

Graphs and thermodynamics

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Abstract Graphs are used in many fields of chemistry for codification and model purposes. One of these fields is widely known under the acronym QSAR/QSPR, i.e., quantitative structure–activity/structure–property relationships. In chemical graph studies directed graphs, known as digraphs, i.e., graphs with a preferred direction, have mainly been used to codify chemical reaction networks. Actually, digraphs, especially directed acyclic graphs together with simple graphs, can be used to draw a meta-language of thermodynamics that codifies rules and properties which can be used to automatically derive many well-known, and less-known, thermodynamic relationships.

Keywords Directed graphs · Simple graphs · Thermodynamic digraphs · Thermodynamic relationships

1 Introduction

“Science has its cathedrals, built by the effort of a few architects and of many workers. In these loftier monuments of scientific thought a tradition has arisen whereby the friendly usages of colloquial speech give way to a certain severity and formality. While this may sometimes promote precise thinking, it more often results in the intimidation of the neophyte.” These are some of the words that Gilbert Newton Lewis and Merle Randall used to introduce their book on thermodynamics, which soon became the most famous book on the subject [1]. Usually one of the aspects of thermodynamics that overwhelms the neophyte, and also the skilled practitioner, is the number of mathematical relations that are scattered throughout any book or paper on thermodynamics.

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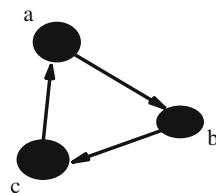
Even if mathematics offers a wonderful shorthand for the precise formulation of well standardized ideas, in thermodynamics it is not rare the feeling of a lack of a unitary formalism that could encompass and order the many equations, which seem to pop out from everywhere. The feeling that there must be a shorter and easier way to derive and order the thermodynamic relationships can be traced back to the beginning of the 20th century, when it was rationalized by a physicist of the caliber of Percy William Bridgman (1882–1961, Nobel prize in 1946). In a paper published in 1914 [2] Bridgman suggested how to encode by the aid of an algebraic method the 720 first derivatives, encompassing three parameters (among a pool of ten fundamental parameters), and the 11,704,365,420 relations between the first derivatives. Bridgman's rather heavy method, was further developed and simplified by Shaw [3] and it is presented in a synthetic and readable form in Appendix 6 of Ref. [1]. It is a method based on mathematical functions known as Jacobians, and on a short-hand way to encode differentials. This first attempt to draw a metalanguage of thermodynamics remained nonetheless a curiosity. A metalanguage (in logic and linguistic) is a language used to make statements about statements in another language, which is called the object language. More broadly it can refer to any terminology used to discuss the language itself (a written grammar for example).

It is told that Max Born (1882–1970, Nobel Prize in 1954) devised in 1929 a 'private' geometrical method to check automatically the Maxwell relations during his thermodynamic lectures. It should be told that Max Born contributed in a significant way to the development of Carathéodory's axiomatic thermodynamics [4]. The Max Born method is reported by Callen [5], but it was known by Koenig [6] and by Tisza [7], who have been students of Max Born. The Born method was further developed into a diagrammatic method for thermodynamic relationship [8,9]. Recently, a straightforward diagrammatic pattern-based method [10–13] has been presented, while, nearly concomitantly, two different vector-based methods have been proposed [14,15], which can be considered a revival of the algebraic methods for short-hand notation in thermodynamics.

2 The digraph

In the following a metalanguage for thermodynamic relationships based on graphs will be developed. Actually, the diagrammatic pattern-based method used geometric tools that bear a resemblance with graphs and directed graphs. Graphs are, indeed, interesting tools for representing a relation by the aid of a pictorial representation. A directed graph, or digraph, consists of a set V of *vertices* (or *nodes*) together with a set E of ordered pairs of elements of V called *edges* (or *arcs*). In a directed graph a *vertex* is represented by a point, and each ordered pair is represented using an edge with its direction indicated by an arrow. In the simple directed acyclic graph, $x \rightarrow y$, vertex x is called the initial vertex (or tail) of the edge (a, b) , and vertex y is called the terminal vertex (or head) of the edge. Vertex x is said to be adjacent to y and y is said to be adjacent from x . The *in-degree* of a vertex, v , denoted by $deg^-(v)$, is the number of edges with v as their terminal. The *out-degree* of v , denoted by $deg^+(v)$, is the number of edges with v as their initial vertex. A vertex with a zero indegree

