THERMODYNAMIC CHARACTERISTICS OF LOW AND INTERMEDIATE MOISTURE FOODS

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ABSTRACT

THERMODYNAMIC CHARACTERISTICS OF LOW AND INTERMEDIATE MOISTURE FOODS

By

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Water comprising about 60 - 95 percent in our food is by far the dominant and the most important component. Thermodynamics related to moisture equilibrium data provides a basis for explaining how the water associates with food at different energy levels. In addition, it provides a macroscopic description of the sorption phenomena.

The Gibbs - Duhem equation allows the computation of total free energy, enthalpy and entropy of the product. Entropy calculations for various foods exhibit a maximum entropy value at some intermediate moisture value. Thermodynamically, a state of the system representing maximum entropy suggests stability. If this hypothesis is applicable to food systems, the moisture level at which entropy is maximum becomes the stable moisture value. The moisture value at which entropy is maximum for a given food closely resembles the monomolecular moisture value computed by using the Brunauer-Emmett-Teller (BET) equation. It is also in good agreement with the moisture level corresponding to the intersection of the local isotherm L I and local isotherm L II, according to Rockland's local isotherm theory.

A procedure was developed with sound thermodynamic basis to predict the thermodynamic parameters of low and intermediate moisture foods using moisture equilibrium isotherm data at single temperature. In developing this procedure the non-idealities existing in the food system were considered and an effective molecular weight was assigned to the solids portion of the food system. Free energy of mixing, entropy of mixing and enthalpy of mixing were computed. Heats of sorption values obtained by this method seem to be in good agreement with the heats of immersion values expected for food product and with the values predicted by the BET analysis. Similar relationships were observed between the heats of sorption values computed by the proposed method and a heat evolution index obtained by sensory panel procedures.

Approved D. R. Heldman

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By

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LIST OF SYMBOLS

a_s --activity of solids

a_w --activity of water

c --energy constant of BET equation

ΔG --integral free energy, cal/g water

$\overline{\Delta G}$ --total free energy of product, cal/g product

$\overline{\Delta G}_w$ --differential free energy, cal/g water

$\overline{\Delta G}_s$ --differential free energy, cal/g solids

$\widetilde{\Delta G}_m$ --free energy of mixing, cal/g mole of mixture

$\overline{\Delta G}_m$ --free energy of mixing, cal/g mixture

ΔH --integral enthalpy of product, cal/g water

$\overline{\Delta H}$ --total enthalpy of product, cal/g product

$\overline{\Delta H}_w$ --differential enthalpy, heat of sorption, cal/g water

$\widetilde{\Delta H}_m$ --enthalpy of mixing, cal/g mole of mixture

$\overline{\Delta H}_m$ --enthalpy of mixing, cal/g of mixture

$\overline{\Delta H}_s$ --contribution of enthalpy due to solids portion of the food, cal/g solids

$\overline{\Delta H}_{s'}$ --enthalpy computed from effective molecular weight and expressed on the basis of product solids, cal/g solids

$\overline{\Delta H}_T$ --total enthalpy of sorption

Δs --integral entropy, cal/g water/° K

$\overline{\Delta s}$ --total entropy of product, cal/g product/° K

$\tilde{\Delta} s$ --entropy of mixing, cal/g mole of product/° K

E_1 --heat of sorption for the monomolecular layer moisture, cal/g water

EMW_s --effective molecular weight of solids

γ_w --activity coefficient of water

γ_s --activity coefficient of solids

K --integration constant of the Clausius-Clapeyron equation

L --latent heat of vaporization, cal/g water

M --moisture content

M_1 --monomolecular moisture content

MW_w --molecular weight of water

NFDM --non-fat dry matter

μ --chemical potential

μ_w --chemical potential of water in a given food

μ_w^0 --chemical potential of pure water

P --vapor pressure of food system

P_0 --saturation vapor pressure

R --universal gas constant

W --weight

X_w --mole fraction of water

X_s --mole fraction of solids

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I. INTRODUCTION

1.1 General Remarks

Water, comprising 60 - 95 percent of the total weight of food, is by far the dominant and the most important component of common foods, which may also contain fat, protein, carbohydrate, mineral and other groups of substances. Water, being a major constituent of common foods, is an important factor to consider in perishability of foods. The water molecule and its association with biological substances is still a subject of controversy in spite of considerable literature available on the subject. Kuprianoff (1958) proposed that moisture associated with biological material could exist as free moisture, chemically bound moisture and adsorbed moisture. Various workers defined bound water on the basis of the technique used for its measurement. No definition of so-called "bound water" is accepted universally. The concept of bound water associated with biological materials cannot be ignored since some characteristic and sometimes irreversible changes take place when water is removed from a biological material by freezing, by evaporation or even by binding chemically. Fennema (1970) gave some guidelines to describe the water associated with biological materials.

> There is no such a thing as free water, all water associated with food is bound. The relative boundness of water associated with a given biological material changes as a continuum. That is at low moisture levels water is less mobile in comparison to the water at higher moisture levels.

It is well known that the latent heat of vaporization increases to a value well above the values known for pure water as food is dried to low moisture levels. Latent heat of vaporization values especially at low moisture level become very important when designing the equipment to be utilized in the dehydration process. The heat of adsorption or the amount of heat released as a product adsorbs moisture may be as important to product quality as the latent heat of vaporization is to design of dehydration process. The most obvious relationship between product quality and thermodynamic parameters is that described by heat of immersion. This particular parameter best describes the heat released and sensed by the person consuming a dry or intermediate moisture food product. Although the magnitude of this value or parameter is relatively small, it must be considered in the overall sensory evaluation of dry food product. Difficulties in direct calorimetric experimental measurement of small thermodynamic quantities such as heat of immersion place increased emphasis on indirect evaluation from moisture equilibrium data.

1.2 Sorption Phenomena and Biological Materials

Sorption is a general term which describes both adsorption and desorption. When a biological material is exposed to a vapor pressure of water it increases or decreases in weight (adsorbs or desorbs moisture) depending on temperature and relative humidity of the surrounding. The moisture content of the product when it is in equilibrium with surrounding temperature and relative humidity is called equilibrium moisture content of the product. The relative humidity corresponding to the equilibrium moisture content of a biological material is called equilibrium relative humidity (Hall, 1964). Rockland (1969) stated that the moisture sorption isotherms of heterogenous biological products represent the integrated hygroscopic properties of numerous constituents which vary with respect to both quality and quantity. Usually Type II isotherms result for biological materials according to Brunauer's classification (Brunauer, 1945). It is now well established that the water activity is more closely related to food stability than the total moisture content of a food product.

Water Activity (a_w)

The ratio of vapor pressure of a food material over the saturation vapor pressure of pure water would probably be the simplest and least meaningful definition of water activity. Numerically water activity is the equilibrium relative humidity divided by one hundred.

From the thermodynamic point of view, the water activity (a_w) has a different meaning. Water activity of a given material means its relative chemical potential with respect to the chemical potential of pure water to which a value of 1 is arbitrarily assigned. The following thermodynamic relation effectively describes the link between the chemical potential of water in a biological material (μ_w) and the chemical potential of pure water (μ_w^0). This link is truly what is called as water activity. The term RT is the product of the universal gas constant (R) and the absolute temperature (T).

$$\mu_w = \mu_w^0 + RT \text{ Ln } a_w \qquad (1-1)$$

In general the smaller the chemical potential of water in food, the smaller the driving force for chemical reactions involving water.

The understanding of water activity in relation to biological material has been partially responsible for the development of "Intermediate Moisture Foods." Brockman (1969) reported that the intermediate moisture foods are a heterogenous group of foods which owe their stability to reduced water activity but contain too much water to be regarded as dry. The moisture contents usually range from approximately 20-50 percent (wet basis). In general an intermediate moisture food can be consumed, without rehydration, and it is shelf-stable without refrigeration or thermal processing. The recent trends toward the development of dry and intermediate moisture foods has created renewed interest in the evaluation of thermodynamic parameters related to the moisture sorption phenomena. It is believed that the thermodynamic energy parameters may play an important role in the improvement and innovation of food quality and processing. There seems to be considerable evidence that the storage stability of dry or intermediate moisture food products may be related in some manner to thermodynamic parameters, although it is difficult to develop an obvious relationship between them. The evidence available indicates that some thermodynamic parameters may be useful in establishing the optimum stability conditions.

1.3 Objectives

The broad objective of this dissertation is to analyze the moisture sorption data for biological materials in terms of thermodynamic energy parameters which describe the various energy levels of the association of water with the food.

1. To determine the various thermodynamic energy parameters connected with the moisture sorption of dry and intermediate moisture foods and interpret them in terms of their usefulness.
2. To explore the possibilities of finding a link between one or more thermodynamic parameters and storage stability of dry and intermediate moisture foods.
3. To develop a procedure with a sound thermodynamic basis to predict the thermodynamic parameters of dry foods utilizing moisture equilibrium data at one temperature.
4. To compare the results obtained from moisture equilibrium isotherms with the calorimetric heat of immersion.

II. GENERAL REVIEW OF LITERATURE

2.1 General Remarks

Water, in many respects, is a unique compound. Chemical reactions and physical interactions in which it participates influence every gross characteristic of a biological material. The moisture content of a biological product controls its mechanical (texture, hardness, chewiness, etc.), enzymic, chemical, physical and even microbiological characteristics. Recently Labuza *et al.* (1970) stated that at moisture contents below those of fresh foods, water still has solvent properties including the ability to dissolve the solids and to allow the diffusion of reactants.

Since the objective of this dissertation is related to the estimation and importance of thermodynamic energy parameters for low and intermediate moisture foods with regards to the moisture sorption phenomena, it is not intended to review the vast amount of literature available on the subject of moisture sorption phenomena.

For convenience, the literature on the subject of moisture sorption phenomena can be divided into two classes, the approach of physical chemists and engineers and the approach of food scientists.

The physical chemists are primarily interested in investigating the underlying principles of moisture sorption phenomena. Their approach is to obtain a theoretical moisture equilibrium isotherm to account for sorptive behavior of biological materials, making use of sound physicochemical laws governing the moisture sorption. Not entirely different from the above mentioned theoretical approach, food scientists rely largely on experimental work and investigate the changes in a given food system with respect to moisture content which is so closely related to equilibrium relative humidity. In general, both the approaches focus on the same goal, namely, better food and the role of water in food quality.

2.2 Moisture Sorption Phenomena

Moisture equilibrium isotherms are the most convenient way to represent the sorption characteristics of a given biological substance. In addition, it proves to be a good starting point for further theoretical analysis of moisture sorption phenomena. Bio-scientists are primarily interested in only one adsorbate (water vapor) and numerous adsorbents (biological materials) which are characterized by great complexity and heterogeneity in physical structure, each being an assemblage of strongly hydrated high molecular weight compounds mostly belonging to classes called proteins, carbohydrates, and lipids. Since the complete quantitative representation of components in a given biological material is difficult, the combined or average behavior of large numbers of individual components is dealt with in relation to water activity and the adsorbent-adsorbate complex. However, it is obvious that the weight of adsorbate adsorbed on a given adsorbent depends on the characteristics of both adsorbent and adsorbate.

Adsorption is commonly divided into two classes, namely, physisorption and chemisorption. Physical adsorption could be relatively rapid as compared to chemisorption. Physical adsorption is caused by intramolecular forces between molecules of water vapor and the surface of adsorbent (polar sites of adsorbent). In general, the polar molecules--the molecules possessing the following polar groups: $-NH_2$, -NH, -OH, -COOH, $CONH_2$, etc.--are considered to be sorptive sites on the adsorbent because the positive and the negative charges in the above molecules are not symmetrically distributed. The formation of a physically adsorbed layer may be similar to condensation of a vapor to form liquid.

Considerable efforts have been devoted to the development of quantitative theories to account for usually sigmoid shaped moisture equilibrium isotherms of biological materials. Labuza (1968) reviewed some of the theories and stated that there are three basic theories to explain the moisture sorption phenomena, (1) the kinetic concept of Langmuir, (2) Polayanis' adsorption potential theory, and (3) Zsigmondy's capillary condensation theory. Recently Ngoddy (1969) critically reviewed several moisture sorption theories in terms of their applicability, assumptions and limitations. According to his hypothesis, if the physical structure of a given biological material is represented mathematically in terms of pore size distribution function and an idealized geometry, its moisture equilibrium isotherm shape can be predicted. Ngoddy (1969) applied his theory to several biological materials and was able to show good agreement between experimental and theoretical moisture equilibrium isotherms. Adamson (1967) noted that the theoretically derived relationships for moisture equilibrium isotherms from different models have been found to yield equations which are graphically and even algebraically identical.

The applicability of theoretical equations explaining the moisture sorption phenomena based on some mathematical model system to real food systems is somewhat limited due to their great complexity. Even if a given theoretical equation does predict a moisture equilibrium isotherm, in most cases it fails to explain the relation between food stability and moisture levels. Finally the general drawback of the theoretical prediction equation is that it depends on the experimental determination of a parameter used in its derivation.

Strasser (1969) reported that the moisture sorption isotherm can be expressed by the following formula:

$$M = f\,(P/P_0)_T$$

Moisture content (M) of food at constant temperature (T) is a function of water activity (a_w). Strasser (1969) further remarked that a more sensitive indication of the sorption properties of food might be obtained if isobars were measured at low temperatures. Sorption isobars can be determined by varying the temperature of a food and keeping the partial vapor pressure of water about the food constant as expressed by the following formula:

$$M = f\,(T)_P$$

Another method of expressing moisture content is by using isosters as expressed by the following equation:

$$P = f\,(T)_M$$

Procedures for obtaining water vapor sorption isotherms have been described in detail by Taylor (1958), Karel et al. (1964), and Hofer and Mohler (1962). Ngoddy (1969) described a more sensitive and accurate method of obtaining the moisture equilibrium. This system uses an electrobalance which records the sorptive changes automatically and continuously.

Biological substances usually exhibit a prominent hysteresis effect. This indicates that the equilibrium moisture content for a given relative humidity is higher during desorption than adsorption (Chung and Pfost, 1967). Several theories have been advanced to account for the phenomena of hysteresis, based mostly on the pore structure of the adsorbent, which is assumed to play a dominant role in hysteresis.

2.3 Water Activity and Food Stability

One of the basic theories of adsorption of gases or vapors was proposed by Brunauer, Emmett and Teller (1938). The BET equation leads to the determination of the amount of gas or vapor adsorbed in the first monomolecular layer (M_1). This monomolecular layer moisture value was first related to optimum moisture content of dehydrated food by Salwin (1959). Whether a BET monomolecular layer value does represent an optimum moisture level is debatable according to Rockland (1969). However, the existence of an optimum moisture level for dehydrated food is well established (Cuendet et al., 1954; Huelsen et al., 1955; Martin, 1958; Mitchell et al., 1957; Roby et al., 1959; and Salwin, 1963). Rockland et al. (1957, 1960, 1961) reported an optimum moisture content of walnut kernels above and below which they deteriorated at a more rapid rate. Deterioration reactions occurring below the optimum moisture value were characterized as auto-oxidative, resulting in the development of typical rancid flavors and odors. Scott (1957) and Webb et al. (1960) demonstrated that microbiological proliferation occurred at high equilibrium relative humidity values.

With the development of intermediate moisture foods in recent years, food stability acquired a much broader meaning than just optimum moisture value commonly expressed for dehydrated foods. There is no reliable theoretical method to predict the stability region for a given food system.

Rockland's Local Isotherm Concept

Rockland (1969) specified three types of local isotherms (Figure 2-1). Type L I is associated with water bound by polar to ionic groups such as carboxyl and amino groups. Type L II may consist of water hydrogen bonded to hydroxyl and amide groups, and Type L III is characterized by unbound or free water. Optimum stability region, according to Rockland (1969), appears to be associated with L II - L III region as shown in Figure 2-1. Some typical

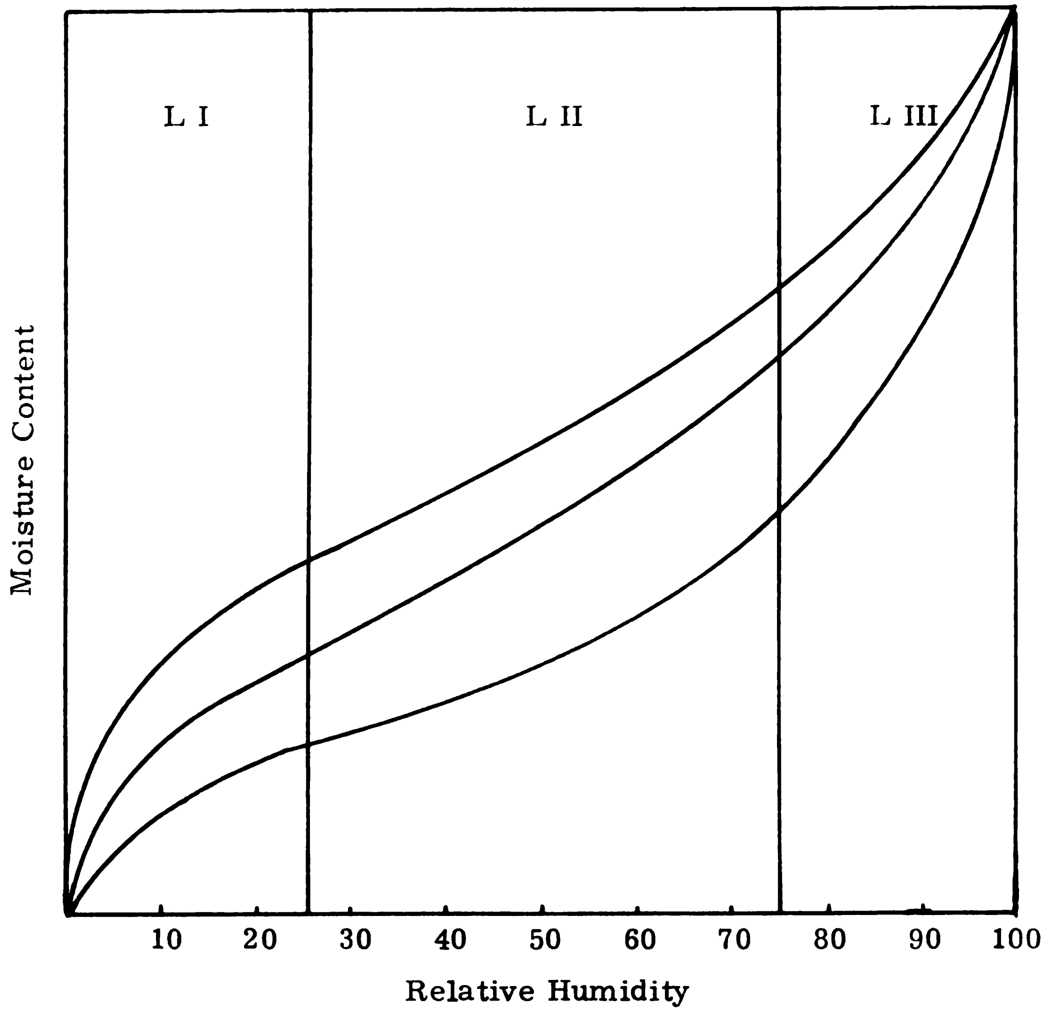

Figure 2-1. --**Hypothetical separation** of local isotherms **(Rockland, 1969).**

physical, chemical and biological changes associated with local isotherm regions L I, L II and L III are shown in Table 2-1.

Table 2-1. --Some product characteristics within localized moisture sorption isotherms (Rockland, 1969).

Local Isotherm I	Local Isotherm II	Local Isotherm III
Dry	Dry	Moist
Hard	Firm	Soft
Crisp	Flexible	Flaccid
Glazed	Normal Dry Surface	Syneresis
Shrunken	Normal Size	Swollen
Static Charge	Non-adherent	Sticky
Darkened	Normal Color	Browning
Rancid Odor	Normal Odor	Off Odor
Rancid Flavor	Normal Flavor	Off Flavor
Autoxidation	Minimal Chemical Changes	Enzymatic Reaction
Microbicidal	Microbiostatic	Microbial Growth

Rockland used Henderson's (1952) semi-empirical equation of the moisture sorption isotherm to establish his local isotherm concept. If this concept should hold for intermediate moisture foods, then the chances for improved shelf stability are increased by structuring the food to obtain the L II type sorption isotherm. An understanding of water activity thus could be tied with food stability, leading to innovation in formulation and processing of food products. It is evident that the available control factors are temperature, vapor pressure and composition of a food.

TABLE 2-2. --Some intermediate moisture foods (Bone, 1970).

Item	% Water	Item	% Water
Mayonnaise	16	Canned Biscuits	39
Canned Bacon	16	Swiss Cheese	39
Margarine	16	Chocolate Syrup	39
Butter	16	Waffles	40
Citron Candy	18	Luncheon Meat	40 - 55
Pound Cake	19	Pork Link Sausage	42
Marshmallow	15 - 35	Cooked Ham	42
Doughnuts	19	Tortillas	42
Honey	20	Canned Sardines	47 - 57
Raw Bacon	20	Cooked Hamburger	47
Fruit Cake	23	Fresh Coconut	47
Dried Fruits	24	Dried or Chipped Beef	48
Foundation Cake	25	Apple Pie	48
Table Syrup	25	Sweetened Cranberry Sauce	48
Biscuits	27	Corn Bread	49
Sweetened Condensed Milk	27	Egg Yolk	49
Jams, Marmalades	28	Cream Cheese	51
Gingerbread	30	Canned Tuna Fish	52
Angel Food Cake	32	Apple Butter	53
Jellies	35	Corned Beef, Uncooked	54
Canned Orange Juice Concentrate	35	Raw Hamburger	55
White Bread	35	Pancakes	56
Cheddar Cheese	39	Baked Macaroni and Cheese	58

Food stability is not an absolute term. In fact, food stability could be visualized as a function of several interdependent factors such as color, texture, flavor, and nutritive value, in addition to moisture content. It seems logical, however, to correlate the food stability with water activity, although it may be difficult to develop a logical relationship between them. Bone (1970) stated that the control of water activity is the basic control factor in the preservation of nonrefrigerated intermediate moisture foods that have extended shelf life. Table 2-2 illustrates some examples of intermediate moisture foods (Bone, 1970). Prevention of microbiological growth is, of course, a dramatic feature of water activity control. Table 2-3 indicates the approximate lower limits of water activity at which growth can occur for various kinds of organisms.

Table 2-3. --Approximate lower limits of a_w for microorganism growth (Bone, 1970).

Microorganism	Lower limits of a_w
Bacteria	0.91
Yeast	0.88
Molds	0.80
Halophillic Bacteria	0.75
Xerophillic Fungi	0.65
Osmophillic Yeasts	0.60

Most species of organisms are limited to a rather small, but characteristic range of water activity values. Each kind of organism apparently has its characteristic optimum water activity at which it grows best.

The control of water activity for a given food system largely depends on the control of its composition. The composition of a given food system is controlled in such a way that water activity is reduced, which results in extension of shelf stability. The water activity of a given food system can be reduced by increasing the concentration of the solution phase. The solutes in a given food system impose changes on the water.

III. EXPERIMENTAL

Experimental phases of this investigation involved preparation of meat samples and its components for the measurements of equilibrium moisture isotherms. The *longissimus dorsi* muscle of beef procured from MSU Food Stores was used for the sample preparations.

Fractionation procedures. --All physically separable fat and connective tissue was removed from the meat sample. The sample was ground twice through a 1 cm plate and twice through a 2 cm plate, using a meat grinder. The water soluble (sarcoplasmic) fraction, water insoluble fraction, actomyosin and connective tissue component of raw beef were fractionated according to the procedures described by Palnitkar and Heldman (1970).

Cooking procedures. --The beef sample, in the form of approximately one-inch cubes, was cooked in a forced convection air oven at 300° F for a period of 30 minutes. The precooked beef cubes were subsequently frozen at 20° F prior to freeze-drying. The freeze-drying was done in a commercial freeze-drier at a required plate temperature and with a pressure of less than 1 mm of mercury. Approximately 15 to 20 hours were required to dry the product to less than 2 percent moisture content on the dry basis.

After drying, the product was ground in a Fritz-Patrick mill using a 0.063-inch screen. The resulting powder was sealed in bottles which were stored in a desiccator at 20° F. Portions of the product to be used for equilibrium moisture content determination were equilibrated to the isotherm temperature prior to the run.

