AN ANALYSIS AND INTERPRETATION OF THERMODYNAMIC PROPERTIES OF FOODS AS DETERMINED FROM MOISTURE SORPTION DATA

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSTY
SERAFIM N. ELVANIDES
1972

This is to certify that the

thesis entitled

AN ANALYSIS AND INTERPRETATION OF
THERMODYNAMIC PROPERTIES OF FOODS AS
DETERMINED FROM MOISTURE SORPTION DATA

presented by

SERAFIM N. ELVANIDES

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Food Science

D. R. Heldman
Major professor

Date March 10, 1972

O-7639

ABSTRACT

AN ANALYSIS AND INTERPRETATION OF THERMODYNAMIC PROPERTIES OF FOODS AS DETERMINED FROM MOISTURE SORPTION DATA

By

Serafim N. Elvanides

Both the food engineer and the food scientist are interested in thermodynamic properties of foods. The engineer is primarily interested in information needed for design of processing equipment whereas the food scientist is concerned with the thermodynamic responses which provide an understanding of the product stability under storage conditions. The purpose of this investigation was to study the thermodynamic properties of foods in the low and intermediate moisture range as evaluated from moisture sorption isotherms.

The thermodynamic relationships which describe the water vapor sorption phenomena were systematically developed and a critical discussion of procedures utilized in published literature was presented. Evidence was presented which revealed that the use of the integral form of the Clausius - Clapeyron equation for evaluating differential enthalpies from two isotherms at widely differing temperatures can lead to errors.

Serafim N. Elvanides

The water vapor sorption isotherms of precooked freeze-dried and raw freeze-dried beef obtained gravimetrically at three different temperatures were used for the thermodynamic analysis. The phenomenon of hysteresis between adsorption and desorption isotherms was present at all temperatures for the products studied. The precooked product had a slightly higher sorptive capacity which was attributed to the heat denaturation of protein and loss of fats during cooking.

The values of integral and differential free energies, enthalpies and entropies of sorption varied considerably with the amounts of water sorbed by the products. All calculations utilized saturated water vapor as the standard state.

The curves of the differential and integral thermodynamic properties obtained in this study were all continuously decreasing or increasing functions when plotted versus moisture content. A theoretical analysis of the integral thermodynamic properties indicated that integral properties will become maximum or minimum at a moisture content which will be a function of the nonideality of the system. A study of the influence of temperature on the differential free energy changes of water and solids with increasing moisture content revealed that the sorptive potential of the products increased with decreasing temperature in the range of temperatures investigated. An analogous study of the effect of temperature on differential entropy changes of the products revealed no significant influence. This was attributed to small differences between the isotherm temperatures.

Isosteric heats of adsorption and desorption ranged from 660 cal/g. water to 50 cal/g. water for the range of moisture contents studied. Differential free energy, enthalpy and entropy changes of water during adsorption and desorption decreased continuously in absolute magnitude with increasing moisture content. The isosteric properties during desorption were consistently greater than the respective properties during adsorption. The net differential thermodynamic properties of water decreased sharply in absolute magnitude with increasing moisture content and leveled off at about 15 percent moisture content approaching zero and indicating that the water may serve as solvent in the low moisture range. The respective net differential properties of solids increased in absolute magnitude during both adsorption and desorption with increasing moisture content. The change of the differential thermodynamic properties of solids were small compared to the change of the respective properties of water. However, it indicated an increased reactivity of the solids with increasing moisture content.

Characteristic peaks on the thermodynamic property curves, which could be correlated to the condition of maximum storage stability of low and intermediate moisture products, were not observed. It was concluded that a simple relationship between thermodynamic properties of low and intermediate moisture foods and their storage stability may not exist.

AN ANALYSIS AND INTERPRETATION OF THERMODYNAMIC PROPERTIES OF FOODS AS DETERMINED FROM MOISTURE SORPTION DATA

By

Serafim Nicolaous Elvanides

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Food Science and Human Nutrition

1972

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Professor D. R. Heldman for his generous assistance in all phases of this study. His genteel guidance, enthusiastic encouragement and constant availability for discussion were largely responsible for the success of this work.

Sincere appreciation is also extended to Professors F. W. Bakker-Arkema, P. Markakis and W. M. Urbain for their advice and help in preparation of this manuscript.

The author feels deeply grateful to the Department of Food Science, Michigan State University, and through it to the generosity of the American people for the financial assistance granted to him during his studies at this university.

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

LIST OF TABLES

LIST OF FIGURES

Figure | Page

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF SYMBOLS

G	Gibbs free energy
$\tilde{G}_w$	free energy of pure water per unit mass (1 mole of 1 g.)
$\bar{G}_w$	partial or differential free energy of a mixture with respect to water cal/mole or cal/g.
ΔG	integral change in net free energy on mixing pure components called free energy of mixing, cal.
ΔG_w	integral net free energy of solution, cal/100 g. solids
ΔG^+	integral net free energy of mixing, cal/g. mixture
$\overline{\Delta G}_w$	change in differential net free energy with respect to water, cal/g. water
$\overline{\Delta G}_s$	change in differential net free energy with respect to solids, cal/g. solids
dG	differential change in free energy on mixing, cal.
H	enthalpy
$\bar{H}_w$	partial or differential enthalpy with respect to water of a mixture
ΔH	integral net change in enthalpy on mixing pure components, cal.
ΔH_w	integral net enthalpy of solution, cal/100 g. solids
ΔH^+	integral net enthalpy of mixing, cal/g. mixture

$\overline{\Delta H}_w$	change in differential net enthalpy with respect to water, cal/g. water
$\overline{\Delta H}_s$	change in differential net enthalpy with respect to solids, cal/g. solids
$\overline{\Delta H}_T$	change in differential total enthalpy with respect to water, cal/g. water
S	entropy
$\bar{S}_w$	partial or differential entropy with respect to water of a mixture, cal/g. water • °K
ΔS	integral change of entropy on mixing pure components, cal/°K
ΔS_w	integral entropy of solution, cal/100 g. solids/°K
$\overline{\Delta S}_w$	change in differential entropy with respect to water, cal/g. water • °K
$\overline{\Delta S}_s$	change in differential entropy with respect to solids, cal/g. solids • °K
J	an extensive thermodynamic property
R	universal gas constant
T	absolute temperature
X_s	adsorbent (solids)
X_w	adsorbate (water)
n_s	mass of solids in moles or g.
n_w	mass of water in moles or g.
N_w	mole fraction of water
N_s	mole fraction of solids
W	weight fraction of water
$(1-W)$	weight fraction of solids
p	vapor pressure
p°	vapor pressure of pure water

p^m	vapor pressure of mixture
P_i	vapor pressure of component i
f_i	fugacity of component i
μ°	chemical potential of pure water
a_w	water activity
λ	enthalpy of vaporization of water
M	moisture content
rh	relative humidity
ΔM	change in moisture content
Δrh	change in relative humidity
V_m	quantity of vapors required for a BET monolayer
C	energy constant in BET equation
k_1, k_2, k, Y	constants
γ	activity coefficient
A	surface area
x	mole fraction
w	work
σ	surface tension or surface free energy

I. INTRODUCTION

I.1. General Remarks

The presence of water is normally essential for life to proceed and the existence of sufficient quantities in food normally leads to spoilage of the products.

Water usually represents 60 to 95 percent of the total mass of food and is by far the dominant and the most important component. Food products normally contain fats and oils, proteins, carbohydrates, acids, minerals and other groups of substances. Many of these (like sugars, many salts, etc.) occur in solution with the water, but others are distributed less uniformly or may be dispersed in these solutions.

Many substances found in the foods of biological origin are organized in characteristic structure (tissue) and adsorb water in different ways.

The association of the water molecule with biological substances is still a subject of controversy in spite of considerable research on the subject. Three types of adsorbed water have been characterized in different terms (Rockland, 1969):

Type 1. Monolayer, frozen or iceberg, hydrate localized polar site, bound, oriented.

Type 2. Multilayer, chemisorbed, intermediate.

Type 3. Mobile, free, capillary, solution.

Evidence supporting the existance of these three types of adsorbed water has come principally from thermodynamic considerations. Additional supporting evidence has been obtained from x-ray studies, infrared and nuclear magnetic resonance spectroscopy, refractive index, water density, and molecular structure investigations.

Type 1 water adsorption is referred to as water molecules adsorbed on the polar sites of components of high molecular weight, such as protein, starch, etc.

Type 2 water adsorption is assumed to involve water molecules, hydrogen bonded to hydroxyl and amide groups.

Type 3 adsorbed water is considered to be water vapor condensed in interstitial pores of the biological tissues.

The interactions of the water molecules with the polar groups of the solid constituents of a food and the capillary effects of the structure of biological tissues lower the vapor pressure of the water in foods. The water vapor pressure depression may be enhanced by the dissolution of solutes such as sodium chloride, citrates, phosphates, sucrose, glycerol and others, due to well known phenomenon which is also responsible for the elevation of boiling point. This is believed to result from increased total hydration of large numbers of solute molecules which decrease the probability of occurrence of unattached water molecules (Potter, 1970). For example, lactose exists in milk powder at least partially as mono-hydrated crystals, which exert a water vapor pressure considerably lower than the vapor pressure of free water (Berlin *et al.*, 1968).

I.2. The Sorption Isotherm and Availability of Water

The fugacity or escaping tendency (f_i) of component i in a mixture was previously established as a measure of its availability for thermodynamic chemical reactions (Rossini, 1950). Since by definition, $f_i = P_i$(P_i = vapor pressure of component i) for ideal gases and $f_i = P_i$ for all gases at low enough pressures, the vapor pressure of water in a food product is a measure of its availability.

The ratio ($\frac{P}{P^\circ}$) between the water vapor pressure of a substance (P) and the saturation vapor pressure of pure water (P°) at the same temperature is known as the activity of the water (a_w) in the substance. It is a measure of the availability of water for chemical reactions or of the escaping tendency of the water in the substance as compared to the fugacity or availability of pure water for chemical reactions. Strictly speaking this is not the thermodynamic activity of water in the product as the latter is given by the fugacity ratio and not by the ratio of vapor pressures. This difference, however, is slight and is being investigated in the field of theoretical thermodynamics (Rossini, 1950).

It can be shown that the water activity (a_w) of a product is equal to the relative humidity of the atmosphere, in thermal and vapor pressure equilibrium with the product, expressed as a decimal. The graphical relationship of the moisture content of a food product to the equilibrium relative humidities of the atmospheres at a given temperature, is called the sorption isotherm of the product. The sorption isotherms of most biological materials are sigmoid curves and are referred to as Type II isotherms, according to Brunauer's classification (Figure 1.1) (Brunauer, 1945). It must be noted here, that sorption is a general term which describes both adsoprtion and desorption.

According to the theory of Brunauer _et al_. (1938), water is bound (strongly sorbed) in a monomolecular layer in the first region of the isotherm (up to point A: Type-1 adsorbed water). Above point A (in the straight-line region) bi- or multi-molecular adsorption occurs (Type-2 adsorbed water). Above point B, water is condensed in capillaries with increasing water activity (Type-3 adsorbed water). Free, unattached water molecules may be present in liquid state and may act as a solvent even at low water activity as has been shown in investigations with model food systems. One characteristic of a solvent is that dissolved materials are permitted to diffuse in it by virtue of a concentration gradient. Water soluble compounds have substantial mobility in dry foods at water contents very close to monolayer

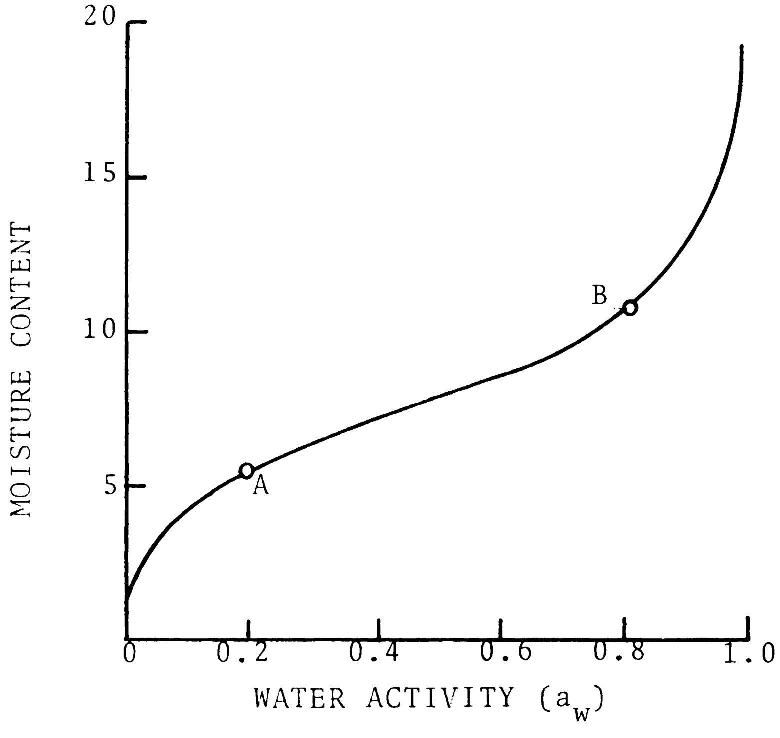


Figure 1.1.--Sorption isotherm of water vapor sorption by biological materials (Acker, 1969)

coverage in spite of important differences in their interaction with the food (Duckworth and Smith, 1963). Thus it is likely that reactants, which are normally within specific sites in cells comprising tissue-derived food, may diffuse out of these sites and react with each other, even at relatively low water contents.

Acker (1963) has demonstrated this effect in terms of enzymatic reactions in various foods. His results illustrate that some reactions occur at very low activities. At higher water activity, especially in the capillary condensation range, the reactions are accelerated.

Chung *et al*. (1967) recently offered additional evidence for the presence of free water at high moisture levels. The net heat of adsorption ($\overline{\Delta H}_w$) approached zero when the heat of vaporization (λ) was subtracted from the differential heat of adsorption ($\overline{\Delta H}$). Thus:

$$\overline{\Delta H}_W = \overline{\Delta H}_T - \lambda$$

indicating that adsorbed water vapor on the adsorbent behaves like pure water. In general, the differential heat of adsorption or desorption indicates the binding energy or the intermolecular force between the molecules of water vapor and the surface of the adsorbent.

I.3. Water Activity and Storage Stability of Low and Intermediate Moisture Foods

Reduction of quality of low and intermediate moisture foods during storage may result from anyone or a combination of undesirable flavor and odor, textural damage and loss of nutritional value. In addition, the food may be rendered unwholesome due to microbial spoilage. Accordingly, the processes leading to quality deterioration of low and intermediate moisture foods may be classified as chemical, enzymatic and microbiological in nature.

A food may be characterized as stable in storage if its quality is preserved during a predefined storage period. It is generally recognized that water activity is more closely related to food product stability than total moisture content. Two foods with the same water content may have very different water activity values depending upon the degree to which the water is free or bound to food constituents.

Water activity, not absolute moisture content, controls bacterial, enzymatic, and chemical reactions and is dependent on the micro-environmental level in food materials. The water activity of optimum storage stability of a food product may be defined as the water activity at which the combined spoilage effect of all deteriorative processes is a minimum during the storage period.

It was reported that the differential coefficient of moisture (M) with respect to humidity (rh) [$\Delta M/\Delta rh$] could be related to chemical characteristics of shelled walnuts and beans during storage (Rockland, 1957). Salwin (1959) suggested that low moisture products would be least susceptible to deterioration, provided their moisture level is kept at the mono-molecular moisture layer determined from BET theory (Brunauer *et al.*, 1938). Below this value, fat oxidation will occur and above the monomolecular layer moisture content, nonenzymatic browning and hydrolytic changes would establish the spoilage pattern. Later investigations have demonstrated that water had an inhibitory effect on nonenzymatic oxidation of fats and promoted the nonenzymatic browning and enzymatic reactions (Acker, 1963; Maloney *et al.*, 1966). There seems to be considerable evidence that the fundamental thermodynamic properties of the vapor sorption process of low and intermediate moisture foods may be related to the water activity (a_w) of optimum storage stability (Rockland, 1969; Kapsalis *et al.*, 1971; Palnitkar, 1970). This might be expected since the water activity of a food is the same as the chemical activity of the water in the food. In addition, thermodynamics of sorption phenomena for low and intermediate moisture foods provide valuable information useful for the design of dehydration equipment with low initial and operation costs.

The current status of research on the relationship between water activity and storage stability for low and intermediate moisture foods however, is not conclusive when considering the existence of a generalized approach to the determination of their optimum storage water activity. As a result of this situation, it seems necessary to follow the time-consuming procedure of establishing the storage behavior of every range of low-moisture foodstuff within its individual critical range of moisture content.

I.4. Objectives

The objectives of this dissertation were:

1. To systematically develop and present the thermodynamic equations which describe the phenomenon of vapor sorption by biological materials.
2. To measure the sorption isotherms of raw and precooked freeze-dried beef at three different temperatures.
3. To determine the various thermodynamic properties of raw and precooked freeze-dried beef from moisture sorption data.
4. To analyze the influence of sorption conditions and product characteristics on thermodynamic properties of food.
5. To explore the possibilities of finding a relationship between one or more thermodynamic parameters and storage stability of foods in the low and intermediate moisture range.
6. To analyze the expressions and procedures used to evaluate the thermodynamic properties of foods as presented in published literature.

II. GENERAL REVIEW OF LITERATURE

II.1. The Mechanism of Sorption

II.1.1. Theories of Sorption Phenomena

Three phenomena may be involved in the sorption of vapors by biological and polymeric materials: monomolecular sorption, multimolecular sorption, and condensation in capillaries or pores. Since there is frequently considerable overlapping of these phenomena, the interpretation of sorption isotherms becomes very complex.

Langmuir (1916) presented the monomolecular theory, which assumes that the film of the adsorbed gas does not grow to a thickness of more than one molecule, even at values of $P/P°$ saturation. Brunauer, Emmett, and Teller (1938) developed the theory of multimolecular adsorption known as BET theory. The derivation of the BET equation involves a detailed balancing of evaporation and condensation phenomena in adjacent layers and assumes that only the energy of sorption for the first layer differs from the energy of condensation for water. The resulting equation is:

$$\frac{P}{V(P^{\circ}-P)} = \frac{1}{V_m c} + \frac{c-1}{V_m c} P/P^{\circ} \qquad (2\text{-}1)$$

where V is the amount of gas adsorbed at an equilibrium pressure (P); P° is the saturation pressure; V_m is the quantity of gas (adsorbed vapor) required to form a monolayer and c is constant which is a function of the difference between the energy of sorption in the first layer and the energy of condensation. Harkins and Jura (1944) established that the thickness of adsorbed films become multimolecular as the vapor pressure (P) increases. Bushuk and Winkler (1957) tested the BET equation utilizing experimental isotherms for flour, starch and gluten.

The BET equation (2-1) was applied in studies of water sorption by proteins and high polymers (Mellon *et al.*, 1947; Smith, 1947). These investigations have shown that the BET equation is applicable only at relative humidities of less than 50 percent. Brunauer *et al.* (1940) established five categories of isotherm. Type II is the sorption isotherm most frequently encountered for biological materials and is referred to as the sigmoid or S-shaped isotherm. The first portion of the curve ($P/P^\circ<0.1$) corresponds to monomolecular adsorption. Capillary condensation occurs in the region above approximately $P/P^\circ=0.4$.

Labuza (1968) reviewed the theory of sorption isotherms and concluded that there are three basic theories which explain the sorption phenomena: (a) the kinetic concept of Langmuir (1916) which was used in deriving the BET theory, (b) Polanyi's (1914) adsorption potential theory, and (c) Zsigmondy's (1941) capillary condensation theory. Ngoddy et al. (1970) developed a generalized theory of sorption phenomena for biological materials and concluded that none of the known theories explain sorption phenomena in biological material satisfactorily.

Hoover and Mellon (1950) found that an equation derived by Bradley (1936) could be used to describe experimental data for relative humidities between 6 and 90 percent for a variety of high polymers. Bradley (1936) derived the following equation:

$$\ln \frac{P^\circ}{P} = K_1 \; K_2^{\alpha} \qquad (2\text{-}2)$$

for the sigmoid isotherms on the basis of polarization theory of Deboer and Zwicker (1929).

In equation (2-2) K_2 and K_1 are constants, and α is the amount of gas adsorbed at pressure (P). Chung and Pfost (1967) tested Bradley's equation and found agreement over the entire range of their experimental data for cereal grains.

Henderson (1952) developed the following isotherm equation:

$$1 - rh = \exp\left(-KTM^{n}\right) \qquad (2\text{-}3)$$

where T is temperature, rh is the relative humidity and K and n are constants. Hall and Rodriquez-Arias (1958) found that the Henderson equation (2-3) described isotherms for relative humidities between 1% and 60%. Rockland (1957) modified the Henderson equation (2-3) as follows:

$$\log \log \frac{1}{1-rh} = n \log M + Y \qquad (2\text{-}4)$$

and found that application of equation (2-4) to experimental sorption data from a wide variety of biological products yielded two or three straight intersecting lines. He suggested that moisture sorption may not necessarily be a uniform continuous process, but a series of two or more independent processes. Each process can be characterized in terms of equation (2-4) if suitable constants, calculated from experimental data are substituted in the equation. Rockland (1957) observed nearly perfect agreement between theoretical curves and all reliable experimental hygroscopic equilibrium data. Local isotherm one (LI-I) is the straight line describing the low moisture range, local isotherm two (LI-II) is the straight line describing the intermediate moisture range and local isotherm three (LI-III) is the line describing the moisture range of capillary condensation.

Chung and Pfost (1967) developed the equation:

$$\ln \frac{P}{P^{o}} = -\frac{A}{RT} \exp\ (-BM) \qquad (2\text{-}5)$$

where A and B are constants and M is moisture content. Equation (2-5) is equivalent to Bradley's equation but was derived on the basis of Polanyi's potential theory and thermodynamic considerations. The authors (1967) found remarkable agreement between experimental data and theoretical isotherms over the entire range of relative humidity investigated for cereal products. Note that no theoretical

equation has been tested at relative vapor pressures lower than 0.05 experimental and higher than 0.95 because there are no reliable methods to give experimental data in these regions.

II.1.2. Physicochemical Aspects of Sorption

Based on physicochemical considerations, adsorption is a means of neutralizing or satisfying the forces of attraction that exist at a surface. Adsorption of a gas by a solid may be classified as physisorption or chemisorption, depending on the nature of the forces involved. Van der Waals forces are considered to be responsible for physical adsorption. Many investigators agree that adsorption of water vapor by biological materials is entirely Van der Walls type of adsorption (Chung and Pfost, 1967: Osipow, 1962). Physical adsorption is caused by intermolecular forces between molecules of water vapor and the surface of the adsorbent (polar sites of adsorbent). In general, polar molecules such as H_2O, NH_3, and alcohol, or molecules possessing the following polar groups: $-NH_2$, -NH-, -OH, -COOH, $-CONH_2$, etc. are considered to be sorption sites on the adsorbent. Pauling (1945) has shown that the number of molecules of water vapor adsorbed in the first layer is related to the total number of polar side chains in certain proteins.

Mellon _et_ _al_. (1947) were able to demonstrate, by benzoylating successively higher numbers of free amino groups in casein, that amino groups are responsible for

approximately one quarter of the total water uptake. The second portion of the sorption isotherm is a linear increase in adsorbed water with increase in relative humidity. The third portion of the isotherm is a rapidly increasing amount of adsorption with increasing of relative humidity and appears to be a condensation of water on water molecules already attached to the amino groups.

The energy change accompanying physical adsorption is of the same order of magnitude as that of the condensation of a vapor to form a liquid. The heat of physical adsorption is of the same order of magnitude as that of condensation. In addition, physically adsorbed layers, particularly those which have a thickness of many molecular layers behave similar to a liquid. Harkins (1952) has shown that the specific energy of immersion of solid anatase ($Ti\ O_2$) in liquid water decreases from 512 erg/cm^2 for the dry crystals to 118.5 erg/cm^2 when the crystals are saturated with vapor (mean thickness of film > 15.0 A°). The same author (1952) reported that the molar energy required to vaporize the first, second and third molecular layer, of water vapor on anatase is 6550, 1380, and 450 cal/mole higher, respectively, than the energy to vaporize pure water. In addition, Harkins (1952) observed an exponential decrease in the energy of desorption with increasing distance from the sorption surface of anatase. It must be emphasized that anatase is a nonporous solid and might behave differently than porous solids, where adsorption and capillary condensation are inextricably mixed. Harkins (1952) has presented evidence that the films of vapors on solids may exist in different states and has proposed the existence of five phases. He indicated three orders for the possible phase transitions of films on solids and observed first and second order phase changes in his experiments.

Bull (1944) determined heats of adsorption for water vapor on a number of proteins. The heats of adsorption decreased rapidly with increasing moisture content. The heat of adsorption tends to decrease rapidly at moisture contents corresponding to BET monomolecular moisture contents (V_m) and increased slightly at $P/P° \simeq 0.7$. Davis and McLaren (1948) computed heats of sorption from Bull's data. These results revealed that the value of differential net enthalpies decreased with increasing moisture content undulations occurring at the BET monolayer region.

Amberg (1957) conducted calorimetric measurements to determine heats of adsorption for water vapor on bovine serum albumin. These results indicated that heats of adsorption of the order of 16 to 18 Kcal/mole for approximately 3 mg/g. solids of adsorbed water. After a rather rapid decrease in the value with increasing moisture content, heats of adsorption became constant at approximately 15 Kcal/mole with a minor increase at moisture contents in the region corresponding to the BET monolayer.

II.2. Water Activity and Food Stability

At low vapor pressures, adsorbed molecules of water vapor may collect on the regions of surface where energy of interaction is highest. Initial adsorption is in the form of single molecules followed by groups of molecules. In these regions surface heterogeneity has a large effect. As moisture adsorption proceeds, the small groups of molecules become larger until there is complete coverage of the surface by one molecular thickness. The forces of interaction between the adsorbed molecules increase as the density of molecules on the surface increases. Harkins (1952) presented data supporting the proposal that the mean molecular area (area occupied by a molecule of the adsorbate) of nonpolar adsorbates is independent of the nature of the solid upon which the adsorption occurs at the BET monolayer. Based on the results, the interactions in the film become very large and the inhomogeneities on the surface of the solid do not influence the adsorption process. At the BET monolayer, the film is mobile and the inhomogeneity theory becomes invalid. Harkins (1952) emphasized that when water vapor is being adsorbed, the limited data available indicate that this is no longer true. The inevestigations of Duckworth and Smith (1963) illustrate that after completion of the monomolecular layer, the adsorbed vapor is considered mobile. The results indicate that diffusion of glucose is possible in dehydrated material (such as dehydrated potato slices) at moisture contents which are 2 to 3 percent above the BET monolayer moisture content.

Acker (1969) observed that enzyme activity begins at moisture contents above the monomolecular adsorption layer and continues along the upper portion of the sorption isotherm which represents the region of capillary condensation. This is not true for enzymatic reactions in which the substrate is mobile enough to establish contact with the enzyme without needing aqueous phase. For example, enzymatic reactions involving oily substrates, such as triglycerides, can occur at water activities lower than the BET monolayer. The results obtained by Acker (1969) indicate that the mobility of the substrate is decisive in promoting the enzyme reaction. The water may participate in enzyme reactions as a reactant, as a medium for the enzyme reactions as a reactant, as a medium for the enzyme reactions or as a vehicle for the substrate movement. Due to these factors, water plays an active role in determining the rate of the enzymic reaction and the extent to which the reaction will proceed.

Salwin (1959, 1963) suggested that the moisture content at the BET monolayer represents a protective film on the surface of the food against attack by oxygen. With the exception of a few foods [mainly high sugar products; Karel and Nickerson (1964)] where complete dehydration was essential for good stability, the BET moisture value was proposed as the final moisture content in dehydration, unless more specific storage stability information is available.

