

# Mathematical Model to Elaborate the Table of Thermodynamic Properties

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## Abstract

**Purpose:** The aim of this scientific contribution is to show the potential that integral calculus has offered to the analysis of thermodynamic processes.

**Method:** Application of Integral Calculus. In this context, the document covers the theoretical principles of integral calculus, such as Theoretical framework and background, Geometric interpretation of the primitive, Primitive existence theorem. **Results:** Integral calculus and generalized thermodynamic models, and their applications in various thermodynamic analysis contacts such as the Generalized Enthalpy Model, the Generalized Entropy Model, and the Generalized Model applied to gas mixtures and the General Model to elaborate the properties table. **Conclusion:** The mathematical analysis developed in this document is very useful in engineering and applied physics environments, a fact that supports its common pedagogical practice in university institutions.

## Keywords

Equations, Curves of Thermal Processes, Thermodynamic Laws, Physics-Mathematics, Energy

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## 1. Introduction

A mathematical expression with an equal sign is called an equation. An equation that includes the derivatives of one or more functions is called a differential equation. In other words, a differential equation expresses a relationship between functions and their derivatives. The term differential equation became known in 1676, when Gottfried Wilhelm Leibniz (1646-1716) used it for the first time; since then, scientists and engineers have used differential equations extensively to model and solve a wide range of practical problems [1].

The integral calculus has its origins in the need to determine the area of a surface with curved contours. The applications of integral calculus can be very diverse. For example, it can determine the center of mass of a body or establishing the amount of fuel used in a space mission. The description of all scientific problems implies relationships that connect changes in some key variables; usually, the smaller the chosen increment in the changing variables, the more accurate the description will be. In the limit case of differential changes in the variables, we obtain differential equations that provide precise mathematical formulations for physical principles and physical laws representing the speed of changes as derivatives [2].

Therefore, differential equations are used to investigate a wide variety of problems in science and engineering. This fact establishes the pertinence of the integral calculation in the analysis of energy transformations [3]. Thermodynamics is precisely the science that is responsible for studying the various processes of energy transformations [1] [2].

The study of thermodynamic phenomena involves two core aspects:

- First: all the variables that affect the phenomena are identified, reasonable assumptions and approximations are made, and the interdependence of these variables is studied. Reference is made to the laws of physics and relevant physical principles, and the problem is formulated mathematically, usually in the form of a differential equation. This equation itself provides a lot of information because it shows the degree of dependence of some variables on others, and the relative importance of various terms.
- Second: the differential equation is solved using a suitable method, and the relationship for the unknown function is obtained in terms of the independent variables.

This document focuses on integral calculus and its relevance in solving problems in thermodynamics. Thermodynamics can be defined as the science of energy. Although everyone has an idea of what energy is, it is difficult to define it precisely [4]. Energy can be considered as the ability to cause change. The term thermodynamics comes from the Greek words *therme* (heat) and *dynamis* (force), which corresponds to the most descriptive of the first efforts to convert heat into energy. Today, the concept is widely interpreted to include aspects of energy and its transformations, including power generation, cooling, and relationships between properties of matter.

One of the most important and fundamental laws of nature is the principle of conservation of energy. It expresses that, during an interaction, energy can change from one form to another, but its total amount remains constant. That is to say, energy is neither created nor destroyed. The first law of thermodynamics can be understood as the principle of conservation of energy, and it holds that energy is a thermodynamic property. The second law of thermodynamics states that energy has quality as well as quantity, and real processes occur in the sense of diminishing the quality of energy.

This scientific contribution is composed of the following sections: 1) Theoretical framework and background. 2) Geometric interpretation of the primitive. 3) Primitive existence theorem. 4) Fundamental integrals. 5) Fundamental rules of integration. 6) Integral calculus and generalized thermodynamic models. 7) Generalized Enthalpy Model. 8) Generalized model applied to the gas mixture. 9) General model to elaborate the property table. 10) Discussion. 11) Conclusions.

## 2. Theoretical Framework and Background

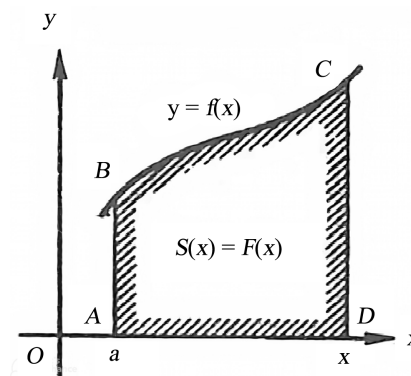
Primitive function or primary function of a given function is a variable  $y = f(x)dx$ , defined in a region whose derivative is equal to  $f(x)$  or, which is the same, whose differential is equal to  $f(x)dx$ :  $F'(x) = f(x)$  or  $dF(x) = f(x)dx$ . In some cases, the field of definition of the primitive function is wider than the field of definition of the initial function. If the field of definition of the function  $f(x)$  is connected, with the exception of some isolated points, of discontinuity,  $x_1, x_2, x_3, x_4, \dots, x_n$  then the field of definition of  $F(x)$  can still contain these points of discontinuity [5].

