# The thermodynamic cube: A mnemonic and learning device for students of classical thermodynamics

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The ''thermodynamic cube,'' a mnemonic device for learning and recalling thermodynamic relations, is introduced. The cube is an extension of the familiar ''thermodynamic square'' seen in many textbooks. The cube reproduces the functions of the usual thermodynamic squares and incorporates the Euler relations which are not as well known. 

## I. MOTIVATION

Students learning thermodynamics need to use the many relations between the various thermodynamic potentials and variables. For simple systems, typically a pure substance with a fixed number of particles $N$ in contact with a heat reservoir, the relevant variables are the pressure $P$, volume $V$, temperature $T$, and entropy $S$, and the usual potentials are the internal energy $U$, Helmholtz free energy $F$, Gibbs free energy $G$, and enthalpy $H$. The other potentials are related to $U$ via Legendre transformations.

Students can rapidly become swamped in the various differentials and partial derivatives which occur in thermodynamics. In particular the Maxwell relations, which arise from the equality of the mixed second-order partial derivatives of the potentials, are important in many contexts. A mnemonic device, the thermodynamic square (see Fig. 1), is often introduced[1,2] to help students summarize these relations. The use of the thermodynamic square can be summarized as follows.

- The four potentials appear on the sides of the square adjacent to their natural variables on which they depend. For example, we have $U(V,S)$ and $F(V,T)$.
- The total differential of a potential is given by inspecting the adjacent variables and assigning a minus sign to those variables to which an arrow points. Hence, $dU=TdS-PdV$ and $dF=-SdT-PdV$.
- The four Maxwell relations are obtained using the corners and arrows only. For example, the relation $(\partial V/\partial S)_P=(\partial T/\partial P)_S$ is obtained by starting at the $V$ corner and going counterclockwise around the square. The variables $V$, $S$, and $P$ are encountered in order, and we say ''partial $V$, partial $S$, constant $P$.'' We then continue to the $T$ corner and reverse direction, picking up $T$, $P$, and $S$ in order and saying ''partial $T$, partial $P$, constant $S$.'' The sign between the two derivatives is assigned to be positive because the two paths we took have a symmetric relation to the two arrows. A relation such as $(\partial S/\partial P)_T=-(\partial V/\partial T)_P$ has a negative sign because of the asymmetric placement of the arrows with respect to the two paths we took around the square.

All of these partial derivatives are taken at constant $N$, but this notation is usually suppressed.

If more than one type of particle or a variable number of particles is considered, the chemical potential $\mu$ must be introduced. Additional squares can be drawn for various subclasses of the additional Maxwell relations, depending on which thermodynamic variables are held constant. For a single component system, the total number of squares that can be drawn is six. Due to the Gibbs–Duhem relation, $Nd\mu=-SdT+VdP$, there are three pairs of variables which cannot be held constant at the same time, and so the total number of Maxwell relations for the single component system is 21 and not 24.[1]

## II. THE THERMODYNAMIC CUBE

Because there are six possible thermodynamic squares for the single component system, a single ''thermodynamic cube'' can contain all of the possible Maxwell relations (see Fig. 2). We note the following characteristics of the cube.

- The potentials are at the corners of the cube (unlike the square where they are on the sides), and the variables are on the faces (unlike the square where they are on the corners).
- The arrows travel through the body of the cube, and the directions are indicated by the ''arrow in'' ($\otimes$) and ''arrow out'' ($\odot$) symbols on the faces. The directions of the arrows are reversed from that used in the squares, because of the different way the cube is manipulated.
- The natural variables of a potential are on the faces adjacent to its corner: $U(S,V,N)$, $F(T,V,N)$, $G(T,P,N)$, $H(S,P,N)$, Landau free energy $\Omega(T,V,\mu)$, $\psi(S,V,\mu)$, and $\chi(S,P,\mu)$. The latter two potentials are not commonly used and do not have a standard name or label. The corner adjacent to the $T$, $P$, and $\mu$ faces has a ''0'' assigned to it, because there is no potential with this combination of independent variables, due to the Gibbs–Duhem relation.
- The marks on some of the edges are negative signs which are important for obtaining the Maxwell relations.

## III. USE OF THE CUBE

Using the cube to recall various thermodynamic relations involves holding the cube in your hand and looking at the various sides and corners. It might be difficult to understand the following discussion without first making a cube (see Sec. IV) to follow the examples.

