COLLAPSE TEMPERATURE OF FREEZE-DRIED CARBOHYDRATE SOLUTIONS: EFFECTS OF COMPOSITION AND MOISTURE CONTENT

by

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ABSTRACT

Knowledge of the collapse temperature of dry fruit juices at different moistures can be used to specify process and storage conditions which will lead to a better quality product with longer shelf life. This work is a study of the collapse temperature for freeze-dried liquid foods. Collapse temperatures were measured for carbohydrate solutions simulating fruit juices and for fruit juices themselves. Collapse temperatures were determined by visual observations. The studies concentrated on evaluating the effect of the following parameters on the collapse temperature: 1) moisture content, 2) concentration of the initial solution, 3) viscosity of the initial solution, 4) molecular weight of the carbohydrate added (in the case of additives), and, 5) the rate of freezing. The results show that collapse temperature increases with decreasing moisture content, with increasing concentration of the initial solution, with increasing viscosity of the initial solution and with increasing molecular weight of the additive. In the case of freezing rate, no set pattern of behavior could be found.

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This study is dedicated to my mother and the memory of my father.

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1. INTRODUCTION

Freeze drying has been, so far, the best method of dehydration for food preservation purposes as it produces the highest quality product obtainable by any drying method. During World War II freeze drying received considerable attention beyond the laboratory scale as a means for preservation of blood plasma (Flosdorf, 1949). In the 1950's the Quartermaster Corps of the U.S. Army together with the USDA initiated research to develop freeze-drying for military foods (King, 1971). Today, freeze drying is mostly used by the food industry in large scale operations for production of foodstuffs of wide variety and for wide consumption.

The principle behind freeze-drying is that under certain conditions of low vapor pressure, water can evaporate from ice without the ice melting. The phenomenon is known as sublimation. Frozen water will sublime if the temperature is below the freezing point of the water and the frozen sample is placed in a surrounding in which the partial pressure of water is below 4.6mm. These conditions can be achieved conveniently by placing the ice in a vacuum chamber at a pressure below 4.6mm (Potter, 1973). Under such conditions, the water will remain frozen and water molecules will leave the ice at a faster rate than water molecules from the surrounding atmosphere re-enter the ice.

Within the vacuum chamber, heat can be applied to the frozen food to speed sublimation and if the vacuum is maintained sufficiently high (0.1-2mm Hg) and the heat is controlled, moisture vapor will sublime at a high rate. In the case of freeze drying of foods sublimation takes place from the surface of the ice and, as the process continues, the ice front recedes towards the center of the food. When the last ice sublimes, the food is usually at a low water content. The average moisture content existing within the food product of the time the ice disappears completely depends on various processing factors and in particular on the temperature at which the drying is conducted and on the modes of heat and mass transfer (Karel, 1974). It is noted that most of the drying time is spent in removing the last 10% of moisture. As many of the degrading chemical changes, occurring in dried foods, occur between 2% and 10% moisture, it is necessary to dry below this point (Charm, 1971).

In this study, the dehydration of fruit juices will be considered as it is related to optimum operation temperatures. The aim in dehydrating fruit juices is to produce a stable, easily handled and stored form of juice which reconstitutes rapidly to give a high quality product resembling the original juice as closely as possible. The factors involved in achieving this aim are the following:

1) Quality - that is the retention of the original attractive color, taste, and aroma of the fruit and the preservation of acceptable texture. This requires avoidance of off-flavor and prevention of structural collapse. The quality varies markedly depending on whether or not the frozen portion of the product was kept below a critical temperature, the <u>collapse temperature</u> during the sublimation step.

2) Stability - Dehydrated juices have a longer storage life at ordinary temperatures than concentrated ones. Requirements of stable natural color and odor for at least 6 months at 100°F or 1 year at 70°F are not unusual, especially for overseas or military uses (Ponting et al, 1973). In terms of drying operations, these requirements imply reduction of moisture content to very low values (~1% for fruit powders).

3) Rapid Reconstitution - Dried juices are convenience foods, which means that they must show "instant" reconstitution; namely they must be dispersible in cold water in a minute or two, in order to compete with frozen juice concentrates.

4) Low weight and volume - Reduction in weight of juices dehydrated to 1% moisture varies between 4:1 and 8:1 (Ponting et al, 1973). This is an important saving in weight and volume, especially if it is followed by compression or grinding of the juice.

The above mentioned factors show the importance of research on dehydration of juices. Of all, the most critical is, maybe, the regulation of operating temperature, namely the collapse temperature. If the temperature of the juice being freeze-dried is higher than the collapse temperature, the final product is in the form of a collapsed solute matrix, that is it loses its shape, it becomes highly viscous, and it has poor aroma retention, poor rehydration characteristics, and uneven dryness. For various aqueous solutions, collapse temperatures vary from -5° to -60°C (Mackenzie, 1965,1966). Thus, maintaining the product below the collapse temperature is an important factor in the final quality of the product.

The objective of this research was to study the collapse temperature of fruit juices as a function of their moisture content, that is, to find the family of curves that will describe the change in collapse temperature due to different moisture levels. Also, it was one of the objectives to simulate juices with meaningful model solutions and show how the collapse temperature of these solutions depends on their concentration of different carbohydrates and the composition of dissolved solutes in the case of additives meant to produce a more stable product. Finally, it intends to give suggestions of practical interest, as to certain additives of the nature of carbohydrates or other, that may improve the quality of certain freeze-dried juices.

2. LITERATURE SURVEY

During freeze-drying, a certain portion of the water remains unfrozen and this is removed by evaporation from the partially dried solute matrix. Because of this unfrozen water, the solute matrix in the case of a food liquid remains somewhat fluid and there exists a temperature Tc above which the solid matrix will collapse before drying is completed.

Many previous investigators of freeze-drying of liquids have studied collapse behavior, because if they operated above the collapse temperature they obtained a poor or unacceptable product. Many workers noticed that higher operating temperatures cause partial melting or puffing but the general treatment of the problem of collapse has been limited.

Before we concentrate on the specific papers, we should mention some basic aspects of freeze-drying as this process is used throughout the experiments to be described, and especially emphasize the variables on which drying time depends.

2.1 Some Basic Aspects of Freeze-Drying

The heat of sublimation of ice during freeze-drying can be provided by radiation to the outer dry layer of a food being freeze-dried or by conduction to the frozen layer. Convective heat transfer is important when drying is conducted at pressures above several torrs. In the radiation method, the drying rate is almost always limited by heat transfer, either by the external heat transfer coefficient for the radiation or by conduction through the dry layer of the food. Also, in the radiation method, there is variability of heating depending upon the view factors and temperatures seen by different food pieces (King, 1971).

To overcome these disadvantages we can provide the heat by conduction through a frozen zone of the food to the sublimation front. This procedure requires good thermal contact between the foodstuff and a contact heating plate. Although the surface area through which vapor can escape is less, the overall time required for drying is less than can be achieved by supplying heat through the dry layer. The only drawback to this method is the necessity for maintaining good contact between the food and the heating plate since, if a gap develops, there will be a vapor escape and formation of an insulating dry layer adjacent to the heating plate. Because of the low plate temperature necessary to prevent melting, drying adjacent to the heating surface will result in a much lower rate of heat supply than would be achieved by supplying heat through the outer dry layer. Good contact with heater can be obtained with frozen liquid foodstuffs (King, 1971). We shall consider a typical vacuum freeze-drying operation in which the material to be dried is heated by radiation to dry surface, and its internal frozen layer temperature is determined by the balance between heat and mass transfer. For simplicity, we can consider a slab geometry with negligible end effects. Karel (1974) gives an analysis of the drying effects in this case. He assumes that the maximum allowable surface temperature T_s is reached instantaneously and remains constant throughout the cycle. Also, that the partial pressure of water p_s in the drying chamber remains constant and that all of the heat is used for sublimation of water vapor.

Under these conditions, the heat transfer is:

(1): $q = Ak_d(T_s-T_i)x_d^{-1}$ where x_d =thickness of dry layer(ft)
k_d =thermal conductivity of dry layer (BTU/ft/h/°F)
T_i =temperature of ice surface

and the sublimation rate is:

(2): $G = -dw/dt = Ab(p_i-p_s)x_d^{-1}$ where w =weight of water in slab (lb)
t =time
b =permeability of dry layer (lb/ft/h/torr)
p_s=partial pressure of water at dry layer surface (torr)

In the case of the slab we also have, for the loss of weight during drying:

(3): $-dw/dt = A\rho(m_i-m_f)dx_d/dt$ where ρ =bulk density of solids in drying slab(lb/ft^3)
m_i=initial moisture content lb-water/lb-solids
m_f=final moisture content lb-water/lb-solids

Karel (1974), combining equations (1), (2), and (3) showed that the drying time is

$$t = \frac{L^2\rho(m_i-m_f)\Delta H_s}{8k_d(T_s-T_i)}$$

where L =thickness of slab(ft)
k_d=thermal conductivity of the dry layer.

This equation shows which variables are important in deciding drying time. In this idealized analysis the frozen layer temperature depends neither on the overall thickness of the drying material, nor on the thickness of the dried layer. The ice temperature is determined by interactions between surface temperature, chamber vapor pressure p_s and the dry layer properties k_d and b. This temperature must be maintained below a critical level, T_c, which depends on the composition of the product and its thermal history. Ideally, it should also be below the eutectic point of the material. It must be noted that the thermal conductivity of the dry layer of freeze-dried food is extremely low. As a consequence, the temperature drop across the dry layer is large, and with surface temperatures often limited to values below 150°F because of danger of discoloration or even below 100°F because of danger of denaturation, the ice temperature is usually well below 0°F (Karel, 1974). Therefore, it is the surface temperature that limits the drying rate. Average drying rates reported in the literature are about 0.30 lb of water removed per ft^2 of surface per hour. Yet, a much more rapid rate can be achieved by decreasing the particle size and loading rates. This lowers both mass and heat transfer resistances.

2.2 The Frozen State

The important change that occurs during freezing is the appearance of at least one new phase, ie., the conversion of part or all of the water into ice, together with other changes which include: 1) dehydration of insoluble solid material, 2) coalescence of droplets of immiscible liquids

3) the crystallization of some solutes, 4) the formation of amorphous precipitates of other solutes, 5) exsolution of dissolved gases, 6) formation of concentrated solute glasses, and 7) the disruption of molecular complexes (lipoproteins) and other (Mackenzie, 1965).

Thus, the ideal frozen state would show a sharp and discrete dividing surface between a region which consists of ice crystals, and a region which consists of concentrated amorphous solution. Aroma molecules remain in this area after freezing. However, there is a considerable amount of contention in recent years regarding the degree of sharpness of this surface, when it is retreating as a frozen front during freeze-drying (King, 1971). Figure 1 shows an idealized cross-section of a frozen liquid where ice has grown into long, thin, parallel cylinders separated by regions of concentrated solute.

2.2.1 Recrystallization Phenomena

Mackenzie (1965) gives a very good description of the structure of the frozen state, and the factors involved in it. The point that deserves discussion in this connection is recrystallization of ice. According to Luyet (1966), rapidly frozen solutions do not remain stable until the temperature is raised to the melting point, but rather when it reaches a certain value, which seems to depend primarily on the molecular weight of the solute and slightly on the concentration, the material changes from transparent to opaque due to a transformation of the pattern of ice from one type to another

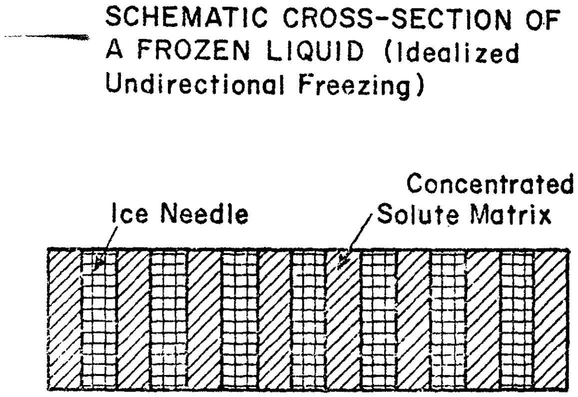


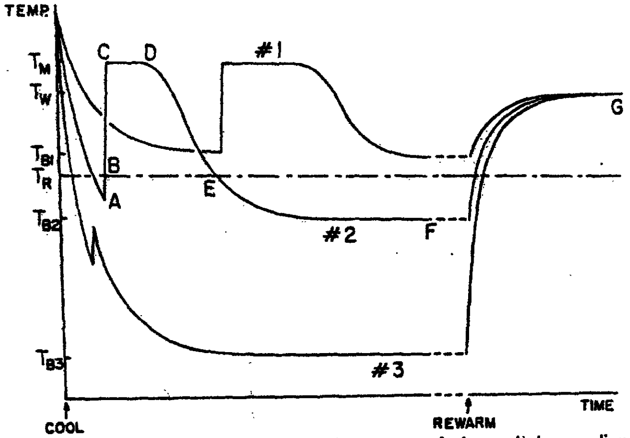
FIGURE 1

From Bellows and King (1972)

of coarser grain. This value of temperature is known as the recrystallization temperature, T_R. Table I shows recrystallization temperatures of some aqueous solutions of importance in this study.

According to Mackenzie (1965) the rapid increase in viscosity of the solute when the temperature approaches T_R prevents further ice crystal growth and crystal size redistribution.

Luyet and co-workers (1962) studied several possible situations of recrystallization in frozen systems which are illustrated in Figure 2. It shows cooling curves for a sample frozen to temperatures above (Curve#1) and below (Curves #2 and #3) the characteristic recrystallization temperature. What they essentially found was that 1) sample frozen in cooling baths warmer than T_R demonstrated a steady recrystallization of ice from the moment of freezing onwards and 2) samples frozen by immersion in cooling baths of temperature colder that T_R showed recrystallization as long as the sample remained above T_R (portion BCDE of Curve #2) but that further crystallization stopped as the sample passed point E. With sufficiently rapid cooling (Curve #3), no detectable recrystallization occured during cooling. Also, when they rewarmed the sample frozen to very low temperature, they found either a resumption of recrystallization (Curve #2) or the initiation of recrystallization (Cruve #3). Another point we should make in this paragraph is the relation of supercooling to recrystallization and water-binding by the solute and their effect on the structure of the final frozen sample. Mackenzie (1965) found (abscissae).



Three model cooling curves for the same sample frozen, i) in a cooling bath at a temperature, T_{B1}, higher than T_R, the recrystallization temperature of the solution in question, ii) in a cooling bath at a temperature, T_{B2}, somewhat lower than T_R, and iii) in a bath at a temperature T_{B3}, much lower (e.g., 100 to 150 degrees C. lower) than T_R. Recrystallization of ice proceeds in each case only when sample is warmer than T_R.

FIGURE 2

FROM MACKENZIE (1965)

TABLE I*

SUBSTANCE	NATURE	THRESHOLD TEMPERATURES (°C)	
		For recrystallization upon rewarming	For collapse upon freeze-drying
Dextran	linear polysaccharide; unpec. m.w.	-10	-9
Dextran 10	linear polysaccharide; m.w:10^4	-	-10
Dextran 110	ditto: 11×10^4	-	-10.5
Dextran 2000	ditto: 2×10^6	-	-9
Ficoll	globular polymer of sucrose; m.w: 4×10^5	-32	-19.5
Fructose	monosaccharide	-48	-48
Gelatin	linear polypeptide	-11	-8
Glucose	monosaccharide	-41	-40
Glycerol	linear triol	-60 to -65	-
Inositol	cyclic hexitol	-	-27
Lactose	disaccharide	-	-31
Maltose	disaccharide	-	-30 to -35
Methocel	methylated cellulose	-10	-9
Ovalbumin	globular protein	-10	-10
Polyethylene glycol	linear polyether; m.w: ca. 6000	-65	-13
Polyvinyl pyrrolidone	linear polymer m.w: ca. 3×10^4	-24	-23
Raffinose	trisaccharide	-27	-26
Sephadex G200	cross-linked dextran	-	-10
Sorbitol	linear hexitol	-	-37
Sucrose	disaccharide	-32	-32

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* From Mackenzie (1965)

that slow cooling causes the temperature of the entire sample to fall more or less uniformly and that once ice starts to form the entire sample is invaded within a few seconds, causing a vertical rise, AC, in the cooling curve (see Fig.2). The ice formed was dendritic in structure corresponding to supercooled surroundings. Further heat transfer to the sample causes a steady increase in the quantity of ice in the sample (plateau CD). Now the total ice structure undergoes a process of further recrystallization (grain growth) until the temperature is lower than T_R (point E). Thus, ice already formed is recrystallizing while further ice is still crystallizing. This essentially goes on throughout the curve part BCDE.

2.2.2 Effect of Moisture on Recrystallization of Sugars

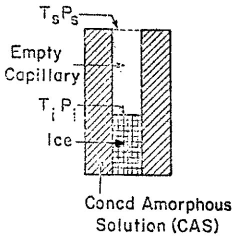
Another point of interest with respect to recrystallization phenomena related to this study is the stability of dehydrated sugars. After rapid dehydration of sugar solutions and juices, the sugars may be present in unstable amorphous or microcrystalline states. Recrystallization may occur when sufficient mobility is imparted to allow re-arrangements. Most often such recrystallization occurs after exposure to water vapor.

Mackower and Dye (1956), studying the preparation of free-flowing powders from fruit juices found that at relative humidities lower than about 12% for sucrose and 5% for glucose, moisture equilibrium was attained and practically no crystallization occurred in nearly 3 years. At higher humidities, the absorbed water initiated crystallization of the sugars with subsequent release of moisture to yield essentially anhydrous materials; thus becoming sticky and forming a hard cake. The rate of crystallization of amorphous sucrose followed an exponential law with respect to time, after an initial induction period.

Palmer, Dye, and Black (1956) used an X-ray diffractometer method to determine the crystalline-to-amorphous ratio in a spray-dried sample of sucrose. They found that crystallization of the amorphous particles proceeds in 2 steps. The surface of the particles crystallizes first, followed by a rapid crystallization of the remaining amorphous sucrose inside each particle. The crystallization of the surface of the particles evidently prevents them from flowing together when the sample is subsequently exposed to a high relative humidity. After the crust is formed, therefore, the sample does not shrink and caking does not occur upon subsequent crystallization of the remaining amorphous sucrose. In other sugars, however, and in fruit juices caking can accompany the recrystallization phenomena.

2.3 The Drying Step and the Concept of Collapse

When the frozen sample is placed in the vacuum chamber of the freeze-drier with radiant heat applied to it, ice nearest the surface sublimes first, leaving a drying front at some level within the material. The region below the drying front is referred to as the frozen zone (see Fig.3).



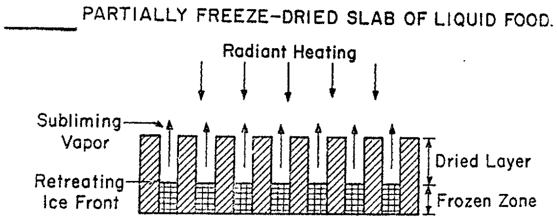


FIGURE 3

FROM BELLOWS AND KING (1972)

The heat of sublimation is supplied to the ice front by conduction across the dry layer. The outer surface of the particle must be kept above the temperature of the ice front for this heat transfer to occur. Sublimed vapor leaves the ice front through the capillaries left behind by sublimed ice needles. The following equation describes the mass transfer occuring during freeze-drying:

$$G = \frac{A(p_i - p_c)}{R_d + R_s + R_o} = \frac{q}{\Delta H_s}$$

where p_i = partial pressure of ice inside the food; p_c = partial pressure of water in the condenser; G = rate of sublimation; R_d = resistance of the "dry" layer in the food; R_s = resistance of space between food and condenser; R_o = constant; ΔH_s = heat of sublimation (Karel, 1974).

The rate of drying of many liquid foods is limited by the rate of diffusion of the vapor to the surface of the drying slab. If we raise the temperature of the ice front mass transfer increases thus limiting heat transfer.

Bellows and King (1972) found in general that the rate of drying increases approximately 11% per degree C rise of ice front temperature. However, there is an upper limit to increasing drying by temperature increase since collapse of the structure due to high temperature is usually highly undesirable.

The collapse temperature (or temperature range of two or three degrees) is the temperature at which viscous flow in the concentrated amorphous layer is possible so that in freeze drying sublimation of ice is attended by the collapse of the freeze-dried matrix. In this case, the ice crystals appear to dissolve rather than to sublime. A potential practical problem due to collapse is the construction of capillaries and thus increase of resistance to vapor flow (see Fig.4). Extreme collapse completely closes the capillaries, so that moisture removal is limited to evaporative mechanisms, with much bubbling and spattering (Mackenzie, 1965; Bellows and King, 1972).

2.4 Collapse of Freeze-Dried Fruit Juices and Related Phenomena

2.4.1 The Glassy State

Meyer and Ferry (1965) and Luyet (1970) have reported that concentrated solutions of sugars can show glass transitions. In fact, this behavior is the basis of hard candies which are mixtures of sugars with low water content and have glass transitions which occur above room temperature. Jones (1956) describes as a glass any liquid or supercooled liquid that has a viscosity of more than 10^{13} poises, thus being able to support its own weight. Breakdown of these glasses leads, in the case of freeze-dried products, to partial liquefaction or caking (White and Cakebread, 1962). It is also suspected that in freeze-dried fruit products the sugars are present in a glassy

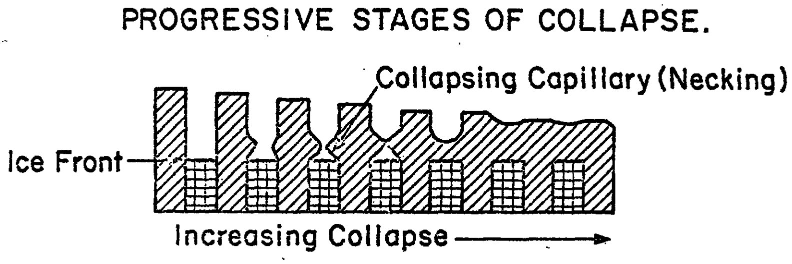


FIGURE 4

FROM BELLOWS AND KING (1972)

form; this accounts not only for the hygroscopicity of part of such products, but also for the phenomenon of puffing (Rey, 1960).

According to Kauzmann (1948), matter in the glassy state is a constrained liquid with molecules unable to achieve certain molecular degrees of freedom. So what we really have in the glass state is a relatively non-ordered structure. Luyet (1939) supports this view with his work on divitrification temperatures of carbohydrate solutions. Glass transition phenomena are of interest to this study as they were initially attributed to be the cause of collapse.

2.4.2 Collapse and Recrystallization Temperatures

An interesting observation that arises from the measurement of collapse temperatures is the close identity of the collapse temperature during freeze-drying with the corresponding T_R. Table I shows T_R and T_C for some solutes. It is, therefore, logical to assume that the same reduction in viscosity of the solute phase with a small increase in temperature that is responsible for recrystallization, is also responsible for the collapse of the matrix.

