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Methods of classical thermodynamics
as they apply to

SIMPLE   SYSTEMS

Introduction. The "methods of thermodynamics" are, from a mathematical point of view, all quite elementary. But because thermodynamics provides no natural independent variable (analog of t in dynamics) to lend it a logical beginning/middle/end,[35] a "conceptual spine"... the blizzard of "patterned relationships" to which it gives rise tends to defy all attempts to achieve reduction to an orderly linear arrangment. In this respect, thermodynamics is a bit like a Chinese dictionary. Moreover, getting from here to there on any web-like structure poses strategic problems not encountered on linear structures: those problems require explicit attention in thermodynamics, and serve in part to explain why thermodynamic manipulations often seem so obscurely *ad hoc* to physicists who come to the subject from dynamics.

It is with the expository intent of keeping semi-simple things as semi-simple as possible that I will be illustrating the characteristic methods of classical thermodynamics as they are encountered in the theory of systems with the

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[35] Rather surprisingly, that role is *not* taken over by T. Something like it, however, is played (not within solitary systems subject to manipulation, but within closed composite systems, within the universe as a whole) by the never-decreasing numerical value of S. It has, in fact, been argued (most notably by Einstein) that it is the growth of S that *accounts* for "time's arrow."

least feasible number of independent state variables. Painting on such a small canvas will serve to reduce the notational and conceptual clutter, but will extract a price: certain topics of interest will have to be set temporarily aside

- no multi-phase systems (no ice cubes floating in icewater);
- no multi-species systems (no equilibrated hydrogen/nitrogen/ammonia mixtures, no hot $\gamma \leftrightarrows e^+ + e^-$ systems).

But the theory that emerges will by itself be rich enough to embrace many systems of practical interest, and will supply us with wealth sufficient to redeem many of the topics we have pawned.

Initially, however, I *will* work on a relatively broad canvas, the better to "frame" the work undertaken in the main body of the text.

1. From 2-function formalism to two flavors of 1-function formalism. Classical mechanics does supply a population of statements about Lagrangians-in-general, but in its principal role the Lagrangian serves as a "system-descriptor." You have only to ascribe some specific structure to $L(\dot{\boldsymbol{q}}, \boldsymbol{q})$—and to describe the physical meanings of the variables q—for me to know all I need to know about whatever mechanical system you may have in mind. Within the Hamiltonian formalism the function $H(\boldsymbol{p}, \boldsymbol{q})$ plays a similar role.

The 1st and 2nd laws of thermodynamics assert that with every system $\mathfrak{S}$ we can associate a *pair* of functions, $U(\boldsymbol{\xi})$ and $S(\boldsymbol{\xi})$. Those functions do enter into a population of general, system-non-specific statements, but in their principal role those functions serve as "conjoint system-descriptors." You have only to ascribe particularized structure to them—and to describe the physical meanings of the variables ξ—to indicate the essentials of whatever thermodynamic system is of momentary interest to you. Evidently the laws of thermodynamics invite us to contemplate what might be called a "2-function formalism."

Suppose, however, that—in reprise of a trick with we enjoyed some success already on page 24—we were to *promote the value of $S(\boldsymbol{\xi})$ to the status of a state variable*; *i.e.*, that we were to proceed as follows:

$$S = S(\xi_1, \xi_2, \ldots, \xi_n)$$
$$\downarrow$$
$$\xi_1 = \xi_1(S, \xi_2, \ldots, \xi_n) \quad \text{by functional inversion}$$
$$\downarrow$$
$$U(\xi_1, \xi_2, \ldots, \xi_n) \equiv U(S, \xi_2, \ldots, \xi_n)$$

We arrive then at a "1-function formalism," within which system-specification can be accomplished by presentation of a *single* function. Which is a conceptual economy, but the principal merit of the formalism lies elsewhere:

Simultaneous statement of the 1st and 2nd laws yields

$$\text{CLAUSIUS' DIFFERENTIAL EQUATION}^\dagger \quad : \quad dU = TdS + \dbar W \qquad (25)$$

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† Seems a reasonable enough name for an *equation among differentials*, but is misleading nonetheless.

Simple calculus, on the other hand, supplies

$$dU = \left(\frac{\partial U}{\partial S}\right)dS + \left(\frac{\partial U}{\partial \xi_2}\right)d\xi_2 + \cdots + \left(\frac{\partial U}{\partial \xi_n}\right)d\xi_n$$

so we have

$$T = \left(\frac{\partial U}{\partial S}\right)_{\xi_2,\ldots,\xi_n} \tag{26.1}$$

$$dW = \sum_{i=2}^{n} \left(\frac{\partial U}{\partial \xi_i}\right)_{S,\xi_2,\ldots,\not\xi_i,\ldots,\xi_n} d\xi_i \tag{26.2}$$

which provide the point of departure for much of the work (applied function theory) that will soon command our attention.

The 1-function formalism comes to us in two primary (and, as will emerge, many secondary) flavors. For by obvious adjustment of the procedure described above (alternatively: by functional inversion of $U(S, \xi_2, \ldots, \xi_n)$) we are led to the system-specific function $S(U, \xi_2, \ldots, \xi_n)$ which we can use in conjunction with this variant of Clausius' equation

$$dS = \frac{dU - dW}{T}$$

to obtain

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{\xi_2,\ldots,\xi_n} \tag{27.1}$$

$$dW = -T \sum_{i=2}^{n} \left(\frac{\partial S}{\partial \xi_i}\right)_{U,\xi_2,\ldots,\not\xi_i,\ldots,\xi_n} d\xi_i \tag{27.2}$$

We will say we are working "in the U-representation" when we work from (26), and "in the S-representation" when we work from (27). The two representations lead ultimately to identical conclusions, but arguments that are simple in one may be complicated in the other: choice of representation—and the list of options will be greatly expanded with the introduction of "thermodynamic potentials"—becomes therefore an "analytical degree of freedom," an issue to be addressed at the outset whenever one sets out to establish some specified thermodynamic relationship/formula/identity. We will—at least initially—work mainly in the U-representation.

> **REMARK: Notational conventions standard to thermodynamics.** Given a function $f(x)$ and change of variable $x = x(y)$ one would, in polite mathematical society, never give the name f to the function $f(x(y))$, for its dependence upon y differs from the dependence of $f(x)$ upon x. One would instead write something like $F(y) = f(x(y))$. That formal nicety is suspended in thermodynamic practice…for the simple reason that we change variables at every turn, and we would both exhaust the resources of the alphabet and become confused if we changed the name

of the function every time we did so. It was with this circumstance in mind that on the preceding page we allowed ourselves to write

$$U(\xi_1, \xi_2, \ldots, \xi_n) \equiv U(S, \xi_2, \ldots, \xi_n)$$

even though the $U(\bullet, \bullet, \cdots, \bullet)$ on the left is a different function of its arguments than is the $U(\bullet, \bullet, \cdots, \bullet)$ on the right. No confusion will result if one bears in mind that, by thermodynamic convention,

$$F(x,y) \begin{cases} \text{is } \underline{\text{not}} \text{ to be read "the function } F \text{ of } x \text{ and } y\text{"} \\ \underline{\text{is}} \text{ to be read "}F \text{ described as a function of } x \text{ and } y\text{"} \end{cases}$$

That practice requires that we depart slightly from some of the notational conventions standard to the calculus. The symbol $\partial F/\partial x$ informs us that we assume x to be an argument of F, but tells us nothing about the other variables upon which F has been presumed to depend. We resolve that ambiguity by writing

$$\left(\frac{\partial F}{\partial x}\right)_y, \left(\frac{\partial F}{\partial y}\right)_x, \text{etc.}$$

and more generally

$$\left(\frac{\partial F}{\partial x}\right)_{\text{explicit list of the variables being held constant}}$$

As, in fact, we did already at (26) and (27).

General cautionary note. Central to the processes that lead from the 2-function formalism to the various alternative 1-function formalisms is a step that calls for *functional inversion*. Functional inversions are, in fact, central to *many* of the arguments and manipulations that are basic to thermodynamics. A point to be borne in mind is that functional inversion, though always easy to talk about, is often difficult or impossible to carry out.

EXAMPLE: Ideal gases in the single-function representations. We found earlier that $\{T, V, N\}$ are variables sufficient to describe the state of an ideal gas, and that presentation of the functions

$$\left. \begin{array}{l} U(T, V, N) = NcT \\ S(T, V, N) = Nc\log\dfrac{T}{T_0} + Nk\log\dfrac{V}{V_0} \end{array} \right\} \tag{28}$$

serves in effect to define *what we mean* by an "ideal gas," to distinguish such systems from all other thermodynamic systems. Here

$$c \equiv k\nu \equiv C_V/N_0 = \text{"isovolumetric specific heat per molecule"}$$
$$= \tfrac{3}{2}k \quad \text{for monomolecular gases}$$

and its occurance in (28) informs us that <u>the term "ideal gas" refers actually to the members of a c-parameterized *family* of systems</u>.

The functional inversion of $S(T, V, N)$ poses in this instance no difficulty: we obtain

$$T(S, V, N) = T_0 \left(\frac{V_0}{V}\right)^{k/c} \exp\left\{\frac{S}{Nc}\right\} \tag{29}$$

giving

$$U(S, V, N) = NcT = NcT_0 \left(\frac{V_0}{V}\right)^{k/c} \exp\left\{\frac{S}{Nc}\right\} \tag{30}$$

This solitary function—notable for its implausible appearance! (and entirely typical in that respect!!)—serves to provide a <u>complete characterization of the thermodynamic theory of ideal gases</u> (in the U-representation).

According to (26.1) we can expect to write

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

and indeed: when we use (30) to work out the derivative we promptly recover precisely (29). But we can go further: according to (26.2) we should have

$$dW = \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN \tag{31.1}$$

$$= \left(\frac{\partial U}{\partial V}\right)_{S,N} dV \quad \text{if } N \text{ is held constant}$$

$$= -p \, dV \tag{31.2}$$

which supplies

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = \frac{k}{c}\frac{U}{V}$$

$$= \frac{k}{c}\frac{NcT}{V}$$

The c's cancel, and we obtain finally—for *all* ideal gases—the familiar statement

$$pV = NkT$$

We will return again and again to the ideal gases to illustrate points of principle, as they arise. Here the lesson has been that
- the single-function formalism seems to work, but
- $U(S, \text{other variables})$ is, even in this simplest of cases, structurally bizarre: it seems highly unlikely that one would, on intuitive grounds, ever *guess* the design of (30)!

2. General properties of bulk systems. Let $\mathfrak{S}'$ be a thermodynamic system (think, for example, of an equilibrated gas sample), and let $\mathfrak{S}$ be a mentally delimited fragment of $\mathfrak{S}'$, as indicated in the following figure. Evidently $\mathfrak{S}'$ constitutes a *scaled-up version/replica* of $\mathfrak{S}$. Let the scale-up—so far as it relates
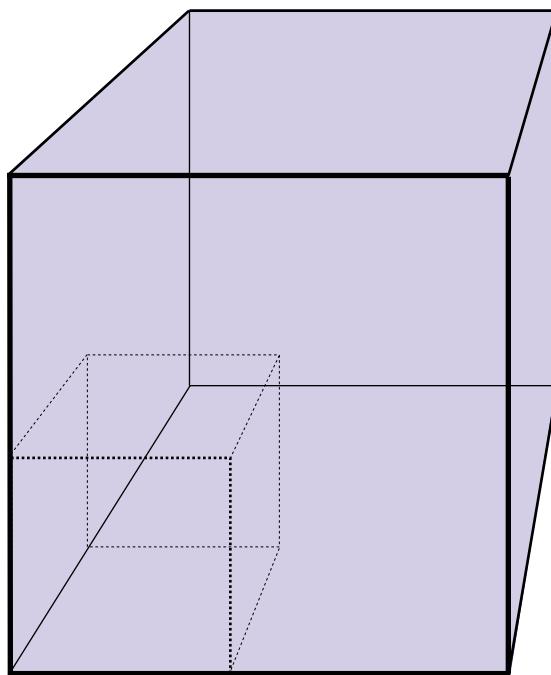
FIGURE 15: *A system $\mathfrak{S}'$ in thermal equilibrium with $\mathfrak{S}$, a mentally delimited fragment of itself.*

to volume—be described

$$V \longmapsto V' = \lambda V$$

Particle number (equivalently : mass and mole number) scales similarly

$$N \longmapsto N' = \lambda N$$

and so—or so we expect, by the argument that gave (17)—does entropy

$$S \longmapsto S' = \lambda S$$

Finally, to the extent that the energetic mechanisms operative within the system hinge on short-range effects that are repeated throughout its volume—that is: to the extent that surface effects (which go as $V^{\frac{2}{3}}$) can be neglected—we expect to have

$$U \longmapsto U' = \lambda U$$

It is, on the other hand, intuitively evident that (for example) temperature and pressure scale by invariance:

$$T \longmapsto T' = T$$
$$p \longmapsto p' = p$$

The preceding remarks relate in the simplest ways—which, as it happens, are also the most important ways—to the question: How do various properties of a thermodynamic system *scale*?[36] And they inspire now the introduction of some terminology:

Extensive state variables (denoted generically by upper-case letters) are variables that—like volume/mass—scale by the rule

$$X \longmapsto X' = \lambda X$$

Intensive state variables (denoted generically by lower-case letters) are variables that—like pressure/temperature—scale by the rule

$$x \longmapsto x' = x$$

A **bulk system** $\mathfrak{B}$ is a thermodynamic system with the property that it can —need not, but *can*—be described in terms of state variables $\{X_1, X_2, \ldots, X_n\}$ <u>all of which are extensive</u>. To describe such a system we (working "canonically" within the U-representation) conventionally identify X_1 with S and assign specific structure to $U(S, X_2, \ldots, X_n)$. But the internal energy is (by prevailing assumption) itself extensive, so we have

$$U(\lambda S, \lambda X_2, \ldots, \lambda X_n) = \lambda^1 U(S, X_2, \ldots, X_n) \tag{32}$$

according to which the function $U(S, X_2, \ldots, X_n)$ is <u>homogeneous of degree one</u>. This fact will exert a major controlling force upon the shape of the ensuing theory.

We have

$$T = \left(\frac{\partial U}{\partial S}\right)_{X_2, \ldots, X_n} \tag{33.1}$$

as a specialized instance of (26.1), and (see again page 8) will take

$$f_i = \left(\frac{\partial U}{\partial X_i}\right)_{S, X_2, \ldots, \cancel{X}_i, \ldots X_n} \tag{33.2}$$

as the *definition* of the **thermodynamic force** conjugate to the variable X_i. In this language "temperature" becomes the "thermodynamic force conjugate to entropy." It is clear (by $\frac{\text{extensive}}{\text{extensive}} = \text{intensive}$) that the f_i are *intensive* : as they

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[36] Though the mechanics of few-particle systems only rarely provokes interest in that question (see, however, Problem 30 at page166 in CLASSICAL MECHANICS (1983)), it is fairly central to the mechanics of distributed systems, especially hydrodynamics and aerodynamics. It is of importance to all engineers who would learn things about real-world systems by studying models, and inspires the widespread interest among engineers in "dimensional analysis" (see, for example, H. L. Langhaar, *Dimensional Analysis & Theory of Models* (1951); C. L. Dym & E. S. Ivey, *Principles of Mathematical Modeling* (1980)). Scaling theory contributes vitally to the understanding of turbulence, to the statistical mechanical theory of critical phenomena, to all physical applications of the theory of fractals.

come to us from (33.2) they are described by functions that are homogeneous of degree zero:

$$f_i(\lambda S, \lambda X_2, \ldots, \lambda X_n) = \lambda^0 f_i(S, X_2, \ldots, X_n) \tag{34}$$

The f_i are dimensionally as diverse as the X's, but in all cases we have

$$[X_i][f_i] = \text{energy}$$

> **NOTATIONAL REMARK:** We will consider ourselves free henceforth to
>
> > write X_1 in place of S
> >
> > write f_1 in place of T
>
> whenever those adjustments serve expository clarity and simplicity. We will, for example, feel free to write $U(\boldsymbol{X})$ in place of $U(S, X_2, \ldots, X_n)$.