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. Figure 3-1 shows a schematic diagram of the vacuum system and electrobalance assembly. The glass chamber containing the balance was connected to the main vacuum line and to a pure water vapor source. The main line was connected to a mechanical pump through a vapor trap. The vapor source consisted of a temperature controlled distilled water reservoir. The temperature of the reservoir was controlled to within 0.05° C using a constant

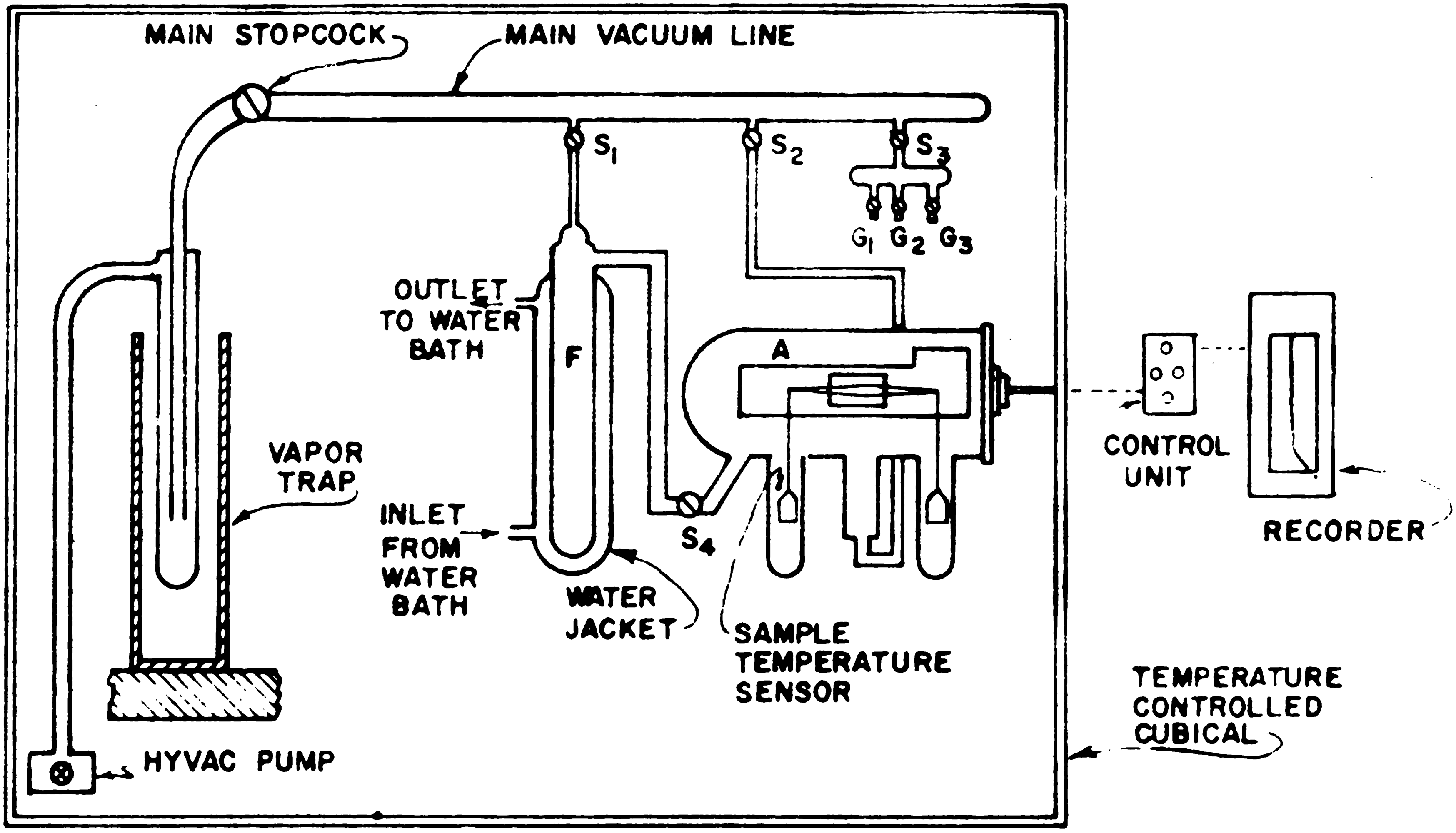

Figure 3-1. --Schematic diagram of moisture sorption apparatus showing electrobalance assembly and related instrumentation.

temperature laboratory bath. The desired relative vapor pressure valves were established by precise temperature control of the free water surface. Three vacuum gauges were utilized by pressure measurements. The entire system except for instrumentation and recorder was enclosed in a 5 ft. × 4 ft. × 9 ft. controlled temperature cubicle.

Sorption isotherms were measured at 10° C, 22.2° C and 37.7° C temperatures. Between 50 and 100 mg of ground freeze-dried material was placed in an aluminum sample container. The system was evacuated to 10 torr in order to establish zero percent relative humidity reference. The sample was then exposed to atmosphere produced by the free water surface. The adsorption isotherm was established by adjusting the vapor pressure of the free water surface to progressively higher values corresponding to higher relative humidities, and allowing sufficient time for each equilibrium level. Approximately 10 to 12 equilibrium points were used to establish each adsorption isotherm. After reaching a relative humidity of approximately 99.5% the vapor pressure was progressively reduced and the desorption isotherm was established. Generally 12 - 15 days were required to complete the adsorption and desorption isotherms for a given sample.

IV. THERMODYNAMICS OF SORPTION

4.1 General Remarks

Numerous methods are available for the computation of thermodynamic quantities for pure substances. Bull (1944), Fish (1958), Stitt (1958), McLaren and Rowen (1951), and recently Kapsalis (1967) used moisture equilibrium isotherm data for the calculation of the thermodynamic quantities for various food substances. In general, the differential and the integral values of free energy, enthalpy and entropy are calculated. It should be mentioned that most of the thermodynamic relations used in this chapter or in Chapter V are obtainable from the standard textbooks of chemical thermodynamics. 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. For the sake of convenience, the results and discussion are included in the same chapter.

4.2 Food as a Binary System

In biological materials, being complex conglomerations of various components, one would expect that each component would exert a "component characteristic influence" on the total isotherm. However, it is well established that biological substances in general give smooth sigmoid-shaped isotherms. The resulting smooth sigmoid shape of moisture equilibrium isotherm could have two possible explanations.

The first explanation is that the equilibrium moisture isotherm disregards that a given biological substance is a multi-component system (e.g., protein, fat, carbohydrate) and treats the solid mass as a homogenous entity in equilibrium with the surrounding water vapor. This essentially means that a biological substance generally behaves as a two-component system, mass of solids and water vapor.

The second explanation is that the components which make up the biological substance do exert an influence on the total shape of the moisture equilibrium isotherm. However, the "component characteristic influence" is additive in nature, or the amount of water adsorbed at a given water activity is derived by the weight percentage of each component times the amount it would adsorb alone (Labuza, 1968).

This generalization that a biological substance is a two-component or a binary homogeneous system happens to be convenient for thermodynamic analysis of moisture equilibrium isotherm. Some food components, however, do exert a "component characteristic influence" on total moisture equilibrium isotherm. Berlin et al. (1968) indicated a classical effect of a component on the shape of isotherm (Figure 4-1). The discontinuity in the isotherm of a foam spray dried whole milk is associated with the crystallization of lactose. Initially the lactose in milk powder is present in the form of an amorphous glass which is very hygroscopic. However, once it adsorbs sufficient water the lactose crystallizes as the monohydrate, which is a relatively nonhygroscopic form. It then loses water upon the completion of the crystallization process. Karel and Nickerson (1964) also reported an example of specific component influence in connection with their studies with dry orange juice powder.

4.3 Assumptions and Other Considerations

At a constant temperature, vapor pressure and a given composition, a given food can be considered as a homogenous mixture of n_s moles of solids and n_w moles of water.

For further development the following assumptions are made:

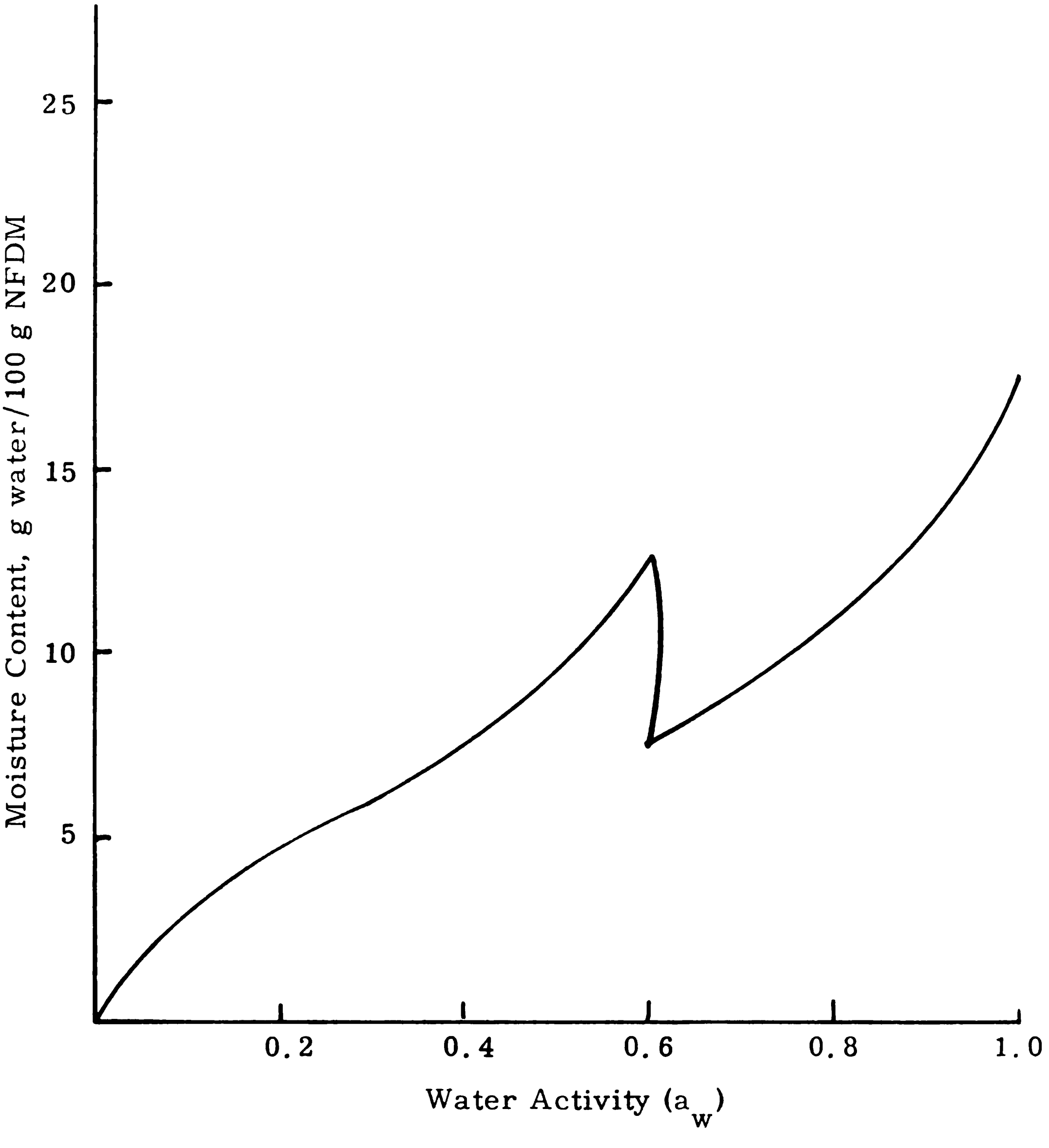

Figure 4-1. --Adsorption moisture isotherm for spray dried whole milk at 24.5° C (Berlin *et al.*, 1968).

a. The standard condition for water is pure water at one atmosphere pressure and $T^\circ K$. Therefore the activity of water (a_w) at standard state is equal to one.

b. The standard condition for solids in a biological substance is the dry solids at one atmosphere pressure and $T^\circ K$. Therefore at the standard condition the activity of solids (a_s) is equal to one.

c. The thermodynamic relations assume that the state of a food system is defined by its temperature and composition, whereas hysteresis signifies the absence of thermodynamic equilibrium or existence of metastable state. This probably is the single conflicting assumption which may explain the anomalies observed in results.

4.4 Theoretical Considerations

Adamson (1967) stated that it is not necessary phenomenologically to state whether the process is adsorption, absorption or solution; the same thermodynamic relations could be applied for all the cases. In general, the thermodynamic processes to be considered are of two general types, integral and differential.

Integral Processes

For adsorbent (Z_1) and adsorbate (Z_2), the following general equation can be written:

$$n_s Z_1 \text{ (adsorbent at T° K)} + n_w Z_2 \text{ (adsorbate liquid at pressure P and temperature T° K)}$$

$$\longrightarrow \text{(system comprising of } n_s Z_1 \text{ and } n_w Z_2\text{)} \qquad (4\text{-}1)$$

This process represents the adsorption of n_w moles of water (Z_2) initially in liquid, upon n_s moles of Z_1 (adsorbent).

Differential Processes

$$n_w Z_2 \text{ (liquid)} \rightleftharpoons n_w Z_1 \text{ (adsorbed on } Z_1\ n'_w/n_s \text{ constant)} \qquad (4\text{-}2)$$

Equation (4-2) represents an adsorption of n_w moles of liquid adsorbate, on the infinitely large amount of Z_1 (adsorbent) which already hold n'_w moles of adsorbate for each n_s moles of adsorbent. The mole ratio n'_w/n_s increases only infinitesimally.

Thermodynamics of Adsorbate

The major portion of the thermodynamic treatment of the moisture sorption phenomena has been devoted to adsorbate (water vapor). In most cases partial free energy, enthalpy and entropy values are reported as cal/g water or cal/g mole of water.

Enthalpy. --Calculation of partial heats of sorption $\overline{\Delta H}_w$ is conveniently carried out by using the Clausius-Clapeyron equation (Kapsalis, 1967).

$$\text{Ln } P = \frac{-\overline{\Delta H}_T}{MW_w \cdot R} \cdot \frac{1}{T} + K \qquad (4-3)$$

where P--partial vapor pressure of water at temperature T,

T--absolute temperature,

R--Universal gas constant,

K--constant of integration,

MW_w--molecular weight of water.

In practice, the isosteric values of equilibrium vapor pressure (P) on a log scale are plotted against 1/T on a linear scale. The slope of any isoster is given by $\frac{\overline{\Delta H}_T}{2.303 \times R\,(MW_w)}$. The $\overline{\Delta H}_T$ obtained from the slope of an isoster is the sum of the enthalpy of sorption $\overline{\Delta H}_W$ and the latent heat of vaporization or condensation (L). The $\overline{\Delta H}_w$, enthalpy of sorption is also the differential heat of wetting and is obtained by subtracting latent heat of vaporization (L) from the $\overline{\Delta H}_T$ value.

Davis and McLaren (1948) and Dole and McLaren (1947) gave the following relation to calculate the integral heat change:

$$\Delta H = \frac{R\,T_1\,T_2}{T_2 - T_1} \int_{o}^{n_w} Ln\,\frac{X_1}{X_2}\,dn \qquad (4-4)$$

where X_2 is relative vapor pressure (P/Po) at the higher temperature (T_2) which produces the same number of moles of water sorption as at lower temperature (T_1) for which X_1 applies and n_w is the moles of water per 100 g of dry substance.

Free energy. --Partial molar free energy for water vapor (adsorbate) is calculated by using the following relation (Kapsalis, 1967):

$$\widetilde{\Delta} G_w = \frac{d\widetilde{G}}{dn} = RT\ Ln\ X = RT\ Ln\,\frac{P}{Po} \qquad (4-5)$$

The integral free energy change for water vapor accompanying the sorption process was calculated by using the following equation:

$$\Delta G_w = -RT \int_{o}^{1} n_w\,d\ Ln\,\frac{P}{Po} \qquad (4-6)$$

where n_w is the number of moles of water sorbed per 100 g of dry substances. The integration of the right hand side of the above equation is commonly carried out by parts as follows:

$$\int_{o}^{1} n_w \, d \, \mathrm{Ln} \left(\frac{P}{Po}\right) = \int_{o}^{1} n_w \frac{P}{Po} \, d \left(\frac{P}{Po}\right) \tag{4-7}$$

In this process P/Po is considered as an independent variable. In practice, a plot of $n_w \frac{P}{Po}$ vs P/Po is made and the total area under the curve multiplied by RT gives the integral free energy ΔG_w.

Entropy. --Calculation of corresponding entropy changes for water vapor (adsorbate) is carried out by using the following relations:

$$\tilde{\Delta} S_w = \frac{(\tilde{\Delta} H_w - \tilde{\Delta} G_w)}{T} \tag{4-8}$$

$$\Delta S_w = \frac{(\Delta H_w - \Delta G_w)}{T} \tag{4-9}$$

Thermodynamics of Adsorbent

Adamson (1967) pointed out that the bulk of thermodynamic treatment of sorption phenomena was focused primarily on the contribution of adsorbate and very little emphasis was placed on adsorbent. The Gibbs-Duhem equation (1875) permits the calculations of the energy contribution of adsorbent from the knowledge of its composition.

Gibbs-Duhem equations. --Houghen et al. (1962) stated that

> the Gibbs-Duhem equations are rigorous thermodynamic relations that are valid for conditions at constant temperature and pressure. They are of particular value in minimizing the number of experimental data necessary to evaluate the properties of a system and for detection of inconsistent and erroneous measurements.

The general form of the Gibbs-Duhem equation can be written as for a constant temperature and pressure:

$$n_1 \, d\mu_1 + n_2 \, d\mu_2 = 0 \qquad (4\text{-}10)$$

where n_1 and n_2 are moles of substances 1 and 2,

μ_1 and μ_2 are chemical potentials or partial properties.

The standard states or reference states are substances described by μ_1^o and μ_2^o.

Thus

$$\mu_1 = \mu_1^o + RT \operatorname{Ln} a_1$$

$$\mu_2 = \mu_2^o + RT \operatorname{Ln} a_2$$

where a_1 and a_2 are the activities of substances 1 and 2.

The derivation of the Gibbs-Duhem equation is given in several textbooks of chemical thermodynamics (Houghen et al., 1962, page 974). Stitt (1958) reported that the thermodynamic quantities pertaining to the sorption process can be obtained from the temperature dependence of sorption isotherms. At equilibrium the Gibbs chemical potential (partial Gibbs free energy) for water must have the same value throughout the system and furthermore this quantity must be the same in the solid material as in the vapor phase. Copeland and Young (1964) and Wu and Copeland (1964) studied the adsorption isotherms for $BaSO_4$-H_2O system. The thermodynamic analysis of the $BaSO_4$-H_2O system by the above authors revealed that the heats of sorption values computed utilizing the Gibbs-Duhem equation were in good agreement with the similar values obtained by calorimetry on the $BaSO_4$-H_2O system. Copeland and Young (1964) reported that the magnitude of surface forces during sorption of water on $BaSO_4$-H_2O system usually is very small and can be ignored. There seem to be similarities between water sorption in the $BaSO_4$-H_2O system and the sorption of water vapor on various foods. In accordance with the above observations, it was felt that the contribution due to surface forces during water vapor sorption of food products need not be included in this investigation.

With reference to liquid water as a standard state, the change in the partial Gibbs function per g of water for a transfer of an infinitesimal quantity from pure liquid (vapor pressure P) to equilibrate solid with vapor pressure $\dot{P}$ is given by:

$$\overline{\triangle G}_w = \frac{RT}{MW_w} \cdot \text{Ln} \frac{P}{Po} \qquad (4\text{-}11)$$

which is similar to equation (4-5).

The corresponding free energy change per g of solids (dry material as standard state) can be found by application of the Gibbs-Duhem equation:

$$N_w \, d\,(\overline{\triangle G}_w) + N_s \, d\,(\overline{\triangle G}_s) = 0 \qquad (4\text{-}12)$$

$$\overline{\triangle G}_s = -\int_o^P \frac{N_w}{N_s} \, d\,(\overline{\triangle G}_w) \qquad (4\text{-}13)$$

where N_w is the weight fraction of water,

N_s is the corresponding weight fraction of solids,

also $N_w + N_s = 1$.

The overall change in Gibbs function for the entire process of dry sorbent combining with water to form 1 g of material at equilibrium pressure P is given by

$$\overline{\triangle G} = N_w \, \triangle G_w + N_s \, \overline{\triangle G}_s \qquad (4\text{-}14)$$

The $\overline{\Delta H_w}$, the change in partial heat function per g of water for the sorption of an infinitesimal quantity from pure liquid to equilibrated material of specific moisture content is obtained by using the equilibrium moisture sorption data at various temperatures. The Clausius-Clapeyron equation can be rewritten in the following form:

$$\left[\frac{d \operatorname{Ln} \frac{P}{Po}}{dT}\right]_M = - \frac{MW_w \overline{\Delta H_T}}{RT^2} \tag{4-15}$$

which is also given as equation (4-3).

The enthalpy due to solids portion ($\overline{\Delta H_s}$) is once again obtained by using the Gibbs-Duhem equation:

$$N_w \, d\,(\overline{\Delta H_w}) + N_s \, d\,(\overline{\Delta H_s}) = 0 \tag{4-16}$$

$$\overline{\Delta H_s} = - \frac{N_w}{N_s} \, d\,(\overline{\Delta H_w}) \tag{4-17}$$

and the total enthalpy contribution of making 1 gm of product by mixing N_w of water and N_s of solids is given by:

$$N_w \overline{\Delta H_w} + N_s \overline{\Delta H_s} = \overline{\Delta H} \tag{4-18}$$

The entropy function can be calculated by using

$$\overline{\Delta S} = \frac{\overline{\Delta G} - \overline{\Delta H}}{T} \qquad (4-19)$$

4.5 Results and Discussion

In general, thermodynamics related to moisture sorption phenomena provides a macroscopic description of the sorption process. Adamson (1967) stated that there has been a great interest in recent years in going beyond the macroscopic description of sorption to obtain the detailed information about the structural and chemical state of solid surface and the adsorbate-adsorbent complex.

Obviously it is important to know as much as possible about the microscopic processes in relation to the adsorbent-adsorbate complex. Various techniques such as optical and electron microscopy, X-ray diffraction, magnetic susceptibility measurements, electron spin resonance and nuclear magnetic resonance have been used in this connection, and the results obtained have been interpreted in terms of microscopic description of sorption phenomena.

No attempt has been made to provide a microscopic description of sorption phenomena in this investigation.

Differential and Integral Energy Values

Differential free energy, enthalpy and entropy values are expressed by equations (4-5), (4-3) and (4-8). Figure 4-2 represents the differential free energy, enthalpy and entropy values for precooked freeze-dried beef (plate temperature 40.6° C) for the moisture adsorption isotherm at 22.2° C. The adsorption isotherms for precooked freeze-dried beef dried at two different freeze-drier plate temperatures are shown in the appendix (Figure A-1 and A-2).