2.4.3 Effect of Freezing Treatment and Solute Concentration on Collapse Temperature

Collapse temperature may vary with the freezing treatment as well as solute concentration and nature of solute. Mackenzie (1965) claims that collapse temperatures were relatively independent of concentration and freezing treatment. Ito (1970,a,b and 1971) reports that preconcentration was not observed to affect the collapse temperature for a given solute, but that collapse temperatures increase as the molecular size of the solute increases. Quast and Karel (1968) reported that a preconcentrated coffee solution with 20% solids could not be dried without collapse above -25°C, and that a 40% solution had a collapse temperature lower by a "few degrees". Their data were based on drying behavior.

With reference to freezing treatment, Mackenzie (1965) reports that freezing techniques do not affect the collapse temperature of a solute. Rey and Bastien (1962), though, suggest a freezing treatment which can raise the collapse temperature of a solution. They, first, freeze their samples quickly with dry ice and then they rewarm them to recrystallization temperature in order to recrystallize (or "devitrify") the CAS. Then, they cool again below the collapse temperature (or range) and finally they freeze-dry, keeping the sample below the collapse temperature just under the bottom of the collapse range.

2.4.4. Effect of Additives on Collapse Temperature

Attempts have been made by some researchers to use various additives as a means of improving the structure of drying material. These additives include sucrose, glucose, corn syrup solids, dextrins, NaCl, etc. Mackenzie (1965) observed that his collapse temperatures were relatively independent of concentration and freezing treatment but varied markedly with composition. He observed that adding macromolecules (with high collapse temperature) to a sucrose solution (with a lower collapse temperature) raised the collapse temperature for the sugar solution. This increase was linear in some cases (dextran) but nonlinear in others (ovalbumin) with a percentage of added macromolecular additive. When he added 10% wt NaCl to sucrose, though, he found that it lowered the collapse temperature up to ~30% NaCl and then it raised it at concentrations of ~45% and higher.

Neuman (1961) patented the addition of macromolecules with high collapse temperatures - such as gelatin, agar-agar, pectin or polyvinylpyrollidone, claiming that these additives will raise low collapse temperatures by several degrees. This agrees with Mackenzie (1965). Stern and Storrs (1969) patented the addition of lactose or low-dextrose corn syrup to raise the collapse temperatures of juices with low collapse temperatures such as apple and grape juice, and honey. Moy (1971) indicates that added sucrose, corn-syrup or maltodextrin will raise the collapse temperatures of various tropical fruit juices. Monzini and Maltini (1971) found that adding sucrose raised the collapse temperature for lemon juice.

2.4.5. Aroma and Flavor Retention as Related to Collapse

Loss of volatile components of aroma and flavor is strongly related to collapse. Saravacos and Moyer (1968) showed that a high concentration of soluble solids (above 30-40%) made the loss of volatile flavor negligible. This suggests a pretreatment of the juice to concentrate it prior to freeze-drying or the addition of sugars as additives. The volatiles responsible for flavor are dispersed in a solid matrix which may be a variety of mixtures of natural gums, gelatin, glycerol, sorbitol, sugars and corn syrup solids. If this matrix collapses, there is a high loss of volatiles (Ponting, 1973). Bellows and King (1972) also worked on this problem using 25%wt sucrose solutions containing 0.2%vol. ethyl acetate as a model aroma.

Flink and Karel showed that there is an entrapment mechanism which immobilizes the volatile compounds within the amorphous solute matrix. They conducted a simple experiment which showed that in freeze-dried carbohydrate solutions the retention phenomena depend on local entrapment rather than absorption as Rey and Bastien (1962) claimed. Maltose solutions were frozen in layers, some of which were volatile containing,other,volatile-free. After freeze-drying the layers were separated and analyzed for the volatile. The results showed that volatile was retained in those areas where it had been initially present (Flink and Karel, 1970 ; Karel and Flink, 1973).

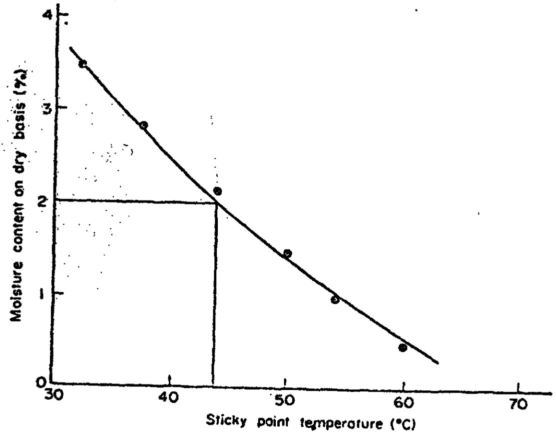
2.4.6. The Sticky Point Temperature in Spray Drying Liquid Foods

A similar situation with respect to flavor retention appears during spray drying of concentrated liquid foods. Lazar, et al (1956), in spray drying tomato juice, encountered problems of scorching of the product and sticking of the powder in the drying and collecting zones of the drier. Scorching was prevented by adding sulfur dioxide to the paste, in a concentration of 200 ppm on the wet basis (20% solids). Salt was also added in a concentration of 2% on a wet basis. Sticking of particles in the drier was decreased by cooling them with dry atmospheric air admitted near the bottom cone of the drier; this permitted transport of the powder to a collector having a low humidity atmosphere. It was then shown that sticky-point temperature varied as a function of the moisture content of the sample. Sticky point was defined as the temperature at which caking is instantaneous with slow stirring.

Brennan et al (1971) worked on spray drying concentrated orange juice. Their findings agreed generally with those of Lazar et al, (1956). They decided that liquid glucose was the most effective additive, reducing the wall deposition markedly and producing a product of acceptable flavor and with good free-flowing properties (Brennan, Herrera, Jowitt, 1971). Figure 5 shows the relationship between sticky point temperature and moisture content or orange juice powder with liquid glucose as additive.

2.4.7. Agglomeration Phenomena

Another phenomenon related to collapse is agglomeration of powdered foods in order to produce an instant product. Powdered foods can be considered as a mixture of organic compounds, and as such they possess no precise melting point. At a given temperature, the food



Relationship between sticky point temperature and moisture content of orange juice powder with liquid glucose as additive.

FIGURE 5

FROM BRENNON, HERRERA AND JOWITT (1971)

particles begin to plasticize and stick together (agglutinate). The point of agglutination is dependent upon the moisture content of the podwer; thus, there exists a requirement for wetting dried powder under closely controlled conditions to make their surfaces sticky. The result is the formation of clusters, which are then dried to the desired moisture content (Masters and Stoltze, 1973).

Agglomeration produces an increase in the amount of air between the particles (interstitial air). The reconstitution process starts by first wetting the particles and then replacing interstitial air by water. If the volume of interstitial air is low as in non-agglomerated powder the amount of water replacing this air will also be low. There will, therefore, be little water available to the large surface area of the powder particles with the result that a very concentrated solution of high viscosity is created around masses of particles, i.e. lumps are formed preventing further access of water. In an agglomerated powder the amount of interstitial air is high so that the particles are dispersed in the liquid before the high viscous solution is formed. Thus, agglomeration improves dispersibility and solubility of powdered foods (Jensen, 1973).

2.4.8. Caking Phenomena

A third phenomenon similar to collapse is caking of foods during storage. The process of caking in powders containing carbohydrates in the amorphous state is described by Pisecky (1973). Moisture absorption starts and continues towards equilibrium with the surrounding air. The material softens and nearly liquifies. Moisture contents can reach about 30%. Once sufficient moisture content has been reached sintering of the particles takes place and the material tends to lose the character of powder. Due to the absence of crystals the first condition for further crystallization is development of crystal nuclei; this takes a considerable time. After termination of crystallization, the vapor tension of powder moisture becomes higher than that of surrounding air so that the moisture absorption is followed by moisture desorption. The sticky and sintered powder formed during moisture increase will become cemented into a hard lump during crystallization and moisture decrease.

Working with whey powder, Pisecky (1973) found that a rich crystallization of lactose (90-95%) can reduce the hygroscopicity considerably. This is true for the degree of caking, too, although there is no straightforward relation between powder hygroscopicity and degree of caking. Yet, a rich crystallization is in itself not enough to prevent caking as this depends not only on the degree of crystallization but also on its quality; i.e. the number and distribution and size of crystals (Pisecky, 1973).

2.4.9. Observation of Collapse

Observation of collapse can be done in several ways. Mackenzie (1965) observed collapse directly with an optical microscope by freeze-drying a thin layer of solution between two microscopic slides. Rey (1960, 1962) tested electrical conductivity and differential thermal analysis (DTA) as alternative methods to determine "incipient melting" temperature analytically (the incipient melting temperature is the collapse temperature). The use of electrical conductivity as a monitor assumes that the conductivity of the concentrated amorphous solution is determined by the mobility of dissolved ions. Ito (1970,a,b and 1971) observed collapse visually in solutions which were freeze-dried in test tubes. Ito's criterion for collapse was unevenness or the appearance of puffs and bubbles at the retreating ice front. He also reports that electrical resistance measurements correlated well with his collapse temperatures. According to Bellows and King (1972), electron microscopy could be used by histologists to observe collapse in freeze-dried tissure. Sometimes the volatilization of a labelled volatile component entrapped in the freeze-dried matrix has been used to indicate matrix collapse. Chirife and Karel (1974) used ^{14}C-labelled 1-propanol to find the effect of structure disrupting treatments on volatile release from freeze-dried maltose.

2.5 Theories of Collapse

Two basic theories have been developed so far to explain collapse phenomena. These theories are based on phase transition phenomena which occur during the initial step of freezing. The first explains collapse for materials that form eutectic solutions, the second examines solutions where nucleation of solute crystals is inhibited.

2.5.1. The Eutectic Melting Theory

A solution is at its eutectic point when the removal of heat results in formation of a solid whose composition is the same as the remaining concentrated solution phase rather, than giving an increase of an ice phase. The temperature at which the solution freezes with a constant composition is the eutectic temperature.

The eutectic theory is based on a phase diagram similar to that shown in Fig. 6 for sucrose and water (Young, 1949). Freezing sucrose solutions of less than 65% wt solids at temperatures between the melting point and the eutectic point (-13.5°C) would produce a mixture of ice and concentrated solution. Cooling this mixture below the eutectic temperature will cause CAS to solidify into an eutectic mixture of ice and sucrose crystals. Freeze-drying above -13.5°C causes all of the rigid eutectic material to re-dissolve into a liquid thus causing collapse as a result of tension and gravity forces.

Rey (1960) generalized the behavior of a two-component system into a multicomponent eutectic mixture, the eutectic temperature of which he calls the cryohydric point. The cryohydric point of juices has been studied by Chandrasekaran and King (1971). They theorectically predicted that any mixture of sucrose, glucose and fructose in water would have the same cryohydric point of -25.4°C. Since juices are primarily composed of these three sugars and water, they have the same

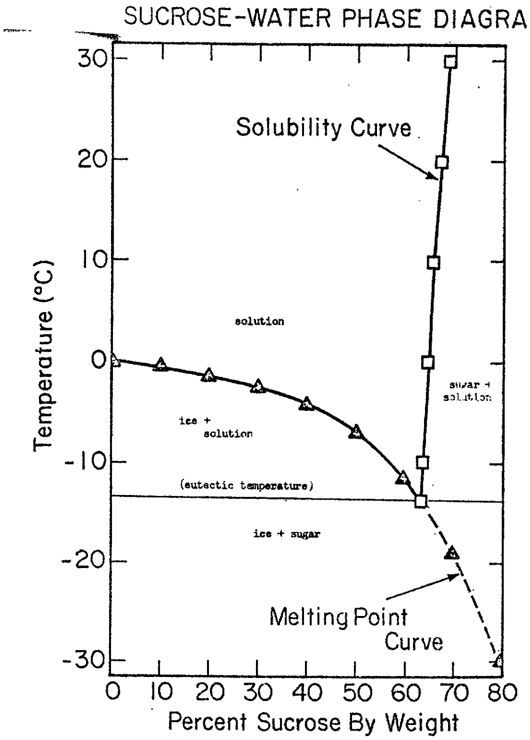


FIGURE 6

FROM BELLOWS AND KING (1972)

cryohydric point.

Ito (1970a,b, 1971) studied collapse of materials that formed eutectic mixtures. He found noticeable changes in the macroscopic appearance of solutions during freezing of some substances which exhibited the eutectic behavior. These changes were classified into four types (Ito, 1970a): 1) no change, 2) slight increase in opacity, 3) very noticeable formation of clear white spots due to eutectic crystallization with very slow rate of growth of spots, 4) high rate of growth of spots. The eutectic temperatures were taken from the temperature at which spots faded or disappeared. The collapsing temperatures were also obtained from the observation during freeze-drying of the temperatures above which the frozen layer of the solution became puffed or collapsed. The mechanism of the collapse during freeze-drying was discussed by Ito (1971) in relation to the state of frozen sample and T_c was classified in three types: the first was related to eutectic point temperature, T_e, the second to a glass transition temperature, T_g, and the third was the temperature below which the gross matrix of crystallized solute persisted even in the presence of a small amount of solution among crystallized solutes and ice crystals. Ito also found that the solution which did not exhibit eutectic crystallization could be freeze-dried if the temperature of sample was controlled below T_c.

2.5.2. Inhibition of Solute Crystallization

Eutectic Melting Theory explains collapse of solutions that readily form eutectics, like solutions of NaCl and other salts (Ito, 1970). For sugars, however, the nucleation of solute crystals is often inhibited. If the solute can not be nucleated, formation of solid eutectic mixture can not occur, no matter how low the temperature is. Further cooling, below T_e, continues to concentrate the CAS by forming more ice. According to Mackenzie (1965) and to White and Cakebread (1962) this leads to high solute concentration, which together with low temperatures causes the matrix to undergo a glass transition and no more ice is found. At the same time, and for the same reasons, the diffusivity of water within the CAS matrix can become so low that any practical rate of freezing does not allow sufficient time for the solute concentration within the bulk of the CAS to adjust to the removal of water as ice from the surfaces of CAS regions. A concentration polarization can thereby occur within the CAS, keeping the solute concentration in the bulk of the CAS lower than that at the CAS-ice interface (Bellows, 1972). This can also prevent ice formation. The dashed curve in Figure 6 shows the equivalent sucrose-water phase diagram for the case where sucrose does not crystallize. Bellows (1972) used differential scanning calorimetry (DSC) to show that sucrose and other sugars as well as fruit juices and coffee do not form an eutectic mixture.

2.5.3. Amorphous Viscosity Theory of Collapse

This theory, which applies to most solutes present in foods, considers the matrix as a concentrated amorphous aqueous solution. As long as the temperature of the matrix is below the collapse temperature, it is sufficiently viscous and acts like a solid. The matrix is further rigidified by the removal of moisture during drying, as water constantly evaporates from that region of the matrix where the ice crystals have already been removed by sublimation. If the temperature of the frozen zone goes above the collapse temperature, the concentrated amorphous solution becomes less viscous as it is now more diluted in water, and thus sufficiently fluid for collapse to occur, before it can be stabilized by sufficient moisture removal due to evaporative drying (Bellows and King, 1972).

According to Bellows (1972) surface tension forces acting at the surfaces of open capillaries left by sublimed ice needles predominate over gravity forces in causing the collapse. He suggests that from balancing the rate of viscous energy dissipation in the collapsing fluid against the rate of surface energy loss due to reduced capillary surface, an equation can be derived to describe collapse:

$$t_c = \frac{\mu R}{2\gamma}$$

where t_c is collapse time, μ viscosity of the matrix, R radius of capillary, and γ surface tension. This equation assumes that there is a drying time t_d necessary for the wet area above the ice front to dry to sufficient rigidity. This drying time is assumed because it is very difficult to be measured. Then, t_c must be longer than t_d to prevent collapse. The magnitude of t_d could presumably vary between 1 sec and 1000 sec (characteristics of overall freeze-drying times for small particles) (Bellows, 1972). Then, the order of magnitude of CAS viscosity that would prevent collapse can be calculated from the above equation. Typical values of γ = 70 dynes/cm and $R = 2\times10^{-3}$cm (Bellows and King, 1972) with t_d between 1 and 1000 sec predict that collapse should occur when the viscosity of the matrix is between 10^7 and 10^{10} cp (Bellows and King, 1972).

This predicted viscosity range for collapse appears to be very large but since the matrix viscosity is a strong function of temperature, this order-of-magnitude estimate of the collapse viscosity is sufficient to predict the collapse temperature.

Generally, the viscosity of a concentrated solution increases as the temperature decreases, as the concentration of water decreases and as the average solute molecular weight increases. At high solute concentrations (as in the matrix), slight decreases in the water content cause very large increases in viscosity. To relate viscosity changes to temperature of ice front, Bellows (1972) showed that there is very little concentration polarization taking place above the collapse temperature and therefore he assumed an equilibrium for water between the matrix and the ice. This means that, at any temperature the viscosity of the matrix containing a given ratio of solutes will be well defined - the viscosity of the matrix in equilibrium with ice (no more phase change of water) at that temperature. Therefore, lowering the temperature increases the viscosity by two effects: the Arhennius effect and the effect of further concentration of the matrix (Bellows and King, 1972). Figure 7 shows the Equilibrium Viscosity Curves for several solutions (after Bellows and King, 1972). These curves were obtained by calculating the equilibrium concentration at a given temperature and then estimating the viscosity from the measured viscosity data. It can be seen that way that the formula suggested by Bellows holds true for estimating of collapse viscosities.

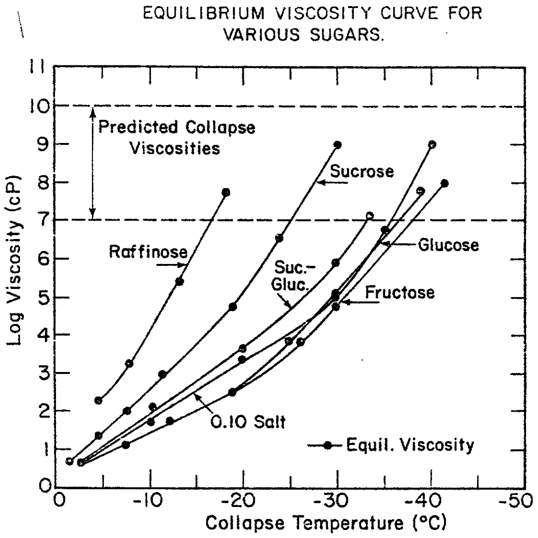


FIGURE 7

FROM BELLOWS AND KING (1972)

3. MATERIALS AND METHODS

3.1 Equipment

A. Freeze-Dryer

The freeze-drier used in this study was a Virtis Laboratory Freeze-Dryer (Model 10-100, Virtis Co., Gardener, New York). The drying chamber is a manifold type which allowed samples to be dried in the main chamber or in flasks attached to the manifold outlets. It was generally operated with a condenser temperature of -60°C, ambient temperature and a chamber pressure below 100 microns. The drying cycle was 48 hours.

B. Water Baths

Two identical water-baths were used to elevate the temperature of the samples in 10°F intervals. Each consisted of a cylindrical stainless-steel container of 9 3/4 inches in height and 8 5/8 inches in diameter. The container was seated on a hot plate and the temperature was regulated by means of a thermocouple type temperature controller which was used to regulate the electrical input to the heating element. One bath had a West-800 controller with a precision of regulation of ±1°F while the other had a Love Controls controller with a precision of ±1°F. A copper coil was put in each one of the containers. By means of a small pump, cold water was forced through the coil as a cooling source when temperatures between 32° and ambient were desired. While the samples were held at a constant temperature in one of the water baths, the other was equilibrating to the next desired temperature, 10°F higher.

3.2 Sample Holder

5-ml long neck glass ampules were used as sample holders. The same sample holder was used throughout each experiment, from freezing to collapse determination. In order to be held in place in the water bath, the ampules were put in a circular rack and weights were placed on their neck.

3.3 Experimental Procedure

The following flow diagram gives the principle steps required for each experiment.

SAMPLE PREPARATION

FREEZING

FREEZE-DRYING

HUMIDIFICATION

MOISTURE CONTENT DETERMINATION

SEALING

COLLAPSE

3.3.1 Sample Preparation

Table II is a list of all systems used in this study and the corresponding concentration:

Table II

	Material	Concentration, w/v
1. Pure systems*		
Carbohydrates	maltose	25%
	lactose	25%
	sucrose	25%
	maltrin M-100	25%
	maltrin M-150	25%
	maltrin M-200	25%
	maltrin M-250	25%
Liquid Foods**	orange juice	14.18%
	apple juice	13.5%
2. Mixed systems*		
	sucrose:maltose	12.5%:12.5%
	sucrose:Lactose	12.5%:12.5%
3. Systems with additives		
	sucrose, 25% + 2% starch	
	apple juice + 10% maltose	
	orange juice + 10% maltose	
	orange juice + 2% starch	
	orange juice + 2.5% maltrin***	
	orange juice + 5% maltrin	
	orange juice + 10% maltrin	
	orange juice + 15% maltrin	
	orange juice + 20% maltrin	
	orange juice + 1% Gum Arabic	
	orange juice + 3% Gum Arabic	
	orange juice + 6% Gum Arabic	
	orange juice + 3% Locust Bean Gum	
	orange juice + 3% Tragacanth Gum	
	orange juice + 3% Karaya Gum	
	orange juice + 3% Tapioca Dextrin	
	orange juice + 6% Tapioca Dextrin	
	orange juice + 10%Tapioca Dextrin	

* all solutions were made in distilled water unless otherwise indicated

** in the case of the juices, frozen concentrated juice was used, reconstituted according to the instructions on the can.

*** Maltrins used were: M-100, M-150, M-200, M-250

After the solution was prepared, preweighed ampules were filled by means of a syringe. 2 ml of solution were delivered to each ampule. The next step was freezing. The samples were frozen in a tilted position so that a greater surface could be obtained which aided the visual determination of collapse. The samples were frozen either overnight in the 0°F room (slow freezing) or in liquid nitrogen (fast freezing). Both methods of freezing were usually used in order to observe the difference in collapse temperature.

After the samples were frozen, they were put in the freeze-drier for 48 hours (either in the main body or in side-flasks). Using an analytical balance, the weight of freeze-dried solids was determined for each sample.

3.3.2 Experimental Procedure for Humidification and Moisture Determination

After freeze-drying, the samples were humidified to different moistures, ranging from 0% to around 10% moisture content. A typical series of samples, meant for the same experiment usually contained 7 or 8 different moistures in the mentioned range. Two ampules were used for each moisture and for each freezing method.

The humidification took place at 32°F to avoid any possible collapse. Two methods of humidification were followed. In the first, the samples were held in a dessicator together with a saturated solution of K_2SO_4 in water (97%RH) under vacuum for different times so that they were allowed to pick up different amounts of water. In the second, a whole series of constant humidity solutions ranging from

LiCl (11%RH) to K_2SO_4 (97%RH) was used, and the holding time was the same for all samples.