Euler's "homogeneous function theorem" asserts that a function $f(\boldsymbol{x})$ will be homogeneous of degree n

$$\lambda^n f(\boldsymbol{x}) = f(\lambda \boldsymbol{x}) \quad \text{if and only if} \quad nf(\boldsymbol{x}) = \sum_i x_i \left(\frac{\partial f}{\partial x_i} \right) \tag{35}$$

From (32) it follows therefore that

$$U(\boldsymbol{X}) = \sum_i X_i \left(\frac{\partial U}{\partial X_i} \right)_{X_1 \cdots \not{X}_i \cdots X_n} = \sum_i X_i f_i(\boldsymbol{X}) \tag{36}$$

Variation of the preceding equation gives

$$dU = \sum_i f_i \, dX_i + \sum_i X_i \, df_i \tag{37}$$

But it is the upshot of Clausius' differential equation (25)—*i.e.*, of the combined 1st and 2nd laws—that

$$dU = T \, dS + \left\{ \sum_{i=2}^n f_i \, dX_i \right\} = \sum_i f_i \, dX_i$$

so from (37) if follows that—not generally, but for all bulk systems—we have the so-called **Gibbs-Duhem relation**

$$\sum_j X_j \, df_j = 0 \tag{38.1}$$

If we write $df_j = \sum_i f_{ij}\, dX_i$ with $f_{ij} \equiv \partial f_j / \partial X_i$ then the Gibbs-Duhem relation becomes

$$\sum_{i,j} dX_i \cdot f_{ij} X_j = 0$$

which by the independent variability of the dX's implies

$$\sum_j f_{ij} X_j = 0 \quad : \quad i = 1, 2, \ldots, n$$
$$\Updownarrow$$
$$\mathbb{F}\boldsymbol{X} = \boldsymbol{0} \quad : \quad \mathbb{F} \equiv \|f_{ij}\| = \|\partial_i f_j\| = \|\partial^2 U / \partial X_i \partial X_j\|$$
$$\Downarrow$$
$$\det \mathbb{F} = 0 \tag{38.2}$$

Evidently (38.1) and (38.2) say, in their separate ways, the same thing … which can be phrased this way: the intensive variables $\{f_1, f_2, \ldots, f_n\}$ cannot be varied independently because they are, according to (38.1), *subject to a solitary differential constraint*, which might be written

$$dT = -\frac{1}{S}\Big\{ \sum_{j=2}^{n} X_j\, df_j \Big\}$$

If (!) the differential form on the right were exact then we would assuredly be able (in principle) to write

$$T = T(f_2, f_3, \ldots, f_n) \tag{39}$$

I will, however, not attempt to establish exactness by direct argument, for in the present instance it is both simpler and more illuminating to proceed by indirection:

Notice first that the intensive variables $\{f_1, f_2, \ldots, f_n\}$—since they are not independent—cannot serve to provide a coordinatization of state space; *i.e.*, that the transformation $\{X_1, X_2, \ldots, X_n\} \longrightarrow \{f_1, f_2, \ldots, f_n\}$ is *singular*

$$\text{Jacobian} \left| \frac{\partial(\, f_1\,,\, f_2\,, \ldots,\, f_n\,)}{\partial(X_1, X_2, \ldots, X_n)} \right| = 0$$

… which is precisely the purport of (38.2). It is therefore evident that by functional inversion of

$$T = T(S, X_2, \ldots, X_n) \tag{40}$$
$$f_2 = f_2(S, X_2, \ldots, X_n)$$
$$\vdots$$
$$f_n = f_n(S, X_2, \ldots, X_n)$$

the best one can hope to achieve is something like

$$X_2 = X_2(S, f_2, \ldots, f_n)$$
$$\vdots$$
$$X_n = X_n(S, f_2, \ldots, f_n)$$

which when inserted back into (40) give an equation of the form

$$T = T(S, f_2, \ldots, f_n) \tag{41}$$

Scale-up induces

$$\downarrow$$
$$T = T(\lambda S, f_2, \ldots, f_n)$$

which by "Euler's trick"[37] becomes

$$0 = S\left(\frac{\partial T}{\partial S}\right)_{f_2, \cdots, f_n}$$

It follows (except at $S = 0$) that the seeming S-dependence of the function on the right side of (41) is illusory, and therefore that (41) has precisely the structure anticipated at (39).

The surviving companions of (40)—rewritten below

$$\left.\begin{array}{l} f_2 = f_2(S, X_2, \ldots, X_n) \\ \qquad \vdots \\ f_n = f_n(S, X_2, \ldots, X_n) \end{array}\right\} \tag{42}$$

—are called the **equations of state** of the system to which they refer . . . somewhat confusingly, because some other things are too. They are $n - 1$ in number.

EXAMPLE: Ideal gases—revisited. How does the preceding formal material play in the "simple" case of an ideal gas? Notice first that the internal energy function encountered at (30) is homogeneous of unit degree if and only if V_0 is included in the list $\{S, V, N; V_0\}$ of extensive variables: we therefore write

$$U(S, V, N; V_0) = NcT_0\left(\frac{V_0}{V}\right)^{k/c} \exp\left\{\frac{S}{Nc}\right\} \tag{43}$$

We then have

$$\left.\begin{array}{lll} T = \left(\dfrac{\partial U}{\partial S}\right)_{V,N,V_0} = \dfrac{U}{Nc} & : & \text{temperature} \\[2mm] f_2 = \left(\dfrac{\partial U}{\partial V}\right)_{S,N,V_0} = -(k/c)\dfrac{U}{V} & : & \text{negative pressure, denoted } -p \\[2mm] f_3 = \left(\dfrac{\partial U}{\partial N}\right)_{S,V,V_0} = \dfrac{U}{N} - \dfrac{US}{N^2 c} & : & \text{"chemical potential," denoted } \mu \\[2mm] f_4 = \left(\dfrac{\partial U}{\partial V_0}\right)_{S,V,N} = +(k/c)\dfrac{U}{V_0} & : & \text{fiducial pressure, denoted } p_0 \end{array}\right\} \tag{44}$$

from which it follows that

$$TS + f_2 V + f_3 N + f_4 V_0 = \frac{US}{Nc} - (k/c)U + \left\{U - \frac{US}{Nc}\right\} + (k/c)U$$
$$= U \quad \text{after simplifications}$$

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[37] Differentiate with respect to λ, then set $\lambda = 1$. See Problem 8.

We have here an instance of (36), by a calculation that would have failed if the f_4V_0-term had been omitted. From the descriptions of f_2 and f_4 it follows readily that

$$pV = p_0V_0$$

while from the descriptions of $f_1 \equiv T$ and f_2 we (again) recover

$$pV = NkT$$

With the invaluable assistance of *Mathematica* we compute

$$\mathbb{F} \equiv \begin{pmatrix} U_{SS} & U_{SV} & U_{SN} & U_{SV_0} \\ U_{VS} & U_{VV} & U_{VN} & U_{VV_0} \\ U_{NS} & U_{NV} & U_{NN} & U_{NV_0} \\ U_{V_0S} & U_{V_0V} & U_{V_0N} & U_{V_0V_0} \end{pmatrix}$$

$$= U \cdot \begin{pmatrix} \frac{1}{c^2N^2} & -\frac{a}{cNV} & -\frac{S}{c^2N^3} & \frac{a}{cNV_0} \\ -\frac{a}{cNV} & \frac{a(a+1)}{V^2} & -\frac{a(cN-S)}{cN^2V} & -\frac{a^2}{VV_0} \\ -\frac{S}{c^2N^3} & -\frac{a(cN-S)}{cN^2V} & \frac{S^2}{c^2N^4} & \frac{a(cN-S)}{cN^2V_0} \\ \frac{a}{cNV_0} & -\frac{a^2}{VV_0} & \frac{a(cN-S)}{cN^2V_0} & \frac{a(a-1)}{V_0^2} \end{pmatrix} \quad : \quad a \equiv k/c$$

and

$$\det \mathbb{F} = \left| \frac{\partial(f_1, f_2, f_3, f_4)}{\partial(S, V, N, V_0)} \right| = 0$$

which provides a concrete instance of the general result reported two pages ago. Now strike the first (which is to say: the Sth) row and column, and compute

$$\left| \frac{\partial(f_2, f_3, f_4)}{\partial(V, N, V_0)} \right| = -U^3 \frac{a^2 S^2}{c^2 N^4 V^2 V_0^2} \neq 0$$

The implication is that—as anticipated at the bottom of page 47—it should in principle be possible to write equations of the form

$$V = V(S, p, \mu, p_0)$$
$$N = N(S, p, \mu, p_0)$$
$$V_0 = V_0(S, p, \mu, p_0)$$

but in point of analytical fact it appers to be unfeasible to do so: the functional inversion problem—even for this simplest of systems—appears to be intractable. That awkward circumstance prevents our obtaining an equation of the form

$$T = T(p, \mu, p_0)$$

contemplated at the top of the preceding page, though by the simplest of arguments one does have

$$T = (p/p_0)T_0 \quad \text{for isovolumetric processes}$$

To summarize: ideal gas systems do conform to the points of general principle developed in the text, but point up this important **MORAL: The functional inversion problem is a beast.**

To the (limited) extent that the results obtained above depend upon the homogeneity assumption they are *special to bulk systems*. Though most of the systems in which we will have physical interest *are* bulk systems (or their lower-dimensional analogs, in which area/length play the role of volume), one does occasionally encounter a system in which the "bulk system assumption" is not justified. Think, for example, of a *bubble* of gas: an accounting of the system energetics will have to include both volume effects and non-negligible *surface effects*, which can be expected to go as $V^{\frac{2}{3}}$. On similar grounds, we expect the thermodynamics of "foam" to require methods beyond those supplied by the theory of bulk systems.

The preceding discussion serves to demonstrate that the 1st and 2nd laws (enriched here by occasional by homogeneity assumptions) place one in position to "do function theory," but supply no compelling evidence bearing on the question "Function theory to what useful purpose?" Before addressing that issue I will install—mainly as a notational convenience—the simplifying assumptions that cause "bulk systems in general" to become "*simple* bulk systems." And it is to place those in context that I present some general remarks pertaining to . . .

3. Systems of ascending complexity. If the state of $\mathfrak{S}$ can be described by a *single* variable ξ then <u>the laws of thermodynamics have nothing useful to say</u>. For then (see again page 19) dW and dQ are both automatically exact. If ξ refers to a mechanical property of the system then the system must necessarily be *purely mechanical*, stripped of all thermodynamic properties (since no variables remain available to describe such properties). The first law reads

$$dU = dW$$
$$dW = W(\xi)\,d\xi = (dU/d\xi)d\xi$$

If, on the other hand, ξ refers to thermodynamic property of the system then the system must necessarily be *purely thermodynamic*, stripped of all mechanical properties. To describe (within the U-representation) the design of such a system we would identify ξ with S and present $U(S)$. Clausius' equation then reads
$$dU = T dS \quad \text{with} \quad T = dU/dS$$

Such systems are almost (not quite) too simple to be interesting.

If the state of $\mathfrak{S}$ can be described by a *pair* of variables, ξ_1 and ξ_2, then the 1st law—which asserts the existence of a $U(\xi_1, \xi_2)$ such that

$$dW + dQ = dU$$

—conveys non-trivial information, but the 2nd law tells us nothing we did not already know, for

the integrability of $dQ = Q_1(\xi_1, \xi_2)d\xi_1 + Q_2(\xi_1, \xi_2)d\xi_2$ is *automatic*

To describe (within the U-representation) the design of such a system we would present $U(S,\xi)$, and write

$$dU = \underbrace{\left(\frac{\partial U}{\partial S}\right)_\xi dS}_{\text{\dj}Q} + \underbrace{\left(\frac{\partial U}{\partial \xi}\right)_S d\xi}_{\text{\dj}W}$$

Under circumstances in which the mechanical variable ξ can be considered "frozen" we recover the (almost) trivial theory considered previously.

The simple point of this discussion:

> The state space of $\mathfrak{S}$ must be at least 3-dimensional if the 1st and 2nd laws are both to contribute non-trivially to the development of the theory.

4. "Simple" bulk systems. These, in a nutshell, are systems $U(S, \xi_2, \xi_3)$ with

$$U(\lambda S, \lambda \xi_2, \lambda \xi_3) = \lambda U(S, \xi_2, \xi_3)$$

In practice, we assign to ξ_2 and ξ_3 the names most commonly natural to physical applications, writing $U(S, V, N)$.

> **REMARK:** We noticed at (43) that to bring the theory of ideal gases into the embrace of the theory of bulk systems we had to write $U(S, V, N; V_0)$, and that the simplest of systems is, by this account, "not simple." The formal theory of simple bulk systems will, however, serve to illuminate most of those aspects of the theory of gases in which V_0 can be considered to be "fixed/frozen."

In this and the next few sections we will be looking to the analytical properties of bulk-systems-in-general. We look to *simple* bulk systems because they require us to keep mental track of only a few, utterly non-exotic variables concerning which we possess already some ripe physical intuitions, variables which—*because* they are few—will cause certain arguments and constructions to resolve into manageably few "cases."

Clausius' differential relation becomes

$$dU = \text{\dj}Q + \text{\dj}W = \big\{ T dS \big\} + \big\{ - p\, dV + \mu\, dN \big\} \tag{45}$$

where

$$\left.\begin{aligned}
T = T(S, V, N) &\equiv \ \ \left(\frac{\partial U}{\partial S}\right)_{V,N} \ : \ \text{absolute temperature} \\
p = p(S, V, N) &\equiv -\left(\frac{\partial U}{\partial V}\right)_{S,N} \ : \ \text{negative pressure} \\
\mu = \mu(S, V, N) &\equiv \ \ \left(\frac{\partial U}{\partial N}\right)_{S,V} \ : \ \text{"chemical potential"}
\end{aligned}\right\} \tag{46}$$

where T, $-p$ and μ are the thermodynamic forces conjugate to the entropy S, volume V and particle number N, respectively.

REMARK: p wears a minus sign because to do mechanical work *on* a system like a gas (*i.e.*, to render $dW > 0$) one must *compress* it ($dV < 0$). Confusion can result when the minus sign built into the defintion of p collides with minus signs that enter into our equations for *other* reasons. To minimize that confusion I will sometimes (rarely) adopt the non-standard notation

$$q \equiv -p$$

and call q the "negpressure."

We can, by Euler's theorem, always write (compare (36))

$$U = TS - pV + \mu N \tag{47}$$

which is sometimes handy, but since the preceding statement follows simply and directly from the assumed *homogeneity* of the function $U(S, V, N)$ it tells us nothing about the *specific* structure of the internal energy function.

Equation (47) acquires diverse interpretations, depending upon how one has elected to coordinatize the space of states. The variables $\{S, V, N\}$ come to us as what might (within the U-representation) be called the "canonical point of departure." Taking classical mechanics as our model, we might contemplate introducing "generalized curvilinear coordinates"

$$q_i \equiv q_i(S, V, N) \quad : \quad i = 1, 2, 3$$

into state space, but in thermodynamics this turns out to be *not* useful, is *not* done. Instead, one confronts in thermodynamics a relatively "crystaline" <u>finite set of coordinate transformations</u> that can be described as follows:

$$\left.\begin{array}{lll} S \longrightarrow & T & : \quad \text{do it or don't} \\ V \longrightarrow & -p & : \quad \text{do it or don't} \\ N \longrightarrow & \mu & : \quad \text{do it or don't} \end{array}\right\} \tag{48}$$

There would appear to be $2^3 = 8$ possibilities, but in fact there are only 7, since "do it, do it, do it" is excluded by

$$\left| \frac{\partial(T, p, \mu)}{\partial(S, V, N)} \right| = 0$$

It will serve my expository purposes to exclude the last-listed option;[38] *i.e.*, to restrict my attention to coordinate transformations of these four basic types:

---

[38] I do this mainly to keep the discussion short, but have in mind also the fact that in physical—as opposed to chemical—problems one often wants to retain a direct and easy way to express the fact that N is a "frozen" parameter.

$$
(S, V, N) \longrightarrow
\begin{array}{l}
\longrightarrow (S, V, N) \; : \; \text{trivial} \\[4pt]
\longrightarrow (T, V, N) \\[4pt]
\longrightarrow (S, p, N) \\[4pt]
\longrightarrow (T, p, N)
\end{array}
\tag{49}
$$

Since T and p came into being at (46) as partial *derivatives* of $U(S, V, N)$ the theory of **Legendre transformations** (see below) provides precisely the tools of which we have just acquired need. The coordinate transformations (49) give rise respectively to functions—partial Legendre transforms of the internal energy function (and of each other)—which are standardly written and designated

$$
U(S, V, N) \longrightarrow
\begin{array}{l}
\longrightarrow U(S, V, N) \; : \; \textbf{energy} \\[4pt]
\longrightarrow F(T, V, N) \; : \; \textbf{free energy} \\[4pt]
\longrightarrow H(S, p, N) \; : \; \textbf{enthalpy} \\[4pt]
\longrightarrow G(T, p, N) \; : \; \textbf{free enthalpy}
\end{array}
\tag{50}
$$

and are known collectively as "thermodynamic potentials." The "home-base" U-representation, natural receptacle for the *laws* of thermodynamics, acquires thus—at least potentially (meaning except when the Legendre transformation in question either fails to exist or cannot be executed)—the companionship of
- the F-representation,
- the H-representation,
- the G-representation, etc.

