

THERMODYNAMICS IN FOOD ENGINEERING

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Summary

In many situations where manufacturing processes are present, as in those frequently found in food processing, or in everyday life situations, a series of energy exchanges occur between systems that entail thermal effects. These exchanges tend to alter the components involved, causing the cooling or heating of such, or generating or stopping of any reaction. These alterations or changes can be described in macroscopic form through the basic concepts of thermodynamics, defined as the area of science concerning energy exchanges among the components of a system or between a system and its surroundings. However, it is important to distinguish two sub-areas within the traditional concept of thermodynamics: thermophysics and chemical thermodynamics. The former area studies the modification of situations in which no changes exist in the chemical structure of the participants during energy exchanges, whereas chemical thermodynamics studies processes presenting structural changes due to chemical reactions. Knowledge of concepts, such as enthalpy, entropy, free energy, equilibrium, etc., is required in describing the thermal treatment and cooling processes in foods, functioning of equipment employed in such processes, characteristics of deterioration or preservation reactions presented in foods, and many other factors that appear in food engineering. These concepts form part of the basis of thermodynamics and will be presented next.

1. Introduction

The Industrial Revolution resulted in the development of a series of devices and machines, for example, the steam engine, internal combustion engine, and electrical engine. However, for many years the principles on which their functioning was based were not recognized. Thermodynamics surged in the middle of a search for solutions to problems present in the design of thermal machines. It is a branch of science related to energy exchange among the components of a system or between a system and its surroundings.

Thermodynamics can be treated purely from the macroscopic point of view through established laws described in terms of system properties that can be macroscopically measured. This has been traditionally called classical thermodynamics. Another view of thermodynamics is based on the derivation of macroscopic behavior of the material through statistical analysis of the properties of atoms and molecules, generating what is known as statistical thermodynamics.

When the thermal effects of an energy exchange between a system and its surroundings are studied, there is a possibility no changes will be generated in the chemical structure of the system. It is here the concepts of the thermodynamics branch, denominated as physical thermodynamics or thermophysics, are applied. On the other hand, when the above mentioned changes do appear, processes are described by chemical thermodynamics.

Nevertheless, thermodynamics can be studied according to some fundamental laws. For example, the first law of thermodynamics allows the determination of how much energy exists in carbon, wood, steam, food, etc. The second law of thermodynamics deals with

the determination of how efficiently one form of energy can be transformed into another. It also determines which changes are possible or not. The combination of these laws leads to relationships that state how much work can be obtained under a given condition.

Additionally, the so-called zero law and third law are useful, the former, to understand temperature measurement concepts, and the latter, to make thermodynamics participate in the analysis of reactions.

Thermodynamics is the most powerful tool available to study natural phenomena. Many of the devices and systems used and controlled today by man base their functioning on the concepts contained in this science.

Thermodynamics is directly related to the field of transport of phenomena disciplines, as in heat and material transfer. Thermodynamics plays a very important role in food engineering, for example, in the selection of the type of refrigerant used in a cooling system, in the humidity control of air, or in the final moisture content of a product. Many phase changes that appear during the processing or storage of food can be described through the principles of thermodynamics. Also, the heat requisites of a heat exchanger employed in pasteurization processes or the equilibrium composition of a multicomponent mixture being separated can be determined through thermodynamic analysis. Furthermore, it is possible to determine the degradation rate of a nutrient with the aid of chemical kinetics. These are some of the examples highlighting the importance of thermodynamics in food processing.

The purpose of this discussion is to present, in a concise form, thermodynamic concepts and functions that serve as background for the study and comprehension of food engineering processes.

2. Thermophysics

2.1. Thermodynamic Concepts

2.1.1. System

A thermodynamic system is that part of the physical universe under consideration. A system is separated from the rest of the universe by limits or boundaries that can be physical or imaginary. Any region outside the system's limits is called surroundings. Thermodynamic systems are subjected to processes that imply material and/or energy exchanges with its surroundings. An open system exchanges mass and energy with its surroundings, as in food dehydration in a hot air dryer. In this process a clear heat flow moves from air to food and a mass flow (mainly water vapor) from food to air. On the other hand, a closed system only exchanges energy, keeping its mass constant, which in food engineering can be exemplified by a hermetically packed food subjected to sterilization or a cooling process. A system that does not exchange material or energy with its surroundings constitutes an isolated system, which from a practical point of view is rarely useful. A special case involving open systems is one in which there is a permanent or steady state flow. In this case, mass enters and leaves the system at the

same rate, such that the mass contained within the limits is constant at all times. A system is considered homogeneous if all of its properties are uniform at any point. Usually this is a one-phase system. A system with more than one phase is called heterogeneous. Practically all foods, whether subjected or not to a preservation process, are included within the last category.

