The THERMODORM© revisited: A thermodynamic didactical tool

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Abstract

The THERMODORM© is a tridimensional mnemonic tool created for learning and using the Maxwell's thermodynamics equations. The development of this device was based on thermodynamic squares with eight energy functions placed on the triangular sides of a rectangular octahedron, and the six independent variables are located at the vertex points. Using modern technology, it is possible to create a digital representation of this device. In this work, Google Scketchup® was used as a virtual environment that allows representing and manipulating this 3D model.

Keywords: Thermodynamics, fundamental equations, derivatives, Maxwell relations, mnemonic device

1. Introduction

The Maxwell relations are an important subject in thermodynamics. Gangi *et al.* [1] developed a mnemonic tool for energy functions and their variables called the THERMODORM© (Thermodynamic Octahedral Display Of the Relations of Maxwell), consisting in a desktop- or pocket-sized device with a complete set of Maxwell relations and energy functions derivatives. These authors provided a detailed pattern for building a folding paper model, and possibly also a hard plastic version.

Specifically, the main energy functions represented are U (internal energy), H (enthalpy), A (Helmholtz free energy), G (Gibbs free energy), TS-PV, TS, $-PV$ (where T is the temperature, P is the pressure and e is the entropy) and μ_i (chemical potential).

2. Theoretical Background

For a homogenous phase of an open system of k components, the fundamental equation associated with the internal energy is given as a function of entropy, volume (V) and the mole number of each component (N_i) (Equation (1)).

$$U = U\left(S, V, N_i\right); \quad i = 1, 2, ..., k \tag{1}$$

The total differentiation of the internal energy is shown in Equation (2).

$$dU = TdS - PdV + \sum_{i=1}^{k} \mu_i dN_i \tag{2}$$

Using Legendre transformations the internal energy can be converted into the others energy functions: $H(S,P,N_i)$, $A(T,V,N_i)$, $G(T,P,N_i)$, *etc*, as presented in Equations (3)-(9). This last expression is called the Gibbs-Duhen equation [2].

$$dH = TdS + VdP + \sum_{i=1}^{k} \mu_i dN_i \tag{3}$$

$$dA = -SdT - PdV + \sum_{i=1}^{k} \mu_i dN_i \tag{4}$$

$$dG = -SdT + VdP + \sum_{i=1}^{k} \mu_i dN_i \tag{5}$$

$$d\left(TS - PV\right) = TdS + VdP - \sum_{i=1}^{k} N_i d\mu_i \tag{6}$$

$$d\left(TS\right) = TdS + VdP - \sum_{i=1}^{k} N_i d\mu_i \tag{7}$$

$$d\left(-PV\right) = -SdT - PdV - \sum_{i=1}^{k} N_i d\mu_i \tag{8}$$

$$0 = -SdT + VdP - \sum_{i=1}^{k} N_i d\mu_i \tag{9}$$

This eight energy functions can be used for deducing Maxwell relations using six independent variables: S, V, P, T, N_i and μ_i. For example, from Equation (4) it is obtained:

$$\left(\frac{\partial S}{\partial V}\right)_{T,N_i} = \left(\frac{\partial P}{\partial T}\right)_{V,N_i} \tag{10}$$

For the seven non-zero energy equations there are two possible relations for each component. Therefore, it is possible to find a total of $7\left(k+2\right)$ relations.

