

## Recursion tables for thermostatic derivatives

Any person working on thermodynamics must eventually master the skill of converting thermodynamic derivatives into expressions involving only measurable material state variables and tabulated material properties. However, a systematic means of doing so is rarely presented in thermodynamics textbooks. Most students take a “random walk” through various nebulous identities, hoping to eventually stumble upon the answer. This document makes the process systematic (guaranteed success).

Classical reversible thermostatics is mostly *math*, not physics. It is a grand application of the calculus of functions of two variables, founded on the constitutive\* assumption that the internal energy per unit mass  $u$  is expressible as a function of the specific volume  $v$  (i.e., volume per mass, which is 1/density) and the entropy  $s$ . This function  $u(s, v)$  is called a *fundamental potential* because all other quantities of interest in thermodynamics can be determined from it. For example, as explained in any undergraduate thermodynamics textbook, the temperature  $T$  and pressure  $P$  can be found by

$$T = \left(\frac{\partial u}{\partial s}\right)_v \quad \text{and} \quad P = -\left(\frac{\partial u}{\partial v}\right)_s \quad (1)$$

To be a fundamental potential, the internal energy must be expressed as a function of  $v$  and  $s$ , so we call these two independent variables the “*natural*” variables for the internal energy.

Equation (1a) implies that  $T$  is a function of  $s$  and  $v$ . In principle, this equation could be solved for  $s$  as a function of  $T$  and  $v$ . You could then substitute  $s(T, v)$  into  $u(s, v)$  to obtain  $u(T, v)$ . Sadly, the function  $u(T, v)$  is not a fundamental potential. It has lost information content. Having only  $u(T, v)$ , you will no longer be able to uniquely determine all thermodynamic quantities. The fact that  $u(T, v)$  embodies less information than  $u(s, v)$  is not obvious — the proof and further information can be found in most advanced thermodynamics textbooks.† Fortunately, all is not lost. Even though  $u(T, v)$  is not a fundamental potential, there is a different energy measure that *is* a fundamental potential when it is expressed as a function of  $T$  and  $v$ . If you seek a fundamental potential for which  $v$  and  $T$  are the independent natural variables (instead of  $v$  and  $s$ ), then you must use a “contact” (Legendre) transformation to introduce an alternative energy measure, called the Helmholtz free energy:

$$a = u - Ts \quad (2)$$

As outlined in any good thermodynamics textbook, this new variable is a fundamental potential function when it is expressed in terms of  $T$  and  $v$ . With it, you may compute entropy and pressure by

$$s = -\left(\frac{\partial a}{\partial T}\right)_v \quad \text{and} \quad P = -\left(\frac{\partial a}{\partial v}\right)_T \quad (3)$$

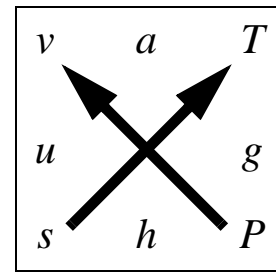
Similar strategies and introductions of new energies (potentials) can be applied to permit construction of fundamental potentials in terms of any convenient pair of thermomechanical state variables. The process leaves us with so many formulas, that mnemonics and executive summary tables are needed to keep everything organized and useful.

\* The word “constitutive” means “relating to a particular material or class of materials, possibly further restricted to certain constraints on service conditions.” For example, many materials can be regarded to be elastic under strict conditions on, say, the magnitude and/or duration of loading. In classical thermostatics, we consider materials and service conditions for which only two independent variables, perhaps entropy and volume, are needed to fix the values of all other quantities of interest (such as pressure and temperature). This constitutive *assumption* is broadly applicable to gases and inviscid fluids and also applicable to isotropic solids when the deformations are constrained to allow changes in size but not changes in shape.

† e.g. **Thermodynamics and an Introduction to Thermostatistics** (1985) by H.B. Callen.

## Thermodynamic square

The thermodynamic square is a mnemonic device that helps you recall the natural variables associated with the energies, as well as many other things such as the Legendre transformations and Maxwell's relations. The square is constructed by placing the state variables on the corners and the energies on the edges, along with two arrows as shown.