We have now to examine the detailed meaning those anticipatory remarks, then to address the question: *What has this excursion into "function theory" purchased for us?* The short answer: Lots!!

5. Theory of Legendre transformations. The mathematical literature provides many instances of rules $f(\bullet) \rightarrow F(\bullet)$ for transforming functions into companion functions (and back again), the point being that properties of $f(\bullet)$ may be more easily developed as properties of $F(\bullet)$. Many of those rules[39] are of the form

$$
f(x) \longrightarrow F(y) = \int f(x) K(x, y) \, dx
$$

but we will be concerned here with a rule that falls outside of that class (though it can be obtained from Fourier's rule by a certain delicate limiting process).

Your assignment, let us suppose, is to lend natural/useful meaning to

$$
f(x) \longrightarrow g(p) \quad \text{with} \quad p \equiv \frac{df(x)}{dx}
$$

---

[39] See Ahmed I. Zayed, *Handbook of Function and Generalized Function Transformations* (1996) for an exceptionally nice and up-to-date survey of the "integral transforms" most commonly encountered in physical applications.
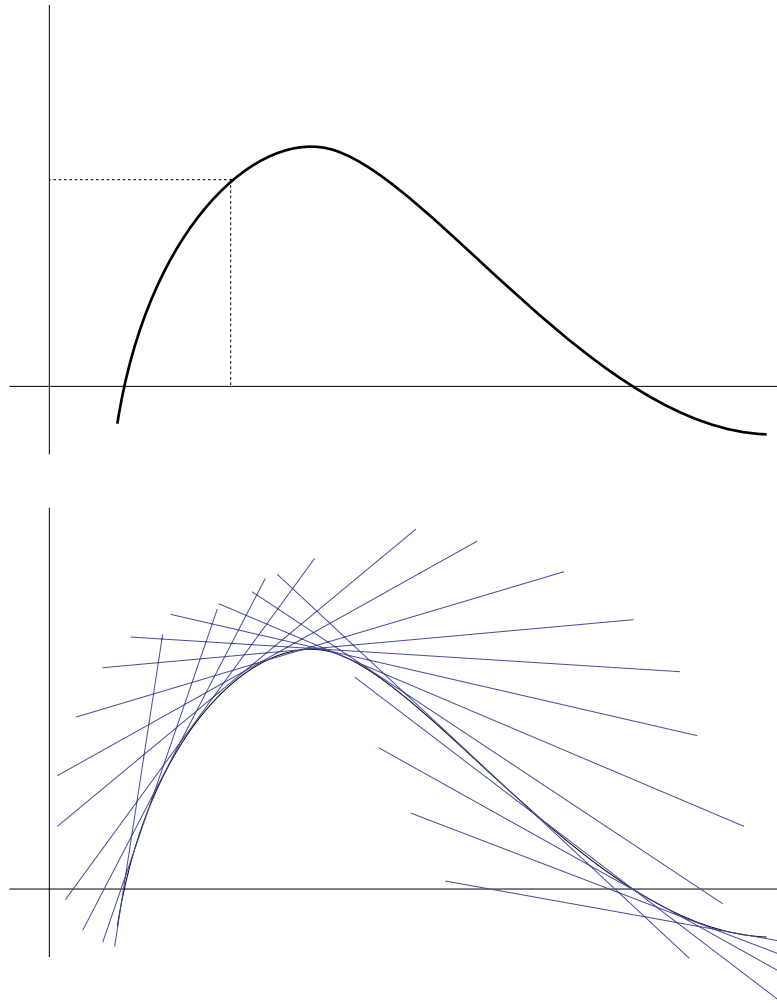
FIGURE 16: *Above: the curve $\mathcal{C}$—the "graph"—that results in the usual way from plotting $y = f(x)$. Below: the same curve displayed as the envelope of its tangents. In the first representation, $\mathcal{C}$ is a property of a set of points; in the second, it is a property of a set of lines. The theory of Legendre transformations formalizes the "duality" of the two constructions.*

You might attempt to "do the obvious"... which is, I take it, to
- write $x = x(p)$ by functional inversion (if possible!) of $p = f'(x)$, then
- construct $g(p) \equiv f(x(p))$

but you would be hard-pressed to list "useful properties" of the transformation $f(x) \rightarrow g(p)$ thus described; you would confront also the fact that the inverse transformation $f(x) \leftarrow g(p)$ is accomplished by quite a *different* procedure.
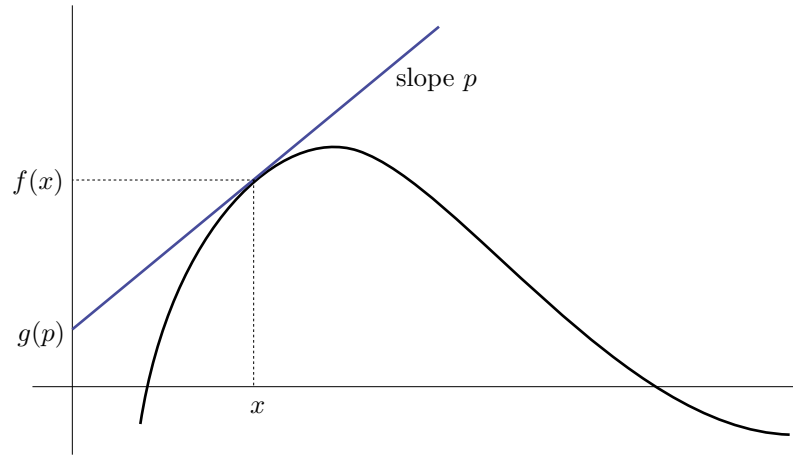
FIGURE 17: *Notations used to describe the relationship between the point-wise and line-wise descriptions of* C. *The function $g(p)$ is the "Legendre transform" of $f(x)$.*

Only a little bit less "obvious"—but culminating in what the experience of two centuries has shown to be, in many applications, the method of choice—is a procedure that takes a plane curve C to be the object that mediates the relation between $f(x)$ and $g(p)$. Figure 16 captures the geometrical essence of the idea, and Figure 17 sets the notation we will use to develop the details. The tangent to C at x has slope $p = f'(x)$ and intercepts the y-axis at a point we will call $g(p)$: it can therefore be described $y = g(p) + px$, and *at the point of tangency* we have

$$g(p) = f(x) - px \tag{51.1}$$

$$p \equiv f'(x) \tag{51.2}$$

The idea now is to write

$$x = x(p) \quad \text{by functional inversion} \tag{51.3}$$

and then to construct

$$g(p) = f(x(p)) - p \cdot x(p) \tag{51.4}$$

EXAMPLE: Look to the case

$$f(x) = \tfrac{1}{2}a(x - b)^2 \tag{52.1}$$

Here $p \equiv f'(x) = a(x - b) \implies x(p) = \dfrac{p + ab}{a}$, so

$$g(p) = \tfrac{1}{2}a\left(\frac{p + ab}{a} - b\right)^2 - p \cdot \frac{p + ab}{a} = -\tfrac{1}{2a}p^2 - bp \tag{52.2}$$

Look now to the differential of (51.1): we find

$$g'(p)dp = \underbrace{\left[f'(x) - p \right]}_{0 \quad \text{by the definition of } p} dx - x\,dp$$

according to which $g'(p) = -x$. What this says is that if we were to construct a graph of $g(p)$ then the slope of the tangent at p is $-x$: the tangent itself could be described $z = (\text{intercept}) - xp$, which *at the point of tangency* becomes

$$g(p) = (\text{intercept}) - xp$$

which upon comparison with (51.1) supplies the information that

$$(\text{intercept}) = f(x)$$

In short: if

$$\left. \begin{array}{l} g(p) = f(x) - px \\ \qquad p = +f'(x) \end{array} \right\} \quad : \quad \text{eliminate } x \text{ to obtain } f(x) \longrightarrow g(p) \quad (53.1)$$

it taken to describe Legendre's rule for "promoting derivatives to the status of independent variables" then

$$\left. \begin{array}{l} f(p) = g(x) + xp \\ \qquad x = -g'(p) \end{array} \right\} \quad : \quad \text{eliminate } p \text{ to obtain } f(x) \longleftarrow g(p) \quad (53.2)$$

informs us that a rule of—except for a reversed sign[40]—identical design accomplishes the inverse transformation.

> **EXAMPLE REVISITED:** Inversion of $x = -g'(p) = \frac{1}{a}p + b$ gives $p = a(x - b)$ whence
>
> $$\begin{aligned} f(x) &= -\tfrac{1}{2a}[a(x-b)]^2 - b[a(x-b)] + x[a(x-b)] \\ &= \tfrac{1}{2}a(x-b)^2 \end{aligned}$$
>
> which is precisely the $f(x)$ introduced at (52.1).

---

[40] Such sign-reversals are the rule rather than the exception. Recall from the theory of Fourier transformations that if

$$g(p) = \tfrac{1}{\sqrt{2\pi}} \int f(x) e^{+ipx}\,dx$$

then

$$f(x) = \tfrac{1}{\sqrt{2\pi}} \int g(p) e^{-ixp}\,dp$$

In multivariable situations one proceeds similarly, writing (for example)

$$
\left.
\begin{aligned}
g(p,q,z) = f(x,y,z) - p\,x - q\,y \\
p = \frac{\partial f(x,y,z)}{\partial x} \\
q = \frac{\partial f(x,y,z)}{\partial y}
\end{aligned}
\right\}
\qquad (54)
$$

By functional inversion of the last pair of equations one obtains

$$
x = x(p,q,z)
$$
$$
y = y(p,q,z)
$$

which when substituted into the first equation produces

$$
f(x,y,z) \xrightarrow[\text{double Legendre transformation}]{} g(p,q,z)
$$

to which the z has been a mere spectator. The functional inversion may, however, be impossible—will be, if

$$
\left| \frac{\partial(p,q)}{\partial(x,y)} \right| = 0
$$

—and, even when possible-in-principle, may well be intractable.

It is, by the way, by just such a scheme that in classical mechanics the Lagrangian $L(\dot{x},\dot{y},x,y) = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2) - U(x,y)$ gives rise to the (negative of the) Hamiltonian:

$$
-H(p,q,x,y) = L(\dot{x},\dot{y},x,y) - p\,\dot{x} - q\,\dot{y}
$$
$$
p = \frac{\partial L}{\partial \dot{x}} = m\dot{x} \;\Rightarrow\; \dot{x} = \tfrac{1}{m}p
$$
$$
q = \frac{\partial L}{\partial \dot{y}} = m\dot{y} \;\Rightarrow\; \dot{y} = \tfrac{1}{m}q
$$
$$
= -\left\{ \tfrac{1}{2m}(p^2 + q^2) + U(x,y) \right\}
$$

Here $\dot{x}$ and $\dot{y}$ are participants in the transformation, x and y are spectators, and the impossibility/intractability problem does not arise. The merit of the exercise is that it converts the system of second-order Lagrange equations into an expanded set of first-order equations of motion (Hamilton's canonical equations).[41]

---

[41] For more on the elementary theory of Legendre transformations see H. B. Callen *Thermodynamics* (1960), §5.2. More advanced material can be found in J. V. José & E. J. Saletan, *Classical Mechanics* (1998), §5.1.2 and V. I. Arnold, *Mathematical Methods of Classical Mechanics* (2$^{\text{nd}}$ edition 1989), pages 61, 366 & 487.

6. Construction of the thermodynamic potentials. It is to establish the pattern of subsequent argument that I begin with a review of some of the already-familiar essentials of the

U-representation Proceeding differentially from $U = U(S, V, N)$ we have

$$dU = T dS - p dV + \mu dN \qquad (55 \cdot U)$$

with

$$\left.\begin{array}{c} T = \left(\dfrac{\partial U}{\partial S}\right)_{V,N} \\[2mm] -p = \left(\dfrac{\partial U}{\partial V}\right)_{S,N} \\[2mm] \mu = \left(\dfrac{\partial U}{\partial N}\right)_{S,V} \end{array}\right\} \qquad (56 \cdot U)$$

The <u>cross-derivative condition</u> $\partial U^2/\partial V \partial S = \partial U^2/\partial S \partial V$ gives[42]

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N} \qquad (57 \cdot U)$$

while the <u>homogeneity condition</u> $\lambda U(S, V, N) = U(\lambda S, \lambda V, \lambda N)$ entails

$$U = TS - pV + \mu N \qquad (58 \cdot U)$$

F-representation The function $F(T, V, N)$ is understood to be the "partial Legendre transform of $U(S, V, N)$ <u>with respect to S</u>," got by eliminating S between

$$T = \frac{\partial U(S, V, N)}{\partial S}$$

and $\qquad F(T, V, N) = U(S, V, N) - TS$

Differentially

$$dF = \big[\,TdS - p dV + \mu dN\,\big] - \big[\,TdS + S dT\,\big] \qquad (55 \cdot F)$$

where the red terms cancel,[43] leaving in their wake the statements

---

[42] This in addition to

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

which I omit because it is our agreed upon intention to hold N constant.

[43] Such a cancellation stands in the middle of *every* Legendre transformation: it comprises the very heart of Legendre's idea.

$$
\left.
\begin{array}{rl}
-p = & \left(\dfrac{\partial F}{\partial V}\right)_{T,N} \\[2ex]
S = & -\left(\dfrac{\partial F}{\partial T}\right)_{V,N} \\[2ex]
\mu = & \left(\dfrac{\partial F}{\partial N}\right)_{T,V}
\end{array}
\right\} \tag{56 $\cdot$ F}
$$

The cross-derivative condition $\partial F^2/\partial V\partial T = \partial F^2/\partial T\partial V$ gives

$$
\left(\frac{\partial S}{\partial V}\right)_{T,N} = +\left(\frac{\partial p}{\partial T}\right)_{V,N} \tag{57 $\cdot$ F}
$$

while—whether one argues from scale-up $\lambda F(T, V, N) = F(T, \lambda V, \lambda N)$ or from

$$
F \equiv U - TS
$$
$$
U = TS - pV + \mu N
$$

—one has

$$
F = -pV + \mu N \tag{58 $\cdot$ F}
$$

$\boxed{\textbf{H-representation}}$ The function $H(S, p, N)$ is produced by eliminating V between
$$
-p = \frac{\partial U(S, V, N)}{\partial V}
$$
and $\qquad H(T, p, N) = U(S, V, N) + pV$

Differentially

$$
dH = \big[TdS - {\color{red}pdV} + \mu\, dN\big] + \big[{\color{red}pdV} + V\, dp\big] \tag{55 $\cdot$ H}
$$

where again the ${\color{red}\text{red terms cancel}}$, leaving in their wake the statements

$$
\left.
\begin{array}{rl}
T = & \left(\dfrac{\partial H}{\partial S}\right)_{p,N} \\[2ex]
V = & \left(\dfrac{\partial H}{\partial p}\right)_{V,N} \\[2ex]
\mu = & \left(\dfrac{\partial H}{\partial N}\right)_{S,p}
\end{array}
\right\} \tag{56 $\cdot$ H}
$$

The cross-derivative condition $\partial H^2/\partial p\partial S = \partial H^2/\partial S\partial p$ gives

$$
\left(\frac{\partial T}{\partial p}\right)_{S,N} = +\left(\frac{\partial V}{\partial S}\right)_{p,N} \tag{57 $\cdot$ H}
$$

while—whether one argues from scale-up or otherwise—one has

$$
H = TS + \mu N \tag{58 $\cdot$ H}
$$

| **G-representation** | Elimination of S <u>and</u> V from amongst

$$T = \frac{\partial U(S, V, N)}{\partial S}$$
$$-p = \frac{\partial U(S, V, N)}{\partial V}$$

and
$$G = U(S, V, N) - TS + pV$$

gives rise to the function of state $G(T, p, N)$. Differentially

$$dG = \big[T dS - p dV + \mu dN\big] - \big[T dS + S dT\big] + \big[p dV + V dp\big] \qquad (55 \cdot G)$$

where the red terms cancel and so do the blue terms, leaving in their wake the statements

$$\left. \begin{aligned} S &= -\left(\frac{\partial G}{\partial T}\right)_{p,N} \\ V &= \left(\frac{\partial G}{\partial p}\right)_{T,N} \\ \mu &= \left(\frac{\partial G}{\partial N}\right)_{T,p} \end{aligned} \right\} \qquad (56 \cdot G)$$

The cross-derivative condition $\partial G^2/\partial p \partial T = \partial G^2/\partial T \partial p$ gives

$$\left(\frac{\partial S}{\partial p}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{p,N} \qquad (57 \cdot G)$$

while—whether one argues from scale-up or otherwise—one has

$$G = \mu N \qquad (58 \cdot G)$$

Several remarks are now in order:

1. By similar manipulations one could "complete the transformational net." Which is to say: though I have, in the text, produced F, H and G as Legendre transforms of U (red arrows in the following diagram), one could by similar maneuvers produce any potential from any other . . . provided only that the
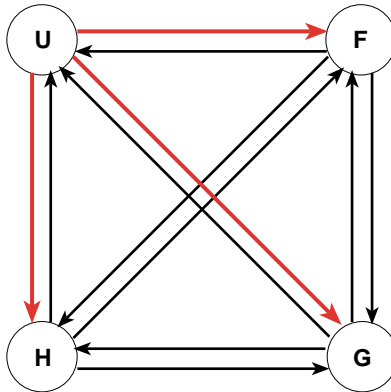
Legendre transformation in question is well-defined (which requires that the relevant Jacobian not vanish). Notice, by the way, that while the existence of U is assured by the *laws* of thermodynamics, we are not similarly protected from the possibility that (say) $U \longrightarrow H$ may *not be well-defined*: in such a case (though I know of no example) we would be forced to the conclusion that the H-potential *does not exist*.