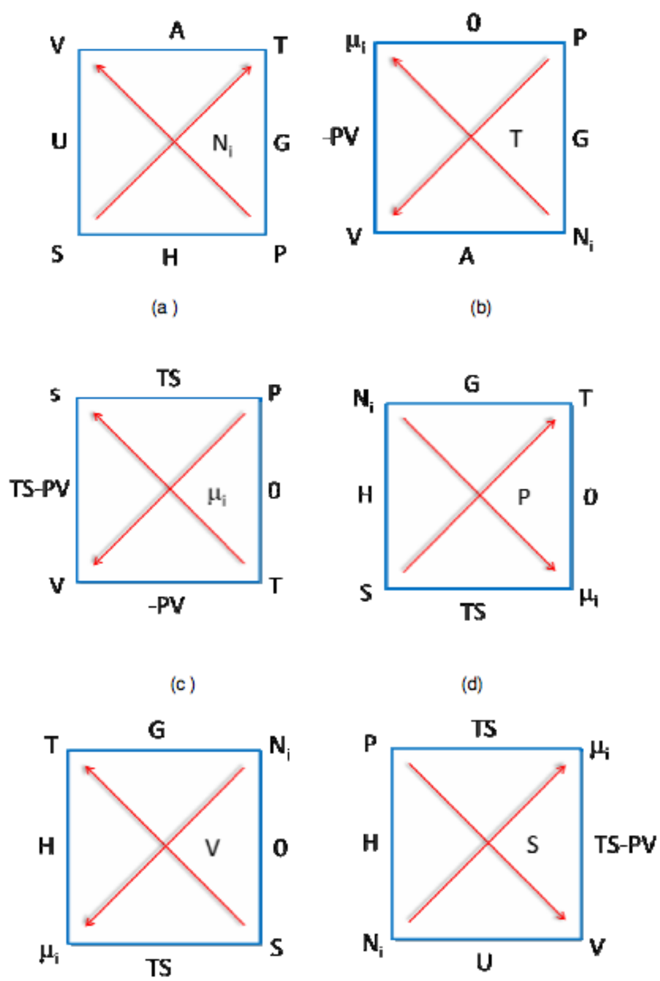

Figure 1: *Thermodynamic squares at constant number of mole (a), temperature (b), chemical potential (c), pressure (d), volume (e) and entropy (f).*

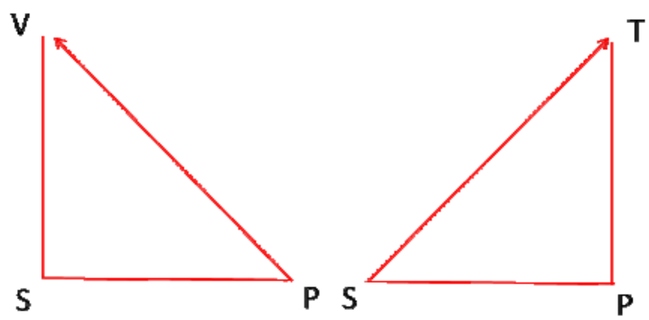

Figure 2: *Thermodynamic square path.*

According to Equation (9), $dT|_{P,\mu_i} = 0$, as a consequence the relations obtained are shown in Equations (11) [1].

$$\left(\frac{\partial T}{\partial S}\right)_{P,\mu_i} = \left(\frac{\partial P}{\partial V}\right)_{T,\mu_i} = \left(\frac{\partial \mu_i}{\partial N_i}\right)_{P,T,\mu_i} \tag{11}$$

3. Development and use

One common mnemonic tool for remembering the Maxwell relations is the use of thermodynamic squares [3], as shown in Figure 1. Gangi *et al.* presented three of this squares (Figure 1 a to c), and here are illustrated the other three, one square for each of the six independent variable listed in the previous section.

These squares have energy functions on each side, flanked by natural variables. In order to obtain a Maxwell relation a path must be followed as the one illustrated in Figure 2, related to the square in Figure 1 (a). Starting from the volume, it can be assured that its partial derivative with respect to S at constant P (and constant N_i, according to this particular square) is equal to the partial derivative of T with respect to P at constant S (Equation (12)). This relation comes from Equation (3). If both arrows in the square point upward or downward, the sign of the relation is positive. The squares can be rotated to apply the same pattern and obtain the remaining relations.

$$\left(\frac{\partial V}{\partial S}\right)_{P,N_i} = \left(\frac{\partial T}{\partial P}\right)_{S,N_i} \tag{12}$$

Moreover, starting from one of the energy functions on the square side, it is possible to obtain the following relations (according to Figure 1b):

$$\left(\frac{\partial G}{\partial P}\right)_{T,N_i} = V; \quad \left(\frac{\partial A}{\partial T}\right)_{V,N_i} = -S \tag{13}$$

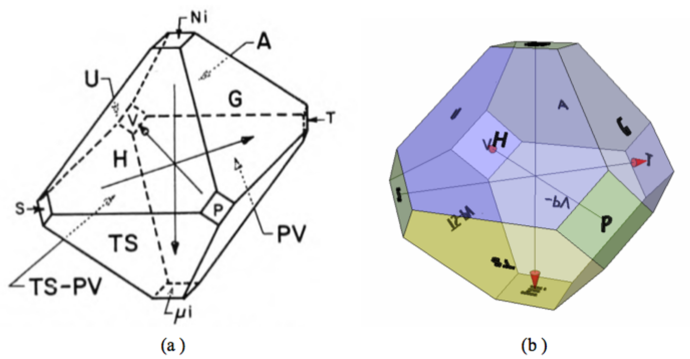

Figure 3: *THERMODORM© representation: a) Gangi et al. [1] b) present work.*

If the pattern concurs with the arrow sense in the square, then the sign is positive.