For the given function there exists an infinite set of primitive functions; the difference between two primitive functions  $F_1(x)$  and  $F_2(x)$  is a constant quantity. The graphs of all the primitive functions  $F_1(x), F_2(x), F_3(x), F_4(x), \dots$  of the given one represent the same curve and are obtained from each other as a result of a parallel translation of the curve in the direction of the ordinate axis, to one side or the other.

### 2.1. Geometric Interpretation of the Primitive

If the given function  $f(x)$  is represented by a row of Cartesian coordinates as shown in **Figure 1**. Then the numerical value of the primitive is equal to the area  $S(x)$  limited by the curve  $y = f(x)$ , by the  $O_x$  axis and by the two ordinates: the constant AB (for  $x = a$ ) and by the variable CD (for the abscissa  $x$ ). By arbitrarily choosing the constant (a), different primitives are obtained [1] [5]. In this case the area  $S(x)$  is understood in the algebraic sense

$$ABCD = \int_a^x f(x)dx.$$



**Figure 1.** Geometric interpretation of the primitive (Bronshtein & Semendiaev, 1973, p. 385).

## 2.2. Primitive Existence Theorem

For every continuous function in a connected region, there is a primitive also continuous in this region [5]. A function that has discontinuities for some isolated values of  $(x)$ , has a primitive that is a continuous function, or is a function that has discontinuities for the same values of  $(x)$ .

## 2.3. Fundamental Integrals

The integration formulas obtained by inverting the derivation formulas are shown in **Table 1**. In solving thermodynamic analysis exercises, we try to reduce the integrals by means of algebraic or trigonometric transformations, or by applying the integration rules [5].

## 2.4. Fundamental Rules of Integration

These rules are based on the properties of the indefinite integrals that allow transforming the integral of a given function into integrals of other functions [5].

- The constant factor can be taken out of the integral sign:

$$\int af(x)dx = a \int f(x)dx \quad (1)$$

- The integral of the sum is equal to the sum of the integrals of the separate terms.  $u, v, w$ , are functions of  $x$ .

**Table 1.** Main integrals. In this table, the integration constants are omitted [5].

Potential functions	Exponential functions
$\int x^n dx = \frac{x^{n+1}}{n+1} (n \neq -1)$	$\int e^x dx = e^x$
$\int \frac{dx}{x} = \ln x $	$\int a^x dx = \frac{a^x}{\ln a}$
Trigonometric functions	Hyperbolic functions
$\int \sin x dx = -\cos x$	$\int \operatorname{sh}x dx = \operatorname{ch}x$
$\int \cos x dx = \sin x$	$\int \operatorname{ch}x dx = \operatorname{sh}x$
$\int \tan x dx = -\ln \cos x ^*$	$\int \operatorname{th}x dx = \ln \operatorname{ch}x ^*$
$\int \cot x dx = \ln \sin x ^*$	$\int \operatorname{cth}x dx = \ln \operatorname{sh}x ^*$
$\int \frac{dx}{\cos^2 x} = \tan x$	$\int \frac{dx}{\operatorname{ch}^2 x} = \operatorname{th}x$
$\int \frac{dx}{\sin^2 x} = -\cot x$	$\int \frac{dx}{\operatorname{sh}^2 x} = -\operatorname{ch}x$

Note: \* In all formulas in which the composition function of the primitive formula contains an expression containing  $\ln f(x)$ , it must be understood that it is  $\ln|f(x)|$ ; For simplicity, the sign of the absolute value the sign of the absolute value is omitted.

$$\int (u + v - w) dx = \int u dx + \int v dx - \int w dx \quad (2)$$

- Substitution rule: if  $x = \varphi(t)$ , we have:

$$\int f(x) dx = \int f[\varphi(t)] * \dot{\varphi}(t) dt \quad (3)$$

- Integration by parts.  $u, v$ , are functions of  $x$ .

$$\int u dv = uv - \int v du \quad (4)$$

### 3. Integral Calculus and Generalized Thermodynamic Models

The equation of state is an equation that relates, for a system in thermodynamic equilibrium, the state variables that describe it; these have the general form:  $f(P, V, T) = 0$ , where  $P$  is pressure,  $V$  is volume and  $T$  is temperature. The ideal gas equation of state can be written in various ways:  $PV = NR_u T$ ,  $Pv = R_u T$ ,  $PV = mRT$ , where  $R_u$  is the universal gas constant and  $R = \frac{R_u}{M}$ . Another useful expression for the ideal gas equation is  $\frac{P_1 * v_1}{T_1} = \frac{P_2 * v_2}{T_2}$ . The variations of internal energy and specific enthalpy for the ideal gas model, using the integral calculation, can be written as:

$$\Delta u = u_2 - u_1 = \int_1^2 c_v dT \quad (5)$$

and

$$\Delta h = h_2 - h_1 = \int_1^2 c_p dT \quad (6)$$

These two equations are valid for any ideal gas process. Specific thermal capacities are only a function of temperature and are related by  $R = c_p - c_v$ . When superheat data is lacking, for engineering calculations  $Pv = ZRT$  can be assumed, where  $Z$  is the compressibility factor. The  $Z$  values are correlated as a function of the reduced pressure  $P_r = \frac{P}{P_c}$  and the reduced temperature

$T_r = \frac{T}{T_c}$ . The compressibility factor and reduced coordinates can be used to

evaluate properties such as enthalpy, entropy and specific heat capacity at constant pressure for gases at very high pressures. The usefulness of this method is that you only need to know the critical pressure and temperature of any substance. This approach is widely used in the thermodynamic analysis of various processes such as: petrochemicals, power plants, heat pumps, among others.