After humidification, the samples were carried in ice to the analytical balance where the moisture pick-up was determined gravimetrically and then expressed as a % of the total weight of dry solids in the ampule.

3.3.3 Experimental Procedure for Collapse Measurement

Immediately after moisture determination, the ampules were sealed by stretching their neck while heating in the flame of a propane torch.

The ampule was wrapped in a towel dipped in ice-water to avoid any collapse due to heat of sealing.

In the meantime, one of the two containers of the bath had been equilibrated to the lowest possible temperature (40°F) and the sealed samples were put in this container while the thermostat of the other container was set 10°F higher (i.e. at 50°F). The elevation of temperature was continued until all samples collapsed or until the maximum capacity of the bath was reached (~210°F).

An oil bath or an oven was used for temperatures above 212°F. Collapse was observed visually from the change of the appearance of the sample's surface. The collapsed sample resembles a highly viscous material rather than a solid. The photograph in Figure 8 indicates the visual difference between a collapsed and an uncollapsed sample.

Samples were allowed 45 min for collapse (See Appendix B).

(A) (B)

FIGURE 8

VISUAL DIFFERENCE BETWEEN AN UNCOLLAPSED (A) AND A COLLAPSED (B) SAMPE OF SUCROSE

3.3.4 Data Treatment

The collapse temperature of each moisture was plotted against the moisture content of that sample. A family of curves was obtained which showed how T_c changes with moisture content.

Also, a correlation of the viscosity of the initial solution with the collapse temperature was attempted.

The effects of initial concentration and molecular weight were investigated to find out if there is a dependence of collapse temperature on these parameters.

The mode of freezing and its effect on collapse temperature was also considered in the results.

4. RESULTS AND DISCUSSION

The major aim of this study is to determine the collapse temperature of various freeze-dried carbohydrate solutions as a function of their moisture content. Carbohydrates were selected as they simulate well fruit juices, which have high sugar contents.

For this purpose, the solutions were first freeze-dried and then humidified to different moisture contents ranging from 0% to around 10%. In this study "0%" moisture content is based on the assumption that the residual moisture after freeze-drying is negligible. This moisture content is defined as "0%". Then, the samples were placed in a water bath and the temperature was elevated at suitable time intervals in steps of 10°F. At each step, the samples were withdrawn and checked for collapse visually.

Presently, there are two theories explaining collapse. The first explains collapse of materials that form eutectic solutions. In this case, collapse comes mainly as a result of gravity forces(Ito 1970 a,b, 1971). The second theory considers the matrix as a concentrated amorphous aqueous solution, which becomes less viscous, as the temperature becomes higher, due to greater dilution in water as well as the temperature effect. Surface forces acting at the surfaces of open capillaries left by sublimed ice needles predominate, in this case, over gravity forces in causing the collapse.(Bellows, 1972).

4.1 Method for Presentation of Results

The experimental results have been divided into 3 major topics:

A) Single-component systems

B) Multi-component systems

C) Fruit juices with additives

Each of these sections have in turn been divided into subdivisions covering each substance individually. A short discussion follows the figure showing the experimental results. A separate section is devoted to the correlation of viscosity to collapse temperature. A general discussion where all the results are taken together, closes this chapter.

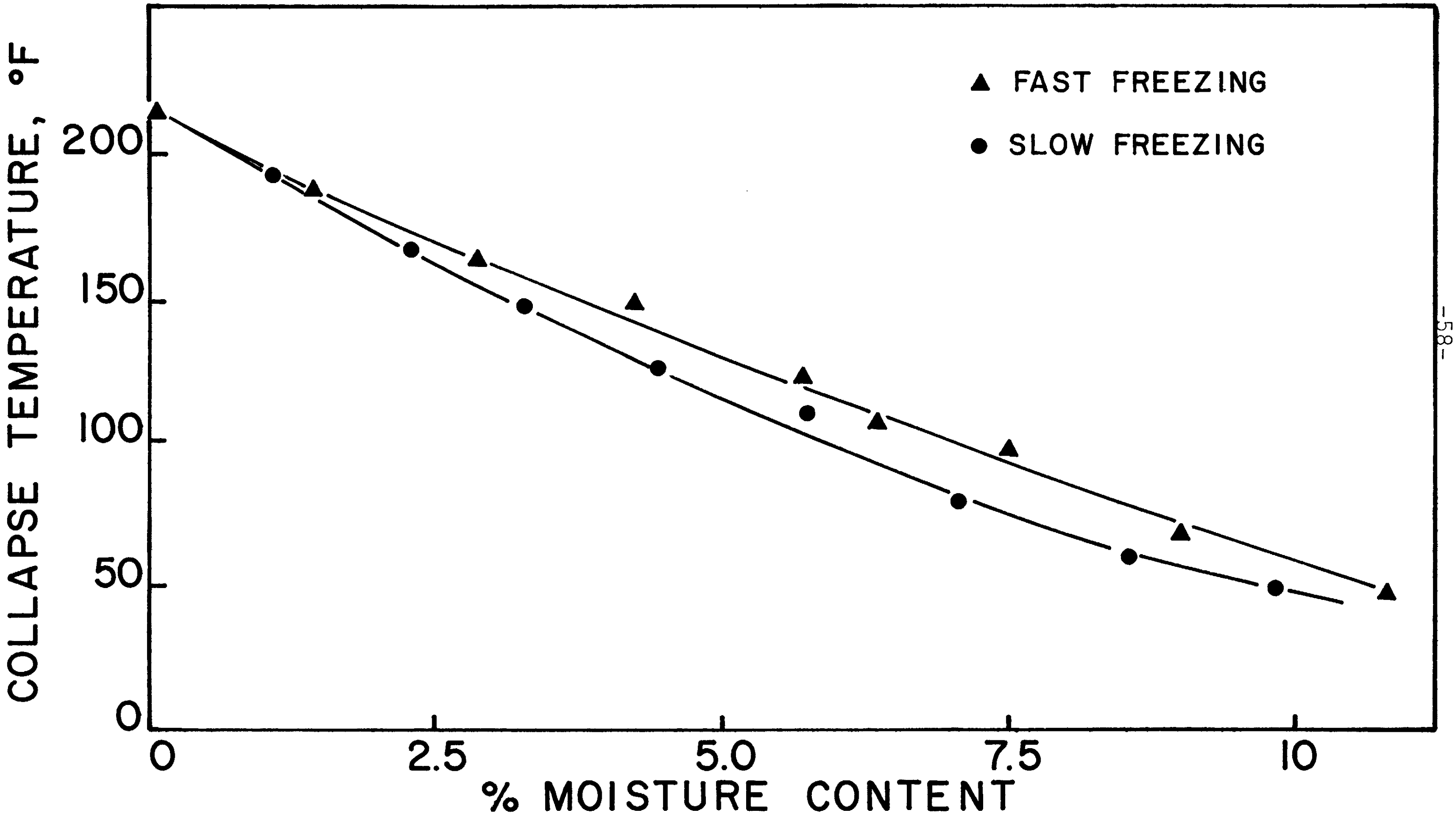
4.2 Single-Component Systems

The data of this section are tabulated in Appendix A.

a) Lactose

Figure 9 shows the change in collapse temperature of freeze-dried solutions of lactose (25% lactose in distilled water, w/v) with varying moisture content. As will be seen, the collapse temperature of lactose is the highest of the three sugars examined, at all moisture contents, being 214°F for the 0% moisture level. There is also a distinct difference between the curve of T_c vs % mc for fast frozen samples and the same curve for slowly frozen samples. Fast frozen samples have a higher collapse temperature than samples of the same moisture content frozen slowly, especially at high moisture contents. The rate of freezing is, therefore,

FIGURE 9. COLLAPSE TEMPERATURE VS. MOISTURE CONTENT FOR LACTOSE (25% SOLIDS, FAST AND SLOW FREEZING)



a factor determining collapse temperature in lactose solutions. It should also be noted that the rate of moisture pick up during humidification was higher in the fast frozen samples than in those slowly frozen. The quality of the freeze-dried lactose cake was good in that there wasn't any observable collapse during freeze-drying. Subsequent references to cake "quality" refer to absence of collapse prior to humidification.

b) Maltose

Figure 10 is a plot of collapse temperature against moisture content for maltose. The collapse temperature of maltose is also high, although, a little lower than that of lactose. Dry maltose collapses at 205°F. The mode of freezing affects the collapse temperature of the freeze-dried and rehumidified solution. In this case, the slowly frozen samples show a slightly higher collapse temperature at all moistures than the fast frozen samples, while in lactose it was the other way around. This difference disappears at 0% moisture content and again at around 8% moisture content. The quality of the freeze-dried maltose cake is also good. There was no observable collapse of the matrix during freeze-drying.

c) Sucrose

The change in collapse temperature with moisture content for sucrose is shown in Figure 11. There is a distinct difference for this sugar from the two examined previously: the collapse temperature is considerably lower, dry sucrose collapsing at 132°F for both fast and slow freezing.

FIGURE 10. COLLAPSE TEMPERATURE VS. MOISTURE CONTENT FOR MALTOSE (25% SOLIDS, FAST AND SLOW FREEZING)

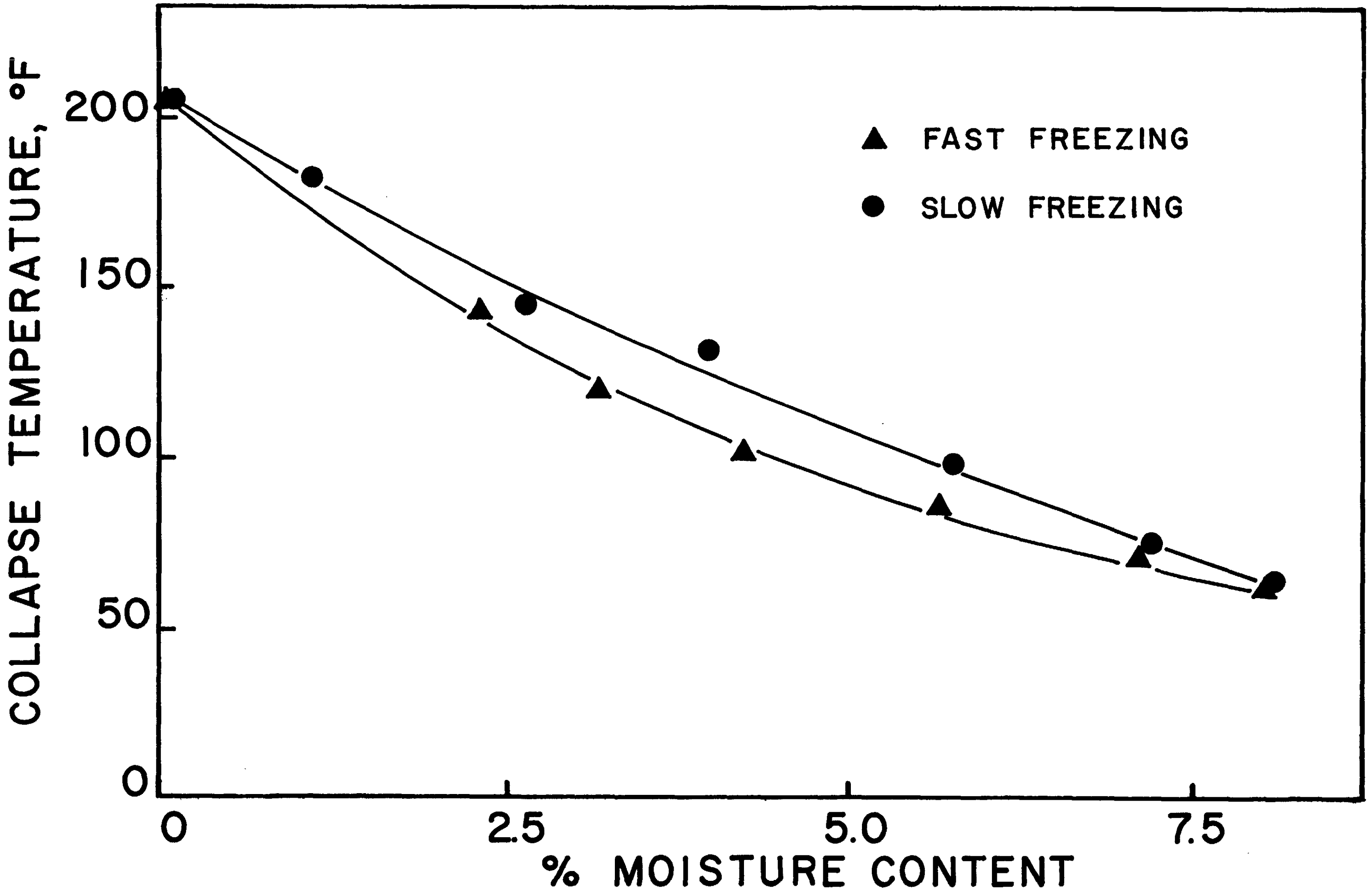
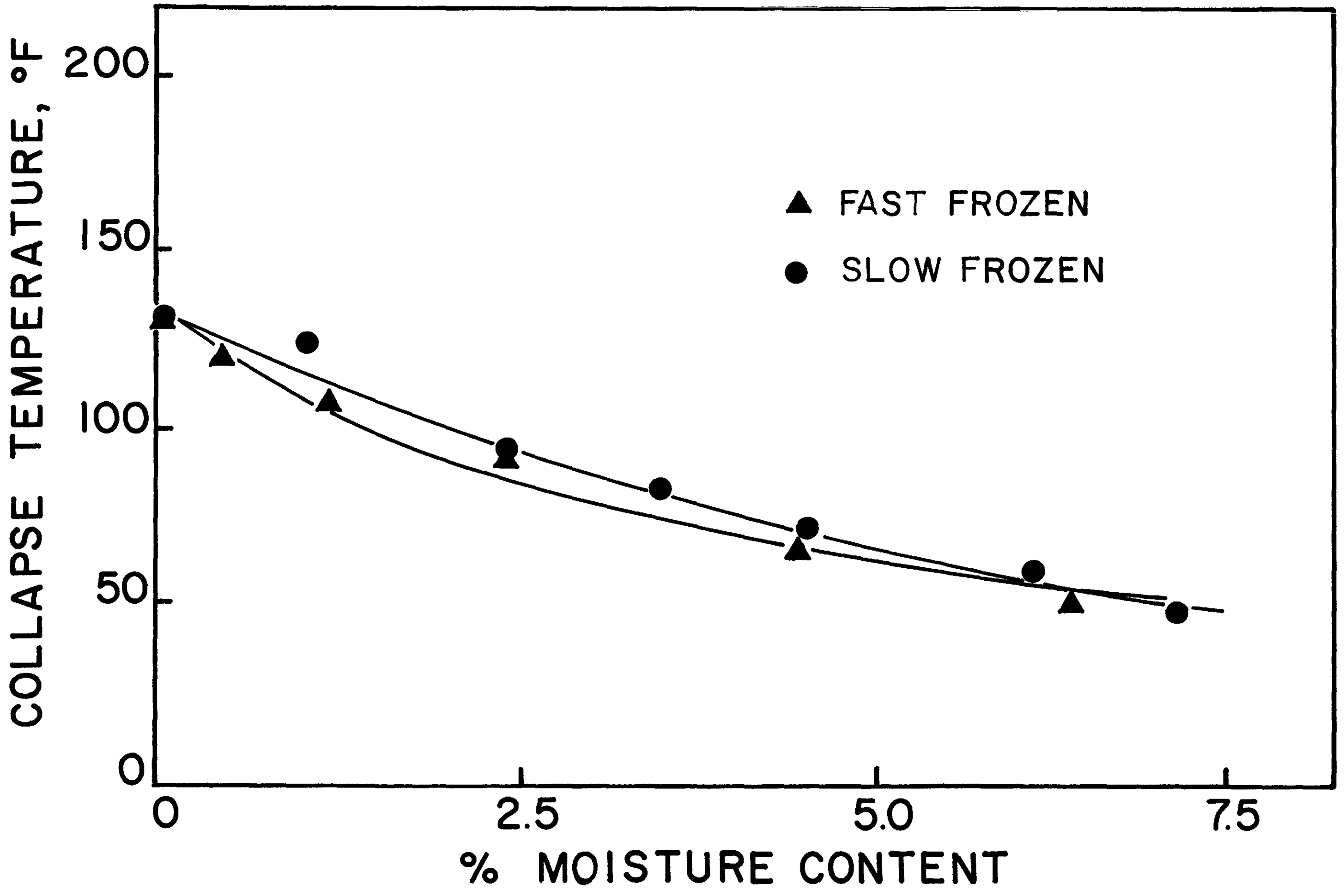


FIGURE 11. COLLAPSE TEMPERATURE VS. MOISTURE CONTENT FOR SUCROSE (25% SOLIDS, FAST AND SLOW FREEZING)



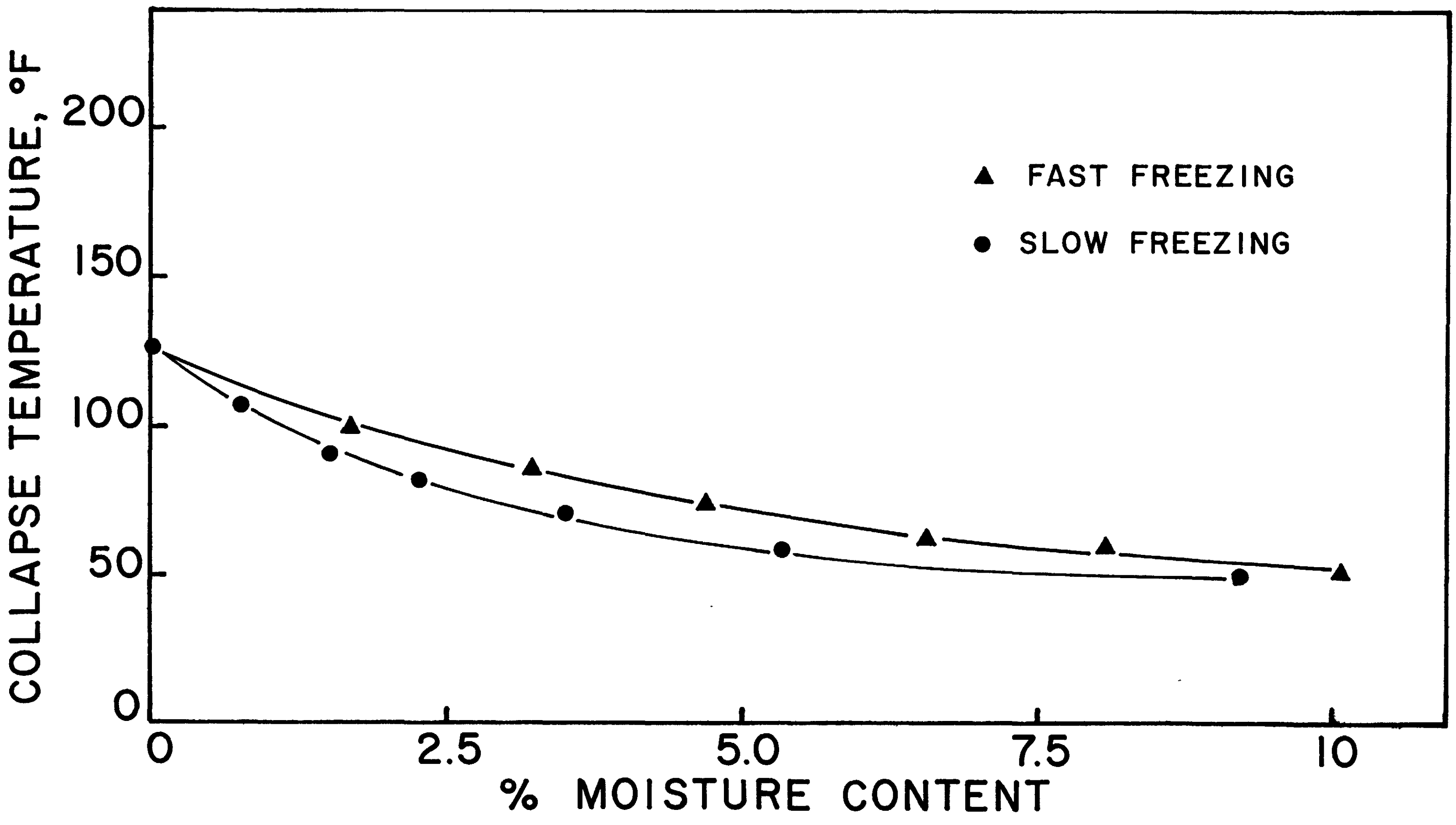
Differences in the collapse curve between samples frozen slowly and samples frozen rapidly are slight. In this case, there is a tendency for samples frozen slowly to show a slightly higher collapse temperature. The quality of the freeze-dried sucrose cake is not as good as in the case of the two previous sugars examined, but it is acceptable.

d) Orange juice

As shown in Figure 12, the collapse temperature of pure orange juice is relatively low, the dry (0% mc) collapsing at 125°F. This collapse temperature is very close to that of sucrose and this is expected due to the high content of sucrose in orange juice. According to Bellows (1972), 50% of the sugar composition of orange juice is sucrose. The orange juice used in this and the following experiments was a commercial one known under the name of Family Care.

