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The Thermodynamic Cuboctahedron

The thermodynamic cuboctahedron is a three dimensional generalization of the thermodynamic square which is a mnemonic device for generating thermodynamic equations, particularly the Maxwell relations. Specifications for the construction of a thermodynamic cuboctahedron are given in this paper.

In 1929, Professor Max Born delivered a lecture on Maxwell's relations in which he used a diagram like the one in Figure 1.[1] F. O. Koenig has elaborated on Born's idea and has provided geometrizations of other thermodynamic relationships.[2] Koenig has even used a thermodynamic octahedron as a geometrical element but in a way very different from the way the thermodynamic cuboctahedron is used in this paper.[2]

The "thermodynamic square" contains a great deal of information:

1) The four fundamental thermodynamical potentials, U, A, H, and G are exhibited at the edges of the square and are flanked at the corners by the thermodynamic parameters upon which they depend

$$\begin{aligned} U &= U(S,V) \\ A &= A(T,V) \\ H &= H(S,P) \\ G &= G(T,P) \end{aligned}$$

2) The two arrows provide plus and minus signs for the differential form of the first law. If an arrow points away from a thermodynamic parameter, then the differential of that parameter has a + sign. If the arrow points toward a thermodynamic parameter, then the differential of that parameter has a − sign. This convention gives

$$\begin{aligned} dU &= TdS - PdV \\ dA &= SdT - PdV \\ dH &= TdS + VdP \\ dG &= SdT + VdP \end{aligned}$$

3) The Maxwell relations can be obtained. They depend only upon the parameters at the corners of the square, and the orientation of the arrows. Figure 2 depicts two situations which lead to the Maxwell's relations

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

The first relation has the same sign on both sides of the equation because the arrows in Figure 2 are oriented symmetrically. The second relation has opposite signs on the two sides of the equation because the arrows are oriented asymmetrically in the corresponding diagram of Figure 2.

In order to include the mole number, N, the chemical potential,[3] μ, and the grand canonical potential, $\Omega = \Omega(T, V, \mu)$,

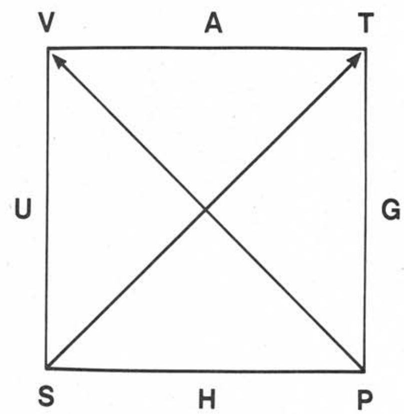

Figure 1. Thermodynamic square.

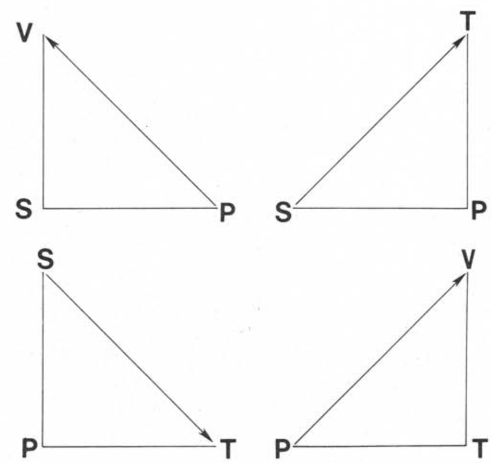

Figure 2. Maxwell relation diagrams.

additional thermodynamic squares are introduced as is depicted in Figure 3.

From the thermodynamic squares in Figure 3, relevant equations for the grand canonical potential are obtained. Using both squares in Figure 3 and the same sign convention as was used in Figure 1, gives

$$d\Omega = SdT - PdV - Nd\mu$$

Note that one square in Figure 3 gives $d\Omega = -SdT - Nd\mu$ while the other square gives $d\Omega = -PdV - Nd\mu$. Consequently, in order to get the full, three parameter dependence for Ω or any of the other thermodynamic potentials, two squares must be used simultaneously. The squares in Figure 3 also provide more Maxwell relations

$$\left(\frac{\partial N}{\partial S}\right)_\mu = -\left(\frac{\partial T}{\partial \mu}\right)_S$$

$$\left(\frac{\partial S}{\partial \mu}\right)_T = \left(\frac{\partial N}{\partial T}\right)_\mu$$

$$\left(\frac{\partial V}{\partial N}\right)_P = \left(\frac{\partial \mu}{\partial P}\right)_N$$

$$\left(\frac{\partial N}{\partial P}\right)_\mu = -\left(\frac{\partial V}{\partial \mu}\right)_P$$

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[1] Callen, H. B., "Thermodynamics," John Wiley & Sons, New York, **1960**, pp. 117–121. In the figure, A denotes the Helmholtz free energy, although Born used the symbol F, as do most physicists.

[2] Koenig, F. O., *J. Chem. Phys.*, **56**, 4556, (1972).

[3] μ, the *chemical* potential is a thermodynamic parameter in a class with S, T, V, P, and N and should not be confused with the *thermodynamic* potentials, U, A, H, G, and Ω.

[4] Callen, H. B., "Thermodynamics," John Wiley & Sons, New York, **1960**, Chap. 3.

