Pressure Variation Due to Heat Shock of CO_2 Hydrate Desserts

T. B. Peters, J. L. Smith, and J. G. Brisson
Dept. of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

DOI 10.1002/aic.12634

CO_2 hydrate desserts are carbonated frozen desserts in which the CO_2 is trapped in a crystalline water-carbon dioxide structure called a CO_2 clathrate hydrate. The CO_2 concentration of the dessert enables strong perception of carbonation, but CO_2 hydrate dissociation during heat shock can cause high package pressures during storage and distribution. In this work, a model is developed for package pressure as a function of temperature, CO_2 content, package volume, dessert mass, and recipe. The model is validated by comparison with an experimental measurement of the pressure and mass of a CO_2 hydrate dessert subjected to heat shock. It is shown that during heat shock a sealed package can reach pressures greater than the ice-CO_2 hydrate equilibrium pressure. At pressures above the ice-CO_2 hydrate equilibrium pressure, the fraction of water crystallized in the dessert can be increased, potentially mitigating heat shock damage. © 2011 American Institute of Chemical Engineers *AIChE J,* 58: 957–966, 2012
Keywords: CO_2 clathrate hydrate, phase equilibrium, freeze concentration, aqueous solution, heat shock

Introduction

Currently carbonated frozen desserts are not commonly available on the market. One challenge in developing a carbonated ice cream or sorbet is trapping CO_2 in the frozen product. In a carbonated beverage CO_2 is dissolved in the aqueous phase, but in a frozen dessert the majority of the water is crystallized, so very little CO_2 can be dissolved. One way to carbonate a frozen dessert is to replace some or all of the ice with a water-carbon dioxide solid structure called a CO_2 clathrate hydrate. CO_2 clathrate hydrates (hereafter CO_2 hydrates) look like snow or ice, but consist of water molecules hydrogen-bonded in a cage structure that is stabilized by CO_2 molecules.[1] The density of CO_2 in CO_2 hydrates is typically 296 kg/m^3, which is about 50 times the typical density of CO_2 in sparkling water, 6 kg/m^3. This high CO_2 concentration enables strongly carbonated frozen desserts.

CO_2 hydrates can be formed in desserts during freezing using a process called CO_2 flash freezing, which is described in Peters et al.[2] The process involves combining liquid CO_2 with liquid dessert mixture at a temperature and pressure of 283 K and 5 MPa respectively, and then flashing the combined fluids to 1–1.5 MPa. The flashing causes CO_2 evaporation and disperses the dessert mixture into fine droplets. The droplets are cooled rapidly and the majority of the water in the droplets crystallizes into CO_2 hydrates. CO_2 flash freezing results in a fine powder with the texture of fresh fallen snow and CO_2 concentrations of 0.12–0.25 kg CO_2/kg powder. A soda contains much less CO_2, typically 0.006 kg CO_2/kg soda.

CO_2 hydrate desserts can be stored in standard home and vendor freezers, but must be packaged under pressure to stabilize the CO_2 hydrates. The minimum pressure for stable CO_2 hydrates in the dessert is the same as the ice-CO_2 hydrate-gas (IHG) equilibrium pressure in a pure water-carbon dioxide system. The IHG equilibrium pressure increases with temperature. For temperatures of 253–258 K the minimum storage pressure is 0.5–0.6 MPa,[1] which is

---

Correspondence concerning this article should be addressed to T. B. Peters at teresab@mit.edu.

only a few tenths of MPa larger than the typical 0.3 MPa storage pressure of a soda. However, CO_2 hydrate desserts contain significantly more CO_2 than carbonated beverages. While this high CO_2 content is beneficial for strong perception of CO_2, it can lead to significant increases in package pressure when the product is warmed.

To design appropriate packaging for CO_2 hydrate desserts it is necessary to develop a model for the variation of package pressure due to heat shock. The objective of this work is to introduce a model for the pressure in a sealed CO_2 hydrate dessert as a function of temperature, recipe, gas volume in the package (headspace) and total CO_2 content. The model is based on thermodynamics and experimental data reported in the literature for CO_2—H_2O and H_2O-sucrose systems. While the model is developed for simple sucrose-water solutions due to the availability of data for the aqueous sucrose freezing curve, the trends in package pressure should be similar for desserts containing a mixture of dissolved ingredients. The model developed here can be used to identify the effect of parameters such as headspace and water content on the pressure and CO_2 content of the CO_2 hydrate dessert during heat shock, enabling successful design of a CO_2 hydrate dessert and its packaging for distribution through the cold chain.

Model

The model for pressure in the packaging is developed assuming that equilibrium is reached throughout the frozen dessert at every temperature. The kinetics of CO_2 transfer between the crystalline, gaseous and aqueous phases are neglected. This assumption is reasonable for the CO_2 flash-freezing powder due to the high specific surface area of the powder, as will be shown later. In large, continuous bodies of CO_2 hydrates this assumption may not be applicable because CO_2 hydrates are known to persist in large agglomerates under metastable conditions below 273 K.[3]

The minimum pressure for stable CO_2 hydrates in the dessert is equal to the IHG equilibrium pressure. This can be inferred by considering Gibb's Phase Rule. In the three-component system of water, CO_2 and sucrose, there are four phases present at the IHG equilibrium pressure (ice, CO_2 hydrate, aqueous solution and gas). According to Gibb's Phase Rule, there is only one degree of freedom. Thus, for a given temperature along the four-phase equilibrium curve, the pressure for equilibrium between ice and CO_2 hydrate is specified and is not a function of solute concentration. The equilibrium pressure should be the same as the pressure in the limit of a dilute solution, which corresponds to the IHG equilibrium pressure curve.

Even with more than one solute, the ice-CO_2 hydrate-aqueous solution-gas equilibrium does not shift because the chemical potential of water in every phase must be equal to the chemical potential of water in ice. The chemical potential of water in ice does not change with solute concentration because ice crystallizes as a nearly pure phase and the chemical potential of a pure substance is a function of temperature and pressure only.[4] Similarly, the chemical potential of CO_2 in each phase must be equal to the chemical potential of CO_2 in CO_2 hydrate ($\mu^h_{CO_2}$). $\mu^h_{CO_2}$ is related to the chemical potential of water in CO_2 hydrate ($\mu^h_{H_2O}$) through the Gibbs-Duhem equation,[4]

$$-SdT + VdP - n_{CO_2}d\mu^h_{CO_2} - n_{H_2O}d\mu^h_{H_2O} = 0, \qquad (1)$$

where S is entropy, T is temperature, V is volume, P is pressure, and n_{CO_2} and n_{H_2O} are the number of moles of CO_2 and H_2O, respectively. Thus μ^h_{CO2} is not changed by the aqueous solution concentration and therefore the equilibrium CO_2 partial pressure, which is a function of CO_2 chemical potential, does not change. (Note that above the freezing point of the dessert mixture only three phases are present and the pressure required for aqueous phase-CO_2 hydrate equilibrium is a function of sucrose concentration; the equilibrium pressure increases with increasing sucrose concentration.)