#### 3.1. Generalized Enthalpy Model

Enthalpy is a thermodynamic quantity, symbolized by the letter  $h$ , whose variation expresses a measure of the amount of energy absorbed or transferred by a thermodynamic system, that is, the amount of energy that a system exchanges with its environment [1] [6]. The entropy of a simple compressible substance

can be evaluated from the generalized equation:

$$dh = c_p dT + \left[ u - T \left( \frac{\partial u}{\partial T} \right)_P \right] dP \quad (7)$$

The first term of the right member of this equation is not difficult to evaluate since it only requires the knowledge of the variation of the  $c_p$  with the temperature at the desired pressure. However, the variation of  $h$  with pressure is not so simple, since it is necessary to know the  $PvT$  behavior of each substance of interest. Since there are no detailed data for many substances, a more general method should be used. The enthalpy variation at constant temperature can be written mathematically as:

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$$dh_T = \left[ v - T \left( \frac{\partial v}{\partial T} \right)_P \right] dP \quad (8)$$

Using the compressibility relation  $Pv = ZRT$ , we have:

$$dh_T = \left[ \frac{ZRT}{P} - \frac{ZRT}{P} - \frac{RT^2}{P} \right] dP = -\frac{RT^2}{P} \left( \frac{\partial Z}{\partial T} \right)_P dP \quad (9)$$

Before integrating this expression, it must be transformed to reduced coordinates, so that the result is generally valid. By definition,  $T = T_c T_r$ ,  $P = P_c P_r$ . Por tanto:  $dT = T_c dT_r$ ,  $dP = P_c dP_r$ . Substituting this expression in the equation  $dh_T$  we obtain:

$$dh_T = -\frac{RT_c^2 T_r^2}{P_c P_r} \left( \frac{\partial Z}{T_c \partial T_r} \right)_{P_r} P_c dP_r = -RT_c T_r^2 \left( \frac{\partial Z}{\partial T_r} \right)_{P_r} d \ln P_r \quad (10)$$

Integrating at constant temperature we have:

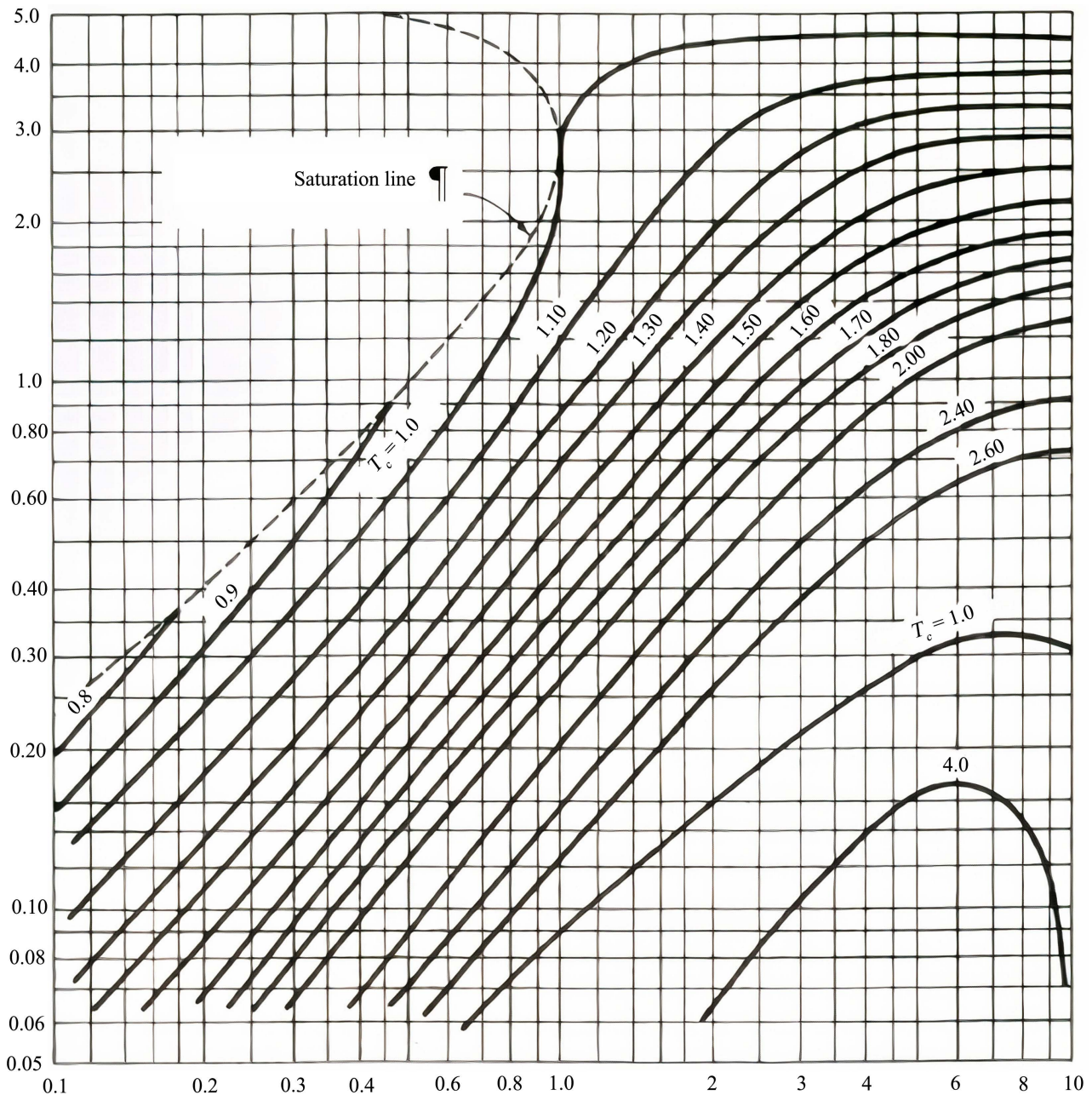
$$\frac{\Delta h_T}{RT_c} = -\int_i^f T_r^2 \left( \frac{\partial Z}{\partial T_r} \right)_{P_r} d \ln P_r \quad (11)$$