2. The so-called **Born diagram** (see the following figure) translates the problem of remembering <u>which variables associate naturally with which potentials</u> into
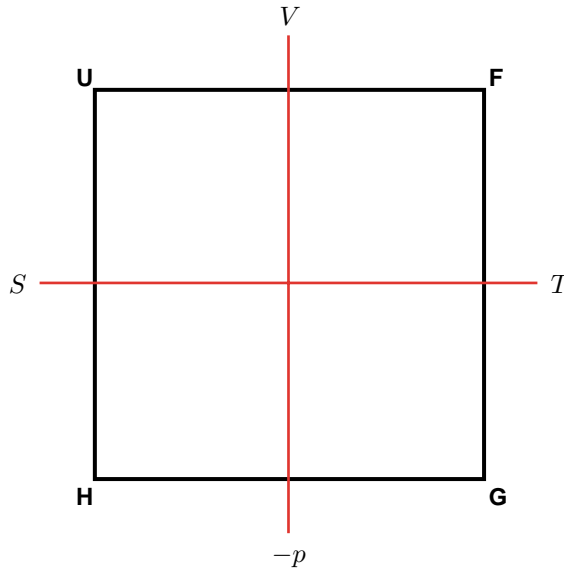

FIGURE 18: *Classic "Born diagram." The potentials appear at the vertices of a square, and the variables upon which they "naturally" depend appear on the adjacent edges. Conjugate variables stand diametrically opposite to one another.*

the problem of <u>remembering how to draw</u> the Born diagram: this is usually accomplished with the aid of personally-devised mnemonics, of which

Good **p**hysicists **H**ave **S**tudied **U**nder **V**ery **F**ine **T**eachers

provides an insipid example (taken from the pages of the American Journal of Physics). If N and μ are brought into play then the square expands into a cube (Figure 19), and mnemonics lose their utility. While the Born diagram serves to identify the variables "natural" to a potential, nothing (unless it be the vanishing of a Jacobian) prevents—and practical considerations sometimes recommend—the use of "unnatural" variables. For example: when developing properties of the isovolumetric and isobaric specific heats we will find it useful to write $U(T, V, N)$ and $U(T, p, N)$, which are obtained from $U(S, V, N)$ not by Legendre transformations but by ordinary "scalar point transformations."
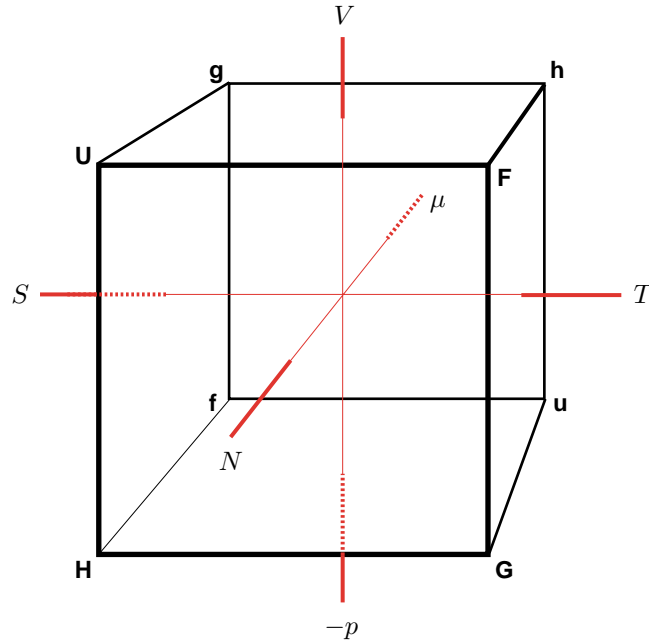
FIGURE 19: *When N is brought into play the Born diagram becomes a "Born cube." There are then 8 potentials (unless homogeneity— via the Gibbs-Duhem relation—intervenes to render* **u** *impossible). We identify those with the vertices of the cube, and the arguments "natural" to each with the faces that meet at that vertex. Conjugate variables are associated with opposite faces.*

3. The potentials U, F, H and G all have the same physical dimension

$$[U] = [F] = [H] = [G] = \text{energy} = [(\text{variable}){\cdot}(\text{conjugate})]$$

and they are intimately interrelated: it follows, for example, from

$$F = U - TS$$
$$H = U + pV$$
$$G = U - TS + pV$$

that

$$U - F - H + G = 0 \tag{59}$$

4. Looking back to equations (55–58·U/F/H/G) we see that the homogeneity assumption (the characteristic "bulk system" assumption) entered into the proof only of (58). The other statements remain in force *even if that assumption is dropped*.

5. A (relatively little used) formally parallel but distinct series of statements/ transformations/relations would have emerged if we had elected to work in the "S-representation:" elected, that is to say, to take not $U(S,V,N)$ but $S(U,V,N)$ as our point of departure (see again page 41).

EXAMPLE: Ideal gas potentials. At (43) we found that the internal **energy** function of an ideal gas can be described

$$U(S,V,N;V_0) = NcT_0\left(\frac{V_0}{V}\right)^a \exp\left\{\frac{S}{Nc}\right\} \tag{60.1}$$

with $a \equiv k/c$. Functional inversion of

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N,V_0} = T_0\left(\frac{V_0}{V}\right)^a \exp\left\{\frac{S}{Nc}\right\}$$

gives

$$\exp\left\{\frac{S}{Nc}\right\} = \frac{T}{T_0}\left(\frac{V}{V_0}\right)^a \quad \text{whence} \quad S = Nc\log\left[\frac{T}{T_0}\left(\frac{V}{V_0}\right)^a\right]$$

so the **free energy** of an ideal gas becomes

$$F(T,V,N;V_0) \equiv U(S,V,N;V_0) - TS$$
$$= NcT\left\{1 - \log\left[\frac{T}{T_0}\left(\frac{V}{V_0}\right)^a\right]\right\} \tag{60.2}$$

In concrete illustration of (56·F) we by quick calculation find

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N,V_0} = \frac{NkT}{V}$$
$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N,V_0} = Nc\log\left[\frac{T}{T_0}\left(\frac{V}{V_0}\right)^a\right]$$

which—gratifyingly—are correct, if not exactly news. Turning our attention now from the free energy F to the enthalpy H... we found that to present ideal gases as "bulk systems" we had to include V_0 among the variables: it seems appropriate, therefore, that if our objective is to eliminate V in favor of p then we should at the same time eliminate V_0 in favor of p_0; *i.e.*, that we should undertake a *double* Legendre transformation. From[44]

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,V_0,N} = a\frac{U}{V} \quad \text{and} \quad p_0 = +\left(\frac{\partial U}{\partial V_0}\right)_{S,V,N} = a\frac{U}{V_0}$$

it follows that $pV = p_0V_0 = aU$ and that $V_0/V = p/p_0$, so from

$$H = U + pV - p_0V_0$$

(in which the red terms cancel) we obtain

---

[44] See again (44).

$$H(S,p,N;p_0) = NcT_0\Big(\frac{p}{p_0}\Big)^a \exp\Big\{\frac{S}{Nc}\Big\} \tag{60.3}$$

In concrete illustration of (56·H) we find

$$T = \Big(\frac{\partial H}{\partial S}\Big)_{p,p_0,N} = T_0\Big(\frac{p}{p_0}\Big)^a \exp\Big\{\frac{S}{Nc}\Big\}$$

$$V = \Big(\frac{\partial H}{\partial p}\Big)_{S,p_0,N} = a\frac{H}{p} = a\frac{U}{p} = \frac{NkT}{p}$$

$$V_0 = -\Big(\frac{\partial H}{\partial p}\Big)_{S,p_0,N} = a\frac{H}{p_0} = a\frac{U}{p_0} = \frac{NkT}{p_0}$$

which are once again "old wine in new bottles." A subsequent Legendre transformation (designed to achieve $S \to T$) would give

$$G(T,p,N;p_0) = NcT\Big\{1 - \log\Big[\frac{T}{T_0}\Big(\frac{p_0}{p}\Big)^a\Big]\Big\} \tag{60.4}$$

7. The stuff we measure in the lab. The *laws* of thermodynamics—as formulated —direct our attention to a certain function $U(S, \text{other state variables})$ from which all the thermodynamic properties of the system $\mathfrak{S}$ can be considered to radiate. But how, in specific physical cases, are we to *discover* U? The issue can be approached in one or another (or some adroit mix) of three principal ways:

- We might, on the basis of our experience, simply <u>guess the structure of U</u>, and then see how implications of our guess compare with the observational facts. We might, for example, proceed from $U_{\text{ideal gas}}$ to a tentatively conjectured $U_{\text{real gas}}$.

- We might attempt to <u>guess the underlying microphysics</u>, then to bring into play the methods of statistical mechanics. Those (as it turns out) deliver into our hands not U but F, which serves quite as well as U as a point of departure for thermodynamnic analysis ...but from which we could (in principle, if we thought it necessary) get to U by Legendre transformation.

- We might <u>go into the lab</u> and observe how $\mathfrak{S}$ responds when "tickled" in various ways, then attempt to devise strategies

$$\text{U(state)} \longleftarrow\! \text{measured data}$$

that enable us to *deduce* the structure of U.

My business in this section and the next will be to describe (within the illustrative context provided by simple systems) the last of those lines of attack. We look here to some shared features of the diverse procedures that result in "measured data" and to the elaborate network of identities that serves invariably/inescapably to interrelate such data.

Let $\mathfrak{S}$ be a simple system (*not* necessarily a "bulk system") of fixed particle number N (which in point of laboratory fact means of fixed *mass*). We ask— because calorimetric techniques would permit us to observe—how $\mathfrak{S}$ responds

to the **injection of differential heat** $đQ$. The 1$^{\text{st}}$ law supplies

$$đQ = dU - \left\{ - p\,dV + \mu\,dN \right\}$$

$$dN = 0 \quad \text{because } N \text{ is experimentally constrained}$$

Writing

$$U = U(T, V, N) \quad : \quad \text{Note the } non\text{-}standard\ arguments \qquad (61)$$

we have

$$đQ = C_V dT + L_V dV \qquad (62)$$

where

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_{V,N} \qquad : \quad \textbf{isovolumetric heat capacity} \qquad (63.1)$$

$$L_V \equiv \left[\left(\frac{\partial U}{\partial V} \right)_{T,N} + p \right] \quad : \quad \textbf{volumetric latent heat} \qquad (63.2)$$

are <u>typical of what thermodynamicists actually measure</u>.

Definitions (63) are particularly well-adapted to the observational realities of gas physics, but if one turns to liquids/solids one finds that *pressure is more susceptible to experimental control than volume*, and is motivated therefore to promote p to the status of independent variable, writing

$$V = V(T, p, N)$$

Returning in this light to (62) we obtain

$$đQ = C_V dT + L_V \left\{ \left(\frac{\partial V}{\partial T} \right)_{p,N} dT + \left(\frac{\partial V}{\partial p} \right)_{T,N} dp \right\}$$

$$= C_p dT + L_p dp$$

with

$$C_p \equiv C_V + L_V \left(\frac{\partial V}{\partial T} \right)_{p,N} \qquad : \quad \textbf{isobaric heat capacity} \qquad (64.1)$$

$$L_p \equiv L_V \left(\frac{\partial V}{\partial p} \right)_{T,N} \qquad : \quad \textbf{barometric latent heat} \qquad (64.2)$$

If, on the other hand, we take (61) as our point of departure and write

$$U = U(T, V(T, p, N), N) \equiv U(T, p, N) \quad : \quad \begin{cases} \text{scalar point transform, used} \\ \text{to obtain a } different \text{ set of} \\ \text{"unnatural arguments"} \end{cases}$$

then by the argument that gave (63) we obtain

$$C_p = \left(\frac{\partial U}{\partial T} \right)_{p,N} + p \left(\frac{\partial V}{\partial T} \right)_{p,N} \qquad (65.1)$$

$$L_p = \left(\frac{\partial U}{\partial p} \right)_{T,N} + p \left(\frac{\partial V}{\partial p} \right)_{T,N} \qquad (65.2)$$

Equations (65) do not much resemble equations (65)! Here we encounter first evidence of the important fact that *quantities of practical thermodynamic interest can always be described in a great many alternative—and non-obviously equivalent—ways* ... of which, inevitably, some are more useful than others; utility is always conditional on the specific application at hand. We will need to become familiar with the transformation-theoretic techniques that enable one to move about efficiently within the **network of equivalent identities**.

Looking to equations (63) and (64), we see that the quantities C_V, L_V, C_p and L_p—which are, in general, <u>not constants but functions of thermodynamic state</u>—are by nature **coefficients of differential susceptibility**: they tell us how, when we hold all-variables-but-one fixed and differentially "tickle the system," the solitary unconstrained variable responds. The coefficients listed above all arise (as it happens) from "tickle processes" that are by nature "calorimetric" (meaning "performed with the aid of a calorimeter").[45, 46]

What follows is a short list of some of the most frequently encountered *non*-calorimetric susceptibility coefficients:

coefficient of (cubic) thermal expansion $\quad : \quad \alpha \equiv +\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N} \qquad$ (66.1)

isothermal compressibility $\quad : \quad \varkappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} \qquad$ (66.2)

adiabatic compressibility $\quad : \quad \varkappa_s \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{S,N} \qquad$ (66.3)

coefficient of tension $\quad : \quad \beta \equiv +\frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_{V,N} \qquad$ (66.4)

$$\vdots$$

$$etc.$$

The constructions C_V, C_p, L_V, L_p, α, $\varkappa$, $\varkappa_s$, β, ... are accorded names because they are intuitively informative and (depending on the system) conveniently measurable functions of state.

They are—as previously remarked—interrelated by an elaborate network of system-independent identities. For example: it follows from (66.1) and (66.2) that

$$d\log V(T,p,N) = \alpha\, dT - \varkappa\, dp + \frac{1}{V}\left(\frac{\partial V}{\partial N}\right)_{T,p} dN$$

and therefore that

$$\left(\frac{\partial \alpha}{\partial p}\right)_{T,N} = -\left(\frac{\partial \varkappa}{\partial T}\right)_{p,N} \tag{67.1}$$

---

[45] It is, by the way, from an instance of $dQ = C_p\, dT$ that calorimetry derives its basic system of units: let C_p refer to the isobaric heat capacity of one gram of H_2O at atmospheric pressure and $T = 15°C$ and let $T + dT = 16°C$. Then, by definition, $dQ =$ one *calorie*.

[46] While C_V, C_p, *etc.* serve well enough the needs of engineers, what one finds tabulated in the handbooks are the corresponding **specific heats**:

$$C_V \equiv m \cdot c_V \equiv \text{(sample mass)} \cdot (\textbf{isovolumetric specific heat})$$
$$C_p \equiv m \cdot c_p \equiv \text{(sample mass)} \cdot (\textbf{isobaric specific heat})$$

Physicists/chemists also speak frequently about the "specific heat per mole" (or "...per molecule"). Note the implicit use made here of the "bulk system" concept.