Rockland (1957) reported that the differential coefficient of moisture with respect to relative humidity ($\Delta M/\Delta rh$) could be related to chemical characteristics of shelled walnuts and beans during storage. Optimum odor, flavor and color stability in walnuts, and minimum phosphatase and catalase activity in beans occurred at a moisture content close to a minimum $\Delta M/\Delta rh$ value. Below this value rancidity occurred, whereas above it fat hydrolysis and browning occurred. Since dehydrated foods are chemically complex, it can be difficult to interpret results of storage stability in terms of specific reactions.

Maloney _et_ _al_. (1966) employed purified freeze-dried model systems of methyl linoleate, microcrystalline cellulose and water to establish that water had an inhibitory effect on the oxidation reaction of methyl linoleate. Based on results presented, this inhibitory effect was not restricted to 19.5 percent RH corresponding to the BET monolayer, but it was evident at 14.5 percent RH, and increased with increasing humidity up to about 50 percent RH. Compared to the BET value, the inhibitory effect was slightly smaller at 14.5 percent RH and it was appreciably higher at 27.7 percent RH. These findings indicate that water exerts a specific protective effect against lipid oxidation. Uri (1956) attributed the inhibition of oxidation to a specific type of solvation of the coordination shells of metal ions by the polar water molecule, whereby the catalytic oxidative effect of these ions is decreased. Lea (1958) suggested that water promotes amino-carbonyl browning which produces intermediate reducing compounds and competition develops between lipid oxidation and Maillard-type of browning. Simatos (1966) revealed that water reacts to reduce the free radical content in serum albumin and it is possible that this is one of the anti-oxidant mechanisms of water action. These results are in agreement with a more recent report by Martinez and Labuza (1968) on the storage stability of freeze-dried salmon. When kept below the level which promoted nonenzymatic browning, water decreased the rate of lipid oxidation and prevented the destruction of the carotenoid pigment astacene.

Karel and Labuza (1968) illustrated that nonenzymatic browning increased with increasing water activity and reached a maximum within intermediate moisture range. The growth of microorganisms, which represents a major limitation to food stability, occurs at higher water activities (a_w>0.85). Scott (1957) and Christian (1963) have reviewed the relationship of the growth of molds, yeasts and bacteria to water activity. Labuza *et al.* (1970) presented Figure 2.1 to illustrate the relationship of mechanisms involved in chemical deterioration to storage stability of foods. Although the authors do not indicate the water activity at which oxidation and browning becomes equal, it is recognized that it occurs slightly above the monolayer moisture content.

Palnitkar (1970) determined thermodynamic parameters for precooked freeze-dried and raw freeze-dried beef

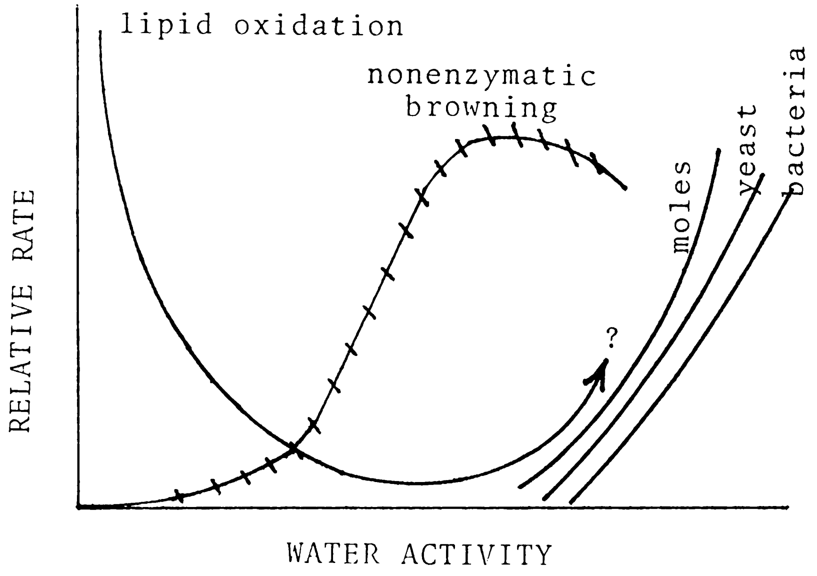


Figure 2.1.--General dependence of rates of deterioration on water activity.

and reported that the entropy becomes maximum at moisture contents slightly above the BET monolayer. He suggested that computation of entropy may provide a tool for determining optimum water activities for low and intermediate moisture foods.

III. EXPERIMENTAL

III.1. Sample Preparation

Experimental phases of this investigation involved preparation of beef samples for the measurements of equilibrium moisture isotherms. The *longissimus dorsi* muscle of beef procured from the Michigan State University Food Stores was used for the sample preparations.

III.1.1. Preparation and Grinding

All physically separable fat and connective tissue was removed from the beef sample. The sample was ground twice through a 1 cm plate and twice through a 2 cm plate, using a meat grinder. A portion of the ground beef was frozen at -15°C prior to freeze-drying while part of it was cooked before freezing at -15°C.

III.1.2. Cooking Procedures

The ground beef samples were formed into 1-inch diameter spheres before cooking in a forced convection air oven at 300°F for a period of 30 min. The precooked beef samples were subsequently frozen at -15°C prior to freeze-drying.

The freeze-drying of both raw and precooked samples was accomplished in a commercial freeze-drier with a 100°F

plate temperature and at a pressure of less than 1 mm of mercury. The drying was completed in 20 to 25 hrs. After drying, the product was ground in a Fritz-Patrick mill using a 0.063-in. screen. The resulting product powder was sealed in bottles which were stored in a desiccator at -20°C. Portions of the product to be used for equilibrium moisture content determination were equilibrated to the isotherm temperature prior to the experiment.

III.2. Measurement of Equilibrium Moisture Isotherms

The moisture adsorption and desorption isotherms were determined gravimetrically by exposing the sample to an atmosphere produced by a temperature-controlled free water surface under vacuum. An electrobalance and associated instrumentation was used to measure and record weight changes automatically and continuously during moisture sorption. The glass chamber containing the balance was connected to a vacuum pump through a freeze-trap and to a pure water vapor source. The vapor source consisted of a temperature controlled distilled water reservoir. The temperature of the water reservoir was controlled to within ± 0.05°C using a constant temperature ethylene glycol laboratory bath. A schematic diagram of the vacuum system and electrobalance assembly is presented in Figure 3.1. The desired relative vapor pressure values were established by precise temperature control of the free water surface.

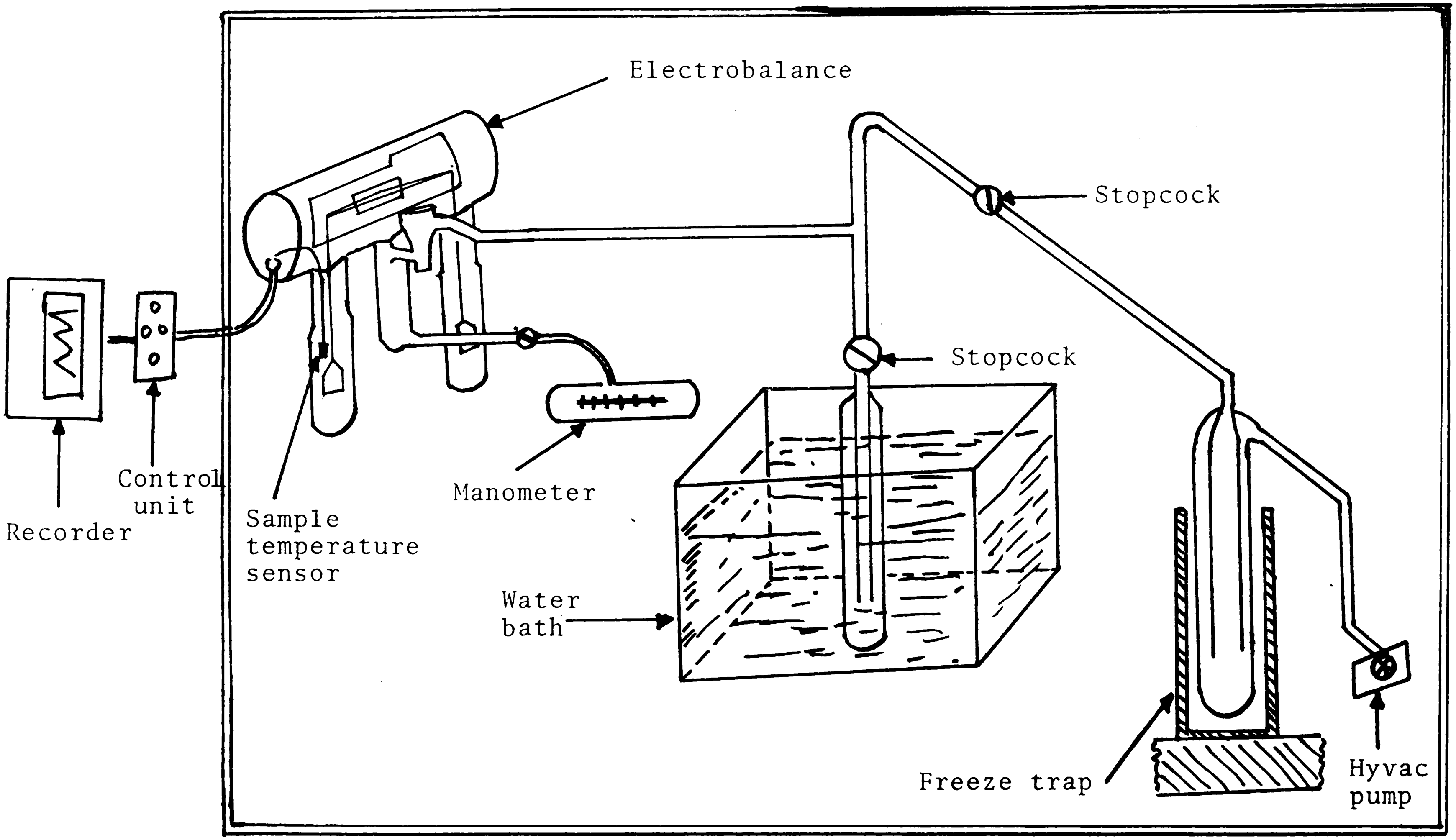


Figure 3.1.--Schematic diagram of moisture sorption apparatus showing electrobalance assembly and related instrumentation.

A vacuum gauge was utilized for pressure measurements. The entire system except for instrumentation and recorder was enclosed in a 5 ft x 4 ft x 9 ft constant temperature cabinet controlled to within ± 1°C. Moisture content of samples was determined independently using the 95°C 5 hr vacuum oven method (Triebold and Aurand, 1963). Sorption isotherms were measured at 10°C, 21.3°C and 31°C. Between 30 and 50 mg of ground freeze-dried material, equilibrated to isotherm temperature for 24 hr, was introduced into an aluminum pan in the electrobalance. The vacuum chamber was sealed and the weight of the sample was recorded. The chamber was then evacuated and the vacuum was drawn until the change in moisture content of the sample was less than 0.01 percent in 1 hr. This usually took 10 to 15 hr of continuous pumping by the vacuum system. The vapor pressure in the chamber after this period was between 7 and 25 μ depending on temperature and was considered the starting point for measurement of the isotherm. The sample was then exposed to progressively higher vapor pressure atmospheres produced by controlling the temperature of the vapor source. The vapor source was distilled water which was degassed by successive freeze-evacuating and thawing. Equilibrium at each vapor pressure atmosphere was assumed when weight changes corresponding to changes in moisture content of less than 0.01 percent occurred in 1 hr. The corresponding equilibrium moisture contents were determined on the basis of moisture content of sample as determined by the vacuum oven method and the weight changes recorded by the electrobalance. Approximately 10 to 12 equilibrium points were used to establish each adsorption isotherm. Completion of the adsorption isotherm required 3 to 4 days. After the completion of the adsorption isotherm, the system was evacuated to remove any air which had diffused into the chamber and resaturated with vapors until the sample showed a moisture gain corresponding to a relative humidity of greater than 95 percent. The desorption isotherm was then measured by progressive reduction of the vapor pressure through control of the temperature of the vapor source reservoir. Generally 6-7 days were required to complete the adsorption and desorption isotherms for a given sample. There was no visible microbial activity or any type of deterioration within the time period required for isotherm measurement.

IV. THERMODYNAMICS OF SORPTION

IV.1. General Remarks

Systems containing macromolecules are subject to the ordinary thermodynamic laws (Hermans, 1949). Gee and Treloar (1942), Bull (1944), Davis and McLaren (1948), Fish (1958) used sorption isotherms for thermodynamic description of binary mixtures of high-polymeric materials with a low molecular weight liquid. Kapsalis (1967) and Palnitkar (1970) employed sorption isotherm data for the calculation of the thermodynamic quantities for various food products. In general, the differential and the integral values of free energy, enthalpy and entropy were calculated. There appears to be a certain amount of disagreement among researchers in the field of adsorption concerning the application of thermodynamics to adsorption data. In this chapter the thermodynamic relations used for the computation of differential and integral quantities are illustrated along with some of the conventional assumptions used.

IV.2. Thermodynamics of Nonreacting Binary Systems

The thermodynamic processes of interest for homogeneous binary systems are of two general types; integral and differential. The integral process related to sorption phenomena can be presented as follows:

$$n_sX_s \text{ (dry at } P=0) + n_wX_w \text{ (at } P=P°) \rightleftarrows n_sX_s \text{ with } n_wX_w$$
$$\text{(system at } P=P^m) \qquad (4\text{-}1)$$

In addition, the differential process corresponding to sorption phenomena may be written as:

$$n_wX_w \text{ (at } P=P°) + \text{system of } n_sX_s \text{ with } n_w'X_w \text{ (at } P=P^m) \rightleftarrows$$
$$\text{system of } n_sX_s \text{ with } (n_w+n_w')\ X_w \text{ and } n_w'/n_s =$$
$$\text{constant, at } P=P^m \qquad (4\text{-}2)$$

Process (4-1) represents the sorption of n_w moles of pure water (vapor pressure P°) on a finite amount (n_s moles) of dry adsorbent (X_s) to produce the system containing n_s moles of X_s and n_w moles of water, at pressure P^m.

Process (4-2) describes the sorption of n_w moles of water on an indefinitely large amount (n_s moles) of X_s which already holds n_w' moles of water for each n_s moles of adsorbent. The ratio n_w'/n_s and the pressure P^m remain constant during the differential process (4-2).

IV.2.1. Thermodynamics of the Differential Process

Free Energy--With reference to liquid water as the standard state, the change in the partial molar free energy ($\overline{\Delta G}_w$) of water is defined as the increase in free energy (G) of the system when one mole of water is transferred isothermally from or to a bulk of liquid water to or from an infinite quantity of solid mixture at definite moisture content (Fish, 1958). When $\tilde{G}_w$ represents the molar free energy of pure water and $\overline{G}_w$ the (partial) molar free energy of the water in the mixture, the change in free energy of the system (dG) for dn_w moles of water being adsorbed is:

$$dG = \overline{G}_w dn_w - \tilde{G}_w dn_w = \overline{\Delta G}_w dn_w \tag{4-3}$$

If the system is in equilibrium with the vapor of the pure water, the molar free energy of the water must be the same in the two phases. Denoting the molar free energy of the equilibrium vapor phase by $\overline{G}'_w$:

$$\overline{G}_w = \overline{G}'_w$$

If the vapor has the properties of an ideal gas and if P is the pressure:

$$\overline{G}'_w = \mu°(T) + RT\ln P$$

where $\mu°$ is a function of temperature alone. Consequently the partial molar free energy in the solution is:

$$\overline{G}_w = \mu°(T) + RT\ln P$$

Considering, in addition, the equilibrium between the pure water and its vapor at the same temperature and pressure ($P°$), the molar free energy of pure water is:

$$\tilde{G}_w = \mu^\circ(T) + RT\ln P^\circ$$

Thus, from the vapor pressure (P) of the mixture and the vapor pressure (P°) of the pure water the differential change of the free energy of the system dG per dn_w moles of adsorbed water can be obtained:

$$dG = \overline{G}_w dn_w - \tilde{G}_w dn_w = \overline{\Delta G}_w dn_w = RT\ln P/P^\circ dn_w \qquad (4\text{-}4)$$

Correspondingly, with reference to pure adsorbent as the standard state, the change of the partial molar free energy ($\overline{\Delta G}_s$) of the adsorbent is defined as the increase in Gibbs free energy of the whole system when 1 mole of pure adsorbent is isothermally transferred from a mass of pure adsorbent to a large quantity of the mixture (process 4-2).

It is well known that in a homogeneous mixture of two components, w and s, the change of $\overline{\Delta G}_w$ with concentration N_w, at constant temperature and pressure, is related to the change in $\overline{\Delta G}_s$ according to the Gibb's-Duhem relation (Hermans, 1949):

$$N_w d\overline{\Delta G}_w + N_s d\overline{\Delta G}_s = 0 \qquad (4\text{-}5)$$

Based on equation (4-5), the partial molar free energy change of solids (G_s) can be derived from the partial molar free energy change of the water. Equation (4-5) can be integrated as follows:

$$N_s\overline{\Delta G}_s = -\int_{-\infty}^{\overline{\Delta G}_w} N_w d\overline{\Delta G}_w \qquad (4\text{-}6)$$

It is apparent from equation (4-4) that $\overline{\Delta G}_w = -\infty$ at $P/P° = 0$ and $\overline{\Delta G}_w$ is finite when $P/P°$ is finite. It follows that equation (4-6) can be integrated graphically if written as:

$$N_s\overline{\Delta G}_s = -RT\int_0^{P/P°} N_w(P°/P)d(P/P°) \qquad (4\text{-}7)$$

Enthalpy--The differential net molar enthalpies ($\overline{\Delta H}_w$, $\overline{\Delta H}_s$) or partial molar net enthalpy changes may be defined in the same way as $\overline{\Delta G}_w$, $\overline{\Delta G}_s$ above, except for the substitution of the concept of enthalpy.

The term "net" is used here to point out that $\overline{\Delta H}_w$ is the difference between the differential heat of adsorption of the adsorbate vapor and the differential heat of condensation of the vapor.

The differential enthalpies can be computed from expressions for the corresponding differential free energies. The partial molar enthalpy of the adsorbate is:

$$\overline{\Delta H}_w = -T^2[\partial(\overline{\Delta G}_w/T)/\partial T]_{n_w,n_s} = -RT^2[\partial \ln(P/P°)/\partial T]_{n_w,n_s} \qquad (4\text{-}8)$$

Equation (4-8) is the well known Gibb's-Helmholtz relation and can be written in the following more explicit form:

$$\overline{\Delta H}_w = [\partial(\overline{\Delta G}_w/T)/\partial(1/T)]_{n_w,n_s} = R[\partial \ln(P/P°)/\partial(1/T)]_{n_w,n_s} \qquad (4\text{-}9)$$

Apparently, for an isoteric process, $\overline{\Delta H}_w$ can be obtained either graphically or by integration from equation (4-9).

The partial molar enthalpy change of the adsorbent can be derived either from the Gibb's-Duhem relation:

$$N_s\overline{\Delta H}_s = -\int_0^{\overline{\Delta H}_w} N_w d\overline{\Delta H}_w \qquad (4\text{-}10)$$

or from the Gibb's-Helmholtz relation:

$$\overline{\Delta H}_s = [\partial(\Delta G_s/T)/\partial(1/T)]_{n_w,n_s} \qquad (4\text{-}11)$$

Entropy--As with enthalpy changes, differential entropy changes may be determined from appropriate temperature coefficients of the corresponding free energy changes. The change in partial molar entropy of the adsorbate and adsorbent are determined directly from the temperature coefficients of the differential process (equation 4-2):

$$\overline{\Delta S}_w = -(\partial\overline{\Delta G}_w/\partial T)_{P,n_w,n_s} \qquad (4\text{-}12)$$

$$\overline{\Delta S}_s = -(\partial\overline{\Delta G}_s/\partial T)_{P,n_w,n_s} \qquad (4\text{-}13)$$

Equations (4-12) and (4-13) are obtained from the well known Maxwell's relations. Differential entropy changes may also be calculated from the thermodynamic relation:

$$\overline{\Delta S}_w = \frac{(\overline{\Delta H}_w - \overline{\Delta G}_w)}{T} \qquad (4\text{-}14)$$

IV.2.2. Thermodynamics of the Integral Process

Sorption experiments are designed to measure finite changes. For example, calorimetric determination of heats of sorption is possible only for finite processes even when using the best instruments available. Harkins and Boyd (1942) determined heats of adsorption by measuring heats of immersion. The immersion process is equivalent to the integral process (equation 4-1) as illustrated with the aid of the following two step process:

A. Immerse a dry adsorbent from a vacuum into a liquid;

adsorbent n_sX_s (dry at $P=0$) + nX_w (water, $P=P^\circ$) →

$$\left[\begin{array}{l}n_sX_s \text{ saturated with and in} \\ \text{an excess of liquid } X_w\end{array}\right]$$

B. Immerse the adsorbent from a vapor, wherein n_s moles of X_s adsorbed n_w moles of X_w in equilibrium with vapor at pressure P^m, into a large amount of liquid adsorbate.

$$\left[\begin{array}{l}n_s \text{ moles of } X_s \text{ with} \\ n_w \text{ moles of } X_w \text{ adsorbed} \\ \text{upon it in equilibrium} \\ \text{with vapor at } P=P^m\end{array}\right] + (n-n_w)X \rightarrow \left[\begin{array}{l}n_s \text{ moles of } X_s \\ \text{saturated with and} \\ \text{in an excess of} \\ \text{liquid } X_w\end{array}\right]$$

The difference between these two steps (A-B) is given by the integral process equation (4-1):

$$n_sX_s \text{ (dry at } P=0) + n_wX_w \text{ (at } P=P°) \rightarrow \begin{bmatrix} n_s \text{ moles of } X_s \text{ with } n_w \\ \text{moles of } X_w \text{ adsorbed} \\ \text{upon it in equilibrium} \\ \text{with vapor at pressure } P^m \end{bmatrix}$$

The integral heat of adsorption (ΔH) per fixed amount of adsorbent is the difference between the heat of immersion of the dry adsorbent and the heat of immersion of the adsorbent with n_w moles of X_w adsorbed upon it.

The value of ΔH obtained by calorimetric measurement depends on the total quantities of the components mixed and their relative amounts, which determine the concentration of the resulting solution. In order to have comparable values for different concentrations, it is necessary to base the measurements on some fixed quantity of solute or solvent or mixture. One approach is the quantity of heat per mole of solute added. If n_1 moles of solvent and n_2 moles of solute are mixed, the quantity ($\Delta H/n_2$) is called the integral heat of solution. Correspondingly the integral heat of dilution is given by the ratio $\Delta H/n_1$ and represents the quantity per mole of solvent added in the mixing process. For dilute solutions (n_1/n_2 large), the values of $\Delta H/n_2$ approach a limiting value referred to as the heat of solution at infinite dilution (Cole and Coles, 1964). It corresponds to the heat adsorbed or desorbed when one mole of solute is added to an infinitely larger quantity of solvent, and represents therefore the heat supplied when solute molecules are transferred from surroundings of other solute molecules to an environment of solvent molecules.

Considering the process of adsorption as mixing of pure water with food solids the integral net heat of solution of the sorption process may be expressed per mole of adsorbent or per unit mass (100 g. solids), assuming a molecular weight cannot be assigned to food solids. The term net is, again, used to point out that ΔH is the difference between the integral heat of adsorption of the adsorbate vapor and the integral heat of condensation of the vapor. The integral heat (net) of solution of the sorption process (ΔH) can be derived either by integration of the differential net heat of sorption or from the temperature coefficient of the integral free energy of solution (ΔG) (Wu and Copeland, 1964).

The integral properties can be obtained from the differential in the following manner: For a differential change, at constant temperature and pressure, with respect to molar concentration of the change of any extensive property J of a homogeneous binary system the following expression can be written:

$$d\Delta J = (\partial \Delta J/\partial n_w)_{T,P,n_s} dn_w + (\partial \Delta J/\partial n_s)_{T,P,n_w} dn_s \qquad (4\text{-}15)$$

where n_w, n_s represents moles of water and food solids, rexpectively. However, by definition:

$$(\partial \Delta J/\partial n_w)_{T,P,n_s} = \overline{\Delta J}_w \text{ and } (\partial \Delta J/\partial n_s)_{T,P,n_w} = \overline{\Delta J}_s$$

Based on derivations presented the differential change of free energy and enthalpy for the entire system can be written as:

$$d\Delta G = \overline{\Delta G}_w dn_w + \overline{\Delta G}_s dn_s \tag{4-16}$$

$$d\Delta H = \overline{\Delta H}_w dn_w + \overline{\Delta H}_s dn_s \tag{4-17}$$

Experiments used to investigate sorption phenomena are conducted at constant mass of solids while varying the amount of sorbed water. For sorption results, equations (4-16) and (4-17) can be used in the following form:

$$d\Delta G = \overline{\Delta G}_w dn_w \tag{4-18}$$

$$d\Delta H = \overline{\Delta H}_w dn_w \tag{4-19}$$

Equations (4-18) and (4-19) prove that the differential change in any extensive property of a sorption system, at constant temperature and pressure, is equal to the partial molar change of the same property of the sorbate. Based on equations (4-18) and (4-19), the following equations are obtained:

$$\Delta G_w = \int_0^{n_w} \overline{\Delta G}_w dn_w \tag{4-20}$$

$$\Delta H_w = \int_0^{n_w} \overline{\Delta H}_w dn_w \qquad (4\text{-}21)$$

where n_w is the number of moles of water sorbed per mole or unit mass of food solids, assuming a molecular weight cannot be assigned to food solids and ΔG_w and ΔH_w indicate integral free energy and enthalpy of solution in cal/unit mass solids. Equations (4-20) and (4-21) have been used by a number of authors (Davis and McLaren, 1948; Wu and Copeland, 1964; Kapsalis, 1967) although they do not give an explicit account of their derivation.

In practice the integrations must be carried out graphically (Kapsalis, 1967). The quantity (ΔH), as already pointed out, is directly accessible to experiment and has been used as a means to study the thermodynamic properties of mixtures and as a check on theoretical formulae (Wu and Copeland, 1964). The significance of the integral heats of solution for final solution concentration other than infinitely dilute is not obvious; as solute is added progressively to pure solvent and to increasingly less dilute solutions. The integral heat is an average ΔH for the total change in solution concentration.

In contrast, the differential heats are values of ΔH which represent the addition to a solution of particular concentration, and are partial molar values. The differential heat of dilution (adding water to a given amount of food solids) must be obtainable from the slope of the curve $\Delta H/n_s$ vs. n_w/n_s (n_w = moles or grams of water; n_s = 1 mole or 100 g. of solids respectively). Thus:

$$[\partial(\Delta H/n_s)/\partial(n_w/n_s)]_{T,P,n_s} = (\partial\Delta H/\partial n_w)_{T,P,n_s} = \overline{\Delta H}_w \qquad (4\text{-}22)$$

Equation (4-22) confirms the correctness of equation (4-21) and its derivation. In practical calorimetry, known amounts of the pure mixture components are mixed and the heat evolved (ΔH) is measured. The integral heat of solution is then obtained from the ratio ($\Delta H/n_s$), while the integral heat of dilution is obtained from the ratio ($\Delta H/n_w$) (Cole and Coles, 1964). The differential heats of dilution and solution are obtained as suggested by equation (4-22). The integral heat of mixing may also be expressed as per unit mass of mixture. Of course the integral heat of mixing per unit mass of mixture (ΔH^+) will vary with varying composition of the fixed amount of mixture.