The pressure in a sealed CO_2 hydrate dessert package at a temperature T can be calculated if the mass of gaseous CO_2 and the volume available to the gas are known. The mass of gaseous CO_2 in the package is the difference between the total mass of CO_2 in the package and the mass of CO_2 in the crystalline and aqueous phases. The mass of CO_2 in the crystalline and aqueous phases depends on the fraction of water that is crystalline (as well as the solubility of CO_2 in the aqueous phase and the fraction of crystalline water that is CO_2 hydrate). Thus, a model for the crystalline water fraction is needed to determine the pressure in the package. Unfortunately, the crystalline water fraction (as well as the CO_2 solubility and the CO_2 hydrate fraction) is a function of pressure in addition to temperature and sucrose concentration. Therefore to calculate the pressure in a package at T one must guess an initial pressure and then iterate to find the actual pressure. A model for the crystalline water fraction as a function of pressure, temperature and sucrose concentration will be developed first, and then an iterative process to determine the pressure in a package will be described.

The temperature dependence of the crystalline water fraction is similar to the temperature dependence in conventional ice confections. At equilibrium, the chemical potential of water in the aqueous phase must be the same as the chemical potential of water in the crystalline phase. Below the freezing point, the chemical potential of solid water is less than the chemical potential of metastable liquid water, so the chemical potential of the liquid water must be lowered by solutes to achieve equilibrium. As the temperature decreases, the aqueous phase solute concentration must increase for water in the aqueous phase and water in the solid phase to be in equilibrium. This requirement results in the familiar freeze concentration of sucrose solutions. As the temperature decreases, more and more water crystallizes as ice, leaving an increasingly concentrated aqueous phase.

The pressure dependence of the crystalline water fraction is also the result of equilibrium between the chemical potential of water in the aqueous and crystalline phases. In an ice confection at a fixed temperature, the crystalline water fraction decreases with increasing pressure. This occurs because under CO_2 pressure, the concentration of solutes in the aqueous phase is increased by dissolved CO_2 in addition to dissolved sucrose. The recipe fixes the total sucrose content of the frozen dessert, but the amount of CO_2 dissolved in the aqueous phase increases with pressure. Thus, at a fixed temperature as the CO_2 pressure increases toward the IHG equilibrium pressure, the crystalline water fraction decreases. More water is needed to dilute the aqueous phase to achieve the equilibrium chemical potential.

In contrast, in a CO_2 hydrate dessert, the (dissolved) total solids concentration in the aqueous phase increases with increasing CO_2 pressure at a fixed temperature. This occurs because the change in $\mu^h_{H_2O}$ is related to the change in $\mu^h_{CO_2}$, as can be seen by simplifying and rearranging Eq. 1 for an isothermal increase of pressure

$$d\mu^h_{H_2O} = \frac{V}{n_{H_2O}}dP - \frac{n_{CO_2}}{n_{H_2O}}d\mu^h_{CO_2}. \tag{2}$$

By assuming that the CO_2 hydrate phase is in equilibrium with a CO_2 vapor phase during the isothermal increase in pressure, the term $d\mu^h_{CO_2}$ can be equated to the change in chemical potential of CO_2 vapor. Based on the Gibbs-Duhem equation for a single component phase

$$d\mu^v_{CO_2} = v^v_{CO_2}dP, \tag{3}$$

where $\mu^v_{CO_2}$ is the chemical potential of CO_2 in the vapor phase and $v^v_{CO_2}$ is the molar volume.[4] Substituting Eq. 3 for $d\mu^h_{CO_2}$, Eq. 2 becomes

$$d\mu^h_{H_2O} = \frac{V}{n_{H_2O}}dP - \frac{n_{CO_2}}{n_{H_2O}}v^v_{CO_2}dP. \tag{4}$$

The first term on the right hand side of Eq. 4 involves the volume of CO_2 hydrate per mole of water, which is on the order of 10^{-5} m^3/mol, similar to the molar volume of ice. The second term on the right of Eq. 4 varies with the molar volume of vapor phase CO_2, which is much larger than the molar volume of ice. Therefore, the right-hand side of Eq. 4 must be negative. In this case, the left-hand side of Eq. 4 (the change in chemical potential of water) must also be negative. (Of course, the chemical potential of a hypothetical pure water phase increases with increasing pressure according to the Gibbs-Duhem equation for a single component phase.) To lower the chemical potential of water in the aqueous phase sufficiently to achieve equilibrium as pressure increases above the IHG equilibrium pressure, the aqueous phase solute concentration must increase. This is achieved by a combination of increased CO_2 concentration in the aqueous phase and removal of water from the aqueous phase to the CO_2 hydrate phase.

The mole ratio in the last term of Eq. 4, $\frac{n_{co_2}}{n_{H_2O}}$, varies between 0.13 and 0.17 with temperature and pressure. The CO_2 hydrate structure consists of six large cages and two small cages per unit cell, which are formed by 46 water molecules. Typically, the fractional occupancy of the large cages is very high while the fractional occupancy of the small cages increases with increasing pressure (above the pressure for incipient CO_2 hydrate formation at a particular temperature). The software program CSMGem,[1] predicts the fractional occupancy of various gas hydrates, including CO_2 hydrates. At temperatures and pressures encountered in this work (243–268 K; pressures up to 1.2 MPa), the predicted fractional cage occupancy for CO_2 hydrates ranges from 96 to 99% in the large cages and 45–73% in the small cages.[1] This corresponds to the ratio varying from 0.14 to 0.16. A constant ratio of 0.15 is assumed for this work.

The crystalline water fraction in a frozen dessert can be estimated using several idealizations. CO_2 is treated as an ideal gas, the volume of CO_2 hydrate per mole of water and the molar volume of water are treated as constant, the aqueous phase is treated as an ideal solution (the activity coefficient (γ_{H_2O}) is equal to 1), and the solubility of CO_2 in water in the aqueous phase is assumed to be equal to the solubility of CO_2 in pure water. The crystallized water fraction is estimated by applying the equation for the freezing point of an ideal solution to a water-sucrose-CO_2 solution and then accounting for the pressure. The freezing point of a solvent (in this case water) is related to the mole fraction of solvent in the solution by

$$\ln\left(\frac{1}{x_{H_2O}}\right) = \frac{h_{sf} - \Delta c_p T_M}{R}\left(\frac{1}{T} - \frac{1}{T_M}\right) + \frac{\Delta c_p}{R}\ln\left(\frac{T_M}{T}\right), \tag{5}$$