### A. Legendre transforms

For the Legendre transforms which relate the various thermodynamic potentials, we need to first find the two potentials which we seek to relate, and inspect which side(s) the

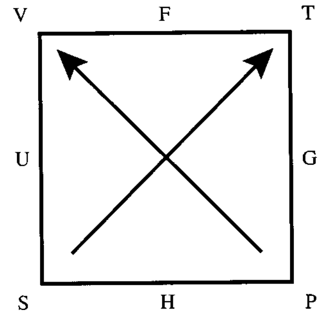


Fig. 1. A thermodynamic square for a system with a fixed number of particles.

two potentials share. Suppose we wish to recall the Legendre transform between the free energy $F$ and the enthalpy $H$. We note that $F$ and $H$ share the $N$ side, which means that $N$ will *not* be involved in the transform—the Legendre transform only involves the variables not in common among the two potentials—so the terms in the transform will be $PV$ and $TS$. The arrows through the cube joining $P$ to $V$ and $T$ to $S$ both point toward the sides adjacent to $H$, so both of these terms have a minus sign if they are on the $H$ side of the equation: $F=H-PV-TS$. One way to recall this expression while holding the cube is to let your eye start at the $F$ corner (''$F$ equals''), then go to the $H$ corner (''$F$ equals $H$''), and then note the arrows pointing out of the $P$ and $S$ sides adjacent to $H$, giving the minus signs (''$F$ equals $H$ minus $PV$ minus $TS$'').

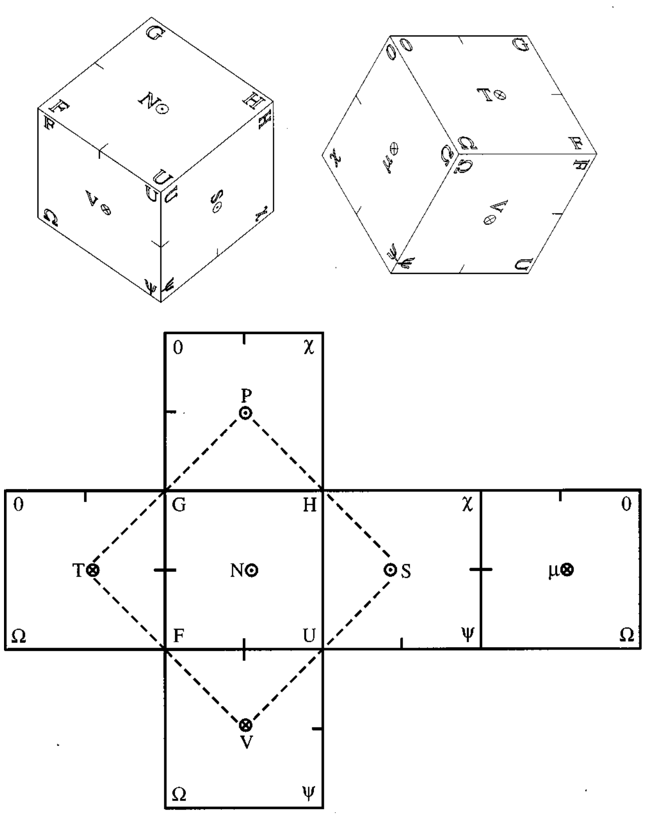


Fig. 2. Two views of the thermodynamic cube, and the cube spread out flat. The dashed line in the flat view shows how the square of Fig. 1 is incorporated into the layout of the cube.

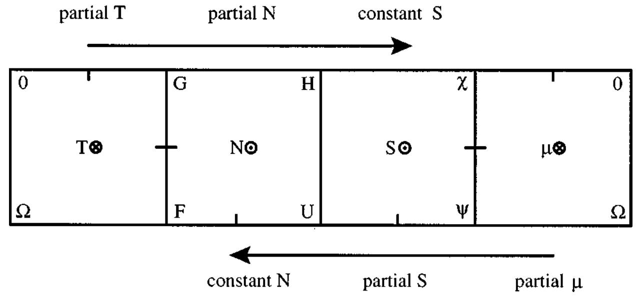


Fig. 3. How to generate the Maxwell relation $(\partial T/\partial N)_S=(\partial \mu/\partial S)_N$.

As another example, consider the Legendre transform between $\Omega$ and $H$. These two potentials do not share any sides (they are at opposite corners), and so the transform will involve three terms $PV$, $TS$, and $\mu N$. Going from $\Omega$ to $H$ (''$\Omega$ equals $H$''), and observing the arrows (''$\Omega$ equals $H$ minus $PV$ minus $TS$ minus $\mu N$''), we obtain $\Omega=H-PV-TS-\mu N$.

### B. Euler form of the potentials

The Euler form[1] for the various potentials can be found by using the cube to obtain the Legendre relation between the zero corner and the potential of interest. Following the above prescription, the internal energy is $U=TS-PV+\mu N$, and the enthalpy is $H=TS+\mu N$.