If J in equations (4-16) and (4-17) is used to replace any extensive property, the general form of the equation becomes:

$$d\Delta J = \overline{\Delta J}_w dn_w + \overline{\Delta J}_s dn_s \qquad (4\text{-}23)$$

At constant temperature and pressure, for a given composition of the mixture, $\overline{\Delta J}_w$ and $\overline{\Delta J}_s$ are constant and equation (4-23) may be integrated for a finite addition of water to yield:

$$\Delta J = \overline{\Delta J}_w dn_w + \overline{\Delta J}_s dn_s \qquad (4\text{-}24)$$

This process of forming a solution of the final composition could have been initiated with an empty beaker. Both n_w and n_s would have been zero initially and:

$$\Delta J = \overline{\Delta J}_w n_w + \overline{\Delta J}_s n_s \qquad (4\text{-}25)$$

where n_w and n_s represent mass of water and food solids respectively. Dividing both sides of equation (4-25) by the total weight of the mixture we have:

$$\Delta J^+ (\text{cal/g. mixture}) = W\overline{\Delta J}_w + (1-W)\overline{\Delta J}_s \qquad (4\text{-}26)$$

where W is the weight fraction of water and (1-W) is the weight fraction of solids in a total mixture.

Fish (1958) and Stitt (1958) used the equation (4-26) to obtain the integral thermodynamic properties of the water vapor adsorption process by dry starch to form 1 g. of equilibrated material with vapor pressure (P^m).

<u>Free Energy</u>--The integral free energy change for the entire system in process (4-1) may be derived by integration of equation (4-20):

$$\Delta G_w = \int_0^{n_w} \overline{\Delta G}_w dn_w$$

The integration of this equation may be carried out as follows:

$$\Delta G_w = n_w\overline{\Delta G}_w - RT\int_0^{P/P^\circ} n_w(P^\circ/P)\,d(P/P^\circ)$$

A plot of $n_w(P^\circ/P)$ vs. P/P° will allow evaluation of the integral (Wu and Copeland, 1964). The integral free energy obtained by this formula will be the integral free energy of solution and will be expressed as cal. per unit mass dry food solids. According to equation (4-26), the integral free energy per unit mass of mixture may be obtained as follows:

$$\Delta G^+ = W\overline{\Delta G}_w + (1-W)\overline{\Delta G}_s \qquad (4\text{-}27)$$

Enthalpy--The integral enthalpy (net) of sorption can be derived in several ways. The method using the temperature coefficient of the integral free energy (ΔG) leads to the following equation:

$$\Delta H_w = [\partial(\Delta G_w/T)/\partial(1/T)]_{P,n_w,n_s} \qquad (4\text{-}28)$$

The method using integration of the differential net heat of sorption employing data at two isotherms only yields the following equation:

$$\Delta H_w = (RT_1T_2/T_2-T_1)\ln(Z_2/Z_1)dn_w \qquad (4\text{-}29)$$

Equation (4-29) is used when sorption isotherms are available at only two temperatures. In this equation, Z_2 is the relative vapor pressure (P/P°) at the higher temperature which produces the same number of moles of water sorption as Z_1 at lower temperature. The integral net enthalpy obtained from the above formulae will be the integral net enthalpy of solution and will be expressed as cal. per unit mass of dry food solids. The integral net heat of sorption per unit mass of mixture can be obtained from equation (4-26) as follows:

$$\Delta H^+ = W\overline{\Delta H}_w + (1-W)\overline{\Delta H}_s \qquad (4\text{-}30)$$

Entropy--The integral net entropy of sorption can be computed from the relationship associating the free energy and enthalpy of a system:

$$\Delta S_w = \frac{(\Delta H_w - \Delta G_w)}{T} \qquad (4\text{-}31)$$

where S is expressed in cal. per unit mass of solids per °K.

The integral net entropy of sorption per unit mass of mixture is given by an equation similar to equation (4-31) when the integral properties per unit mass of solids are replaced by the corresponding properties per unit mass of mixture as follows:

$$\Delta S^+ = \frac{(\Delta H^+ - \Delta G^+)}{T} \qquad (4\text{-}32)$$

IV.3. Food as Binary System

When deriving the thermodynamic relations for non-reacting binary systems, the following implicit assumptions are made :

a) The system is nonreacting since there appears to be no chemical reactions and the changes in free energy are associated with changes in surface free energy only.

b) The surface area can be varied reversibly to obtain the relation:

$$w = \sigma \cdot d\,A, \qquad (4\text{-}29)$$

where w refers to work, A is the surface area and σ is the surface tension or the surface free energy (Cole and Coles, 1964).

c) The system is homogeneous mixture of a single solid substance with a pure liquid.

Biological substances considered food components are mixtures of macromolecules. It appears to be well established that sorption of water on them is a means of neutralizing or satisfying the forces of attraction that exist at surface (Pauling, 1945; Bull, 1944).

In general it seems evident that assumption (a) will not introduce errors when evaluating the sorption thermodynamic properties of biological substances as long as sorption isotherms are obtained within short periods of time. If, however, sorption isotherms require long periods of time, chemical reactions (enzymatic, autoxidative) unrelated to the sorption process, may alter the system and the thermodynamic properties determined will not describe the original system.

There is evidence that the surface area (sorptive sites of biological substances), as related to sorption phenomena, is not constant. Chung and Pfost (1967) associated the phenomenon of hysteresis to changes in available sorptive sites on the biological substances. Since hysteresis, as far as is known, occurs invariable in all biological substances the surface area cannot be varied reversibly and consequently, there is no expression such as equation (4-29) [Guggenheim, 1967, p. 166]. In view of the fact that the integral free energy of the solid is related to the surface free energy (Copeland and Young, 1964) by the following equation:

$$\overline{\Delta G}_s = A\Delta\sigma,$$

it must be expected that assumption (b) will introduce some error in evaluation of thermodynamic properties of foods. However, Copeland and Young (1964) pointed out that the changes in surface area are usually small and ignored.

A system may be considered homogeneous when the equilibrium bulk properties vary in a continuous fashion throughout the entire system with no regions of discontinuity.

Based on observations, biological substances may be visualized as homogeneous mixtures of solids with water. In addition, food components are not expected to exert a "component characteristic influence" on total moisture isotherm. Berlin _et_ _al_. (1968) indicated a classical effect of a component on the shape of isotherm. In general, however, biological substances yield smooth sigmoid-shaped isotherms. This indicates that the components of the solid mixture of biological substances follow the same mechanism with respect to sorption and any differences are of a quantitative nature. We may accordingly regard the sorption isotherm as made up additively by quantitative contributions of the components. The solid mixture of biological substances may therefore be considered as a single component with respect to the qualitative behavior during sorption of vapors.

The considerations above indicate that biological substances may be treated as binary systems with respect to their sorption thermodynamic properties.

V. RESULTS AND DISCUSSION

V.1. Moisture Sorption Isotherms

The adsorption and desorption isotherms of precooked freeze-dried and raw freeze-dried beef at 10, 21.3 and 31°C are presented in Figure 5.1 and in the appendix (Figures A.1 through A.3). The isotherms are sigmoid and belong to the type II isotherm according to the classification of Brunauer (1945). The adsorption isotherms of raw freeze-dried beef are similar to those obtained in previous investigations (Saravacos and Stinchfield, 1965; Kapsalis, 1967; Palnitkar, 1970) when examining the influence of temperature on isotherm position. The quantity of water adsorbed by all samples increased to a maximum as the temperature decreased from 30 to 10°C. The adsorption and desorption isotherms of precooked freeze-dried and raw freeze-dried beef at 10.0°C and 31°C respectively are shown in the appendix (Figures A.4 and A.5). These isotherms illustrate that hysteresis between adsorption and desorption is exhibited over a wide range of relative humidities. The hysteresis effect is exhibited at 21.3 and 31°C, also. The comparison of isotherms of precooked freeze-dried and raw freeze-dried beef reveals that their sorptive capacities for water vapor

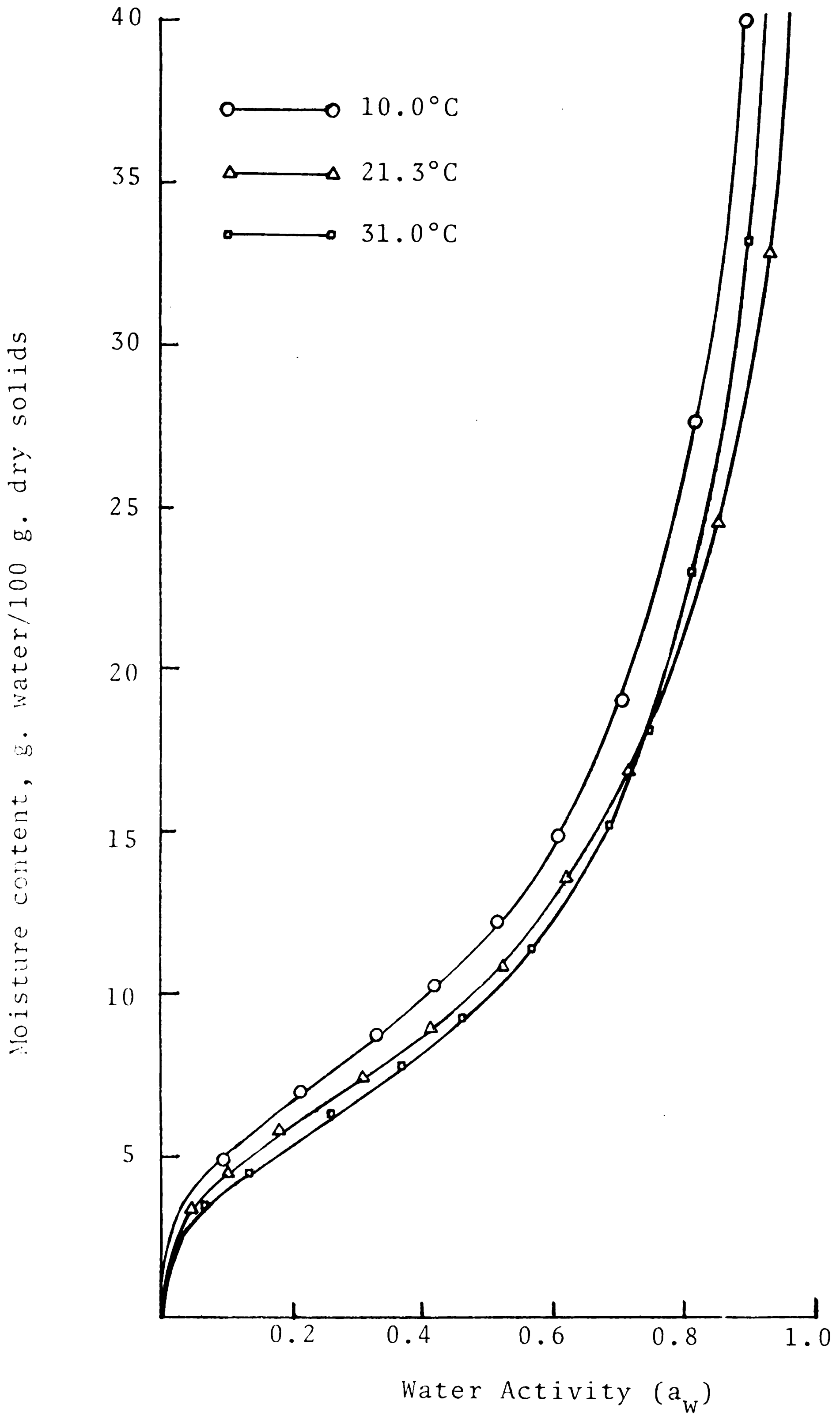


Figure 5.1.--Adsorption isotherms for precooked freeze-dried beef.

are nearly of the same order with the precooked product being slightly higher. The small differences in sorptive capacity of the two products should be due primarily to the differences in the availability of polar sites. It is certain that the cooking temperature denatured the protein components of the precooked samples, which also lost considerable amount of fat during cooking.

V.2. Physicochemical Properties

V.2.1. Differential Thermodynamic Properties

Differential net free energy changes ($\overline{\Delta G}_w$), ($\overline{\Delta G}_s$). For any process at constant temperature, the definition of free energy ($G \equiv H - TS$) may be used to write:

$$\Delta G = \Delta H - T\Delta S \tag{5-1}$$

Based on equation (5-1), the free energy change of a system combines the changes of enthalpy and entropy of the system. The change of free energy between two states of a system is a measure of the feasibility or "spontaneity" of the process taking the system from the initial to final state.

The change in free energy (ΔG) represents a difference of potential between the two states of the system considered and could equal the negative of the work done by a reversible isothermal engine as a result of the isothermal flow of the system from the initial to final state. A negative change in free energy would indicate that the process is spontaneous

and capable of producing work. For example, a negative free energy change indicates that the adsorption of water vapor by the dry food and the concomitant structural changes will occur spontaneously at the specified temperature and other conditions. If the free energy change were positive, the process would have occurred in the opposite direction, i.e., the food system would have desorbed its residual water into the vapor phase and the structure of the food would have changed accordingly.

The integral free energy of a two component mixture however, is related to the partial molar free energies of the components. according to equation (4-25):

$$\Delta G = n_w \overline{\Delta G}_w + n_s \overline{\Delta G}_s \qquad (5\text{-}2)$$

Equation (5-2) is derived directly from equation (4-25) by replacing G for the general extensive thermodynamic property J. In equation (5-2), ΔG refers to free energy for the entire mass of mixture. The partial molar free energy change of sorption per g. of sorbed water ($\overline{\Delta G}_w$) is expressed by:

$$\overline{\Delta G}_w = \pm \frac{RT}{18} \ln P/P^\circ \qquad (5\text{-}3)$$

Where the positive sign refers to adsorption and the negative sign refers to desorption. Equation (5-3) is obtained from equation (4-4). The values of differential free energies with respect to sorbed water were calculated

for the adsorption and desorption processes using equation (5-3) and experimental data. The corresponding differential free energy changes with respect to the solids (adsorbed) ($\overline{\Delta G}_s$) were determined using the convenient form of the Gibbs-Duhem equation (4-5).

Values of differential free energy changes ($\overline{\Delta G}_w$ and $\overline{\Delta G}_s$) for precooked freeze-dried and raw freeze-dried beef at 10, 21.3 and 31°C were plotted against moisture content as shown in Figure 5.2 and in the appendix (Figures A.6 to A.8). The differential free energy values ($\overline{\Delta G}_w$) of adsorption and desorption decreased continually in magnitude with increasing moisture content. A comparison of differential free energy ($\overline{\Delta G}_w$) of desorption with values from adsorption indicates that desorption values are consistently greater in magnitude. This is in agreement with the published literature (Chung and Pfost, 1967). The differential free energy values ($\overline{\Delta G}_s$) of adsorption and desorption for both products increased continually in magnitude with increasing moisture. This same relationship was observed by Palnitkar (1970).

The values of $\overline{\Delta G}_w$ decreased or increased to infinity for the adsorption or desorption processes respectively, as the dry state was approached. The property values approached zero, assymptotically, with increasing moisture content. These findings agree with those of other investigators (Fish, 1958; Kapsalis, 1967). The values of $\overline{\Delta G}_s$ increased negatively to a limiting value with increasing moisture content. The relatively small changes in free

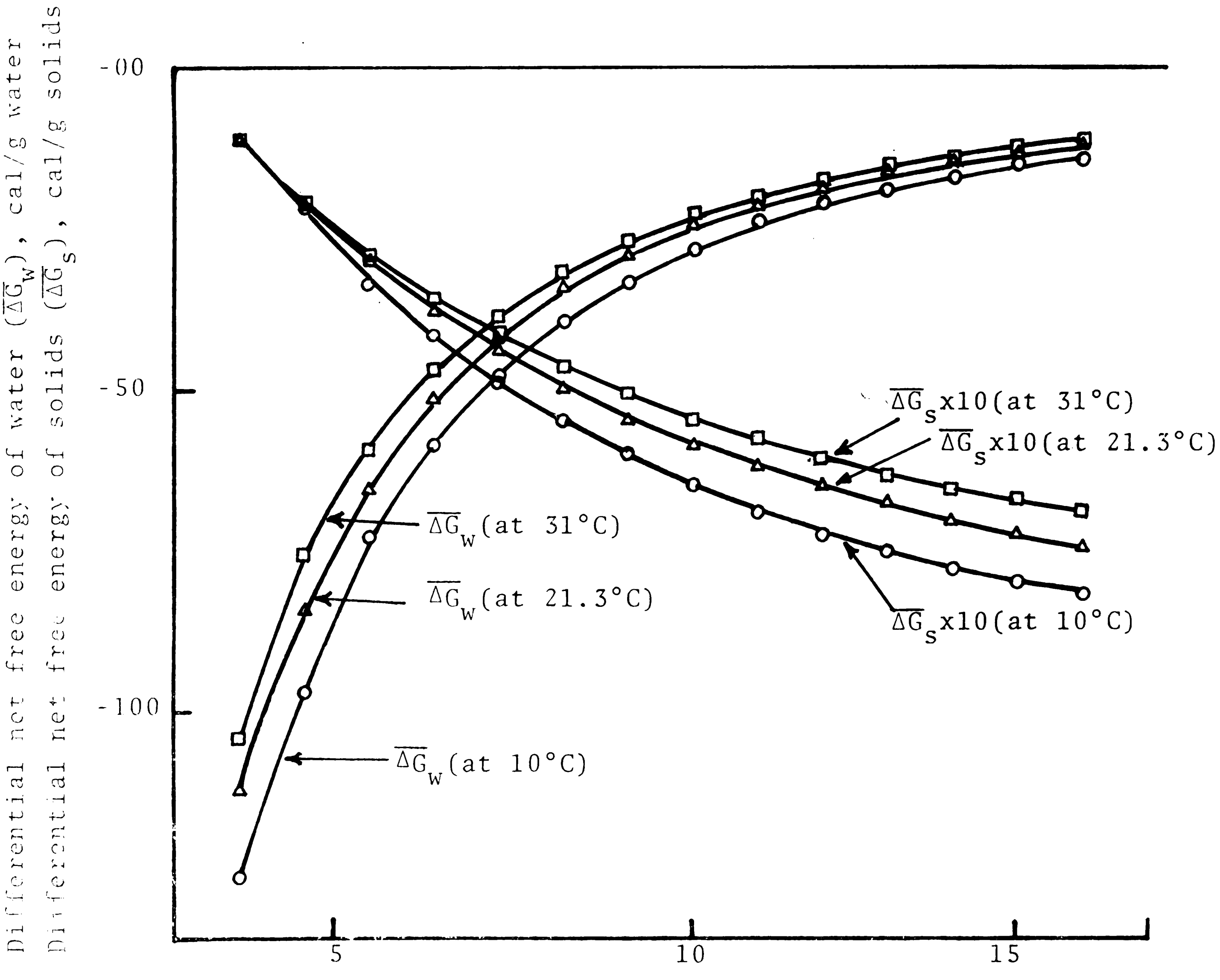


Figure 5.2.--Influence of temperature on the differential net free energy values of water and solids for adsorption of water vapors on precooked freeze-dried beef (plate temperature 100°F).

energy with respect to solids may be attributed to limited extent on changes due to the stretching, bending and tortional vibrations of the macromolecules comprising the solids. The results essentially imply that the polymer molecules comprising the beef gel are interlinked in junction points which are not accessible to the swelling agent. These links may represent covalent ponds (e.g., disulfite bridges), or noncovalent bonds (e.g., electrostatic interaction, hydrogen bonding, hydrophobic interaction, dipole-dipole interaction), which impedes unlimited swelling. When the volume of the gel is increased, the structural units of the gel scaffolding connecting successive junction points are brought into configurations of lower entropy and tend to reassume the original configuration to attain minimum Gibb's free energy (Hermans, 1949, p. 88).

Both differential free energy with respect to water ($\overline{\Delta G}_W$) and the differential free energy with respect to solids ($\overline{\Delta G}_S$) were higher in magnitude at lower temperature than the corresponding values at higher temperature. In practical terms this implies that the adsorption process will proceed to a larger extent (more water will be adsorbed) at the lower temperatures ($\overline{\Delta G}_W$ more negative) for a given relative humidity. Saravacos _et al._ (1967) observed this relationship over the range of temperatures from 50 to 0°C, but the amount of adsorbed water remained almost constant for temperatures below 0°C.

Palnitkar (1970) reported the same relationship between free energies ($\overline{\Delta G}_w$ and $\overline{\Delta G}_s$) for water vapor adsorption on biological materials and temperature and concluded that a given food system is more stable thermodynamically at a lower temperature than the higher temperature. This conclusion seems very questionable when discussing the vapor pressure adsorption process.

As discussed previously, the change in free energy is related to the potential of chemical reactions. The change in free energy will be zero at thermodynamic equilibrium. The more negative $\overline{\Delta G}_w$ of adsorption at low moisture level indicates that the adsorption of vapors on solids is more spontaneous at the lower moisture level than at the higher levels. This equilibrium should not necessarily be related to the stability of foods as proposed by Palnitkar (1970, p. 40).

Figure 5.3 demonstrates the influence of product characteristics on the free energy. The isosteric free energy values of precooked product are higher than the respective properties of the raw product both for water and solids. This indicates a higher sorptive potential for precooked product due probably to protein denaturation and loss of fats during cooking.

Differential net enthalpy changes ($\overline{\Delta H}_w$), ($\overline{\Delta H}_s$). $\overline{\Delta H}_w$ and $\overline{\Delta H}_s$ were evaluated using equations (4-9) and (4-11), respectively. The use of equation (4-9) for computing $\overline{\Delta H}_w$ for the water vapor adsorption by precooked freeze-dried beef is illustrated in the appendix (Figure A-7a). Using

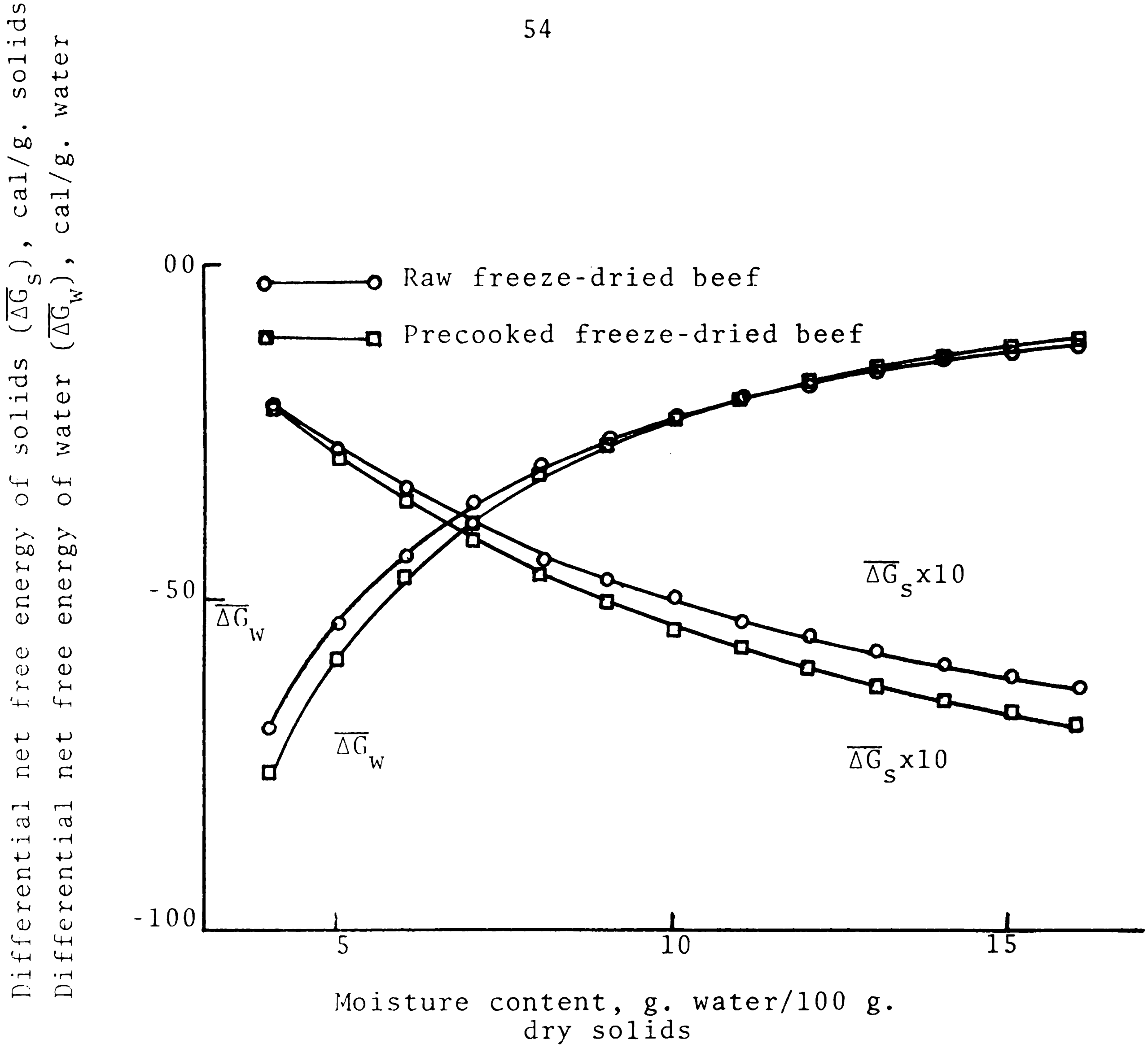


Figure 5.3.--Isosteric differential net free energies with respect to water ($\overline{\Delta G}_W$) and solids ($\overline{\Delta G}_S$) for adsorption of water vapors on precooked and raw freeze-dried beef at 31°C.

equation (4-9) does not assume that $\overline{\Delta H}_w$ is invariant with temperature.

Isosteric differential net heats of adsorption and desorption of precooked freeze-dried and raw freeze-dried beef with respect to water are plotted as a function of moisture content in Figure 5.4 and in the appendix (Figures A.9 to A.11). The isosteric heats ($\overline{\Delta H}_w$) of adsorption and desorption ranged from 660 cal/g to 50 cal/g for the range of moisture contents studied and are in agreement with values obtained by Kapsalis (1967) and Palnitkar (1970) for precooked freeze-dried beef. The high negative values of $\overline{\Delta H}_w$ of adsorption at low moisture contents indicates the formation of more or stronger bonds, such that the system moves to a state of lower energy accompanied by the evolution of heat. The high heats of sorption also indicate nonideal behavior of vapor pressure. Based on thermodynamic considerations, ideal solutions will not adsorb or evolve heat when the species are mixed (Cole and Coles, 1964). Plots of $\overline{\Delta H}_w$ for adsorption and desorption processes of all samples demonstrate that heats of sorption decrease continually in magnitude with increasing moisture content. Since the heats of sorption can be considered as indicative of intermolecular attraction forces between sorptive sites and water vapor, plotted values of $\overline{\Delta H}_w$ vs. moisture content can be used to study the magnitude of binding energy or the availability of polar sites to water vapor as sorption

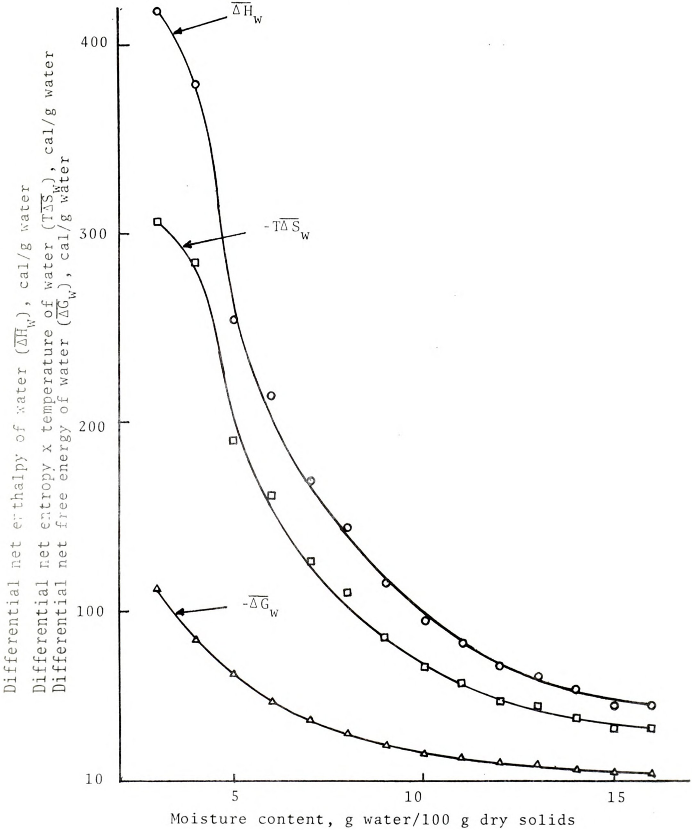


Figure 5.4.--Differential net thermodynamic values of water vapor adsorption from precooked freeze-dried beef (plate temperature 100°F) at 21.3°C.

proceeds. Accordingly, the high $\overline{\Delta H}_w$ values at low moisture content may be due to sorption (possibly by hydrogen bond formation) on polar groups of the protein side chains and of other substances, as proposed first by Pauling (1945), Davis and McLaren (1948) and Dole and McLaren (1947). The differential net heat $\overline{\Delta H}_w$ of adsorption for all samples drops rapidly at low moisture contents and then gradually in magnitude as the water is adsorbed and approaches a low value at moisture contents greater than that required for a complete monolayer of adsorbed moisture. The nonzero value of net $\overline{\Delta H}_w$ at water contents greater than necessary for the first monolayer violates the assumptions of the BET theory which is based on the idea that the heat of adsorption on layers above the first is equal to the heat of condensation in pure water. This violation of the BET theory has also been observed by Kapsalis (1967) and Dole and McLaren (1947). Note that there is no break in the $\overline{\Delta H}_w$ curve at the point where the amount of water sorbed is equal to that required for one monolayer. As is well known, the BET theory permits the onset of multilayer sorption before sorption on the first layer is complete.