Differential enthalpy change ($\overline{\Delta H}_w$). --Differential enthalpy change is expressed as cal/g water, is plotted versus moisture content (g water/100 g NFDM). Of all the differential thermodynamic values, the differential enthalpy change is very significant. Differential enthalpy ($\overline{\Delta H}_w$) of about 700 cal/g water was observed for precooked freeze-dried beef at low moisture; this total enthalpy of adsorption decreased as more water was adsorbed by the precooked freeze-dried beef. The use of the Clausius-Clapeyron equation for computing differential enthalpies is illustrated in the appendix (Figure A-3). The high enthalpy value at low moisture indicates that sorbed water on precooked freeze-dried beef is not equivalent to liquid water. If the sorbed water by the biological substance was equivalent to liquid water, the heat of sorption ($\overline{\Delta H}_w$) or the heat of

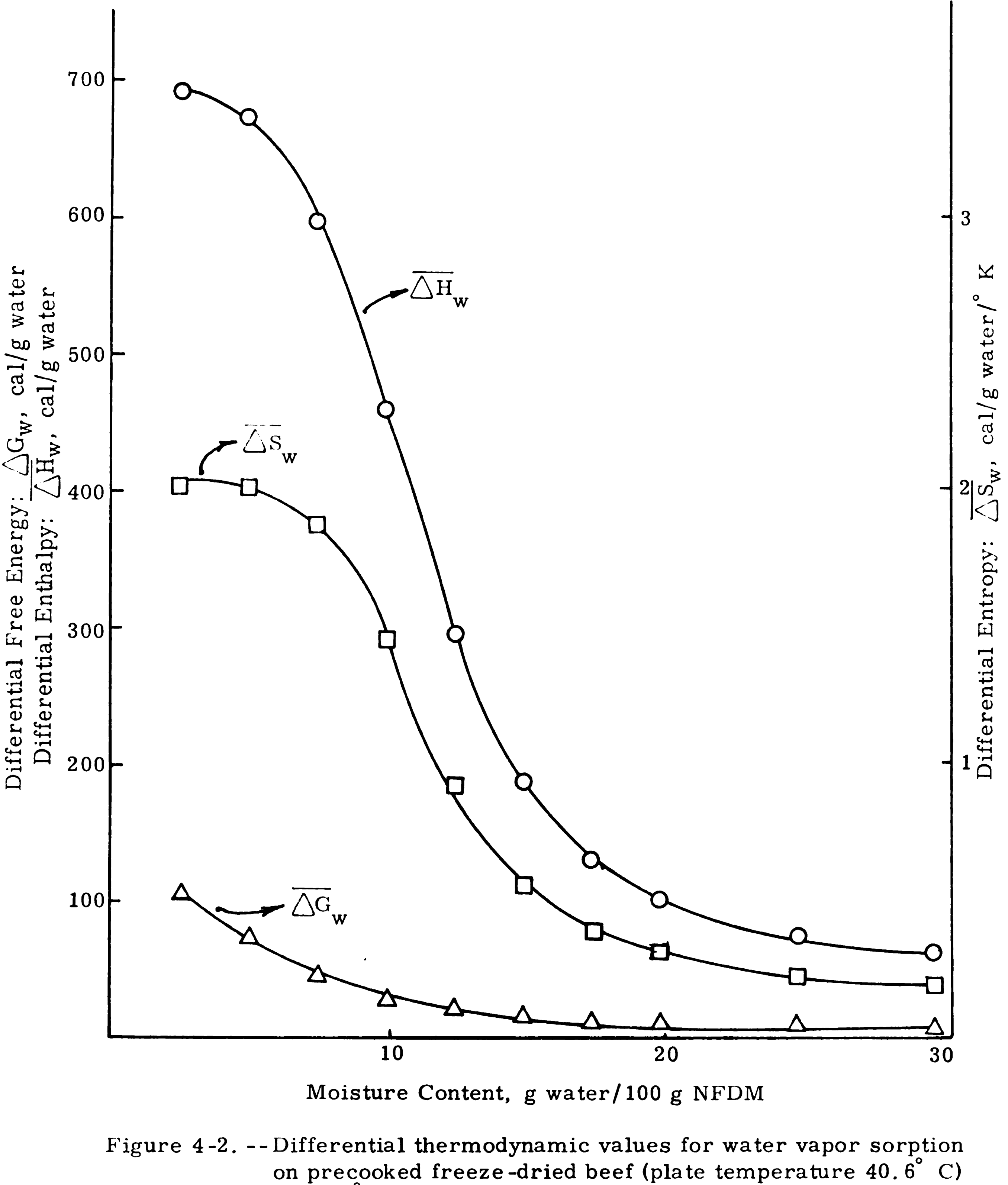

Figure 4-2. --Differential thermodynamic values for water vapor sorption on precooked freeze-dried beef (plate temperature 40.6° C) at 22.2° C adsorption isotherm.

wetting would have been zero. In a way, this emphasizes the importance of knowing the heats of sorption for various biological substances. Fish (1958) reported the differential heat of wetting for dry potato starch gel desorption to be about 270 cal/g water. Bull (1944) cautioned about the use of enthalpy calculations from free energy change (using the Clausius-Clapeyron equation). This should be done very carefully because the isotherm shift with change in temperature is not always significant. The accuracy of the heats of sorption obtained by this method is low. Stitt (1958) stated that high heats of sorption ($\overline{\Delta H_w}$), for most of the biological materials, indicate that the sorbed water is bound by energies characteristic of hydrogen bonding in the low moisture region. At higher relative humidities the value of $\overline{\Delta H_w}$ approaches the latent heat of vaporization or condensation. Even at the higher relative humidities, however, there is a residual heat of sorption slightly higher than zero. Kapsalis et al. (1964) discussed the presence of residual heat of sorption at higher relative humidities on the basis of the "Zipper Mechanism" of water sorption in Mucopolysacchrides, which was first proposed by Ehrlich and Bettelheim (1954).

Differential free energy change ($\overline{\Delta G_w}$). --Figure 4-2 illustrates the relation between $\overline{\Delta G_w}$ and moisture content of precooked freeze-dried beef moisture adsorption isotherm at 22.2° C.

The differential free energy values ($\overline{\Delta G_w}$) were decreased as the moisture content increased (Figure 4-2). Kapsalis (1967), McLaren and Rowen (1952) and Bull (1944) analyzed the moisture equilibrium data for several biological products in terms of partial and integral energy values. Upon examination of equation (4-5), it is evident that partial free energy values ($\overline{\Delta G_w}$) are not particularly useful and even could be misleading (McLaren and Rowen, 1952). Partial free energy values are independent of adsorbent or any food solids. The free energy function, however, is related with thermodynamic equilibrium and useful in computation of enthalpy and entropy. Thermodynamic equilibrium is reached when the free energy change for a given system is zero. The more negative free energy value at low moisture level indicates that escaping tendency is less or the food at low moisture level is more stable than at the higher moisture. Close observation of equation (1-1) suggests that the chemical potential of water in food system at low moisture is less at low equilibrium relative humidities.

Differential entropy change ($\overline{\Delta S_w}$). --Figure 4-2 represents, in addition to differential energy values of free energy and enthalpy, the differential entropy values expressed as cal/g water/degree versus the moisture content for precooked freeze-dried beef at 22.2° C. The differential entropy of water ($\overline{\Delta S_w}$) in precooked freeze-dried beef seems to have high negative values at low moisture contents and decreases in magnitude with increasing hydration in a similar manner to heat of sorption ($\overline{\Delta H_w}$). The decrease in entropy indicates degree of orientation and rigidity of water molecule in the sorbed state over that in liquid water. High negative entropy values may be due to chemisorption as postulated by Pauling (1945).

Integral energy values. --Figure 4-3 indicated that the integral values of free energy, enthalpy and entropy increased with the moisture content. Davis and McLaren (1952) stated that the integral free energy, enthalpy and entropy values are possibly a summation of several chemical and mechanical effects.

Thermodynamics of Mixing

The energy values calculated in this section are usually expressed as cal/g product, unlike cal/g water as in the case of differential energy values. The following approach was used for the computation of total energy quantities expressed as cal/g product. For a given set of equilibrium moisture data, first the differential energy quantities for the aqueous phase (adsorbate) are calculated. The corresponding contribution of solids (adsorbent) was determined using the convenient form of the Gibbs-Duhem equation (4-10). Finally the total energy of mixing was obtained by multiplying the

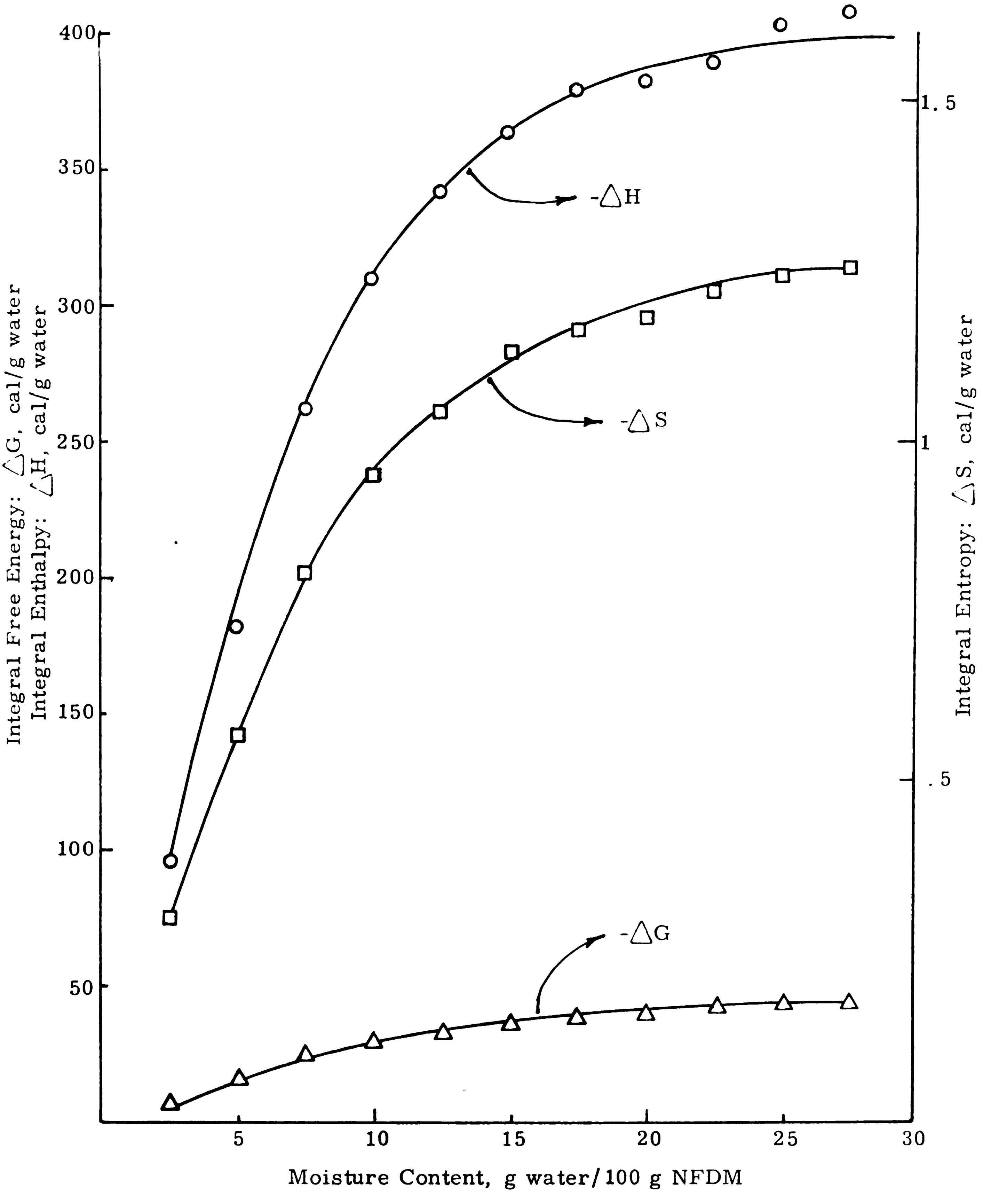

Figure 4-3. --Integral thermodynamic values for water vapor sorption in precooked freeze-dried beef (plate temperature 40.6° C) at 22.2° C adsorption isotherm.

differential energy values of aqueous phase and the solids phase by their respective weight fractions. The computation of total free energy ($\overline{\Delta G}$) expressed as cal/g product is illustrated in Table 4-1. Adsorption moisture equilibrium isotherm at 20° C for raw freeze-dried beef (Saravacos and Stinchfield, 1965) was utilized in this computation. The differential free energy of the aqueous phase ($\overline{\Delta G_w}$) was determined by using equation (4-11). Knowing the weight fraction of water (N_w) and the weight fraction of solids (N_s), the free energy contribution of the solids phase was computed by integration of the Gibbs-Duhem equation as given by equation (4-13). Finally the total change in free energy was obtained by using equation (4-14).

Table 4-1 illustrates several interesting observations. As the moisture content was increased, the weight fraction of water (N_w) was increased and the weight fraction of solids (N_s) was decreased. While the differential free energy value for the water phase ($\overline{\Delta G_w}$) was decreased in magnitude and the corresponding contribution of the solids phase ($\overline{\Delta G_s}$) was increased slightly as the moisture content was increased. The differential free energy value for the water phase ($\overline{\Delta G_w}$) was changed from -63 to -2.3 cal/g water while the corresponding $\overline{\Delta G_s}$ was changed from -0.96 to -6.8 cal/g solids. First the higher negative value of free energy suggests more tendency towards equilibrium; the dry food is more stable than the wet food.

Table 4-1. --Some thermodynamic parameters for raw freeze-dried beef at 20° C (Saravacos and Stinchfield, 1965).

M	N_w	N_s	$\overline{\Delta G}_w$	$-\frac{N_w}{N_s}$	$\overline{\Delta G}_s$	$N_w \cdot \overline{\Delta G}_w$	$N_s \cdot \overline{\Delta G}_s$	$\overline{\Delta G}$
5.0	0.048	0.952	63.633	0.05	0.00	3.030	0.0	3.030
7.0	0.065	0.936	47.566	0.070	0.964	3.112	0.901	4.013
10.0	0.091	0.909	31.316	0.100	2.345	2.847	2.132	4.979
12.0	0.107	0.893	23.087	0.120	3.250	2.474	2.902	5.376
14.0	0.123	0.877	17.077	0.140	4.032	2.097	3.536	5.634
16.0	0.138	0.862	12.482	0.160	4.721	1.721	4.070	5.791
18.0	0.153	0.847	9.745	0.180	5.186	1.486	4.395	5.882
20.0	0.167	0.833	7.222	0.200	5.665	1.203	4.721	5.925
25.0	0.200	0.800	4.137	0.250	6.360	0.827	5.087	5.915
30.0	0.231	0.769	2.349	0.300	6.851	0.542	5.270	5.812

The larger contribution of free energy by the water phase ($\overline{\Delta G_w}$) than the corresponding contribution by the solids phase ($\overline{\Delta G_s}$) could be explained on the basis that it is the water portion of the food which undergoes changes in a sorption process.

Table 4-1 also shows that the total free energy change ($\overline{\Delta G}$) was increased from -5 to -8 cal/g product; this is somewhat similar to the free energy contribution due to the solids part ($\overline{\Delta G_s}$). This means for a given food system, at constant pressure, temperature and given composition, the total free energy is composed of higher contribution due to water phase and relatively smaller contribution due to solids portion. The total property (free energy change) of the product does not change significantly with the compositon (moisture content). This dicussion could be related to chemical potential of pure water (μ_w^o) and the water associated with the food (μ_w) as described by equation (1-1). Essentially it implies that the chemical potential or escaping tendency or chemical potential of water in a given food system changes drastically with the moisture content, the chemical potential of solids portion in a given food product and the chemical potential of the product does not change significantly.

Contribution of Adsorbents

Proteins, carbohydrates, fats, minerals and several other substances account for the solids portion of a given food system. In some thermodynamic treatments, the solids portion of the system are considered inert and less important. It is necessary to critically evaluate the significance of the adsorbent for sorption process when applied to food systems.

Figure 4-4 illustrates the influence of temperature on free energy change of aqueous phase ($\overline{\Delta H}_w$) and the corresponding free energy change for adsorbent ($\overline{\Delta H}_s$) for adsorption isotherms of precooked freeze-dried beef (plate temperature 40.6° C) at 10, 20 and 37.7° C. As the beef solids adsorbed more moisture, $\overline{\Delta G}_w$ was decreased and $\overline{\Delta G}_s$ was increased in magnitude. Both differential free energy of aqueous phase ($\overline{\Delta G}_w$) and the differential free energy of solids ($\overline{\Delta G}_s$) values were higher (more negative) at lower temperature than the corresponding $\overline{\Delta G}_w$ and $\overline{\Delta G}_s$ values at higher temperature. Differential free energy for aqueous phase ($\overline{\Delta G}_w$) values were in the range of -6 to -124 cal/g water and $\overline{\Delta G}_s$ values in the range of -1 to -11 cal/g solids.

Both Table 4-1 and Figure 4-4 indicate that the free energy contribution of solids portion ($\overline{\Delta G}_s$) is significantly lower than that of the aqueous phase. This observation may be the reason for considering the adsorbent to be inert (Copeland and Young, 1961) in thermodynamic treatment of sorption phenomena. At lower temperature both $\overline{\Delta H}_w$ and $\overline{\Delta H}_s$ were higher and negative; once again

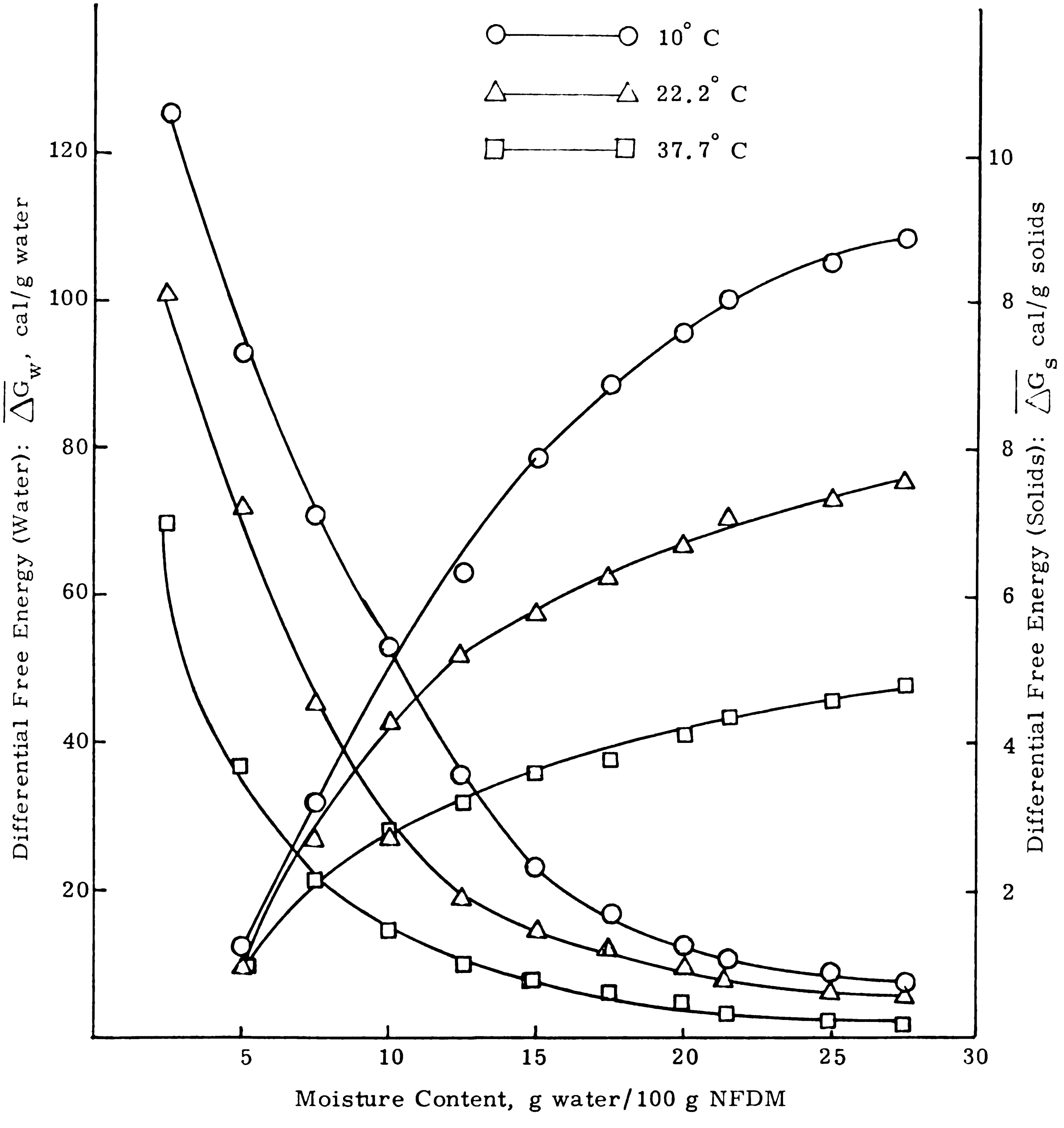

Figure 4-4. --Influence of temperature on the differential free energy values for the aqueous phase ($\overline{\Delta G_W}$) and corresponding contribution by solids portion ($\overline{\Delta G_S}$) in precooked freeze-dried beef (plate temperature 40.6° C).

equation (1-1) could explain this in terms of chemical potential. The escaping tendency for water portion at low temperature was less (free energy was more negative) than that of the higher temperature. In other words a given food system is more stable thermodynamically at a lower temperature than the higher temperature. Figure 3-4 also illustrates that $\overline{\Delta G}_w$ and $\overline{\Delta G}_s$ curves intersect each other in the region of 10-12 percent moisture (g water/100 g NFDM). These values are relatively close to the monomolecular moisture content (MC_1) as calculated by the BET equation (Brunauer et al., 1938).

Figure 4-4 does point out the contribution of adsorbent with respect to aqueous phase and temperature. Intuitively it could be visualized that the total enthalpy and entropy properties of a given food system would be related similarly with the contribution of adsorbent and the adsorbate. Copeland and Young (1961) and Wu and Copeland (1961) provided the best explanation of the contribution due to the adsorbent in a sorption process. They reported that only a limited number of reports have dealt with the changes in escaping tendency of adsorbent, and in many treatments the effect of adsorbent is ignored entirely. According to Copeland and Young (1961) the change in escaping tendency of adsorbent must occur during dispersal of material and adsorption of another substance on it. If the substance (X_1) attracts another substance (X_2), then X_2 also has to attract X_1.

They approximately divided the solid material into interior matter and the surface matter. In general, the escaping tendency of the surface matter may exceed that of material in the interior. There is a possibility of continuous gradation of escaping tendency over a wide range. Copeland and Young (1961), however, assumed that the escaping tendency of the material in the interior had a single value of average tendency and the surface matter had another, possibly slightly higher, value of escaping tendency.

Total Thermodynamic Properties

Total free energy ($\overline{\Delta G}$) enthalpy ($\overline{\Delta H}$) expressed as cal/g product are plotted versus moisture content for precooked freeze-dried beef (Figure 4-5). In addition, absolute temperature multiplied by total entropy values ($T \cdot \overline{\Delta S}$) are plotted in the same figure.

Figure 4-5 reveals that the enthalpy and entropy of mixing one gram of product increased with the moisture content up to about 10 percent and then decreased as the moisture content was increased.

Figure 4-6 presents similar results for raw freeze-dried beef (Saravacos and Stinchfield, 1965) adsorption data. Both Figures 4-5 and 4-6 reveal that at certain intermediate moisture the entropy was maximum (entropy inversion peak). For raw freeze-dried beef the entropy inversion peak was observed at about 7 percent

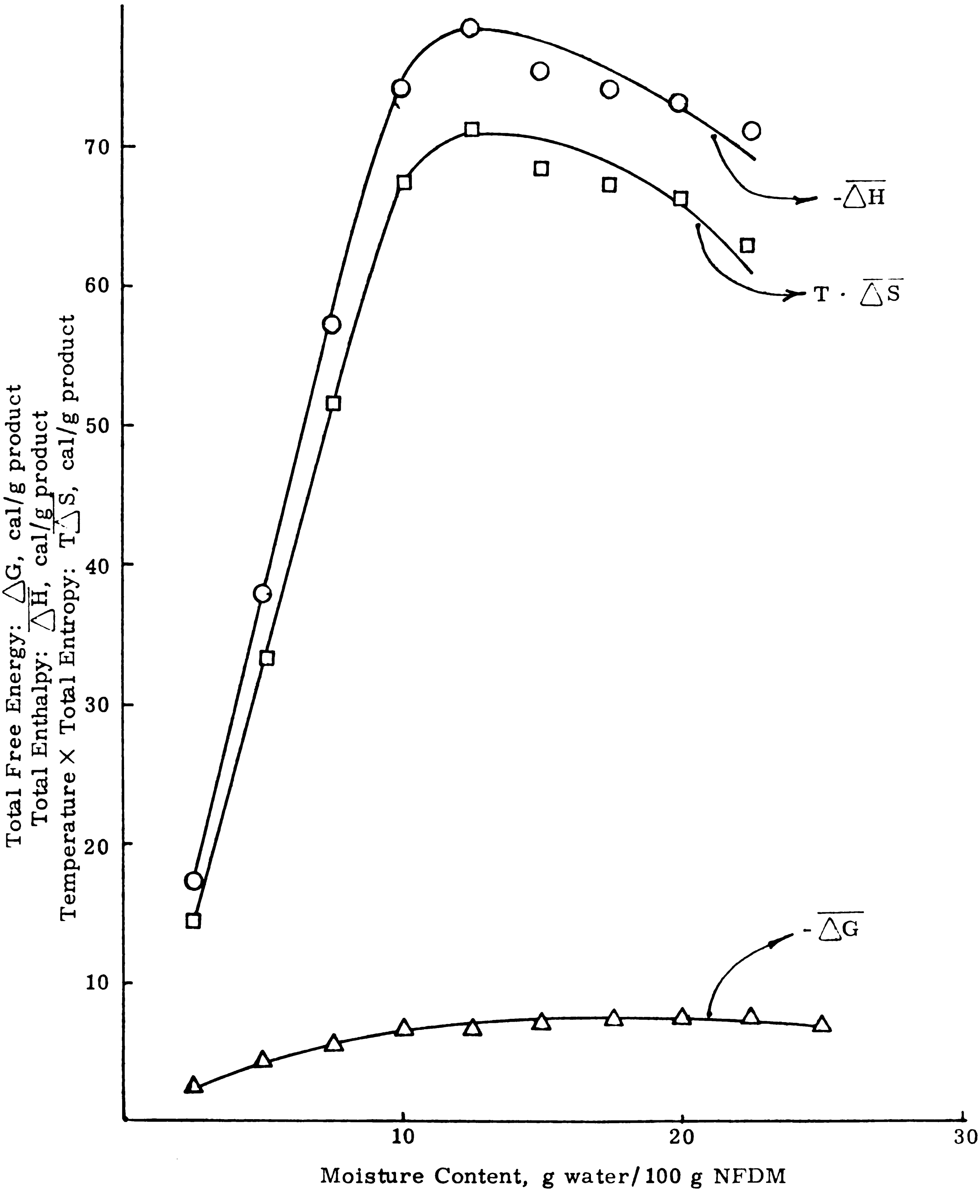

Figure 4-5. --Thermodynamic functions describing precooked freeze-dried beef as computed from moisture adsorption data (plate temperature 40.6° C).