### C. Differentials of potentials

Suppose we want to obtain the differential for the internal energy $U$. We find the $U$ corner and observe which sides are adjacent to it. The variables on these sides are the dependent variables of the potential and so they will occur as differentials in the resulting expression. The $U$ corner is adjacent to $V$, $S$, and $N$, and so the differential for $U$ will involve $PdV$, $TdS$, and $\mu dN$. If an arrow points into a side, the term associated with that side receives a minus sign: $dU=\mu dN+TdS-PdV$. As another example, the Gibbs–Duhem relation can be recalled by finding the differential of the zero corner.

### D. Maxwell relations

Figure 3 shows how to reconstruct the Maxwell relation $(\partial T/\partial N)_S=(\partial \mu/\partial S)_N$. Starting at the $T$ side, we rotate the cube to see in order the $N$ and $S$ sides (''partial $T$, partial $N$, constant $S$''), and then continue to the $\mu$ side and reverse direction to see again the $S$ and $N$ sides (''partial $\mu$, partial $S$, constant $N$''). Because the common edge of the two expressions, the $N$-$S$ edge, does not have a minus sign on it, the Maxwell relation does not pick up a minus sign. (We can derive the sign in the expression by studying the arrows joining the variables, just as in the case of the thermodynamic square, so the minus signs on the edges of the cube are unnecessary.)

We also can easily recall that $(\partial V/\partial T)_P=-(\partial S/\partial P)_T$ by spinning the cube about the $\mu-N$ axis and following the above prescription.

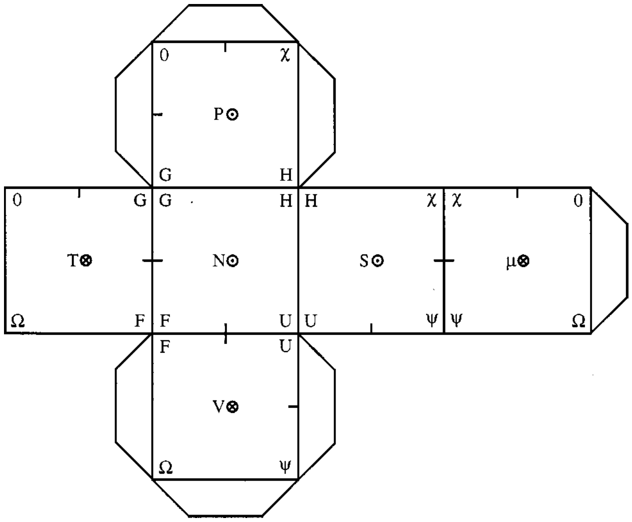


Fig. 4. Do it yourself. A cut-out figure of the cube which can be glued into shape at the tabs.

For a multicomponent system, the terms $\mu N$, $Nd\mu$, and $\mu dN$ would become summations over the particle species; for example, $\mu N$ would become $\Sigma_k \mu_k N_k$.

## IV. MAKING YOUR OWN CUBE

There are several ways of making the thermodynamic cube. The simplest way is to cut out an outline from a sheet of paper and glue the edges together. Figure 4 can be copied (and perhaps enlarged) and cut out for this purpose, and the tabs used as gluing points. This cube is not very sturdy, but it can be filled with tissue paper to prevent it from collapsing under normal use. A better cube can be made from a cube of wood and the letters and symbols painted on it. The Japanese art of paper-folding, known as origami, provides several techniques for making robust cubes from paper alone. Most hobby and craft stores have introductory origami kits, and some book stores have more advanced books on the subject.[3]

## V. CONCLUSION

A simple mnemonic device for learning and recalling a variety of thermodynamic relations has been introduced. The main benefits to students and teachers arise not only from the simple ways of recalling the relations, but also in the visual realization that the various thermodynamic potentials are not independent of each other and can be closely related geometrically.


## ACKNOWLEDGMENTS

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[1]H. B. Callen, *Thermodynamics* (Wiley, New York, 1985), 2nd ed.
[2]K. Huang, *Statistical Mechanics* (Wiley, New York, 1987), 2nd ed.

[3]Note that the cube is not the only polyhedron which could be used to represent these thermodynamic relations. The truncated octahedron, for example, could be used equally well.

### POINCARÉ'S METHOD

[Poincaré] knew, as every mathematician does, that if you have to solve a difficult problem, you first spend time looking at it from different angles. A number of ideas present themselves, which you pursue conscientiously, but you fail to solve your problem. How then do you proceed? Here is what may happen: ''One evening I took black coffee, contrary to my custom. I could not go to sleep. Ideas came up in swarms, I sensed them clashing until a pair would hook together, so to say, to form a stable combination. By morning...I had just to write the results, which only took me a few hours.''

David Ruelle, in a review of Henri Poincaré's *Science et Méthode*, Nature **391**, 760 (1988).