where the symbols  $i$  and  $f$  identify the initial and final reduced pressure limits. For convenience, enthalpy is evaluated from the ideal gas state to the real gas state at the same temperature. The lower limit of the left hand of the equation is zero pressure, a state for which  $P_r$  is equal to zero. The enthalpy of an ideal gas is indicated by an asterisk, that is,  $h^*$ . The upper limit is the enthalpy  $h$  of the real gas at high pressure  $P$ . Therefore:

$$\frac{h^* - h}{RT_c} = \int_0^P T_r^2 \left( \frac{\partial Z}{\partial T_r} \right)_{P_r} d \ln P_r \quad (12)$$



The value of the integral is obtained by graphical integration, using the data from the generalized compressibility diagram. The integration results in values of the deviation source  $\frac{h^* - h}{RT_c}$  in source of  $P_r$  and  $T_r$ . The state graph is called a generalized enthalpy diagram, and a characteristic diagram is shown in **Figure 2**.



**Figure 2.** Generalized enthalpy diagram. On the horizontal axis, we have the reduced pressure values  $P_r$ , while on the vertical axis we have the relationship  $\frac{\bar{h}^* - \bar{h}}{RT_c}$ . Reduced temperature  $T_r = \frac{T}{T_c}$ . Reduced pressure  $P_r = \frac{P}{P_c}$ . Critical temperature  $T_c$ . Critical pressure  $P_c$ . Ideal gas enthalpy  $h^*$ . Real gas enthalpy  $h$ . [7].

### 3.2. Generalized Entropy Model

Entropy, symbolized as  $S$ , is the physical quantity that measures the part of energy that cannot be used to produce work. In a broader sense it is interpreted as the measure of the uniformity of the energy of a system. It is an extensive state function and its value, in an isolated system, grows in the course of a process that occurs naturally [8] [9] [10].

It is of interest to scientists and engineers to have a generic entropy diagram. The entropy diagram is based on the generalized equation for the entropy variation of a simple compressible substance, as shown in the following equation:

$$ds = \frac{C_p dT}{T} - \left( \frac{\partial v}{\partial T} \right)_p dP \quad (13)$$

As in the case of the enthalpy function, it is pointed out that the first term of the right side of the equation requires only information on the specific thermal capacity of the substance at the required pressure. The second term of the right member of this equation is in some cases difficult to evaluate, because not always enough  $PvT$  information is available for the substances of interest. Therefore, in these cases a generalized approximation is necessary. Following the procedure carried out in the previous section for the enthalpy source, the equation is integrated from practically zero pressure to the desired pressure, keeping the temperature constant. The resulting equation is written as:

$$(S_p - S_0^*)_T = - \int_0^P \left( \frac{\partial v}{\partial T} \right)_p dP \quad (14)$$

Normally, the next step would be to introduce into this expression the definition of the compressibility factor and the reduced pressure and temperature. However, it cannot be used directly in the above equation, because the entropy of the ideal gas in the zero-pressure state is infinite. This dilemma is obviated as follows: Equation (13) is applied to an isothermal change between zero pressure and the given pressure  $P$ , but assuming that the gas behaves like an ideal gas at all times. As for an ideal gas  $\left( \frac{\partial v}{\partial T} \right)_p = \frac{R}{T}$ , then:

$$(S_p^* - S_0^*)_T = - \int_0^P \left( \frac{\partial v}{\partial T} \right)_p dP = -R \int_0^P \frac{dP}{P} \quad (15)$$

The state presented by  $S_p^*$  is a fictitious state, since the ideal gas exists only at zero pressure. However, you can still assign values to this state even though it is not successful, if you now subtract the Equation (14) from the. Equation (15), we have:

$$(S_p^* - S_p)_T = - \int_0^P \left[ \frac{R}{P} - \left( \frac{\partial v}{\partial T} \right)_p \right] dP \quad (16)$$