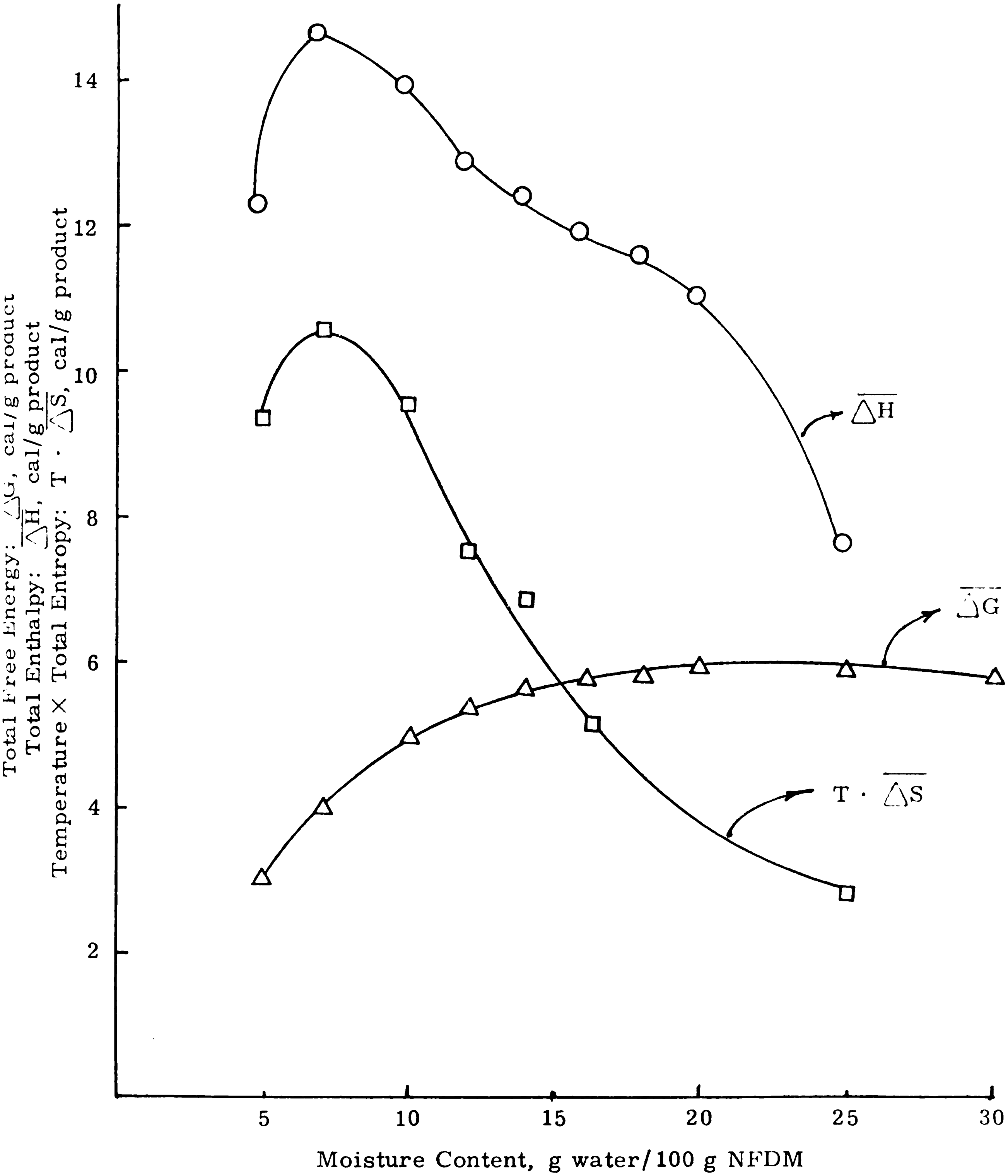

Figure 4-6. --Thermodynamic functions describing raw freeze-dried beef (Saravacos and Stinchfield, 1965) moisture adsorption data.

moisture, while for precooked freeze-dried beef the entropy inversion peak was observed at about 10 percent moisture. Adsorption isotherm data at different temperatures was utilized for the computation of total energy parameters in Figures 4-5 and 4-6. Stitt (1958) and Cardew and Eley (1958) observed the similar behavior for potato starch gel and haemoglobin, respectively. This observation of entropy inversion peak or maximum entropy has a special meaning in thermodynamics in relation to equilibrium. A maximum entropy of the system essentially signifies thermodynamic equilibrium according to the second law of thermodynamics. Moore (1965) stated that the drive or tendency of physicochemical systems towards equilibrium is compound of two factors: One is the tendency towards minimum energy and the other is the tendency towards maximum entropy. This discussion may be of considerable significance when evaluating food stability of low and intermediate moisture foods. First, it was observed that food materials tend to give an entropy inversion peak at low moisture levels. From a thermodynamic standpoint, it represents the maximum work obtainable from the system. Secondly, this peak occurs at some intermediate moisture, indicating that there seems to be an intermediate moisture content for a given food system at which the food system is more stable than any other moisture level. In a way it confirms the optimum moisture concept first proposed by Salwin (1959).

It should be emphasized that the entropy inversion peak merely suggests that thermodynamically the food system is relatively more stable at that moisture value than any other lower or higher moisture level. It is evident that the accuracy of the moisture value corresponding to entropy inversion peak will depend upon the accuracy of the moisture equilibrium data. Secondly, the entropy inversion point only suggests stability from a thermodynamic point of view. This moisture level may not be stable with respect to color, flavor, texture or some other criteria. At this point it should be indicated that there seems to be remarkable resemblance between the moisture content value at the entropy inversion peak and the BET monomolecular moisture content as proposed by Brunauer et al. (1938). Table 4-2 illustrates the monomolecular moisture values (M_1) and the moisture values at the entropy inversion peak for various products. Rockland's (1969) stability local isotherm L I and L II intersection seems to be related with the entropy inversion moisture level and monomolecular moisture content (M_1). Hence this discussion brings about a new hypothesis, namely the moisture content corresponding to entropy inversion peak is related to the stability of food system from a thermodynamic point of view. The value of this hypothesis could be only proven when it is utilized with respect to actual food systems.

Table 4-2. --Comparison of BET monomolecular moisture value (M_1) with the moisture value at the Entropy Inversion Peak (EIP).

Product	M_1	EIP
1. Precooked freeze-dried beef (plate temperature 40.6° C)		
adsorption isotherm at 10° C	10.63	11.3
adsorption isotherm at 22.2° C	7.50	10.1
adsorption isotherm at 37.7° C	4.59	5.8
desorption isotherm at 22.2° C	6.97	7.2
2. Raw freeze-dried beef (Saravacos and Stinchfield, 1965)		
adsorption isotherm at 20° C	6.94	7.0
3. Precooked freeze-dried beef (plate temperature 62.8° C)		
adsorption isotherm at 22.2° C	6.29	8.2
4. Gelatin (Bull, 1944)		
adsorption isotherm at 25° C	8.70	8.5

In this connection it is necessary to review one of the assumptions made in section 4-2 which stated that the hysteresis occurring commonly in biological products signifies the absence of thermodynamic equilibrium or existence of metastable state. It is very difficult to distinguish between the adsorption equilibrium moisture content and desorption equilibrium moisture content, from the food stability point of view. In general, a system is said to be in equilibrium when it has no further tendency to change its properties. In order to clarify this equilibrium concept further, let us first consider the mechanical stability via a simple example.

Figure 4-7a and 4-7b illustrate the mechanical stability of a box resting on a table. In positions A and C, the center of gravity of the box is lower than in any slightly displaced position, and if the box is tilted slightly it will try to return spontaneously to its original equilibrium state.

The gravitational potential energy of the box in positions A or C is at a minimum, and both positions represent a stable equilibrium state.

Yet it appears that position C is more stable than position A, and a certain large tilt of A will suffice to push it over into C. In position A, therefore, the box is said to be in metastable equilibrium.

Position B is also an equilibrium position, but it is a state of unstable equilibrium. The center of gravity of the box in B is higher than in any slightly displaced position, and a slight tilt will send the box into either position A or C.

The above example of mechanical stability indicates two stable equilibrium positions and one unstable equilibrium. It could

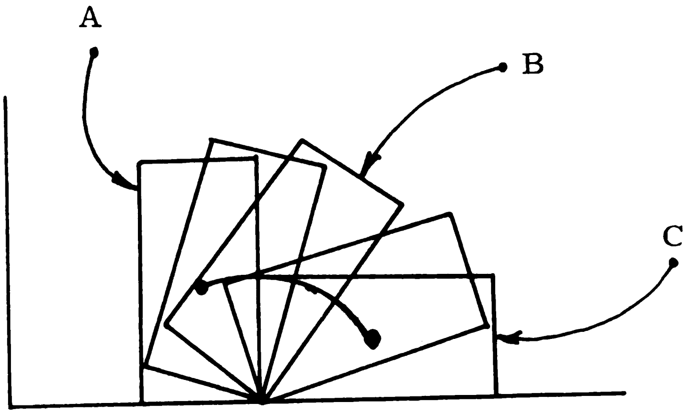

Figure 4-7a

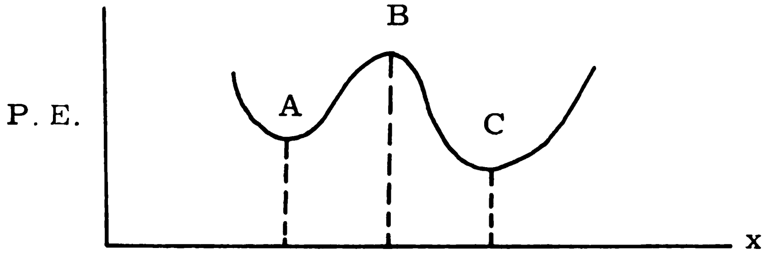

Figure 4-7b

Figure 4-7. --Mechanical stability of a box resting on a flat surface.

be visualized that an entropy inversion peak moisture level due to adsorption represents one stable moisture level, and the other stable moisture level is given by the entropy inversion peak due to desorption. The answer to the question of which equilibrium moisture level is more stable, the adsorption equilibrium moisture or desorption equilibrium moisture, could be provided by precise storage studies of the food system. The problem of defining precise moisture level stability becomes more complicated when applied to actual food products. The food products, when exposed to the surroundings, may undergo adsorption, desorption or a combination of both, making the optimum moisture level prediction much more difficult.

The close observation of Table 4-2 reveals several interesting observations. In general the BET monomolecular moisture values were similar to the moisture values at the entropy inversion peak.

Influence of isotherm temperatures. --For precooked freeze-dried beef (plate temperature 40.6° C) adsorption isotherms at 10, 22.2 and 37.7° C (Figure A-1), the entropy inversion peak moisture values and the BET monomolecular layer moisture values (M_1) are shown in Table 4-2. As the isotherm temperature was increased, the M_1 values decreased and the moisture values at the entropy inversion peak were decreased also. The moisture values corresponding to the entropy inversion peak were slightly higher than the BET monomolecular moisture values.

It appears that the precooked freeze-dried beef at 10° C could be more stable even with about 10 percent moisture; however, as the temperature was increased to 37.7° C the stability moisture level was reduced to about 5 percent. The accuracy of moisture level at which entropy inversion peak occurs depends upon the accurate moisture equilibrium isotherm data at several temperatures.

The effect of adsorption and desorption. --The adsorption and desorption moisture equilibrium data for the precooked freeze-dried beef was analyzed using the BET equation (Brunauer *et al.*, 1938), while the entropy inversion peak was obtained by the procedures described earlier. The results are shown in Table 4-2. Figures 4-5 and 4-8 show the total enthalpy ($\overline{\Delta H}_T$) total free energy ($\overline{\Delta G}$) and the product of the absolute temperature and total entropy ($T \cdot \overline{\Delta S}$) plotted versus moisture content for adsorption and desorption moisture equilibrium data of precooked freeze-dried beef (plate temperature 40.6° C) respectively. The results obtained as shown in Figures 4-5 and 4-6 and Table 4-2 reveal that BET monomolecular value for adsorption (7.5 percent) was slightly higher than the corresponding desorption moisture value (6.97 percent).

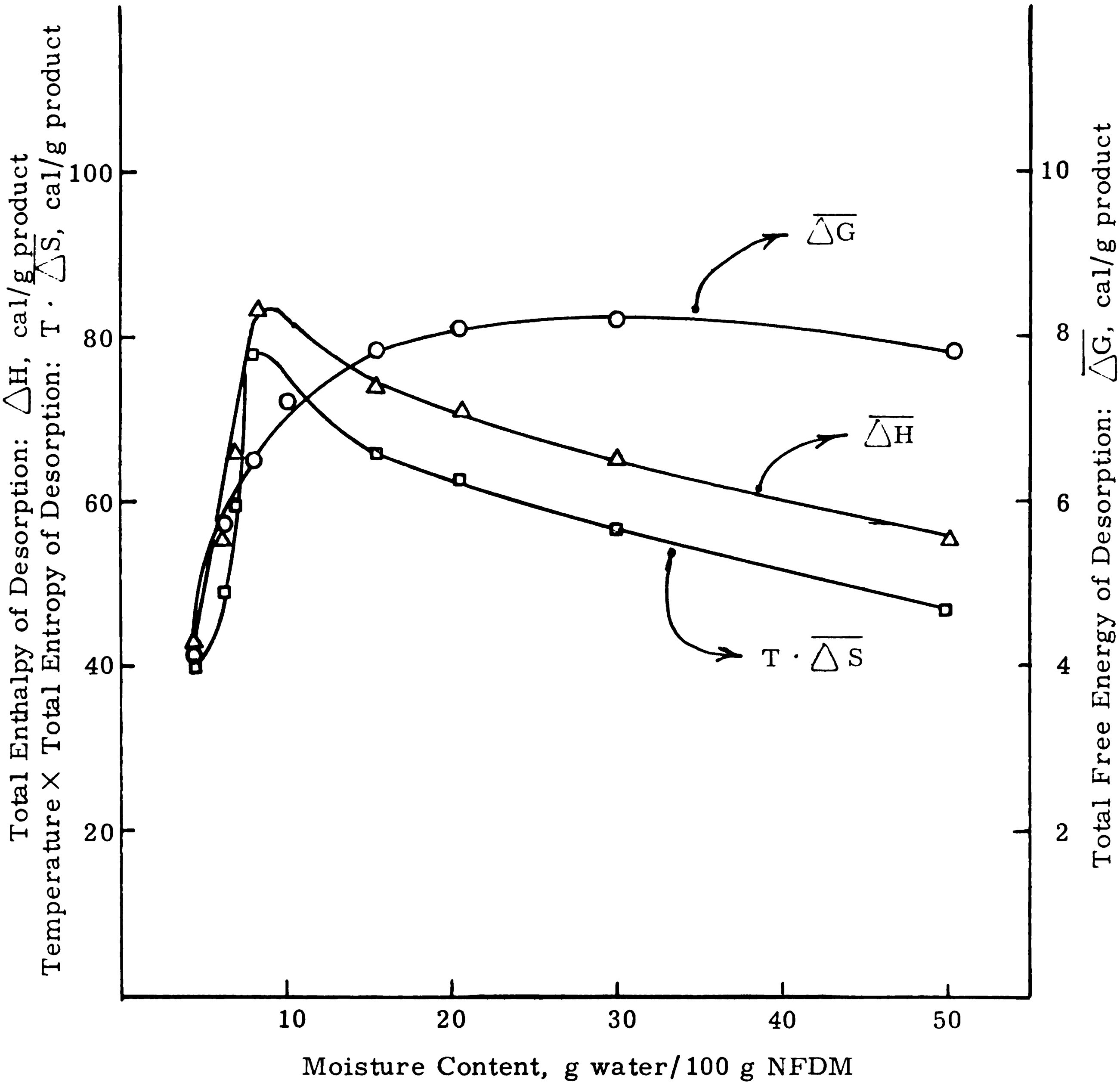

Figure 4-8. --Thermodynamic functions describing precooked freeze-dried beef as computed from moisture desorption date (plate temperature 40.6° C).

It is interesting to observe that the moisture level corresponding to the entropy inversion peak changed similarly. The thermodynamic analysis of moisture adsorption and desorption equilibrium data indicate a relative stability at the moisture level corresponding to the entropy inversion peak. Which equilibrium moisture value, the adsorption equilibrium moisture or desorption equilibrium moisture, should represent a true moisture value with respect to stability of food is difficult to predict. Chung and Pfost (1967) suggested that the desorption equilibrium moisture value could be considered as a metastable state. The low stability moisture value obtained for desorption isotherms both by BET analysis and the entropy values supports the argument of Chung and Pfost (1967). Precise storage studies and a clear definition of food stability are needed for further clarification.

Effect of freeze-drying temperature. --Table 4-2 shows the influence of temperatures employed for freeze-drying precooked beef on the monomolecular moisture values (M_1) obtained by the Brunauer, Emmett and Teller equation (1938) and the moisture levels corresponding to the entropy inversion peak. When the freeze-drying temperature was increased from 40.6° C to 62.8° C the BET monomolecular moisture values were decreased slightly from 7.5 to 6.94 percent, and the entropy inversion peak values also decreased from 10.1 to 7.2 percent. For precooked freeze-dried beef (plate temperature 62.8° C), both the BET monomolecular moisture value and the moisture content corresponding to the entropy inversion peak were in close agreement. It is difficult to explain the effect of freeze-drying temperature on the product in terms of stability moisture values due to several reasons. As mentioned earlier, it takes about 10 - 15 days to measure an adsorption and desorption isotherm for one sample; during this time the product may undergo physiochemical changes, for example, browning was very evident. The faster rate of freeze-drying at 62.8° C plate temperature may have altered the pore structure of the product. Since the product was cooked before freeze-drying, it is not likely that protein denaturation due to freeze-drying could have influenced the results.

Table 4-2 also indicates the effect of precooking on the stability moisture value of the product. Raw freeze-dried beef seems to have lower monomolecular moisture value and lower moisture value corresponding to the entropy inversion peak than the similar moisture values for the precooked freeze-dried beef. It may be possible that the precooking of the product makes it more stable at slightly higher moisture values than the raw product; in addition, protein denaturation during cooking may expose more active sites for water vapor sorption, thus accounting for higher entropy inversion moisture value.

Thermodynamic Quantities and Food Stability

It seems that the term "food stability" could be considered in two ways. First, it is the optimum moisture value at which dehydrated food is considered to be more stable. Secondly, in connection with the intermediate moisture foods, food stability could be visualized as a range of moisture rather than a specific moisture value. However, no absolute meaning should be attributed to food stability, since the food stability could be with respect to texture, flavor, color, taste and a number of other factors. Thermodynamics does not necessarily take into account such factors. It merely describes the various energy levels with which the water associates with the food. The accuracy of thermodynamic analysis of moisture equilibrium data is directly dependent upon the accuracy of the moisture sorption data itself.

Free energy quantities are generally considered less meaningful, but more accurate. Free energy calculations are dependent upon the measurement of vapor pressure of foods and vapor pressure of pure water (water activity). They are more related to surrounding relative humidities of a food substance. Enthalpy and entropy values are probably the most important and are directly related to the product under consideration. Bull (1944) remarked that the accuracy of enthalpy values is generally low.

The isotherms especially at low relative humidities are very close to each other and may overlap at times, making the application of the classical Clausius-Clapeyron equation to enthalpy calculations very difficult. Since the computation of entropy is directly dependent upon the computation of enthalpy values, all the difficulties mentioned above are carried forward.

However, thermodynamic quantities, especially entropy values calculated on the basis of the weight of the product, showed a moisture value at which entropy becomes maximum. Thermodynamically this moisture level could be considered more stable than any other moisture level. This moisture value may explain the optimum moisture value concept for foods proposed by Salwin (1959).

With regard to intermediate moisture foods, if food stability is visualized as an optimum stability moisture range, then it could be explained thermodynamically. It could be suggested that an intermediate moisture food should be formulated in such a way that entropy inversion peak should be uniform over the desired moisture range.

V. PREDICTION OF THERMODYNAMIC PARAMETERS

5.1 Effective Molecular Weight of Solids in Biological Substances

Thermodynamic treatment of moisture sorption on biological products would be simplified and more meaningful if the effective molecular weight of solids (EMW_s) in the biological substances was known. Stitt (1958) first observed the need of knowing the effective molecular weight of solids and indicated that if this value was known, then it would be possible to express the thermodynamic parameters on a molar basis.

It is well known from the thermodynamics that the free energy changes, enthalpy changes and entropy changes are best discussed when a process is described as follows:

$$aA + bB \rightleftharpoons cC + dD \qquad (5-1)$$

where a moles of substance A and b moles of substance B react to form c moles of C and d moles of D.

Such a description for a biological process would be very difficult because of the complex nature of the biological product.

We have already assumed that the solids in a given biological material form one phase of the system while the other phase is water under equilibrium conditions. By extending this analogy, an effective mole fraction which would be representative of the solids portion of the biological substance can be defined. It should be noted, however, that an effective molecular weight of solids in a biological substance has no relation with the molecular weight as used in chemical terms.

The purpose of knowing the effective molecular weight of solids in biological substances is to develop a procedure with a sound thermodynamic basis to predict the thermodynamic parameters of low and intermediate moisture food utilizing moisture equilibrium data at a single temperature and to compare the results obtained by this procedure with the known method.

5.2 Possible Methods of Estimating the Effective Molecular Weight

a. Colligative Properties

Freezing point depression, boiling point elevation and osmotic pressure measurements are some of the common methods used in the estimation of molecular weight of pure substances. If such data is available for biological products, it could be used for the estimation of the effective molecular weight of solids. This approach could be somewhat risky because much emphasis is placed on a single point whose experimental accuracy could be questionable.

b. Differential Thermal Analysis

The use of differential thermal analysis should be discounted since a food system changes significantly as the temperature is changed.

c. Apparent Specific Heats in Frozen Region

Hohner and Heldman (1970) used an interesting approach to determine the effective mole fraction in their studies with freezing rates of food systems by computer simulation. They developed the effective molar solute concentration by knowing the apparent specific heat and temperature relationship in the frozen product. This approach is probably more sound, since the computation involves the use of available data of apparent specific heats at various temperatures. They reported that the value of the effective molar concentration of solutes for cod fish was 0.0009 and for lean sirloin beef was 0.0007.

d. Use of Raoult's Law at High Relative Humidities

The validity of this approach will depend upon the extent to which the solution may be ideal at the composition corresponding to equilibrium relative humidities higher than 90 percent. Raoult's Law is defined as:

$$P = X_w P_0 \tag{5-2}$$

and states that the vapor pressure of food (P) is proportional to mole fraction (X_w) and the saturation vapor pressure (P_0). Labuza (1968) stated that about 80-90 percent of the water in food exerts a vapor pressure equal to that of pure water ($a_w < 1$). At higher equilibrium relative humidities, therefore, it may be assumed that Raoult's Law is valid.