Fig. 1 A directed graph with three vertices and three directed edges



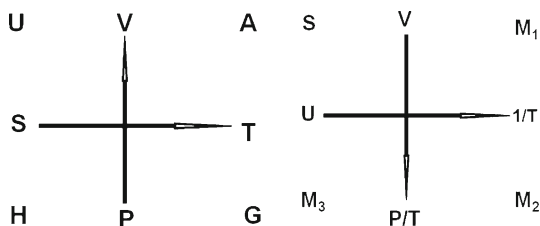
is called a *source* (vertex x , since one can only leave it) and a vertex with a zero outdegree is called a *sink* (vertex y , since one cannot leave it). A relation R on a set A is represented by the digraph that has the elements of A as its vertices and the ordered pair (a, b) as edges [where $(a, b) \in R$]. In Fig. 1 is shown the digraph of the relation $R = \{(a, b), (b, c), (c, a)\}$ on the set $\{a, b, c\}$. In simple undirected graphs, instead, edges have no direction (no arrow) and the degree of a vertex, denoted by $deg(v)$, is the number of edges incident with it. Isolated vertices have, in any type of graph, $deg^+(v) = deg^-(v) = deg(v) = 0$ [16].

3 The thermodynamic digraphs

Two sets of eight fundamental thermodynamic quantities will be considered as the vertices of two digraphs. The first set is the energy set, $\{A, G, H, U, P, S, T, V\}$, where A is the Helmholtz function, G the Gibbs function, H the Enthalpy, U the internal energy, P the pressure, S the entropy, T the temperature, and V the Volume. These quantities build the Energy-digraph, or E -digraph (Fig. 2, left). These eight quantities of the energy set build two subsets: an energy-dimensioned subset of four *zero*-degree thermodynamic potentials, $\{A, G, H, U\}$, and a subset of their natural variables, $\{P, S, T, V\}$, which are the *one*-degree (out and in) vertices of the E -digraph. The E -digraph can be considered the digraph of the relation $R = \{A, G, H, U, (P, V), (S, T)\}$. Notice that multiplying either the source P and the sink V , or the source S and the sink T an energy-dimensioned quantity is obtained (i.e., PV and ST). In this digraph the thermodynamic labels of the zero-degree vertices are ordered clockwise (clockwise rotations is here considered positive), while the labels of the natural variables have a slanted ‘Z’ order.

The second set of eight quantities is the entropic set, $\{M_1, M_2, M_3, S, P/T, U, 1/T, V\}$, where M denotes the Massieu entropic functions, which are useful in the theory of irreversible thermodynamics and in statistical mechanics. These functions

Fig. 2 Left: the E -digraph; right: the S -digraph



were introduced by the French mineralogist François–Jacques Dominique Massieu in 1869 [5, 12]. These eight quantities build the second digraph, the Entropy-digraph, or *S*-digraph (Fig. 2, right). They can be arranged into two subsets, an entropy-dimensioned subset of four *zero*-degree entropic functions $\{M_1, M_2, M_3, S\}$, and a subset of their natural variables, $\{P/T, U, 1/T, V\}$, which are the *one*-degree vertices of the *S*-digraph. The *S*-digraph is the digraph of the relation $R = \{M_1, M_2, M_3, S, (P/T, V), (U, 1/T)\}$. Multiplying together the source V and the sink P/T , or the source U source and the $1/T$, an entropy-dimensioned quantity is obtained (i.e., PV/T , and U/T). In this digraph the thermodynamic labels for the zero-degree vertices are ordered clockwise, while the labels for the natural variables have a slanted ‘Z’ order. The two digraphs and the following three properties can be considered the main tools of the present metalanguage of thermodynamics, which opens with the following three properties,

Property 1 (Neighborhood property) *The corner parameters are functions of their nearby natural variables (in the standard exposition of classical thermodynamics of simple systems),*

$$A = A(V, T), G = G(T, P), H = H(P, S), U = U(S, V) \quad (1)$$

$$M_1 = M_1(V, 1/T), M_2 = M_2(1/T, P/T), M_3 = M_3(P/T, U), S = S(U, V) \quad (2)$$

From these functional relations the total differentials of the corner quantities can easily be derived.