where T_M is the melting temperature of pure water, h_{sf} is the enthalpy of melting (on a molar basis) at T_M, Δc_p is the difference between the heat capacity of water in liquid and solid phase (on a molar basis), x_{H_2O} is the mole fraction of water, and T is the freezing point of the solution of concentration x_{H_2O}.[4] The moles of water that must be aqueous at temperature T and pressure P are the moles of water necessary to dilute the aqueous phase to $x_{H_2O}(T)$. The moles of sucrose present are known from the recipe. The moles of CO_2 present are estimated by extrapolating the CO_2 solubility model of Diamond and Akinfiev[5] to T and P, neglecting the effect of sucrose on the solubility of CO_2. The solubility model gives the mole fraction of CO_2 in water, x_{CO2}(T,P). The mole fraction is

$$x_{CO_2} = \frac{mol_{CO_2}}{(mol_{CO_2} + mol_{H_2O,aq})}, \tag{6}$$

where mol_{CO_2} is the moles of CO_2 dissolved in the water and $mol_{H_2O,aq}$ is the moles of water in the aqueous phase. For the water mole fraction in the aqueous phase to match x_{H_2O}, the moles of water in the aqueous phase must be

$$mol_{H_2O,aq} = \frac{x_{H_2O} \cdot mol_{suc}}{1 - x_{H_2O} - \left(\frac{x_{H_2O} \cdot x_{CO_2}}{1 - x_{CO_2}}\right)}, \tag{7}$$

where mol_{suc} is the moles of sucrose in the dessert. Given the total moles of water in the dessert, the crystallized water fraction can be calculated as

$$f_{xtal} = \frac{mol_{H_2O,tot} - mol_{H_2O,aq}}{mol_{H_2O,tot}}, \tag{8}$$

where $mol_{H_2O,tot}$ is the total moles of water in the dessert.

For pressures greater than the IHG pressure, the water mole fraction in the aqueous phase at the desired pressure, $x_{H_2O}(T,P)$, can be related to the water mole fraction in the aqueous phase at the IHG equilibrium pressure, $x_{H_2O}(T,P_{IHG})$ by calculating the change in chemical potential of water in the aqueous phase with change in pressure. The chemical potential of aqueous water is given by

$$\mu_{H_2O,aq} = \mu^0_{H_2O,l} + RT\ln(\gamma_{H_2O}x_{H_2O}), \tag{9}$$

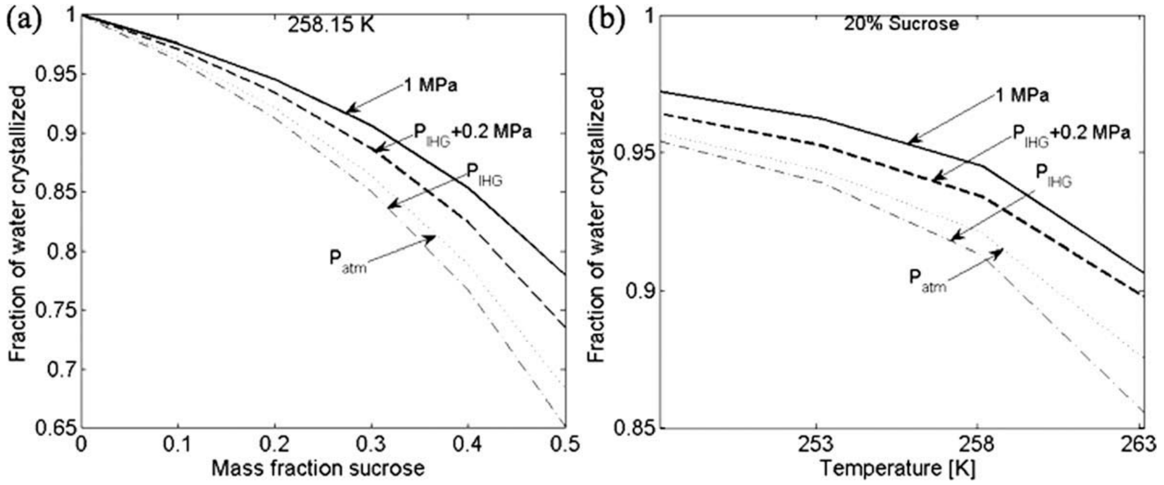

Figure 1. Ideal fraction of water crystallized (ice or CO_2 hydrates) as a function of pressure and (a) sucrose mass fraction at a fixed temperature of 258.15 K or (b) temperature at a fixed sucrose mass fraction of 20%.

Plots represent trends correctly, but not the actual crystallized fractions because the crystallized fractions here are calculated using several idealizations.

where T is the temperature, $\mu^0_{H2O,l}$ is the chemical potential of pure liquid water at T, R is the universal gas constant, γ_{H_2O} is the activity coefficient of water, and x_{H_2O} is the mole fraction of water in solution.[4] The change in chemical potential of aqueous water, $\Delta\mu_{H_2O,aq}$, due to an isothermal change in pressure is then

$$\Delta\mu_{H_2O,aq} = \Delta\mu^o_{H_2O,l} + RT\ln\left(\frac{\gamma_{H_2O}(P)x_{H_2O}(P)}{\gamma_{H_2O}(P_{IHG})x_{H_2O}(P_{IHG})}\right), \quad (10)$$

where $\Delta\mu^o_{H2O,l}$ is the change in chemical potential of hypothetical pure liquid water and R is the universal gas constant. The term $\Delta\mu_{H_2O,aq}$ is equated to Eq. 4 and $\Delta\mu^o_{H2O,l}$ is calculated according to the Gibbs-Duhem equation for a single component phase. The water mole fraction in the aqueous phase at the IHG equilibrium pressure is calculated using Eq. 5. The fraction of water crystallized is again found by determining the amount of water that must remain in the aqueous phase to achieve $x_{H_2O}(T,P)$, accounting for both the mole fraction of solutes in the recipe and the mole fraction of dissolved CO_2, as in Eqs. 6–8.

Using Eqs. 1–10 the ideal fraction of water crystallized in a sucrose solution is calculated and plotted in Figure 1 at atmospheric pressure, the IHG equilibrium pressure (P_{IHG}), and two higher pressures. The plots show several important trends. As expected, the fraction of water crystallized increases with decreasing temperature as well as decreasing sucrose concentration. Owing to the increased CO_2 concentration in the aqueous phase at P_{IHG}, the fraction of water crystallized at P_{IHG} is lower than the fraction crystallized at atmospheric pressure, but the fraction of water crystallized increases with pressure above P_{IHG}. Thus in a system with CO_2 hydrates, freeze concentration occurs both with decrease in temperature and with increase in pressure.

As a result of the idealizations used in Eqs. 1–10, the curves in Figure 1 only show a theoretical fraction of water crystallized. In particular, the solubility of CO_2 in the aqueous phase is taken from Diamond and Akinfiev's[5] data for CO_2 solubility in pure water. The actual CO_2 solubility in the aqueous phase is lower, both due to sucrose in the aqueous phase and due to the presence of CO_2 hydrates.[5] The lower solubility would be expected to increase the predicted fraction of water crystallized. However, the effect of sucrose and CO_2 on the activity coefficient of water (γ_{H_2O}) in the aqueous phase has also been neglected. Including γ_{H_2O} in the calculations would decrease the predicted fraction of water crystallized. The actual fraction of water crystallized in an ice confection is typically found to be lower than the theoretical fraction,[6] especially at low temperatures where the sucrose concentration is high in the aqueous phase. For example at −20°C, the measured sucrose concentration in the aqueous phase is about 10% lower than predicted by theory, corresponding to a crystallized water fraction 6% lower than predicted by theory for a 25% sucrose solution. Thus the actual fraction of water crystallized in the CO_2 hydrate confection is also likely to be lower than shown in Figure 1 by 5–20%, particularly at high sucrose concentrations.