From the definition of compressibility factor  $Z = \frac{Pv}{RT}$ :

$$\left( \frac{\partial v}{\partial T} \right)_p = \frac{RZ}{P} + \frac{RT}{P} \left( \frac{\partial Z}{\partial T} \right)_p \quad (17)$$



Using this equation allows Equation (16) to be written as:

$$(S_p^* - S_p)_T = -R \int_0^P \left[ \frac{1-Z}{P} - \frac{T}{P} \left( \frac{\partial Z}{\partial T} \right)_P \right] dP \quad (18)$$

This last result can now be expressed in terms of reduced properties as:

$$(S_p^* - S_p)_T = -R \int_0^{P_r} \frac{1-Z}{P_r} dP_r + RT_r \int_0^{P_r} \left( \frac{\partial Z}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r} \quad (19)$$

By comparing the last term of the right side of this equation with Equation (12), it is found that this term can be written as a source of  $h^* - h$ . The final result is:

$$\frac{(S_p^* - S_p)_T}{R} = \frac{h^* - h}{RT_r T_c} - \int_0^{P_r} (1-Z) \frac{dP_r}{P_r} \quad (20)$$

The value of the first term of the right side of the equation can be obtained by means of the generalized enthalpy diagram. The last term of the right-hand side of the equation must be evaluated through a graphical integration of the information of the compressibility factor. Equation (20) allows evaluating the deviation of the entropy value with respect to that of the ideal gas at the same pressure and temperature. A graphical representation of the deviation function  $\frac{(S_p^* - S_p)_T}{R}$  versus reduced pressure and temperature is shown in **Figure 3** as a generalized entropy diagram.

The deviation function that is presented as a graph in **Figure 3** is used as follows. Since entropy is a property, its variation is independent of the path chosen to evaluate it. Thus, between two states of the real gas we can write:

$$S_2 - S_1 = (S_{P_1}^* - S_{P_1})_{T_1} + (S_2^* - S_1^*) - (S_{P_2}^* - S_{P_2})_{T_2} \quad (21)$$

The first and third terms of the right-hand side of the equation are obtained from the generalized entropy diagram for the initial and final states. The remaining term is determined by the entropy variation of an ideal gas between the initial and final states. This term is given by:

$$S_2^* - S_1^* = C_{p,m} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \quad (22)$$