2.1.2. System Variables

A system's thermodynamic variable or property is one of its defining characteristics. The properties are extensive if their magnitude is directly proportional to the system size, as are mass, volume, internal energy, enthalpy, entropy, etc. On the other hand, the properties are intensive when their magnitude is independent of size, as are temperature and pressure. The relationship between two extensive variables yields an intensive variable. For example, density is the relationship between the mass and volume of the system. The state of a system describes its condition. The values of the properties are used to characterize the system's state, and it is important to note that those properties only depending on the system's state, not on the way in which the system reached such a state, are denominated as state variables or state properties. Pressure (P), volume (V), and temperature (T) of a system, and many expressions of its energetic content are state variables. However, heat and work are not state variables, since they depend specifically on the way in which change from one state to another occurs. Any equation that relates state variables is a state equation, and it is important to note that few state variables are enough to define other variables. The most common variables present in a state equation are P, V, and T.

2.1.3. State Equations for Ideal Gases

In the case of gaseous systems, volume noticeably changes as a function of temperature and pressure. However, this variation is almost independent of the gas. Thus, to describe the relationship of the mentioned variables, an approximate state equation that describes the behavior of all gases has been proposed. This equation is known as the ideal or perfect gas equation, and is expressed as

$$PV = nRT \quad (1)$$

In this equation, R is the general constant of gases and n the number of moles of gas.

When a determined quantity (n moles) of gas that behaves according to Equation (1), is subjected to a process where volume, temperature, or pressure change is present, and because the product nR is a constant, it follows that

$$\frac{PV}{T} = constant \quad (2)$$

Therefore, when the initial conditions of a gas (T_1 , P_1 , and V_1) are known, the gas properties under other conditions are as follows:

$$\frac{PV}{T} = \frac{P_1V_1}{T_1} \quad (3)$$

The ideal conditions presented in Equations (1) and (3) are used to describe the behavior of gases at conditions near those of the environment, which occurs in many food preservation processes or during its packaging. For this reason, such expressions can be very useful to Food Engineers.

However, when temperature and pressure conditions deviate from environmental conditions, the gases tend to deviate from the ideal, thus they are called real gases. A state equation used to describe this behavior is one by Van der Waal, and is expressed as

$$\left[P + \left(\frac{n^2 a}{V^2} \right) \right] (V - nb) = nRT \quad (4)$$

In this equation, a and b are constants that characterize each gas. Equations (1) and (4) are applied only to systems containing one component. For gas mixtures, the state equation depends on the concentration of each component. For perfect gases, the mixture equations are simple; thus, if gases do not react chemically in the mixture, the partial pressure of a component (i) becomes

$$P_i = \frac{n_i RT}{V} \quad (5)$$

The total pressure of the mixture is the sum of partial pressures, so

$$P_{total} = \sum P_i = \frac{n_{total} RT}{V} \quad (6)$$

The partial pressure can be obtained from the total pressure and the molar fraction (X_i) of each component as follows:

$$P_i = X_i P_{total} \quad (7)$$

$$X_i = \frac{n_i}{\sum n_i} \quad (8)$$

In some food preservation processes (humidification, controlled atmospheres, etc.) the partial pressure is useful, since it is interesting to know the individual behavior of each component in a mixture.

2.1.4. Thermodynamic Variables

The energy participating in thermodynamic transformations is expressed in terms of heat (Q) and work (W). Q is the energy passing across the limits of a system due to a temperature difference between the system and its surroundings, and W is the energy

transfer associated with a force that is applied to the system along a distance. Internal energy (U) is a concept used to define the system energy not associated with work or heat, and is usually defined as an addition to all microscopic energy forms in the system. This type of energy is related to the structure and degree of molecular activity, and can be seen as the sum of kinetics and potential energies of the molecules. Entropy (S) is a variable that measures the number of possibilities or options for the system. The mathematical relationship between these thermodynamic variables allows the expression of the first and second law of thermodynamics.