Previous attempts were made in order to condense the thermodynamic squares into one figure in order to have one simple practical tool [4,5]. Gangi *et al.* used an octahedron with the six independent variables located at the vertex points and the energy functions at the triangular sides (THERMODORM©).

As can be seen in Figure 1, some of the squares have common variables at the vertex point and thus this is used as an advantage when locating the squares in a tridimensional structure. The vertexes where flattened and each of them represents a constant variable; when sighting directly to them a mnemonic square can be observed.

Using modern technology it is possible to recreate this tool in a digital environment. In this case we used Google Sketchup® to build an easy to use 3D virtual model that can be manipulated in order to understand or recall thermodynamic relations. In Figure 3 it is shown a comparison between the original model proposed by Gangi *et al.* and the one developed in this work.

As this model is based on a free-software philosophy, it can be downloaded and modified to the user's needs, and uploaded again for further improvements and modifications (see Figure 4). The present implementation is available from the authors on request.

As a last example, it is demonstrated the use of the tridimensional tool. Using the constant temperature square (as the one in Figure 1b), the THERMODORM© must be rotated in order to look directly into the T vertex. The relations are obtained using the red and yellow arrow as shown in Figure 5, therefore:

$$\left(\frac{\partial \mu_i}{\partial V}\right)_{T,N_i} = -\left(\frac{\partial P}{\partial N_i}\right)_{T,V} \tag{14}$$

According to the rules explained before, and the internal arrow direction, the sign is negative.

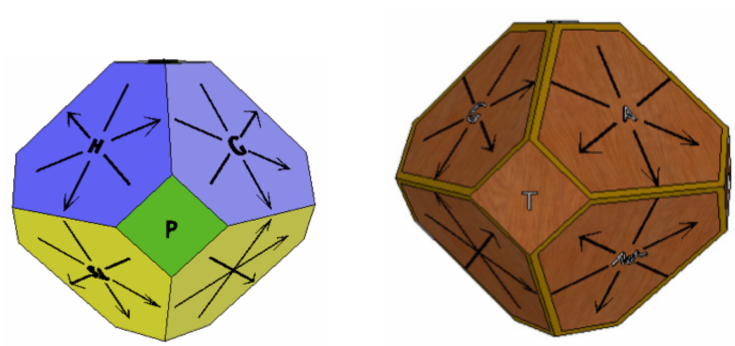

Figure 4: *Two different representations of a digital THERMODORM©, following the pocket size model described by Gangi et al. [1].*

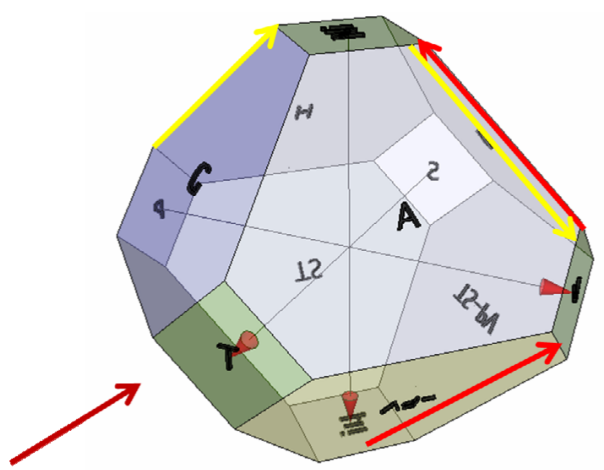

Figure 5: *Using the digital THERMODORM©.*

Conclusions

Modern software allows to create virtual environments with tridimensional visualisation options. Some techniches and devices developed in the past are being revisited and carried to the digital world. In this work it was possible to use the idea of an octahedron for learning and using the Maxwell's thermodynamic equations. The main advantage of this representation is to have an usefull and user-friendly tool that can be manipulated and modified using a free-software philosophy.

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