Using the model for crystallized water fraction in the dessert, the pressure in the package at a temperature T can be calculated. The calculation has been implemented in several Matlab (The MathWorks, Matlab version R2007a, Natick, MA) scripts. The basic steps for each iteration are to assume a pressure, calculate the fraction of water crystallized and solubility of CO_2 at that pressure (and temperature T), determine the amount of gaseous CO_2, determine the volume of the dessert and the corresponding headspace and then calculate the pressure using the resulting molar volume and the Peng-Robinson equation of state for CO_2.[7] The volume of dessert in the package is given by the mass of water crystallized divided by the density of ice or CO_2 hydrate at T and the mass of aqueous solution divided by the density of the concentrated aqueous solution. The densities of ice, CO_2 hydrate and the sucrose solution are calculated using best-fit

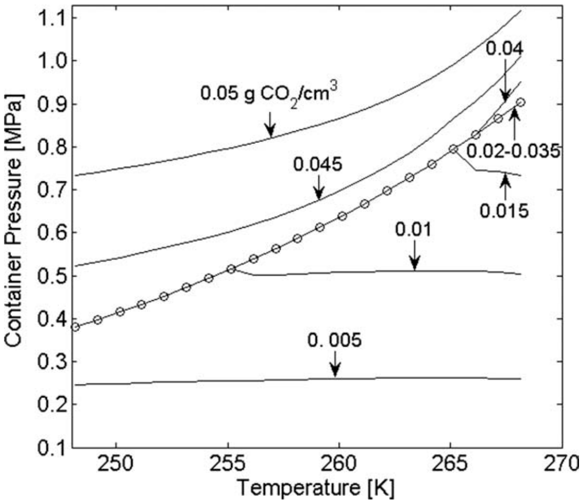

Figure 2. Predicted pressure in a CO_2 hydrate dessert package containing 0.125 g/cm^3 of 20% sucrose solution and varying total mass of CO_2 in the package.

Open circles indicate the IHG equilibrium curve.

curves for tabulated data in the CRC Handbook of Chemistry and Physics.[8]

In the Matlab scripts, the first pressure assumed is the IHG equilibrium pressure at T, $P_{IHG}(T)$. It is initially assumed that the crystallized water is all ice to determine if there is enough CO_2 in the package to stabilize CO_2 hydrates. If the new calculated pressure is less than P_{IHG}, then the package does not contain enough CO_2 to stabilize CO_2 hydrates at T. The basic steps of the iteration are repeated, using the new calculated pressure to estimate the fraction of water crystallized and the solubility of CO_2. The scripts continue iterating using the most recent pressure calculation until the pressure changes by less than 0.01 MPa through an iteration. If the new calculated pressure is greater than or equal to P_{IHG}, then there is enough CO_2 in the package to have CO_2 hydrates at T. The pressure in the package is recalculated assuming that all of the crystallized water is CO_2 hydrate and no ice is present. If the resulting pressure is less than P_{IHG}, then the pressure in the container is P_{IHG}, but there is a mixture of ice and CO_2 hydrate. If the pressure in the container is still greater than P_{IHG}, then the dessert contains CO_2 hydrates and no ice. The scripts again iterate using the most recently calculated value of pressure until the pressure changes by less than 0.01 MPa. Throughout this work it is assumed that the dessert is packed in a CO_2 environment (i.e. no air is present in the package) and water vapor pressure is neglected.

To predict more realistic container pressures, the water mole fraction at temperature T is calculated using experimental data, rather than the ideal solution equation (Eq. 5). Blond et al.[6] measured the aqueous phase sucrose concentration in equilibrium with ice as a function of temperature at atmospheric pressure. By using the experimental data of Blond et al.[6] the effect of the nonideality of a frozen sucrose-water solution on the fraction of water crystallized as a function of temperature is accounted for. Fortunately, the variation of activity coefficient with pressure is very small.[4] Equation 10, which is used to calculate the crystallized water fraction at a pressure greater than P_{IHG}, does not include the activity coefficient of water, but since the term x_{H_2O} is in both the numerator and denominator of Eq. 10, the effect of the activity coefficient on the fraction of water crystallized as a function of pressure should nearly cancel out.

Figure 2 shows a plot of the pressure in a package with varying CO_2 content. The dessert recipe for this calculation is 20% sucrose and 80% water by mass. The package contains 0.125 g of dessert mixture per cubic cm of internal volume. This packing density is much lower than the density of typical ice confections because it is modeled after a container filled with the low bulk density powder formed by CO_2 flash freezing. In Figure 2, as the mass of CO_2 in the package increases, the pressure increases. At the lowest CO_2 content, CO_2 hydrates are never stable. As the CO_2 content increases, stable CO_2 hydrates are present at low temperatures, but during heat shock all of the CO_2 hydrates dissociate until only ice remains and the pressure falls below the IHG equilibrium curve. For a range of CO_2 contents (0.02–0.035 g/cm^3), the pressure in the package follows the IHG equilibrium curve and at least some CO_2 hydrates are present at all temperatures. For CO_2 contents greater than 0.035 g/cm^3, the package pressure exceeds the IHG equilibrium curve and increases with increasing temperature.

The model described here has a limited range. The crystallized water fraction can only be calculated below the freezing point of the dessert mixture. In the model, the crystallized water fraction is calculated using the measured water mole fraction in a sucrose water solution at atmospheric pressure. Between the freezing point of the dessert mixture and 283 K, water can still be crystallized as CO_2 hydrate, but ice is not stable. It is not possible to simply apply Eq. 5 with the latent heat and specific heat capacity of CO_2 hydrates because the melting temperature, T_M, of CO_2 hydrates is a strong function of pressure. A model for the aqueous solution-CO_2 hydrate equilibrium curve, as a function of solute concentration, would be needed.