In this case, there is less difference between the two curves (slow-fast freezing) than in the previous cases. Both curves start at the same temperature at 0% moisture (125°F) and meet again at around 10% moisture content, the slow frozen samples giving collapse temperatures several degrees lower at all moistures. A point of interest in this case is the quality of freeze-dried orange juice. During the initial steps of freeze-drying there is melting and puffing which give a second-rate quality to the final freeze-dried product. It is interesting to see how different additives affect this quality. This will be examined in experiments described later. It is also interesting to note that fast frozen juice takes

FIGURE 12. COLLAPSE TEMPERATURE VS. MOISTURE CONTENT FOR ORANGE JUICE (14.2% SOLIDS, FAST AND SLOW FREEZING)



up moisture faster than the slowly frozen juice (Rate 1:2).

e) Apple juice

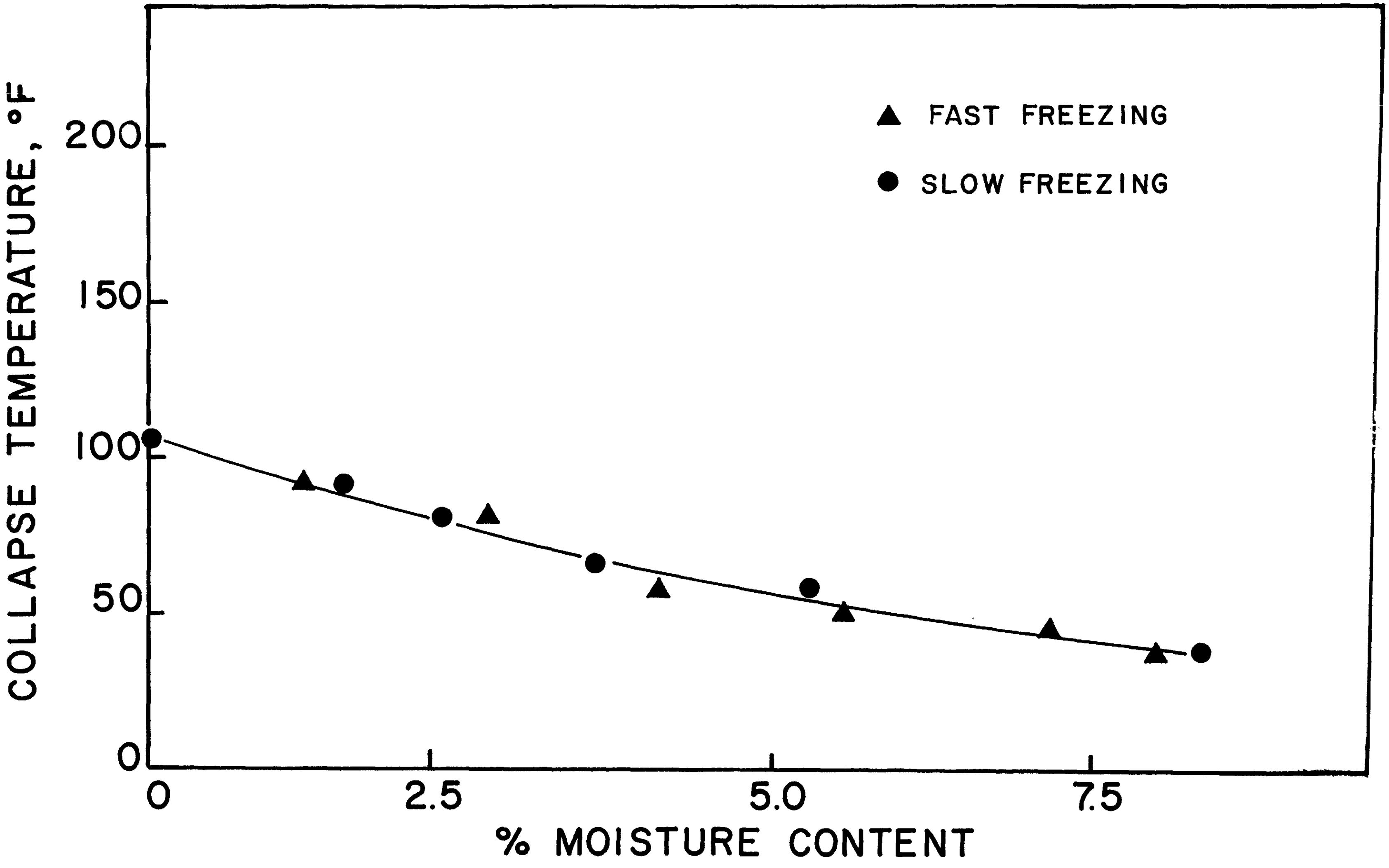
Figure 13 shows the collapse temperature of apple juice as a function of moisture content. Apple juice exhibits the lowest collapse temperature of all the systems examined so far. Dry apple juice collapses at 109°F. Different modes of freezing do not affect the collapse temperature much. There is a little difference in the intermediate moistures (2.5% - 7.5%), the slowly frozen samples having a slightly higher collapse temperature than the fast frozen. Both curves start at the same point (0% mc) and meet again at around 7.5% mc.

The major problem in freeze-drying apple juice is the low collapse temperature (-41.5°C according to Bellows). This makes the material difficult to freeze-dry and the result is a poor quality of the final freeze-dried cake - due to partial collapse during freeze-drying and also due to excessive puffing. This behavior of the apple juice is expected as 54-67% of its sugar content is fructose which has a low collapse temperature.

f) Maltodextrins

Maltodextrins are starch hydrolysates characterized by a number known as dextrose equivalent. The dextrose equivalent denotes the total reducing sugar content on a dry basis and for the maltodextrins it ranges from 5 to 95 D.E. (dextrose equivalent). The following table gives an idea

FIGURE 13. COLLAPSE TEMPERATURE VS. MOISTURE CONTENT FOR APPLE JUICE (13.5% SOLIDS, FAST AND SLOW FREEZING)



of the composition of the maltodextrins (see Table III).

TABLE III

Composition of Corn Starch Hydrolysates

	Hydrolysate			
	9-12 D.E.	13-17 D.E.	18-22 D.E.	23-27 D.E.
Carbohydrate Composition				
Dextrose	0.5	1.0	1.0	2.5
Disaccharides	3.5	3.5	6.0	5.0
Trisaccharides	6.5	7.5	8.0	8.5
Tetrasaccharides and higher	89.5	88.0	85.0	84.0

As it can be seen from the table, the properties of dextrose are approached at higher D.E., and the properties of starch are approached as D.E. decreases.

Viscosity of solutions (at equal concentration) increase with decreasing D.E., and the low level of reducing sugars results in less browning, lower hygroscopicity and lower sweetness. D.E. generally decreases with increasing molecular weight of the substance.

The maltodextrins examined in this study, are sold commercially under the trade mark MALTRINS (Grain Processing Co., Murcotine, Iowa) and they are characterized by the letter M followed by a number ten times their average D.E. number. Thus, an M-150 is a maltodextrin with a D.E. of 15 (Murray and Luft, 1973).

The maltrins used in this experiment are: M-100, M-150, M-200, M-250. They all have a common characteristic: an extremely high collapse temperature. As it can be seen from Figure 14, all four maltrins collapse in the dry state, between 400°F and 480°F. These values refer to freeze-dried solutions of 25% w/v in distilled water. The collapse temperature is a function of the D.E. of the maltrin. Maltrins with higher D.E., that is, with lower molecular weight, show a lower collapse temperature (M-250 at 400°F) while maltrins with lower D.E. (higher molecular weight) have a higher T_c (M-100 at 480°F). Maltrins with intermediate D.E. collapse at intermediate temperatures (M-200 and M-150 collapse at 450°F).

Rate of freezing was not found to have any effect on the collapse temperature of maltrins. The freeze-dried cake showed no melting or puffing but it had low bulk structural strength and it broke into pieces upon gentle agitation.

4.3 Multi-component systems

The data of this section are tabulated in Appendix A.

a) Lactose-Sucrose

Figure 15 shows the curve of collapse temperature vs moisture content

FIGURE 14. COLLAPSE TEMPERATURE VS. MOISTURE CONTENT OF MALTODEXTRINS (25%, W/V)

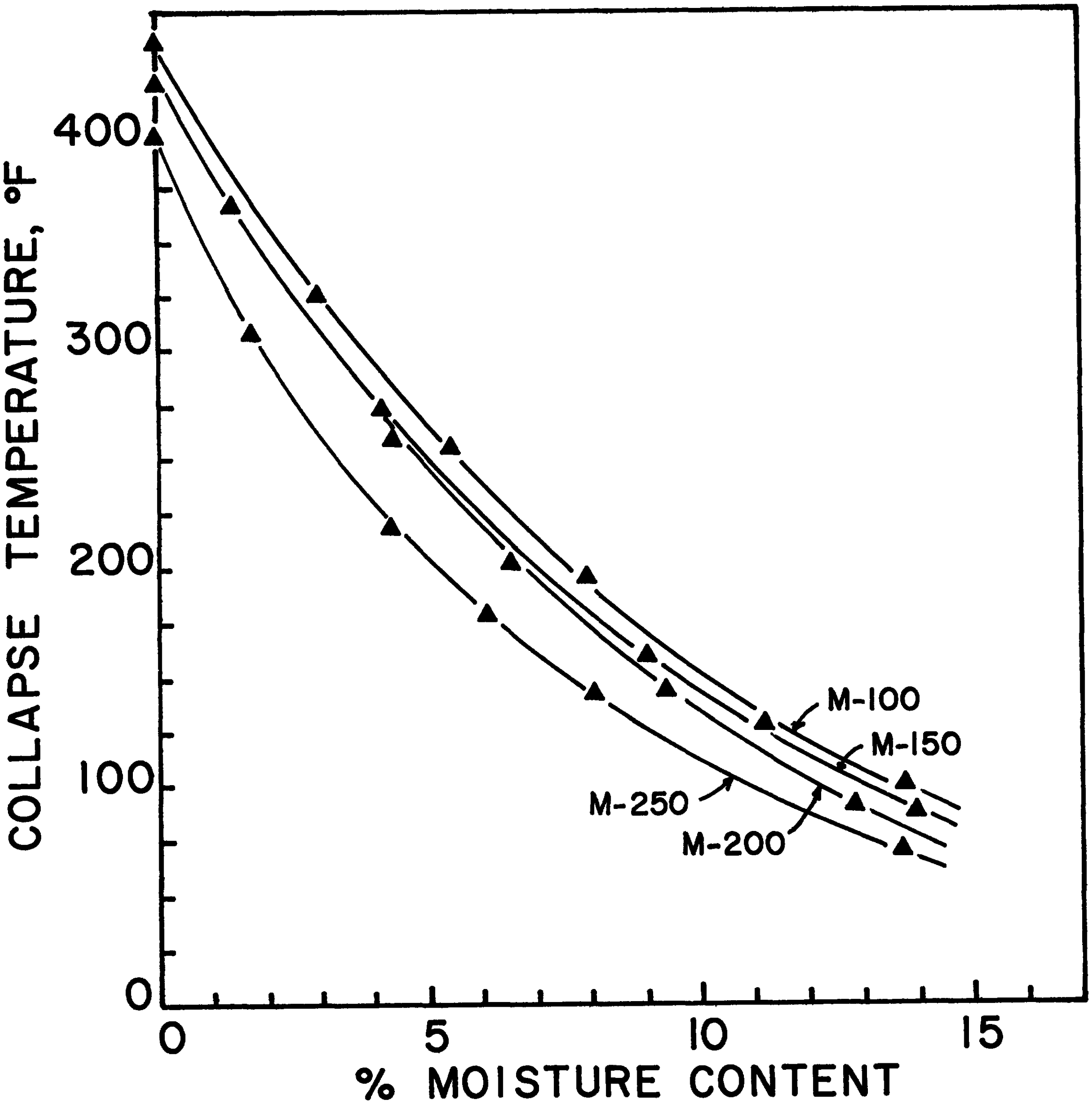
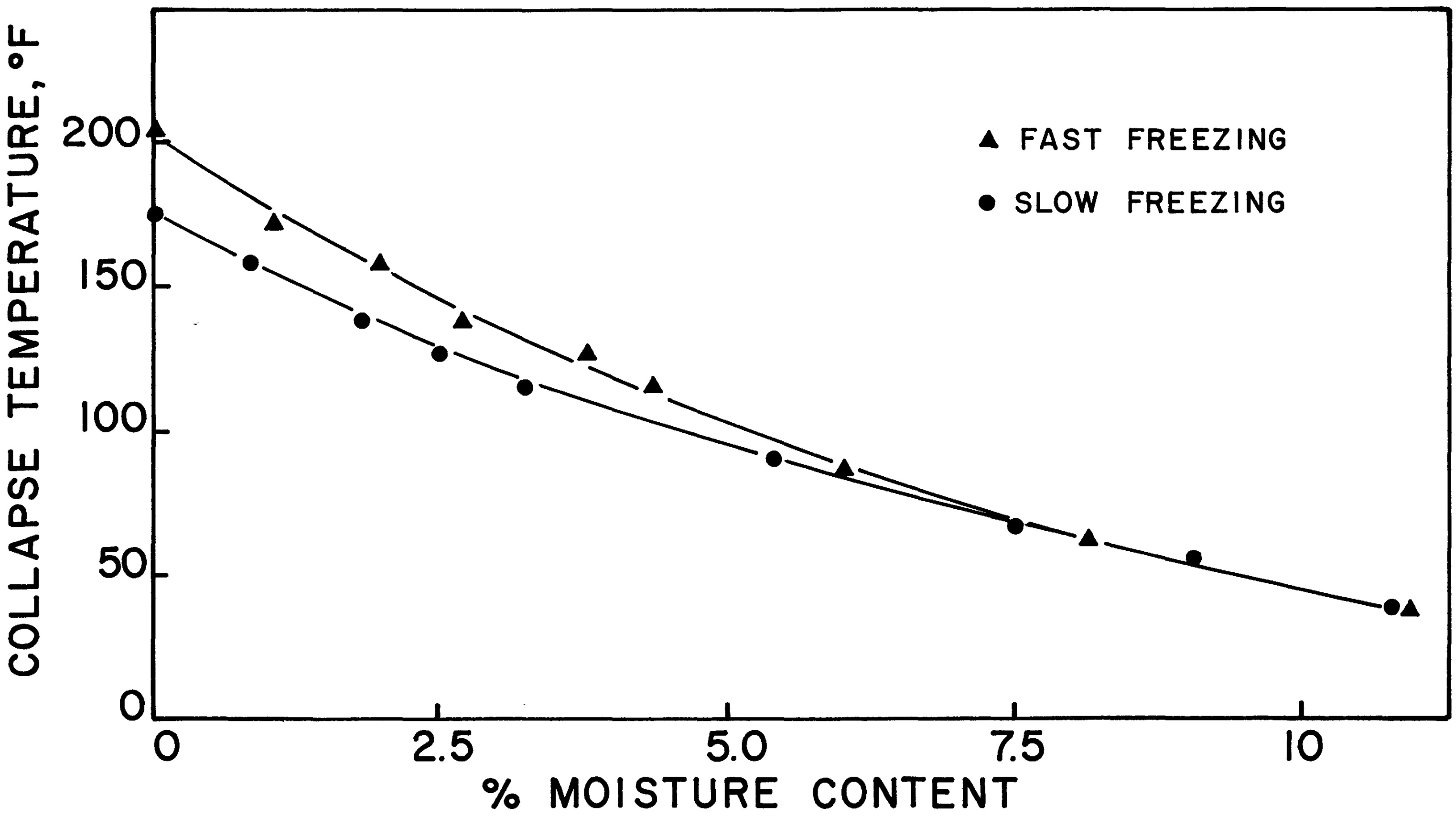


FIGURE 15. COLLAPSE TEMPERATURE VS. MOISTURE CONTENT FOR A MIXTURE OF SUCROSE-LACTOSE (12.5% - 12.5% SOLIDS, FAST AND SLOW FREEZING)

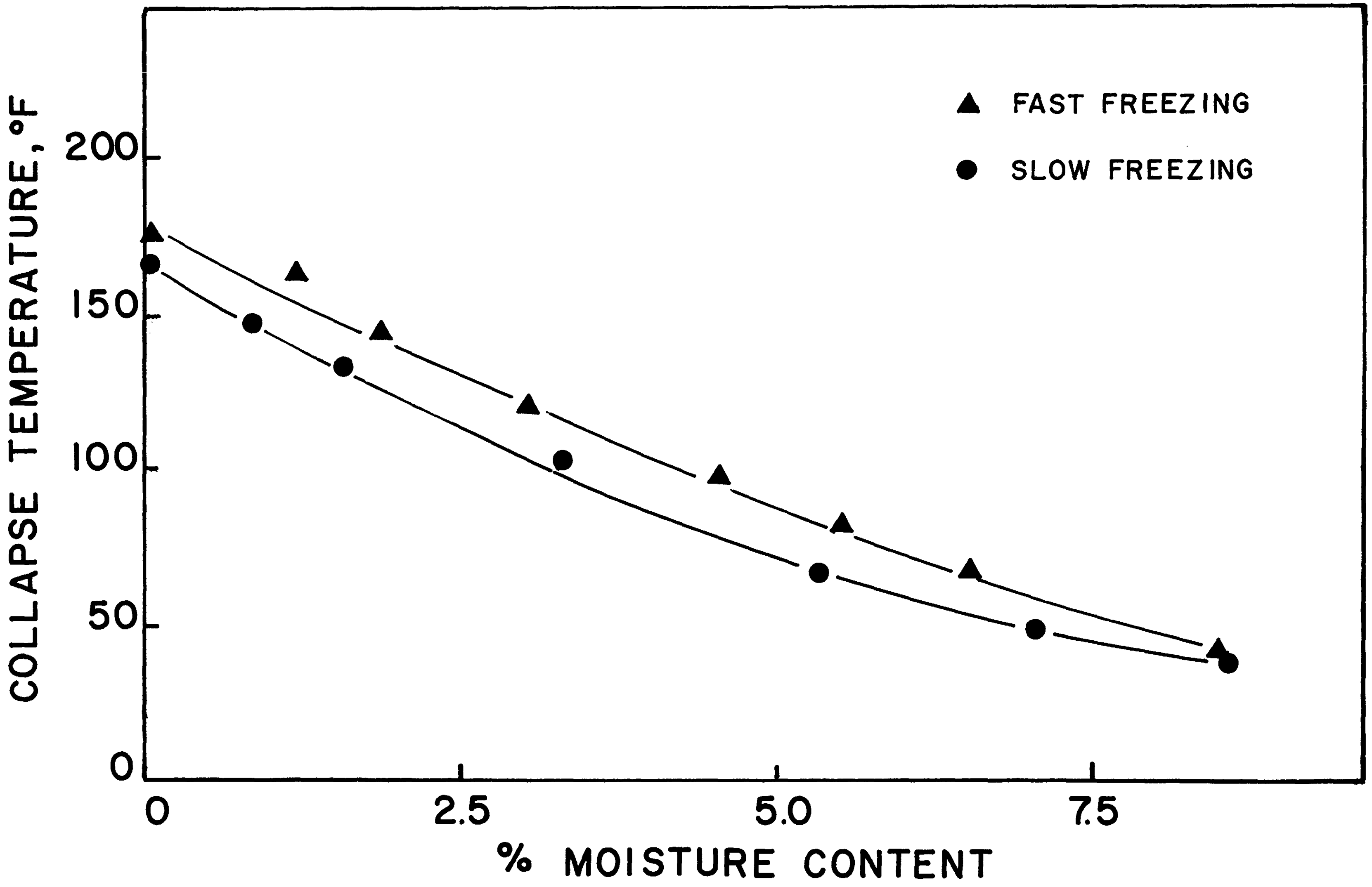


for a mixture of lactose with sucrose (12.5%-12.5% in the original solution). This curve is found to be approximately halfway between the curves of lactose and sucrose (see Fig.9 and Fig.11). The same is true for both modes of freezing, slow and fast, although in fast freezing the curve of the mixture is closer to lactose than to sucrose. The dry mixture is found to collapse at 174°F for the slowly frozen sample and at 204°F for the fast frozen samples. Fast freezing exhibits a higher collapse temperature until around 7% moisture content. At that point the curves meet and there is no dependence of T_c on mode of freezing for higher moistures. The freeze-dried cake is of good quality, similar to that of lactose.

b) Maltose-Sucrose

The curve of T_c vs moisture content for a solution of a mixture of maltose with sucrose exhibits behavior intermediate between those of pure maltose and pure sucrose (see Figure 16). In the case of slow freezing, the curve of the mixture is approximately in the middle between the curves of the two sugars. In fast freezing, the curve appears to be closer to maltose, the sugar with the highest collapse temperature. The same pattern appeared in the mixture of sucrose-lactose discussed previously.
The mode of freezing also affects the collapse temperature. Dry samples (0% mc), that have been frozen slowly, have a T_c of 164°F while the fast frozen samples collapse at 176°F. The curve representing fast freezing is higher at all moistures than the curve of the slow freezing. The freeze-dried cake of the mixture is of good quality, similar to that of maltose

FIGURE 16. COLLAPSE TEMPERATURE VS. MOISTURE CONTENT FOR A MIXTURE OF SUCROSE-MALTOSE (12.5% - 12.5% SOLIDS, FAST AND SLOW FREEZING)



(rather than sucrose).