This is typical of the population of **partial differential identities**, and—since latent in the *definitions* of α and $\varkappa$—is clearly system-independent. Typical of a population of **algebraic identities** are the statements

$$C_p - C_v = \alpha\beta pVT \tag{67.21}$$

$$\alpha = \varkappa\beta p \tag{67.22}$$

—the derivations of which will be postponed.[47] Results like (67) would seem immensely surprising if presented as "experimental discoveries," extracted from data produced by laboratory study of a system $\mathfrak{S}$, and the further discovery that study of a second system $\mathfrak{S}'$ yields the *same* relationships might seem astounding. Their derivation from first principles—as implications of the laws of thermodynamics and of the relevant definitions—serves

- *to render transparent their system-independent generality*, and (since such relations serve typically to declare that one measurement is obviated by a suitably-chosen set of other measurements, that information about difficult-to-measure system-properties may be inferred from easier-to-measure other properties)
- *to simplify the work of experimentalists*.

8. Inferring potentials from measured data. While the functions of state S, U, F *etc.* are "conceptually most primitive" (in the sense that it is they which enter into the postulated foundations of thermodynamics), it is a distinct population of objects—the "coefficients of differential susceptibility"—that are emperically most accessible. The problem before us: *How—from experimental knowledge of the latter—does one deduce the structure of the former?* An illustrative example will serve to make clear the essence of the general procedure:

Suppose the system $\mathfrak{S}$ before us has (like an enclosed sample of gas) the property that
- N is fixed (and will therefore be notationally surpressed), while
- T and V are subject to easy control.

Our stated objective—quite natural in such a circumstance—is to describe U as a function of the (unnatural) variables T and V, and also to describe $S(T, V)$.

Differentially

$$dU(T,V) = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

But $\left(\frac{\partial U}{\partial T}\right)_V \equiv C_V(T, V)$, while by a yet-to-be-established identity[48]

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = T^2\left(\frac{\partial}{\partial T}\frac{p}{T}\right)_V \tag{68}$$

Suppose $C_V(T, V)$ and $p(T, V)$ to be known—because measured—along some

---

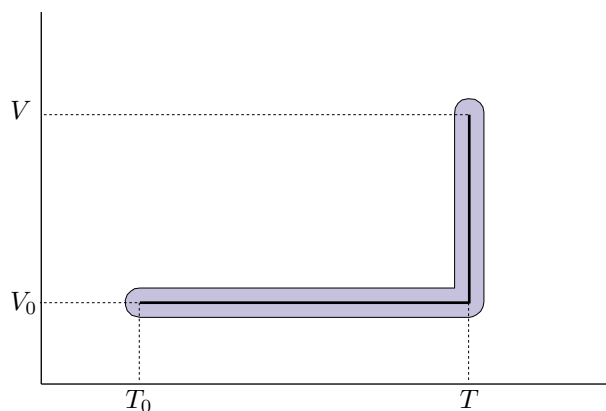[47] See below, page 80.
[48] See (86) page 77.

FIGURE 20: *Specialized path* $(T_0, V_0) \longrightarrow (T, V)$ *used in (69) to construct* $U(T, V)$, *and in (71) to construct* $S(T, V)$. *The path has been made "fat" to provide a schematic reminder that the integrands ask us to* <u>*differentiate the data*</u> $p(T, V)$.

curve $\mathcal{C}$ that on the $\{T, V\}$-plane links $(T_0, V_0) \longrightarrow (T, V)$: then

$$
\begin{aligned}
U(T, V) - U(T_0, V_0) &= \int_{\mathcal{C}} dU \\
&= \int_{\mathcal{C}} \left\{ C_V(T, V) \, dT + T^2 \Big(\frac{\partial}{\partial T} \frac{p(T, V)}{T} \Big)_V dV \right\}
\end{aligned}
$$

If, in particular, we take $\mathcal{C}$ to have the form shown in the figure, then

$$
U(T, V) = U_0 + \int_{T_0}^{T} C_V(T, V_0) \, dT + T^2 \int_{V_0}^{V} \Big(\frac{\partial}{\partial T} \frac{p(T, V)}{T} \Big)_V dV \qquad (69)
$$

A similar argument—one that that exploits the identities

$$
\Big(\frac{\partial S}{\partial T} \Big)_V = \frac{C_V}{T} \qquad (70.1)
$$

$$
\Big(\frac{\partial S}{\partial V} \Big)_T = \Big(\frac{\partial p}{\partial T} \Big)_V \qquad (70.2)
$$

—gives

$$
S(T, V) = S_0 + \int_{T_0}^{T} \frac{C_V(T, V_0)}{T} \, dT + \int_{V_0}^{V} \Big(\frac{\partial p(T, V)}{\partial T} \Big)_V dV \qquad (71)
$$

EXAMPLE: Sitting on our lab bench is (let us say) a fixed sample $\mathfrak{S}$ of ideal gas. By experiment we discover
  • that $C_V(T, V)$ is actually a *constant*, and
  • that $p(T, V) = KT/V$, where K is a second constant.
Equations (69) and (71) then supply

$$U(T, V) = U_0 + C_V \cdot (T - T_0)$$
$$S(T, V) = S_0 + C_V \cdot \log \frac{T}{T_0} + K \cdot \log \frac{V}{V_0}$$

Experiments with scaled replicas of $\mathfrak{S}$ lead us to write

$$C_V = N c_v \quad \text{and} \quad K = N k$$

Exercising our options to set $U_0 = N c_v T_0$ and $S_0 = 0$, we have

$$U(T, V) = N c_v T$$
$$S(T, V) = N c_v \left\{ \log \frac{T}{T_0} + a \cdot \log \frac{V}{V_0} \right\} \quad : \quad a \equiv k/c_v$$

Eliminating T between those two equations we obtain finally

$$U(S, V, N) = U_0 \left(\frac{V_0}{V} \right)^a \exp \left[a \frac{S}{Nk} \right]$$

This equation—which describes U as a function of its "thermodynamically natural" variables $\{S, V, N\}$—is familiar already from (43), but was extracted here from (idealized) "observational data."[49]

The strategy—described above—for accomplishing

$$\text{U(state)} \longleftarrow \text{measured data}$$

admits of many variations;[50] the trick, of course, to select the variation appropriate to the situation at hand, and for that the only guide is experience.

It was remarked on page 29 that "...any system can be made to serve as an 'absolute thermometer.'" *How one might proceed to do so* is an issue that has much in common with the issue discussed above, and that we are in position now to discuss in more general terms what was possible in §13 of Chapter 1. Suppose that for purposes of thermodynamic experimentation/measurement we have adopted some conveniently/arbitrarily-graduated emperical temperature scale $\mathfrak{T}$. Our problem is to execute the transformation

$$\mathfrak{T} \longrightarrow T = T(\mathfrak{T})$$

Though $T(\mathfrak{T})$ is unknown, we do know (by the clever argument concluded on page 26) that

$$\frac{1}{T} \frac{dT}{d\mathfrak{T}} \equiv G(\mathfrak{T}) \quad \text{is system-independent, universal}$$

and that <u>if $G(\mathfrak{T})$ were known then $T(\mathfrak{T})$ could be readily computed</u>. We will

---

[49] In more realistic situations the lab data would be discrete, and one would be obliged to resort to *numerical* differention/integration techniques. One might, however, proceed analytically if the data could be fit to conjectured formulæ.

[50] For discussion of some of those see STATISTICAL PHYSICS (1969), Chapter 3, page 61 or—better—A. H. Wilson, *Thermodynamics & Statistical Mechanics* (1960), pages 37–39.

proceed—non-obviously!—from a yet-to-be-established identity[51] of such general importance that it is known to some authors as the

thermodynamic equation of state   : $\left(\dfrac{\partial U}{\partial V}\right)_T = T\left(\dfrac{\partial p}{\partial T}\right)_V - p$ (72)

We proceed more particularly from the observation that our tentative adoption of the $\mathfrak{T}$-scale entails that in place (72) we should write

$$\left(\frac{\partial U}{\partial V}\right)_{\mathfrak{T}} = T\left(\frac{\partial p}{\partial \mathfrak{T}}\right)_V \frac{d\mathfrak{T}}{dT} - p$$

from which it follows quite simply that

$$G(\mathfrak{T}) \equiv \frac{1}{T}\frac{dT}{d\mathfrak{T}} = \frac{\left(\dfrac{\partial p}{\partial \mathfrak{T}}\right)_V}{\left(\dfrac{\partial U}{\partial V}\right)_{\mathfrak{T}} + p}$$ (73.1)

So $G(\mathfrak{T})$ <u>is</u> known, in the sense *susceptible to direct emperical determination.* Upon feeding this *experimental* information into (compare (15))

$$T(\mathfrak{T}) = C \cdot \exp\left\{ \int^{\mathfrak{T}} G(\mathfrak{T})\, d\mathfrak{T} \right\}$$ (73.2)

we find that we have accomplished a program that might be symbolized

$$\text{T(state)} \longleftarrow\!\!\!\text{—————}\quad \text{measured data}$$

It is on the basis of (73) that frontier thermodynamicists—those not in position to employ off-the-shelf thermometers—do in fact conduct their business.

EXAMPLE: Suppose our "working substance" were (unbeknownst, perhaps, to us) were a fixed sample of ideal gas, and that we had come experimentally to the realization that (compare (18))
  • $U(\mathfrak{T}, V)$ is actually V-independent
  • $p\,(\mathfrak{T}, V) = V^{-1} \cdot \mathfrak{F}(\mathfrak{T})$, with $\mathfrak{F}(\mathfrak{T})$ known from data.
It would follow then from (73.1) that

$$G(\mathfrak{T}) = \frac{V^{-1} \cdot \mathfrak{F}'(\mathfrak{T})}{0 + V^{-1} \cdot \mathfrak{F}(\mathfrak{T})} = \frac{d\log \mathfrak{F}(\mathfrak{T})}{d\mathfrak{T}}$$

<div align="center">NOTE that all variables except $\mathfrak{T}$ have dropped
away, as by general theory they must.</div>

and therefore that $T(\mathfrak{T}) = [C/\mathfrak{F}_0]\cdot\mathfrak{F}(\mathfrak{T})$. From this point the story continues as it continued at the bottom of page 31: the point is that we have here managed to achieve by swift and general means a result that was there obtained by a relatively *ad hoc* line of argument.

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[51] See (86 page 77. We have encountered this same identity already at (68).

9. Identity factories. Generalized "coefficients of susceptibility" (things like C_V: see (63.1)) possess (or are assembled from objects of) the characteristic form

$$\left(\frac{\partial A}{\partial B}\right)_C \tag{74}$$

while "coefficients of *relative* susceptibility" (things like α: see (66.1)) possess the form

$$\frac{1}{A}\left(\frac{\partial A}{\partial B}\right)_C = \left(\frac{\partial \log A}{\partial B}\right)_C$$

where $\{A, B, C\}$ are drawn from the list

$$S, T, V, p; U, F, H, G$$

It will serve the illustrative purposes of the present discussion to consider only coefficients of the former type, of which there are a total of $8 \cdot 7 \cdot 6 = 336$ (most of which are of little or no practical interest). Our remarks will pertain to <u>simple systems with N held fixed</u>: if N (and its conjugate μ) were included in the list of variables then the four potentials $\{U, F, H, G\}$ would be joined by four others (see again Figure 19), and the number total number of such coefficients would expand to $14 \cdot 13 \cdot 12 = 2184$.

Independent state variables can be selected from the short list

$$S, T, V, p$$

in a total of 6 ways:

$$
\begin{array}{lll}
U & : & (S, V) \quad \text{both variables } \textbf{extensive} \\
G & : & (T, p) \quad \text{both variables } \textbf{intensive} \\
F & : & (T, V) \\
H & : & (S, p) \\
  &   & (S, T) \\
  &   & (V, p)
\end{array}
\left.\begin{array}{l}\\\\\\\\\\\\\end{array}\right\} \text{one extensive, other intensive}
$$

$\left.\begin{array}{l}\\\end{array}\right\}$ **non-conjugate** pairs

$\left.\begin{array}{l}\\\end{array}\right\}$ **conjugate** pairs

The selected pair will, for purposes of generic argument, be called $\{x, y\}$. Coordinate transformations can, in this context, be described

$$\begin{pmatrix} x \\ y \end{pmatrix} \longmapsto \begin{pmatrix} a \\ b \end{pmatrix} \equiv \begin{pmatrix} a(x, y) \\ b(x, y) \end{pmatrix} \tag{75}$$

The notations

$$\frac{\partial(a, b)}{\partial(x, y)} = \begin{vmatrix} \left(\frac{\partial a}{\partial x}\right)_y & \left(\frac{\partial a}{\partial y}\right)_x \\ \left(\frac{\partial b}{\partial x}\right)_y & \left(\frac{\partial b}{\partial y}\right)_x \end{vmatrix} = \left(\frac{\partial a}{\partial x}\right)_y \left(\frac{\partial b}{\partial y}\right)_x - \left(\frac{\partial b}{\partial x}\right)_y \left(\frac{\partial a}{\partial y}\right)_x$$

provide alternative descriptions of the "Jacobian" of the transformation (75),

and **Jacobian algebra** provides a powerful means of extracting what are for our purposes the most important implications of (75). The key facts are the following:

$$\frac{\partial(a,b)}{\partial(x,y)} = -\frac{\partial(b,a)}{\partial(x,y)} \tag{76.1}$$

$$= -\frac{\partial(a,b)}{\partial(y,x)} \tag{76.2}$$

$$= \frac{\partial(a,b)}{\partial(u,v)} \cdot \frac{\partial(u,v)}{\partial(x,y)} \tag{76.3}$$

$$= \left[\frac{\partial(x,y)}{\partial(a,b)}\right]^{-1} \tag{76.4}$$

$$= \frac{\partial(a,b)}{\partial(u,v)} \cdot \left[\frac{\partial(x,y)}{\partial(u,v)}\right]^{-1} \tag{76.5}$$

$$\left(\frac{\partial a}{\partial x}\right)_y = \frac{\partial(a,y)}{\partial(x,y)} = \frac{\partial(a,y)}{\partial(u,v)} \cdot \left[\frac{\partial(x,y)}{\partial(u,v)}\right]^{-1} \tag{76.6}$$

$$\frac{\partial(x,y)}{\partial(x,y)} = 1 \tag{76.7}$$

I interpose here some remarks which will serve simultaneously to illustrate the utility of (76) and to establish a property of the **Maxwell relations** which will prove to be of high importance. Drawing upon (76.6) we find that the generic Maxwell relation

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{57·U}$$

can be formulated $\dfrac{\partial(T,S)}{\partial(V,S)} = -\dfrac{\partial(p,V)}{\partial(S,V)}$ or, which is a bit neater (use (76.1/2))

$$\frac{\partial(S,T)}{\partial(S,V)} = \frac{\partial(V,p)}{\partial(S,V)}$$

Multiplication by $\dfrac{\partial(S,V)}{\partial(x,y)}$ gives (by (76.3))

$$\frac{\partial(S,T)}{\partial(x,y)} = \frac{\partial(V,p)}{\partial(x,y)} \quad : \quad x \text{ and } y \text{ arbitrary} \tag{77}$$

Remarkably, we have only to

$$\text{set } (x,y) = \begin{cases} (S,V) \text{ to recover the Maxwell relation } (57\cdot U) \\ (T,V) \text{ to recover the Maxwell relation } (57\cdot F) \\ (S,p) \text{ to recover the Maxwell relation } (57\cdot H) \\ (T,p) \text{ to recover the Maxwell relation } (57\cdot G) \end{cases}$$

