crystallizes, the colors and flavors are concentrated, which leads to a change in appearance. Regions of bright color appear as the dyes become concentrated in a localized region (excluded from the sugar crystals). This phenomenon also can be seen when the candy is eaten, leaving a ring of saliva around the point of consumption. The moisture in the saliva dissolves the sugar glass and recrystallization is rapid. As collapse occurs, the volume occupied by the fine threads of cotton candy also decreases and the cone shrinks in size.

2.11.2.1 Rock Candy

The simplest candy form of crystallized sucrose is rock candy. Rock candy can be found either as individual clusters of crystals sold in a box, as swizzle sticks, where the crystals are attached to a stick for sweetening a drink (e.g., tea), or as rock candy on a string. In some cultures, large individual sugar crystals are grown for direct consumption.

Traditionally, rock candy is made on a relatively small scale in a batch process. Granulated sucrose is dissolved in warm water, about 60–70 °C (140–158 °F) to a concentration around 70%. At this temperature, the solution is still below the solubility concentration for sucrose. The sugar syrup is then removed from the heat and allowed to cool, typically to room temperature. As the solution cools, it becomes supersaturated since the solubility of sucrose is lower at room temperature (only 67%). To promote crystal formation, either a stick or a string is inserted into the solution and crystals form preferentially on the nucleation sites provided by this foreign material. To optimize the growth of sugar crystals on the stick, the correct concentrations (supersaturations) must be used. If concentration is too high, the solution is too supersaturated, and nucleation will occur randomly throughout the solution, not just on the stick. Numerous crystals will be formed and they will remain small, with too few formed on the stick. On the other hand, if concentration is too low, very few nuclei will be

formed and they will grow very slowly. Although good rock candy will be formed, the time required will be excessive. Thus, control of concentration is important in rock candy manufacture – it must be high enough to get fast growth but low enough that extraneous nucleation is not a problem.

In comparison to cotton candy, rock candy has an extended shelf life due to the stability of the sugar crystals. Crystalline sugar does not pick up moisture from the environment very readily. At low relative humidity, water vapor molecules in the air adsorb to the surface of the crystal, but the amount of water that can adsorb is based on the available hydrogen bonding sites on the surface of the crystal. The number of such sites is limited, so at relative humidity less than about 75%, there is very little increase in water content of rock candy (or any crystalline sucrose product). At slightly higher relative humidity (above 85%), though, there is sufficient water at the surface of the crystal to actually start dissolving the surface layers. The deliquescent point, or the point where a solid adsorbs sufficient water to become a solution, occurs when relative humidity reaches 86% for sucrose. At this point, the sucrose crystal dissolves, leaving a sucrose syrup.

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