4.4 Fruit juices with additives

The data of this section are shown in Appendix A.

a) Orange juice + 10% maltose

Figure 17 shows the collapse temperature of orange juice(14.2% solids) with 10% w/v of maltose as additive. The addition of maltose, a sugar with high collapse temperature, causes an elevation of the curve T_c vs % mc towards higher collapse temperatures. This elevation is greater at the lower moisture content. As it can be seen from Figures 12 and 17, the curves that represent fast freezing for orange juice with maltose and for pure juice differ only at the lower moisture content, between 0 and 1.5% mc, while the curves for slow freezing show a difference in T_c of 25°F at 0% mc and a difference of only 6°F at 7.5% mc. Maltose as an additive proves to be more effective at slow rates of freezing (difference of 25°F at 0% mc) than at high rates of freezing (difference of 13°F at 0% mc). Fast frozen samples show a lower T_c in comparison to the slowly frozen ones. The addition of 10% maltose gives a freeze-dried cake of better quality in comparison with the quality of freeze-dried pure orange juice. There is less puffing and melting, but still the quality is far from resembling that of pure maltose at a concentration of 25% solids.

b) Orange juice with 2% starch

Figure 18 shows the effect of addition of 2% starch on the collapse

FIGURE 17. COLLAPSE TEMPERATURE VS. MOISTURE CONTENT FOR ORANGE JUICE WITH 10% MALTOSE (FAST AND SLOW FREEZING)

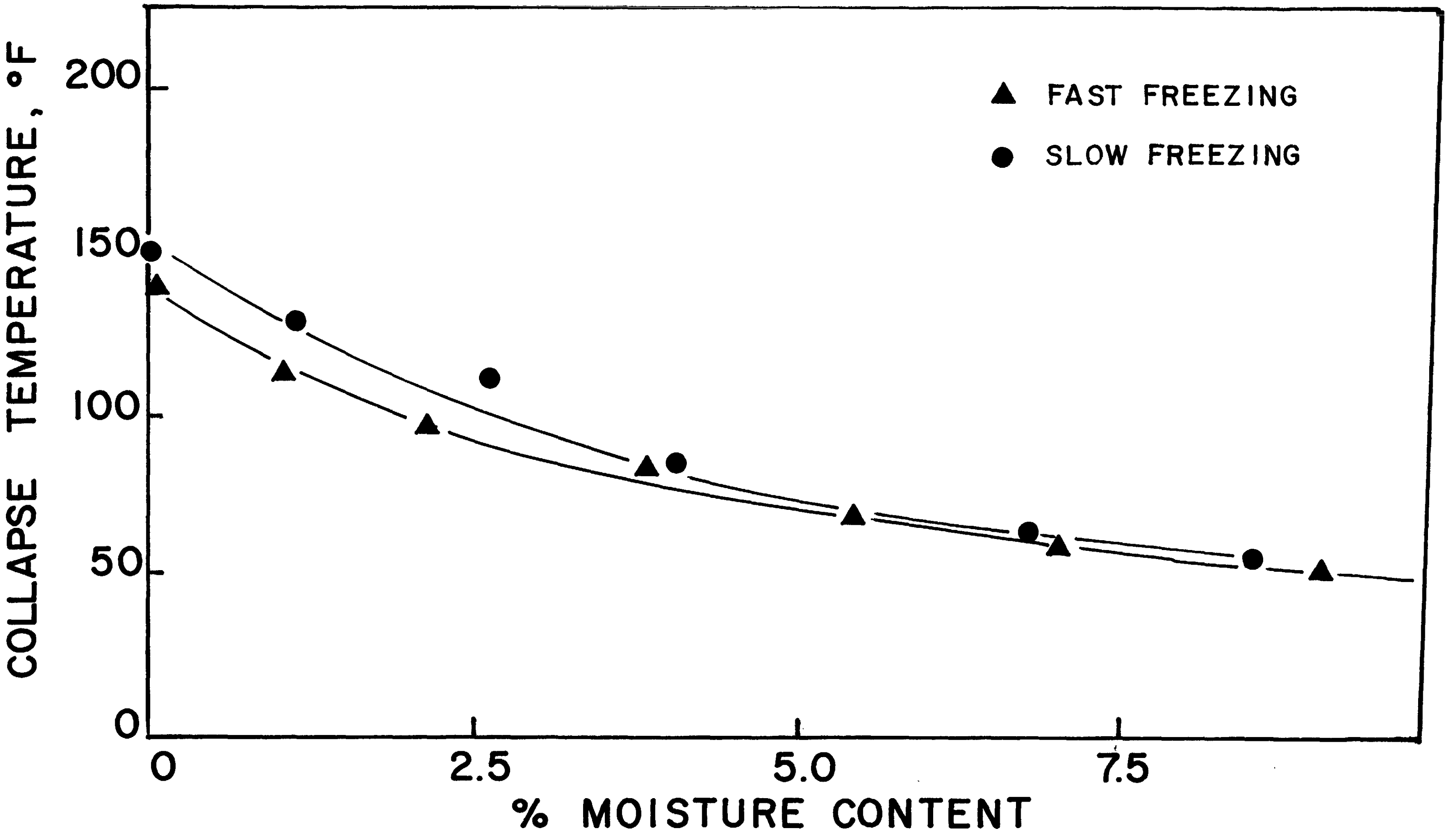
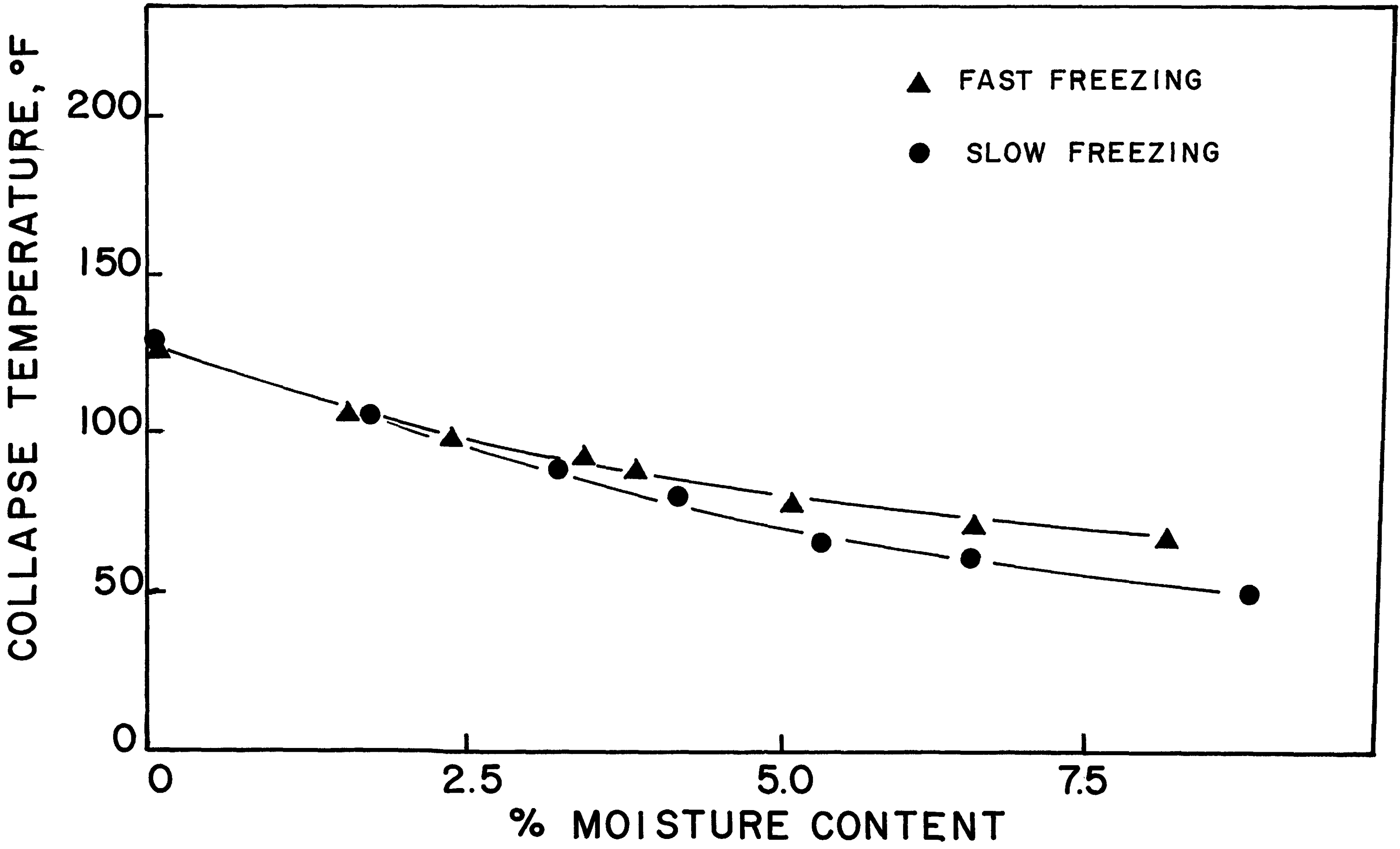


FIGURE 18. COLLAPSE TEMPERATURE VS. MOISTURE CONTENT FOR ORANGE JUICE WITH 2% STARCH (FAST AND SLOW FREEZING)

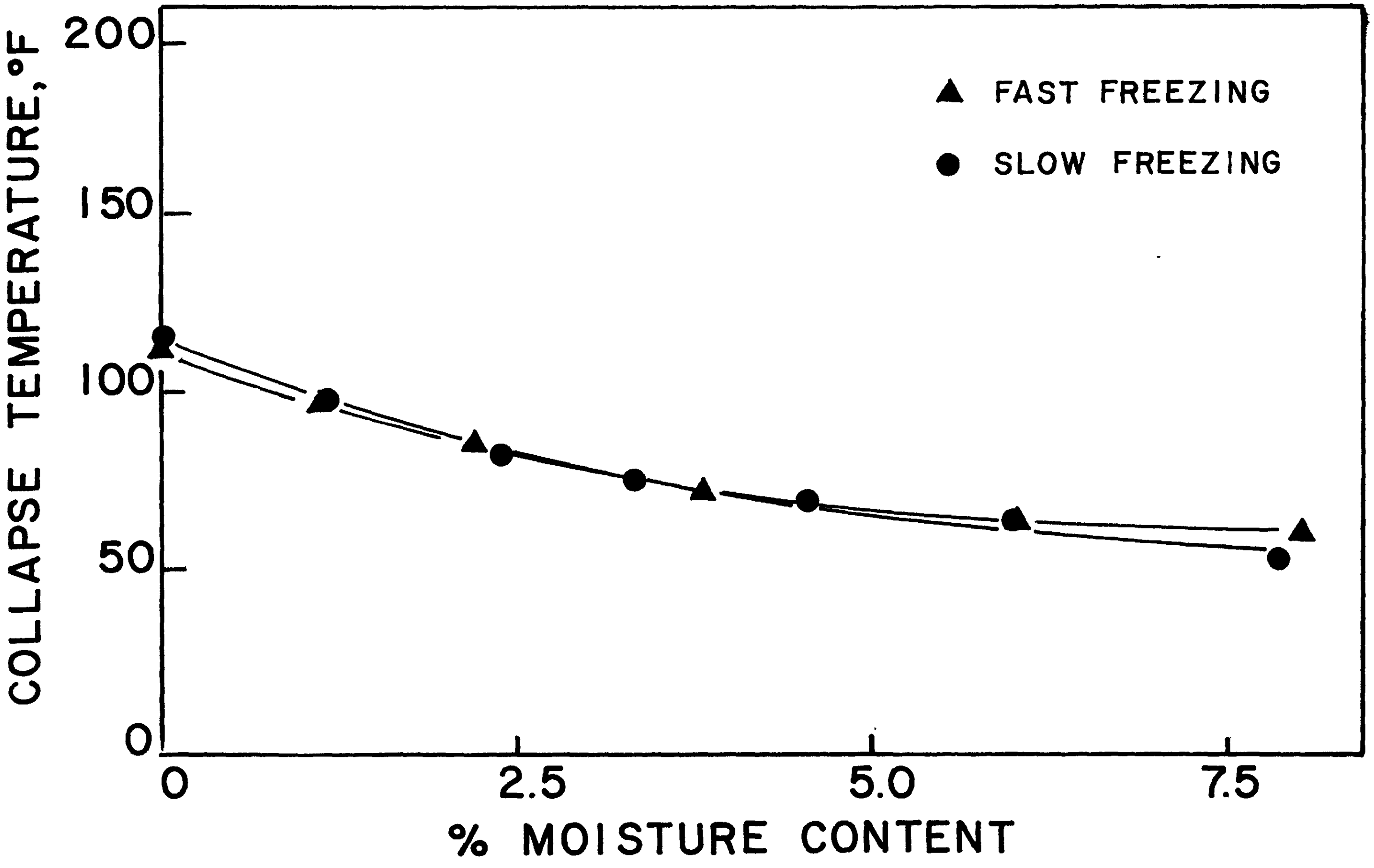


temperature of orange juice (see also Fig.12). Again, as in the case of maltose there is an elevation of the curve towards higher temperatures of collapse for both rates of freezing. This elevation is more intense, as in the case of maltose, in the curve for slow freezing but the greater elevations are now at moisture contents between 2% and 6%. At 0% moisture, there is little rise in T_c (from 125°F to 128°F) for both rates of freezing. The curves for slow freezing (representing pure juice and juice with starch) meet at around 8% mc. Fast frozen samples have a higher collapse temperature than the slowly frozen ones. The quality of the freeze-dried cake is not affected by starch as additive.

c) Apple juice with 10% maltose

The collapse temperature of apple juice is affected slightly by addition of maltose, as indicated in Figure 19 (see also Fig.13). For 0% moisture content, there is an elevation in T_c of approximately 10°F. This is the same for both rates of freezing. The elevation seems to be greater at higher moisture content that at lower moistures. This is true for the fast frozen and the slowly frozen samples. Also, the rate of freezing slightly affects the collapse temperature of the mixture, the larger difference being 5°F at the higher moistures. The curves go together until around 5% moisture and then split. Maltose does not have any effect on the quality of the freeze-dried cake at the concentration used, which is, as in the case of pure apple juice, unacceptable.

FIGURE 19. COLLAPSE TEMPERATURE VS. MOISTURE CONTENT FOR APPLE JUICE WITH 10% MALTOSE (FAST AND SLOW FREEZING)



d) Sucrose with 2% starch

Addition of 2% w/v of starch in solutions of sucrose (25% solids, w/v) has a substantial effect on the collapse temperature of sucrose, as indicated in Figure 20 (also, see Figure 11). The mode of freezing does not seem to substantially affect this mixture, so that both curves can appear as one. In both cases of freezing, the temperature of collapse is elevated, at most, 32°F (from 132°F to 164°F) at the lower moistures, when compared to the pure sucrose system. The quality of the freeze-dried cake is improved but there is still some degree of puffing.

e) Orange juice with maltodextrins

In this experiment, four maltrins (M-100,M-150, M-200, M-250) were used at different concentrations, as additives to orange juice, and the change of collapse temperature with increasing concentration was studied. The experiment was conducted at 0% moisture content. As Figure 21 shows, there is a considerable effect on the collapse temperature of dry juice with different concentrations of maltodextrins added. M-100, at a concentration of 20% w/v gives a T_c of 212°F, while M-250, at the same concentration elevates T_c of orange juice to 184°F. The same maltrins, at a concentration of 10% w/v give collapse temperatures of 183°F and 155°F respectively. M-150 and M-200 give values that lie in-between the ones mentioned above. These two maltrins give curves that are very close together with an average difference of approximately 5°F. Between 0 and 3% w/v

FIGURE 20. COLLAPSE TEMPERATURE VS. MOISTURE CONTENT FOR SUCROSE WITH 2% STARCH (FAST AND SLOW FREEZING)

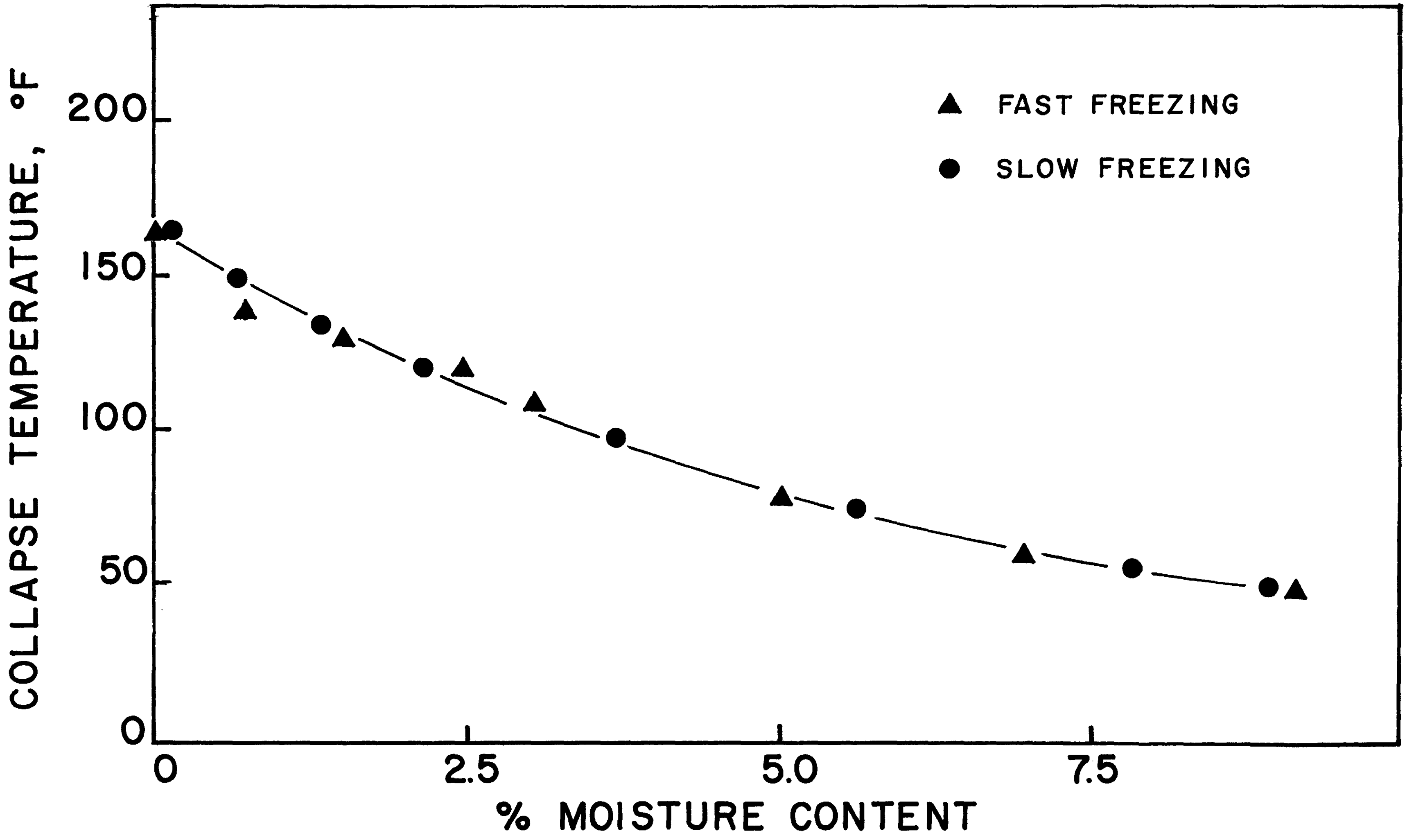
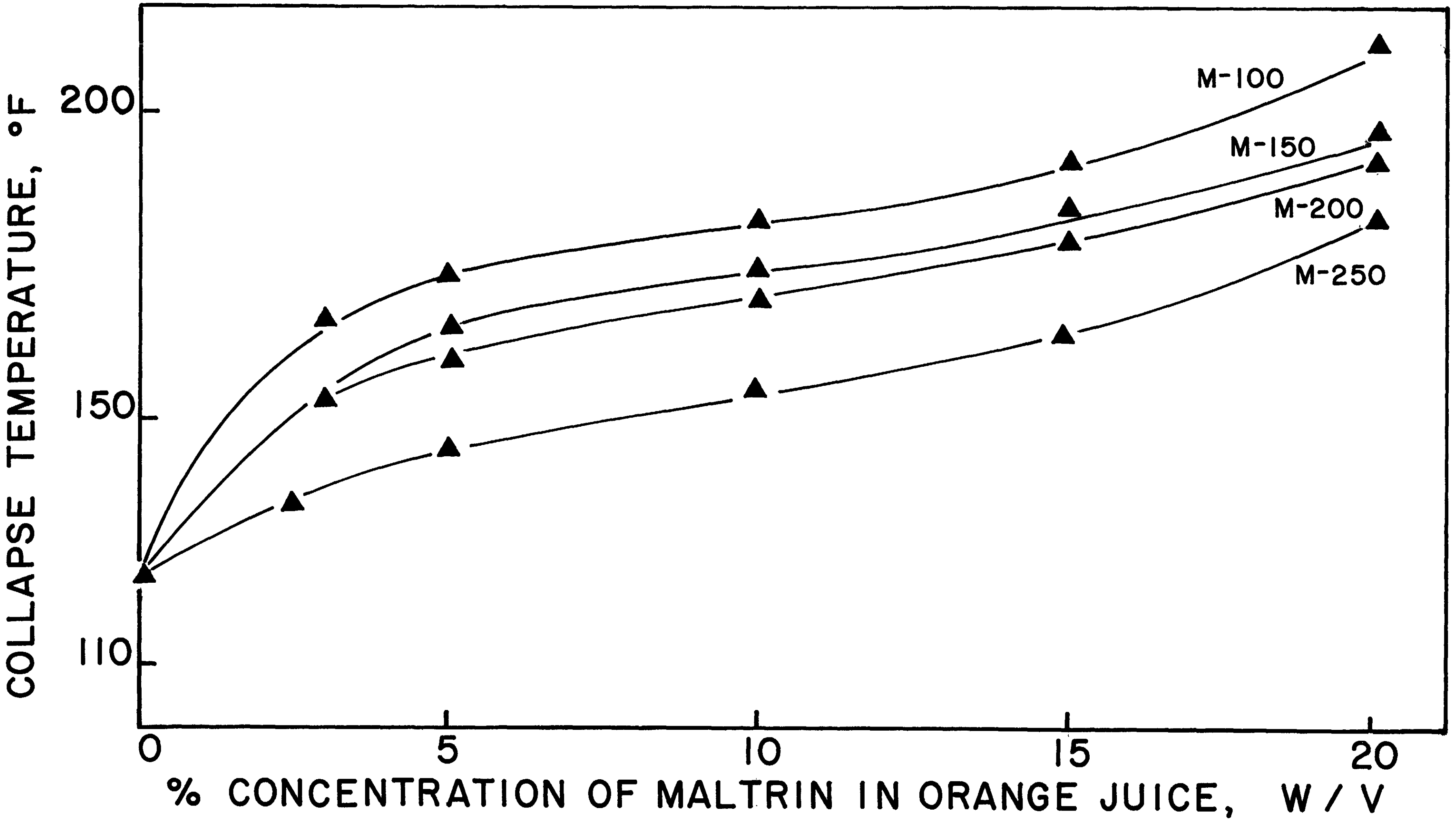


FIGURE 21. COLLAPSE TEMPERATURE VS. CONCENTRATION OF ORANGE JUICE WITH MALTRINS



of maltrin, M-150 and M-200 give the same curve. Another approach to considering these results is to note the way the collapse temperature changes with molecular weight. Low D.E. maltrins (higher average molecular weight) give higher collapse temperatures than high D.E. maltrins (at a given concentration). The quality of the orange juice freeze-dried cake is also greatly improved by the addition of maltrins. At higher concentrations there is no puffing and the cake resembles that of lactose and maltose.

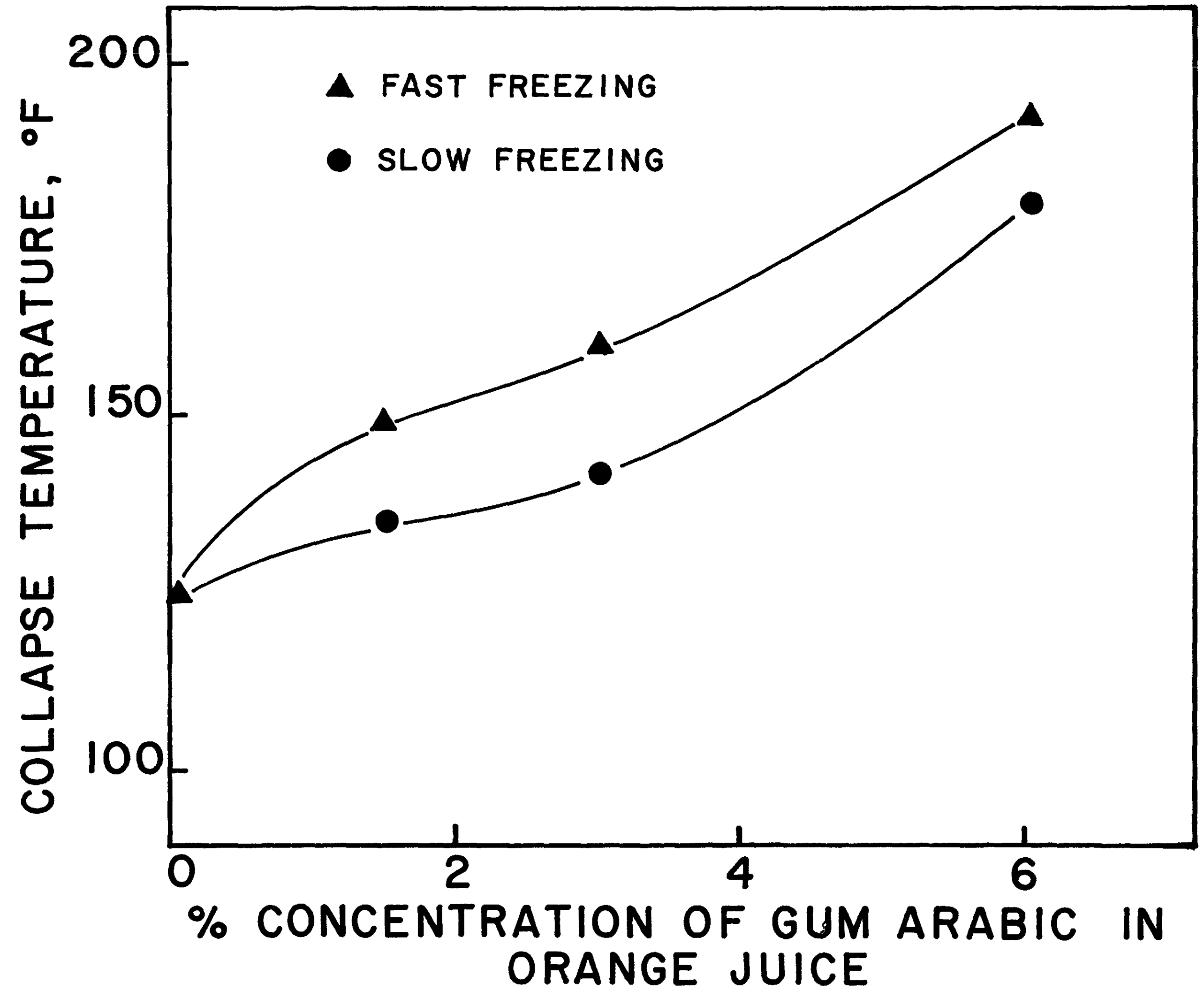
f) Orange juice with various gums

Five gums have been used in this experiment to study the effect of gum concentration in the collapse temperature of orange juice. The upper limit of the concentration was set by the amount of the specific gum that could be dissolved in orange juice with fixed stirring conditions. In all cases, the samples used contained no moisture (0% moisture content).