It should be emphasized that at all moisture contents, the $\overline{\Delta H}_w$ curve for desorption lies above the respective curve for adsorption (Figure 5.5) indicating that adsorption and desorption are essentially different processes. The results indicate that the heat required to remove one gram of water from an infinitely large quantity of food solids

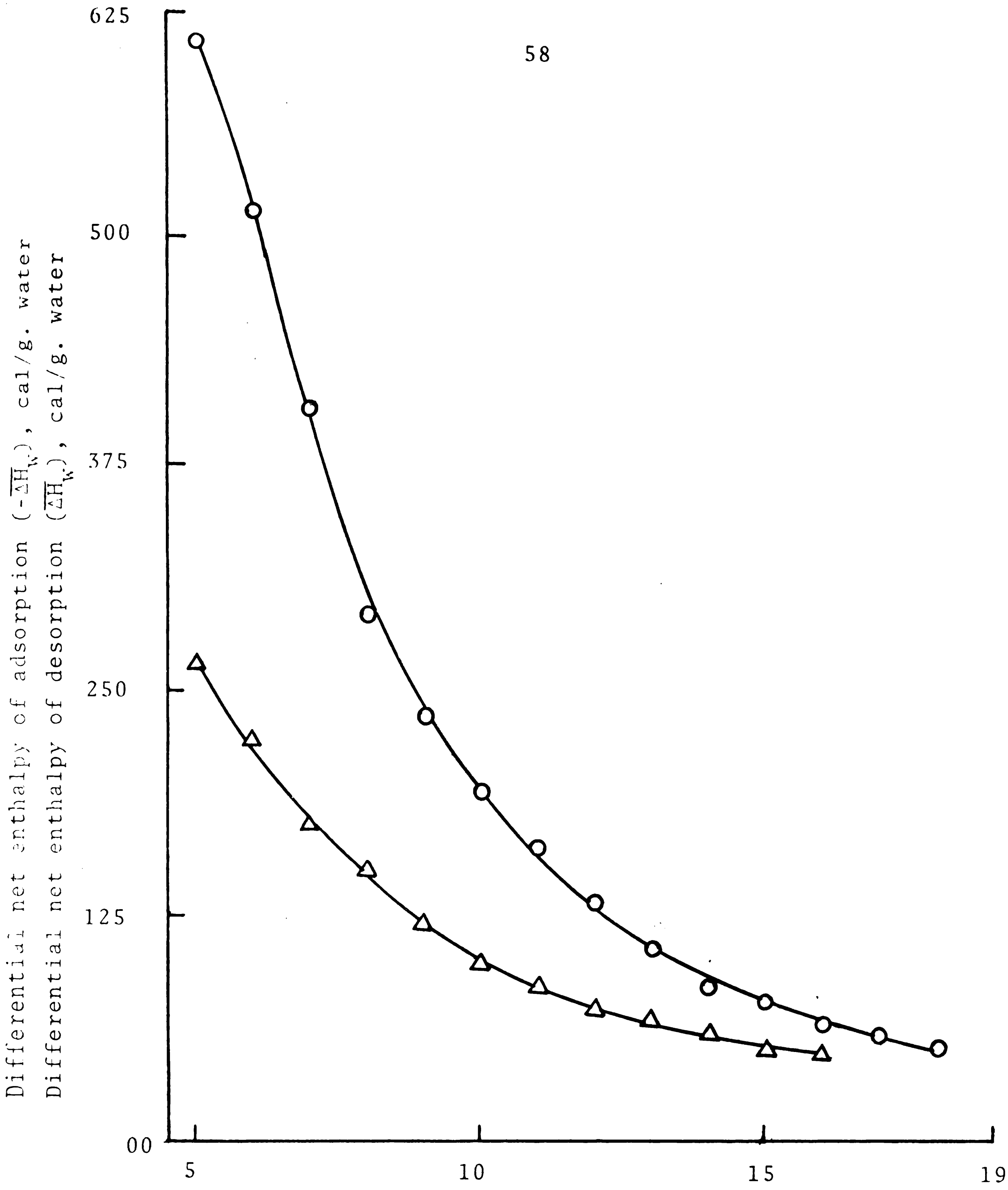


Figure 5.5.--Isosteric differential net enthalpies with respect to water $(\overline{\Delta H}_w)$ for desorption and adsorption of water vapors on precooked freeze-dried beef at 21.3°C.

is greater than that required to place the gram of water in the solids at the same moisture content. This is in agreement with the concept that more sorption sites, which possess the adsorption potential on the surface of an adsorbent, are available to water vapor during the desorption process than during adsorption. This hypothesis has been advanced by Simril and Smith (1942) and recently by Chung and Pfost (1967) to explain the hysteresis effect.

The change in net differential enthalpy of precooked freeze-dried beef with respect to solid component ($\overline{\Delta H}_s$) during adsorption is illustrated in Figure 5.6. Isosteric differential net heats with respect to solid component ($\overline{\Delta H}_s$) of adsorption and desorption of precooked freeze-dried and raw freeze-dried beef were plotted as a function of moisture content. In general, the changes in partial molar thermodynamic properties of adsorbents are smaller than for adsorbates over the ranges of moisture content studied. This behavior should be expected since partial molar properties are average properties of the respective components (Wu and Copeland, 1961). The values of $\overline{\Delta H}_s$ of desorption were consistently greater than those of adsorption for all materials investigated, indicating that inter- and intra-molecular structural changes in adsorbent during desorption are greater than occur during adsorption.

Figure 5.7 illustrates the influence of product characteristics on the net differential enthalpy ($\overline{\Delta H}_w$) of water vapor adsorption. The differential net enthalpy values of

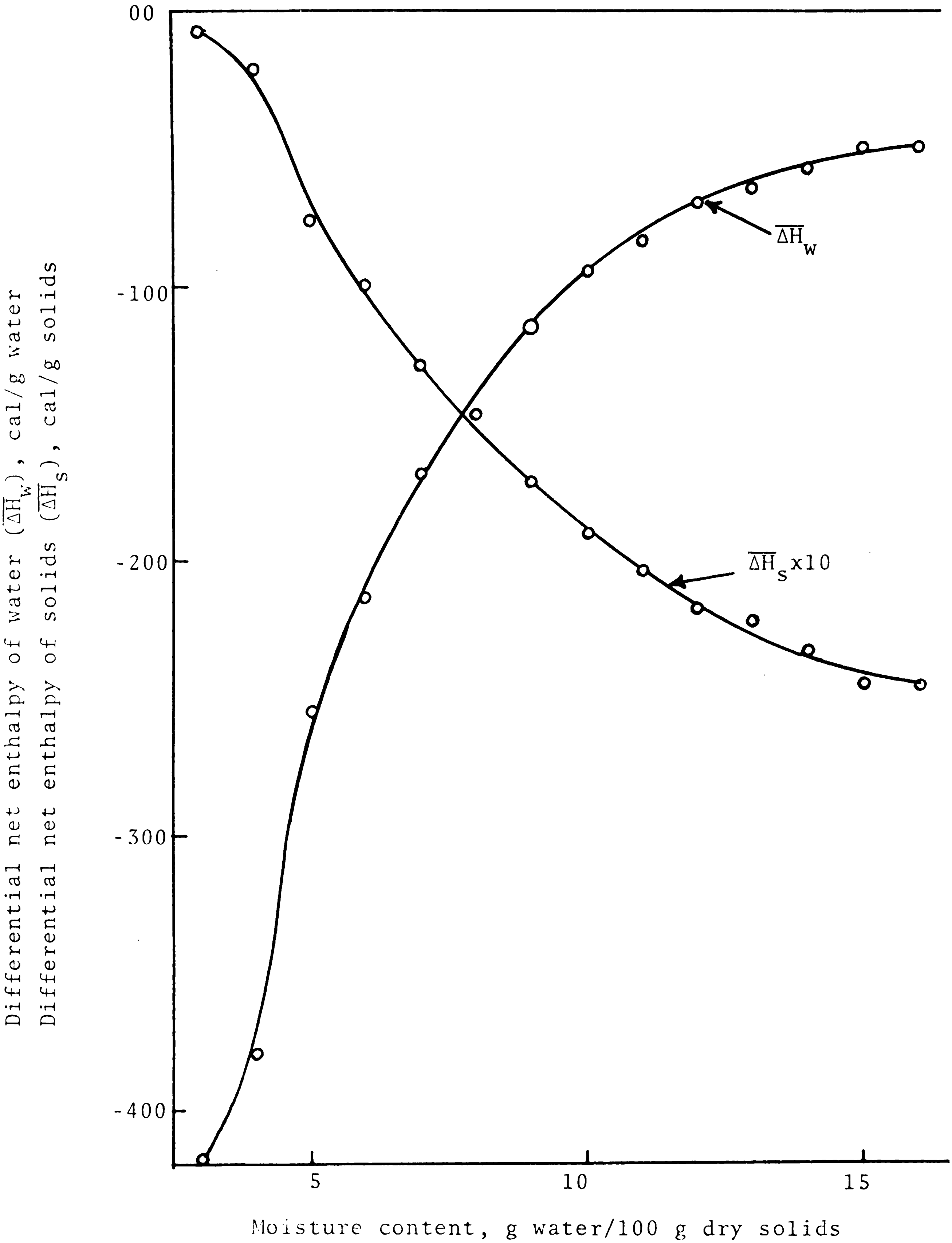


Figure 5.6.--Differential net enthalpy changes for adsorption of water vapor on precooked freeze-dried beef (plate temperature 100°F) at 21.3°C.

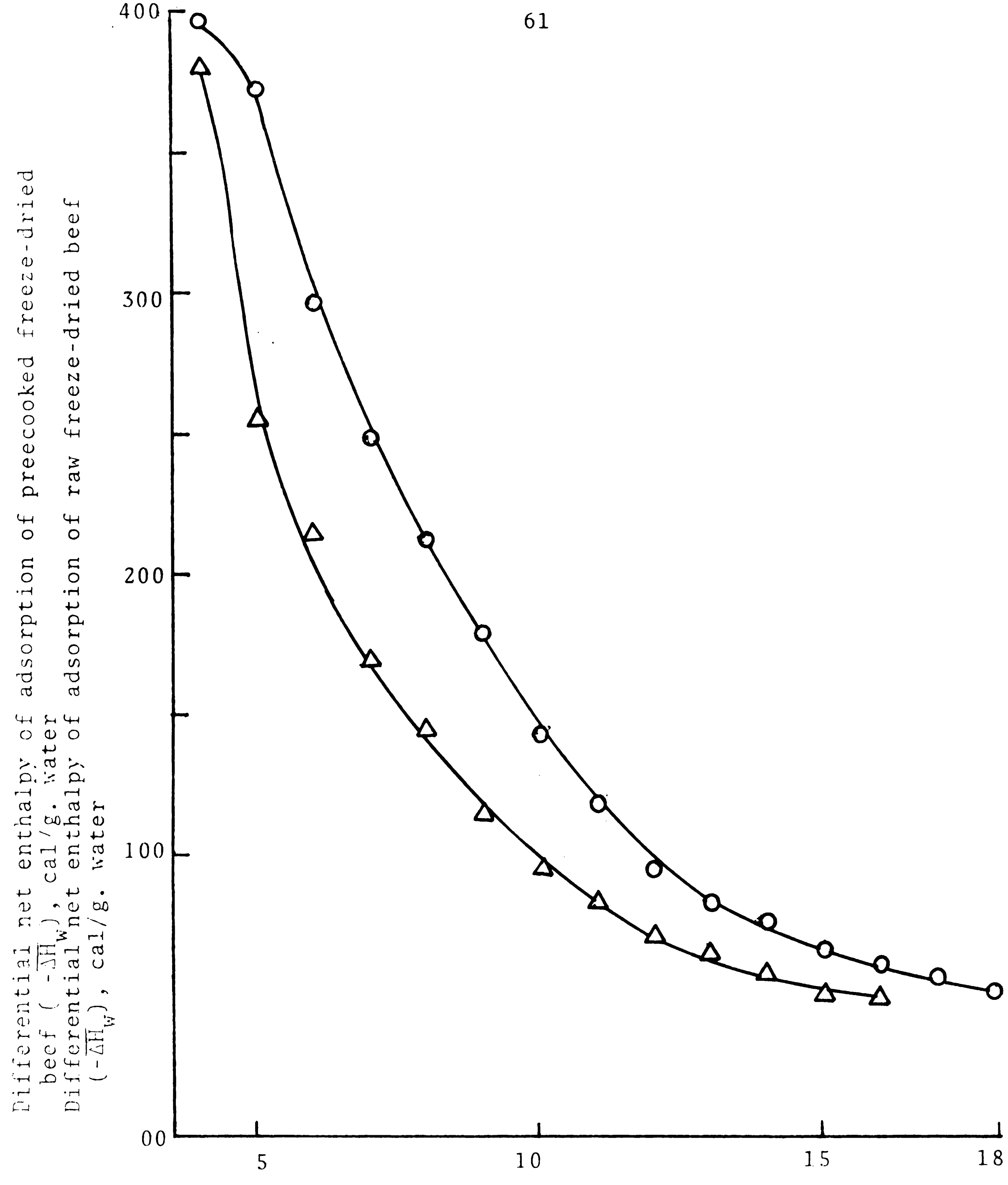


Figure 5.7.--Isosteric differential net enthalpies ($\overline{\Delta H}_w$) with respect to water for adsorption of water vapors on precooked and raw freeze-dried beef at 21.3°C.

water vapor adsorption and desorption (see appendix, Figures A.9 and A.10) by raw freeze-dried beef were consistently higher in absolute magnitude than the differential net enthalpy values for the respective processes of precooked freeze-dried beef. This suggests that more polar sites were available and chemisorption proceeded to a larger extent in raw freeze-dried product than in precooked freeze-dried. More energy will be required to dehydrate the raw freeze-dried beef than the precooked freeze-dried.

<u>Differential net entropy changes ($\overline{\Delta S}_w$), ($\overline{\Delta S}_s$).</u> Differential net entropy changes ($\overline{\Delta S}_w$) were calculated using equation (4-14). The corresponding differential net entropy changes with respect to solids ($\overline{\Delta S}_s$) were calculated using the same equation and the values of $\overline{\Delta H}_s$ and $\overline{\Delta G}_s$ at 21.3°C. The computation of $\overline{\Delta S}_w$ for water vapor adsorption by precooked freeze-dried beef at 21.3°C is illustrated in Table 5-1. In the same table the calculation of integral entropy per unit mass of mixture (ΔS^+) with varying water content is also illustrated. Equation (4-30) was employed for these calculations.

The product of differential net entropies with temperature ($T\overline{\Delta S}_w$) of adsorption and desorption of precooked freeze-dried and raw freeze-dried beef are plotted as a function of moisture content in Figure 5.4 and in the appendix (Figures A.9 to A.11). The differential net entropy changes for the adsorption and desorption processes

Table 5.1 Thermodynamic parameters for water vapor adsorption on precooked freeze-dried beef

%M.C.	N_w	N_s	$\frac{N_w}{N_s}$	Adsorption isotherm at 10°C						
				$\frac{P}{P°}$	$\frac{P°}{P} x \frac{N_w}{N_s}$	$-\overline{\Delta G}_s$	$-\overline{\Delta G}_w$	$-N_w \overline{\Delta G}_w$	$-N_s \overline{\Delta G}_s$	$-\Delta G^+$
3.0	0.029	0.971	0.0299	0.018	1.659	1.133	125.6	3.642	1.100	4.742
4.0	0.038	0.962	0.0395	0.045	0.878	2.204	97.0	3.684	2.120	5.804
5.0	0.048	0.952	0.0504	0.097	0.520	3.340	72.9	3.501	3.180	6.680
6.0	0.057	0.943	0.0604	0.153	0.395	4.141	58.7	3.345	3.905	7.250
7.0	0.065	0.935	0.0695	0.217	0.320	4.856	47.8	3.104	4.540	7.645
8.0	0.074	0.926	0.0799	0.284	0.281	5.485	39.3	2.912	5.079	7.991
9.0	0.083	0.917	0.0905	0.346	0.261	6.011	33.2	2.754	5.512	8.266
10.0	0.091	0.909	0.1001	0.407	0.246	6.494	28.1	2.557	5.903	8.460
11.0	0.099	0.901	0.1099	0.460	0.239	6.896	24.3	2.403	6.213	8.616
12.0	0.107	0.893	0.1198	0.507	0.236	7.245	21.2	2.265	6.470	8.735
13.0	0.115	0.885	0.1299	0.546	0.238	7.533	18.9	2.175	6.667	8.842
14.0	0.123	0.877	0.1403	0.582	0.241	7.803	16.9	2.081	6.843	8.924
15.0	0.130	0.870	0.1494	0.611	0.245	8.023	15.3	1.995	6.980	8.975
16.0	0.138	0.862	0.1601	0.638	0.251	8.233	14.1	1.939	7.097	9.036

Table 5.1 (Continued)

Adsorption isotherm at 31°C							Adsorption isotherm at 21.3°C						
$\frac{P}{P°}$	$\frac{P°}{P} x \frac{N_w}{N_s}$	$-\overline{\Delta G}_w$	$-\overline{\Delta G}_s$	$-N_w\overline{\Delta G}_w$	$-N_s\overline{\Delta G}_s$	$-\Delta G^+$	$\frac{P}{P°}$	$\frac{P°}{P} x \frac{N_w}{N_s}$	$-\overline{\Delta G}_s$	$-\overline{\Delta G}_w$	$-N_w\overline{\Delta G}_w$	$-N_s\overline{\Delta G}_s$	$-\Delta G^+$
0.045	0.664	104.1	1.171	3.020	1.137	4.157	0.032	0.933	1.151	112.0	3.245	1.118	4.363
0.104	0.380	76.0	2.206	2.888	2.118	5.006	0.075	0.526	2.171	84.2	3.200	2.089	5.289
0.170	0.296	59.5	2.955	2.856	2.813	5.669	0.133	0.379	3.024	65.6	3.148	2.879	6.027
0.245	0.247	47.2	3.641	2.692	3.433	6.125	0.204	0.296	3.803	51.7	2.945	3.586	6.532
0.314	0.221	38.9	4.183	2.528	3.911	6.439	0.274	5.254	4.429	42.1	2.736	4.141	6.877
0.389	0.205	31.7	4.720	2.346	4.370	6.717	0.350	0.228	5.024	34.1	2.525	4.652	7.178
0.448	0.202	27.0	5.123	2.238	4.698	6.936	0.412	0.220	5.475	28.8	2.392	5.021	7.413
0.503	0.199	23.1	5.493	2.100	4.993	7.093	0.476	0.210	5.923	24.1	2.196	5.384	7.580
0.549	0.201	20.1	5.795	1.993	5.221	7.215	0.521	0.211	6.231	21.1	2.092	5.614	7.706
0.591	0.203	17.7	6.087	1.890	5.436	7.325	0.564	0.212	6.526	18.6	1.992	5.828	7.820
0.628	0.207	15.6	6.342	1.796	5.613	7.409	0.600	0.216	6.777	16.6	1.910	5.998	7.908
0.658	0.213	14.1	6.553	1.729	5.747	7.476	0.638	0.220	7.046	14.6	1.797	6.179	7.976
0.683	0.219	12.8	6.735	1.664	5.859	7.524	0.664	0.225	7.234	13.3	1.724	6.294	8.018
0.706	0.227	11.7	6.907	1.613	5.954	7.567	0.694	0.231	7.456	11.8	1.639	6.427	8.066

Table 5.1 (Continued)

Adsorption isotherms at 10, 21.3 and 31°C						
$-\overline{\Delta H}_w$	$-\overline{\Delta H}_s$	$-N_w\overline{\Delta H}_w$	$-N_s\overline{\Delta H}_s$	$-\Delta H^+$	$-T\overline{\Delta S}_w$	$-T\Delta S^+$
418.0	0.619	12.123	0.601	12.724	306.1	8.361
378.6	1.987	14.386	1.911	16.298	294.4	11.009
254.1	7.583	12.197	7.219	19.416	188.5	13.389
213.1	9.854	12.147	9.297	21.440	161.4	14.908
168.0	12.782	10.922	11.951	22.873	125.9	15.996
143.4	14.618	10.615	13.536	24.151	109.3	16.973
114.8	17.063	9.525	15.647	25.171	85.9	17.758
94.3	19.016	8.578	17.286	25.863	70.1	18.283
81.9	20.307	8.115	18.297	26.411	60.8	18.705
69.7	21.719	7.455	19.395	26.850	51.1	19.030
65.6	22.230	7.541	19.673	27.215	48.9	19.307
57.4	23.338	7.057	20.467	27.525	42.7	19.549
49.2	24.525	6.397	21.337	27.730	35.9	19.712
49.2	24.525	6.787	21.141	27.927	37.3	19.861

($\overline{\Delta S}_w$) have rather high negative and positive values, respectively at low moisture contents. The values decrease in absolute magnitude with increasing hydration in a manner similar to the corresponding differential net enthalpies. The negative value of $\overline{\Delta S}_w$ for adsorption is due to the decrease in randomness of the system when water molecules from the vapor phase are adsorbed on the surface. When water molecules possessing high translational, rotational and vibrational energies in the vapor phase are adsorbed on the surface of food solids, they lose their translational energy, become "ordered" and the entropy of the system decreases. Since it has been suggested (Pauling, 1945; Stitt, 1958) that the adsorbed water molecules are hydrogen bonded to polar sites of the adsorbent before the completion of the BET monolayer the initial adsorption will impose an increased order to water molecules resulting in the higher negative entropy values at lower moisture contents. As the adsorption proceeds however, it is possible that the adsorbent surface does not remain intact but undergoes configurational changes; a local solubilization or incipient solution, which tends to increase the randomness of solids and contributes positively to the entropy of mixing (Davis and McLaren, 1948). Positive entropies were not observed in this investigation indicating that the beef gels are highly interlinked and tend to maintain their original configuration in the range of moisture contents studied.

The change in net differential entropy of raw freeze-dried beef with respect to solid component ($\overline{\Delta S}_s$) during adsorption is illustrated in Figure 5.8. The differential net entropies with respect to solid component ($\overline{\Delta S}_s$) of adsorption and desorption of all materials investigated were plotted as a function of moisture content in a similar manner. The change in differential entropy of raw freeze-dried beef with respect to water ($\overline{\Delta S}_w$) during the adsorption process is also plotted in Figure 5.8. As illustrated, the change in $\overline{\Delta S}_w$ increases monotonically to a value near zero (absolutely decreases) with increasing amount of adsorbed water. The differential entropy of the solid component $\overline{\Delta S}_s$ decreases (becomes more negative) with increasing moisture content during adsorption.

As was the case with differential enthalpy values with respect to solid component, the differential entropy values ($\overline{\Delta S}_s$) are smaller in magnitude than the differential entropy values with respect to water ($\overline{\Delta S}_w$) over the range of moisture contents studied. This is particularly true for both differential enthalpy and differential entropy changes at moisture contents below the BET monolayer. Within this range of moisture contents therefore, the integral enthalpy and entropy changes of mixing are mainly contributed by the water component while the opposite is true for moisture contents over the BET monolayer as can be seen from $-N_w\overline{\Delta H}_w$, $-N_s\overline{\Delta H}_s$ and $-\Delta H^+$ values in Table 5-1. Obviously, any undulations of the integral free energy,

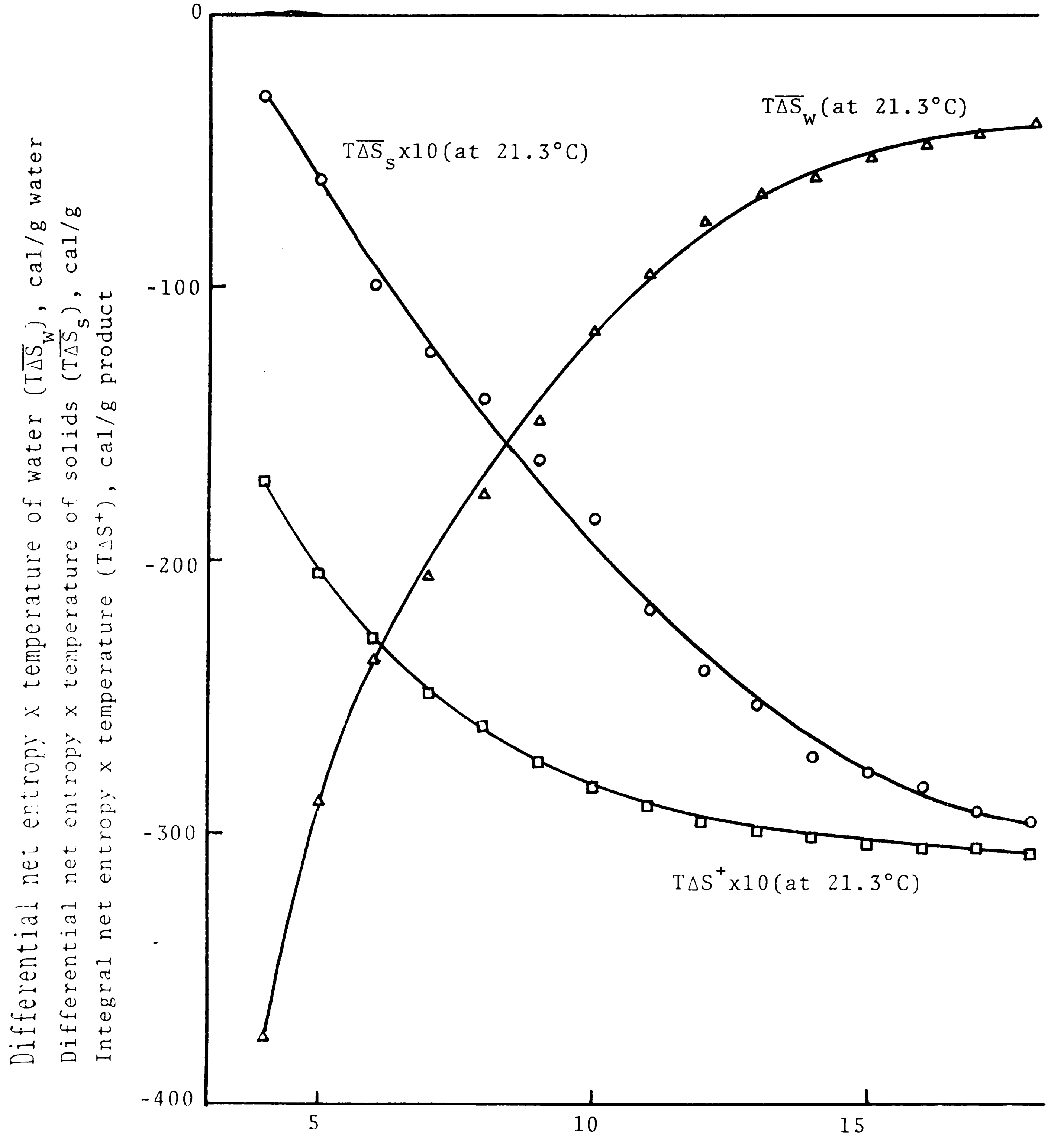


Figure 5.8.--Change in net entropy for adsorption of water vapors on precooked freeze-dried beef (plate temperature 100°F) at 21.3°C.

enthalpy and entropy curves at low moisture contents will manifest analogous more intense undulations of the respective partial molar property curves of water (Davis and McLaren, 1948). In a similar manner undulations in the integral curves at high moisture contents (above the BET monolayer) will manifest more intense undulations of the respective partial molar properties of the solid components.