5.3 Theoretical Considerations

There are several methods available to be used in the evaluation of thermodynamic parameters from moisture equilibrium data. In addition to direct use of the Clausius-Clapeyron equation, the Othmer procedure (1940) can be used if moisture equilibrium data is available at no less than two temperatures. The Brunauer, Emmett and Teller (BET) equation (1938) has been used widely to evaluate monomulecular moisture contents and allows the computation of latent heat values at that specific moisture content from equilibrium data at one temperature. In addition to the indicated limitations, these methods do not account for non-idealities existing in food products and do require careful use to obtain consistent results.

The Clausius-Clapeyron method is the most widely used method for the computation of total enthalpy ($\overline{\Delta H_T}$). The Clausius-Clapeyron equation was presented as equation (4-3). It may be recalled that the total enthalpy of sorption ($\overline{\Delta H_T}$), when applied to adsorption data, represents the sum of the heat of adsorption and latent heat of condensation. If the procedure is applied to desorption data, the heat of sorption value would be the sum of latent heat of vaporization for pure water plus heat of desorption at any moisture content level. The Clausius-Clapeyron equation has been utilized by Kapsalis (1967) to determine the partial molal heat of sorption for various dry foods including freeze-dried beef. As would be expected, the heat of sorption increased dramatically as the moisture content was reduced to low levels.

An alternate approach to determination of latent heat values was proposed by Othmer (1940), who utilized the Clausius-Clapeyron equation to derive the following expression:

$$\text{Log}\,\frac{P_2}{P_1} = \frac{L}{L'}\,\text{Log}\,\frac{P'_2}{P'_1} \qquad (5\text{-}3)$$

where L and L' represent latent heat of vaporization for the product and the latent heat of vaporization for pure water respectively. Obviously equilibrium data is required for at least two temperatures.

Preferably, the equilibrium data would be available at more than two different levels. Rodriguez-Arias (1956), Heldman et al. (1965) and Strohman and Yoerger (1967) have applied the Othmer method to computation of latent heats of vaporization for various biological substances. In all of these applications the method has been applied to desorption data in an effort to evaluate the latent heats of vaporization necessary for design of dehydration equipment.

The method of Brunauer, Emmet and Teller (1938) utilizes the following equation:

$$\frac{P}{M\,(P_0 - P)} = \frac{1}{M_1\,c} + \frac{c - 1}{M_1\,c} \cdot \frac{P}{P_0} \qquad (5\text{-}4)$$

where M_1 and c are the constants evaluated from the BET analysis. In most applications to food products, the constant M_1 has been computed and is referred to as the moisture content of the product when a monomolecular layer of moisture is adsorbed on surfaces of the material. Salwin (1959) utilized this monomolecular layer value to define a minimum moisture content for the stability of a food product in storage. The second constant (c) is defined by the following expression:

$$c = \mathrm{Exp}\ \frac{(E_1 - L)}{RT} \qquad (5\text{-}5)$$

where E_1 represents the heat of sorption for the moisture in the monomolecular layer and L is the latent heat of vaporization or condensation for a free water surface. It is interesting to note that the energy constant of the BET equation as defined by equation (5-5) has not been utilized to compute the heats of sorption for food products.

Proposed Method

The approach to be presented in this investigation is considerably different than the approach utilized by previous methods for computation of thermodynamic parameters in food products. The approach will utilize basic thermodynamic expressions and will assume initially that a dry food or intermediate moisture food product can be treated as a two-phase system. The two phases are the liquid phase and the solid phase of the product. Utilizing this assumption, any dry or intermediate moisture food product will exist due to the mixing of two phases. This so-called mixing process lends itself to description by two thermodynamic expressions. The first of these expressions is the free energy of mixing as follows:

$$\tilde{\Delta} G_m = X_w \, RT \, \mathrm{Ln}\, a_w + X_s \, RT \, \mathrm{Ln}\, a_s \tag{5-6}$$

Equation (5-6) is expressed in terms of mole fraction of water (X_w), mole fraction of solids (X_s), activity of water (a_w) and activity of solids (a_s). The second expression is the entropy of mixing expressed as:

$$\tilde{\Delta} S_m = -X_w R \,\mathrm{Ln}\, X_w - X_s R \,\mathrm{Ln}\, X_s \qquad (5\text{-}7)$$

which defines the entropy value in terms of the mole fraction of the two phases in the system. Utilizing these two expressions and experimental equilibrium moisture data, the necessary thermodynamic parameters and other parameters describing the food system can be computed.

Equations (5-6) and (5-7) deserve somewhat more discussion at this point. First of all, it must be pointed out that equation (5-6) is a rigorous thermodynamic equation and is applicable to both ideal and non-ideal systems, while equation (5-6) is applicable to a class of non-ideal solutions which Hildebrand and Scott (1929) called "regular solutions." For ideal solutions the enthalpy of mixing is zero, while for regular solutions the enthalpy of mixing is relatively small. The concept of mixing as applied to an adsorption process may be somewhat more difficult to explain. Since mixing of two phases results in a free energy change and an increase in entropy, the assumption at this point is that the adsorption process (the mixing of liquid and solids) results in the same type of free energy change and entropy increase within a food system.

An examination of equations (5-6) and (5-7) reveals that evaluation of free energy change or entropy increase can only be accomplished if the mole fraction values for water and solids are known. In general, mole fraction can be defined in the following manner:

$$X_1 = \frac{\frac{W_1}{MW_1}}{\frac{W_1}{MW_1} + \frac{W_2}{MW_2}} \qquad (5\text{-}8)$$

which defines the mole fraction value in terms of the weights and the molecular weights of each component. In a given food system, as defined in this investigation, all parts of equation (5-8) would be known except the molecular weight of the solid phase of the system. This molecular weight value must be considered an effective molecular weight (EMW) rather than one which would be defined in a chemical manner. As described earlier, Raoult's Law [equation (5-2)] can be used in a region of high equilibrium relative humidity (> 90 percent). Using equation (5-2), all the quantities in equations (5-6) and (5-7) can be defined except the activity of solids (a_s). The desired water activity and corresponding equilibrium moisture content values can be selected from the equilibrium moisture isotherms. The remaining quantity, the solids activity (a_s), is not readily available in order to compute the changes in free energy defined in equations (5-6).

Since the solutions or food systems considered in this investigation are not ideal, procedures which will account for this non-ideality must be considered. In thermodynamics, the procedure normally utilized to account for non-ideality is to introduce an activity coefficient defined for solids in the following manner:

$$a_s = X_s \cdot \gamma_s \qquad (5\text{-}9)$$

where the activity coefficient (γ_s) accounts for the non-ideality in the system. An activity coefficient of one would indicate that the water activity and mole fraction are equal. Unfortunately, equation (5-9) alone will not allow computation of solids activity in the food system. An additional equation must be introduced in order to accomplish this objective.

In a two-component system (solids and water), it is possible to ascertain the thermodynamic changes in one component from the thermodynamic changes of the second component by using the convenient form of the Gibbs-Duhem equation (4-10) as follows:

$$X_w \, d \, \mathrm{Ln} \, \gamma_w + X_s \, d \, \mathrm{Ln} \, \gamma_s = 0 \qquad (5\text{-}10)$$

Using equations (5-9) and (5-10), the activity coefficient of solids can be determined by graphical integration. Since the dry solids in a given food system is considered a standard state, the activity of solids at this point is considered equal to one. This explanation will become more evident as an actual example is illustrated. By knowing the activity coefficient of solids, activity of solids can be calculated using equation (5-9). The free energy of mixing ($\widetilde{\Delta G}_m$) can be computed using equation (5-6). The procedure outlined up to this point allows evaluation of free energy change and an increase in entropy for the mixing of two phases. Evaluation of these two thermodynamic parameters allows the evaluation of a third parameter, enthalpy of mixing ($\widetilde{\Delta H}_m$), as follows:

$$\widetilde{\Delta H}_m = \widetilde{\Delta G}_m + T\, \widetilde{\Delta S}_m \qquad (5\text{-}11)$$

Equation (5-11) represents the molar change in enthalpy of mixing of two phases in the system. There are several factors which must be emphasized when examining equation (5-11). The first concerns the acceptability of this expression to describe the enthalpy change which occurs during adsorption or desorption of moisture in a food system. The acceptability of this approach seems very likely but can only be proven by comparing results with known acceptable methods. The second factor is related to a distinct advantage of equation (5-11). Close examination of equations (5-6) to (5-11) indicates that equilibrium data are required at only one temperature for evaluation of latent heats of sorption results. Most procedures require at least three separate equilibrium moisture isotherms at three different temperatures. The success of utilizing this procedure could reduce the requirements for conducting of equilibrium moisture isotherm experiments to no more than one temperature.

5.4 Computation Procedure

The following example will illustrate the procedures used to compute total heats of sorption ($\overline{\Delta H_T}$) by the proposed method. The example will utilize equilibrium moisture adsorption data (Figure A-1) for precooked freeze-dried beef at 22.2° C (plate temperature 62.8° C).

1. Computation of effective molecular weight (EMW_s)
    a. From the equilibrium isotherm, the moisture content at the water activity of 0.95 is equal to 37.5 g water/100 g NFDM.
    b. Using Raoult's Law (equation 5-2)

$$X_w = \frac{P}{P_0} = 0.95$$

c. Using equation (5-8) for mole fraction

$$.95 = \frac{\frac{37.5}{18}}{\frac{37.5}{18} + \frac{100}{EMW_s}}$$

Solving above, $EWW_s = 057.98$ for $X_w = 0.95$.

2. Computation of mole fraction of water (X_w) and mole fraction of solids (X_s) for a series of water activities.

By knowing the effective molecular weight of solids (950) and a given composition ($a_w = 0.5$, $M = 8.5$ g water/ 100 g NFDM) and using equation (5-8):

$$X_w = \frac{\frac{8.5}{18}}{\frac{8.5}{18} + \frac{100}{950}} = 0.818$$

and

$$X_s = \frac{\frac{100}{950}}{\frac{8.5}{18} + \frac{100}{950}} = 0.182$$

3. Computation of activity coefficient for water (γ_w)

The activity coefficient of water is expressed in terms of activity of water (a_w) and mole fraction of water (X_w)

similar to equation (5-9) as follows:

$$\gamma_w = \frac{a_w}{X_w} = \frac{0.5}{.818} = 0.611$$

Values of γ_w at each moisture level are presented in Table 5-1.

4. Activity coefficient of solids (γ_s)

The calculation of activity coefficient of solids involves the integration of the Gibbs-Duhem equation (5-10). The integration of equation (5-10) was carried out by CDC 3600 digital computer. Figure 5-1 illustrates the method of integration. Results presented in Table 5-2 show the thermodynamic parameters obtained for the moisture equilibrium isotherm of precooked freeze-dried beef (plate temperature 62.8° C). In order to find the lower limit of integration of equation (5-9), the standard state of beef solids was considered as dry beef solids (low moisture content). Therefore the activity of precooked freeze-dried beef with moisture content of 2.7 g water/100 g NFDM corresponding to $\frac{P}{P_0} = 0.05$ was considered to be equal to one. Equation (5-9) was utilized to calculate the activity coefficient of solids (γ_s). For the moisture content of

Table 5-1. --Adsorption equilibrium moisture isotherm data for precooked freeze-dried beef (plate temperature 62.8° C) and some thermodynamic quantities.

$\frac{P}{P_0}$	M	X_w	X_s	$\frac{-X_w}{X_s}$	γ_w	$\ln\gamma_w$
0.050	2.100	0.526	0.474	-1.108	0.095	-2.353
0.100	3.200	0.628	0.372	-1.689	0.159	-1.838
0.150	4.300	0.694	0.306	-2.269	0.216	-1.532
0.200	5.200	0.733	0.267	-2.744	0.273	-1.299
0.300	6.400	0.772	0.228	-3.378	0.389	-0.945
0.400	7.100	0.789	0.211	-3.747	0.507	-0.680
0.500	8.500	0.818	0.182	-4.486	0.611	-0.492
0.600	10.900	0.852	0.148	-5.753	0.704	-0.351
0.700	14.200	0.882	0.118	-7.494	0.793	-0.231
0.800	18.400	0.907	0.093	-9.711	0.882	-0.125
0.900	27.400	0.935	0.065	-14.461	0.962	-0.038
0.950	35.700	0.950	0.050	-18.842	1.000	0.000

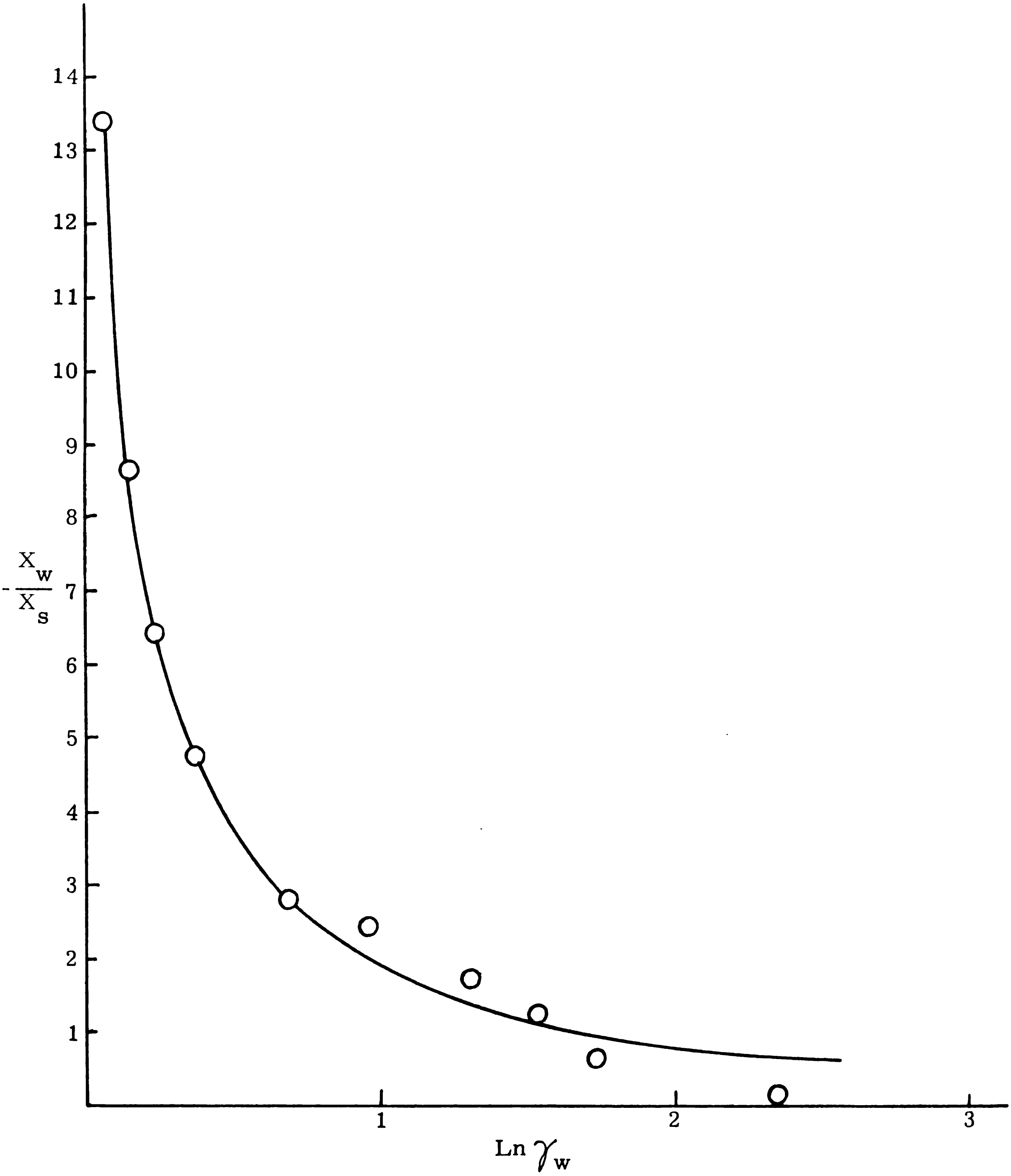

Figure 5-1. --Evaluation of activity coefficient for solids (γ_s) of precooked freeze-dried beef (plate temperature 40.6° C) by graphical integration.

Table 5-2. --Some thermodynamic parameters of precooked freeze-dried beef (plate temperature 62.8° C).

P/P_0	M	a_s	γ_s	$-\Delta\tilde{G}_m$	$\Delta\tilde{S}_m$	$-\Delta\tilde{H}_m$	$\overline{\Delta G}_m$	$\overline{\Delta S}_m$	$-\overline{\Delta H}_m$	$\overline{\Delta H}_w$
.05	2.1	1.000	2.106	923.701	1.375	517.595	2.008	.003	1.126	53.6
.1	3.2	0.381	1.026	1058.510	1.312	671.011	2.903	.004	1.841	57.5
.15	4.3	0.171	.560	1088.829	1.224	727.321	3.593	.004	2.401	55.8
.2	5.2	0.083	.312	1081.050	1.153	740.512	4.050	.004	2.775	53.4
.3	6.4	0.024	.106	1043.888	1.068	728.455	4.521	.005	3.156	49.3
.4	7.1	0.009	.041	1011.024	1.023	708.881	4.717	.005	3.308	46.6
.5	8.5	.003	.019	938.351	0.994	644.774	4.994	.005	3.512	41.3
.6	10.9	.001	.009	828.398	0.833	582.372	5.310	.005	3.733	34.2
.7	14.2	.0009	.004	710.537	0.720	497.855	5.563	.006	3.899	27.5
.8	18.4	.0006	.002	598.547	0.617	416.317	5.700	.006	3.967	21.6
.9	27.4	.0004	.001	443.902	0.476	303.316	5.671	.006	3.875	14.1
.95	35.7	.0002	.0008	355.958	0.397	238.705	5.470	.006	3.676	10.3

2.1 g water/100 g NFDM, $X_s = 0.474$ (Table 5-2); therefore the activity coefficient of solids at the standard state is:

$$\gamma_s = \frac{1}{0.474} = 2.109, \text{ where } \frac{X_w}{X_s} = 1.108$$

Above values fix the lower limit of integration and the constant of integration in equation (5-10) as follows:

$$\ln \gamma_s = \int_{1.108}^{\frac{X_w}{X_s}} - \frac{X_w}{X_s} \, \mathrm{Ln} \quad {}_w + \mathrm{Ln}\ 2.106$$

The γ_s values at each moisture level are tabulated in Table 5-2. For example, at $a_w = 0.5$ the $\gamma_s = 0.019$

and $\quad a_s = X_s \cdot \gamma_s \qquad$ (equation 5-9)

$$= (0.182)(.019) = .003$$

5. Computation of $\widetilde{\Delta G}_m$, $\widetilde{\Delta H}_m$ and $\widetilde{\Delta S}_m$

From previous computations, all parameters in equations (5-6), (5-7) and (5-11) are known.

a. Molar free energy of mixing ($\widetilde{\Delta G_m}$) is calculated by using equation (5-6):

$$\widetilde{\Delta G_m} = (1.98726)\ (295.35)\ \left[0.818 \text{ Ln } (0.5) + 0.182 \text{ Ln } (.003)\right]$$

$$= -938.351 \text{ cal/g mole of mixture}$$

b. Using equation (5-7), the molar entropy of mixing was computed:

$$\widetilde{\Delta S_m} = -(1.98726)\ \left[0.818 \text{ Ln } (.818) + .182 \text{ Ln } (.182)\right]$$

$$= 0.994 \text{ cal/g mole of mixture/}^\circ \text{ K}$$

c. Using equation (5-11), the molar enthalpy of mixing was computed:

$$\widetilde{\Delta H_m} = -938.351 + 295.35\ (0.994)$$

$$= 644.744 \text{ cal/g mole of mixture}$$

6. Computation of $\overline{\Delta G_m}$, $\overline{\Delta H_m}$ and $\overline{\Delta S_m}$

a. The thermodynamic quantities expressed on molar basis are converted to mass basis by utilizing the quantity ($X_w \cdot MW_w + X_s \cdot EMW_s$) as a conversion factor.

$$\overline{\Delta G}_m = \frac{-938.351}{(0.818)(18) + (.182)(950)}$$

$$= 4.944 \text{ cal/g product}$$

Similarly $\overline{\Delta S}_m$ = .005 cal/g product/° K and

ΔH_m = 3.512 cal/g product were obtained.

7. Computation of $\overline{\Delta H}_w$ and $\overline{\Delta H}_T$

   a. The moisture content value was used to express the heat of adsorption values in terms of water as follows:

$$\overline{\Delta H}_w = \frac{\overline{\Delta H}_m}{0.085} = \frac{3.512}{.085} = 41.3 \text{ cal/g water}$$

   b. The total enthalpy of adsorption is computed by adding the latent heat of condensation to the $\overline{\Delta H}_w$ value:

$$\overline{\Delta H}_T = 41.3 + 583.6 = 624.9 \text{ cal/g water}$$

5.5 Results and Discussion

The results obtained in this portion of the investigation will be presented as total enthalpy ($\overline{\Delta H}_T$) (cal/g water) versus moisture content in most cases. The total enthalpy value ($\overline{\Delta H}_T$) represents the sum of $\overline{\Delta H}_w$ and the latent heat of vaporization or condensation.

The Clausius-Clapeyron method and the Othmer procedure. -- Figure 5-2 shows the $(\overline{\Delta H}_T)$ values for moisture adsorption for precooked freeze-dried beef (plate temperature 40.6° C) as determined by using the Clausius-Clapeyron method and the Othmer method (1940). As expected, the $\overline{\Delta H}_T$ decreased from about 1250 to 600 cal/g water as the moisture content increased from 2.5 to 30 percent (g water/100 g NFDM). At lower moisture levels, values were significantly higher and approached the latent heat of vaporization for pure water as the moisture content was increased. Figure 5-2 also reveals close agreement between total enthalpy of adsorption values $(\overline{\Delta H}_T)$ determined by the Clausius-Clapeyron method and values determined by the Othmer method. This is as expected and can be attributed to the fact that Othmer (1940) developed the equation (5-3) from the Clausius-Clapeyron equation (4-3).

Comparison of the proposed method with the known method. -- Adsorption isotherm data for raw freeze-dried beef (Saravacos and Stinchfield, 1965) was used to compute $\overline{\Delta H}_T$ values by various methods. Figure 5-3 presents, in addition to $\overline{\Delta H}_T$ values by the Clausius-Clapeyron method and the Othmer method, the values of $\overline{\Delta H}_T$ by the proposed method for raw freeze-dried beef. The $\overline{\Delta H}_T$ values by the proposed method were significantly lower than the

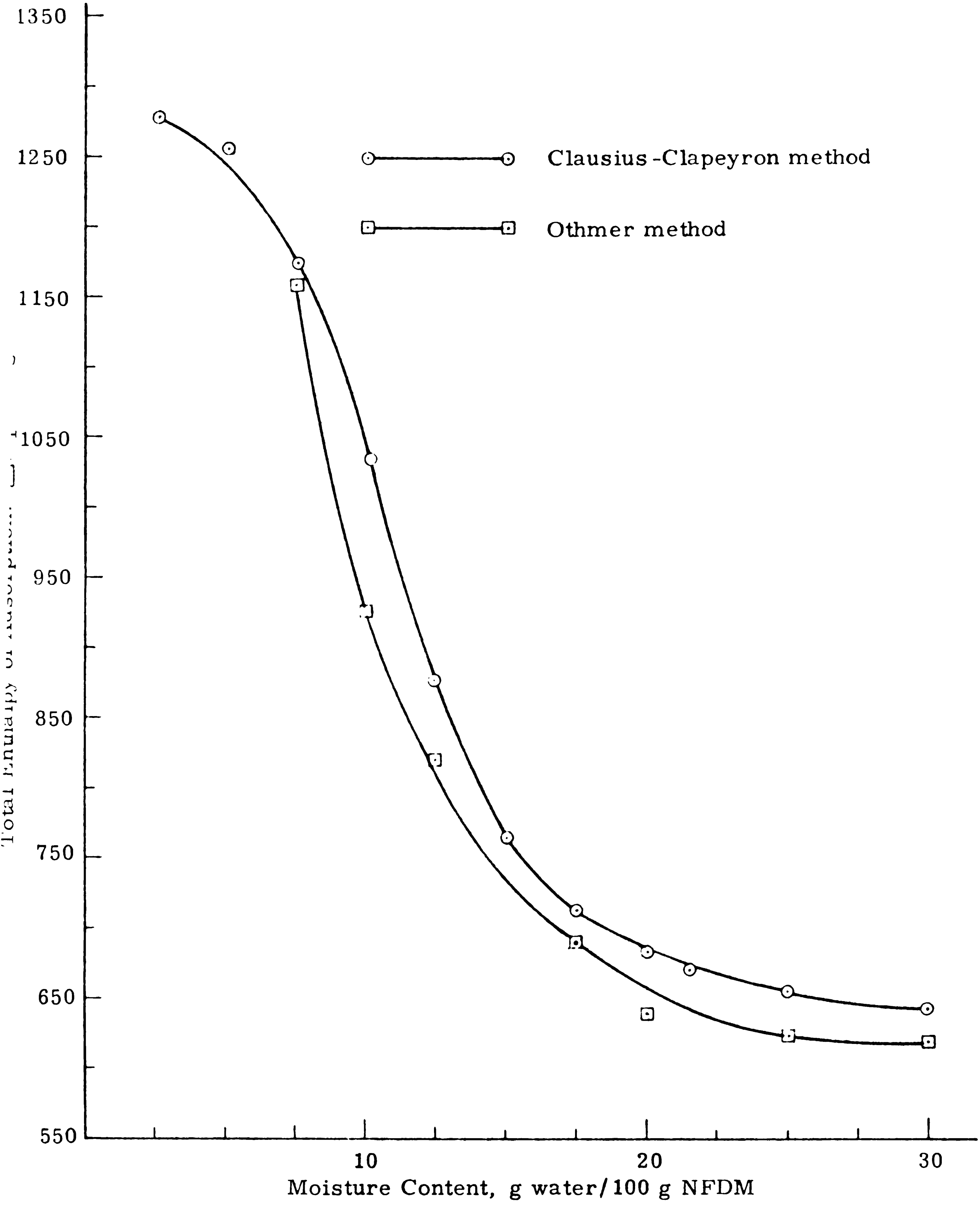

Figure 5-2. --Comparison of total enthalpy values ($\overline{\Delta H_T}$) by the Othmer method and the Clausius-Clapeyron method for precooked freeze-dried beef moisture equilibrium isotherms.