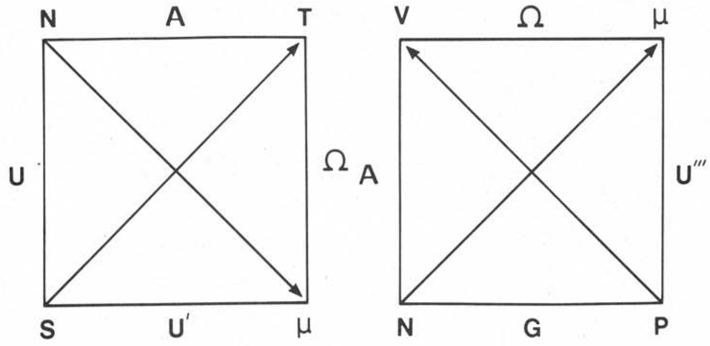

Figure 3. Additional thermodynamic squares.

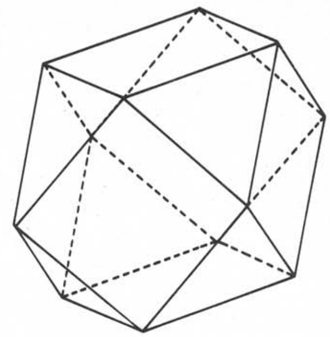

Figure 4. Cuboctahedron.

The additional thermodynamic potentials, U', U'', , U''', which appear in Figure 3 are defined by the Legendre transformations of U given by

$$U' \equiv U - N\mu$$
$$U'' \equiv U + PV - N\mu$$
$$U''' \equiv U - TS + PV - N\mu \equiv 0$$

The first law in differential form, $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N$, and U''' lead to the Gibbs-Duhem relation: $S\mathrm{d}T - V\mathrm{d}P + N\mathrm{d}\mu = 0$. $U''' \equiv 0$ because of the Euler relation for first-order homogenous functions which implies that: $U = TS - PV + N\mu$.[4]

All of the preceding results and kindred others can be represented simultaneously using the surface of a cuboctahedron, which is one of the 13 regular Archimedean solids, and which is comprised of six equal squares and eight equal, equilateral triangles. The cuboctahedron is the solid one gets by successively truncating both a cube and an octahedron until the two truncated solids become identical. Figure 4 depicts the cuboctahedron.

The six thermodynamic parameters, S, T, V, P, N, and μ are placed on the squares, and the eight thermodynamic potentials, U, A, H, G, Ω, U', U'', and U''' are placed on the triangles. Any particular triangle shares an edge with three squares, and any particular square shares an edge with four triangles. It is possible to fill the squares with parameters, and the triangles with potentials, so that the three squares adjacent to the triangle containing a particular potential contain together all three parameters upon which the potential functionally depends. The cuboctahedron tells at a glance that

$$U = U(S,V,N)$$
$$A = A(T,V,N)$$
$$H = H(S,P,N)$$
$$G = G(T,P,N)$$
$$\Omega = \Omega(T,V,\mu)$$

The effect of arrows, as used in thermodynamic squares, can also be achieved with the cuboctahedron by placing a cross, X, with the parameters T, V, and μ and by placing a dot, •, with the parameters S, P, and N. The cross denotes the arrow head while the dot denotes the arrow shaft. The rules for plus and minus signs are then the same as for the thermodynamics squares. All Maxwell relations are readily written and the full parameter dependence is manifested. For example

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N$$
$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}N$$

$$\left(\frac{\partial V}{\partial S}\right)_{P,N} = \left(\frac{\partial T}{\partial P}\right)_{S,N}$$
$$\left(\frac{\partial S}{\partial P}\right)_{T,\mu} = -\left(\frac{\partial V}{\partial T}\right)_{P,\mu}$$

In order to read off Maxwell relations such as in the examples above, the cuboctahedron should be held in such a position

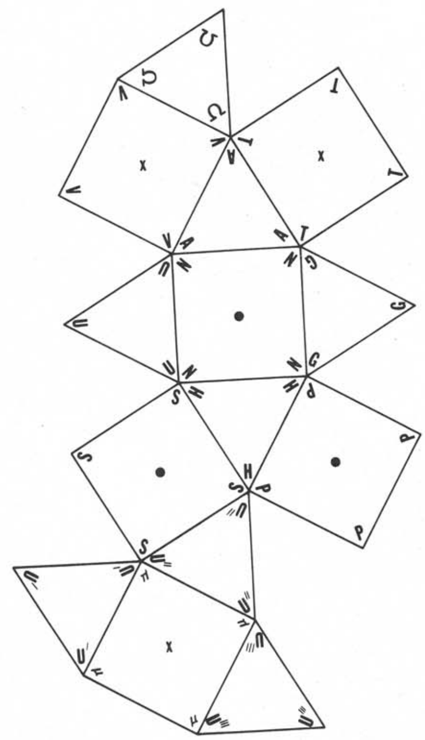

Figure 5. Cut and fold thermodynamic cuboctahedron.

that the four thermodynamic potentials of interest are visible. The associated four parameters will then be found on the squares which connect the visible potentials. A fifth square will connect all four triangles containing the potentials of interest and it provides the additional fixed parameter; or its conjugate parameter which is on the opposite square face of the cuboctahedron can be taken as fixed. Therefore

$$\left(\frac{\partial V}{\partial S}\right)_{P} \longrightarrow \left(\frac{\partial V}{\partial S}\right)_{P,N} \text{ or } \left(\frac{\partial V}{\partial S}\right)_{P,\mu}$$

Figure 5 will be helpful in constructing a thermodynamic cuboctahedron out of stiff paper or thin cardboard. Only a straight edge and a compass are necessary for the construction because every edge is of the same length as every other edge and only squares and equilateral triangles occur in the construction.

Students, in the thermodynamics class which I taught during the Winter quarter of 1974, did very well in the solution to problems requiring thermodynamic formulas, by using their cuboctahedra as compact information sources. The mere act of construction brought to bear a healthy attitude towards Maxwell relations and Legendre transformed potentials which would otherwise probably have been lacking as has been the case with students I have taught who did not construct cuboctahedra.