Property 2 (Orthogonal property) *Natural variables belonging to the same arrow can be multiplied between them to obtain either energy-dimensioned terms (*E*-digraph: PV and ST) or entropy-dimensioned terms (*S*-digraph: U/T and PV/T). Quantities belonging to orthogonal arrows cannot be multiplied with each other. For the same reason, zero-degree quantities cannot be multiplied with each other.*

Property 3 (Directional property) *Flow towards an arrowhead (from a source to a sink) is positive while flow towards an arrowtail (from a sink to a source) is negative.*

4 Simple graphs and the thermodynamic relationships

Let us now superpose on these two digraphs a set of simple graphs (SSG = superimposed simple graph) which have the shape of an alphabetical capital letter: F, M, N, and P. The thermodynamic quantities are the vertices of these letter-shaped graphs. Each superposition gives rise to a simple graph relation, R , among the encompassed vertices of the SSG, which will be used to characterize a thermodynamic relationship.

4.1 The SSG-N and the fundamental relationships of the zero-degree quantities

Be the *E*-digraph and the SSG with shape N (SSG-N) of Fig. 3, left. The well-known relation between H and U , $H = U + PV$, which obeys properties 2 and 3, could be

rewritten in a succinctly way with the following encoding relation,

$$R_{EN} = \{H: U, (P, V)\} \tag{3}$$

Now, either by successive 90° clockwise C_4 rotations or 180° C_2 rotations of the SSG-N [also by reflections through the PV (σ_{PV}) or ST (σ_{ST}) arrows, or by $C_4 + \sigma_{PV,ST}$], it is possible to obtain the other seven encoding relations (there are two relations for each vertex). From these relations the well-known thermodynamic relationships among the different potentials can easily be derived. Some of them are,

$$C_4R_{EN} = \{U: A, (S, T)\} \rightarrow U = A + ST \tag{4}$$

$$\sigma_{ST}C_4R_{EN} = \{H: G, (S, T)\} \rightarrow H = G + ST \tag{5}$$

$$\sigma_{PV}R_{EN} = \{G: A, (P, V)\} \rightarrow G = A + PV \tag{6}$$

$$-C_4\sigma_{PV}R_{EN} = \{A: U, (T, S)\} \rightarrow A = U - TS \tag{7}$$

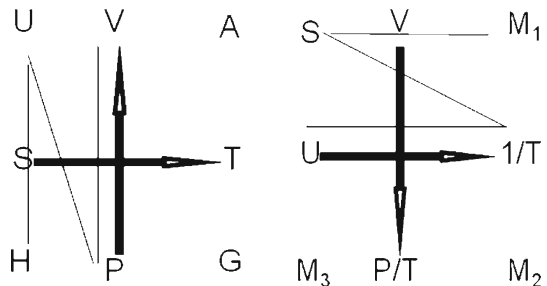
The SSG-N of the S-digraph (Fig. 3, right) encodes the relation and the corresponding thermodynamic relationship for M_1 (after what has been said there is no need for an initial equation to get started),

$$R_{SN} = \{M_1: S, (1/T, U)\} \rightarrow M_1 = S - U/T = (TS - U)/T = -A/T \tag{8}$$

The last result ($-A/T$) was obtained by the aid of Eq. 7. A new relation R can be obtained with a C_4 rotation of the SSG-N, which after insertion of $M_1 = -A/T$, and G from Eq. 6 let us discover the explicit thermodynamic meaning for M_2 (the arrowhead is vertex P/T !),

$$\begin{aligned} C_4R_{SN} &= \{M_2: M_1, (P/T, V)\} \rightarrow M_2 = M_1 - PV/T \\ &= -(A + PV)/T = -G/T \end{aligned} \tag{9}$$

Fig. 3 Left: the SSG-N on the E-digraph; right: the SSG-N on the S-digraph



The obtained relation $-G/T = Y$ is the well-known Planck function [5]. A C_2 operation on the SSG-N of Fig. 3, right, let us uncover, after insertion of $M_2 = -G/T$, the explicit thermodynamic meaning for M_3 ,

$$C_2R_{SN} = \{M_3 : M_2, (U, 1/T)\} \rightarrow M_3 = M_2 + U/T = (U - G)/T \quad (10)$$