Experiments

Several experiments were carried out to support the above model. The experiments were done in an apparatus for measuring the pressure, temperature and mass of a sample of CO_2 flash-freezing powder over time. The pressure-temperature-mass apparatus (PTM) is shown schematically in Figure 3. The PTM consists of a 300 g capacity aluminum single-point load cell (Vishay Tedea-Huntleigh, Model 1004, Malvern, PA) mounted in the base of a three-piece stainless steel (SS) chamber. The SS upper cap and SS base of the SS chamber are bolted to the SS mid-plate, with 3.2 mm (0.125″) silicone *o*-rings forming the pressure seals. The sample sits in an aluminum can resting on an aluminum tray in the upper section of the chamber. The aluminum tray is bolted to the load cell through a hole in the mid-plate, as shown in the figure. There is no contact between the connecting bolts and the mid-plate. The sample mass and volume capacities are 250 g and 250 cm^3, respectively. The internal volume of the PTM is 625 cm^3. A 1.6 mm (0.0625″), SS sheathed T-type thermocouple (Omega Engineering, TTSS-116U, Stamford, CT) is

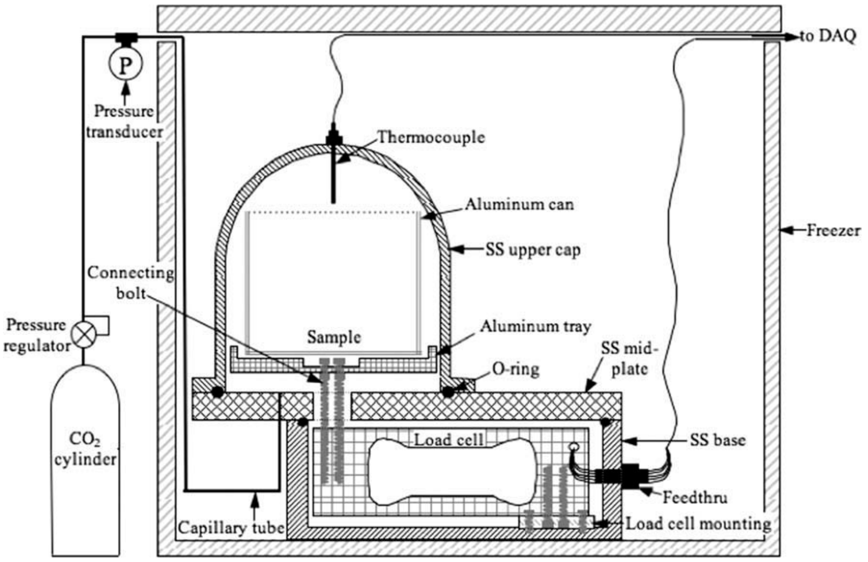

Figure 3. Schematic of pressure-temperature-mass apparatus (the PTM).

mounted in the upper cap of the chamber. The thermocouple tip is close to the top of the sample, but does not touch the sample so that it does not influence the mass measurement. A 1.6 mm (0.0625″) outer diameter capillary tube is connected to the upper section of the chamber. The capillary tube is 0.5 mm (0.02″) inner diameter, 1.5 m (60″) long and connects to a tee joint outside the freezer. The second port of the tee contains a pressure transducer (Kulite Semiconductor Products, XTL-123B-190-15bara, Centerville, OH) and the third connects to a 2.3 kg (5 lb.) CO_2 cylinder. Because of the bolt size and arrangement, the maximum operating pressure in the PTM is 1.2 MPa. The stainless steel chamber containing the load cell is placed at the bottom of a variable temperature chest freezer (Frigor A/S, GLE20, Viborg, Denmark) with a 228–273 K (−45°C to 0°C) range.

Pressure, temperature and mass signals are recorded using a National Instruments Compact FieldPoint system (National Instruments Corporation, cFP-1804 Ethernet interface with cFP-SG140 and cFP-TC120, Austin, TX).

The load cell supplied by Vishay Tedea-Huntleigh comes with an encapsulation material to provide protection against dust and temporary flooding (IP66 environmental protection). Vishay specially provided the load cell for the PTM without encapsulation because the encapsulation causes transients in the load cell response to rapid changes in pressure. The unencapsulated load cell is calibrated as a function of temperature and pressure using standard masses (10–100 g). The load cell signal decreases with increasing pressure. Due to corrections for pressure and temperature effects as well as uncertainty due to vibrations in the freezer, the resolution of the load cell in the PTM is 0.1 g. The load cell is calibrated at atmospheric pressure using the standard masses before each experiment to ensure that it has not been affected by moisture and temperature changes in the freezer.

CO_2 flash-freezing powder is used in the PTM because the powder has a high specific surface area and can nearly completely absorb and release CO_2 within 20–40 hours of storage. Figure 4 shows an example of CO_2 release and reabsorption in CO_2 flash-freezing powder made from water. The PTM sample can was filled with fresh powder and placed in the PTM with the freezer maintaining a temperature of 238 K. The mass of the sample was monitored for ~4 hours as the CO_2 originally in the powder escaped. Starting at hour 3 the PTM was flushed with CO_2 for about an hour and then sealed, indicated by the spikes in the mass data. At hour 4 the PTM was pressurized with CO_2 to 1 MPa. The mass of the sample was monitored for 35 hours as CO_2 hydrates reformed in the powder. Just before hour 20, the pressure in the PTM was boosted to compensate for CO_2 lost from the gas phase due to CO_2 hydrate formation. The mass data has been filtered to remove acoustic signals caused by the freezer compressor. The oscillations in the temperature data are due to the cycling of the freezer

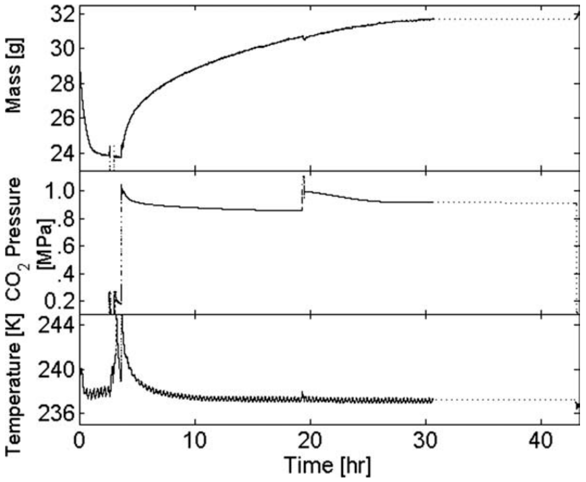

Figure 4. CO_2 hydrate dissociation and reformation in PTM apparatus at 238 K and 1 MPa, showing nearly complete CO_2 hydrate formation during storage.

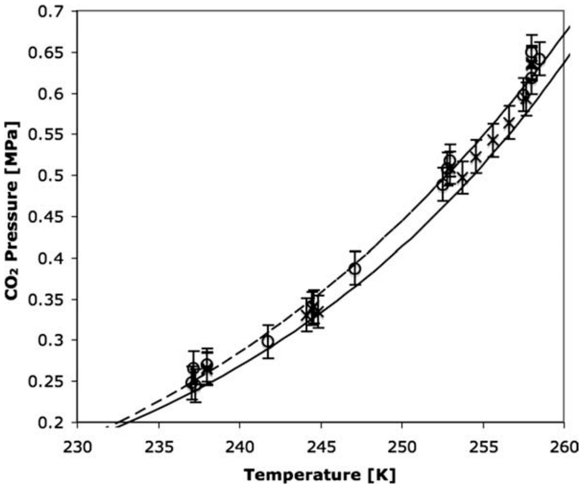

Figure 5. Measured IHG equilibrium pressures.