For all materials investigated, $\overline{\Delta S}_w$ for desorption was consistently greater in absolute magnitude than for adsorption. The same relation was true for the differential net entropies with respect to food solids ($\overline{\Delta S}_s$). This reflects the phenomenon of hysteresis and may be explained in terms of the usual theory of the sorption of moisture by biological materials. Considering the adsorption of water molecules on the exposed polar sites together with condensation in the structural interstices, the observed entropy difference between adsorption and desorption may be explained in either of two ways: (a) the number of available polar sites may be greater for desorption than for adsorption or (b) the interstitial space may be redistributed with an increase in the proportion of water condensed in small pores. It can be shown that the decrease in entropy produced by transferring water from a plane surface to the concave surface of water condensed in a capillary is inversely proportional to the radius of curvature of the concave surface. Such transfer of water should be considered responsible for the observed continuous

decrease of entropy. During this process, however, the solid component will experience structural and configurational changes which produce more sorptive sites available for the desorption process (Chung and Pfost, 1967) and equalizes the interstices in which water is held by capillary condensation. After on desorption, the adsorption process is reversed except that the spatial distribution produced on adsorption persists to lower moisture contents, with the result that the desorption entropy is always higher than the adsorption entropy.

The differential net entropy values with respect to water ($\overline{\Delta S}_w$) obtained from the adsorption isotherms of precooked freeze-dried beef agree very closely with values obtained by Kapsalis (1967) and Palnitkar (1970). In Figure 5.9 the effect of temperature on entropy change with moisture content is illustrated. For all materials investigated the differential entropy ($\overline{\Delta S}_w$) changes with moisture content as well as the differential entropy changes with respect to solids ($\overline{\Delta S}_s$) on adsorption and desorption were uneffected by the temperature. This is in disagreement with the findings of Stamm and Loughborough (1935). These authors however, studied isotherms at widely varying temperatures which is not the case in this study and this may explain the disagreement.

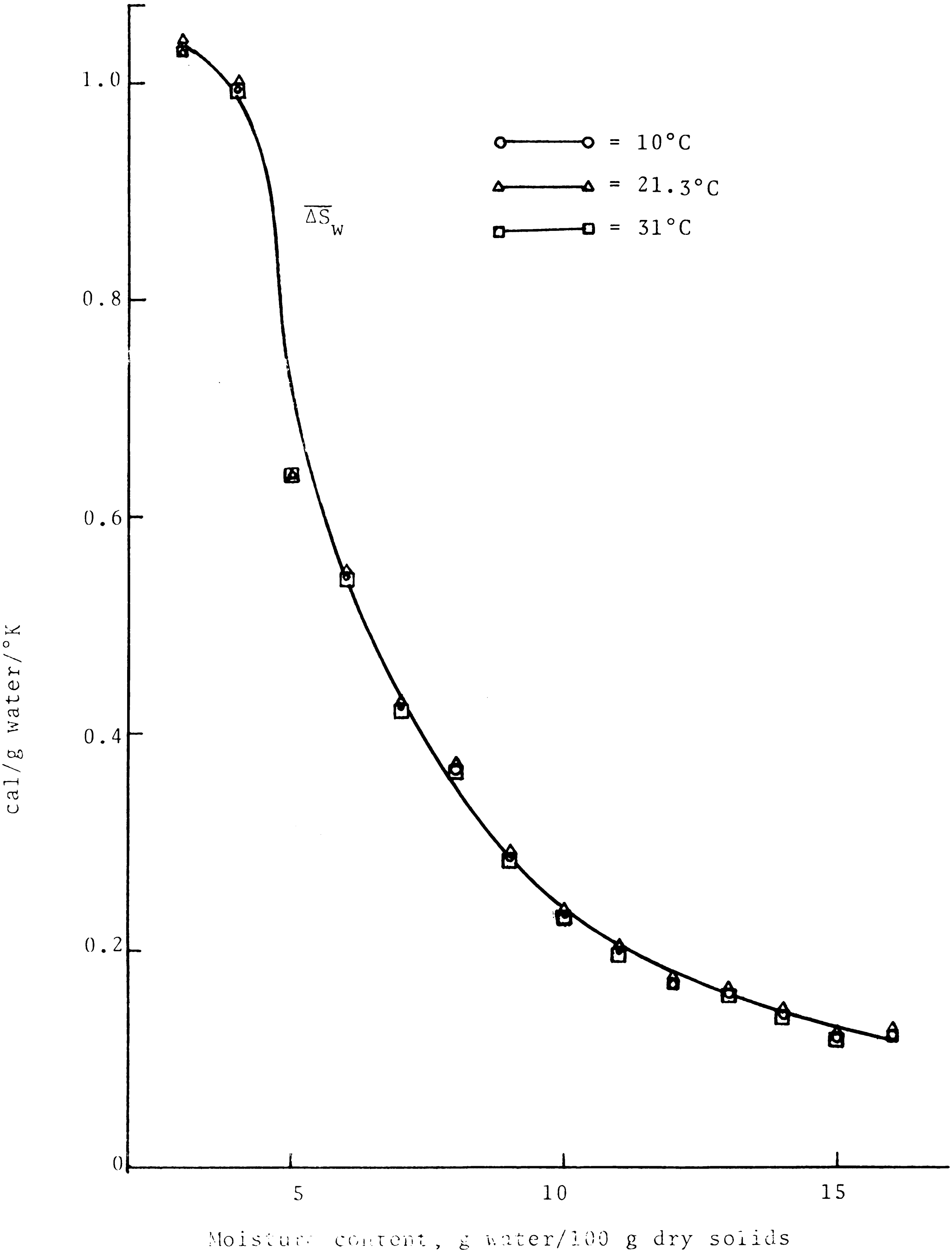


Figure 5.9.--Influence of temperature on the differential net entropy values of water for adsorption of water vapors on precooked freeze-dried beef (plate temperature 100°F)

V.2.2. An Analysis of Procedures Used to Compute Differential Properties

As it can be seen from Figures 5.1 to 5.9 the $\overline{\Delta G}_w$, $\overline{\Delta G}_s$, $\overline{\Delta H}_w$, $\overline{\Delta H}_s$, $\overline{\Delta S}_w$, $\overline{\Delta S}_s$ curves are all smooth curves without any indication of discontinuation. There is no sign of sharp transition between the bound or surface adsorbed water and capillary condensed water or water held by Van der Waals forces. This is in keeping with the moisture content-relative humidity curves (isotherms) which do not reveal sharp discontinuity. The smoothness of the curves is in agreement with the BET theory, which permits the onset of multilayer sorption before sorption on the first layer is complete, and is supported by the findings of Duckworth _et al_. (1963). The latter author demonstrated that at low moisture content water is very strongly adsorbed and becomes loose enough to serve as solvent only at moisture contents 2 to 3 percent higher than the BET monolayer.

The shape of the curves representing the change of the differential net thermodynamic properties of precooked freeze-dried and raw freeze-dried beef during water vapor adsorption and desorption obtained in this study is similar to the shape of the curves of the respective properties of the same or other biological materials obtained by Stamm and Loughborough (1934), Simril and Smith (1942), Fish (1958), Kapsalis (1967), Kapsalis _et al_. (1970a), Chung and Pfost (1967) and Palnitkar (1970). Other authors [Masuzawa and Sterling, 1968; Volman _et al_., 1960; Bettelheim

and Volman, 1957; Davis and McLaren, 1948; and Kapsalis, 1970b], when working with a variety of biological materials, obtained smooth $\overline{\Delta G}_w$ curves but their curves for $\overline{\Delta H}_w$ and $\overline{\Delta S}_w$ were characterized by many peaks, some of which were close to BET monolayer.

In the first four of the latter papers the authors studied strongly swelling substances (Pectins, etc.) and interpreted the peaks as signs of stepwise swelling processes. Bettelheim _et al_. (1963) proposed that during swelling, either previously nonhydrogen bonded polar sites open and give rise to greater second minima or previously existing hydrogen bonds are first cloven and subsequently establish such bonding with water molecules giving rise to lesser second minima [the authors call the peaks maxima referring to absolute values]. The authors pointed out that the differential entropy change of sorbate represents changes in entropy of adsorbent due to the fact that it undergoes configurational changes during adsorption. Since it is very improbable that subsequently adsorbed water is more strongly bonded than the previously adsorbed (at least in the region of moisture contents before the BET monolayer), the minima in their $\overline{\Delta H}_w$ and $\overline{\Delta H}_s$ curves before the monolayer are necessarily attributable to configurational changes of the sorbent. The decrease in entropy and enthalpy of sorbent at the minimum points must apparently be very great in order to arrest the monotonically decreasing

contributions of the sorbate to $\overline{\Delta H}_w$ and $\overline{\Delta S}_w$ and yield minimum peaks. Such changes probably are possible with highly swelling materials not being subject to a solvation process at relatively low vapor pressures. Materials dissolving at low relative vapor pressure, such as salmine, show positive entropy change (ΔS_w) long before they dissolve due to incipient solution as pointed out by Davis and McLaren (1948). These authors studied the thermodynamic properties of water vapor adsorption on a number of proteins and concluded that much credence should not be given to the many undulations observed for the heat and entropy curves since only the major maxima and minima lie outside the experimental errors of the measurements. Dole and McLaren (1947) discussed the accuracy of $\overline{\Delta H}_w$ values and concluded that their graphical estimates are uncertain to about 15 to 20 percent at the lower relative humidities with the uncertainty decreasing to about 5 percent at intermediate $P/P°$ values and rising again at the higher $P/P°$ values. The error inherent in the experimental data is not included in the above uncertainties.

Kapsalis (1970) studied the relationship between the mechanical properties and thermodynamic properties of precooked freeze-dried beef. The author obtained isotherms at three temperatures (7°C, 25°C and 37°C) and calculated total differential properties instead of net values; the standard state of water vapors was considered to be vapors

at one atmosphere pressure and temperature of the experiment. Due to these factors, his values include the heat of condensation for water vapor. For reasons not explained in the report, the author employed the integrated form of Clausius -Clapeyron equation [equation 5-5] and used only the isotherms at 7 and 37°C, to calculate total differential enthalpies. The differential form of the same equation [equation 5-4] could have been employed and used all three isotherms for the above calculation. Using the two-isotherm approach, which is the same as that used by Bettelheim and Ehrlich (1963), Masuzawa and Sterling (1968), Volman et al. (1960), Bettelheim and Volman (1957), Kapsalis et al. (1970) obtained a curve for the total differential enthalpy, which showed two peaks one before and one after the BET monolayer. It should be emphasized that the same author applied the differential form of the Clausius -Clapeyron equation to his 1967 data (Kapsalis, 1967) and obtained smooth curves.

To illustrate the differences in differential net enthalpy which result from the use of two isotherms and the integrated Clausius -Clapeyron equation, differential net enthalpies were calculated from the isotherms of this investigation. The analysis was conducted on the 10 and 21.3°C isotherms and then the 21.3 and 31°C isotherms. The results are presented in Table 5.2. To compute differential net enthalpies by the integrated form of Clausius-Clapeyron equation a convenient form of this equation was derived as follows:

Table 5.2. Differential net enthalpies of water vapor adsorption by precooked freeze-dried beef as calculated by the integral form of Clausious-Clapeyron equation and the equation used in this investigation.

Moisture content g. water per 100 g. dry solids	Differential net enthalpies obtained by the application of equation (5-6) to isotherms at 10 and 21.3°C	Differential net enthalpies obtained by the application of equation (5-6) to isotherms at 21.3 and 31°C	Differential net enthalpies obtained in this investigation by the application of equation (4-9)
3	468.753 cal/g.	347.559 cal/g.	418.033
4	416.171 "	333.263 "	378.600
5	257.150 "	250.235 "	254.098
6	234.376 "	186.713 "	213.114
7	190.011 "	136.920 "	168.033
8	170.239 "	107.699 "	143.443
9	142.231 "	85.399 "	114.754
10	127.599 "	56.150 "	94.262
11	101.449 "	53.357 "	81.967
12	86.798 "	47.676 "	69.672
13	75.337 "	46.502 "	65.574
14	74.894 "	31.479 "	57.377
15	67.777 "	28.756 "	49.180
16	68.545 "	17.464 "	49.180

The net enthalpy of adsorption is by definition the enthalpy of adsorption minus the enthalpy of condensation of the water vapors at the same temperature.

The differential form of Clausius - Clapeyron equation is:

$$\frac{d \ln P}{d\ (1/T)} = -\frac{\Delta H_w}{R} \qquad (5\text{-}4)$$

(Dye, 1969; Weber and Meissner, 1957). Integration of this equation between two temperatures, T_1 (initial) and T_2 (final), where the respective vapor pressures are P_1 and P_2, will yield:

$$\Delta H_w = \frac{R\ T_1\ T_2}{T_2 - T_1} \ln \frac{P_2}{P_1} \qquad (5\text{-}5)$$

Note that this equation was developed for single component homogeneous systems (pure water) and for such systems $\Delta H = \overline{\Delta H}_w$ (molar properties are equal to partial properties). There is no reason to expect acceptable results when this equation is applied to mixtures. If the vapor pressures of pure water at the same two temperatures, T_1 and T_2, are P_1^o and P_2^o respectively, the net enthalpy ΔH_w will be given by the following equation:

$$\Delta H_w\ (\text{net}) = \frac{R\ T_1 T_2}{18(T_2 - T_1)} \ln \frac{P_2}{P_1} - \frac{R\ T_1 T_2}{18(T_2 - T_1)} \ln \frac{P_2^o}{P_1^o}$$

The value of 18 was introduced to allow calculation of ΔH_w per unit mass of water. This equation can be written as follows:

$$\overline{\Delta H}_w = \frac{RT_1T_2}{18(T_2-T_1)} \ln \frac{P_2P_1^\circ}{P_1P_2^\circ} = \frac{RT_1T_2}{18(T_2-T_1)} [\ln \frac{P_2}{P_2^\circ} - \ln \frac{P_1}{P_1^\circ}] \qquad (5\text{-}6)$$

Equation (5-6) was used to calculate the results of Table 5-2.

The results of Table 5-2 appear to be very convincing in that it is not sound practice to calculate differential enthalpies from two isotherms by using the integrated form of Clausius - Clapeyron equation.

The differences indicate that either the assumption of constant ΔH over small temperature differences for integrating equation (5-4) is wrong, in the case of water vapor adsorption by biological materials, or that the integrated form of Clausius - Clapeyron equation should not be applied in this case. Saravacos and Stinchfield (1965) found that the vapor pressures of raw freeze-dried beef followed the differential form of Clausius - Clapeyron equation from -20 to 20°C, and from 20 to 50°C. This, also, indicates that use of two isotherms one of which is at temperature below 20°C and the other at a temperature higher than 20°C for computing $\overline{\Delta H}_w$ values will lead to incorrect results. Since the computation of entropy is directly dependent upon the computation of enthalpy values [see equations (4-14) and (4-32)] errors in enthalpy values will be carried forward.

V.2.3. Integral Thermodynamic Properties

The integral free energy and enthalpy changes for the entire process of dry sorbent combining with water to form a mixture equilibrated with vapor pressure (P) were obtained using the equations (4-25) and (4-28). The integral free energies calculated in this manner are expressed as cal/g. of mixture (product). The following discussion deals with the approach used for the computation of integral free energy (ΔG^+) and enthalpy (ΔH^+) values. For a given set of equilibrium moisture content data, first the differential thermodynamic values for the aqueous phase (adsorbate) are calculated. The corresponding contribution of solids (adsorbent) was determined using the convenient form of the Gibb's-Duhem equation (4-6). The integral free energy (ΔG^+) and enthalpy (ΔH^+) values were computed by multiplying the differential values of the components with their respective weigh fractions followed by summation. The integral entropy values were calculated using equation (4-30). The computation of integral free energy (ΔG^+), integral enthalpy (ΔH^+) and the product of integral entropy and temperature ($T\Delta S^+$) is illustrated in Table 5-1. Data from water vapor adsorption isotherms at 10, 21.5 and 31°C for precooked freeze-dried beef were utilized in these computations. The critical part in these computations is the calculation of $\overline{\Delta G}_s$ and ΔH_s at low moisture contents. In the calculations presented, equation (4-8) is used for computing ΔG_s. A plot of $\frac{N_w}{N_s} \cdot \frac{P^o}{P}$ vs. $\frac{P}{P^o}$ was used and the straight curve at low relative vapor pressure ($\frac{P}{P^o}$) values was extrapolated to

cross the $\frac{N_w}{N_s} \cdot \frac{P^\circ}{P}$ axis. The area beneath the curve was computed by using the trapezoidal rule. A similar approach was used for ΔH_s.

Integral free energy (ΔG^+), enthalpy (ΔH^+) and the product of absolute temperature with integral entropy ($T\Delta S^+$) for adsorption and desorption processes of all product studied are plotted in Figures 5.10 and in the appendix (Figures A.12 to A.14). The figures reveal that the integral thermodynamic properties of adsorption and desorption increase in absolute value with increasing moisture content. The change is rapid at low moisture contents but gradually levels off at higher moisture contents, at least for the range and mixture contents investigated in this study. Fish (1958) studied the integral thermodynamic properties (ΔG^+, ΔH^+, $T\Delta S^+$) of water vapor adsorption on starch and the curves obtained for the above properties showed minima at about 10 g. of water per 100 g. of dry starch. This moisture content is higher than the BET monolayer which was found to be about 6 g. of water per 100 g. of dry starch (Stitt, 1958). It must be mentioned that using the differential enthalpy curve of Fish (1958) the curve for integral ΔH^+ can be reproduced very clearly. Palnitkar (1970) investigated the thermodynamic properties of water vapor adsorption and desorption by precooked freeze-dried beef and reported minima in the curves for integral enthalpy (ΔH^+) and entropy ($T\Delta S^+$) which coincided rather closely with the BET monolayer values. On the basis

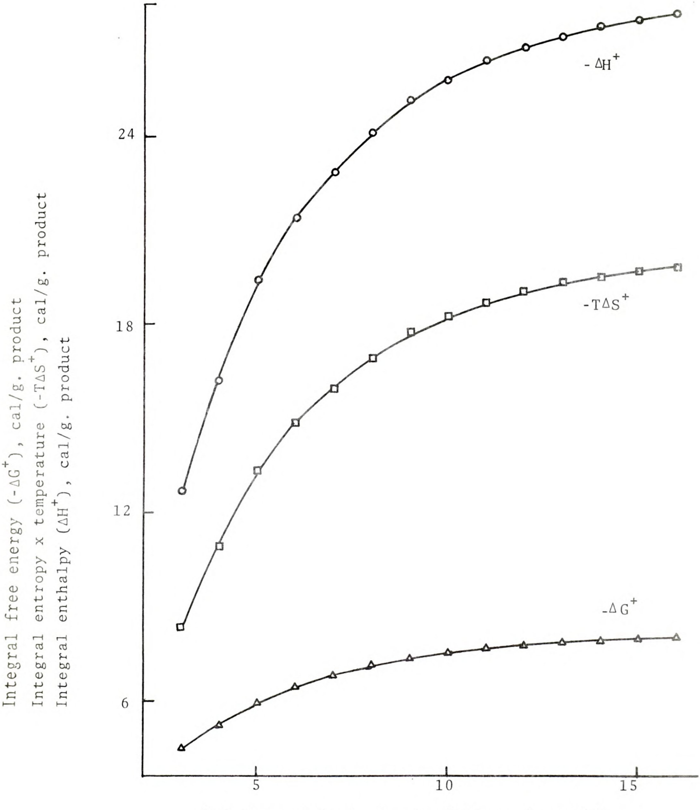


Figure 5.10.--Integral change in net thermodynamic values for water vapor adsorption on precooked freeze-dried beef solids to form 1 g. of mixture with the indicated composition.

of these findings Palnitkar (1970), suggested that there may be a relationship between the minimum entropy moisture content and optimum stability moisture level as proposed by Salwin (1959). An analysis of the data and procedures used by Palnitkar (1970) revealed that the minimum entropy values could not be reproduced. The data used by Palnitkar (1970) produced results very similar to relationships obtained in this investigation. Discussions with Palnitkar (1972) indicate that errors in computer programs used for data analysis probably produced the results presented by Palnitkar (1970).

V.2.4. An Analysis of Procedures Used to Compute Integral Properties

As previously mentioned, the curves for the differential thermodynamic properties of water vapor adsorption by starch obtained by Fish (1958) were smooth curves similar in shape to those obtained by Palnitkar (1970) and in present investigation when analyzing data from vapor adsorption on precooked freeze-dried and raw freeze-dried beef. The difference in shape between the integral thermodynamic properties of water vapor adsorption by starch and those for water vapor adsorption by precooked freeze-dried and raw freeze-dried beef requires explanation. Consider a real two-component liquid solution. Assuming the perfect-gas laws to apply to the vapor phases of the liquids and considering the pure liquids, at the same temperature and pressure as the solution, to be their standard states, the differential free energy changes are given by equation (4-5):

$$\overline{\Delta G}_1 = RT\ln\frac{P_1}{P_1^\circ} \qquad \overline{\Delta G}_2 = RT\ln\frac{P_2}{P_2^\circ}$$

Subscripts 1 and 2 refer to components and P and P° are the vapor pressures of the subscribed component over the solution and at its standard state.

According to Henry's law (Weber and Meissner, 1957, p. 347),

$$P_1 = \gamma_1 P_1^\circ x_1$$

and

$$P_2 = \gamma_2 P_2^\circ x_2 \qquad (5\text{-}7)$$

where γ and x are the activity coefficient and the mole fraction respectively of the subscripted component.

Combining equations (5-7) with equations (4-5) the following equations are obtained:

$$\overline{\Delta G}_1 = RT\ln\gamma_1 x_1, \qquad \overline{\Delta G}_2 = RT\ln\gamma_2 x_2 \qquad (5\text{-}8)$$

By substitution in equation (4-24):

$$\Delta G^+ = x_1 RT\ln\gamma_1 x_1 + x_2 RT\ln\gamma_2 x_2 \qquad (5\text{-}9)$$

where ΔG^+ in the above equation represents the change in free energy of system per mole of solution.

For an ideal solution, all activity coefficients are unity at all concentrations; hence (5-9) becomes

$$\Delta G^{+} = x_1 RT\ln x_1 + x_2 RT\ln x_2 \tag{5-10}$$

Analysis of equation (5-8) indicates that for both real and ideal-liquid solutions, $\overline{\Delta G}_1$ approaches minus infinity as x_1 approaches zero. On the other hand, it can be shown that the product $x_1\overline{\Delta G}_1$ approaches zero as x_1 approaches zero (Weber and Meissner, 1957, p. 447). It can be shown (Weber and Meissner, 1957, p. 347) that the predominant component of both a real- and ideal- liquid solution will follow Raoult's law as its mole fraction approaches unity, and hence its activity coefficient must also approach unity with increasing mole fraction. As x_1 approaches unity, the term $\overline{\Delta G}_1$ must approach zero both for real- and ideal-liquid solutions, as is clear from an inspection of equation (5-8). The above arguments are also true for $\overline{\Delta G}_2$. The change in $\Delta G^{+}/RT$, $\Delta G_1/RT$ and $\Delta G_2/RT$ when one mole of solution is produced by mixing two liquids yielding an ideal solution at varying concentrations as shown in Figure 5.11.

It is apparent from Figure (5-11) that ΔG^{+} must have a minimum, which for an ideal solution will occur at a concentration of 100 moles of component 1 per 100 moles of component 2. The composition of a nonideal binary solution at which ΔG^{+} will become a minimum will probably be determined from the degree of nonideality of the solution.

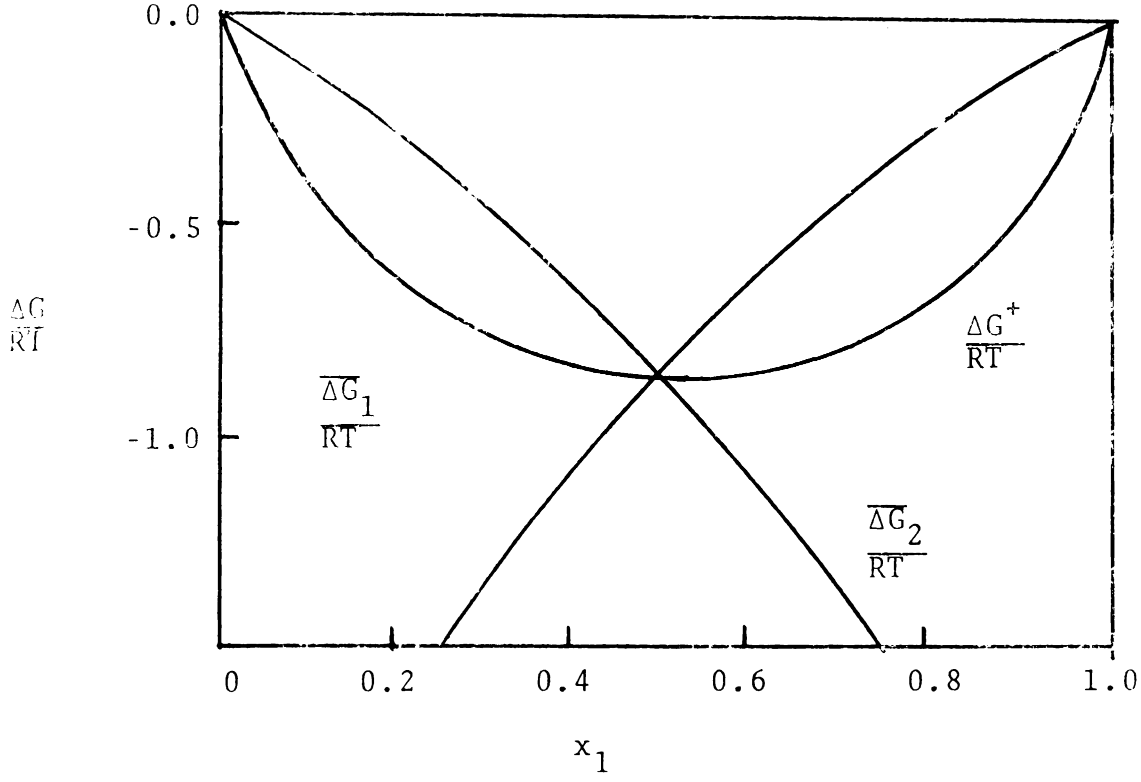


Figure 5.11.--Variation of free-energy quantities with composition in an ideal binary mixture at constant temperature and total pressure (Weber and Meissner, 1957).

The proceeding discussion and equations were derived by considering a binary liquid solution. Obviously it also applies to a binary solution when one of the components of which is liquid in its standard state while the other is solid in its standard state. The vapor pressure of the solid component may not be measurable but Gibb's-Duhem equation provides an acceptable procedure for determining the changes of free energy of these components. It would appear as those minima must occur in the curves of integral properties but it is highly unlikely that these minima will occur at the BET monolayer or if they occur at this moisture content it will be a coincidence.