4.2 The SSG-P and the differentials of the zero-degree quantities as a function of the one-degree quantities

Be the SSG-P and the E-digraph of Fig. 4, left. By the aid of this graph-digraph superposition together with properties 2 and 3, it is possible to encode the central thermodynamic relationship, $dU = dS \cdot T - dV \cdot P$ (i.e., $dU = TdS - PdV$). The encoding relation is,

$$R_{EP} = \{U: (S, T), (V, P)\} \quad (11)$$

Performing first a σ_{PV} and then a σ_{ST} on the SSG-P the following relations and thermodynamic relationships can be derived,

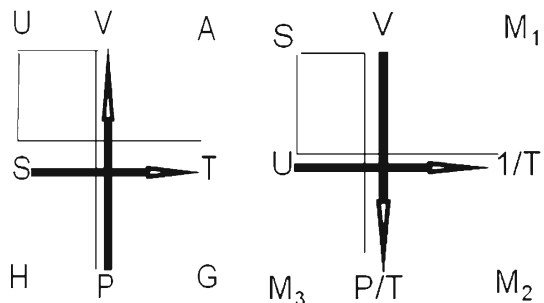
$$\sigma_{PV}R_{EP} = \{A: (T, S), (V, P)\} \rightarrow dA = -dT \cdot S - dV \cdot P = -SdT - PdV \quad (12)$$

$$\begin{aligned} \sigma_{ST}\sigma_{PV}R_{EP} &= \{G: (T, S), (P, V)\} \rightarrow dG = -dT \cdot S + dP \cdot V \\ &= -SdT + VdP \end{aligned} \quad (13)$$

The SSG-P and the S-digraph of Fig. 4, right, give rise to the following encoding relation and thermodynamic relationship (P/T is the arrowhead vertex !),

$$\begin{aligned} R_{SP} &= \{S: (U, 1/T), (V, P/T)\} \rightarrow dS = dU \cdot (1/T) + dV \cdot (P/T) \\ &= dU/T + (P/T)dV \end{aligned} \quad (14)$$

Fig. 4 *Left:* the SSG-P on the E-digraph; *right:* the SSG-P on the S-digraph



With successive SSG-P operations other relationships can be derived, among which,

$$\begin{aligned} \sigma_{PV/T}R_{SP} &= \{M_1 : (1/T, U), (V, P/T)\} \rightarrow dM_1 \\ &= -d(1/T) \cdot U + dV \cdot (P/T) \end{aligned} \tag{15}$$

$$\sigma_{U/T}R_{SP} = \{M_3 : (U, 1/T), (P/T, V)\} \rightarrow dM_3 = dU \cdot (1/T) - d(P/T) \cdot V \tag{16}$$

4.3 The SSG-F and the partial differentials among the zero- and one-degree quantities

The SSG-F and the E-digraph of Fig. 5, left, together with a result from Eq. 12, i.e., $(\partial A/\partial V)_T = -P$, allow to derive the following encoding relation (the 1st and 3rd quantity in parenthesis determine the sign of the relation),

$$R_{EF} = \{A, (V, T: P)\} \tag{17}$$

Now, all other partial differential relationships can be derived. Two new R relations and their thermodynamic relationships can be obtained with a C_4 operation on SSG-F followed by a σ_{ST} operation,

$$-C_4R_{EF} = \{U, (S, V: T)\} \rightarrow (\partial U/\partial S)_V = T \tag{18}$$

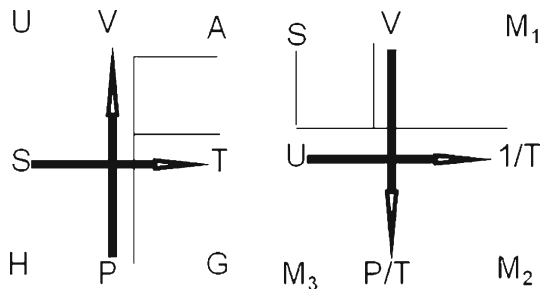
$$\sigma_{ST}(-C_4R_{EF}) = \{H, (S, P: T)\} \rightarrow (\partial H/\partial S)_P = T \tag{19}$$