Dashed curve—IHG model from Sloan and Koh.[1] Black curve—logarithmic fit to literature data.[1] Circles—data for powder formed from water. X's—data for 10–35% total solids mixtures containing sucrose, corn syrup, CarboGain (a powdered maltodextrin) and or citric acid.

compressor. There is a gap in the data between hour 31 and hour 43 because the data acquisition system was accidentally turned off. The temperature increases at the start of the experiment are due to handling of the thermocouple during sealing and checking for leaks.

The mass of water in the sample is 23.5 g. The maximum mass of the sample if all of the water were converted to CO_2 hydrates would be 32.3 g. It can be seen that over ~34 hours of storage the sample mass approaches 32 g, which is similar to the mass expected for pure CO_2 hydrate powder. This indicates that the flash-freezing powder has sufficient surface area to achieve nearly complete CO_2 hydrate formation in the PTM apparatus on the time scale of a day. Therefore it is reasonable to assume that during heat shock tests the CO_2 flash-freezing powder approaches equilibrium when the sample mass approaches a constant value. In other words, the release and absorption of CO_2 occur throughout the powder. The interiors of the particles do not remain in a metastable state and the steady state pressure and mass measured during a heat shock experiment can reasonably be compared to the equilibrium models developed in this work. Of course, during heat shock and storage, some surface area will be lost due to recrystallization processes, and therefore the assumption that equilibrium is reached throughout the powder would become less reasonable if the powder were reused.

The minimum pressure for stable CO_2 hydrates in the dessert has also been verified using the PTM. Flash-freezing powder is placed in the PTM sample can and CO_2 hydrates are allowed to dissociate for a few hours. The PTM is then flushed with CO_2 gas, pressurized to a pressure a few tenths of MPa greater than the predicted IHG equilibrium pressure and sealed. After the pressure approaches a stable value the pressure is perturbed slightly by adding or venting CO_2 to confirm that the equilibrium pressure has been obtained. This procedure is repeated at multiple temperatures between 230 and 260 K with powder formed from several different solutions. Figure 5 shows the pressures measured for powder made from water and powder made from a variety of aqueous solutions. The measured pressures are all close to the IHG equilibrium curve.

A heat shock experiment was carried out with flash-freezing powder made from a 25% sucrose recipe to provide support for the model presented above. The temperature, pressure and mass measured during the experiment are shown in Figure 6. CO_2 flash-freezing powder was placed in the sample can and the SS top of the PTM was bolted in place. The PTM was pressurized with CO_2 gas to 0.38 MPa and then 0.7 MPa. Over the next 10 hours the sample absorbed CO_2 due to CO_2 hydrate formation. The PTM was periodically repressurized to ensure sufficient CO_2 available in the gas phase. At hour 12 the freezer temperature was increased from 251 to 263 K. As the temperature increased in the PTM, the sample mass decreased, indicating CO_2 hydrate dissociation, which caused the pressure to increase. While the sample was at 251 K, the pressure in the PTM was greater than P_{IHG} by at least 0.25 MPa. As the temperature in the PTM apparatus increased, the pressure increased such that it was always greater than P_{IHG}. At the end of the experiment, the pressure in the PTM apparatus was greater than P_{IHG} by more than 0.1 MPa.

Discussion

In Figure 5 it was shown that the minimum pressure for stable CO_2 hydrates does not change with the concentration of dissolved solutes, as predicted by Gibb's Phase Rule. Therefore the minimum storage pressure for a CO_2 hydrate dessert is given by the IHG equilibrium curve.

The heat shock measurement that is shown in Figure 6 supports the model for crystallized water fraction as a function of temperature and pressure. As predicted in the model, CO_2 hydrates dissociate with increasing temperature even above the IHG equilibrium pressure to maintain equilibrium with the aqueous phase. This is indicated by the pressure

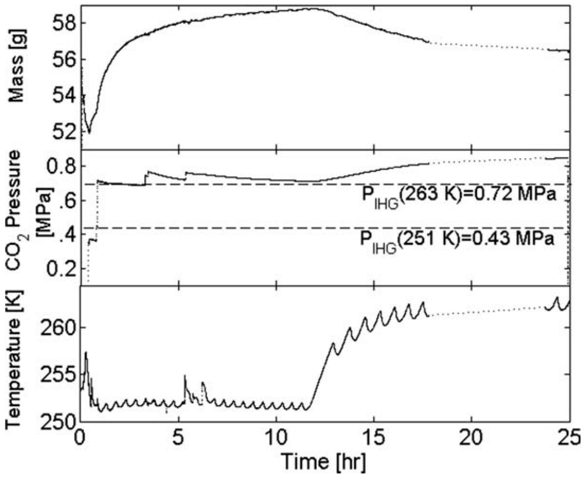

Figure 6. Temperature, pressure and mass of flash-freezing powder heat shocked with sufficient CO_2 to avoid ice formation at the warmest temperature.

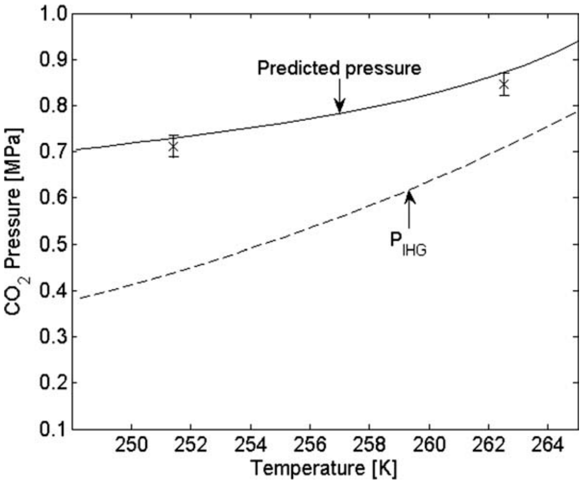

Figure 7. Measured and predicted pressure of flash-freezing powder with heat shock.

The stars indicate the measured PTM pressure at 251 K and at 263 K, the solid curve is the predicted pressure and the dashed curve is the IHG equilibrium curve.

increase in the PTM during heat shock and the concurrent decrease of the mass of the sample. In Figure 7, the PTM pressures measured before and after heat shock are compared to the pressure predicted using the model for package pressure introduced above. In Figure 7, the measured pressure is only plotted at the starting and ending temperature of the heat shock experiment. In between, the system is not in equilibrium and the pressure model is only applicable for equilibrium systems. The measured pressures at 251 K and at 263 K are both within 0.02 MPa of the model prediction and the change in pressure is on the order of 0.15 MPa for both the model and the experiment. Although ~3 grams of CO_2 are added to the gas phase due to the temperature increase, the pressure only increases about 0.1 MPa because the volume of the PTM is large compared to the volume of powder (625 cm^3 vs. 35 cm^3).