By this argument, *all four Maxwell relations are implicit in any one of them*, and can be obtained *without* reference to cross-derivative properties of collateral potentials. But the annotated list on the middle of the preceding page displays

two further possibilities: if we set $(x, y) = (S, T)$ we are led from (77) to what, in the absence of any standard terminology, I will call the **unimodularity condition**

$$\frac{\partial(V, p)}{\partial(S, T)} = \left(\frac{\partial V}{\partial S}\right)_T \left(\frac{\partial p}{\partial T}\right)_S - \left(\frac{\partial p}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1 \qquad (78)$$

while if we set $(x, y) = (V, p)$ we obtain its reciprocal:

$$\frac{\partial(S, T)}{\partial(V, p)} = 1$$

My terminology derives from the observation that if $\mathcal{R}$ is the region bounded by a loop inscribed on the (S, T)-plane, and if $\mathcal{R}'$ is its image on the (V, p)-plane,
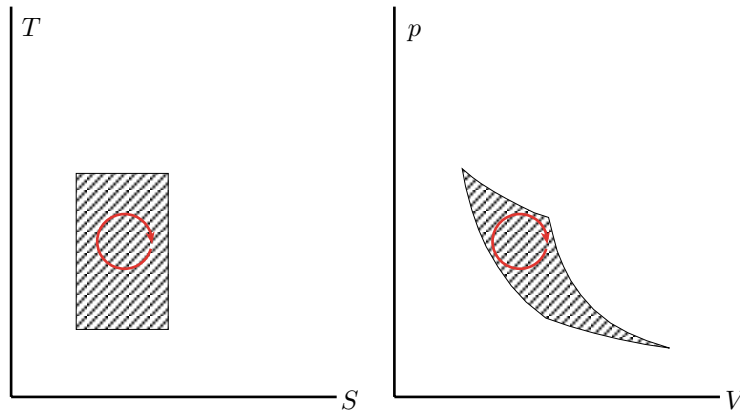

FIGURE 21: *At left: an isolated set $\mathcal{R}$ of states identified by their (S, T)-coordinates. (The set $\mathcal{R}$ is, as it happens, bounded by a pair of isotherms and a pair of adiabats.) At right: the same set of states—identified by their (V, p)-coordinates—define a region $\mathcal{R}'$. The unimodularity condition (78) asserts that*

$$\text{area of } \mathcal{R} = \text{area of } \mathcal{R}'$$

Because (S, T) are conjugate *variables—and so also are (V, p)—one has*

$$[\text{area of } \mathcal{R}] = [\text{area of } \mathcal{R}'] = \text{energy}$$

Orientation of the regions leads to easy physical interpretation of the unimodularity condition.

then (see the figure)

$$\text{area of } \mathcal{R} = \iint_{\mathcal{R}} dS\, dT = \iint_{\mathcal{R}'} \left|\frac{\partial(S, T)}{\partial(V, p)}\right| dV\, dp = \iint_{\mathcal{R}'} dV\, dp = \text{area of } \mathcal{R}'$$

The situation is clarified by the observation that

$$\text{area of } \mathcal{R} = \oint T dS = \oint dQ = \text{heat injected into } \mathfrak{S}, \text{ per cycle}$$

while

$$\text{area of } \mathcal{R}' = \oint p dV = -\oint dW = -(\text{work done on } \mathfrak{S}, \text{ per cycle})$$

$$= \text{work done } by \ \mathfrak{S}, \text{ per cycle}$$

We can, in this light, look upon the unimodularity condition as a ramification of the elementary observation that

$$dQ + dW = dU \quad \Longrightarrow \quad \oint dQ + \oint dW = 0$$

And we can look upon the Maxwell relations as consequences ultimately of that same circumstance.[52]

We are in position now to address what might be called the **fundamental problem in identity-generation theory**, which is to write

$$\left(\frac{\partial A}{\partial B}\right)_C = f\left(x, y, a(x,y), b(x,y), \left(\tfrac{\partial a}{\partial x}\right)_y, \left(\tfrac{\partial a}{\partial y}\right)_x, \left(\tfrac{\partial b}{\partial x}\right)_y, \left(\tfrac{\partial b}{\partial y}\right)_x\right) \qquad (79)$$

where
- x and y are selected from $\{S, T, V, p\}$
- a and b refer to the unselected elements of $\{S, T, V, p\}$
- the partials $\left(\tfrac{\partial a}{\partial x}\right)_y, \left(\tfrac{\partial a}{\partial y}\right)_x, \left(\tfrac{\partial b}{\partial x}\right)_y$ and $\left(\tfrac{\partial b}{\partial y}\right)_x$ are subject to a single Maxwell relation, so only three need/should appear, which is to say: an arbitrarily selected one can/should be discarded.

The expression on the right side of (79) exists in $6 \cdot 4 = 24$ variant formulations, so we confront a population of $336 \cdot 24 = 8064$ potential identities. The inclusion of one or several additional state variables would increase dramatically the size of the identity population. For present purposes it matters little that one has practical interest in very few members of that population, for *to analyse one identity efficiently one must possess technique adequate to the analysis of all.*

How to proceed? All "identity factories" are abstractly identical (and lead, of course, to identical results); they differ one from another only in their computational layout. I present a method that is more straightforward than some others, and is due in outline to A. Tobolsky.[53] We begin by writing

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[52] For further discussion, see pages 45–47 in the class notes cited previously.[50] The unimodularity condition, and its relationship to Maxwell's relations, is discussed in D. J. Ritchie, "A simple method for deriving Maxwell's relations," AJP **36**, 760 (1968).

[53] "A systematic method for obtain the relations between thermodynamic derivatives," J. Chem. Phys. **10**, 644 (1942).

$$dA = \mathfrak{X}_1 dB + \mathfrak{X}_2 dC \quad \text{where} \begin{cases} \mathfrak{X}_1 \equiv \left(\dfrac{\partial A}{\partial B}\right)_C & \text{is the coefficient of interest} \\[2mm] \mathfrak{X}_2 \equiv \left(\dfrac{\partial A}{\partial C}\right)_B & \text{is its "mate"} \end{cases} \tag{80}$$

Additionally

$$\left. \begin{aligned} dA &= a_1 dx + a_2 dy \\ dB &= b_1 dx + b_2 dy \\ dC &= c_1 dx + c_2 dy \end{aligned} \right\} \tag{81}$$

where $\{a_1, a_2, b_1, b_2, c_1, c_2\}$ can be either
  • read directly, or
  • obtained by quick calculation
from the equations

$$dU = +TdS - pdV \tag{82·U}$$
$$dF = -SdT - pdV \tag{82·F}$$
$$dH = +TdS + Vdp \tag{82·H}$$
$$dG = -SdT + Vdp \tag{82·G}$$

and/or the equations

$$\left. \begin{aligned} da &= \left(\dfrac{\partial a}{\partial x}\right)_y dx + \left(\dfrac{\partial a}{\partial y}\right)_x dy \\ db &= \left(\dfrac{\partial b}{\partial x}\right)_y dx + \left(\dfrac{\partial b}{\partial y}\right)_x dy \end{aligned} \right\} \tag{83}$$

Returning with (81) (wherein the a's, b's and c's can now be considered to be known) to (80) we obtain

$$(\mathfrak{X}_1 b_1 + \mathfrak{X}_2 c_1)dx + (\mathfrak{X}_1 b_2 + \mathfrak{X}_2 c_2)dy = a_1 dx + a_2 dy$$

which (since dx and dy are independent) entails

$$\begin{pmatrix} b_1 & c_1 \\ b_2 & c_2 \end{pmatrix} \begin{pmatrix} \mathfrak{X}_1 \\ \mathfrak{X}_2 \end{pmatrix} = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

By matrix inversion

$$\begin{pmatrix} \mathfrak{X}_1 \\ \mathfrak{X}_2 \end{pmatrix} = \frac{1}{b_1 c_2 - b_2 c_1} \begin{pmatrix} c_2 & -c_1 \\ -b_2 & b_1 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

of which

$$\left(\frac{\partial A}{\partial B}\right)_C = \mathfrak{X}_1 = \frac{a_1 c_2 - a_2 c_1}{b_1 c_2 - b_2 c_1} \tag{84.1}$$

is the result of particular interest, while

$$\left(\frac{\partial A}{\partial C}\right)_B = \mathfrak{X}_1 = \frac{a_1 b_2 - a_2 b_1}{c_1 b_2 - c_2 b_1} \tag{84.2}$$

is its B/C-reversed tag-along mate.

A. N. Shaw[54] has arrived at the same results by deft use of the properties (76) of Jacobian determinants. He writes

$$
\left(\frac{\partial A}{\partial B}\right)_C = \frac{\partial(A,C)}{\partial(B,C)} = \frac{\dfrac{\partial(A,C)}{\partial(x,\,y)}}{\dfrac{\partial(B,C)}{\partial(x,\,y)}} = \frac{\begin{vmatrix} \left(\frac{\partial A}{\partial x}\right)_y & \left(\frac{\partial A}{\partial y}\right)_x \\[2mm] \left(\frac{\partial C}{\partial x}\right)_y & \left(\frac{\partial C}{\partial y}\right)_x \end{vmatrix}}{\begin{vmatrix} \left(\frac{\partial B}{\partial x}\right)_y & \left(\frac{\partial B}{\partial y}\right)_x \\[2mm] \left(\frac{\partial C}{\partial x}\right)_y & \left(\frac{\partial C}{\partial y}\right)_x \end{vmatrix}} = \frac{\begin{vmatrix} a_1 & a_2 \\ c_1 & c_2 \end{vmatrix}}{\begin{vmatrix} b_1 & b_2 \\ c_1 & c_2 \end{vmatrix}}
$$

which clearly reproduces (in point of historical fact anticipates) precisely (84.1). In any event—whether one follows in Shaw's footsteps or Tobolski's—one must appeal to (82/83) to *evaluate* the a's, b's and c's appropriate to the specific problem in hand.

EXAMPLE: Our assignment is to describe $C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V$ as a function of T and V —variables which are, as it happens, not "natural" to U. Into

$$dU = a_1 dT + a_2 dV = TdS - pdV$$

we insert
$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

to obtain
$$a_1 = T\left(\frac{\partial S}{\partial T}\right)_V \quad \text{and} \quad a_2 = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

Trivially,
$$dT = b_1 dT + b_2 dV \quad \Longrightarrow \quad b_1 = 1, b_2 = 0$$
$$dV = c_1 dT + c_2 dV \quad \Longrightarrow \quad c_1 = 0, c_2 = 1$$

so by Tobolski's (84.1) we have

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \tag{85.1}$$

Though (T,V) are not natural to U, they are natural to F: drawing upon $S = -\left(\frac{\partial F}{\partial T}\right)_V$ (see again (56·F)) we find that we can, if we wish, write[55]

$$= -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V \tag{85.2}$$

---

[54] "The derivation of thermodynamic relations for a simple system," Phil. Trans. Roy. Soc. **A234**, 299 & 378 (1935). A more lucid account of what has come to be called "Shaw's method" has been given by F. H. Crawford, "Jacobian methods in thermodynamics," AJP **17**, 1 (1949). See also page 450 of the same volume, and additional papers cited there.

[55] The following equation evidently serves to relate C_V/T to the *curvature* of isovolumetric curves inscribed on the (F,T)-plane.

We have—without further labor—also the "mate" of (85.1)

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

which with the aid of the Maxwell relation $(57 \cdot F)$ assumes the form

$$= T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{86}$$

$$= T^2\left(\frac{\partial}{\partial T}\frac{p}{T}\right)_V$$

of what at (72) we called the **thermodynamic equation of state**, and of which we made use already at (68).

> **REMARK:** Equations (56) can be summarized
>
> $$\left.\begin{array}{r}
> \left(\dfrac{\partial U}{\partial S}\right)_V = +T = \left(\dfrac{\partial H}{\partial S}\right)_p \\[2mm]
> \left(\dfrac{\partial F}{\partial V}\right)_T = -p = \left(\dfrac{\partial U}{\partial V}\right)_S \\[2mm]
> \left(\dfrac{\partial G}{\partial T}\right)_p = -S = \left(\dfrac{\partial F}{\partial T}\right)_V \\[2mm]
> \left(\dfrac{\partial H}{\partial p}\right)_S = +V = \left(\dfrac{\partial G}{\partial p}\right)_T
> \end{array}\right\} \tag{87}$$
>
> and, because they yield Maxwell's relations (57) by cross-partial identification, are called the **integrated Maxwell relations**. They often (as just above) prove quite useful.

EXAMPLE: At (64.1) we had

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

Our assignment is to bring this to—compare (79)—the form

$$= f\left(T, p, S(T,p), V(T,p), (\tfrac{\partial S}{\partial T})_p, (\tfrac{\partial S}{\partial p})_T, (\tfrac{\partial V}{\partial T})_p, (\tfrac{\partial V}{\partial p})_T\right)$$

where it is Maxwell's $\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$ that has rendered the stricken term redundant and supplied our *de facto* point of departure:

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V - \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial S}{\partial p}\right)_T$$

We will again use Tobolski's method,[56] and though I write out the details it is to draw attention to how *tedious* they are ... from which very fact we will learn

---

[56] For an account of Shaw's approach to the same problem see STATISTICAL PHYSICS (1969), Chapter 3, page 49.

something. Turning now to those details, we have

$$dU = TdS - pdV$$

$$= T\Big[\Big(\frac{\partial S}{\partial T}\Big)_p dT + \Big(\frac{\partial S}{\partial p}\Big)_T dp\Big] - p\Big[\Big(\frac{\partial V}{\partial T}\Big)_p dT + \Big(\frac{\partial V}{\partial p}\Big)_T dp\Big]$$

$$= a_1 dT + a_2 dp \quad \text{with} \quad \begin{cases} a_1 = T\Big(\frac{\partial S}{\partial T}\Big)_p + p\Big(\frac{\partial S}{\partial p}\Big)_T \\ a_2 = T\Big(\frac{\partial S}{\partial p}\Big)_T - p\Big(\frac{\partial V}{\partial p}\Big)_T \end{cases}$$

$$dT = b_1 dT + b_2 dp \quad \text{with} \quad \begin{cases} b_1 = 1 \\ b_2 = 0 \end{cases}$$

$$dV = \Big(\frac{\partial V}{\partial T}\Big)_p dT + \Big(\frac{\partial V}{\partial p}\Big)_T dp$$

$$= c_1 dT + c_2 dp \quad \text{with} \quad \begin{cases} c_1 = -\Big(\frac{\partial S}{\partial p}\Big)_T \\ c_2 = \Big(\frac{\partial V}{\partial p}\Big)_T \end{cases}$$

which, by (84.1), is found after simplification to give

$$\Big(\frac{\partial U}{\partial T}\Big)_V = \frac{a_1\Big(\frac{\partial V}{\partial p}\Big)_T + a_2\Big(\frac{\partial S}{\partial p}\Big)_T}{\Big(\frac{\partial V}{\partial p}\Big)_T}$$

$$\Big(\frac{\partial U}{\partial V}\Big)_T = \frac{a_2}{\Big(\frac{\partial V}{\partial p}\Big)_T}$$

Returning with this information to our announced point of departure, we find

$$C_p = \left[a_1 + a_2\frac{\Big(\frac{\partial S}{\partial p}\Big)_T}{\Big(\frac{\partial V}{\partial p}\Big)_T}\right] - \left[a_2\frac{\Big(\frac{\partial S}{\partial p}\Big)_T}{\Big(\frac{\partial V}{\partial p}\Big)_T} + p\Big(\frac{\partial S}{\partial p}\Big)_T\right]$$

$$= T\Big(\frac{\partial S}{\partial T}\Big)_p \tag{88.1}$$

And since (56·G) supplies $S = -\Big(\frac{\partial G}{\partial T}\Big)_p$ we can, if we wish, write

$$= -T\Big(\frac{\partial^2 G}{\partial T^2}\Big)_p \tag{88.2}$$

Equations (88) describe C_p in terms that bear a remarkable resemblance to the descriptions (85) of C_V, yet issue from an argument that is markedly more tedious. Why? Because, while the variables (T, V) are semi-natural to U, the variables (T, p) are totally *un*natural. The potential that stands to (T, p) in the

same semi-natural relationship that $U(S, V)$ stands to (T, V) is $H(S, p)$. The implication is that we might fare better if we attempted to construct an H-based theory of C_p. And that, indeed, is easily accomplished: write[57]

$$\mathchar'26dQ = d(H - pV) + p\,dV = C_p dT + L_p dp$$

and (note again the non-standard variables) $H \equiv H(T, p)$. Then

$$\left.\begin{array}{l} C_p = \left(\dfrac{\partial H}{\partial T}\right)_p \\[4mm] L_p = \left[\left(\dfrac{\partial H}{\partial p}\right)_T - V\right] \end{array}\right\} \tag{89}$$

mimic the design of (63). C_p is now simple, and it is the description of C_V that has become relatively complicated:

$$C_V = C_p + L_p \left(\frac{\partial p}{\partial T}\right)_V$$

Proceeding in direct imitation of the argument on page 76 we have

$$dH = a_1 dT + a_2 dp = T\,dS + V\,dp$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

giving

$$a_1 = T\left(\frac{\partial S}{\partial T}\right)_p \quad \text{and} \quad a_2 = T\left(\frac{\partial S}{\partial p}\right)_T + V$$

while trivially

$$dT = b_1 dT + b_2 dp \quad \Longrightarrow \quad b_1 = 1, b_2 = 0$$
$$dp = c_1 dT + c_2 dp \quad \Longrightarrow \quad c_1 = 0, c_2 = 1$$

Tobolski's (84.1) now leads immediately to

$$C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p \tag{90}$$

which is (88.1) without sweat![58]

> **MORAL:** Representation-selection enters as a potentially important consideration into in the efficient generation of thermodynamic identities.