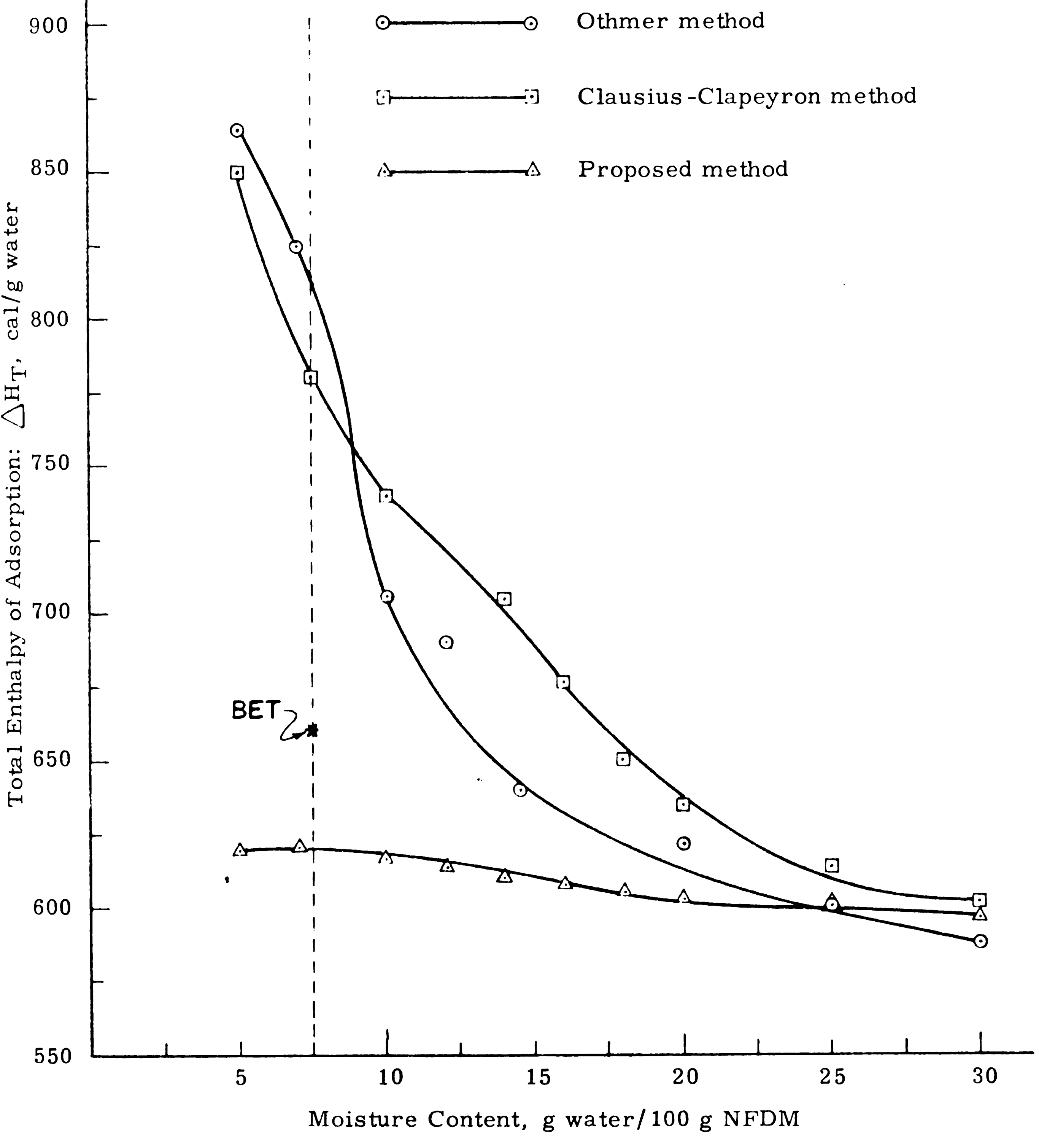

Figure 5-3. --Comparison of total enthalpy values ($\overline{\Delta H}_T$) by the Othmer method, the Clausius-Clapeyron method and the proposed method at 20° C for raw freeze-dried beef moisture adsorption data (Saravacos and Stinchfield, 1965).

$\overline{\Delta H_T}$ values obtained by both the Clausius-Clapeyron method and the Othmer method. Above 25 percent moisture content all the three methods yielded similar values of $\overline{\Delta H_T}$. The total enthalpy values by the proposed method were computed utilizing an effective molecular weight of raw beef solids of 1075 which was obtained by using Raoult's law at the water activity of 0.95. It must be pointed out that the $\overline{\Delta H_T}$ values obtained by the proposed method were computed using isotherm data at a single temperature (20° C), while the Clausius-Clapeyron method and the Othmer method required the use of isotherm data at several temperatures. Use of the Brunauer, Emmett, and Teller (BET) (1938) method allows evaluation of monomolecular moisture contents (M_1) and an energy constant (c). Figure 5-3 indicates the monomolecular moisture value was 6.94 g water/100 g NFDM and the corresponding $\overline{\Delta H_T}$ was 659.21 cal/g water. It is interesting to note that at the monomolecular moisture value, both the Clausius-Clapeyron and the Othmer method predicted significantly higher values of $\overline{\Delta H_T}$ than the proposed method and the BET method which were in close agreement.

The observed agrement between the $\overline{\Delta H_T}$ values obtained by the proposed and BET methods is more evident in Table 5-3. Total heats of sorption values obtained by the four methods were tabulated in Table 5-3 for precooked freeze-dried beef, low heat

Table 5-3. --Comparison of total enthalpy values by various methods (total enthalpy values are expressed as cal/g water).

Temp.	M_1	BET	C-C[a]	Othmer Method	Proposed Method
a. Precooked Freeze-dried Beef					
10° C	10.63	671	983	922	648[b]
22.2° C	7.50	663	1173	1160	646
37.7° C	4.59	641	1257	1197	615
b. Raw Freeze-dried Beef (Saravacos and Stinchfield, 1965)					
10° C	6.87	659	791	830	636[c]
20° C	6.94	659	782	825	632
30° C	6.41	655	798	835	635
40° C	5.47	658	828	853	640
50° C	4.50	650	862	875	646
c. Low Heat Non-fat Milk (Heldman *et al.*, 1965)					
1.66° C	10.06	676	889	833	627[d]
15.55° C	7.51	679	922	849	632
30° C	7.02	678	938	864	633
37.7° C	6.73	680	1021	922	634

[a] Clausius-Clapeyron method

[b] From adsorption data at 22.2° C (EMW_s = 775)

[c] From adsorption data at 20° C (EMW_s = 1075)

[d] From desorption data at 15.5° C (EMW_s = 725)

non-fat dry milk and the raw freeze-dried beef. Once again, $\overline{\Delta H}_T$ values obtained by the Clausius-Clapeyron and the Othmer methods are significantly higher than the BET and the proposed method values.

5.6 Features of the Proposed Method

As indicated earlier in this section, the proposed method computes the $\overline{\Delta H}_T$ values using the equilibrium moisture isotherm data at one temperature. The values computed by the proposed method are expressed as cal/g mole of mixture which can be converted to cal/g of product while the $\overline{\Delta H}_T$ values obtained from the Clausius-Clapeyron method and the Othmer method are customarily expressed as cal/g mole water or cal/g water.

Figure 5-4 illustrates the significant change in shape of the curve when the $\overline{\Delta H}_w$ values were plotted on a mixture, solids and water basis. Figure 5-4 was plotted using moisture adsorption isotherm data for precooked freeze-dried beef at 22.2° C (plate temperature 42.6° C). First it should be pointed out that $\overline{\Delta H}_w$ can be converted to $\overline{\Delta H}_T$ by adding 583.6 cal/g water (latent heat of vaporization at 22.2° C). Close examination of results in Figure 5-4 leads to several interesting observations. $\overline{\Delta H}_w$ expressed as cal/g water decreased from 58 cal/g water to 10 cal/g water as the moisture content was increased from 3 percent to 44.5 percent. The heat of

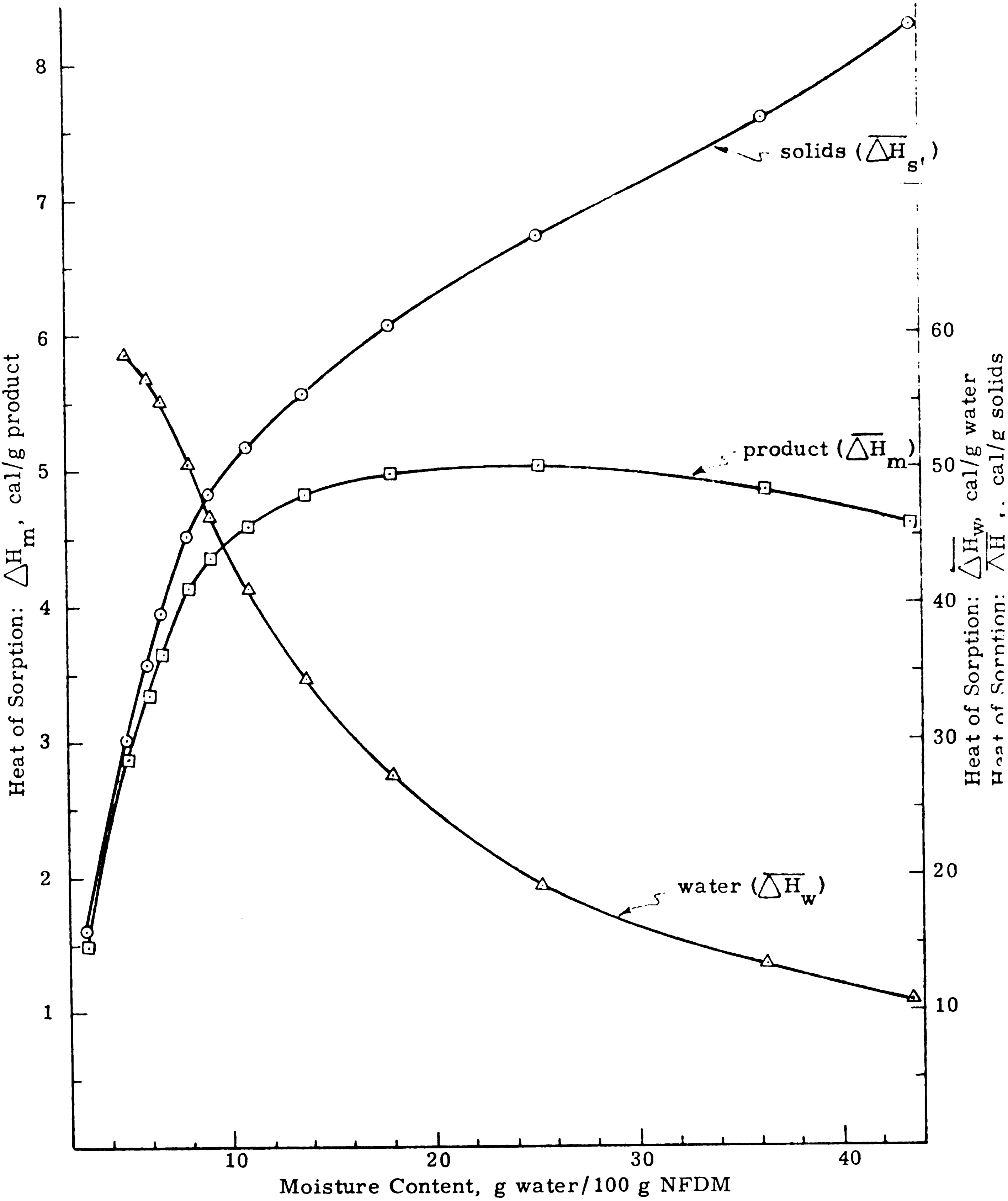

Figure 5-4. --Heat of adsorption values ($\overline{\triangle H}_W$) per g of product, per g of solids and per g of water for precooked freeze-dried beef adsorption isotherms (plate temperature 40.6° C).

sorption expressed as cal/g product, however, results in an opposite relation; $\overline{\triangle H_w}$ (cal/g product) increased with the moisture content. Considerable similarity existed between $\overline{\triangle H_s'}$ expressed as cal/g solid and cal/g product.

Figure 5-5 presents the heats of sorption values expressed as cal/g product, for precooked freeze-dried beef (plate temperature 42.6° C) adsorption isotherms at 10° C, 22.2° C and 37.7° C. Figure 5-6 shows the similar results for precooked freeze-dried beef (plate temperature 62.8° C). In general, the heat of sorption increased with decrease in temperature. The plate temperature used in freeze-drying the product did not affect the magnitude of the heats of sorption values. However, as the freeze-drying temperature was increased, the heats of sorption values decreased somewhat. The relationship of those heats of sorption values with the heat evolved as sensed by a person when product is consumed will be discussed later. One significant observation from Figures 5-4, 5-5 and 5-6 would be the correlation between $\overline{\triangle H_w}$ values, expressed as cal/g product, with the calorimetric heats of immersion. Thompson (1969) and Morrison and Hanlan (1957) indicated that the calorimetric values for heats of immersion for the precooked freeze-dried beef are approximately 1 cal/g product. This emphasizes the validity of the proposed method. It could be argued that the proposed method,

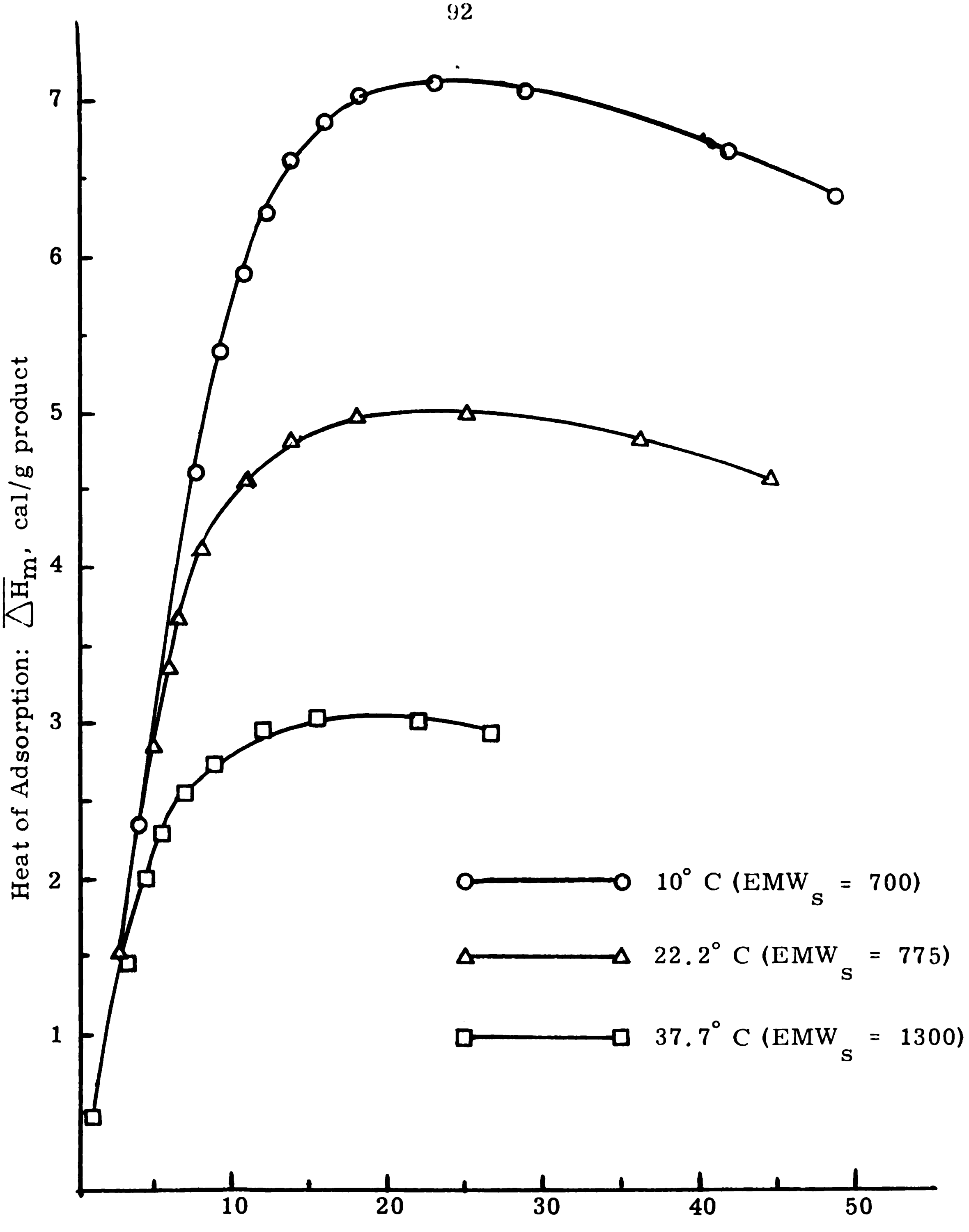

Figure 5-5. --Heat of adsorption values ($\overline{\triangle H_m}$) cal/g product by the proposed method for precooked freeze-dried beef adsorption isotherms (plate temperature 40.6° C).

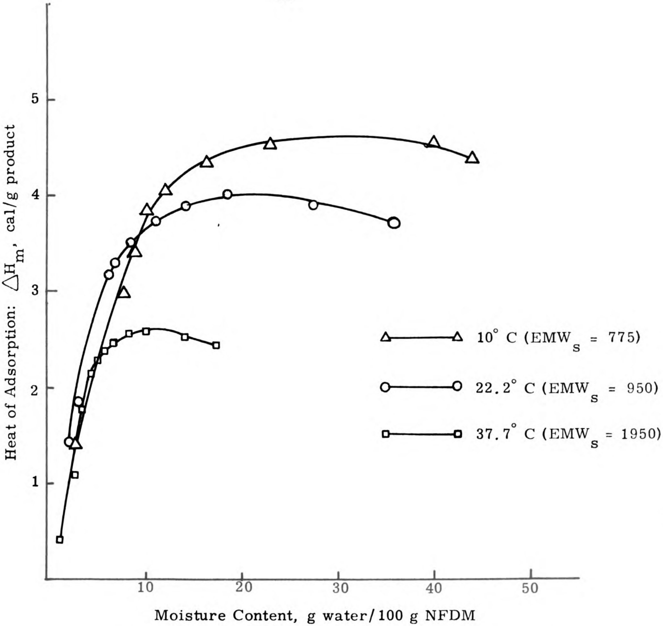

Figure 5-6. --Heat of adsorption values ($\overline{\triangle H_m}$) cal/g product by the proposed method for precooked freeze-dried beef adsorption isotherms (plate temperature 62.8° C.

due to its significant agreement with the BET values and the possible agreement with calorimetric heat of immersion values, is a better estimate of heats of sorption and hence the latent heats of vaporization. This also would mean that the more common methods of measuring the latents of vaporization and heats of sorption are predicting $\overline{\Delta H}_w$ values which are too high. Additional calorimetric investigations are needed to provide clarification of the situation.

At this point it may be worthwhile to closely examine the assumptions of the proposed method and the Clausius-Clapeyron method. Probably the most objectionable assumption of the proposed method would be the use of Raoult's law for the evaluation of the effective molecular weight of the solids in a given food. An outstanding advantage of the proposed method, however, would be the use of non-ideality concept for food products. Reference to the development presented indicates that by setting activity of solids equal to one (dry solids as standard state) and the computation of activity coefficients for solids from the Gibbs-Duhem equation, non-ideality of food systems is accounted for. The use of Raoult's law for computation of effective molecular weight of solids can be justified since the partial heat of mixing or heat of immersion values were in the range of 1-5 calories for most food products. In addition, the close agreement of $\overline{\Delta H}_T$ values by the proposed method and the BET method provides additional evidence. The Clausius-Clapeyron method and the Othmer method assume that the liquid water in a given food system is in equilibrium with its vapor at the temperature of the isotherm. This assumption may be questionable due to the fact that food systems normally have water soluble components present which tend to lower the vapor pressure of the system. In addition, the vapor pressure exerted by the liquid water in the given food system could be lower than the one exerted by the pure water at the same temperature. The integrated form of the Clausius-Clapeyron equation assumes that the $\overline{\Delta H_T}$ is constant over the range of temperature studied. This assumption is somewhat questionable on the basis that the enthalpy change with respect to temperature for food systems may be significant. Finally, the Clausius-Clapeyron equation is applicable to only a reversible process, while the hysteresis commonly associated with biological products suggests that the sorption process for biological products is not strictly reversible.