Since the experimental results support the model of CO_2 hydrate evolution in desserts during heat shock, it is worth considering the model more carefully. Figure 8 is a plot of the CO_2 content of the dessert (grams CO_2/gram dessert) as a function of temperature and CO_2 charge in a package containing 0.125 g of 20% sucrose dessert mixture per cm^3. According to Figure 8 the CO_2 concentration in the dessert itself decreases significantly with warming, even for total CO_2 contents at which the pressure in the package follows the IHG equilibrium curve. The CO_2 content in the dessert is a function of temperature and total CO_2 present in the package. In general, the CO_2 concentration in the dessert decreases with increasing temperature. The CO_2 concentration decreases due to both the decreasing fraction of water crystallized and dissociation of CO_2 hydrate to ice. The curves for 0.01 and 0.015 g CO_2/cm^3 have minimums at the temperature at which the pressure in the package becomes too low for CO_2 hydrates. The subsequent increase in CO_2 concentration occurs because the mass of aqueous phase available to dissolve CO_2 increases with warming. At the highest package CO_2 contents the CO_2 concentration in the dessert approaches saturation. At high pressure, the CO_2 concentration decreases less significantly with warming because all of the crystallized water in the dessert is CO_2 hydrate and the fraction of water crystallized is increased by the "excess" pressure in the package.

In sensory analysis tests of the dessert, a minimum CO_2 concentration of 0.03 g CO_2/g dessert was identified. In Figure 8 it can be seen that with less than 0.02 g CO_2/cm^3 (which corresponds to 4 g of CO_2 in a 200 cm^3 container with 25 g of dessert mixture), the CO_2 content becomes too low to ensure a well-carbonated product as the temperature rises above 267 K. Referring back to Figure 2 it can be seen that for CO_2 contents of 0.02 g/cm^3 or more the pressure in the container increases along the IHG equilibrium curve or above the curve. It has also been observed that CO_2 redistributes rapidly in the dessert if ice is present, which can lead to inhomogeneity in the product. To avoid ice in the dessert during heat shock it is necessary to have more than 0.04 g CO_2/cm^3. For this CO_2 content the pressure in the container increases from at least 0.55 MPa at 253 K to 0.85 MPa at 265 K. While this pressure increase is large, it does not exceed the operating pressure of some carbonated water bottles (e.g. Soda-Club – http://www.sodaclub.com), so it should be reasonable to design a dessert for this total CO_2 content.

However, the pressure at temperatures typical for home and vendor freezers is not the whole story. It is important to remember that if the dessert is warmed to room temperature without venting any gas, the pressure will be significantly higher. In Figure 9 the plot of pressure in the package is extended to include the pressure at room temperature for each package CO_2 content. Even for the minimum package CO_2 content for sensory purposes (0.02 g CO_2/cm^3), the pressure at room temperature is greater than 1 MPa, so a pressure relief device is likely to be necessary.

In addition to considering pressure, the solute concentration in the aqueous phase is of interest. If the sucrose

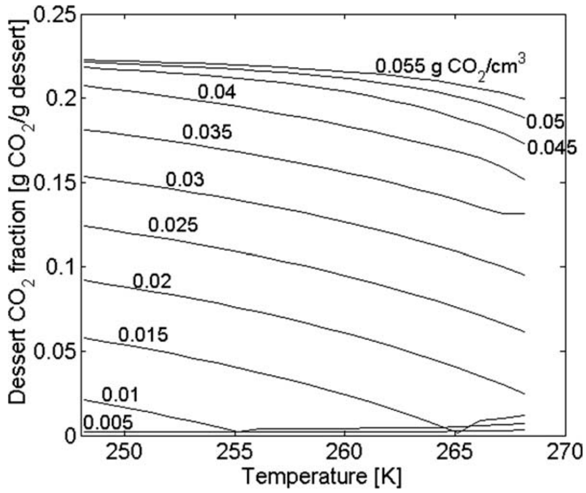

Figure 8. CO_2 fraction in the dessert (rather than in the gas phase) as a function of temperature and package CO_2 content.

Curves correspond to constant grams of CO_2 per cm^3 in a package with 0.125 g/cm^3 of 20% sucrose solution.

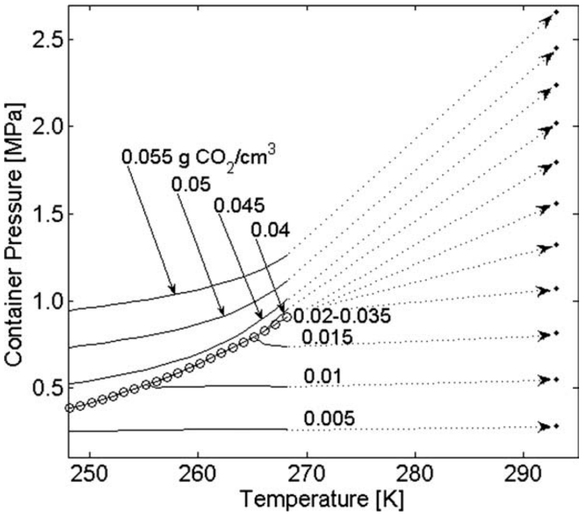

Figure 9. Pressure in a container with 0.125 g/cm^3 of 20% sucrose CO_2 hydrate dessert at room temperature in addition to 248–268 K.

Open circles show CO_2 hydrate-ice equilibrium curve.

concentration in the aqueous phase is increased sufficiently the phase will become very viscous, slowing recrystallization compared to the rates in a dessert at atmospheric pressure. The sucrose concentration in the aqueous phase is plotted in Figure 10. The dashed curve labeled T_m shows the sucrose concentration measured by Blond et al.[6] at atmospheric pressure. With increasing package CO_2 content the curves initially shift to lower aqueous phase sucrose concentrations, reaching a minimum at CO_2 contents that give a pressure equal to the IHG equilibrium pressure. The shift to lower aqueous phase sucrose concentrations occurs because the pressure in the package increases with increasing CO_2 content, which increases the moles of CO_2 dissolved in the aqueous phase. For CO_2 contents greater than 0.04 g/cm^3, the curves begin to shift in the opposite direction, toward higher sucrose concentrations. Referring to Figure 2, the pressure in the package increases above the IHG equilibrium pressure for CO_2 contents greater than 0.04 g/cm^3. For high CO_2 contents (greater than 0.05 g/cm^3) the aqueous phase sucrose concentration is greater than the concentration in a conventional ice confection. The sucrose concentration is shifted toward the glass transition curve (the dashed line indicated by T_g). As the sucrose concentration in the aqueous phase increases, water mobility is decreased and ice recrystallization is slowed. Although at the CO_2 contents shown in Figure 10 the concentration is not shifted to the glassy region, it is likely that at higher pressures recrystallization processes in the dessert could be mitigated over its shelf life.