2.1.5. Thermodynamic Transformations

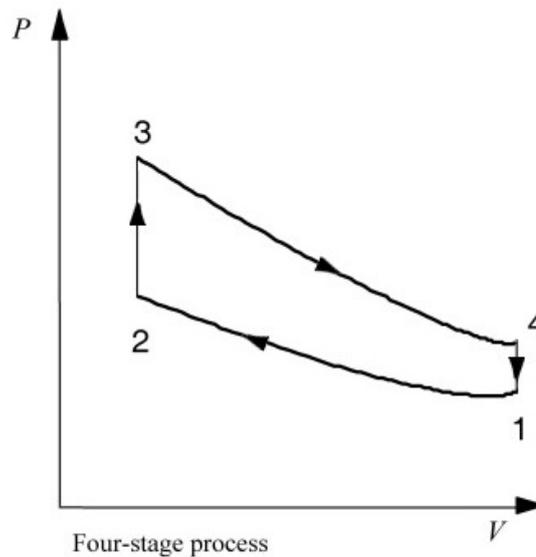
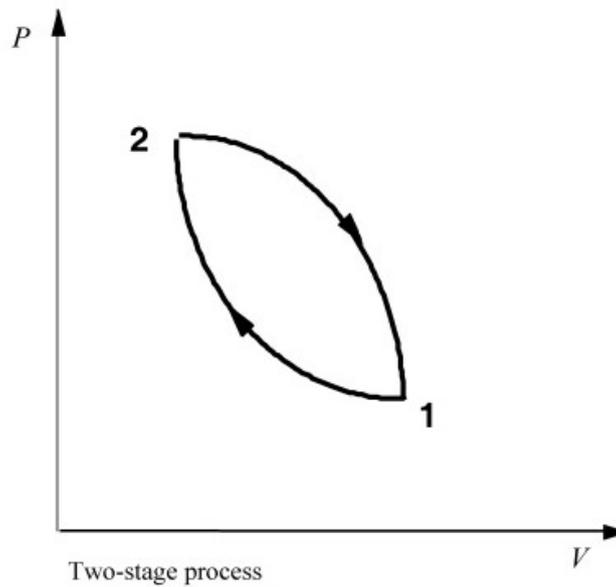


Figure 1: Two thermodynamics cycles.

Whenever a system changes from one thermodynamic state to another, a process occurs. When a system returns to its initial state after experiencing a consecutive series of processes, it is said to have described a thermodynamic cycle. Figure 1 shows two thermodynamic cycles, in which the variables changing in the system are pressure and volume. In this way, a process is called isocoric when the volume of the system remains constant ($\Delta V = 0$), which in Figure 1 is represented by stages 2 to 3 and 4 to 1 in the four-stage cycle. On the other hand, the process is called isothermal when the temperature of the system remains constant ($\Delta T = 0$), and isobaric when the process occurs at constant pressure ($\Delta P = 0$). Additionally, if the process does not give place to thermal interactions, it is denominated as adiabatic ($Q = 0$). Finally, it is said that a system reaches a thermodynamic equilibrium state when its thermodynamic properties remain invariable over time. This equilibrium condition is difficult to reach in many food systems, whether fresh or processed. However, for practical purposes, such equilibrium is usually considered in the design of processing systems or in the selection of storage conditions.

2.2. Zero Law of Thermodynamics

It is traditional to discuss the three fundamental laws of thermodynamics. However, the so-called zero law exists, which was formulated by R. H Fowler in 1931, and although obvious, it is essential in describing thermal equilibrium concepts.

Thus, when a body contacts another body with different temperature, heat from the one having the highest temperature is transferred to the one with the lowest, until both reach the same temperature. Heat transfer stops at this point and it is said that both have reached thermal equilibrium. Thus, it can be understood that temperature equality is the only requirement for thermal equilibrium. In this way, the zero law of thermodynamics states that if two bodies are in thermal equilibrium with a third body, they are in equilibrium with each other. These simple concepts, which are not considered in other thermodynamic laws, are the basis behind temperature measurement systems and a fundamental principle in many food preservation processes in which heat is transferred from or to the food, as in pasteurization, refrigeration, and freezing.