---

[57] Compare page 65.

[58] Since (T, p) are the variables natural to G it might seem reasonable to anticipate that a G-based theory of C_p would be even more efficient than the H-based theory (and similarly: that a F-based theory of C_V would be more efficient than the U-based theory). But try it: you will discover soon enough that—for informative reasons—this is a pretty idea that leads nowhere.

On page 67 I postponed the derivations of a pair of illustrative "*algebraic identities*" which, as it happens, are so important—and the derivation of which involves methods so important—as to merit close attention. At (64.1) we had

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

while the "thermodynamic equation of state" (86) supplies

$$\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] = T\left(\frac{\partial p}{\partial T}\right)_V$$

So we have (recall the definitions (66) of α and β)

$$C_p - C_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \cdot \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V \cdot pVT$$
$$= \alpha\beta pVT$$

... which is (67.21). The derivation of (67.22) is more interesting (because our point of departure is so obscurely related to our destination): From (76.3) it follows in particular that

$$\frac{\partial(S,T)}{\partial(p,T)} = \frac{\partial(S,T)}{\partial(V,T)} \cdot \frac{\partial(V,T)}{\partial(p,T)}$$

which by (76.6) becomes

$$\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial S}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial p}\right)_T$$
$$\downarrow$$
$$-\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial p}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial p}\right)_T \quad \text{by Maxwell relations}$$

Therefore[59]

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \left[-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T\right]\left[\frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V\right]p$$
$$\downarrow$$
$$\alpha = \varkappa\beta p$$

... which is (67.22), and places us in position to write

$$C_p - C_V = (\alpha^2/\varkappa)VT \tag{91.1}$$

Since $\varkappa$, V and T are—for *physical* reasons—necessarily positive, it follows that

$$C_p \geqslant C_V, \text{with equality if and only if } \alpha = 0 \tag{91.2}$$

(which in H_2O occurs at about 4°C). A quantity of major importance—

---

[59] For an entirely different line of argument leading to this same equation, see pages 120 & 133 in MATHEMATICAL THERMODYNAMICS (1967).

especially to the theory of gases—is the *ratio* of heat capacities

$$\gamma \equiv \frac{C_p}{C_V} = \frac{\text{isobaric specific heat}}{\text{isovolumetric specific heat}} \geqslant 1 \qquad (92)$$

which can be described in a variety of ways: from (85.1) and (88.1) we have

$$\gamma = \frac{\left(\frac{\partial S}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_V}$$

which by $\frac{\partial(S,p)}{\partial(T,p)} \cdot \frac{\partial(p,T)}{\partial(V,T)} = \frac{\partial(S,V)}{\partial(T,V)} \cdot \frac{\partial(p,S)}{\partial(V,S)} \implies \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial p}{\partial V}\right)_S$ becomes

$$= \frac{\left(\frac{\partial p}{\partial V}\right)_S}{\left(\frac{\partial p}{\partial V}\right)_T}$$

and by $\left(\frac{\partial x}{\partial y}\right)_z = \left[\left(\frac{\partial y}{\partial x}\right)_z\right]^{-1}$—a corollary of (76.6) & (76.4)—assumes the form

$$= \frac{\left(\frac{\partial V}{\partial p}\right)_T}{\left(\frac{\partial V}{\partial p}\right)_S} = \frac{\varkappa}{\varkappa_s}$$

We will later have occasion to consider why it is that γ occurs commonly in the description of *adiabatic* processes, and why in particular it makes a famous appearance in the formula that describes the velocity of sound in gases.

The "integrated Maxwell relations" (87) describe the first partial derivatives of U, F, H and G with respect to their "natural" variables. But also of importance are the various "unnatural" first partials of the potentials, as became apparent when we wrote

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \text{and again later} \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

Such constructs yield to analysis by (for example) Tobolski's method, which directs our attention also to their "mates"

$$\left(\frac{\partial U}{\partial V}\right)_T \quad \text{and} \quad \left(\frac{\partial H}{\partial p}\right)_T$$

and it is these latter (and objects like them) that I want now to approach by an alternative method: write

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial [F + TS]}{\partial V}\right)_T \quad : \quad T \text{ and } V \text{ are natural to } F$$

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

$$= -p + T\left(\frac{\partial p}{\partial T}\right)_V \quad : \quad \begin{cases} \text{by a Maxwell relation: we have at} \\ \text{this point recovered precisely the} \\ \text{"thermodynamic equation of state"} \end{cases}$$

$$= T^2\left(\frac{\partial}{\partial T}\frac{p}{T}\right)_V$$

and notice that this equation can be rendered

$$\left(\frac{\partial}{\partial V}\frac{U}{T^2}\right)_T = \left(\frac{\partial}{\partial T}\frac{p}{T}\right)_V$$

But the preceding equation can be read as an *exactness condition*, an assertion that there assuredly exists a function $A(T,V)$ such that

$$\left(\frac{\partial A}{\partial T}\right)_V = \frac{U}{T^2} \quad \text{and} \quad \left(\frac{\partial A}{\partial V}\right)_T = \frac{p}{T}$$

and a little tinkering leads to the function that does the job:

$$A(T,V) \equiv -\frac{F(T,V)}{T}$$

What we have, in short, discovered is that

$$d\left(\frac{F}{T}\right) = -\frac{U}{T^2}\,dT - \frac{p}{T}\,dV$$

from which (72)—the "thermodynamic equation of state"

$$\left(\frac{\partial U}{\partial V}\right)_T = T^2\left(\frac{\partial}{\partial T}\frac{p}{T}\right)_V$$

—follows as a statement of the equality of cross-derivatives; *i.e.*, as a kind of "eccentric Maxwell relation." So much for the "mate" of C_V: if we look similarly to the mate of C_p we are led to

$$\left(\frac{G}{T}\right) = -\frac{H}{T^2}\,dT + \frac{V}{T}\,dp$$
$$\Downarrow$$
$$\left(\frac{\partial H}{\partial p}\right)_T = -T^2\left(\frac{\partial}{\partial T}\frac{V}{T}\right)_p$$
$$= V - T\left(\frac{\partial V}{\partial T}\right)_p$$

which we may look upon as an unnamed sibling of (72).[60]

---

[60] $F(T,V)/T$ is a *simple* "assembled function" of T and V. Of course, one could use the material at hand to construct *assembled functions of arbitrary complexity*, give names X and Y to their partials, and stand back amazed by the resulting "eccentric Maxwell relations"

$$\left(\frac{\partial X}{\partial V}\right)_T = \left(\frac{\partial Y}{\partial T}\right)_V$$

but one cannot, in general, expect such activity to serve any useful purpose. The lesson of the preceding discussion is that, however, it once in awhile does.

9. New identities from old by appeal to the formal symmetry-structure of thermodynamics.[61] The "identity-generation engines" described in the preceding section are general-purpose tools, capable in principle of assembling a vast array of products (made vaster still if one looks to derivatives of higher order, and/or increases the number of thermodynamic variables and potentials). We notice, however, the presence of certain <u>repeated patterns</u> in the design of those products (compare, for example, (85) with (90)), and that (see again page 75) the engines <u>accept as input only the following very simple raw material</u>:

$$
\left. \begin{array}{l}
dU = +T\,dS - p\,dV \\
dF = -S\,dT - p\,dV \\
dG = -S\,dT + V\,dp \\
dH = +T\,dS + V\,dp
\end{array} \right\} \tag{93.1}
$$

$$
\left. \begin{array}{llll}
U & = F + TS & = G + TS - pV & = H - pV \\
U - TS & = F & = G - pV & = H - TS - pV \\
U - TS + pV & = F + pV & = G & = H - TS \\
U + pV & = F + TS + pV & = G + TS & = H
\end{array} \right\} \tag{93.2}
$$

$$
U - F + G - H = 0 \tag{93.3}
$$

Equations (93.1) inform us what we consider to be the variables "natural" to each of the potentials, while the highly redundant system (93.2) describes stipulated relationships among the potentials.[62] Equation (93.3)—encountered already at (59)—is an immediate but particularly useful implication of (93.2). The point to which I would lay stress, however, is that **all identities are latent implications of (93)** or, for more general systems (systems with more degrees of freedom), latent in some expanded variant of (93). Our plan is

- to <u>identify the substitutional symmetries</u> inherent in the system (93), then
- to exploit the observation that <u>those must be symmetries *displayed also by the collective implications*</u> of (93).

And to "identify the substitutional symmetries" we will press Born's diagram (Figure 18) into a new kind of service.[63]

The following operations send $\square \to \square$, and in that sense serve to describe the symmetries of a square:

---

[61] What follows is an elaboration of material presented on pages 36–40 of J. S. Lomont's *Applications of Finite Groups* (1959). Lomont cites no source, and his pretty idea (or whose? See the note on page 90.) seems never to have found its way into the standard thermodynamic literature.

[62] The second/third/fourth lines of (93.2) are mere rearrangements of the first line: they have been included to provide escape from the "U-chauvinism" seemingly latent in the standard formulation of *laws* of thermodynamics; *i.e.*, to underscore our determination to treat the potentials as *formally co-equal entities*.

[63] In this respect my line of argument departs from Lomont's.

$$
\begin{aligned}
\mathbf{I} \quad &: \quad \text{identity transformation} \\
\mathbf{R}_1 \quad &: \quad \text{central } \circlearrowleft\text{-rotation through } 90° \\
\mathbf{R}_2 \quad &: \quad \text{central } \circlearrowleft\text{-rotation through } 180° \\
\mathbf{R}_3 \quad &: \quad \text{central } \circlearrowleft\text{-rotation through } 270° \\
\mathbf{A}_1 \quad &: \quad \text{reflect in horizontal axis } \longleftrightarrow \\
\mathbf{A}_2 \quad &: \quad \text{reflect in vertical axis } \updownarrow \\
\mathbf{D}_1 \quad &: \quad \text{reflect in } \nearrow \text{ diagonal} \\
\mathbf{D}_2 \quad &: \quad \text{reflect in } \searrow \text{ diagonal}
\end{aligned}
$$

These operators (see Figure 22) can be looked upon as the elements of a finite *group* of order 8—the so-called **square group**—but that interesting aspect of the situation is of no direct concern to us. The point of interest is that if we decorate the square *a la* Born, then the operations described above serve to *permute* those symbols. Looking for the moment just to the potentials, we have

$$
\begin{aligned}
\mathbf{I} \quad &\longleftrightarrow \quad \{U, F, G, H\} \\
\mathbf{R}_1 \quad &\longleftrightarrow \quad \{F, G, H, U\} \\
\mathbf{R}_2 \quad &\longleftrightarrow \quad \{G, H, U, F\} \\
\mathbf{R}_3 \quad &\longleftrightarrow \quad \{H, U, F, G\} \\
\mathbf{A}_1 \quad &\longleftrightarrow \quad \{H, G, F, U\} \\
\mathbf{A}_2 \quad &\longleftrightarrow \quad \{F, U, H, G\} \\
\mathbf{D}_1 \quad &\longleftrightarrow \quad \{G, F, U, H\} \\
\mathbf{D}_2 \quad &\longleftrightarrow \quad \{U, H, G, F\}
\end{aligned}
$$

Notice that in all cases either U and G share the 1st & 3rd positions or they share the 2nd & 4th positions in the string,[64] from which it follows that (93.3) is **permutationally invariant**. But to describe the permutational transforms of (93.1) and (93.2) we must adjoin $\{V, T, p, S\}$ variables to the preceding list: we must, in other words, work from

$$
\begin{aligned}
\mathbf{I} \quad &\longleftrightarrow \quad \{U, F, G, H; V, T, p, S\} \\
\mathbf{R}_1 \quad &\longleftrightarrow \quad \{F, G, H, U; T, p, S, V\} \\
\mathbf{R}_2 \quad &\longleftrightarrow \quad \{G, H, U, F; p, S, V, T\} \\
\mathbf{R}_3 \quad &\longleftrightarrow \quad \{H, U, F, G; S, V, T, p\} \\
\mathbf{A}_1 \quad &\longleftrightarrow \quad \{H, G, F, U; p, T, V, S\} \\
\mathbf{A}_2 \quad &\longleftrightarrow \quad \{F, U, H, G; V, S, p, T\} \\
\mathbf{D}_1 \quad &\longleftrightarrow \quad \{G, F, U, H; T, V, S, p\} \\
\mathbf{D}_2 \quad &\longleftrightarrow \quad \{U, H, G, F; S, p, T, V\}
\end{aligned}
$$

---

[64] The circumstance just described is, as it happens, realized in all possible ways, and reflects the elementary fact that symmetry operations can not disturb the "diametric oppositeness" of U and G.
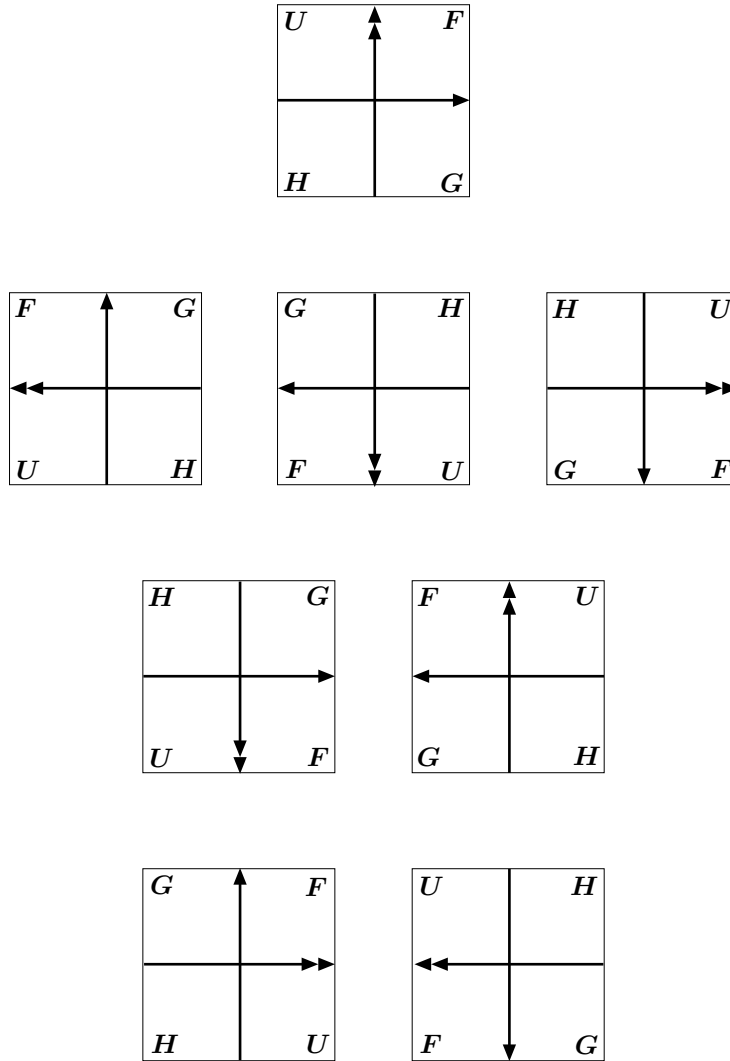
FIGURE 22: *Explicit action of the elements of the* **square group**, *displayed in the sequence*

$$\mathbf{I}$$
$$\mathbf{R}_1 \quad \mathbf{R}_2 \quad \mathbf{R}_3$$
$$\mathbf{A}_1 \quad \mathbf{A}_2$$
$$\mathbf{D}_1 \quad \mathbf{D}_2$$

The arrows proceed $S \longrightarrow T$ *and* $p \longrightarrow V$, *and will acquire an importance evident in Figure 23.*