In case calorimetric investigations indicate that the Clausius-Clapeyron method gives the more correct ($\overline{\Delta H_T}$) predictions, the difference from the proposed method must be attributed to low effective molecular weights used in the computation. Figure 5-7 illustrates the influence of the effective molecular weight (EMW_s) on the heats

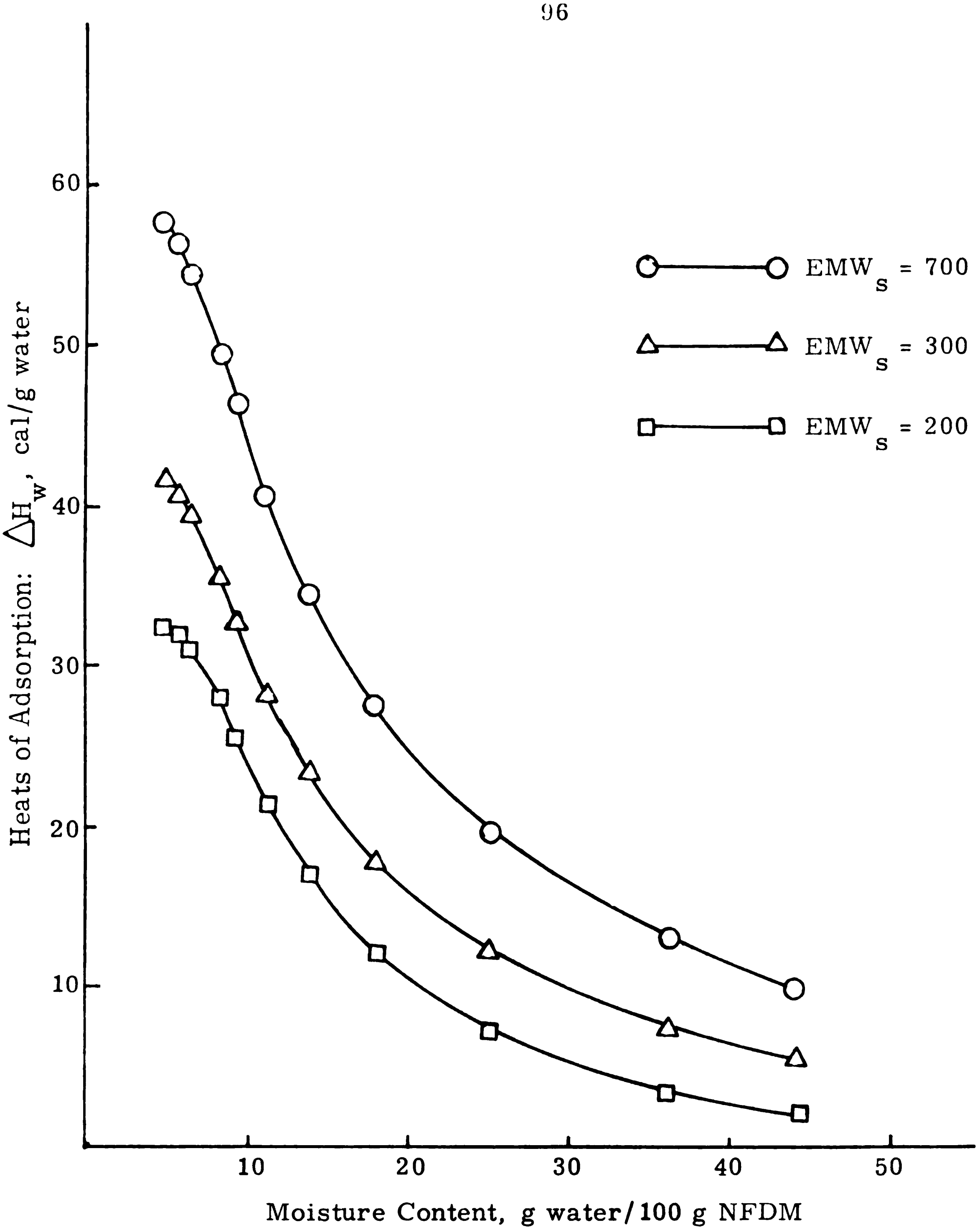

Figure 5-7. --Effect of effective molecular weight of solids (EMW_s) on heats of sorption for adsorption data at 22.2° C of precooked freeze-dried beef (plate temperature 40.6° C).

of sorption $\overline{\triangle H_w}$, expressed as cal/g water for precooked freeze-dried beef isotherm at 22.2° C. As the value of EMW_s was increased, the $\overline{\triangle H_w}$ values increased for a given moisture content. It appears from this discussion that the heats of sorption values obtained by using the proposed method are in good agreement with the calorimetric measurement values (about 1-6 cal/g product). This would also mean that the Raoult's law assumption to compute the effective molecular weight (EMW_s) is a reasonable assumption.

Additional investigations should reveal a more acceptable method of predicting these EMW_s values.

5.7 Applications of the Proposed Method

a. The Effect of Products on Total Enthalpy ($\overline{\triangle H_T}$)

The total enthalpy values ($\overline{\triangle H_T}$) for precooked freeze-dried beef and raw beef were computed by the proposed method from the moisture equilibrium data and plotted versus moisture content (g water/100 g NFDM) as shown in Figure 5-8. The higher values of $\overline{\triangle H_T}$ were obtained for the precooked freeze-dried beef (22.2° C adsorption isotherm). Values from raw freeze-dried beef for adsorption data 20° C gave considerably lower values. Based on these observations, preheat treatments may tend to increase the heats of adsorption.

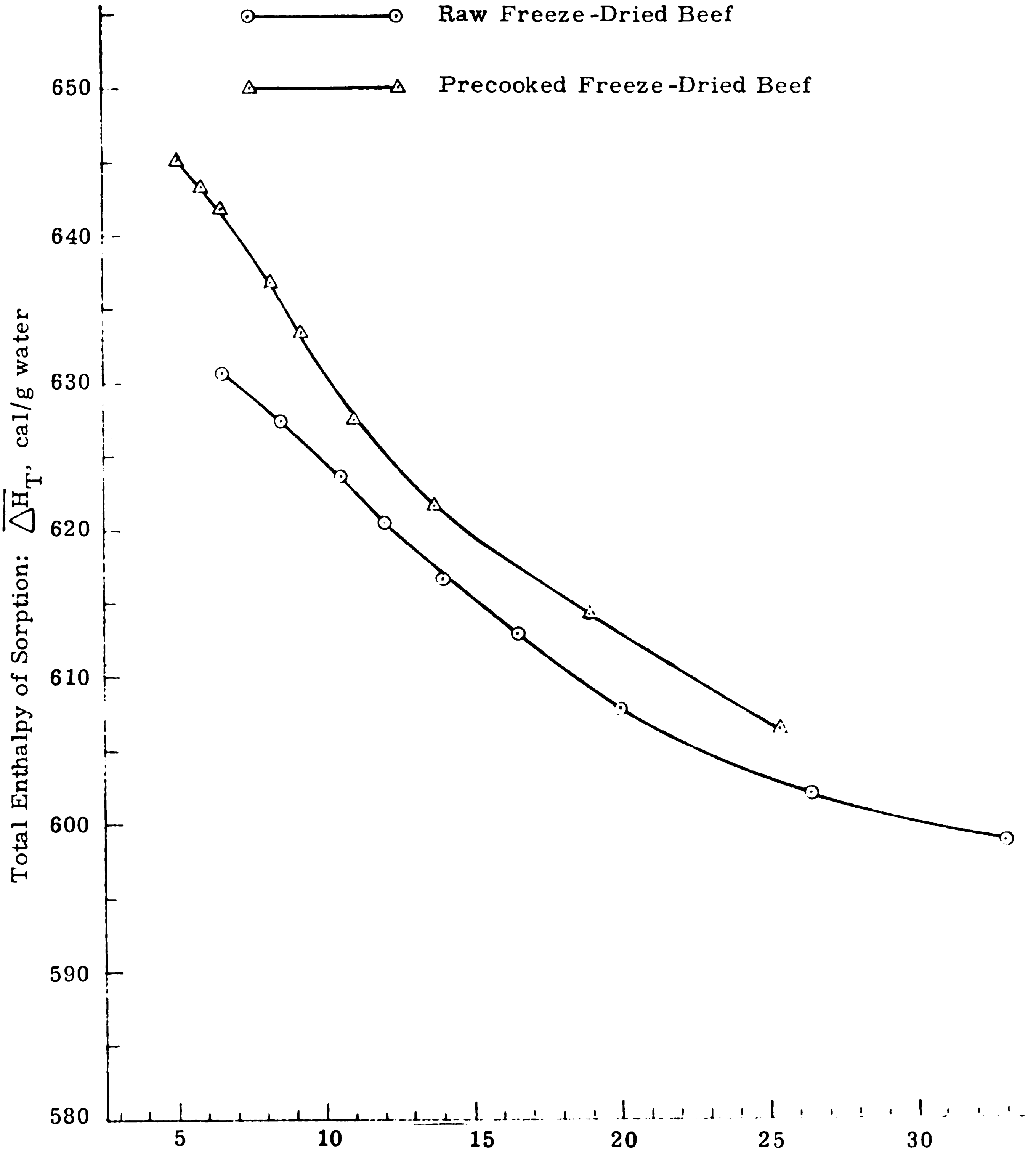

Figure 5-8. --Total enthalpy values of sorption (H_T) for a raw freeze-dried beef adsorption isotherm at 20° C (EMW_s = 1025) and precooked freeze-dried beef adsorption isotherm (plate temperature 40.6° C) at 22.2° C (EMW_s = 775).

b. The Effect of Temperature on Total Enthalpy ($\overline{\Delta H_T}$)

Table 5-3 illustrates the effect of temperature of sorption isotherm on $\overline{\Delta H_T}$ values by the proposed method. $\overline{\Delta H_T}$ values for the raw freeze-dried beef (Saravacos and Stinchfield, 1965) and low heat non-fat dry milk (Heldman et al., 1965) seem to have increased slightly with the increase in sorption temperature. While the $\overline{\Delta H_T}$ values for the precooked freeze-dried beef have decreased with the increase in temperature, this behavior is difficult to explain. It may be recalled that the total enthalpy values ($\overline{\Delta H_T}$) represent a sum of the heat of sorption ($\overline{\Delta H_w}$) and the latent heat of vaporization. The latent heat of vaporization values are 10 to 100 fold higher than the $\overline{\Delta H_w}$ values, depending on moisture content. In addition, the heats of sorption values ($\overline{\Delta H_w}$) do not change significantly from product to product when calculated by using the proposed method.

Figures 5-5 and 5-6 also illustrate the influence of temperature on values of the same product, precooked freeze-dried beef, at two different plate temperatures of freeze drying. As mentioned previously, when the temperature of the isotherm measurement was increased, the $\overline{\Delta H_w}$ values decreased slightly. With the increase in plate temperature of freeze-drying the $\overline{\Delta H_w}$ value was decreased. There is a significant effect of temperature on the shape of the isotherm; at lower isotherm temperature normally the product adsorbs more moisture.

c. Effect of Adsorption and Desorption on Total Enthalpy ($\overline{\Delta H}_T$) Values

In Figure 5-9 heats of sorption values ($\overline{\Delta H}_w$) expressed as cal/g water are plotted versus the moisture content (g water/ 100 g NFDM) utilizing the adsorption and desorption data at 22.2° C for precooked freeze-dried beef (plate temperature 40.6° C). Figure 5-9 revealed, first, as expected, the $\overline{\Delta H}_w$ value decreased as the moisture content was increased for both adsorption and desorption. Secondly, the values of the heats of desorption were slightly higher than the corresponding values of heats of adsorption. This is similar to the common observation that the desorption equilibrium moisture values are higher than the corresponding adsorption equilibrium moisture values. The higher values of heats of desorption than the corresponding values of heats of adsorption may be due to molecular shrinkage occurring during desorption (Chung and Pfost, 1967).

d. Effect of Total Enthalpy ($\overline{\Delta H}_T$) on a Product and Its Components

Figure 5-10 presents the total enthalpy of adsorption ($\overline{\Delta H}_T$) for raw freeze-dried beef, the water insoluble component of beef, and the water soluble component of beef (Palnitkar and Heldman, 1970). The contribution to total enthalpy of adsorption $\overline{\Delta H}_T$ by the water insoluble component of beef was higher than that of the water

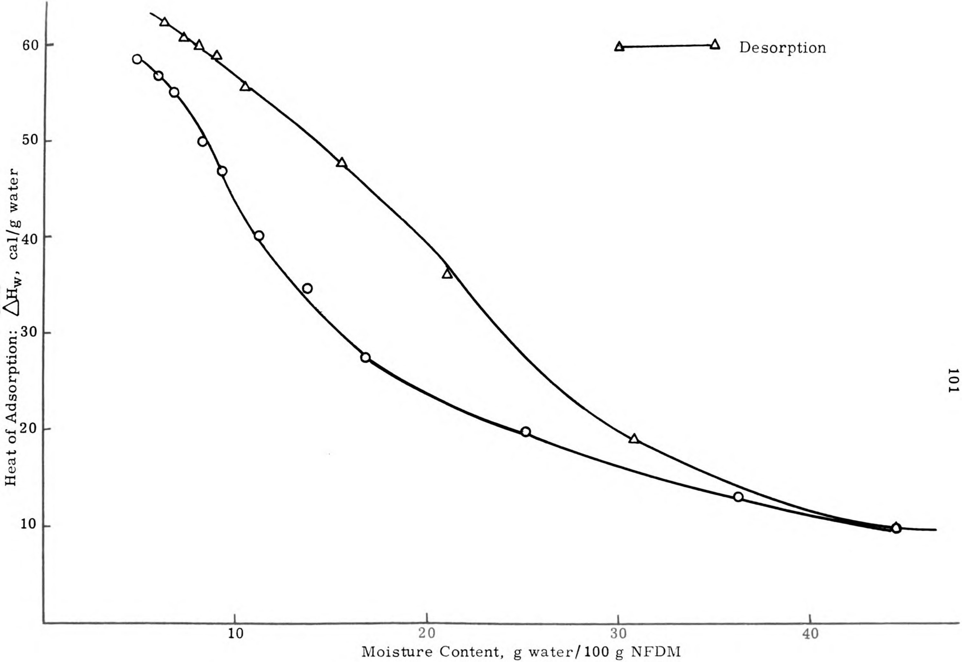

Figure 5-9. --Heat of adsorption and heat of desorption values (cal/g water) for precooked freeze-dried beef at 22.2° C isotherm (plate temperature 40.6° C).

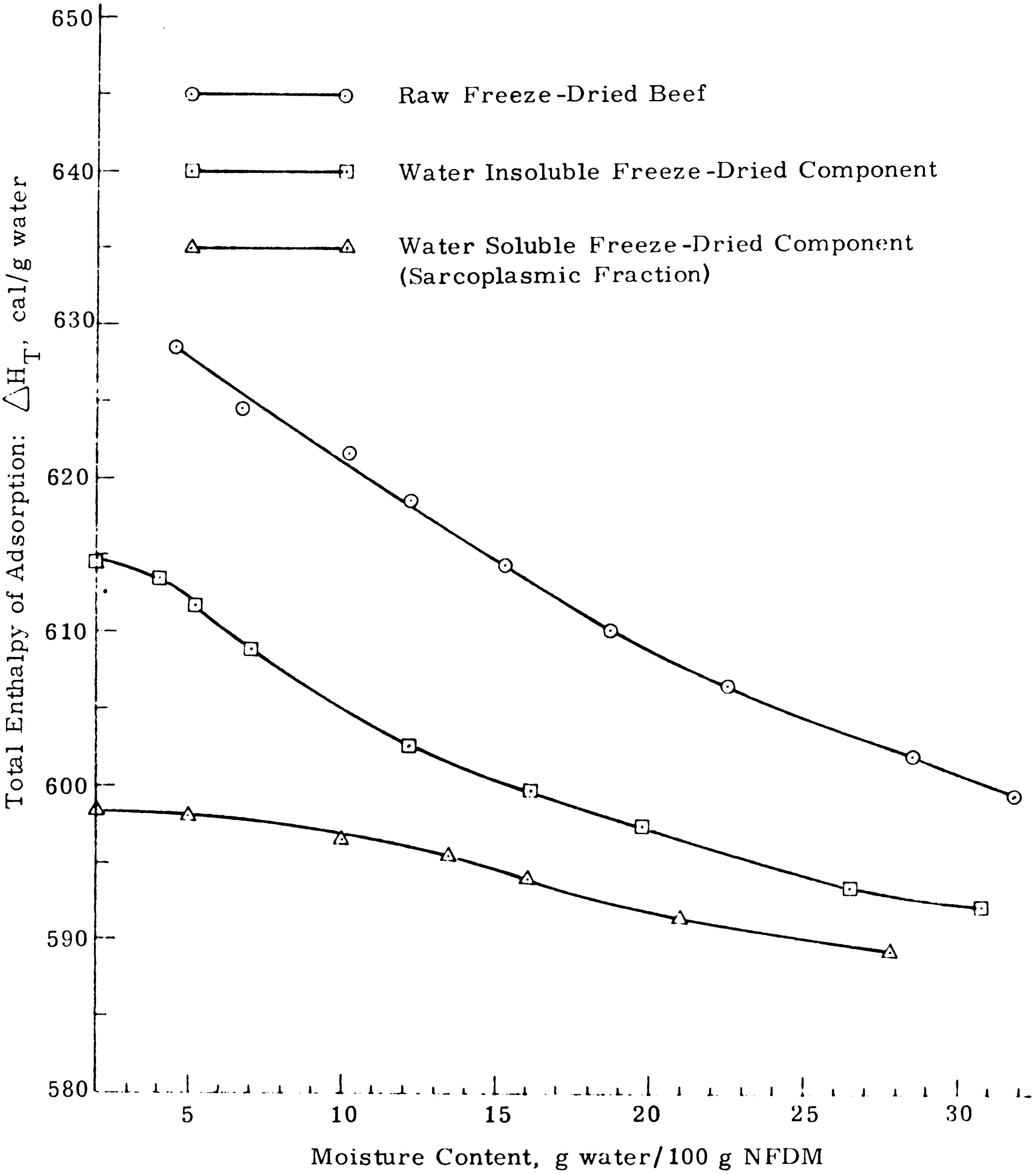

Figure 5-10. --Total enthalpy values of adsorption ($\overline{\triangle H_T}$) at 22.2° C for raw freeze-dried beef (EMW_s = 1100), water soluble freeze-dried component (EMW_s = 1175) and water insoluble freeze-dried component (EMW_s = 1300).

soluble component (Sarcoplasmic fraction) of beef. The $\overline{\Delta H}_T$ values were computed using the proposed method for the adsorption isotherm data at 22.2° C for raw freeze-dried beef, water soluble component and water insoluble component. These results would indicate that a higher proportion of the total heat of adsorption $\overline{\Delta H}_T$ for freeze-dried beef is from the water insoluble component.

Figure 5-11 illustrates the total enthalpy of adsorption ($\overline{\Delta H}_T$) for raw freeze-dried beef, actomyosin, collagen and water soluble component of beef (Palnitkar and Heldman, 1970). The contribution to the total enthalpy of adsorption by collagen was higher than that of the water soluble components and the actomyosin. Collagen represents a portion of water insoluble portion of raw beef and may explain the larger contribution of both water insoluble component and collagen in the total enthalpy value of raw beef. Somewhat higher values of heats of sorption for water insoluble components than the water soluble components may be due to the fact that less energy is required to remove water from solution than solids.

e. Correlation Between Heats of Sorption and Heat Evolved During Sensory Evaluation

A trained taste panel consisting of eight members was asked to evaluate the heat evolved during mastication of beef cubes

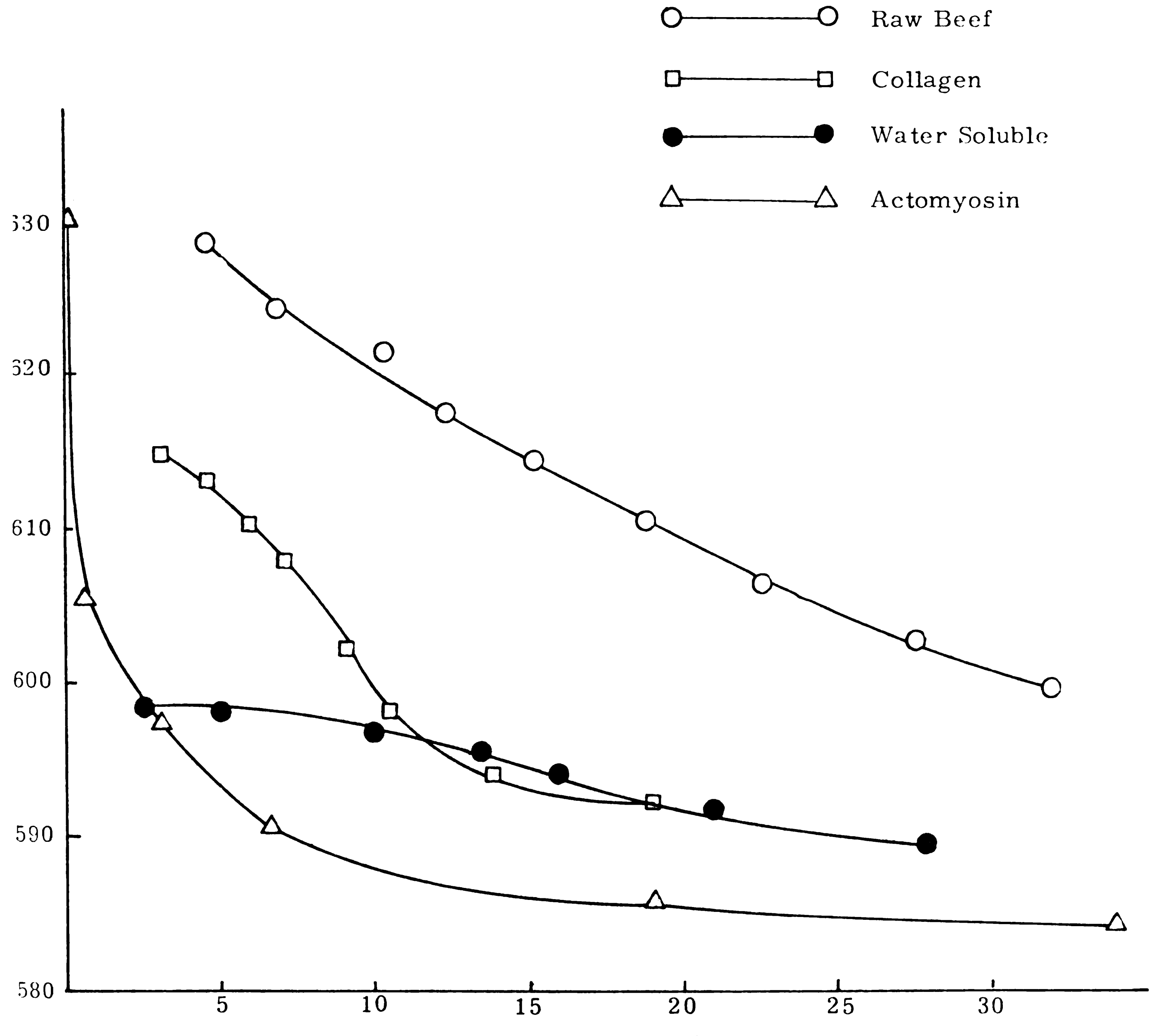

Figure 5-11. --Total enthalpy values of adsorption ($\overline{\Delta H_T}$) at 22.2° C for raw freeze-dried beef (EMW_S = 1100), water soluble freeze-dried component (EMW_S = 1300), freeze-dried collagen (EMW_S = 2000) and freeze-dried actomyosin (EMW_S = 1050).

on a four-point scale from none (1) to evident (4). Table A-1 illustrates the sample score sheet used in the sensory evaluation. The precooked freeze-dried beef cubes were equilibrated to a given conditioning temperature and relative humidity. Four conditioning temperatures and five relative humidity conditions were employed in equilibrating the beef cubes. The panel members reported the heat evolved during mastication of a preconditioned beef cube as heat evolution index. Table A-2 shows the heat evolution index values obtained from the sensory evaluation.

As mentioned previously, the heats of sorption values ($\overline{\Delta H}_w$) were obtained by using the proposed method and the moisture adsorption isotherm data at three different isotherm temperatures for precooked freeze-dried beef. Figures 5-5 and 5-6 illustrate the heats of sorption values for precooked freeze-dried beef powder freeze-dried at 40.6° C and 62.8° C respectively.

Figure 5-12 represents the general trend of the heat of sorption as determined by the proposed method and the heat evolved as sensed by taste panel members. It appears that the heat of sorption and the heat evolved as sensed by a person are indirectly related. The heat of sorption increased with the moisture content up to about 25 percent moisture level and then decreased slightly, while the heat evolved as sensed by the panel members decreased with an increase in moisture content.