The sucrose concentration in the aqueous phase is related to the fraction of water crystallized. The sucrose concentration and fraction of water crystallized vary inversely. In Figure 10 it can be seen that the sucrose concentration in the aqueous phase changes less between 248 and 268 K in the high CO_2 content packages than in the packages at pressures lower than the IHG equilibrium pressure. This means that less water melts during heat shock at high pressure than at atmospheric pressure. Thus more water crystals survive heat shock and when the dessert is recooled the remaining water crystals will not grow as much. Packaging the dessert at pressures many tenths of MPa in excess of the IHG equilibrium pressure should reduce the damage to the dessert texture that is caused by heat shock.

Conclusion

CO_2 hydrates are valuable for creating carbonated frozen desserts. The solid water-carbon dioxide structure traps CO_2 at a high concentration, enabling a strong perception of carbonation when the dessert is eaten. However, based on the model developed and experimentally supported in this work, the dessert packaging must differ from conventional frozen dessert packaging. The package must be pressurized. It must be designed to maintain a CO_2 pressure of at least 0.5–0.6 MPa. The model for the sucrose-water system shows that the package pressure can increase by several tenths of MPa during heat shock, and the pressure can exceed the IHG equilibrium pressure. To keep the dessert carbonated through heat shock the total CO_2 content should be adjusted for the warmest temperature expected in routine storage and distribution of the product. A pressure of 1 MPa may be more than sufficient for the typical freezer temperature fluctuations in the cold chain. However, to ensure that the desserts can be melted safely, it is likely that a pressure relief device will be necessary because the pressure in the package increases significantly when the dessert is completely melted.

It has been shown that increasing the CO_2 content of the package increases the pressure and this may have beneficial effects for mitigating heat shock. If the pressure is increased

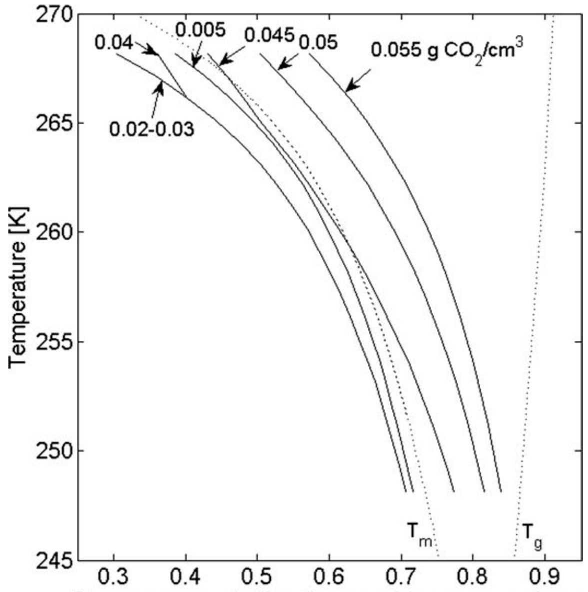

Figure 10. Sucrose concentration in the aqueous phase corresponding to curves in Figure 2.

The glass transition temperature (T_g) and melting temperature (T_m) of a sucrose-H_2O system at atmospheric pressure are plotted for reference.[6]

sufficiently above the IHG equilibrium pressure, the fraction of water crystallized increases above the fraction in a conventional ice confection. With the increased fraction of water crystallized, the sucrose concentration in the aqueous phase increases, which increases the viscosity of the aqueous phase and may slow recrystallization. It is likely that high package pressures are necessary to take advantage of this trend. However, even in the example trends plotted here, the fraction of water crystallized changes by a smaller magnitude in the high-pressure dessert compared to the conventional dessert. Less water melts during heat shock, which should mitigate heat shock damage by reducing the destruction of small crystals. Thus CO_2 hydrates provide not only a mechanism for carbonating frozen foods, but also a potential method of protecting frozen foods during heat shock.

In addition to applications in CO_2 hydrate dessert packaging, the model developed here may be useful in design of two-phase secondary refrigerants containing gas hydrates for loops operating below ~265 K. Several researchers have investigated gas hydrate slurries for secondary refrigerants, but typically only at temperatures of 265 K and warmer.[9,10] Gas hydrates are of interest because they can be formed by gas injection rather than mechanical processing and the latent heat of dissociation is the same order of magnitude as the latent heat of ice melting. At lower temperatures the latent heat of gas hydrate dissociation to ice and gas could provide improvements over use of a single phase working fluid. An appropriate carrier fluid would be needed.

The model presented here may also be useful in development of gas hydrate transportation vessels where temperatures below 273 K are used to reduce system pressures. Currently efforts are more focused on developing economic methods of forming and dissociating gas hydrates at the source and point of delivery.[11,12]

Acknowledgments

The support of Nestle S.A. for this research is gratefully acknowledged.

Literature Cited

1. Sloan ED, Koh CA. *Clathrate Hydrates of Natural Gases*, 3rd ed. Boca Raton, FL: CRC Press, 2008.
2. Peters TB, Smith JL, Brisson JG. Production of CO_2 clathrate hydrate frozen desserts by flash freezing. *J Food Eng*. 2010;100: 669–677.
3. Circone S, Stern LA, Kirby SH, Durham WB, Chakoumakos BC, Rawn CJ, Rondinone AJ, Ishii Y. CO_2 hydrate: synthesis, composition, structure, dissociation behavior, and a comparison to structure I CH_4 hydrate. *J Phys Chem B*. 2003;107:5529–5539.
4. Denbigh K. *The Principles of Chemical Equilibrium*, 4th ed. Cambrige, UK: Cambridge University Press, 1981.
5. Diamond LW, Akinfiev NN. Solubility of CO_2 in water from −1.5 to 100°C and from 0.1 to 100 MPa: evaluation of literature data and thermodynamic modeling. *Fluid Phase Equilibria*. 2003;208:265–290.
6. Blond G, Simatos D, Catte M, Dussap CG, Gros JB. Modeling of the water-sucrose state diagram below 0°C. *Carbohydr Res*. 1997;298:139–145.
7. Tester JW, Modell M. *Thermodynamics and its Applications*. Upper Saddle River, NJ: Prentice Hall, 1996.
8. Lide D. *CRC Handbook of Chemistry and Physics*, 90th ed. Boca Raton, FL: CRC Press, 2009.
9. Fournaison L, Delahaye A, Chatti I, Petitet J-P. CO_2 hydrates in refrigeration processes. *Ind Eng Chem Res*. 2004;43:6521–6526.
10. Delahaye A, Fournaison L, Marinhas S, Martinez MC. Rheological study of CO_2 hydrate slurry in a dynamic loop applied to secondary refrigeration. *Chem Eng Sci*. 2008;63:3551–3559.
11. Hao W, Wang J, Fan S, Hao W. Evaluation and analysis method for natural gas hydrate storage and transportation processes. *Energy Conversion Manage*. 2008;49:2546–2553.
12. Brown TD, Taylor CE, Bernado MP. Rapid gas hydrate formation processes: will they work? *Energies*. 2010;3:1154–1175.

Manuscript received Feb. 21, 2010, revision received Oct. 19, 2010, and final revision received Mar. 17, 2011.