Another relation R and its thermodynamic relationship can be obtained with a σ_{PV} operation on SSG-F,

$$\sigma_{PV}R_{EF} = \{U, (V, S: P)\} \rightarrow (\partial U/\partial V)_S = -P \tag{20}$$

When the SSG-F is applied to the S-digraph in Fig. 5, right, the following relation R and the corresponding thermodynamic relationship can be obtained (compare with Eq. 18),

Fig. 5 *Left:* the SSG-F on the E-digraph; *right:* the SSG-F on the S-digraph



$$R_{SF} = \{S, (U, V: 1/T)\} \rightarrow (\partial S/\partial U)_V = 1/T \quad (21)$$

Performing reflection operations on this SSG-F the following relationships can be obtained,

$$\sigma_{VP/T}R_{SF} = \{M_1, (1/T, V: U)\} \rightarrow (\partial M_1/\partial(1/T))_V = -U \quad (22)$$

$$\sigma_{U/T}R_{SF} = \{M_3, (U, P/T: 1/T)\} \rightarrow (\partial M_3/\partial U)_{P/T} = 1/T \quad (23)$$

4.4 The SSG-M and the maxwell relations among the one-degree quantities

The encoding of the Maxwell relations with ‘geometrical’ rules was first attempted by Max Born. These relations concern the E-digraph only. The SSG-M on the E-digraph of Fig. 6 and the known fact that these relations concern the partial derivatives of the one-degree quantities (where the third one-degree quantity is held constant) allow us to write the R_{EM} relation, and its corresponding Maxwell relationship. The other three relations can be derived performing C_4 rotations of the SSG-M graph (the sign is given by property 3, which concerns the first and the third quantity in each subset),

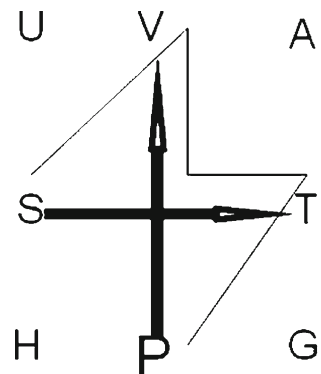
$$R_{EM} = \{(P, T, V): (S, V, T)\} \rightarrow (\partial P/\partial T)_V = (\partial S/\partial V)_T \quad (24)$$

$$-C_4R_{EM} = \{(T, V, S): (P, S, V)\} \rightarrow -(\partial T/\partial V)_S = (\partial P/\partial S)_V \quad (25)$$

$$-C_4^2R_{EM} = \{(V, S, P): (T, P, S)\} \rightarrow -(\partial V/\partial S)_P = -(\partial T/\partial P)_S \quad (26)$$

$$-C_4^3R_{EM} = \{(S, P, T): (V, T, P)\} \rightarrow (\partial S/\partial P)_T = -(\partial V/\partial T)_P \quad (27)$$

Fig. 6 *Left:* the SSG-M on the E-digraph



5 Other applications

Be the Gibbs–Helmholtz relationship, $[\partial(G/T)/\partial(1/T)]_P = H$, substitute G with A and ask about the other changes this relation should undergo. To solve this problem look at the E-digraph of Fig. 2, left, and draw a simple graph, which starts at G goes through T and P and ends in H. Apply to this simple graph a σ_{ST} operation and you notice that V and U should replace P and H respectively. As the sign should be negative on both sides of the relation the overall relation is positive. Rotating this last graph a less-known relation between G and A can be obtained.

6 Conclusions

The use of digraphs and simple graphs and their properties not only widens the applicability of the geometric mechanism that Max Born thought to be useful for the Maxwell relations only but let us uncover the possibility to draw a metalanguage of thermodynamics, which may preside, like a grammar, over the mathematical aspects of thermodynamics.

The reader has noticed that the starting move was normally done by the aid of a well-known thermodynamic relationship. Actually, once properties 1–3, the digraph type and the superimposed simple graph are known, there is no need to know the starting relationship, which can easily be guessed.

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