The integral change in free energy (ΔG^+) and the contribution to ΔG^+ by water $N_w\overline{\Delta G}_w$, and food solids, $N_s \cdot \overline{\Delta G}_s$, for the water vapor adsorption by precooked freeze-dried beef are plotted in Figure 5.12. The integral change in free energy (ΔG^+) decreases monotonically with increasing coverage, as it must in the region of moisture contents studied. The adsorption process is spontaneous for an increase in vapor pressure of the adsorbate (Wu and Copeland, 1964). The curve for $N_w \cdot \overline{\Delta G}_w$ decreases with increasing coverage in the low coverage region, but passes through a minimum and increases with increasing coverage approaching zero. The curve for the contribution of solids, $N_s\overline{\Delta G}_s$, decreases monotonically with coverage, and shows that the beef solids are not an "inert adsorbent" for water. Since N_s approaches zero with increasing moisture content,

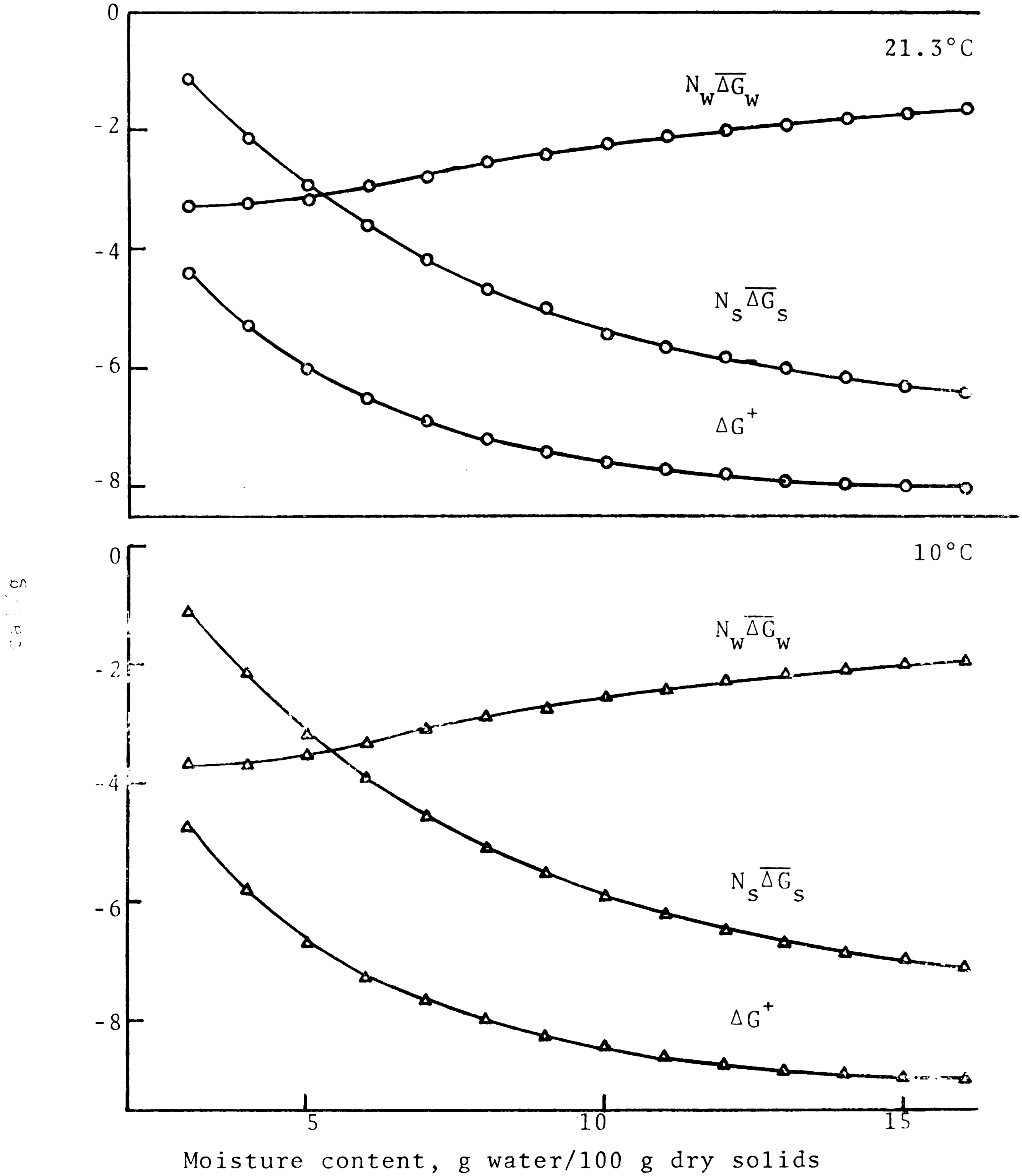


Figure 5.12.--Free energy change of adsorption of water vapors on precooked freeze-dried beef.

Integral change in free energy, G^+, is for the process of mixing appropriate amounts of dry solids and water to form 1 g of mixture with the indicated composition. T=294.45°K and at T=283.15°K.

at $N_w = 1$, $N_s\overline{\Delta G}_s$ will become zero and obviously both $N_s\overline{\Delta G}_s$ and ΔG^+ will pass through a minimum at some higher moisture content and both start increasing tending towards zero.

Figure 5.13 for precooked freeze-dried beef and similar plots for raw freeze-dried beef show that the values of integral net enthalpies of desorption are consistently greater than those for adsorption. It could be suggested that in the design of dehydration equipment, the integral enthalpy of desorption at a moisture content where it becomes a maximum must be considered.

V.2.5. Thermodynamic Properties of the Water Vapor Sorption by Dry Food Solids and Food Stability

The water vapor sorption by dry or low moisture content food solids is of particular importance with respect to preserving the quality characteristics of the food product. The moisture content of a food product has a significant influence on the chemical enzymatic and microbiological activities in the product and determines rates of change of such quality attributes as color, flavor, odor, vitamin content, texture, wholesomeness and physical appearance (agglomeration of sugar, soapiness in oils, sogginess in biscuits). It is uncertain whether loss of these qualities (even in the case of similar foods) becomes evident simultaneously at a given moisture content, or whether all these factors are equally important (Heiss and Eichner, 1971). It seems likely that one of the quality factors will be the

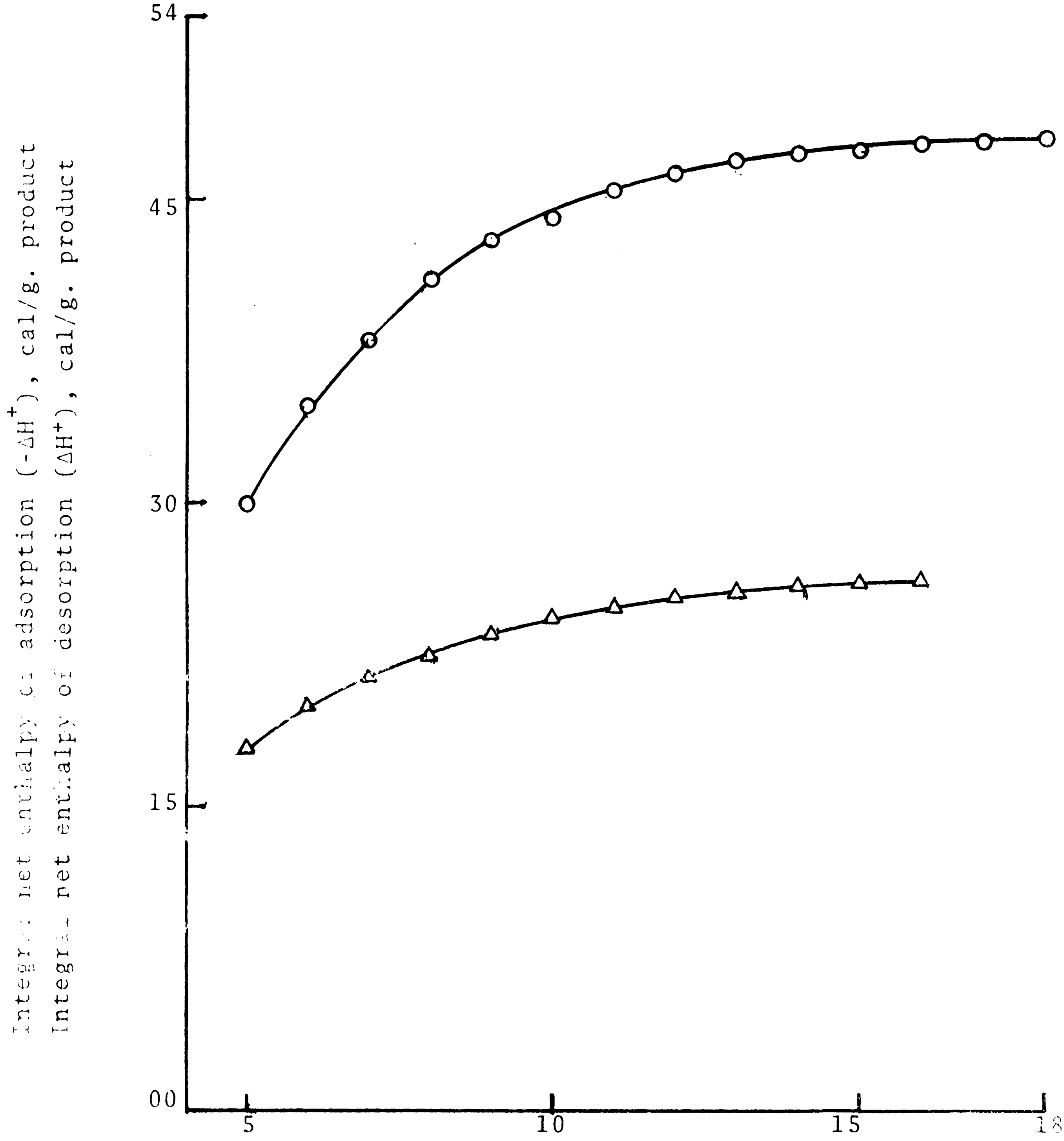


Figure 5.13.--Isosteric integral net enthalpies per g. of mixture (ΔH^+) of desorption and adsorption for precooked freeze-dried beef at 21.3°C.

one which will set the permissible moisture level for each type of food. For example, the relative humidity of the storage atmosphere at low values will not influence any of the quality attributes of refined sugar but has a significant influence on product appearance. A very small moisture uptake can cause agglomeration of sugar. It is apparent that the moisture content at which sugar will be stable from the consumer's point of view will be determined from the relationship "moisture content-sugar agglomeration." In practice the moisture content of sugar will be determined from the relative humidity of storage atmosphere and the stability determining relationship of interest then is "storage relative humidity-sugar agglomeration." The foregoing discussion makes it evident that "food stability" is a general term which signifies different "storage relative humidity-quality factor(s)" relationships for each type of food. The optimum moisture content for a given dehydrated food, which may be defined as the one at which the food has the maximum stability, will apparently be determined by accounting for all quality factors of concern. To understand the role of water and the manner in which it causes undesirable changes in quality factors will require knowledge of the mechanism of the deteriorative reactions and its relation to water content.

The thermodynamics of water vapor adsorption and desorption merely describe the various energy levels with which the water associates with the food solids. The curves representing the relationship between thermodynamic functions of interest and moisture content of the food solids compare the values of the respective functions at a number of "relative humidity-moisture content" equilibrium positions within the range of moisture content studied. It is a thermodynamic axiom as pointed out in the discussion of entropy changes, the change in free energy (dG) of the system is zero at each equilibrium position at constant temperature and pressure. Since dG = 0, G is a minimum at equilibrium. An inference about the entropy value of the system alone at equilibrium cannot be made although the entropy of the system plus the entropy of the surroundings will be a maximum (Denbigh, p. 82; King, 1969, p. 10-12). Any maxima or minima occurring in the entropy curve cannot be interpreted in terms of system stability at various equilibrium positions, since the entropy function is not specifically associated to equilibrium.

In addition, it must be kept in mind that the equilibria referred to the process of water vapor sorption and their comparative stability conveys the easiness by which the system may be thrown out of the respective "moisture content-vapor pressure" equilibria. In other words, if any thermodynamic function was a measure of relative stability of the various possible "moisture content-vapor pressure" equilibria and indicated a given "moisture content-vapor pressure" equilibrium as the most

stable, it would merely imply that at this moisture level the increment of vapor pressure needed for additional adsorption would be a maximum compared to other moisture levels.

Although it is very hard to visualize any simple relationship between thermodynamic stability and the quality stability of a food product, no thermodynamic treatment associates a certain function to relative stability of equilibria of a system. The only meaningful implication which may be assigned to entropy curve undulations is the degree of orientation or orderliness of the system molecules compared to a datum level (Kapsalis *et al.*, 1970a).

VI. SUMMARY AND CONCLUSIONS

The thermodynamic properties of water vapor sorption by foods at low and intermediate moisture contents were investigated. Raw freeze-dried and precooked freeze-dried beef were studied in this investigation. The sorption isotherms of the products at three different temperatures were smooth sigmoid curves. The desorption isotherms followed the respective adsorption isotherms with considerable hysteresis indicating that the processes of adsorption and desorption are not equivalent. The sorption isotherms obtained in this investigation were in good agreement with published data.

The equilibrium moisture content increased with decreasing temperature from 31 to 10°C. This was reflected in the differential free energy values of the water and the solids. The differential free energy values of water and solids were more negative (larger in absolute magnitude) at lower temperatures than at higher. This suggests a larger driving force for water vapor adsorption at lower temperatures for the products studied and leads to the conclusion that the equilibrium moisture content will be higher at lower temperatures.

The differential free energy, enthalpy and entropy of water decreased sharply in absolute magnitude for both adsorption and desorption with increasing moisture content and leveled off at about 15 percent moisture content. This suggests that water may behave similar to free water and serve as a solvent for reactants in the solid mixture at very low moisture range.

The respective differential properties of solids increased in absolute magnitude with increasing moisture content for both adsorption and desorption. The differential thermodynamic properties of solids changed very little with increasing moisture content and tended to level off at higher moisture contents. This suggests that although the reactivity of the macromolecular components of the solid mixture increases with increasing moisture content no extensive structural changes take place in the range of moisture contents studied.

The differential enthalpy values were obtained from Maxwell's relationship between free energy and enthalpy and their curves were smooth without sharp transitions or peaks. The application of the integrated form of Clausius-Clapeyron equation for evaluating differential enthalpies from two isotherms was considered. It was concluded that errors can result from its application when isotherms at widely differing temperatures were employed.

The differential enthalpy values of water and solids for the desorption process were consistently higher in absolute magnitude than the respective values for the adsorption process for all products considered reflecting the phenomenon of hysteresis. The integral enthalpy values (ΔH^+) for desorption of water vapor were also consistently higher than the respective property values of adsorption for all products. This suggests that in the design of dehydration equipment, the maximum integral enthalpy of desorption and the corresponding moisture content must be considered.

The differential entropy changes of water were large in absolute magnitude at low moisture content for both adsorption and desorption and decreased sharply with increasing moisture content. The high entropy changes of water at low moisture content supports the theory that chemisorption takes place at low moisture contents.

The curves of the integral thermodynamic properties were also smooth and changed rapidly with increasing moisture contents at low moisture contents but leveled off at higher moisture content. The change of the integral curves reflect the change of the respective contributing differential curves of water and solids. A theoretical analysis of the integral thermodynamic properties was carried out. It was concluded that the integral thermodynamic property curves will become maximum or minimum at a moisture content which will be a function of the nonideality of the system.

Evidence of special responses of the thermodynamic property curves of water vapor sorption by dehydrated foods which could be related to the storage stability of foods was not revealed in this investigation. It was concluded that a simple relationship between thermodynamic properties of low and intermediate moisture foods and their storage stability may not exist.

REFERENCES

Acker, L. 1963. Enzyme activity at low water contents. Section 5, Vol. III. Recent Advances in Food Science, edited by J. M. Leitch and D. N. Rhodes. Butterworths, London.

Acker, L. W. 1969. Water activity and enzyme activity. Food Technol. 23:1257.

Amberg, C. H. 1957. Heats of adsorption of water vapor on bovine serum albumine. J. Am. Chem. Soc. 79:3980.

Berlin, E., B. A. Anderson and M. J. Pallansch. 1968. Comparison of water vapor sorption by milk powder components. J. Dairy Sci. 51:1912.

Bettelheim, F. A. and S. H. Ehlrich. 1963. Water vapor sorption of mucopolysaccharides. J. Phys. Chem. 67: 1948.

Bettelheim, F. A. and D. H. Volman. 1957. Pectic substances--water. II. Thermodynamics of water vapor sorption. J. Polymer Sci. 24:445.

Bradley, R. S. 1936. Polymolecular adsorbed films. II. The general theory of the condensation of vapors on finely divided solids. J. Am.

Brunauer, S., P. H. Emmett and E. Teller. 1939. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60:309.

Brunauer, S. 1945. The Adsorption of Gases and Vapors, Vol. I. Princeton University Press, Princeton.

Bull, H. B. 1944. Adsorption of water vapor by proteins. J. Am. Chem. Soc. 66:1499.

Bushuk, W. and A. C. Winkler. 1957. Sorption of water vapor on wheat flour, starch and gluten. Cer. Chem. 34.73.

Christian, J. H. B. 1963. Water activity and the growth of microorganisms. Section 5, Vol. III. Recent Advances in Food Science, edited by J. M. Leitch and D. N. Rhodes. Butterworths, London.

Chung, S. D. and B. H. Pfost. 1967. Adsorption and desorption of water vapor by cereal grains and their products. Parts I, II and III. Transactions of the ASAE 10:552.

Cole, R. H. and J. S. Coles. 1964. Physical Principles of Chemistry. W. H. Freeman and Company, London.

Davis, S. and A. D. McLaren. 1948. Free energy, heat and entropy changes accompanying the sorption of water vapor by proteins. J. Polymer Sci. 3:16.

Debeer and Zwicker. 1929. The polarization theory. Z. Physik. Chem. B3:407.

Denbigh, K. 1955. The Principles of Chemical Equilibrium University Press, Cambridge.

Dole, M. and A. D. McLaren. 1947. The free energy, heat and entropy of sorption of water vapor by proteins and high polymers. J. Am. Chem. Soc. 69:651.

Duckworth, R. B. and M. G. Smith. 1963. Diffusion of solutes at low moisture levels. Vol. III. Biochemistry and Biophysics, pp. 230-238. Recent Advances in Food Science, edited by J. M. Leitch and D. N. Rhodes. Butterworths, London.

Dye, L. J. 1969. Thermodynamics and Chemical Equilibrium. W. A. Benjamin Publishers, Inc.

Fish, B. P. 1958. Diffusion and thermodynamics of water in potato starch gel. Fundamental Aspects of Dehydration of Foodstuffs. London, England: Society of Chemical Industries.

Gee, G. and L. R. G. Treloar. 1942. The interaction between rubber and liquids. 1. A thermodynamical study of the system rubber-benzene. Trans. Faraday Soc. 38:147.

Guggenheim, E. A. 1967. Thermodynamics. An Advanced Treatment for Chemists and Physicists. North-Holland Publishing Co., Amsterdam.

Hall, C. W. and H. J. Rodriquez-Arias. 1958. Equilibrium moisture content of shelled corn. Agr. Eng. 39:466.

Harkins, W. D. and G. Jura. 1944. Determination of the decrease (π) of free surface energy of a solid by a adsorbent film. J. Am. Chem. Soc. 66:1356.

Harkins, D. W. 1952. The Physical Chemistry of Surface Films. Reinhold Pub. Comp., New York.

Heiss, R. and K. Eichner. 1971. Moisture content and shelflife. Food Manufacture 46:(5):53.

Henderson, S. M. 1952. A basic concept of equilibrium moisture. Agr. Eng. 33:29.

Hermans, J. J. 1949. Thermodynamics of long-chain molecules. Vol. II, p. 49. Colloid Science, edited by H. R. Kruyt. Elsevier Publ. Co., New York.

Hoover, S. R. and F. E. Mellon. 1950. Application of polarization theory to sorption of water vapor by high polymers. J. Am. Chem. Soc. 72:2562.

Kapsalis, J. G. 1967. Hygroscopic equilibrium and texture of freeze-dried foods. Investigation of the relationships between moisture content-water vapor equilibrium and textural parameters in special freeze-dried foods. Defense Documentation Center, Tech. Report AD 655488. Clearinghouse for Federal Scientific and Tech. Information, U.S. Dept. of Commerce, Springfield, Va.

Kapsalis, J. G., B. Drake and B. Johansson. 1970a. Textural properties of dehydrated foods. Relationships with the thermodynamics of water vapor sorption. J. Texture Studies 1:285.

Kapsalis, J. G., J. E. Walker, Jr. and M. Wolf. 1970b. A physicochemical study of the mechanical properties of low and intermediate moisture foods. J. Texture Studies 1:464.

Kapsalis, J. G., M. Wolf and J. E. Walker. 1971. The effect of moisture content on the flavor and texture stability of dehydrated foods. ASHRAE Journal, January 1971, p. 93.

Karel, M. and J. T. R. Nickerson. 1964. Effect of relative humidity, air and vacuum on browning of dehydrated orange juice. Food Technol. 18:104.

Karel, M. and T. P. Labuza. 1968. Nonenzymatic browning in model systems containing sucrose. J. Agr. Food Chem. 16:717.

King, M. B. 1969. Phase Equilibrium in Mixtures. Pergamon Press, Oxford.

Labuza, T. P. 1968. Sorption phenomena in foods. Food Technol. 22:15.

Labuza, T. P., S. R. Tannenbaum and M. Karel. 1970. Water content and stability of low-moisture and intermediate-moisture foods. Food Technol. 24:543.

Langmuir, I. 1916. Adsorption of gases by solids. J. Am. Chem. Soc. 38:2267.

Lea, C. H. 1958. Chemical changes in the preparation and storage of dehydrated foods. Fundamental Aspects of Dehydration of Foodstuffs. London, England: Society of Chemical Industries.

Maloney, J. F., T. P. Labuza, D. H. Wallace and M. Karel. 1966. Autoxidation of methyl linoleate in freeze-dried model systems. I. Effect of water on the auto-catalyzed oxydation. J. Food Sci. 31:878.

Martinez, F. and T. P. Labuza. 1968. Rate of deterioration of freeze-dried salmon as a function of relative humidity. J. Food Sci. 33:241.

Masuzawa, M. and C. Sterling. 1968. Gel-water relationships in hydrophilic polymers: thermodynamics of sorption of water vapor. J. App. Polymer Sci. 12:2023.

Mellon, E. F., A. H. Korn and S. R. Hoover. 1947. Water adsorption of proteins. I. J. Am. Chem. Soc. 69:827.

Ngody, P. O. and F. W. Bakker-Arkema. 1970. A generalized theory of sorption phenomena in biological materials. I. The isotherm equation. Transactions of the ASAE, p. 612.

Osipow, L. I. 1962. Surface Chemistry. Theory and Industrial Applications. Am. Chem. Soc. Monograph Series. Reinhold Publishing Corp., New York.

Palnitkar, M. P. 1970. Thermodynamic characteristics of low and intermediate moisture foods. Ph.D. thesis, Dept. of Food Science, Michigan State University, East Lansing, Michigan.

Palnitkar, M. P. 1972. Personal communications.

Pauling, L. 1945. The adsorption of water vapors by proteins. J. Am. Chem. Soc. 69:646.

Polanyi, M. 1914. Verbandl Deutsch. Physik. Ges 18:55.

Potter, N. 1970. Intermediate moisture foods: principles and technology. Food Product Development. Nov. 1970, p. 38.

Rockland, L. B. 1957. A new treatment of hygroscopic equilibria application to walnuts (Juglas Regia) and other foods. Food Res. 22:604.

Rockland, L. B. 1969. Water activity and storage stability. Food Technol. 23:1241.

Rossini, F. D. 1950. Chemical Thermodynamics. John Wiley and Sons, Inc., New York.

Salwin, H. 1959. Defining minimum moisture contents for dehydrated foods. Food Technol. 13:594.

Salwin, H. 1963. Moisture levels required for stability in dehydrated foods. Food Technol. 17:34.

Saravacos, G. D. and R. M. Stinchfield. 1965. Effect of temperature and pressure on the sorption of water vapor by freeze-dried food materials. J. Food Sci. 30:779.

Scott, W. J. 1957. Water relations of food spoilage organisms. Advan. Food Res. 7:83.

Simatos, D. 1966. Origine et role des radicaux libres dans les produits biologiques liophilises. Advances in freeze-drying. L. Rey, ed. Herman Publ., Paris.

Simril, V. L. and S. Smith. 1942. Sorption of water by cellophane. Industrial and Engineering Chemistry 34:226.

Smith, S. E. 1947. The sorption of water vapor by high polymers. J. Am. Chem. Soc. 69:646.

Stamm, A. J. and W. K. Loughborough. 1935. Thermodynamics of the swelling of wood. J. Phys. Chem. 39:121.

Stitt, F. 1958. Moisture equilibrium and the determination of water content of dehydrated foods. Fundamental Aspects of the Dehydration of Foodstuffs. Society of Chemical Industries, London, England.

Triebold, H. O. and L. N. Aurand. 1963. Food Composition and Analysis. Van Nostrand Reinhold Co., New York.

Uri. 1956. Metal ion catalysis and polarity of environment in the aerobic oxidation of unsaturated fatty acids. Nature 177:1177.

Volman, D. H., J. W. Simons, J. R. Seed and C. Sterling. 1960. Sorption of water vapor by starch. Thermodynamics and structural changes for dextrin, amylose, and amylopectin. J. Polymer Sci. 46:355.

Weber, C. H. and H. P. Meissner. 1957. Thermodynamics for Chemical Engineers. Second Edition. Wiley and Sons, New York.

Wu, Y. C. and L. E. Copeland. 1961. Thermodynamics of adsorption. The barium sulfate-water system. Advan. in Chem. Series 33:357.

Zsigmondy, R. [illegible]. Z. Anorg. Chem. 71:356.

APPENDIX A

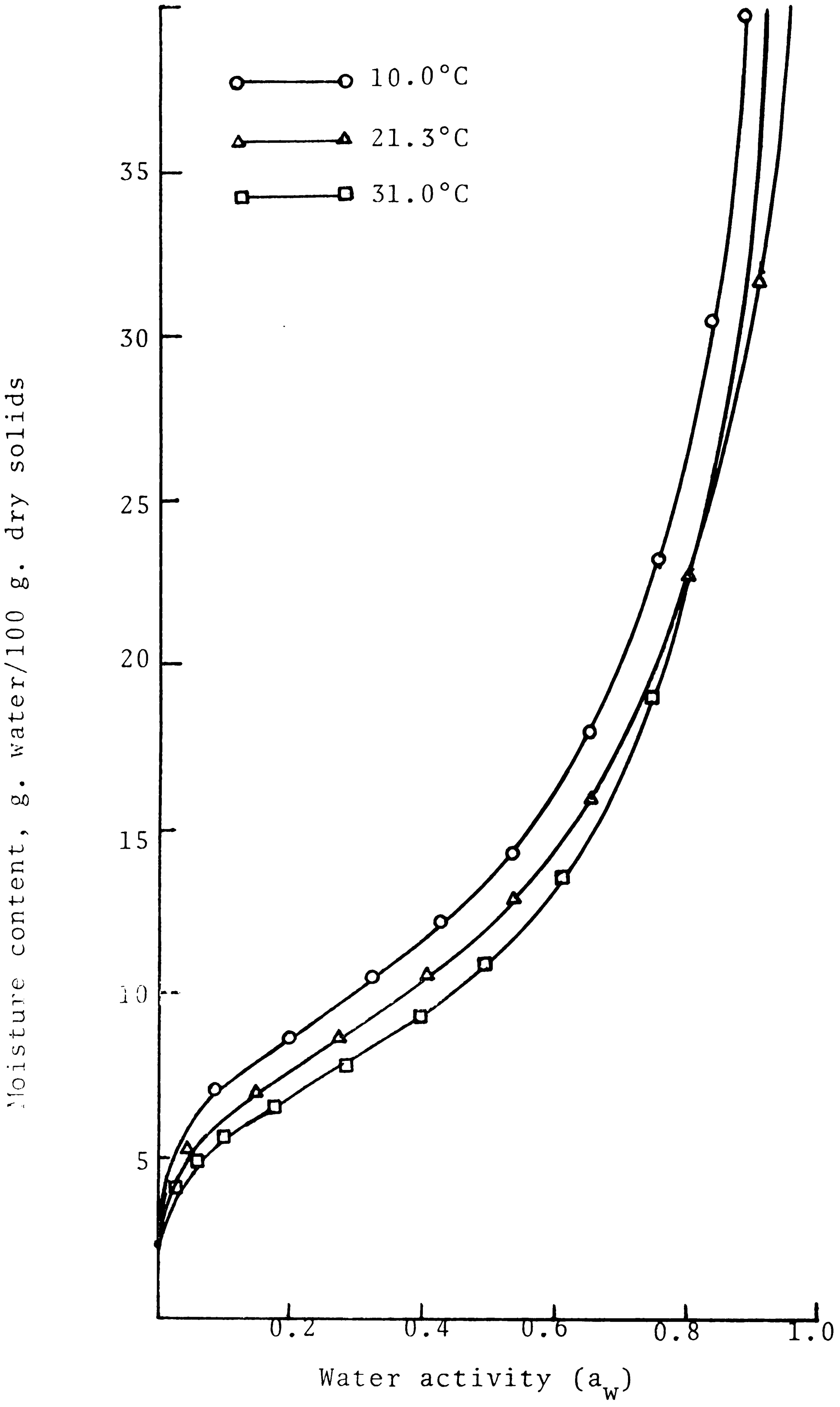


Figure A.1.--Desorption isotherms of precooked freeze-dried beef. Plate temperature 100°F.