1. Gum Arabic

Figure 22 shows the increase in collapse temperature of orange juice with increasing concentration of Gum Arabic for 0% moisture content. There is a considerable increase in collapse temperature and it is affected by the mode of freezing. 6% Gum Arabic elevates the collapse temperature to 180°F for slow freezing and 193°F for fast freezing. Samples frozen slowly have a lower collapse temperature at all concentrations than samples frozen fast. There is also a con-

FIGURE 22. COLLAPSE TEMPERATURE VS. CONCENTRATION FOR ORANGE JUICE WITH GUM ARABIC



siderable effect on the quality of the freeze-dried cake. Puffing and cracking is very much limited in comparison to pure orange juice.

2. Tapioca Dextrin

This gum is usually used for flavor encapsulation. Its effect on collapse temperature of orange juice is shown in Figure 23. The curve T_c vs %C consists of two parts. The first part shows that there is elevation of the collapse temperature but it is independent of the concentration of the gum, up to 5%. After that point, a higher concentration will give a higher collapse temperature reaching 149°F for fast frozen samples and 173°F for slowly frozen samples. The collapse temperature in the region where T_c is independent of gum concentration is 133°F for fast freezing and 152°F for slow freezing. Tapioca Dextrin dissolves easily in orange juice and at high concentration (relative to other gums) but its effect on T_c is considerably less that the other gums examined. Also, the quality of the freeze-dried cake is not as good as in other cases involving gums.

3. Locust Bean Gum

This gum has a pronounced effect on the collapse temperature of orange juice. As Figure 24 shows, within a relatively narrow concentration range (up to 3%), T_c rises from 125°F (pure orange juice) to 212°F. The freezing rate has an effect on T_c, slowly frozen samples showing a lower collapse temperature than fast frozen samples, the greatest difference being about 10°F. The freeze-dried cake is of

FIGURE 23. COLLAPSE TEMPERATURE VS. CONCENTRATION FOR ORANGE JUICE WITH TAPIOCA DEXTRIN

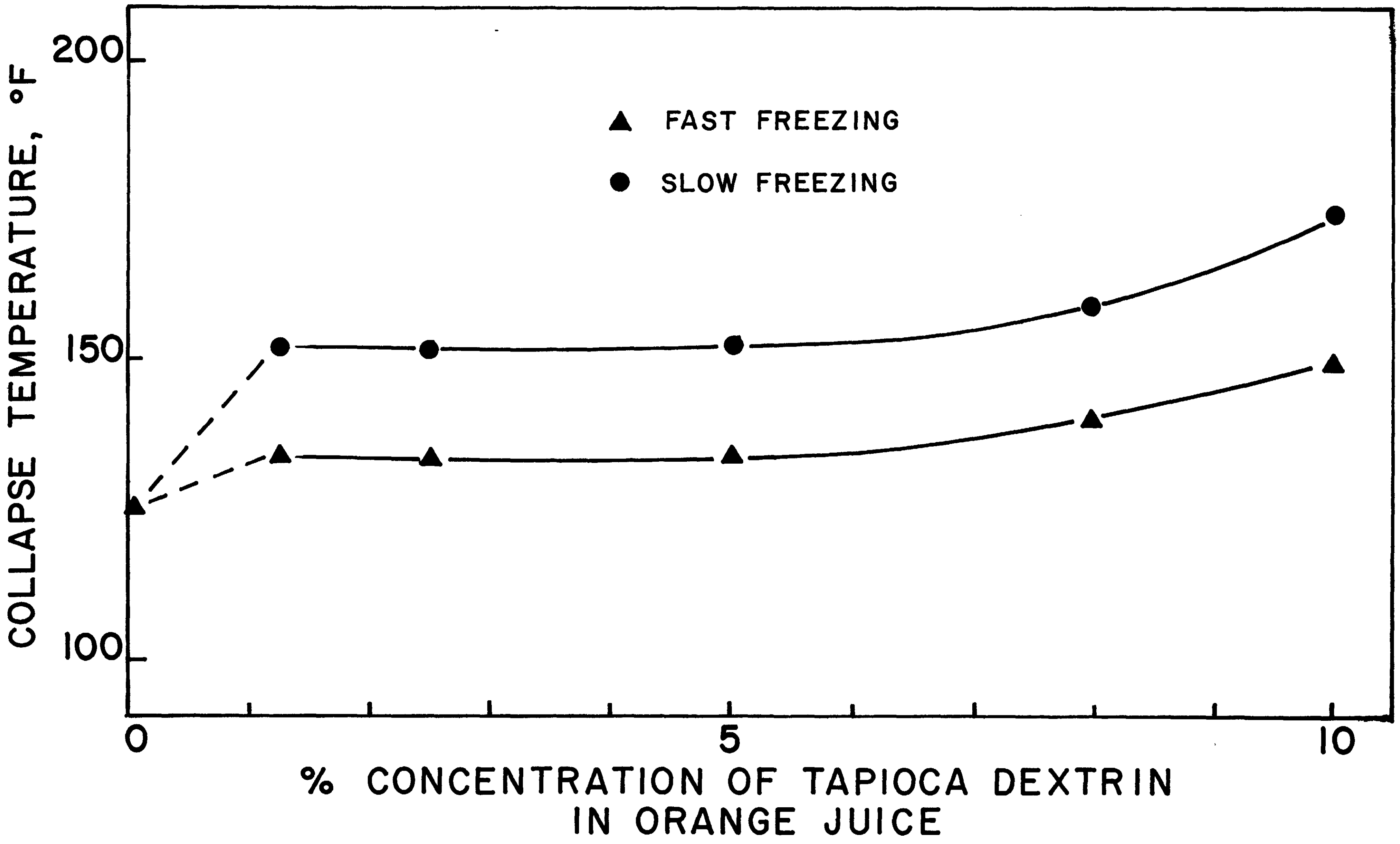
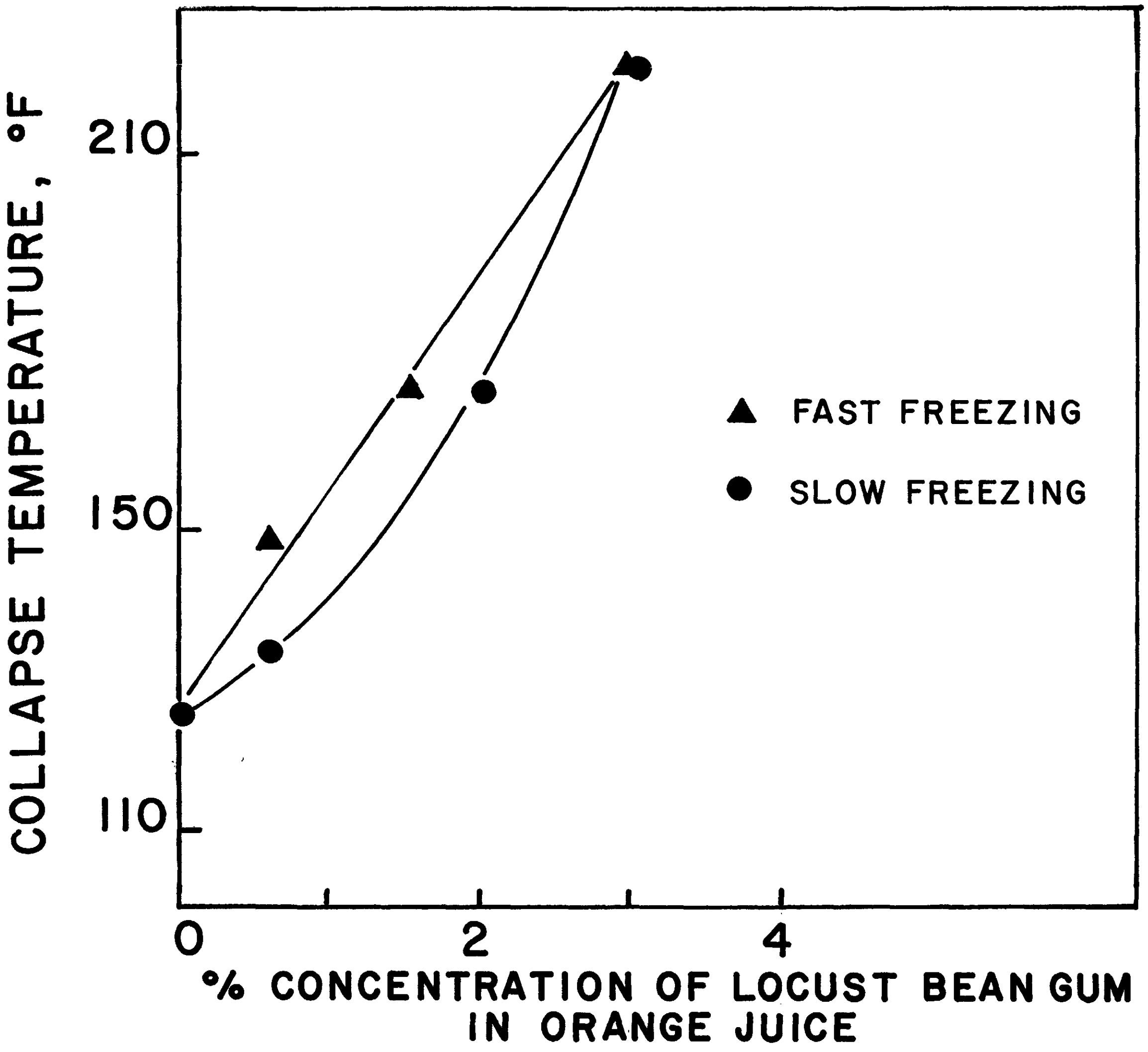


FIGURE 24. COLLAPSE TEMPERATURE VS. CONCENTRATION FOR ORANGE JUICE WITH LOCUST BEAN GUM



good quality,especially that of 3% gum in orange juice.

4. Karaya Gum

Karaya Gum has the same effect on collapse temperature at all concentrations tested (up to 4%). As Figure 25 shows, a small amount of Karaya Gum (around 0.5%) will elevate the collapse temperature of orange juice from 125°F to 152°F. This T_c remains constant for the whole range of concentrations from 0.5% to 4%. The mode of freezing does not affect the collapse temperature at all. However, there is an improvement in the quality of the freeze-dried cake with respect to pure orange juice.

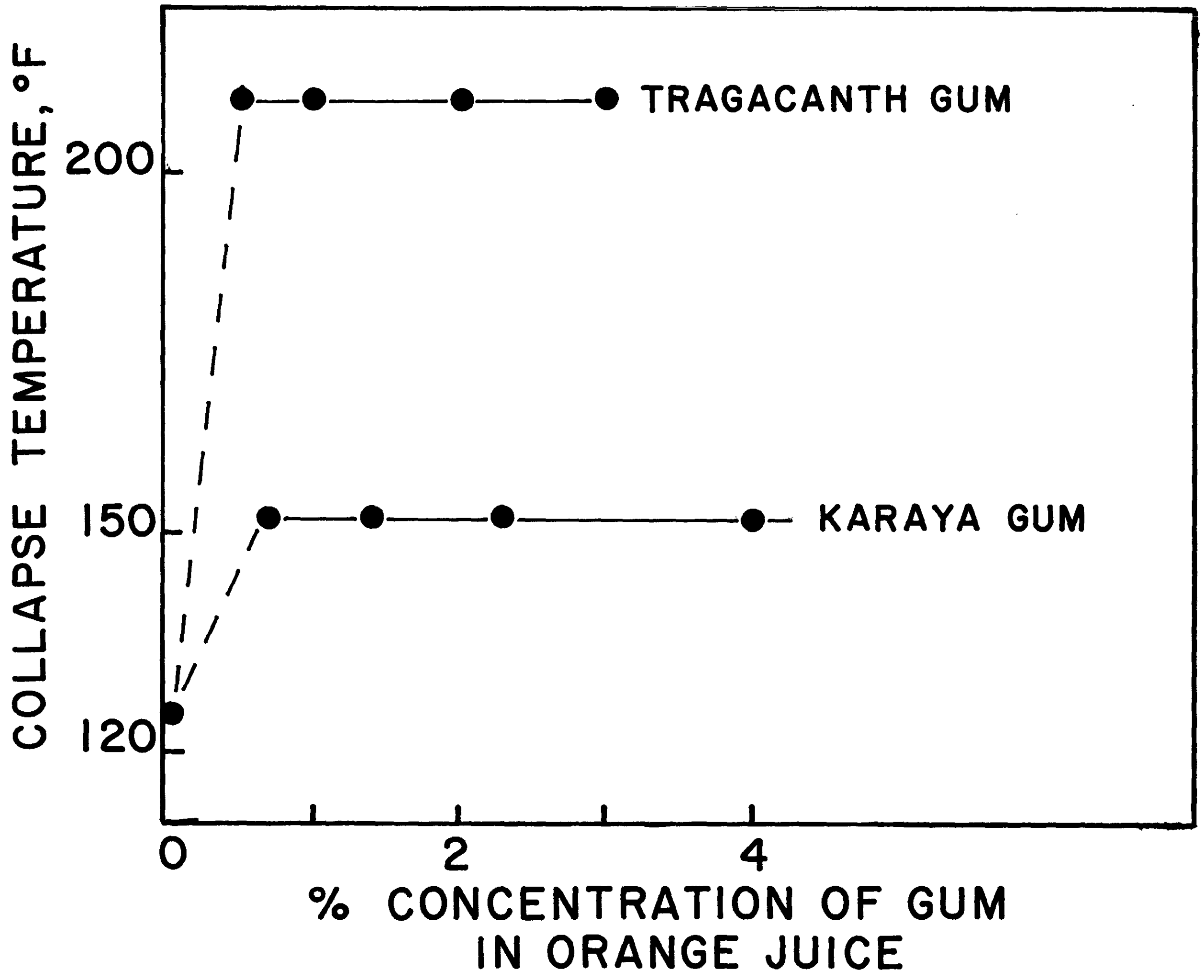
5. Tragacanth Gum

This gum behaves much the same as Karaya Gum, only the elevation of collapse temperature is much higher. As shown in Figure 25, 0.5% of the gum elevates T_c from 125°F to 210°F and the collapse temperature remains the same through a gum concentration of 3%. The mode of freezing does not seem to affect T_c. The quality of the freeze-dried cake is, again, considerably improved.

4.5 Correlation of Viscosity to Collapse Temperature

The Amorphous Viscosity Collapse Theory, introduced by Bellows (1972), provides a model which explains collapse phenomena in terms of viscous flow of the matrix due to surface tension forces, before evaporation can sufficiently dry the concentrated solution. According to this theory, it is the viscosity of the concentrated amorphous matrix that determines

FIGURE 25. COLLAPSE TEMPERATURE VS. CONCENTRATION FOR ORANGE JUICE WITH TRAGACANTH GUM AND WITH KARAYA GUM



whether or not the partially dried matrix will collapse or maintain its shape. The equation developed in the above theory can be used to predict that a viscosity of at least 10^7 cP would be necessary to prevent collapse.

As the viscosity was the important issue in the above theory, it was attempted, in this study, to measure the viscosity of the solutions used and correlate it to collapse temperature, on the assumption that solutions showing a high viscosity before freeze-drying would also have a higher resistance to collapse at low moisture contents (high solids content).

A Brookfield Viscometer was used to measure the viscosity of nearly all the initial solutions used in these experiments, at their actual concentration of use (prior to freeze-drying). The results of the various viscosity experiments are presented in Table IV as a function of their composition, molecular weight, and collapse temperature. For all the samples in this viscosity dependency experiment the collapse temperatures were determined only on samples which were slowly frozen and at 10% mc. The effective molecular weight of the various systems used was determined on a percentage basis depending on their composition. For the maltrins, the "MW" was calculated on basis of their dextrose equivalents. All measurements of viscosity were taken at ambient temperature.

As it can be seen from Table IV, collapse temperature, almost always, increases with increasing viscosity. This is a general phenomenon, independent of differences of the nature of the solute or its concentration

TABLE IV

System	MW	Viscosity, cp	T_c, °F
A. Pure Systems			
Lactose, 25% w/v	342	2.2	214
Maltose, 25% w/v	342	2.2	205
Sucrose, 25% w/v	342	2.2	132
Orange juice, 14.2% w/v	277	4.0	125
Maltrin-100, 25%	1710	6.2	480
Maltrin-150, 25%	1140	3.4	450
Maltrin-200, 25%	855	3.3	450
Maltrin-250, 25%	684	3.1	400
B. Mixed Systems			
Sucrose-Lactose,12.5%-12.5%	342	2.0	174
Sucrose-Maltose,12.5%-12.5%	342	2.1	164
C. Systems with Additives			
Orange + 10% maltose	283	4.8	150
Orange + 2% starch	-	4.1	128
Sucrose + 2% starch	-	2.3	164
Orange juice+3% M-100	320	5.1	167
Orange juice+5% M-100	349	5.4	173
Orange juice+10% M-100	420	7.1	183
Orange juice+15% M-100	492	8.3	192
Orange juice+20% M-100	564	11.6	212
Orange juice+2.5% M-250	287	4.7	137
Orange juice+5% M-250	297	5.4	145
Orange juice+10% M-250	317	6.7	155
Orange juice+15% M-250	338	7.1	164
Orange juice+20% M-250	358	9.3	183
Orange juice+1% Gum Arabic	-	6.5	135
Orange juice+3% Gum Arabic	-	12	142
Orange juice+6% Gum Arabic	-	13	180
Orange juice+3% Locust Bean Gum		1060	212
Orange juice+3% Tragacanth Gum		>2000	210
Orange juice+3% Karaya Gum		>2000	152
Orange juice+3% Tapioca Dextrin		7.4	152
Orange juice+6% Tapioca Dextrin		8.0	153
Orange juice+10% Tapioca Dextrin		9.9	174

for the same sample liquid. However, there are exceptions where different aqueous solutions show the same viscosity but different collapse tmeperatures. These differences must be attributed to varying molecular weight or to different molecular configurations. Table IV shows that lactose, maltose, and sucrose at a concentration of 25% solids, w/v and at 0% moisture content, have different T_c of 214°F, 205°F, and 132°F respectively while their solutions have the same viscosity of 2.2 cp. Considering that these three sugars have the same molecular weight (342) the differences in their T_c must be attributed to differences in the molecular configuration and to different degrees of bonding of the molecules in the freeze-dried state. The same is also true for mixtures of sugars since sucrose-lactose and sucrose-maltose collapse at different temperatures but have the same viscosity and the same molecular weight.

An attempt was made to correlate viscosity and collapse temperature for different concentrations of two maltrins and two gums. The results are shown in Figures 26 and 27 repsectively. The Maltrins (M-100 and M-250) give straight lines while the two gums (Tapioca Dextrin and Gum Arabic) give curves. This type of behavior is expected for both systems, if their curves of T_c vs %concentration is considered. Viscosity is of course a function of concentration, but not a linear function. In the case of the gums, there is a critical viscosity (and therefore, a critical concentration) above which T_c increases rapidly with increasing viscosity. As shown in Figure 27, this critical viscosity for Tapioca Dextrin is around 8 cp and for Gum Arabic around 12 cp. The corresponding critical concentrations are 6% and 3% respectively. These values are good for gums and maltrins dissolved in orange juice. Other solvents might show different behavior. (See Figures 26 and 27).

Another correlation attempted was that of viscosity and collapse temperatures for different systems at the same concentration and the same moisture content. This attempt showed that there is no set pattern of behavior followed in such cases.

As mentioned above, the initial viscosity of the solution affects the collapse temperature of the final-freeze-dried product. This effect is, in part, indirect because the viscosity increase is brought about through changes in concentration of the initial solution. For any given solute, higher viscosities are the result of higher concentrations and, therefore, what is really examined here is the effect of solution concentration on collapse temperature. This aspect will be discussed in the following paragraph.