2.3. Thermodynamic Equilibrium

As mentioned in section 2.1.2., a chemical or food system can be macroscopically described according to a set of thermodynamic variables, which can be considered coordinates that define the system's state. When these coordinates are modified for some circumstance, whether spontaneously or due to external actions, it is said that the system experiences a state change. It is important to note that these alterations do not represent phase changes (solid to liquid, liquid to gas, etc.).

Usually, when the state of a system is modified interactions between the system and its surroundings take place, which can originate mechanical, chemical, or thermal non-equilibrium conditions.

If a lack of equilibrium of forces does not exist inside a system, including between the system and its environment, it is said that the system is under a mechanical equilibrium

state. When these conditions are not complied with, whether in the system alone or the system and its surroundings, the system experiences a state change, which will only stop when the mechanical equilibrium is reached again.

On the other hand, if a system under mechanical equilibrium tends not to experience spontaneous change in its internal structure, as a chemical reaction or mass transfer from one part of the system to another (e.g., diffusion or solution), although it can be slow (as happens in many processed foods), it is said to be under a chemical equilibrium state.

A system not under chemical equilibrium suffers a state change, which in some cases is very slow. Change stops when chemical equilibrium is reached again.

The possibility of thermal equilibrium and its importance in food processing was commented on in section 2.2. However, it is important to understand that in this type of equilibrium the entire system has the same temperature, which is equal to that of the environment.

When conditions are met for the three types of equilibrium, mechanical, chemical, and thermal, the system is said to present thermodynamic equilibrium, and under these conditions will not exhibit a tendency toward change of state, neither in the system nor in the surroundings.

Thus, thermodynamic equilibrium states can be described in terms of macroscopic coordinates, without time intervention, meaning as a function of thermodynamic variables.

Classic thermodynamics does not deal with problems in which the velocity of the process intervenes. Investigation of such problems is performed through other science branches (chemical kinetics, hydrodynamics, and kinetics theory of gases, among others) that, when related to thermodynamics, are essential to understanding the many changes and reactions that occur in foods during handling and processing.

A process that tends to drive a system not in equilibrium to an equilibrium state is called an irreversible or natural process. Irreversible modifications are the only changes that occur in reality, which justifies their alternate name (natural changes).

In an isolated system, the original state cannot be re-established after a natural change, while in a non-isolated system the original state can be restored, but only through an irreversible change in some other system.

If change occurs in such way that the system remains in equilibrium, it will be carried out in an extremely slow manner and will be capable of generating the maximum work quantity. This idealized process is called reversible change. On the other hand, as demonstrated in section 2.7., a system absorbs the maximum quantity of heat from its surroundings and gives the maximum quantity of work to the environment during a reversible change. A natural process absorbs less heat and makes less work than does a reversible process.

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Biographical Sketches

Jorge Welti-Chanes was born in Puebla City, Mexico; he obtained his B.S. in Biochemical Engineering (1976) and Master of Science in Food Engineering (1979) at the Instituto Tecnológico y de Estudios Superiores de Monterrey (ITESM) in his birth country. In 1979 he moved to Spain to obtain a Ph.D. degree in Chemical Sciences, with a major in Food Technology, from the Universidad de Valencia. He has been professor at the ITESM and, since 1977, the University of the Américas-Puebla (UDLA). At UDLA, he has taught at undergraduate and graduate levels in the Departments of Chemical and Food Engineering and Chemistry and Biology. He was Head of the department for one year, and then Dean of the Engineering School (1986-1988). He was Academic Vice-President of UDLA (1988-2002) and currently is Professor and Researcher at the last institution and Visiting Research Scholar at Texas Christian University. His research areas are focused mainly on food and biological polymers, candy technology food drying, water activity, minimal processing of foods and biological materials, process simulation, and emerging technologies. He has been coordinator of diverse international research projects and advisor for different industries within the mentioned research areas. He was the World President of the International Association of Food and Engineering (1997-2000). Dr. Welti-Chanes is author of more than 140 scientific publications in refereed journals and books, and more than 150 presentations at international meetings. He is author or coeditor of the books: *Food Preservation by Moisture Control*, *Inventario de Alimentos de Humedad Intermedia Tradicionales de Iberoamérica*, *Engineering and Food for the 21st Century*, *Transport Phenomena in Food Engineering*, and *Harvesting, Handling, and Preservation of Fruits and Vegetables by Combined Methods at Rural and Village Levels (Technical Manual of FAO)*. He is a member on the Editorial Boards of different journals and book-series, and

evaluator of research projects in Argentina, Chile, Uruguay, Venezuela, Mexico, and USA. He is advisor for different food enterprises in areas such as processing, quality assurance, and process optimization. Also, he has advised different universities in Mexico and Latin-America in Strategic Planning of Educational Processes.