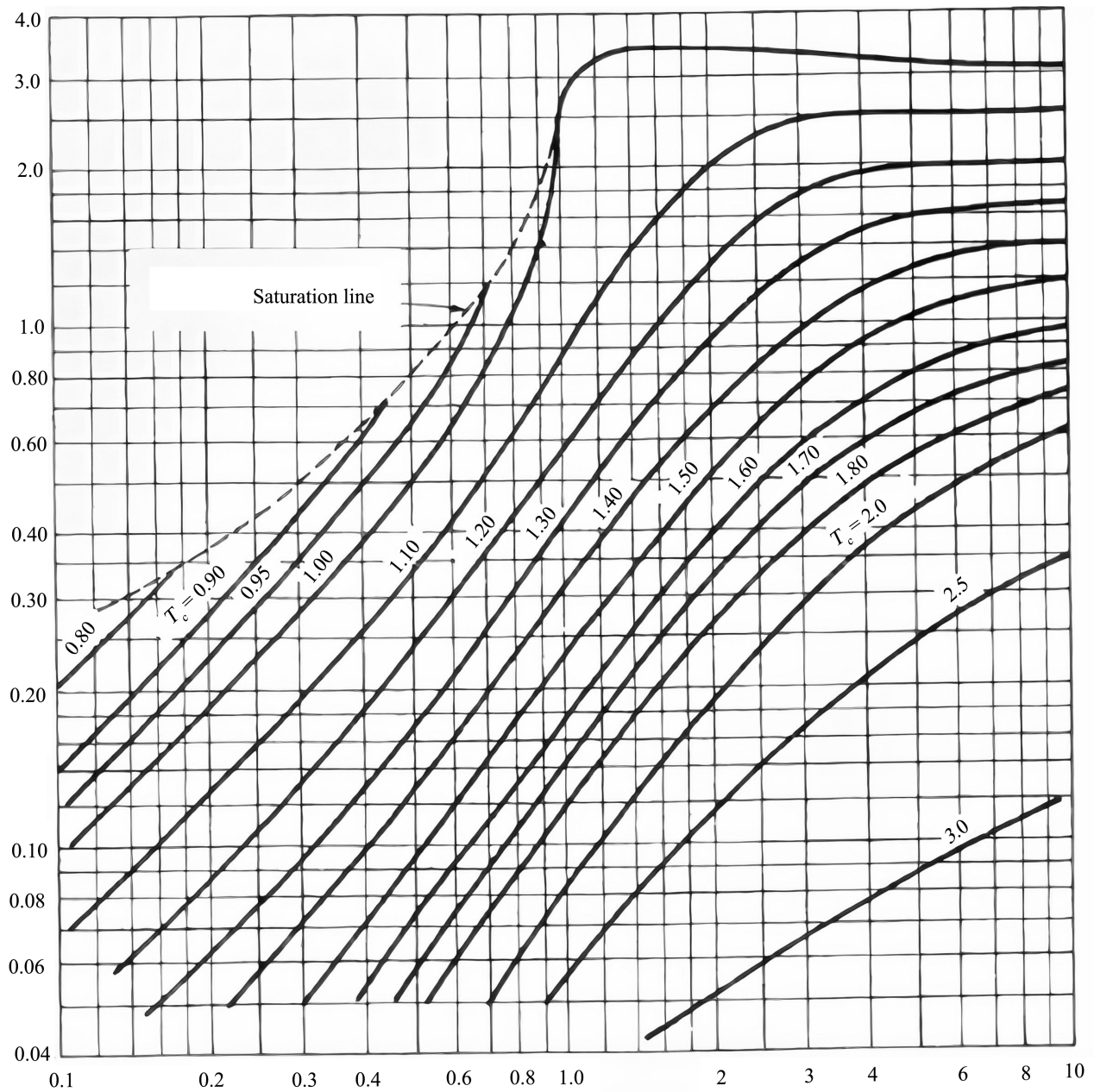
or

$$S_2^* - S_1^* = S_2^0 - S_1^0 - R \ln \frac{P_2}{P_1} \quad (23)$$

Substituting Equation (23) into Equation (21), for example, shows that:

$$S_2 - S_1 = (S_{P_1}^* - S_{P_1})_{T_1} + S_2^0 - S_1^0 - R \ln \frac{P_2}{P_1} - (S_{P_2}^* - S_{P_2})_{T_2} \quad (24)$$

In this analysis it is evident that Equation (22) can be used instead of Equation (23). Besides the evaluation of the entropy variations for real gases, Equation (24) is also very useful for the evaluation of isentropic processes of these gases.



**Figure 3.** Generalized entropy diagram. On the horizontal axis we have the reduced pressure values  $P_r$ , while on the vertical axis we have the relationship  $\frac{(\overline{S}_p^* - \overline{S}_p)}{R_u T}$ . Reduced temperature  $T_r = \frac{T}{T_c}$ . Reduced pressure  $P_r = \frac{P}{P_c}$ . Critical temperature  $T_c$ . Critical pressure  $P_c$ . Ideal gas entropy  $S_p^*$ . Real gas entropy  $\overline{S}_p$ . [7].

### 3.3. Generalized Model Applied to Gas Mixture

The concept of enthalpy, entropy, has already been discussed. in this section is important declares the concept of internal energy. The internal energy is the result of the contribution of the kinetic energy of the molecules or atoms that constitute it, of their energies of rotation, translation and vibration, in addition to the intermolecular potential energy due to the forces of gravitational, electro-

magnetic and nuclear type [11] [12] [13].

The internal energy, enthalpy and entropy of an ideal gas mixture can be determined by subtracting the contribution of each of the components separately. That is, per unit of substance:

$$u_m = \sum y_i u_i, \quad h_m = \sum y_i h_i, \quad s_m = \sum y_i s_i \quad (25)$$

This rule can be applied to a real gas mixture, with some caveats.

- First, the properties  $u_i, h_i, s_i$  of each component must be evaluated at the pressure and temperature of the mixture, and not at the pressures and temperatures of the components. If the volume and temperature of the mixture are known data, Dalton's law (John Dalton 1766-1844) of adiabatic pressures should first be used to obtain the approximate pressure of the mixture.
- Second, this addition rule provides approximate results for  $u_m, h_m, s_m$ , analogously to when applying Dalton's rule to real mixes for  $PvT$ .

The values of  $u_i, h_i, s_i$  are determined from the relationships generated from properties developed in [14]. Alternatively, the data from the generalized diagrams can be used. In this case the reduced pressure  $P_r$  of each component must be evaluated as the pressure of the mixture.

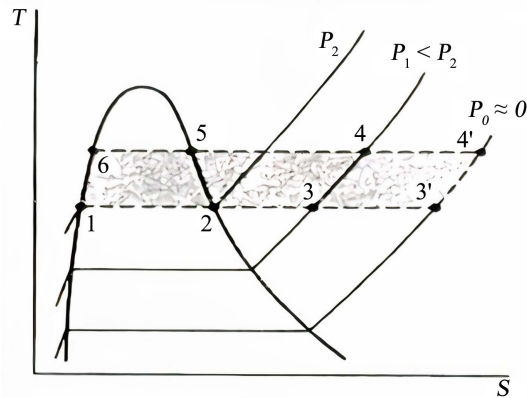
### 3.4. General Model to Elaborate the Property Table

The tables of saturation and superheated steam are very useful for thermodynamic analysis in various contexts. Considering the analysis carried out up to this section of the document, we have the necessary and pertinent information to develop the general method for the elaboration of tables containing  $v$ ,  $u$ ,  $h$  and  $s$  as a function of  $P$  and  $T$ . The method requires three sets of experimental data that are represented analytically by the following equations:

- An equation of state for  $PvT$  accurate for the saturation and superheated steam regions based on experimental data.
- An equation for vapor pressure similar to Equation (26), based on experimental vapor pressure data. The constants  $A, B, C, D, E$ , etc; are adjusted to obtain the best agreement with the experimental data.
- From experimental measurements, you must develop an equation for the ideal gas  $C_{p,0}$  data in the defined temperature range.

$$\ln P_{sat} = A + \frac{B}{T} + C \ln T + DT + ET^2 + \dots \quad (26)$$

The first point of those declared above allows the evaluation of the data of  $v$  in previously defined states. To illustrate the general method, arbitrary values of  $h$  and  $s$  are assigned in a given reference state. These reference values can be, for example, zero. As a clarification, the state of saturated liquid at a defined temperature is chosen for the reference state. This reference state is indicated as state 1 in the  $Ts$  diagram of **Figure 4**. It is intended to determine with respect to this state, the values of the properties in the arbitrary saturation states 2, 5, and 6. And the superheated steam states 3 and 4. The values in other states can be determined in a similar way.