When (for example) the permutation $\mathbf{R}_1$ is applied to (93.1) one obtains

$$
\left.
\begin{aligned}
dF &= \oplus p\,dV - S\,dT \\
dG &= \ominus V\,dp - S\,dT \\
dH &= \ominus V\,dp + T\,dS \\
dU &= \oplus p\,dV + T\,dS
\end{aligned}
\right\}
\qquad \mathbf{R}_1(93.1)
$$

in which I have circled <u>signs that are in disagreement</u> with (93). All could be rectified by the simple adjustment $p \to -p$, which (compare Figures 22 & 23) we might associate diagramatically with a restoration of $\longleftarrow$ to its "canonical" orientation. Similarly, the permutation $\mathbf{R}_2$ gives

$$
\left.
\begin{aligned}
dG &= \oplus S\,dT \ominus V\,dp \\
dH &= \ominus T\,dS \ominus V\,dp \\
dU &= \ominus T\,dS \oplus p\,dV \\
dF &= \oplus S\,dT \oplus p\,dV
\end{aligned}
\right\}
\qquad \mathbf{R}_2(93.1)
$$

in which *all* the signs are wrong, a circumstance that we associate with the fact that now (compare Figures 22 & 23) *both* arrows are misdirected, and rectify by double adjustment: $p \to -p, T \to -T$. Look finally to the $\mathbf{A}_1$ permutation, which gives

$$
\left.
\begin{aligned}
dH &= +T\,dS \ominus V\,dp \\
dG &= -S\,dT \ominus V\,dp \\
dF &= -S\,dT \oplus p\,dV \\
dU &= +T\,dS \oplus p\,dV
\end{aligned}
\right\}
\qquad \mathbf{A}_1(93.1)
$$

We associate the incorrect signs here with (compare Figures 22 & 23) a single misdirected arrow, which when rectified leaves $p \to -p$ in its wake. So it goes ...though in fact we need go no farther, for from the group table

I	$\mathbf{R}_1$	$\mathbf{R}_2$	$\mathbf{R}_3$	$\mathbf{A}_1$	$\mathbf{A}_2$	$\mathbf{D}_1$	$\mathbf{D}_2$
$\mathbf{R}_1$	$\mathbf{R}_2$	$\mathbf{R}_3$	**I**	$\mathbf{D}_1$	$\mathbf{D}_2$	$\mathbf{A}_2$	$\mathbf{A}_1$
$\mathbf{R}_2$	$\mathbf{R}_3$	**I**	$\mathbf{R}_1$	$\mathbf{A}_2$	$\mathbf{A}_1$	$\mathbf{D}_2$	$\mathbf{D}_1$
$\mathbf{R}_3$	**I**	$\mathbf{R}_1$	$\mathbf{R}_2$	$\mathbf{D}_2$	$\mathbf{D}_1$	$\mathbf{A}_1$	$\mathbf{A}_2$
$\mathbf{A}_1$	$\mathbf{D}_2$	$\mathbf{A}_2$	$\mathbf{D}_1$	**I**	$\mathbf{R}_2$	$\mathbf{R}_3$	$\mathbf{R}_1$
$\mathbf{A}_2$	$\mathbf{D}_1$	$\mathbf{A}_1$	$\mathbf{D}_2$	$\mathbf{R}_2$	**I**	$\mathbf{R}_1$	$\mathbf{R}_3$
$\mathbf{D}_1$	$\mathbf{A}_1$	$\mathbf{D}_2$	$\mathbf{A}_2$	$\mathbf{R}_1$	$\mathbf{R}_3$	**I**	$\mathbf{R}_2$
$\mathbf{D}_2$	$\mathbf{A}_2$	$\mathbf{D}_1$	$\mathbf{A}_1$	$\mathbf{R}_3$	$\mathbf{R}_1$	$\mathbf{R}_2$	**I**

we learn that all group elements can be assembled from $\mathbf{R}_1$ and $\mathbf{A}_1$:

$$
\mathbf{R}_1\mathbf{R}_1 = \mathbf{R}_2, \quad \mathbf{R}_1\mathbf{R}_2 = \mathbf{R}_3
$$

$$
\mathbf{R}_1\mathbf{A}_1 = \mathbf{D}_1, \quad \mathbf{R}_1\mathbf{D}_1 = \mathbf{A}_2, \quad \mathbf{R}_1\mathbf{A}_2 = \mathbf{D}_2
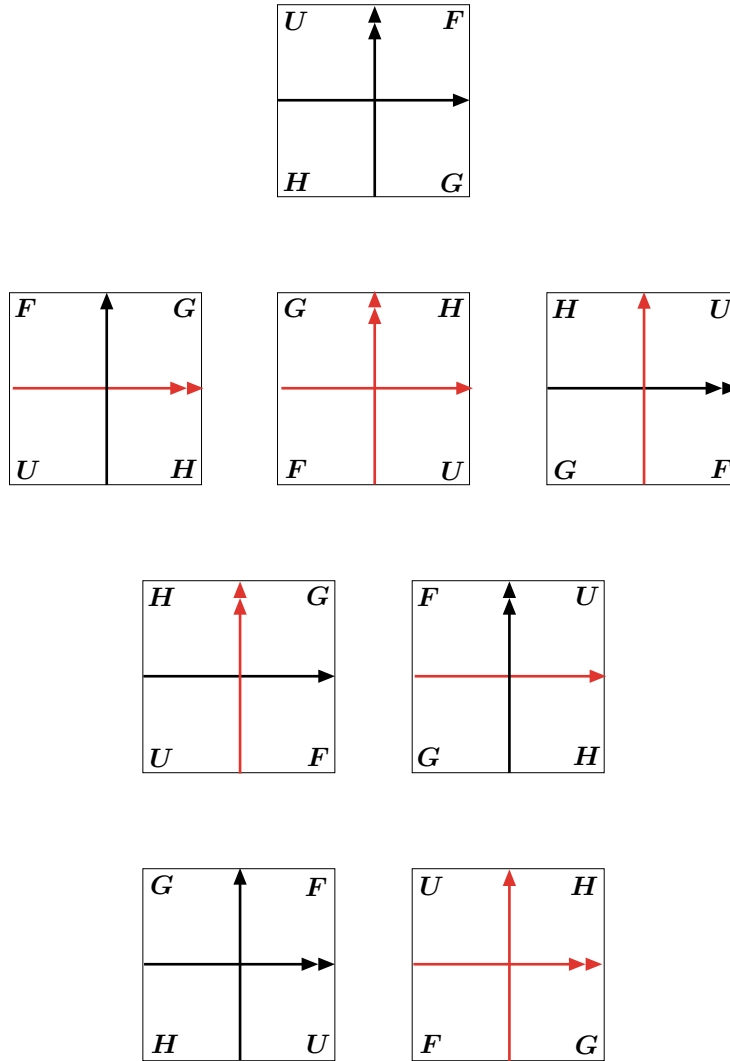$$

FIGURE 23: *Shown in* red *are* <u>arrows that had to be flipped</u> *to be restored to "canonical orientation." Flipping is associated in the text with installation of a minus sign, and with the installation of those signs we achieve permutational invariance—collectively, not individually—of the fundamental equations* (93).

It is easy to show, though I will omit the detailed demonstration, that the permutations that preserve (93.1) also preserve (93.2), and therefore preserve all corollaries of (93).

Much more could be said concerning the formalism sketched above. Suppose, for example, we introduce matrices

$$
\mathbb{R}_1 \equiv \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \quad
\mathbb{R}_2 \equiv \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \quad
\mathbb{R}_3 \equiv \begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}
$$

$$
\mathbb{A}_1 \equiv \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \quad
\mathbb{A}_2 \equiv \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}
$$

$$
\mathbb{D}_1 \equiv \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad
\mathbb{D}_2 \equiv \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}
$$

to describe how the operations of Figure 23 act (permutationally) upon the elements of the

$$
\text{"potential vector"} \quad \begin{pmatrix} U \\ F \\ G \\ H \end{pmatrix}
$$

and that we introduce matrices

$$
\mathbb{R}_1 \equiv \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \quad
\mathbb{R}_2 \equiv \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}, \quad
\mathbb{R}_3 \equiv \begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}
$$

$$
\mathbb{A}_1 \equiv \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad
\mathbb{A}_2 \equiv \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}
$$

$$
\mathbb{D}_1 \equiv \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \quad
\mathbb{D}_2 \equiv \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}
$$

to describe the *signed* permutational action of those operations upon elements of the

$$
\text{"state-variable vector"} \quad \begin{pmatrix} V \\ T \\ p \\ S \end{pmatrix}
$$

We are not surprised to discover that the matrices $\{\mathbb{I}, \mathbb{R}_1, \mathbb{R}_2, \mathbb{R}_3, \mathbb{A}_1, \mathbb{A}_2, \mathbb{D}_1, \mathbb{D}_2\}$ compose in conformity with the group table (page 86); *i.e.*, that they provide

a 4×4 "matrix representation" of the square group. We may, however, be surprised by the observation that the set $\{\mathbb{I}, \mathbb{R}_1, \mathbb{R}_2, \mathbb{R}_3, \mathbb{A}_1, \mathbb{A}_2, \mathbb{D}_1, \mathbb{D}_2\}$ does *not* supply a representation: it is, in fact, not even multiplicatively closed, as the following examples serve to illustrate:

$$\mathbb{R}_1^4 = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

$$\mathbb{A}_1^2 = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & +1 \end{pmatrix}, \quad \mathbb{A}_2^2 = \begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

Clarity is brought to the matter by the realization that

$$\begin{pmatrix} V \\ T \\ p \\ S \end{pmatrix} \rightarrow \begin{pmatrix} -V \\ -T \\ -p \\ -S \end{pmatrix}, \text{ else } \begin{pmatrix} -V \\ T \\ -p \\ S \end{pmatrix}, \text{ else } \begin{pmatrix} V \\ -T \\ p \\ -S \end{pmatrix}$$

describe an additional, *trivial* invariance property of the system (93). But I will resist the temptation to pursue this and related (group-theoretic) matters, and cut directly to the bottom line ... which is that

Equations (93)—and therefore all implications of (93)—are collectively invariant under the following **rules of substitution** (or "signed permutations"):

$$
\begin{array}{rcccccccccl}
\{ & U & F & G & H & V & T & p & S & \} & : & \text{original sequence} \\
 & & & & & & & & & & \downarrow \\
\{ & F & G & H & U & T & -p & S & V & \} & : & \text{rule } \mathbf{r}_1 \\
\{ & G & H & U & F & -p & S & V & -T & \} & : & \text{rule } \mathbf{r}_2 \\
\{ & H & U & F & G & S & V & -T & p & \} & : & \text{rule } \mathbf{r}_3 \\
\{ & H & G & F & U & -p & T & V & S & \} & : & \text{rule } \mathbf{a}_1 \\
\{ & F & U & H & G & V & S & p & -T & \} & : & \text{rule } \mathbf{a}_2 \\
\{ & G & F & U & H & T & V & S & p & \} & : & \text{rule } \mathbf{d}_1 \\
\{ & U & H & G & F & S & -p & -T & V & \} & : & \text{rule } \mathbf{d}_2 \\
\end{array}
$$

EXAMPLE: At (85) we had

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$$

Intuition suggests that a rule that sends $V \rightarrow p$ while preserving T should provide information relevant to the description of C_p. Inspection of the list shows the only candidate to be $\mathbf{a}_1$, which gives

$$\overset{\downarrow}{\left(\frac{\partial H}{\partial T}\right)_p} = T\left(\frac{\partial S}{\partial T}\right)_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p$$

But this is precisely (90)! Notice also that if we apply $\mathbf{a}_1$ to the equations that *led* to the former identity we obtain a *derivation* of (90).

EXAMPLE: If we apply the rules serially to the first of the "integrated Maxwell relations" (87) we obtain

$$
\left(\frac{\partial U}{\partial S}\right)_V = +T = \left(\frac{\partial H}{\partial S}\right)_p \qquad \mathsf{a}_1 \quad : \quad \left(\frac{\partial H}{\partial S}\right)_p = +T = \left(\frac{\partial U}{\partial S}\right)_V
$$

$$
\mathsf{r}_1 \quad : \quad \left(\frac{\partial F}{\partial V}\right)_T = -p = \left(\frac{\partial U}{\partial V}\right)_S \qquad \mathsf{a}_2 \quad : \quad \left(\frac{\partial F}{\partial T}\right)_V = -S = \left(\frac{\partial G}{\partial T}\right)_p
$$

$$
\mathsf{r}_2 \quad : \quad \left(\frac{\partial G}{\partial T}\right)_p = -S = \left(\frac{\partial F}{\partial T}\right)_V \qquad \mathsf{d}_1 \quad : \quad \left(\frac{\partial G}{\partial p}\right)_T = +V = \left(\frac{\partial H}{\partial p}\right)_S
$$

$$
\mathsf{r}_3 \quad : \quad \left(\frac{\partial H}{\partial p}\right)_S = +V = \left(\frac{\partial G}{\partial p}\right)_T \qquad \mathsf{d}_2 \quad : \quad \left(\frac{\partial U}{\partial V}\right)_S = -p = \left(\frac{\partial F}{\partial V}\right)_T
$$

which is to say: we obtain *two* copies of *each* of the relations (87). In general we can expect (for basic group-theoretic reasons) to obtain either

- one copy of each of a total of 8 identities;
- two copies of each of a total of 4 identities;
- four copies of each of a total of 2 identities, or
- eight copies of a single identity ((93.3) provides an example).

The previously-noted tendency of thermodynamic identities to coagulate into structurally similar families begins to seem not so mysterious.

The Born diagram came to us (page 61) as a rudimentary mnemonic device, but has been revealed to have latently a much deeper significance, to empower us to do much more than remember a short list. In higher dimension (*i.e.*, for systems with $n > 2$ thermodynamic degrees of freedom) it loses its mnemonic utility, but its identity-generating power is correspondingly enhanced: we find ourselves talking then[65] about the "symmetries of a hypercube," which give rise to a group of order $2^n n!$. Though the theory was thermodynamically motivated, it pertains to multivariable Legendre transform systems in *whatever* context they may be encountered, and also (with only slight modifications) to multivariable Fourier transform systems.[66]

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[65] This topic is developed in my " Hyper-octagonal Born diagrams" (Notes for the Physics Seminar of 20 October 1971, reprinted in TRANSFORMATIONAL PHYSICS & PHYSICAL GEOMETRY, 1971–1983).

[66] When I worked out the preceding material I was aware only of the Lomont's work,[61] which it was my objective to clarify. I have since learned that the basic ideas were described a long time ago by F. O. Koenig in "Families of thermodynamic equations. I. The method of transformations of the characteristic group," J. Chem. Phys. **3**, 29 (1935). See also H. A. C. McKay, "A generalized thremodynamic notation," J. Chem. Phys. **3**, 715 (1935) and J. A. Prins, "On the thermodynamic substitution group and its representation by the rotations of a square," J. Chem. Phys. **16**, 65 (1948), where it is suggested that the *entire* subject was known already to Born. C. E. Reid, in his *Principles of Chemical Thermodynamics* (1960), speaks in passing of **Koenig-Prins transformations** . . . though I think very few poeple would know what you were talking about if you alluded to those. Of these authors, only McKay gives any attention to the *n*-dimensional case.

Every well-trained musician should know *something* about the crumhorn, but of that subject enough becomes easily too much. The same, I think, can be said of the "theory of thermodynamic identities," which seductively invites—but does not reward—extended close attention. Some such identities are absolutely indispensable, but they are well-known, and hardly need to be rederived every time they are used. Others can be discovered in various dusty handbooks.[67]

10. Concluding remarks. We have acquired some familiarity with the basic principles of classical thermodynamics, and with some of its characteristic methods, at least as they relate to simple systems. But we have yet to consider any of the major *applications* of those ideas. Before we are done we will want to look in particular to

- the thermodynamics of some specific systems (especially real gases, blackbody radiation);
- the theory of multi-phase systems and of phase transitions;
- the theory of heat engines and refrigerators (and to what the latter has to say about the unattainability of absolute zero);
- the theory of superfluids and superconductors;
- the theory of irreversible processes;
- the theory of reactions in multi-component systems . . . the list goes on and on.

But it has come time to cross to the statistical mechanical side of the street, for our knowledge of thermodynamics is already sufficient to permit us to recognize when statistical lines of argument have begun to say "thermodynamic" things. And many of the topics listed above are most usefully illuminated by considerations marked by a *balanced interplay* of statistical and thermodynamic concepts and methods.

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[67] The classic compilation is P. W. Bridgman, *A Condensed Collection of Thermodynamic Formulas* (1925).