4.6 General Discussion

4.6.1 Effects of Composition and Molecular Weight

Collapse temperature of the systems examined is a function of their moisture content. As a general trend, the higher the moisture content the lower the collapse temperature of the sample. The highest collapse temperature is shown by the dry (% moisture content) samples of all systems. This is consistent with the Equilibrium

FIGURE 26. COLLAPSE TEMPERATURE VS. VISCOSITY OF MALTRIN-100 AND M-250

(0% MOISTURE CONTENT)

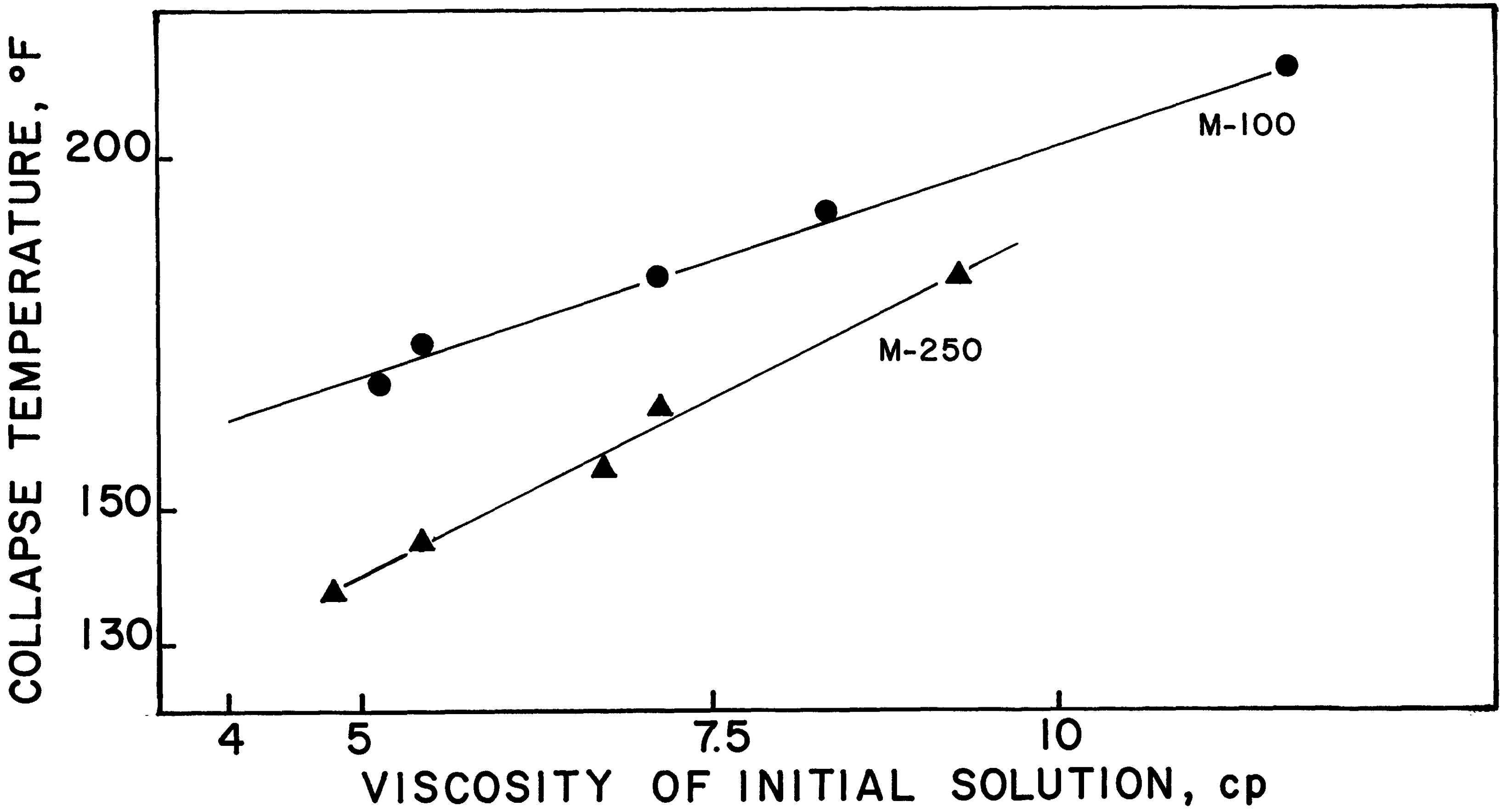
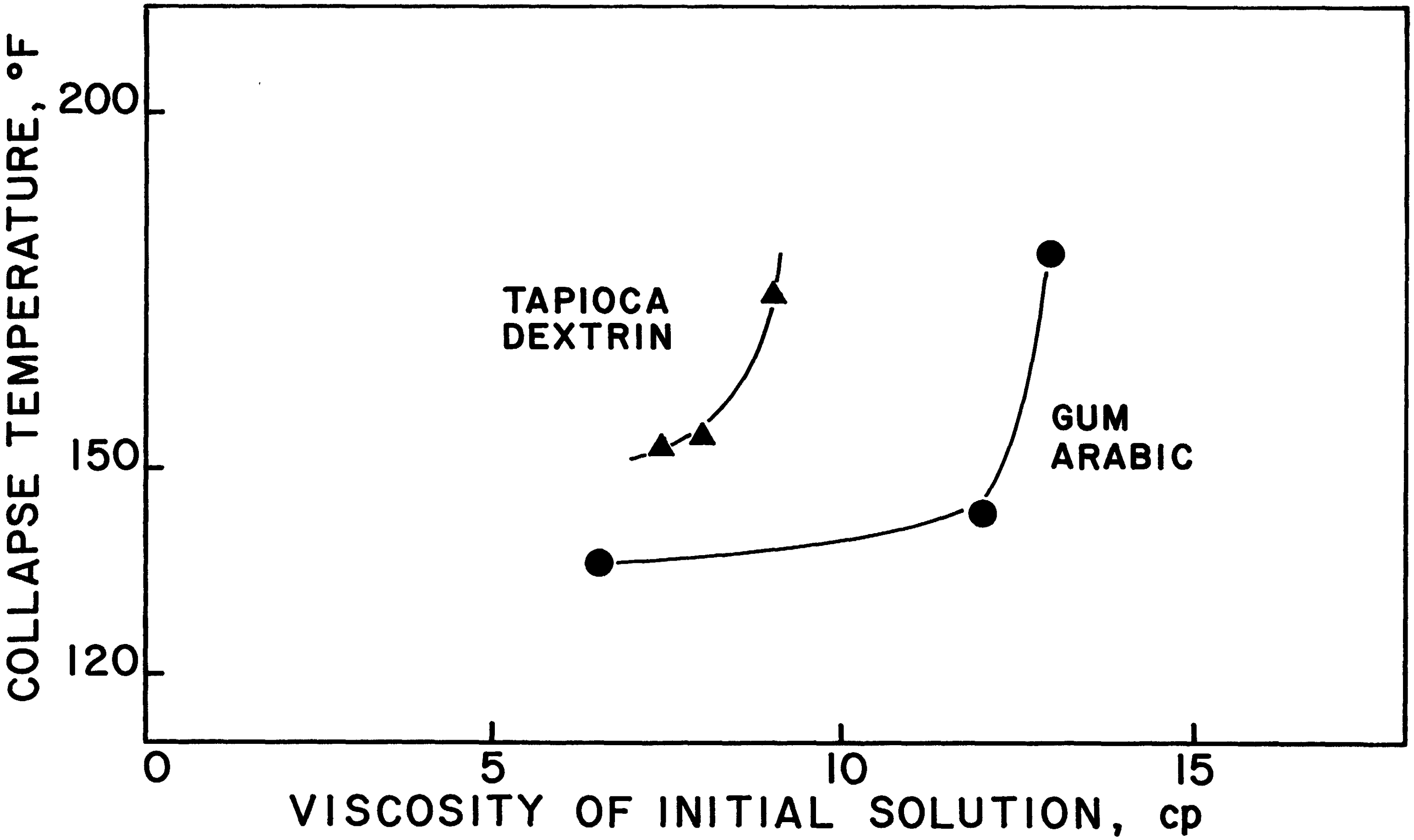


FIGURE 27. COLLAPSE TEMPERATURE VS. VISCOSITY OF GUM ARABIC AND TAPIOCA DEXTRIN (0% MOISTURE CONTENT)



Viscosity argument as moisture dilutes the matrix and lowers viscosity, thus causing collapse to take place at lower temperatures.

As shown in the case of gums and maltodextrins, the initial concentration of the solution affects collapse temperature.

Generally, the higher the concentration of the initial solution, the higher the collapse temperature. The initial composition of the solute determines the amount of water which remains unfrozen at any given temperature. Thus concentrated initial solutions will form less ice than more dilute solutions. The space occupied by ice in the frozen liquid will ultimately become voidage in the dried matrix, as long as no collapse occurs. Presumably, the system with larger fraction of total volume occupied by the concentrated amorphous matrix is capable of developing a more collapse resistant structure. Less voidage means a smaller number of capillaries, and, therefore, less internal surface area. If surface tension is the driving force for collapse, this would lead to higher collapse temperatures. However, there is an upper limit to the use of preconcentration as a means of achieving higher collapse temperatures, due to the kinetic inhibition of ice nucleation. Omran (Ph.D. Dissertation, 1972) showed, as stated by Bellows, that the supercooling required to nucleate ice in a given solution increases as the wt% solids content increase. At some high solids content it often becomes kinetically impossible to nucleate ice before it becomes thermodynamically impossible. That is, the ice can not be spontaneously nucleated at any temperature and, therefore, there is no freeze-drying. DSC studies on sucrose showed that no ice could be nucleated in a 70 wt% solution (Bellows, 1972).

Molecular weight, especially that of additives, plays an important role in collapse temperature determination. Table IV shows the relation of MW to T_c. Disaccharides show different collapse temperatures, although their molecular weight is the same. This, can be attributed to different configurations of the molecule. Maltrins, as pure systems, show a distinct increase in T_c with D.E. decrease. Also, they affect the collapse temperature of orange juice as additives. 20% w/v of M-100 raises T_c of orange juice from 125°F to 212°F. Mixed sugar systems (sucrose-lactose, sucrose-maltose) give collapse temperatures intermediate between those of the pure systems. High molecular weight polysaccharides, also cause an increase in T_c. 2% w/v of starch macromolecules raise the sucrose collapse temperature from 132 to 164°F. Gums also result in substantial changes of T_c of orange juice. Relatively low concentrations can increase T_c by as much as 87°F (3%, w/v of Tragacanth Gum).

4.6.2 Effect of the Mode of Freezing

The mode of freezing affects the collapse temperature of the system, at least for systems of solutes with low molecular weight, The maltodextrins and the Gums that have a high viscosity (Tragacanth, Karaya) do not show any differences in collapse temperature with the rate of freezing. All other systems, though, are affected by it, but the pattern of behavior is not always the same not only among different but also among similar systems. In the case of lactose, for example, fast frozen samples have a slightly higher T_c than slowly frozen ones, while sucrose and maltose show the inverse behavior. Orange juice shows the same behavior as lactose although 50% of its content is sucrose. The difference, though, is small in this case. Differing patterns of influence of the freezing rate can also be shown in mixed systems of sugars such as lactose with sucrose and lactose with maltose. Both show higher collapse temperatures in fast frozen samples than in slowly frozen samples. (Pure lactose shows a higher T_c with fast freezing, while the reverse is true for sucrose and maltose). In the case of additives, like maltose and starch in orange juice,the effectiveness of the additive in elevating temperature of collapse depends on the mode of freezing. Fast frozen samples of orange juice with 10% maltose show a lower T_c in comparison to the slowly frozen ones and the difference in T_c elevation is greater at low rates (25°F) than at high rates (13°F) of freezing. Three of the gums, namely Gum Arabic, Locust Bean Gum, and Tapioca Dextrin are affected by the mode of freezing, but, again, there is no set pattern of behavior. Fast frozen samples of Gum Arabic and Locust Bean Gum have higher T_c than slowly frozen samples. However, the situation is reversed in the case of Tapioca Dextrin .

Any attempt to explain phenomena of freezing rate differences in relation to collapse temperature would probably require consideration of history of the samples during freezing and drying. In particular ice nucleation rate and growth rate of ice crystals are affected by freezing rate.

Nucleation rate influences the number of ice crystals formed and, therefore, the size of ice crystals. Thijssen and Rulkens (1969) have shown that for maltodextrin solutions the number of ice crystals per unit area increases as the rate of cooling is increased. Omran (1972), as stated by Bellows, showed that ice nucleation takes place as a sudden shower of nuclei and that larger supercooling causes more nuclei to form. So, fast freezing increases the number of nuclei formed and means that the distance between ice crystals decreases. Therefore, fast freezing could cause decreased collapse temperature because of thinner lamellae. But at the same time, faster nucleation, according to Thijssen and Rulkens (1969) reduces the permeability thus limiting the rate of freeze-drying by blocking internal mass transfer. This leads to a reduction in viscosity and, therefore, an increase in the drying time, t_d, which lowers the collapse temperature during freeze-drying. This lowering of T_c during drying does not necessarily mean that T_c of the dry material should be lower, but it would affect cake quality and may weaken the structure thus possibly influencing collapse of the humidified systems. It has, in fact, been observed that cake quality following freeze-drying has some relation to level of T_c of humidified system. From the above analysis, it is not clear if either of these two competing effects have a predominating effect on the collapse temperature.

The rate of cooling below the nucleation temperature determines the geometry and growth rate of ice crystals. According to Bellows (1972), the growth rate during freezing is especially important near the freeze-drying collapse temperature because it affects the extent of concentration polarization within the CAS. Rapid growth of ice crystals causes extended concentration polarization between the growing ice and the bulk of the concentrated matrix. An equilibrium amount of ice is prevented from forming and further cooling lowers the diffusion coefficients enough to prevent further freezing. The matrix then has lower solids contents and therefore a lower viscosity which leads to lower collapse temperatures.

Taking under consideration the above analysis, it is obvious that the predictability of the collapse behavior of samples frozen in different freezing rates is very difficult if not impossible, especially when the systems are not pure and interactions take place between their various components.

4.6.3 Correlation of $\ln T_c$ to Moisture Content

The natural logarithm of collapse temperature of different solutions was plotted against their moisture content. The result was a family of straight lines with a slope range of 6.28° to 9.65° and high coefficients of determination (.94 to .99). Table V shows the slopes and the coefficients of determination for the systems examined. The results are plotted in Figures 28,29,30, and 31.

As shown in Figure 28, maltose, lactose, and sucrose show a bend in their straight lines at around 6% moisture content. This change in slope might be due to experimental factors, relating to time required for humidification in the cold room prior to elevation of temperature to desired levels. When the cold room temperature was close to the T_c for the higher moisture smaples,this time may have initiated some collapse thus affecting the measured T_c.

The correlation referred to above shows that a common pattern of behavior can be found for all systems examined in this work with regard to their collapse temperature change with the moisture content.

4.6.4 Quality of the Freeze-Dried Cake

A final point to be made in this study is that of the quality of the freeze-dried cake. There are cases, like orange and apple juice, that give a low quality freeze-dried cake due to puffing and partial collapse in the drying process. Generally, the lower the quality of the freeze-dried cake, the lower the collapse temperature of the product. Addition of macromolecules, like starch, high molecular weight maltrins or gums affects the quality of the cake considerably and, at the same time, the collapse temperature of the

TABLE V

System	Slope	Coefficient of Determination
Lactose, 25%	-8.53°	.98
Maltose, 25%	-7.97°	.99
Sucrose, 25%	-7.97°	.99
Orange juice, 14.18%	-7.41°	.94
Apple juice, 13.50%	-6.84°	.99
M-250, 25%	-6.84°	.99
M-200, 25%	-6.84°	.99
M-100, 25%	-6.28°	.99
Lactose-Sucrose, 12.5%-12.5%	-7.41°	.99
Maltose-Sucrose, 12.5%-12.5%	-9.65°	.99
Orange juice + 10% maltose	-6.84°	.99
Orange juice + 2% starch	-6.28°	.99
Apple juice + 10% maltose	-6.28°	.98
Sucrose + 2% starch	-7.97°	.99