**Figure 4.** *Ts* diagram illustrating the evaluation of the data for the saturation and superheated steam tables.

The data of the properties in state 2 are obtained from the Clapeyron equation. The differentiation of the vapor pressure equation provides data for  $\left(\frac{dP}{dT}\right)_{sat}$ . Substituting that magnitude in the Clapeyron equation, written as:

$$h_2 - h_1 = h_{fg} = -T(v_g - v_f)\left(\frac{dP}{dT}\right)_{sat} \tag{27}$$

you get a value for  $h_2$ .

The values of  $v_f$  and  $v_g$  in states 1 and 2 are found from the equation of state. The entropy and internal energy in state 2 is obtained from:

$$s_2 = s_1 + \frac{h_{fg}}{T_1} \tag{28}$$

and

$$u_2 = u_1 + h_{fg} - P_1(v_2 - v_1) \tag{29}$$

The same type of calculation provides  $\Delta h$ ,  $\Delta s$ , and  $\Delta u$  between states 5 and 6. State 3 is at the same temperature as state 2, but at different pressures. Constant temperature calculations of this type are most easily performed using the concept of deviation source discussed in the section entitled: Generalized Enthalpy Model. The deviation function  $y^R$  is defined as:

$$y^R \equiv y^* - y \tag{30}$$

where  $y$  is the desired value of  $y$  at  $(P, T)$ , and  $y^*$  is the value of the property that the fluid would have a  $(P, T)$ , if it were an ideal gas. Since the equations of state are usually explicit in pressure, we start from the general Helmholtz relation  $da_r = -Pdv$ . Through proper manipulation, this equation leads to the Helmholtz residual function of the form:

$$a^* - a = \int_{\infty}^v \left( P - \frac{RT}{v} \right) dv + RT \ln Z \tag{31}$$

Like  $da = -Pdv - sdT$ , it will have to  $s = -\left(\frac{\partial a}{\partial T}\right)_v$  or:

$$S^* - S = -\frac{\partial}{\partial T}(a^* - a)_v \quad (32)$$

Substitution of Equation (31) in Equation (32) is obtained:

$$S^* - S = -\int_{\infty}^v \left[ \left( \frac{\partial P}{\partial T} \right)_v - \frac{R}{v} \right] dv - \ln Z \quad (33)$$

Considering  $h = a + Ts + Pv$ , Equations (31) and (33) can be used to show that:

$$h^* - h = -\int_{\infty}^v \left[ T \left( \frac{\partial P}{\partial T} \right)_v - P \right] dv + RT(1 - Z) \quad (34)$$

by definition

$$u^* - u = h^* - h - P^* v^* - Pv \quad (35)$$

So

$$u^* - u = h^* - h + RT(Z - 1) \quad (36)$$

Equations (33), (34) and (36), together with the equation of state  $PvT$ , allow us to evaluate the values of  $s$ ,  $h$ , and  $u$  in a given state. For the change of state in the superheated steam region, for example:

$$y_3 - y_2 = (y_2^* - y_2) - (y_3^* - y_3) + (y_3^* - y_2^*) \quad (37)$$

$y$  is any property of interest. The third term of the right member of Equation (37) is the variation of the property between the two states if the gas were ideal. Remember that for an ideal gas:

$$h_y^* - h_x^* = \int_x^y C_{P,0} dT \quad (38)$$

$$S_y - S_x = \int \frac{C_{P,0} dT}{T} - R \ln \frac{P_y}{P_x} \quad (39)$$

where  $x$  and  $y$  are two arbitrary states. To determine the values of the properties in state 4, the calculation must be carried out along the path 3-3'-4'-4 of **Figure 4**. This is necessary since the  $C_{P,0}$  data is known only along the pressure line  $P_0$ , which is low enough for the gas to behave like an ideal gas. This analysis is expressed as:

$$h_4 - h_3 = (h_3^* - h_3) - (h_4^* - h_4) + \int_3^4 C_{P,0} dT \quad (40)$$

$$S_4 - S_3 = (S_3^* - S_3) - (S_4^* - S_4) + \int_3^4 \frac{C_{P,0} dT}{T} - R \ln \frac{P_4}{P_3} \quad (41)$$

Once the data for state 4 is known, those for states 5 and 6 are determined by the reverse process to that of states 1, 2, and 3. In this way, through the series of calculations previously analyzed, the values of the properties in any desired state relative to the reference values for  $h$  and  $s$ .