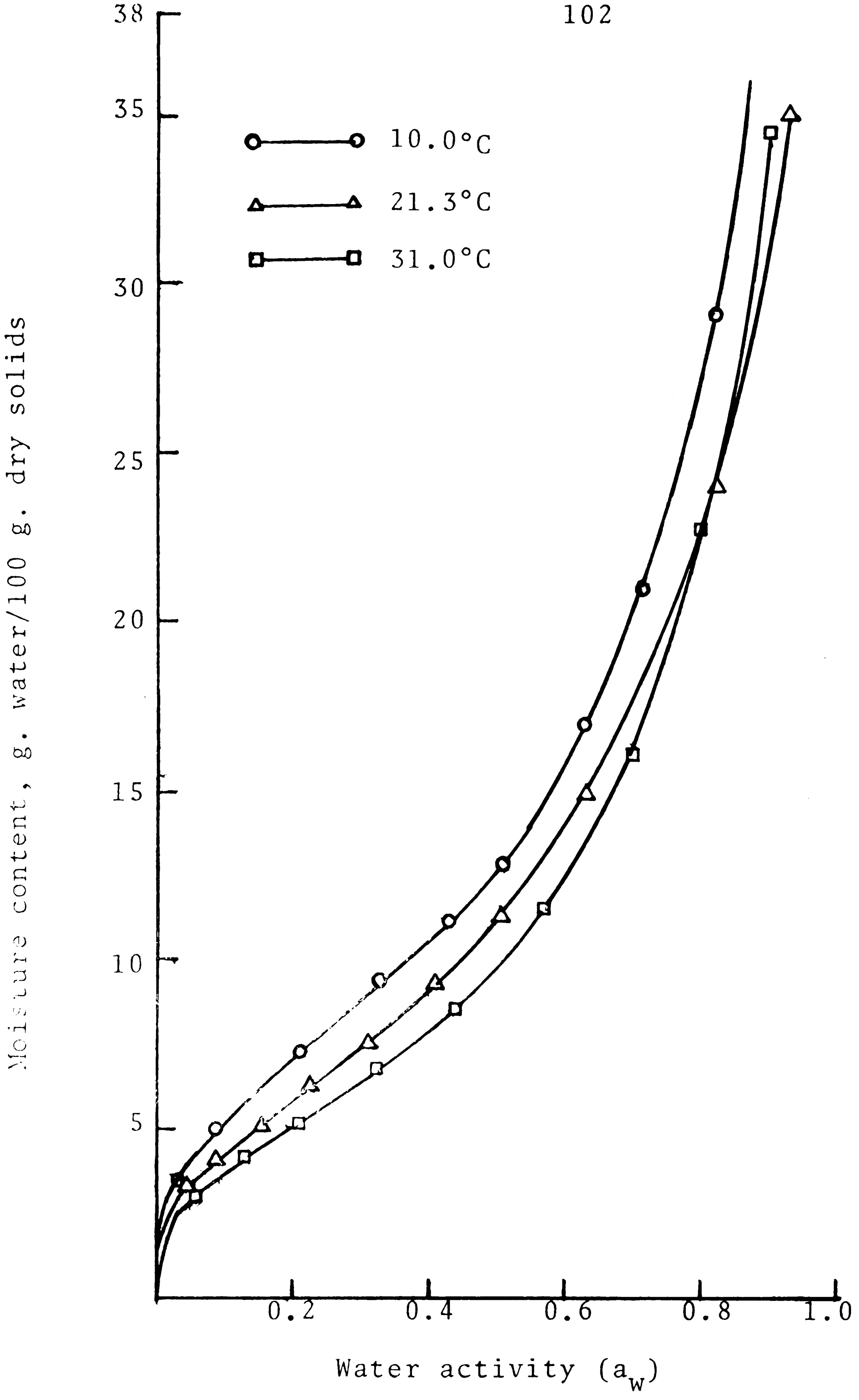


Figure A.2.--Adsorption isotherms of raw freeze-dried beef. Plate temperature 100°F.

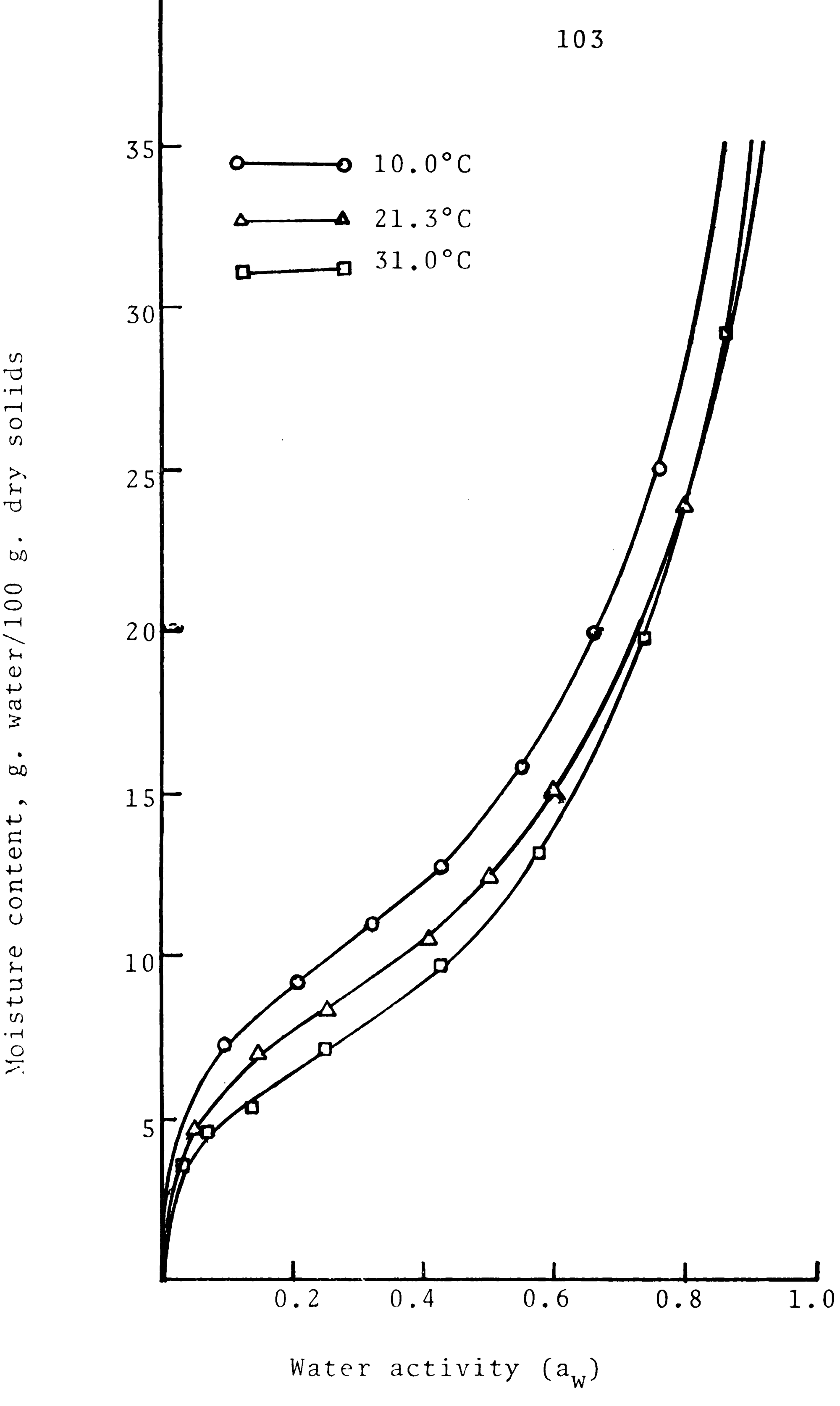


Figure A.3.--Desorption isotherms of raw freeze-dried beef. Plate temperature 100°F.

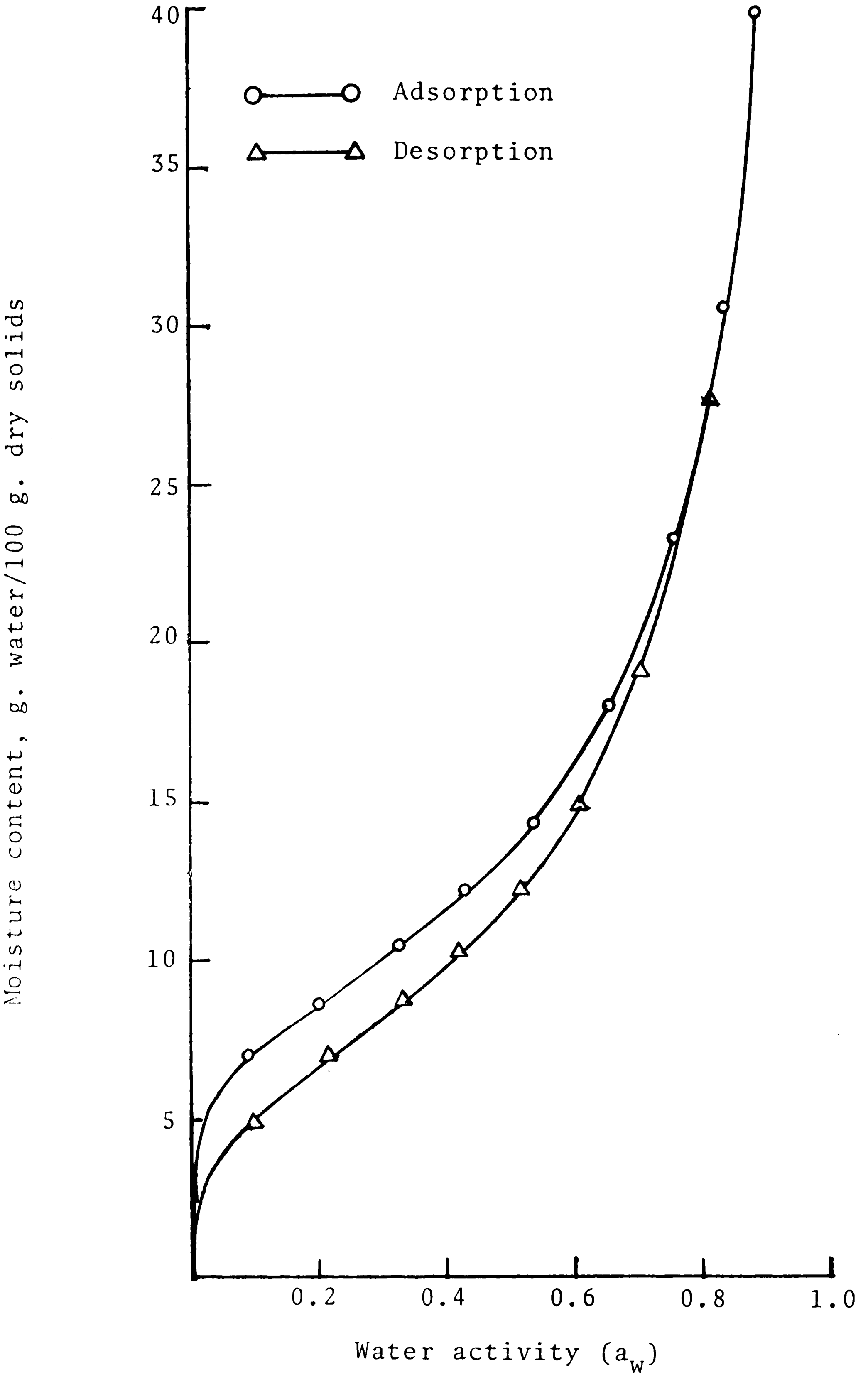


Figure A.4.--Adsorption and desorption isotherms of precooked freeze-dried beef at 10.0°C.

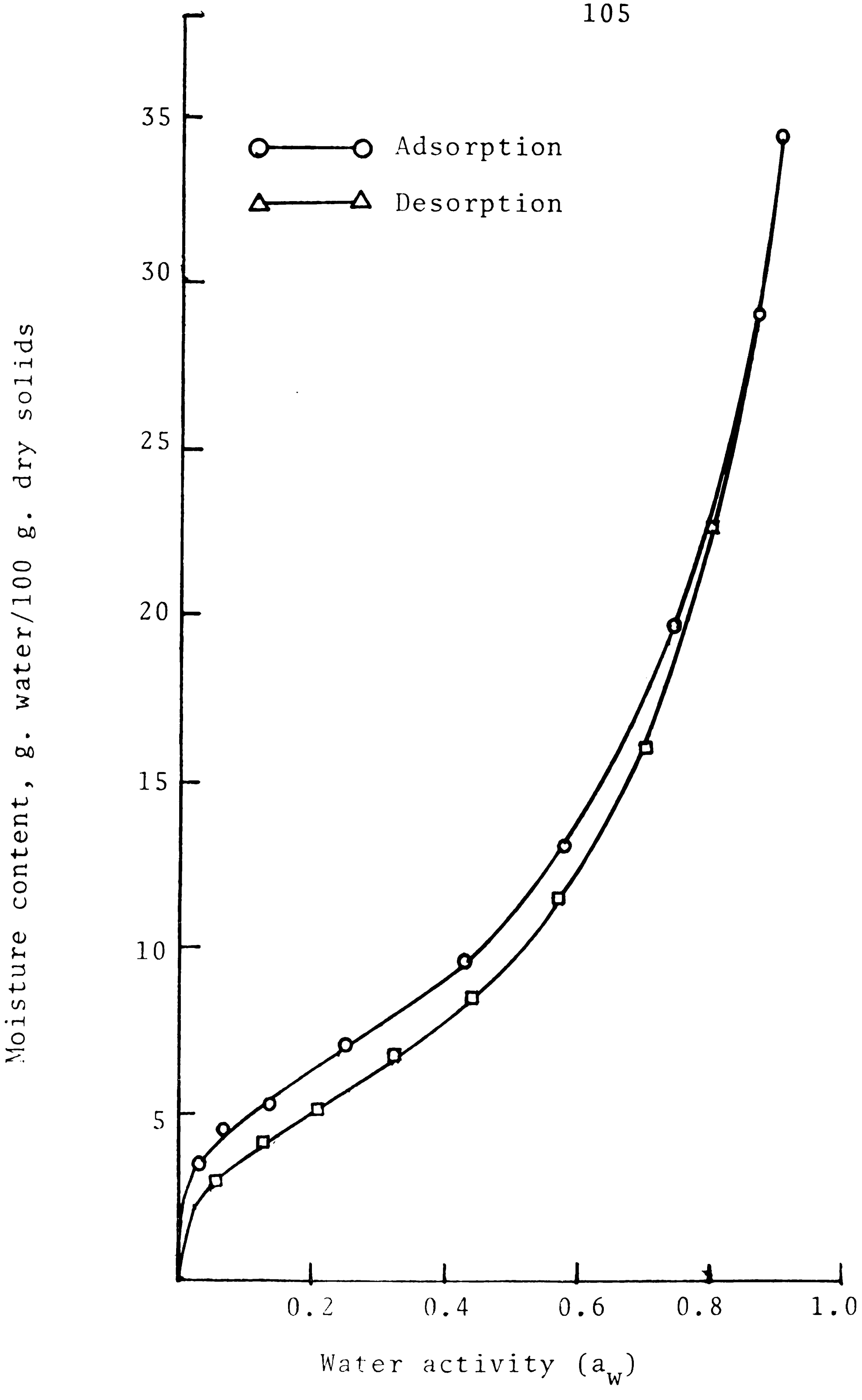


Figure A.5.--Adsorption and desorption isotherms of raw freeze-dried beef at 31.0°C.

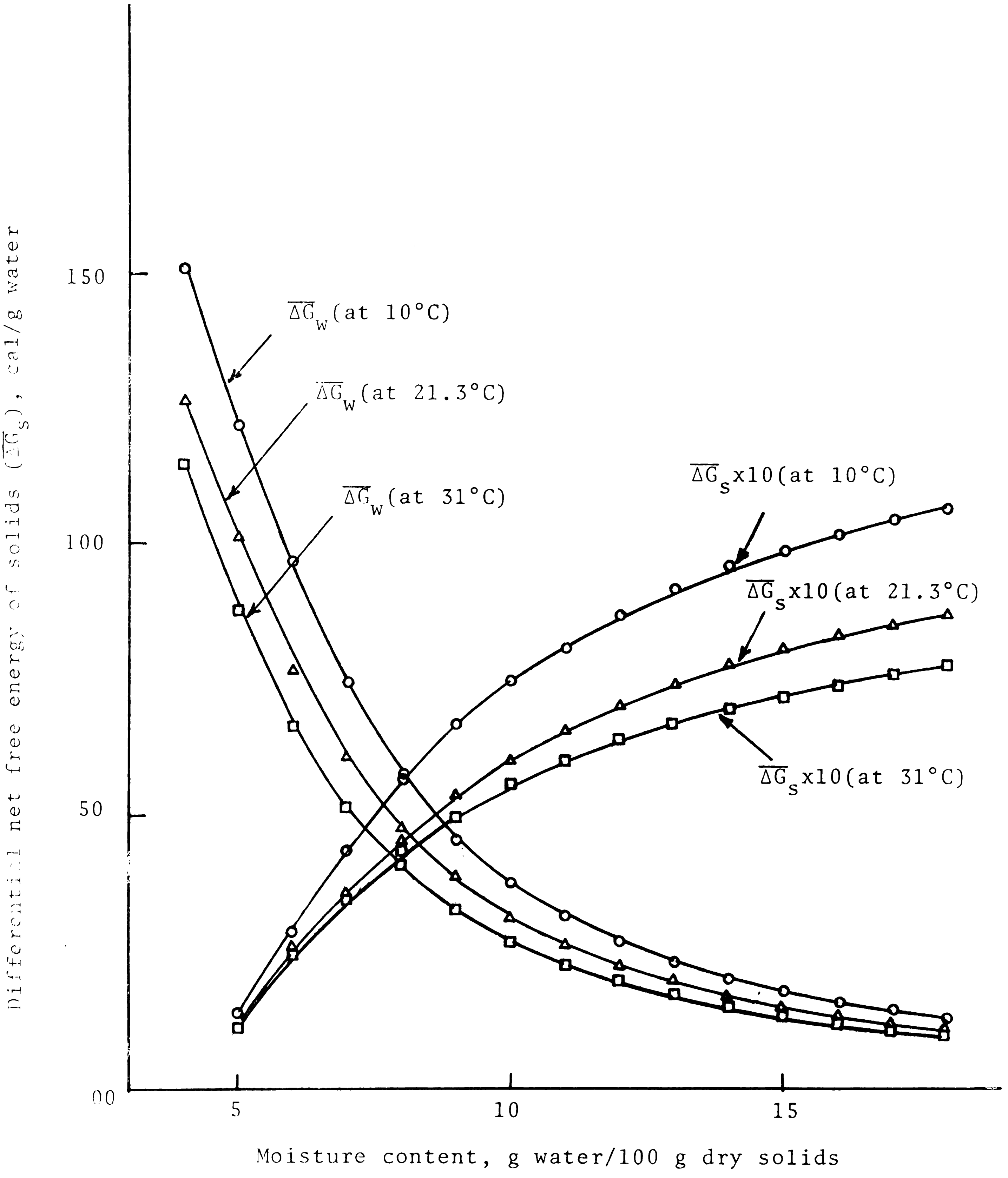


Figure A.6.--Influence of temperature on the differential net free energy values of water and solids for desorption of water vapors from precooked freeze-dried beef (plate temperature 100°F).

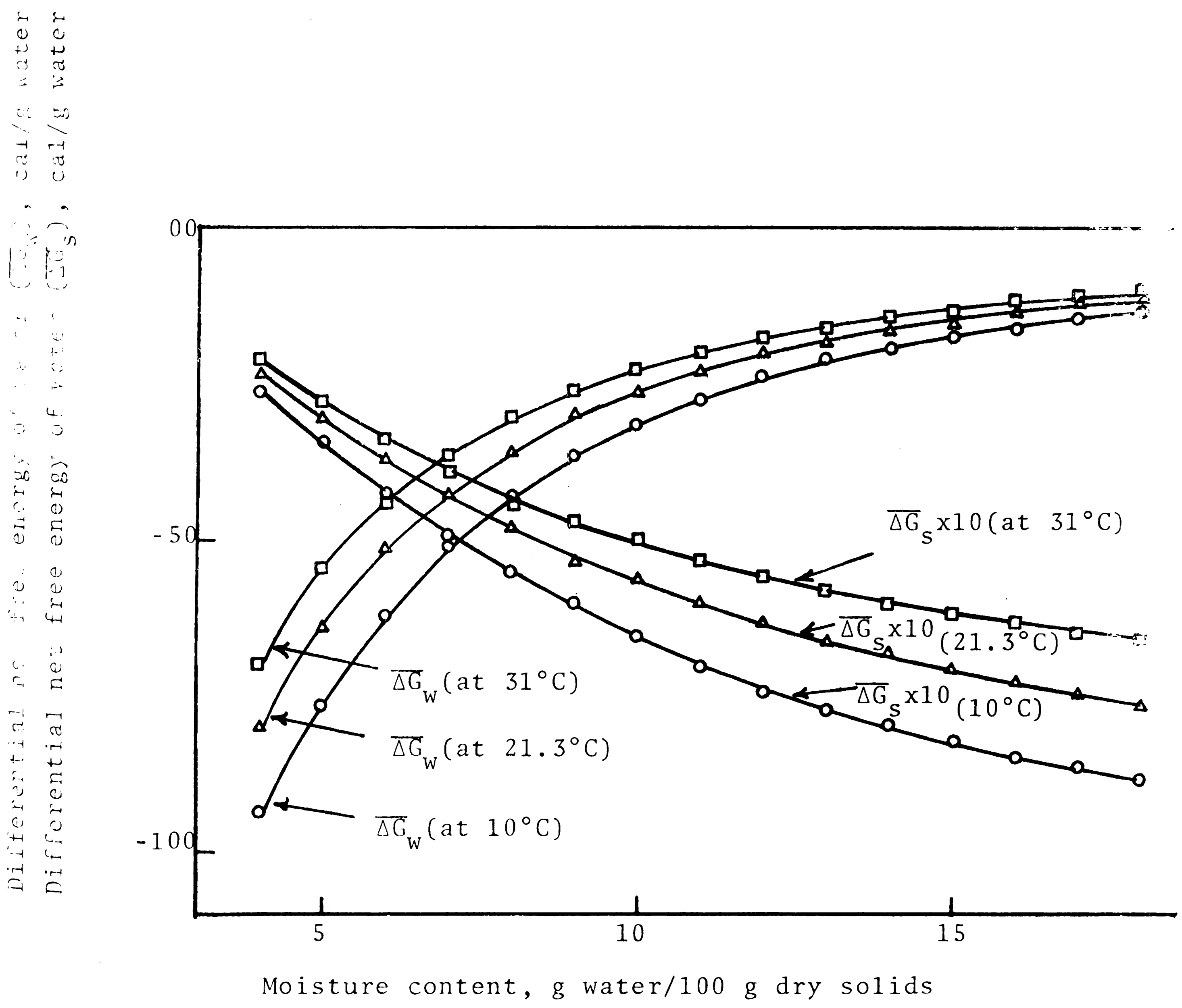


Figure A.7.--Influence of temperature on the differential net free energy values of water and solids for adsorption of water vapors on raw freeze-dried beef (plate temperature 100°F).

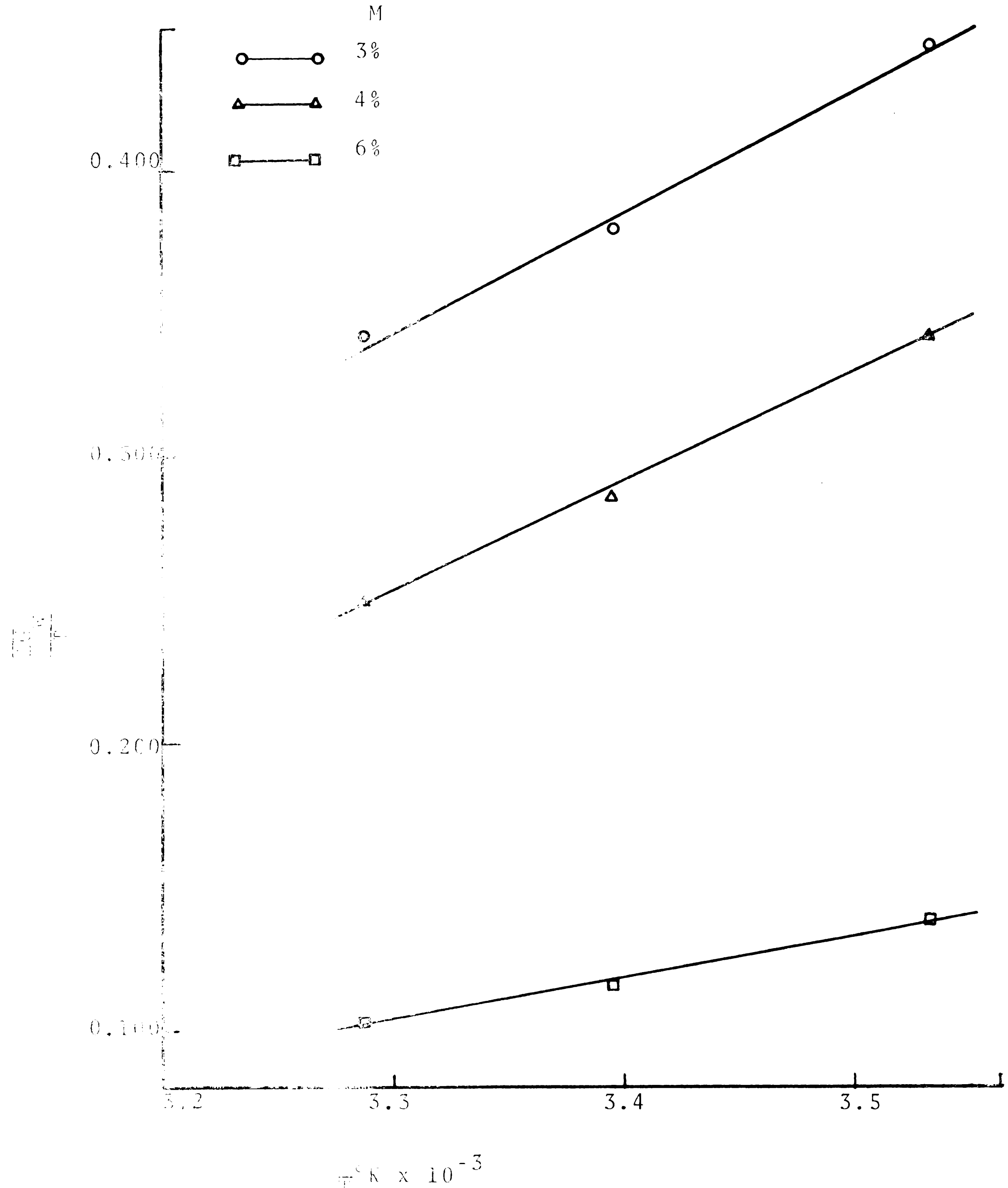


Figure A.7$_a$.--Adsorption isosteres for precooked freeze-dried beef.