FIGURE 28. ln T_c VS. MOISTURE CONTENT FOR SINGLE COMPONENT SYSTEMS

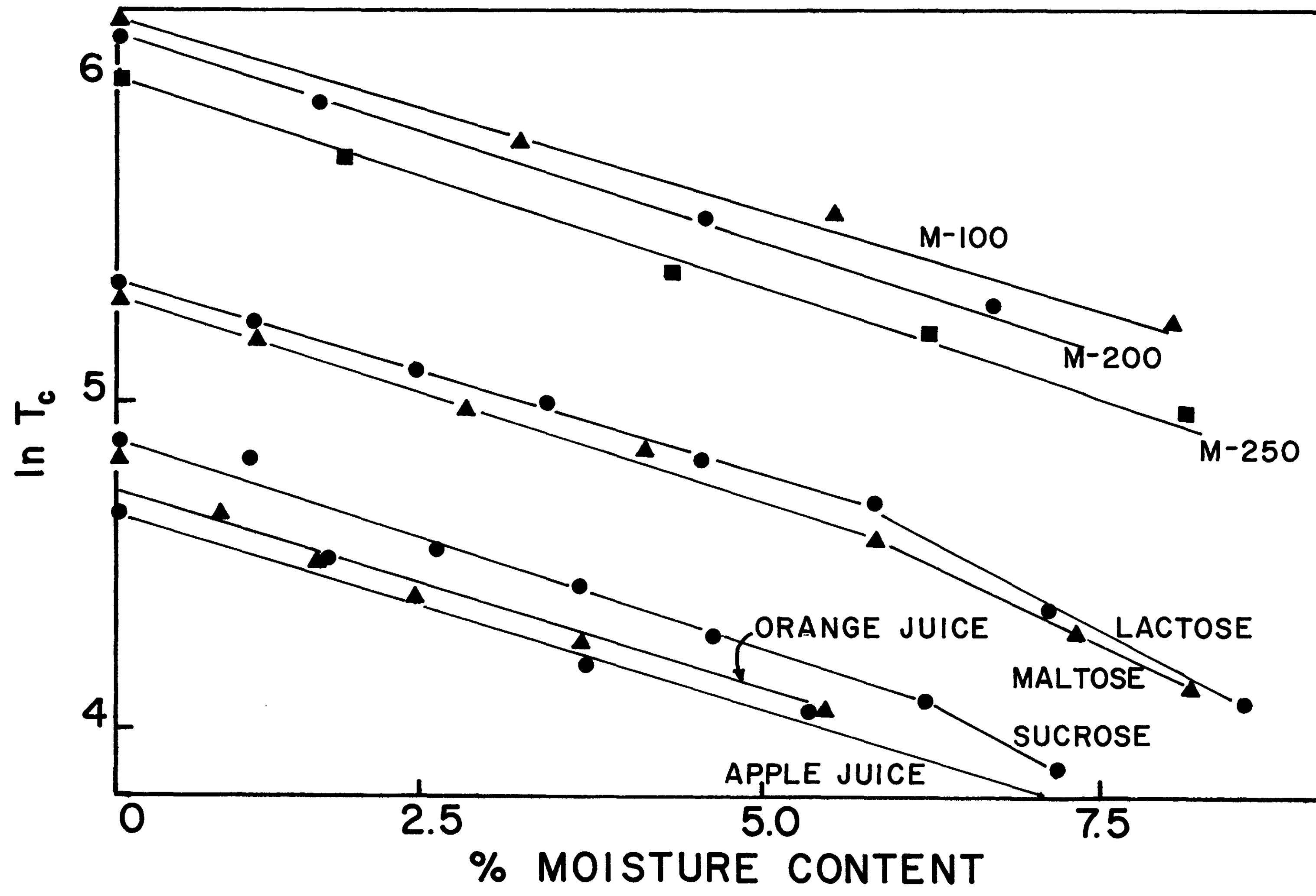


FIGURE 29. ln T_c VS. MOISTURE CONTENT FOR JUICES WITH ADDITIVES

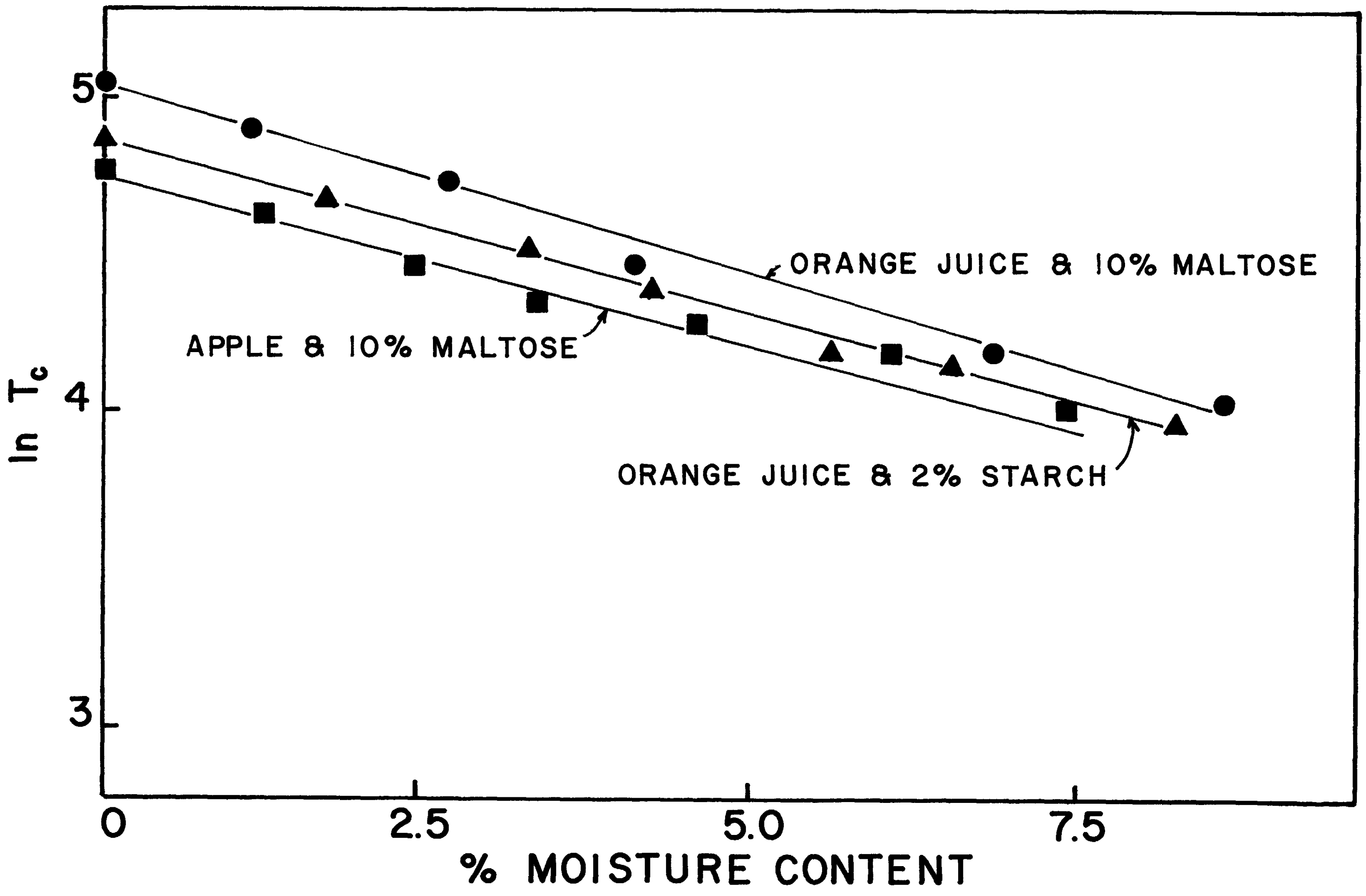


FIGURE 30. ln T_c VS. MOISTURE CONTENT FOR SUCROSE WITH 2% STARCH

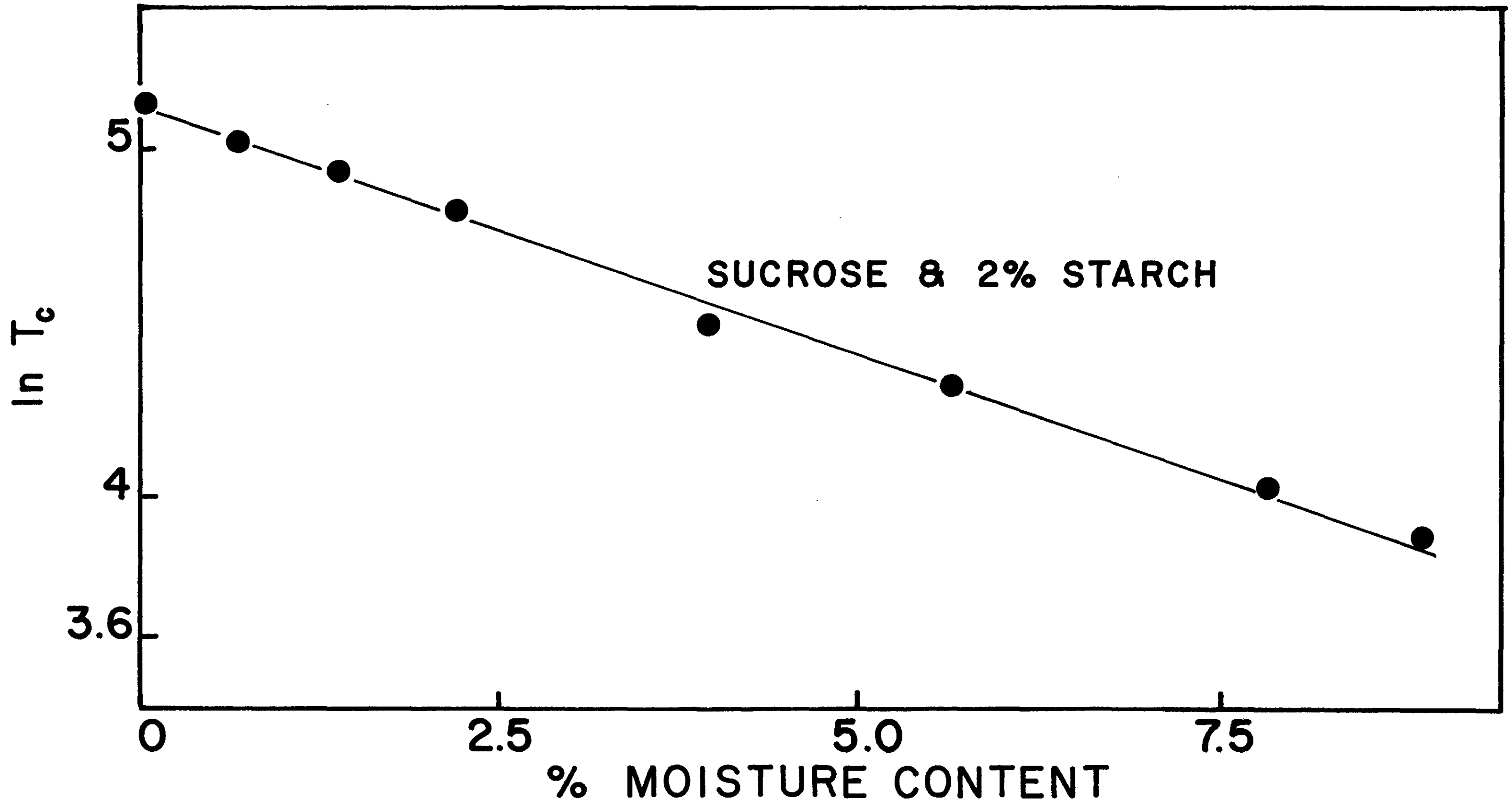
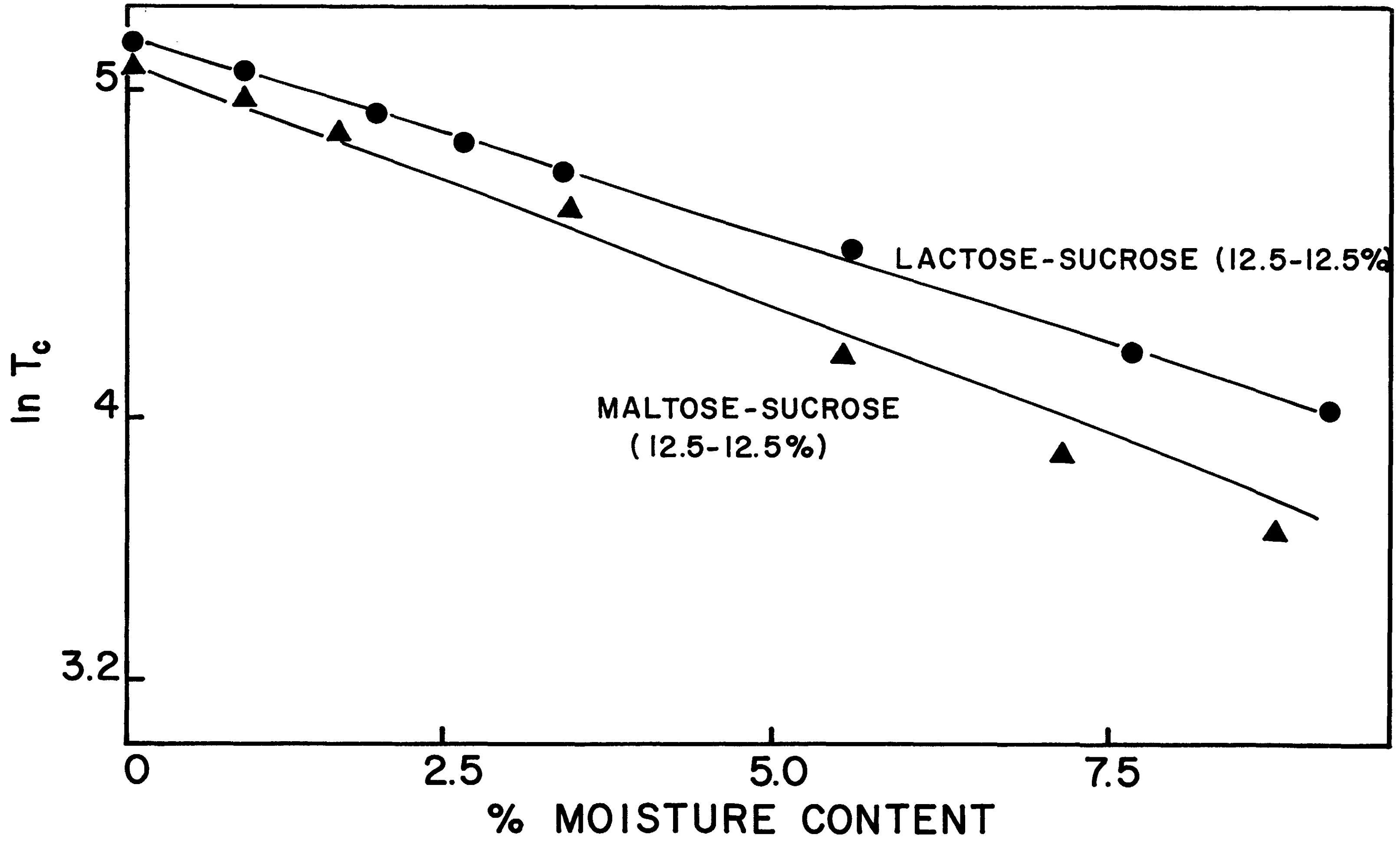


FIGURE 31. ln T_c VS. MOISTURE CONTENT FOR MIXED SYSTEMS



freeze-dried product increases at all moistures. Therefore, the quality of the freeze-dried cake is a first indication of the magnitude of the product's collapse temperature.

5. CONCLUSIONS

Five parameters are postulated as being important in affecting the collapse temperature of juices and juice-simulating carbohydrate solutions.

1) The moisture content of the freeze-dried sample: Moisture was found to be an important factor in determining collapse temperature. As a general rule, the collapse temperature decreases substantially with increasing moisture content of the sample. This holds true for single and multi-component systems and for systems of juice with additives.

2) The initial concentration of the solution before freeze-drying: The initial concentration of the solution before freeze-drying was also found to have an important effect on collapse temperature. The phenomenon was investigated for the case of maltodextrins and gums dissolved in orange juice and it showed different pattern of behavior between the two additives. The collapse temperature of orange juice increased with increasing maltodextrin concentration for all four maltrins tested. When gums were used, however, in some cases, T_c increases with increasing initial concentration (Gum Arabic, Locust Bean Gum), while in others, T_c is independent of initial concentration (Gum Karaya, Gum Tragacanth).

3) The molecular weight of additives: Addition of various carbohydrate substances of similar structure in orange juice increases the collapse temperature. The magnitude of the increase depends in part,

on the molecular weight of the additive. A high molecular weight carbohydrate raises collapse temperature more than a low molecular weight carbohydrate at the same initial concentration. The increase is found at all moistures. The data on maltodextrins illustrate this result.

4) The rate of freezing: Evidence was found that the rate of freezing affects collapse temperatures of the systems tested. However, no set pattern of behavior could be determined. In some cases, rapidly frozen samples show a higher collapse temperature than slowly frozen samples at the same moisture content. In other cases, the situation is reversed. The difference in collapse temperature between the two freezing rates is usually slight, but in a few cases it was found to be considerable.

5) The viscosity of the initial solution: The viscosity of the initial solution was also found to be important in collapse temperature determination. As a general rule, the higher the viscosity of the initial solution, the higher the collapse temperature. Yet, there were cases where solutions of the same initial viscosity and concentration gave considerable differences in T_c (for example, lactose vs sucrose).

Finally, it must be noted that the quality of the freeze-dried cake gave an initial indication of the magnitude of the collapse temperature. If the quality was acceptable, relatively high collapse temperatures were expected.

6. SUGGESTIONS FOR FUTURE RESEARCH

1. Some of the systems which it would by desirable to examine could not be tested, because they could not be freeze-dried without collapse using process conditions imposed by the freeze-drier used. For example, glucose and fructose, having a low collapse temperatures, collapsed durying freeze-drying. A small glass freeze-drier was devised where the condenser was kept at very low temperature by means of liquid nitrogen and the samples were in dry ice so as to have a low sample temperature and still retain a large temperature gradient between sample and condenser, and, therefore, a high mass transfer. Also, the solutions were freeze-dried in the form of a film on microscope slides. This method was partially successful but the amount of freeze-dried glucose finally obtained was small. It is suggested that future research include devising a freeze-drier that would freeze-dry larger amounts of low collapse temperature substances.

2. If this type of freeze-drier is built, other fruit juices, with low collapse temperatures, could be examined as well. Fruit juices like apple, grape, lemon, pineapple which failed to give an acceptable freeze-dried cake and, therefore, were not used, can be tested for the effect of additives on their collapse temperature and their results compared to those of orange juice.

3. Some experiments of these studies should be conducted in more than duplicate experiments and a statistical analysis made. A thorough sta-

tistical analysis will help decide of the differences in the collapse temperature between slow and fast freezing are significant.

4. The effect of more than one additive in orange juice or other juices should be studied. It is possible that the combination of two or more additives used for different purposes (i.e. tapioca dextrin for flavor encapsulation, maltose for elevation of collapse temperature) might give a better quality product.

5. For samples where this work was confined in the study of dry systems ("0%" moisture content), as in gums added to orange juice, an extension should be made to a full range of moisture, from 0% to 10% mc, so that the curve T_c vs mc can be obtained for gums as well as the other carbohydrates used. This could be extended not only to orange juice as the solution medium but also to other juices and to distilled water.

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APPENDIX A

1. Lactose (25% solids, w/v)

RUN A

Slow Freezing:

% mc	0	1	2.23	3.22	4.38	5.70	7.03	8.52	9.80
T_c, °F	214	187	163	146	124	110	78	59	48

Fast Freezing:

% mc	0	1.38	2.80	4.22	5.70	6.34	7.48	9.01	10.85
T_c, °F	214	187	163	150	124	107	98	69	48

RUN B

Slow Freezing:

% mc	0	0.76	1.53	2.60	4.03	5.51	7.62
T_c, °F	214	194	186	150	140	101	60

Fast Freezing:

% mc	0	1.05	3.0	4.15	6.03	7.52	9.83
T_c, °F	214	185	171	148	120	82	51

2. Maltose (25% solids, w/v)

RUN A

Slow Freezing:

% mc	0	1.05	2.60	3.97	5.74	7.20	8.10
T_c, °F	205	182	143	132	98	75	62

Fast Freezing:

% mc	0	2.28	3.15	4.22	5.63	7.10	8.05
T_c, °F	205	143	120	101	87	70	60

RUN B

Slow Freezing:

% mc	0	1.25	3.21	5.07	6.32	7.52
T_c, °F	205	171	142	100	89	63

Fast Freezing:

% mc	0	1.08	2.11	3.77	5.09	6.95
T_c, °F	205	159	140	118	83	62

3. Sucrose (25% solids, w/v)

RUN A

Slow Freezing:

% mc	0	1	2.41	3.48	4.50	6.10	7.10
T_c °F	132	125	94	84	72	60	48

Fast Freezing:

% mc	0	0.38	1.15	2.41	4.44	6.35
T_c, °F	132	119	105	92	64	50

RUN B

Slow Freezing:

% mc	0	1.25	2.48	3.09	4.82	7.0
T_c, °F	132	121	103	88	59	48

Fast Freezing:

% mc	0	0.47	1.89	3.05	6.80
T_c, °F	132	118	81	70	48

4. Orange Juice (14.2% solids, w/v)

RUN A

Slow Freezing:

% mc	0	.75	1.50	2.23	3.51	5.35	9.20
T_c, °F	125	106	90	82	71	58	50

Fast Freezing:

% mc	0	1.65	3.17	4.64	6.50	8.02	10
T_c, °F	125	98	84	73	60	58	49

RUN B

Slow Freezing:

% mc	0	1.33	2.62	4.05	6.08	8.85
T_c, °F	125	97	86	72	61	52

Fast Freezing:

% mc	0	1.08	2.31	3.80	4.51	7.32
T_c, °F	125	100	92	80	74	58

5. Apple Juice[1] (13.5% solids, w/v)

RUN A

Slow Freezing:

% mc	0	1.53	2.30	3.55	5.24	8.37
T_c, °F	106	91	80	66	58	38

Fast Freezing:

% mc	0	1.25	2.66	4.06	5.51	7.13	8
T_c, °F	106	91	81	58	51	45	38

RUN B

Slow Freezing:

% mc	0	1.02	2.52	3.86	5.12	6.82
T_c, °F	106	100	82	72	54	40

Fast Freezing:

% mc	0	2.12	3.17	5.14	7.51
T_c, °F	106	80	90	55	39

6. Maltodextrins (25% solids, w/v)

RUN A

a. M-250

% mc	0	1.68	4.15	6.10	8.05	13.7
T_c, °F	400	307	218	187	145	70

b. M-200

% mc	0	1.4	4.4	6.6	9.4	12.8
T_c, °F	450	365	260	205	145	90

c. M-150

% mc	0	1.4	4.2	9	11.2	13.9
T_c, °F	450	365	272	160	127	90

d. M-100

% mc	0	3	5.4	7.9	11.2	13.8
T_c, °F	480	325	265	190	130	100

RUN B

a. M-250

% mc	0	1.58	4.55	5.82	7.02
T_c, °F	400	307	210	185	157

b. M-200

% mc	0	1.52	3.08	5.0	9.52	13.80
T_c, °F	450	360	307	250	132	79

c. M-150

% mc	0	1.4	4.80	8.81	10.35	12.89
T_c, °F	450	365	250	160	130	97

d. M-100

% mc	0	1.82	4.10	7.12	10.42	13.05
T_c, °F	480	370	300	225	132	105

7. Lactose-Sucrose (12.5% - 12.5% solids, w/v)

RUN A

Slow Freezing:

% mc	0	0.83	1.82	2.5	3.25	5.43	7.52	9.08	10.85
T_c, °F	174	159	139	126	116	92	67	56	39

Fast Freezing:

% mc	0	1.02	1.91	2.63	3.76	4.34	6.01	8.13	10.50
T_c, °F	204	172	159	138	127	116	87	61	39

RUN B

Slow Freezing:

% mc	0	1.09	2.21	3.68	4.99	7.33
T_c, °F	174	150	139	103	90	70

Fast Freezing:

% mc	0	1.52	3.72	5.24	6.75	9.37
T_c, °F	204	153	131	101	89	49

8. Maltose-Sucrose (12.5% - 12.5% solids, w/v)

RUN A

Slow Freezing:

% mc	0	0.83	1.55	3.30	5.35	7.02	8.60
T_c, °F	164	145	132	105	66	49	39

Fast Freezing:

% mc	0	1.14	1.85	3.0	4.52	5.50	6.52	8.52
T_c, °F	176	163	145	120	98	84	69	45

RUN B

Slow Freezing:

% mc	0	1.08	2.51	3.81	4.98	7.10
T_c, °F	164	135	121	100	69	49

Fast Freezing:

% mc	0	1.52	3.02	4.80	5.28	7.03
T_c, °F	176	151	115	100	89	62

9. Orange Juice + 10% maltose, w/v

RUN A

Slow Freezing:

% mc	0	1.12	2.60	4.04	6.73	8.50
T_c, °F	150	128	110	84	64	55

Fast Freezing:

% mc	0	0.98	2.12	3.82	5.41	7.01	9
T_c, °F	138	112	95	83	66	58	52

RUN B

Slow Freezing:

% mc	0	.95	2.05	3.44	5.14	6.25	7.51
T_c, °F	150	121	113	98	69	60	49

Fast Freezing:

% mc	0	1.24	2.64	3.99	8.51
T_c, °F	138	100	81	81	50

10. Orange Juice with 2% starch

RUN A

Slow Freezing:

% mc	0	1.70	3.22	4.13	5.27	6.45	8.17
T_c, °F	128	105	89	79	65	62	52

Fast Freezing:

% mc	0	1.5	2.30	3.34	3.75	4.98	6.40	7.97
T_c, °F	128	108	99	94	89	79	71	66

RUN B

Slow Freezing:

% mc	0	1.15	2.30	3.91	5.09	7.5
T_c, °F	128	110	101	85	71	52

Fast Freezing:

% mc	0	1.30	2.28	3.31	4.78	5.91
T_c, °F	128	108	95	90	86	73

11. Apple Juice with 10% maltose

RUN A

Slow Freezing:

% mc	0	1.13	2.37	3.28	4.50	5.96	7.29
T_c, °F	114	99	84	75	70	65	54

Fast Freezing:

% mc	0	1.08	2.27	3.80	6	8
T_c, °F	114	99	89	75	65	62

RUN B

Slow Freezing;

% mc	0	1.08	2.34	3.79	4.58	5.98	7.48
T_c, °F	114	96	88	77	69	60	55

Fast Freezing:

% mc	0	2.11	3.27	4.51	5.25	6.18
T_c, °F	114	79	79	70	70	59

12. Sucrose (25% solids, w/v) with 2% starch

RUN A

Slow Freezing:

% mc	0	0.64	1.33	2.15	3.65	5.60	7.80	8.89
T_c, °F	164	147	134	119	87	74	56	49

Fast Freezing:

% mc	0	0.7	1.51	2.43	3.01	4.98	6.93	9.15
T_c, °F	164	138	129	120	110	79	59	49

RUN B

Slow Freezing:

% mc	0	0.98	2.28	4.10	5.11	6.75	8.10
T_c, °F	164	140	117	95	82	65	49

Fast Freezing:

% mc	0	1.12	2.37	3.48	4.90	7.14	8.08
T_c, °F	164	137	118	99	80	59	49

13. Orange Juice with varying maltrin concentration at 0%mc

RUN A

a. M-250

% C	0	2.5	5	10	15	20
T_c, °F	125	137	145	155	164	183

b. M-200

% C	0	3	5	10	15	20
T_c, °F	125	153	159	170	179	193

c. M-150

% C	0	3	5	10	15	20
T_c, °F	125	153	165	175	184	197

d. M-100

% C	0	3	5	10	15	20
T_c, °F	125	167	173	183	192	212

RUN B

a. M-250

% C	0	2.5	5	10	15	20
T_c, °F	125	135	142	151	168	188

b. M-200

% C	0	3	5	10	15	20
T_c, °F	125	155	163	170	175	191

c. M-150

% C	0	3	5	10	15	20
T_c, °F	125	155	168	175	181	199

d. M-100

% C	0	3	5	10	15	20
T_c, °F	125	165	171	182	192	212

14. Orange Juice with varying concentrations of gums

a. Gum Arabic

RUN A

Slow Freezing:

% C	0	1.5	3	6
T_c, °F	125	135	142	180

Fast Freezing:

% C	0	1.5	3	6
T_c, °F	125	149	160	193

RUN B

Slow Freezing:

% C	0	1.5	3	6
T_c, °F	125	131	140	177

Fast Freezing:

% C	0	1.5	3	6
T_c, °F	125	153	163	195

b. Locust Bean Gum

RUN A

Slow Freezing:

% C	0	0.60	2	3
T_c, °F	125	133	168	212

Fast Freezing:

% C	0	0.60	1.5	3
T_c, °F	125	149	179	212

RUN B

Slow Freezing:

% C	0	0.60	2	3
T_c, °F	125	129	171	212

Fast Freezing:

% C	0	0.60	1.5	3
T_c, °F	125	151	183	212

c. Tapioca Dextrin

RUN A

Slow Freezing:

% C	1.25	2.50	5	8	10
T_c, °F	152	152	152	169	174

Fast Freezing:

% C	1.25	2.50	5	8	10
T_c, °F	133	133	133	140	149

RUN B

Slow Freezing:

% C	1.25	2.50	5	8	10
T_c, °F	151	152	151	169	179

Fast Freezing:

% C	1.25	2.50	5	8	10
T_c, °F	136	136	133	142	148

d. Tragacanth Gum

RUN A

% C	0.50	1	2	3
T_c, °F	210	210	210	210

RUN B

% C	0.50	1	2	3
T_c, °F	211	210	209	211

e. Karaya Gum

RUN A

% C	0.70	1.40	2.30	4
T_c, °F	152	152	152	152

RUN B

% C	0.70	1.40	2.30	4
T_c, °F	151	149	149	149

APPENDIX B

Since collapse is a time and temperature dependent phenomenon, a determination of collapse temperature depends on the length of time that is alloted to observation of the sample. In general, the observed collapse temperature decreases with increasing time of exposure, up to a given time at which no further reduction is observed.

A time-temperature study was conducted to determine the minimum exposure time needed to assure that measured collapse temperature did not depend on heating time.

For this study the bath, containing samples of freeze-dried 25% sucrose solution, was maintained at a certain temperature and the time necessary for the samples to collapse was determined. This procedure was repeated for identical samples for a number of heating temperatures. The table below shows the time required to achieve collapse at various heating temperatures.

T_c, °F	Residence time, min.
161	2
151	9
131	25
123	31
116	40
114	48
112	125

The accompanying figure shows that heating samples for 45 minutes will give collapse temperatures which are essentially independent of further heating time. As shown in the figure, collapse temperature decreases rapidly with increasing residence time until around 40 min. From then on, collapse temperature varies very little with time.

COLLAPSE TEMPERATURE VS. RESIDENCE TIME FOR SUCROSE (25% SOLIDS, FAST FREEZING)