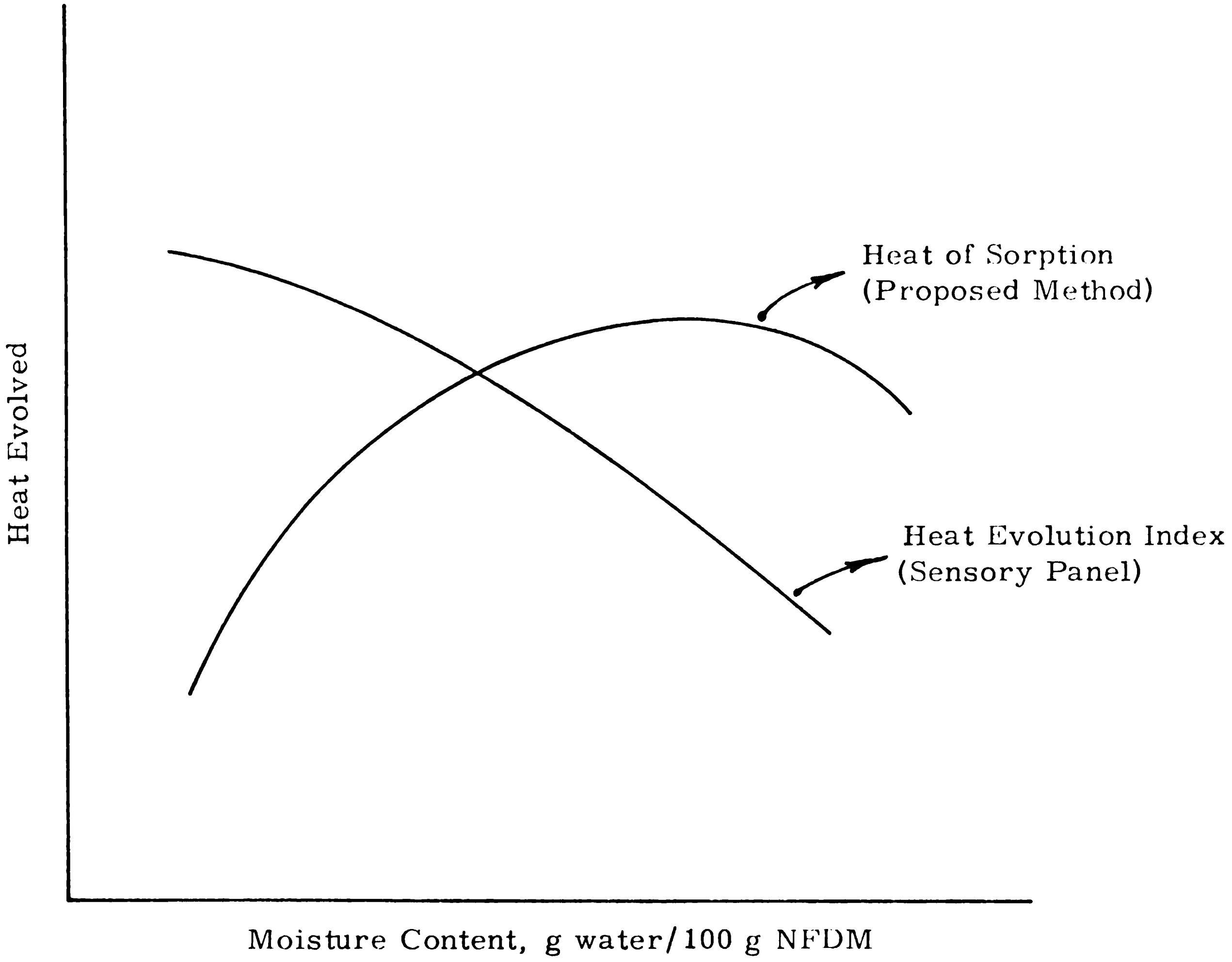

Figure 5-12. --General trends of heat evolved as measured by the sensory panel and the heat of sorption computed from moisture equilibrium isotherm data by the proposed method for precooked freeze-dried beef (plate temperature 40.6° C).

Table A-2 indicated that the heat evolved as sensed by the judges decreased with the increase in equilibrium relative humidity or water activity for all the three conditioning temperatures. The panel members assigned slightly higher value of heat evolved to a dry product (low moisture level) than a wet product. Table A-2 did not show the consistent influence of plate temperature (40.6° C and 62.8° C) used in the freeze-drying of the beef cubes on the heat evolved during mastication of the product. However, the heats of sorption values (cal/g product) calculated by utilizing the proposed method indicated that the values are slightly influenced by the plate temperature used in freeze-drying.

Careful examination of Figure 5-12 revealed that the panel members sense the heat evolved while masticating the beef cubes in a peculiar manner. In order to illustrate this, the heats of immersion values (heats of sorption) obtained by the proposed method were plotted as difference in the maximum heat of immersion (which occurred at some intermediate moisture value) and the heats of immersion values at various moisture levels versus the equilibrium relative humidity. In addition to the differences in the heats of immersion, the heat evolved as sensed by the panel members was also plotted against the equilibrium relative humidity in the same Figure 5-13.

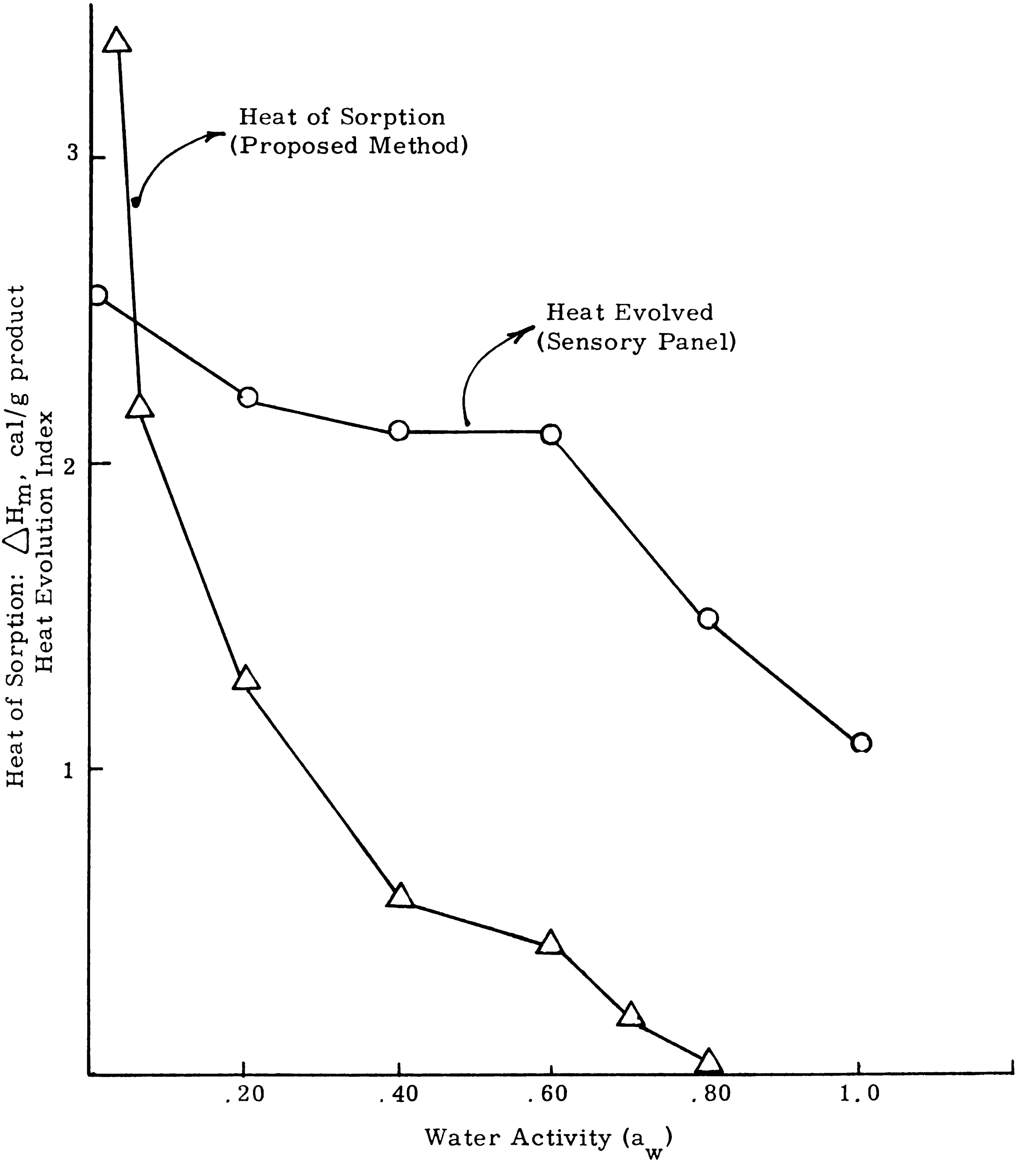

Figure 5-13. --Correlation between the difference in heat of sorption from moisture sorption data as calculated by the proposed method and the heat evolution index from the sensory panel for precooked freeze-dried beef (plate temperature 40.6° C).

Figure 5-13 indicated that there seems to be a similar relation between the heats of immersion values expressed as differences and the manner in which the judges sensed the heat evolved during mastication of beef cubes. It seems that the panel members sensed the heat evolved as difference in taking preconditioned beef cube from its initial conditions (temperature and water activity) to some optimum condition existing in their mouth before swallowing the sample. This results in the panel members reporting higher amounts of heat evolved for a dry beef cube and somewhat lower values of heat evolved for the wet beef cubes. It should be pointed out that the judges experienced difficulties in judging the small differences in heat evolved during mastication of the beef cubes. Also, the heats of sorption values were based on the powder form of the product and were expressed as cal/g product while the heat evolved as sensed by the panel members was based on the beef sample in the form of cubes, the weight of which was dependent upon the conditioning temperature and relative humidity at which it was equilibrated.

VI. SUMMARY AND CONCLUSIONS

A. Even though thermodynamics provides only macroscopic description of the moisture sorption phenomena, it provides a basic explanation of various energy levels with which water associates with the biological substance. The Gibbs-Duhem equation allows the determination of energy contribution due to solids portion of a food (adsorbent). Thermodynamic energy parameters, when expressed on the basis of product weight, become important in explaining the thermodynamic stability of a given food system. One of the most important criterion of the thermodynamic stability of a system is the state of the system at which the entropy function is maximum. Various food systems tend to show an entropy maxima at some intermediate moisture level.

The following conclusions become evident based on a portion of the investigation.

1. Total entropy values for various food systems expressed in terms of product weight become maximum at some intermediate moisture value. The state of the system

(moisture content of the food) at which entropy becomes maximum represent a thermodynamically stable condition (optimum moisture content). This observation supports the concept that an optimum moisture value for a food occurs at some intermediate moisture value.

2. The moisture level at which entropy reaches maximum is close to the BET monomolecular moisture (M_1). Secondly, this moisture value is in close agreement with the Rockland's (1969) local isotherms L I and L II intersection.
3. Thermodynamic quantities for a food expressed on the basis of the weight of the product are more important than the ones expressed on the basis of weight of water or weight of solids.

The total energy parameter for a food can be divided into two, contribution due to solids portion (adsorbent) and the corresponding energy contribution due to water portion (adsorbate).

B. A procedure was developed to predict the thermodynamic parameters of a food system using the moisture equilibrium data at one temperature. In developing this procedure the non-idealities existing in the food system were considered and the solids portion of a food was assigned an effective molecular weight.

Based on the results of this portion of the investigation, several conclusions related to thermodynamic properties of a food system become evident.

1. A procedure developed from thermodynamic basis allows the prediction of heats of sorption in food systems with reasonable accuracy and requires equilibrium moisture data at only one temperature.
2. The magnitude of the heats of sorption values are dependent upon the basis used for the expression (water, solids or product).
3. Heat of adsorption values predicted by the proposed method seem to be in close agreement with heat of immersion values expected for the product.
4. Heats of adsorption values predicted by the proposed method are in good agreement with the heats of adsorption value at the monomolecular moisture value computed by the BET method (Brunauer *et al.*, 1938).
5. Precooking or preheating of food before drying may increase heat of sorption.
6. Water insoluble components of freeze-dried beef seem to contribute more significantly to heats of sorption of the product than the water soluble component.

7. Heat evolved as sensed by sensory panel members did not change significantly with the plate temperature used for precooked freeze-dried beef. However, the heats of sorption as computed by the proposed method were slightly higher at lower freeze-drying temperatures of the product.
8. A direct relationship between the difference in heats of immersion values at two different moisture contents and the evolved heat sensed by sensory panel members when preparing the product for swallowing.

VII. SUGGESTIONS FOR FUTURE WORK

This investigation revealed that there are several areas which need further investigation.

1. There is a pressing need for a suitable method which can accurately determine the moisture equilibrium isotherms in a short period of time. The aspect of time is very critical for the biological products, which undergo several physicochemical changes with respect to time.
2. There is almost complete absence of reliable experimental data on calorimetric values for the biological products. Accurate calorimetric values can furnish additional information on the various energy levels with which water associates with the biological products.
3. Raoult's law was used in this investigation in establishing effective molecular weight of biological substances. Further investigations are needed to determine whether the effective molecular weight of a biological substance should be constant over the entire moisture range or whether the effective molecular weight changes with a parameter such

as moisture content. Alternate approaches of establishing effective molecular weight should be investigated.

4. Differential thermal analysis techniques could furnish important information about the energetics of water in biological substances. Further investigations in this area are desirable.

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APPENDIX

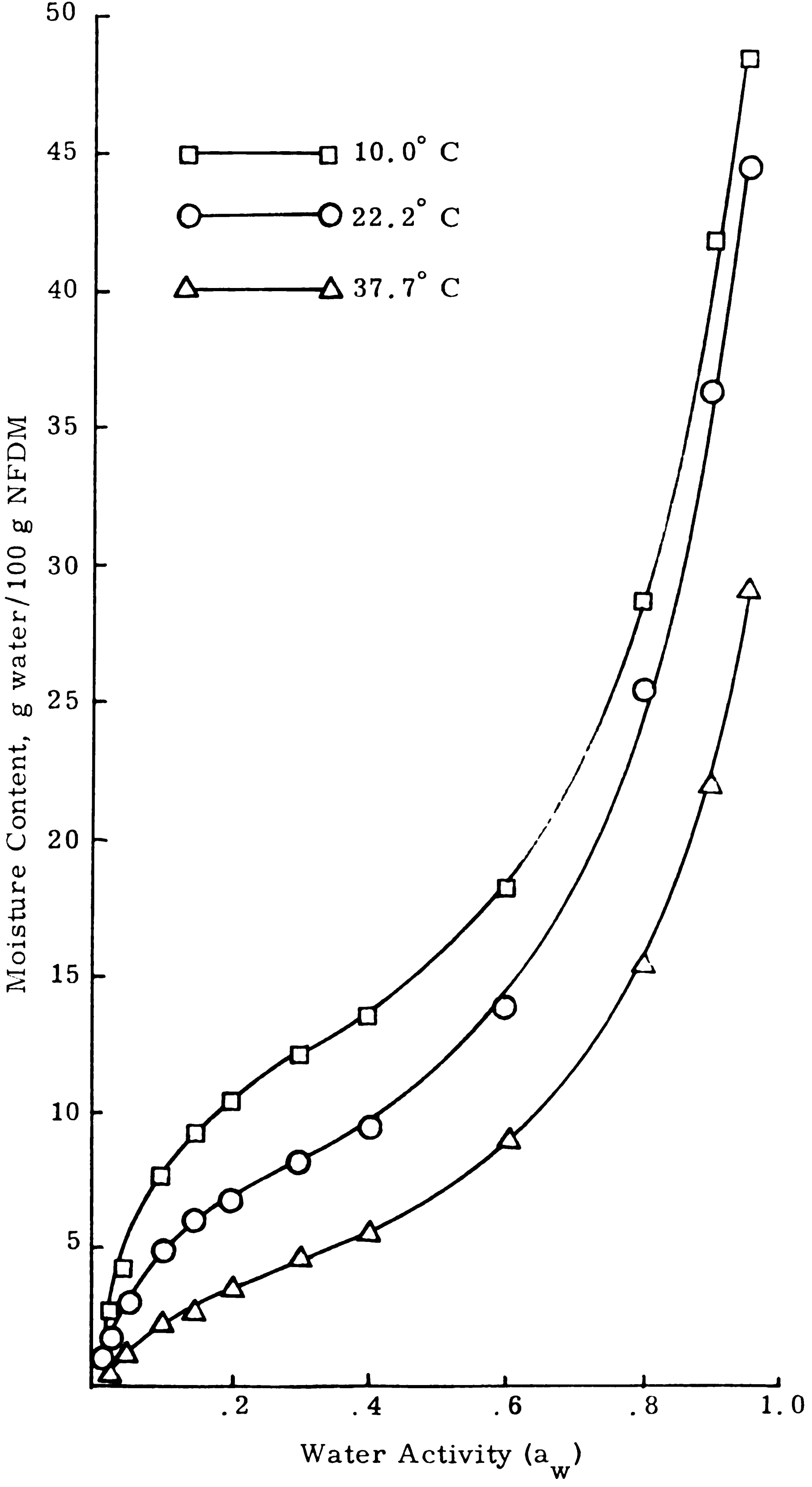

Figure A-1. --Adsorption isotherm for precooked beef powder freeze-dried at 40.6° C plate temperature.

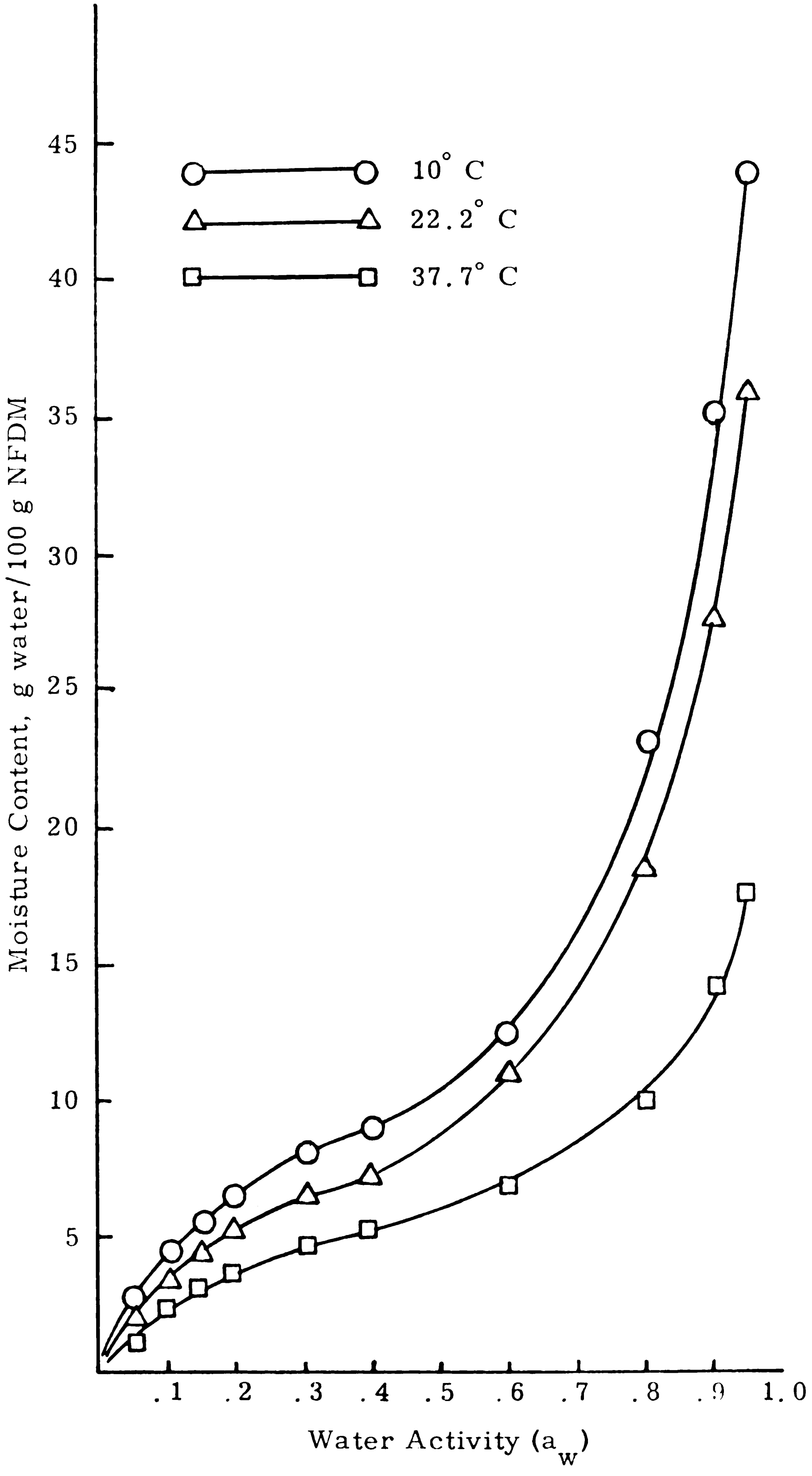

Figure A-2. --Adsorption isotherms for precooked beef powder freeze-dried at 62.8° C plate temperature.

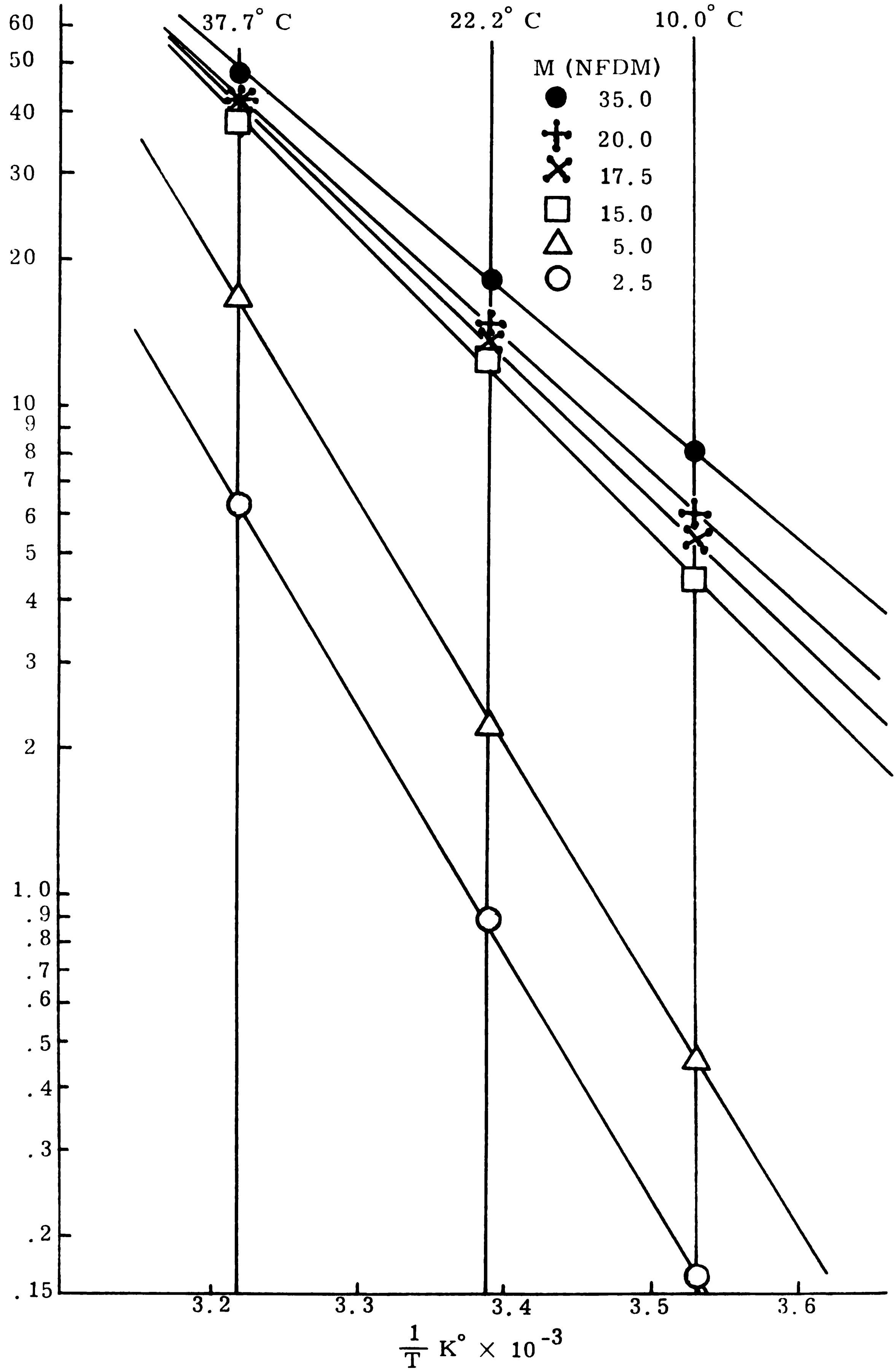

Figure A-3. --Adsorption isosteres for precooked beef freeze-dried at 40.6° C plate temperature.

Table A-1. --Sample score sheet used to evaluate heat evolved while chewing a sample.

Name Date

Instructions:

A. While chewing the sample, try to sense an increase in temperature in the mouth (on tongue or palate).

B. Use the four-point scale on the score sheet to indicate your evaluation.

Heat evolved:	I	II	III	IV
1. None				
2.				
3.				
4. Evident				

Comments:

Table A-2. --Heat evolution index values obtained from sensory panel.

Temp. (° C)	0%	20%	40%	60%	80%	100%
Plate Temperature 40.6° C						
10	2.9	2.4	1.8	1.4	1.0	1.1
22.2	2.55	2.21	2.10	2.1	1.5	1.10
37.7	2.4	2.21	2.2	2.3	1.38	1.0
Plate Temperature 62.8° C						
10	2.36	2.58	2.1	1.2	1.0	1.0
22.2	2.9	2.5	2.417	2.2	2.3	1.0
37.7	2.8	2.68	2.35	2.2	1.8	1.0