Fidel T. Vergara-Balderas was born in Puebla City, Mexico; he obtained his B.S. in Food Engineering (1977) from the Universidad de las Américas A.C. (Mexico) and Master of Food Science (1980) from the Instituto Tecnológico y de Estudios Superiores de Monterrey, ITESM (Mexico). He was professor at ITESM, and since 1981, he has been professor and researcher at the Universidad de las Américas, Puebla (Mexico) where he teaches several courses in the Department of Chemical and Food Engineering. He was head of this department for 3 years (1996-1999). He is co-author of several scientific publications and presentations, and has offered consulting services and courses within the Food Industry in Mexico.

Luis Gabriel Ríos Casas was born in Mexico. He obtained a B.S. in Chemical Engineering from the Universidad Iberoamericana (1974, Mexico City) and a M.S. in Chemical Engineering from the Universidad de las Américas-Puebla (1992). Professor Ríos worked at the Instituto Mexicano del Petróleo from 1973 to 1980; in his last position as head of the area for Equipment Design by Computer, he developed important projects such as The General Process Simulator of the IMP (SIMPROC), Systematic Methods for Process Synthesis and Optimization for Chemical and Petrochemical Process, and Synthesis Optimal for the Auxiliary Services Plant. At the same time, Professor Ríos taught different courses related to Chemical Engineering at the Universidad Iberoamericana, ENEP-Cuautitlán, and the Universidad La Salle. He has advised some industries such as Ciba Geigy Mexicana (1991 and 1992) and Bendix-Pemsa (1986). He has been Associate Professor of the Department of Chemical and Food Engineering at the Universidad de las Américas-Puebla (UDLA) since 1981. His interests are focused on physicochemistry, thermodynamics, process engineering, and simulation of chemical processes. He has advised around 50 undergraduate theses, given several conferences at national and international congresses, and published papers in refereed journals and other periodic publications. At the present, he heads two important research projects at the UDLA: Solar Energy and Development of Software for Chemical Engineering.

Aurora Valdez Fragoso received her B.S. in Food Engineering from the Universidad Autónoma de Chihuahua in 1984, and her Master in Sciences in Food Engineering from the Universidad de las Américas-Puebla, México. She received her doctorate from the Ecole Nationale Supérieure des Industries AgroAlimentaires-Massy, France. She served at several public universities in Mexico before joining the staff of the Facultad de Ciencias Químicas at the Universidad Autónoma de Chihuahua. She has been involved in educational, research, and science diffusion activities for more than 12 years. Professor Valdez Fragoso has taught courses in biochemistry, food chemistry, and technology of fruits and vegetables to both undergraduate and graduate students. Areas of focus include food physical properties, food processing (especially minimally processing), and biochemistry of foods. She is author and co-author of many chapters and journal articles on food process engineering. Dr. Valdez Fragoso is a member of the Institute of Food Technologists and the American Institute of Chemical Engineers.

Hugo Mújica Paz received his Bachelor degree in Chemical Engineering from the Instituto Politécnico Nacional (México) and Master and Doctorate degrees in Food Engineering from the Universidad de las Américas-Puebla (México) and the Institute National Polytechnique de Toulouse (France), respectively. Dr. Mújica Paz began teaching chemical engineering at the Universidad de Nayarit (México) in 1985. Since then, he has been involved in higher education in his country, lecturing on topics in unit operations of food engineering, chemical reaction engineering, food technology, etc. Currently, Dr. Mújica Paz is a faculty member at the Universidad Autónoma de Chihuahua. Professor Mújica's research interest has been in mass transport phenomena in foods, food packaging, and minimal processing of fruits and vegetables. He has contributed to 9 chapters and has published several papers in these areas. He is a member of the Institute of Food Technologists and the American Institute of Chemical Engineers. He has presented several lectures at national and international meetings. He is fluent in Spanish and French and has some conversation ability in English and Italian.