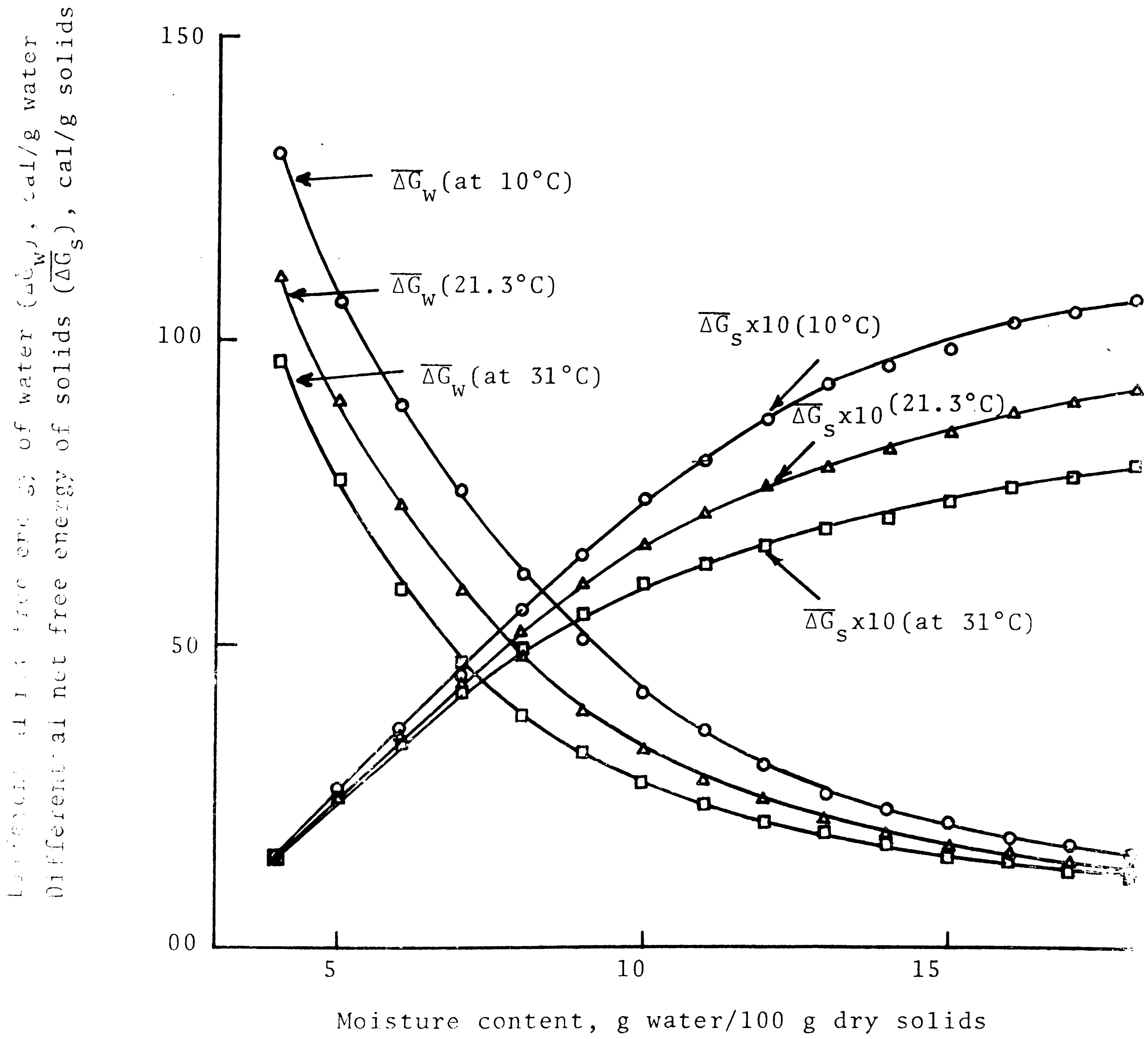


Figure A.8.--Influence of temperature on the differential net free energy values of water and solids for desorption of water vapors from raw freeze-dried beef (plate temperature 100°F).

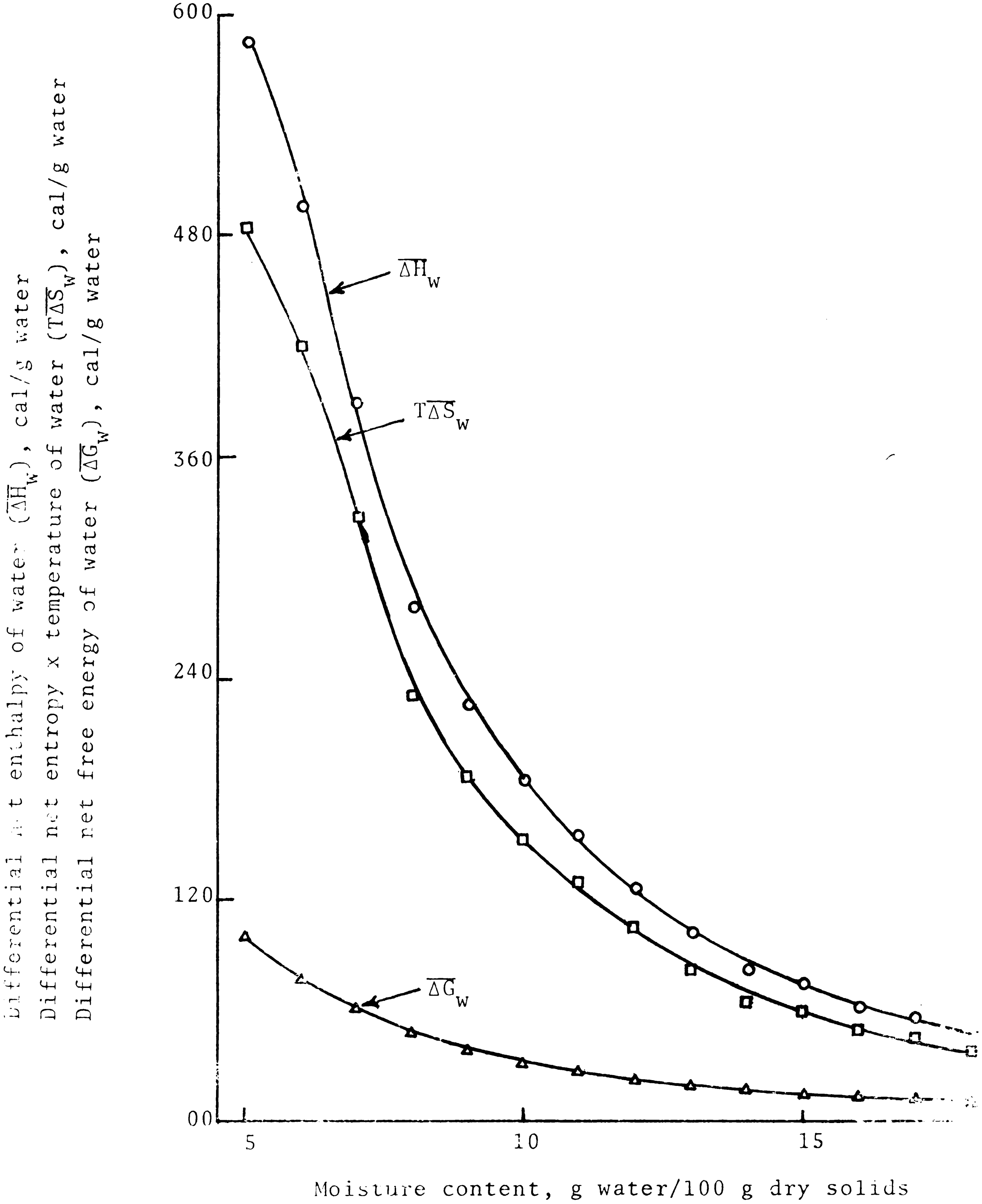


Figure A.9.--Differential net thermodynamic values of water vapor desorption from precooked freeze-dried be[illegible] temperature 100°F) at 2[illegible]°C.

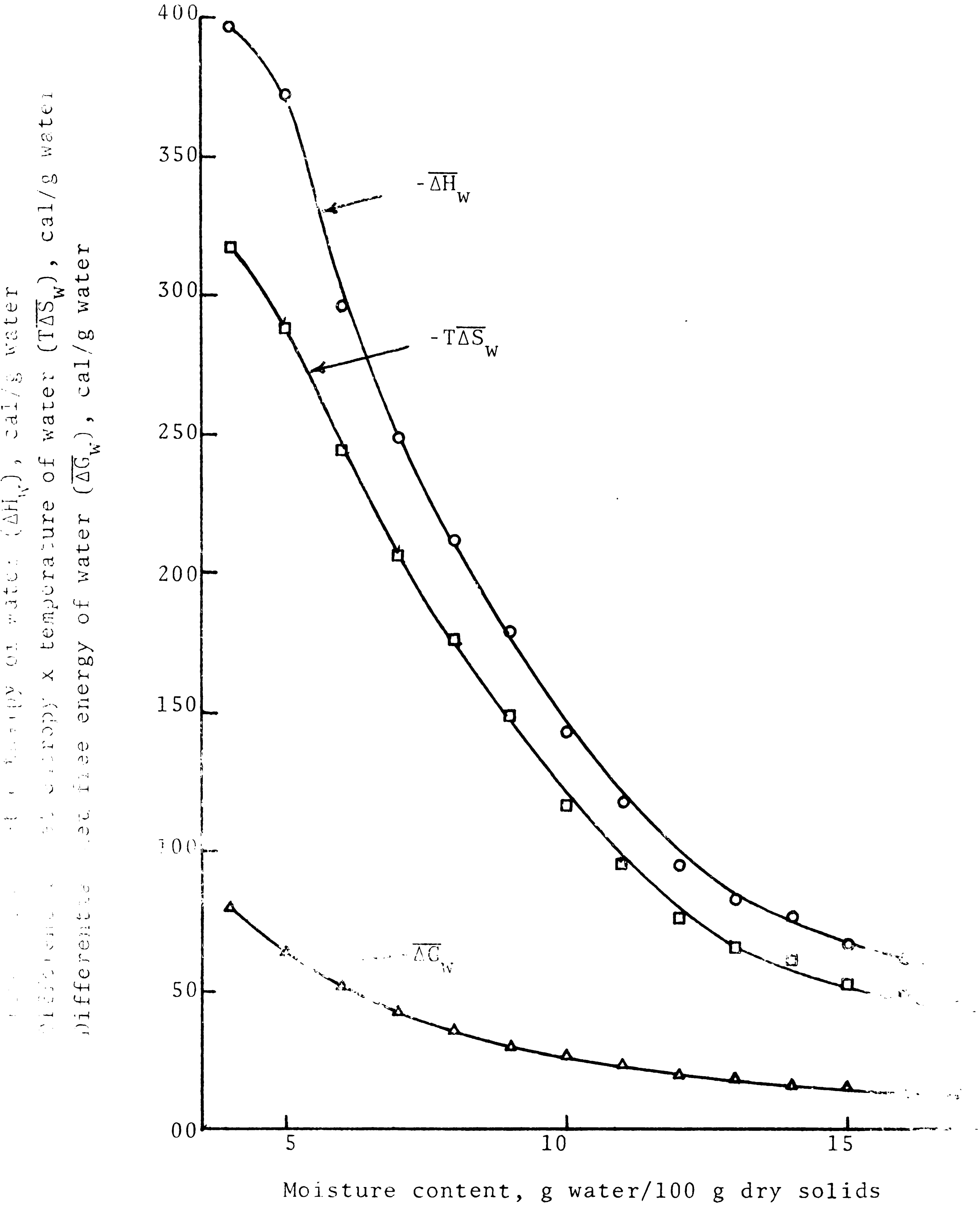


Figure A.10.--Differential net thermodynamic values of water vapor adsorption on raw freeze-dried beef (plate temperature 100°F) at 21.3°C.

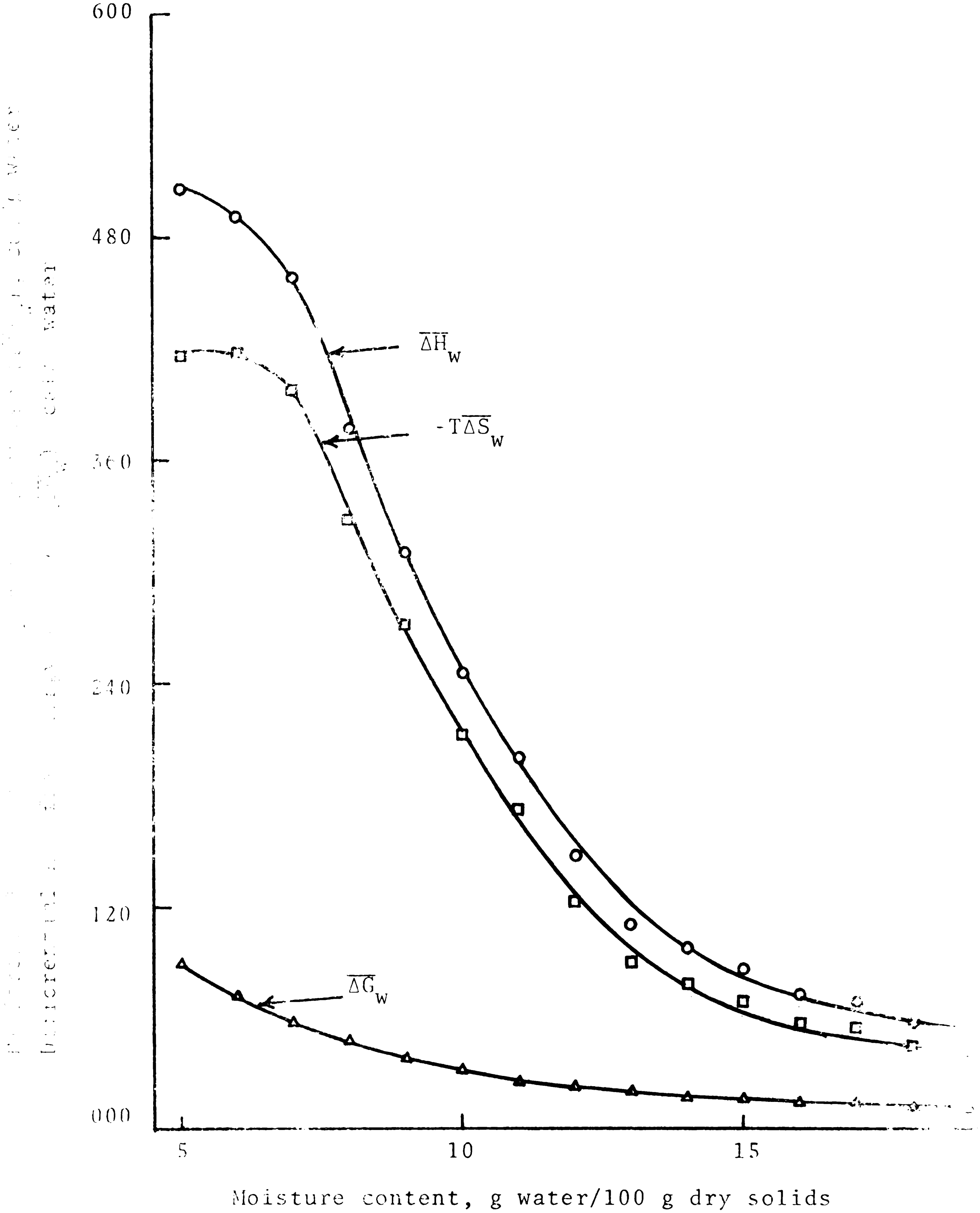
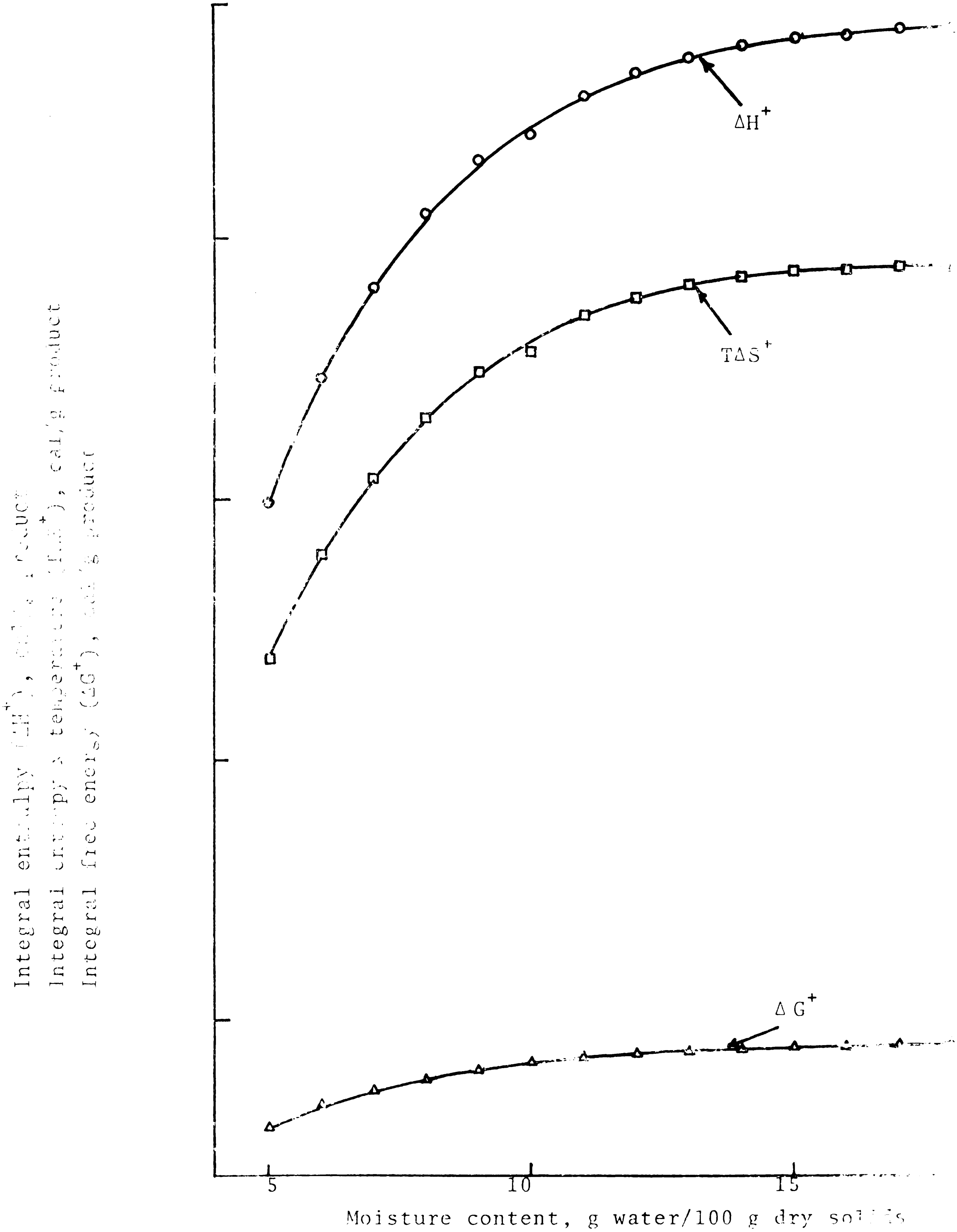


Figure A.11.--Differential net thermodynamic values for water vapor desorption from raw freeze-dried beef ([illegible] temperature 100°F) at 21.3°C.



[illegible] change in net thermodynamic [illegible] from [illegible] mixture [illegible] from [illegible] solids with water [illegible] composition to form dry solids and pure [illegible]

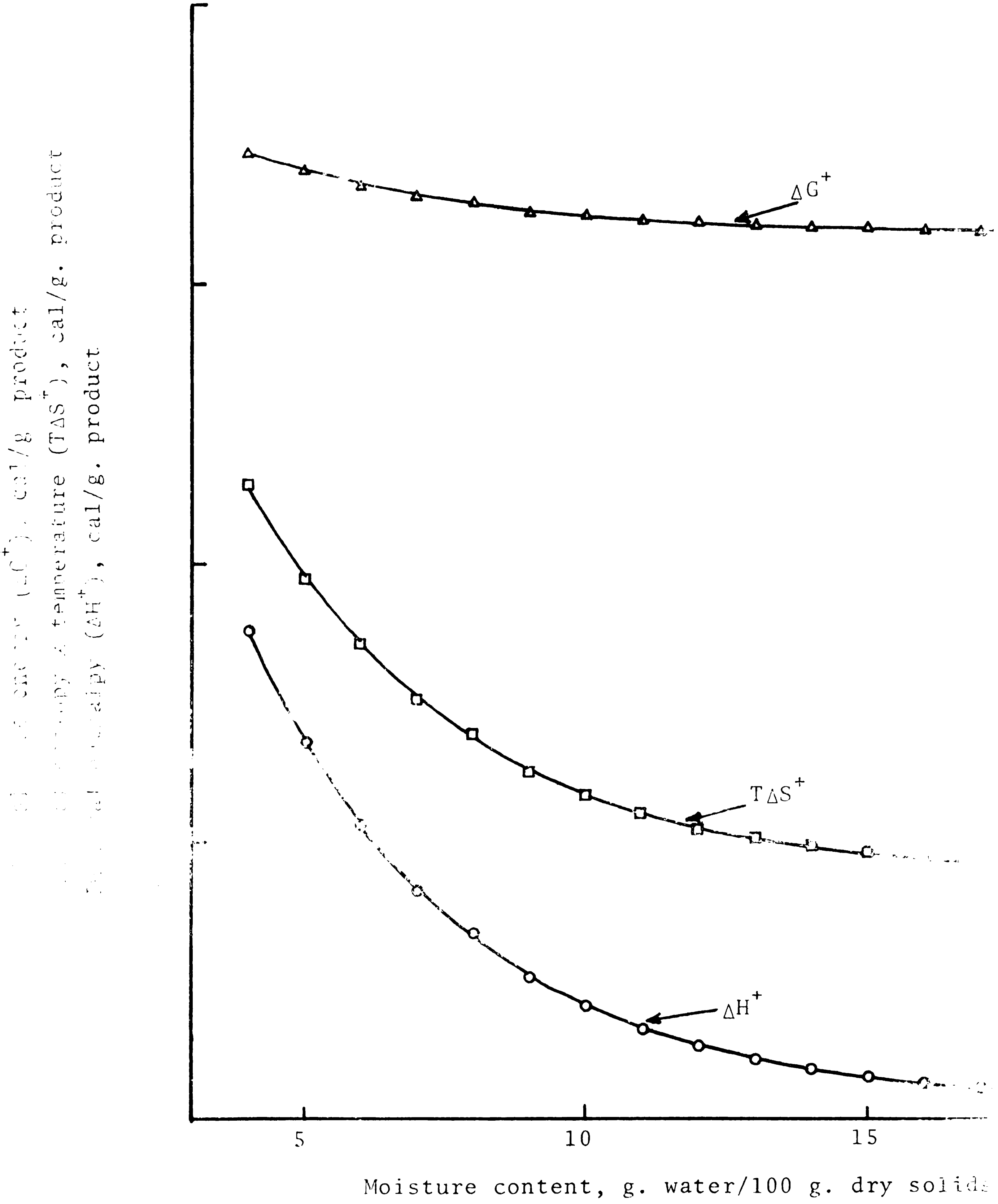


Figure A.13.--Integral change in net thermodynamic values for water vapor adsorption on raw freeze-dried bea solids to form 1 g. of mixture with the indicated composition

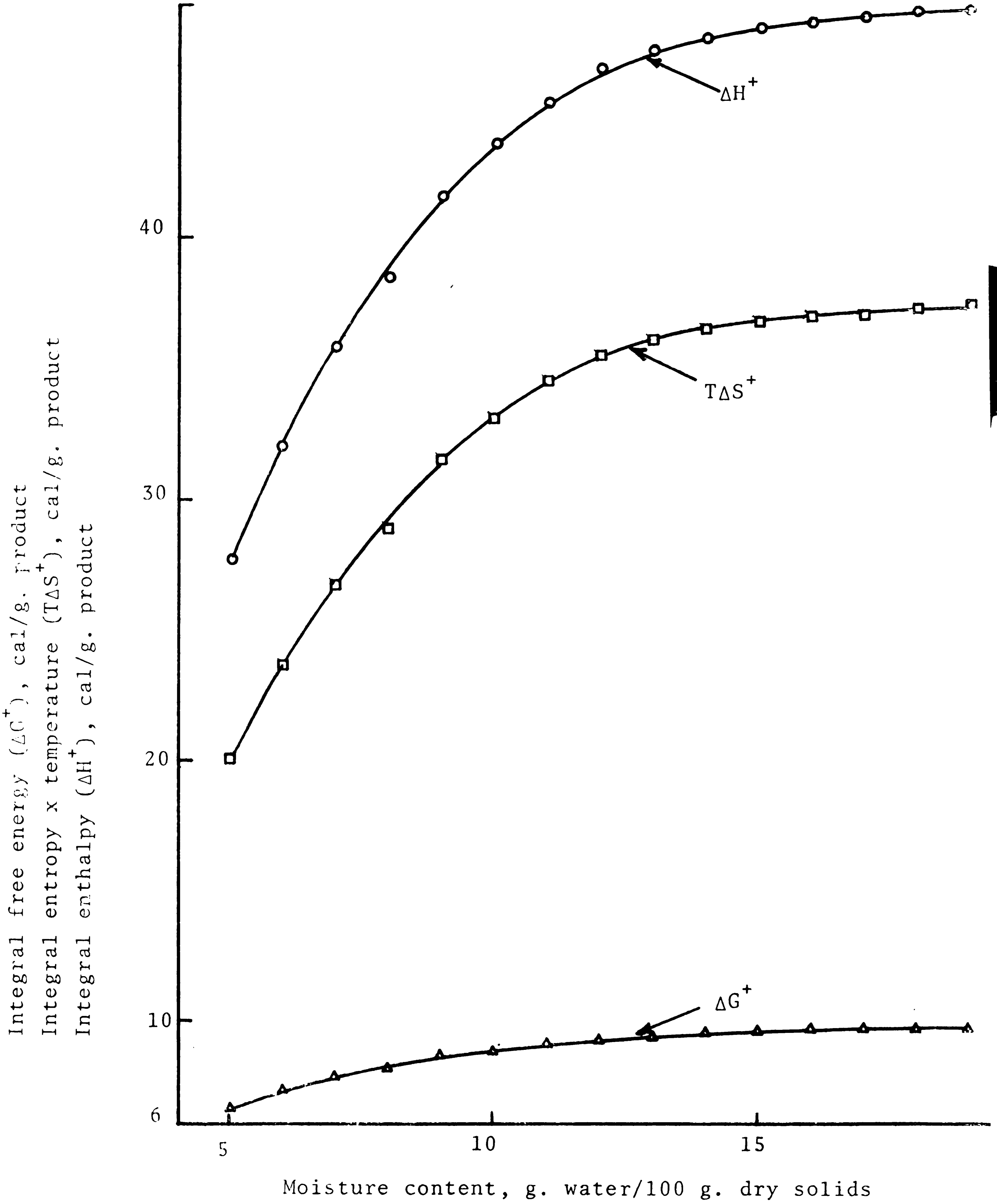


Figure A.14.--Integral change in net thermodynamic values for water desorption from 1 g. of mixture of raw freeze-dried beef solids with water at the indicated composition to form dry solids and pure