## 4. Discussion

Only a few of the many generalized diagrams that can be devised are shown in

this contribution. When the generalized equation is available for a property in relation to the variables  $P$  and  $T$ , it is possible to develop many diagrams. In the absence of abundant  $PvT$  data for a substance, generalized diagrams are powerful tools for predicting the properties of a liquid or gas.

According to the concepts developed from the energy transformation laws and the definitions of the Helmholtz (a) and Gibbs (g) functions, four very useful relationships between properties of simple compressible substances can be inferred. These are:

$$du = Tds - Pd v \quad (42)$$

$$dh = Tds + v dP \quad (43)$$

$$da = -Pd v - s dT \quad (44)$$

$$dg = v dP - s dT \quad (45)$$

From these relationships, the four additional actions given below have been deduced:

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P \quad (46)$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial s}{\partial P}\right)_T \quad (47)$$

This group of equations is known as Maxwell's relations. Two very important relationships of the specific thermal capacities are:

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{C_v}{T} \quad (48)$$

and

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{C_P}{T} \quad (49)$$

When these expressions and the Maxwell relations are substituted in the total differentials of  $du$ ,  $dh$  and  $ds$ , the following generalized relations are obtained:

$$du = C_v dT + \left[ T \left(\frac{\partial P}{\partial T}\right)_v - P \right] dv \quad (50)$$

$$dh = C_P dT + \left[ v - T \left(\frac{\partial v}{\partial T}\right)_P \right] dP \quad (51)$$

$$ds = \frac{C_v dT}{T} + \left(\frac{\partial P}{\partial T}\right)_v dv = \frac{C_P dT}{T} - \left(\frac{\partial v}{\partial T}\right)_P dP \quad (52)$$

They are called Generalized Equations because they are not restricted to any particular substance or any particular phase. However, these equations are restricted to simple compressible substances. The generalized relationships for  $cp$  and  $cv$  can be written as:

$$\left(\frac{\partial C_v}{\partial v}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_v \quad (53)$$



$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 v}{\partial T^2}\right)_P \quad (54)$$

$$C_p - C_v = -T \left(\frac{\partial v}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial v}\right)_T \quad (55)$$

The experimental data applications, together with the last equation, show that  $0 \leq C_p - C_v$ . The slope of the vapor pressure curve in a PT diagram is theoretically given by the Clapeyron equation. This can be written as:

$$\left(\frac{\partial P}{\partial T}\right)_{sat} = \frac{h_{fg}}{Tu_{fg}} \quad (56)$$

An approximation of this equation, which does not contain the specific volume, is:

$$\ln\left(\frac{P_2}{P_1}\right)_{sat} = -\frac{h_{fg}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (57)$$

This equation is one of the forms of the Clausius-Clapeyron equation. This equation expresses that  $\ln P_{sat}$  is a linear function of  $\frac{1}{T}$ . The generalized relationship of the Joule-Thomson coefficient is written as:

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_h = \frac{1}{C_p} \left[ T \left(\frac{\partial v}{\partial T}\right)_P - v \right] \quad (58)$$

This equation is useful for predicting when the temperature of a gas will decrease during a throttling process. This analysis is of great importance to re-determine the efficiency of a refrigerant substance. Well, the refrigerant effect consists of extracting the thermal energy of a body to reduce its temperature. Due to thermodynamic properties, this energy is transferred to another material [15] [16].

The generalized diagrams and tables have been developed based on the generalized data for  $Z$  as a source of the reduced pressure and temperature and in accordance with the generalized equations for  $dh$  and  $ds$ . Normally, the values of the deviation functions  $\frac{h^* - h}{RT_c}$  and  $\frac{(S_p^* - S_p)_T}{R}$  are represented for selected values of  $P_r$  and  $T_r$ . This allows the estimation of  $h$  and  $s$  exclusively from the initial and final pressures and temperatures and from the critical data of the substance. This concept is also applicable to real gas mixtures.

It could be said that almost all human activities have some kind of connection with mathematics. These links may be obvious, as in engineering, or less conspicuous, as in medicine or music. Thermodynamics is a science that has a close relationship with mathematics and its evolution.

## 5. Conclusion

The aim of this scientific contribution is to show the potential that integral calculus has offered to the analysis of thermodynamic processes. In this context, the

document ranges from the theoretical principles of the integral calculus, such as Theoretical framework and background, Geometric interpretation of the primitive, Primitive existence theorem, Integral calculus and generalized thermodynamic models; to its applications in various contexts of thermodynamic analysis, such as Generalized py Model, Generalized Entropy Model, Generalized model applied to gas mixture and General model to elaborate the property table. The mathematical analysis developed in this document is very useful in engineering and applied physics environments, and this fact supports their common pedagogy practice in university institutions. The main argument that develops throughout this work is focused on the mathematical demonstration of obtaining the model from the saturation and superheated steam tables. The tables of saturation and superheated steam are very useful for thermodynamic analysis in various contexts ranging from steam generation, refrigeration processes, and petrochemical processes to applied physics and earth science studies. The study of thermodynamic laws is essential in the training process of energy engineers and studies in applied physics. Mathematical analysis is the pillar that supports the cognitive development of the very diverse processes of energy transformation.

### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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