### State variables (corners of the thermodynamic square):

$v$  = specific volume ( $= \frac{1}{\rho}$ , where  $\rho$  is mass density)  
 $T$  = temperature  
 $P$  = pressure  
 $s$  = specific entropy

$\text{m}^3/\text{kg}$   
 $\text{K}$   
 $\text{N}/\text{m}^2 = \text{J}/\text{m}^3$   
 $\text{J}/(\text{kg}\cdot\text{K})$

### Energies\* (edges of the thermodynamic square):

$a$ = Helmholtz free energy	= natural function of $v$ and $T$	$\text{J}/\text{kg}$
$g$ = Gibbs free energy	= natural function of $T$ and $P$	$\text{J}/\text{kg}$
$h$ = enthalpy	= natural function of $P$ and $s$	$\text{J}/\text{kg}$
$u$ = specific internal energy	= natural function of $s$ and $v$	$\text{J}/\text{kg}$

The Legendre transformations (i.e., the relationships between the energies) are inferred from the thermodynamic square by subtracting energies in the off-diagonals in the same directions as the arrows:

$$u - a = h - g = Ts \quad \text{and} \quad h - u = g - a = Pv \quad (4)$$

In the thermodynamic square, the energies are surrounded by their natural variables. Looking at the square, for example,  $u(s, v)$  is a fundamental potential because  $u$  is surrounded by  $s$  and  $v$ . Gibbs free energy is a fundamental potential when it is written in the form  $g(T, P)$ . Similarly, according to the thermodynamic square,  $a(v, T)$  and  $h(s, P)$  are fundamental potentials. With a fundamental potential, you can get “everything else.” For example, the **Gibbsian relations** give

$$\left(\frac{\partial u}{\partial v}\right)_s = -P \quad \left(\frac{\partial a}{\partial v}\right)_T = -P \quad \left(\frac{\partial g}{\partial P}\right)_T = v \quad \left(\frac{\partial h}{\partial P}\right)_s = v \quad (5a)$$

$$\left(\frac{\partial u}{\partial s}\right)_v = T \quad \left(\frac{\partial a}{\partial T}\right)_v = -s \quad \left(\frac{\partial g}{\partial T}\right)_P = -s \quad \left(\frac{\partial h}{\partial s}\right)_P = T \quad (5b)$$

These equations apply when differentiating with respect to an energy's natural variable, holding the *other* natural variable constant. The final result is found by moving diagonally across the square, setting the  $\pm$  sign based on whether you move *with* or *against* the arrow. If  $e$  denotes any of the energies ( $u, a, h, \text{ or } g$ ) and if  $x$  and  $y$  are the natural variables associated with  $e$ , then

$$\left(\frac{\partial e}{\partial x}\right)_y = x^* \quad (6)$$

where  $x^*$  is the variable diagonally opposite from  $x$  on the thermodynamic square multiplied by +1 if traversing the diagonal moves *with* the arrow, or -1 if *opposing* the arrow. Specifically,

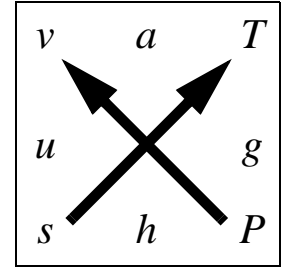
$$s^* = T, \quad T^* = -s, \quad P^* = v, \quad \text{and} \quad v^* = -P. \quad (7)$$

The formulas listed explicitly in Eq. (5) are specific instances of the generic Eq. (6).

\* The energies are also “state variables” in the sense that they return to their original value for any closed path of variations in the other state variables.

The thermodynamic square can also be used to recall Maxwell's relations:

$$\begin{aligned}
 \left(\frac{\partial v}{\partial s}\right)_P &= \left(\frac{\partial T}{\partial P}\right)_s & \left(\frac{\partial v}{\partial T}\right)_P &= -\left(\frac{\partial s}{\partial P}\right)_T \\
 \left(\frac{\partial s}{\partial v}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_v & \left(\frac{\partial T}{\partial v}\right)_s &= -\left(\frac{\partial P}{\partial s}\right)_v \\
 \left(\frac{\partial v}{\partial s}\right)_T &= \left(\frac{\partial T}{\partial P}\right)_v & \left(\frac{\partial v}{\partial T}\right)_s &= -\left(\frac{\partial s}{\partial P}\right)_v \\
 \left(\frac{\partial s}{\partial v}\right)_P &= \left(\frac{\partial P}{\partial T}\right)_s & \left(\frac{\partial T}{\partial v}\right)_P &= -\left(\frac{\partial P}{\partial s}\right)_T
 \end{aligned}$$



These formulas all involve derivatives of a state variable with respect to another state variable on the same edge of the thermodynamic square. The variable held constant can be either of the two state variables on the other side of the square. An edge derivative like this is equated to its mirror-image edge derivative across the square with the  $\pm$  sign assigned to be “+” if the symmetry of the edges is the same as that of the arrows or “-” otherwise. For example, in Maxwell's relations,

$\frac{\partial v}{\partial s}$  involves variables  $v$  and  $s$ , which are on a vertical edge

$\frac{\partial T}{\partial P}$  uses the corresponding “mirror-image” variables on the other vertical edge

In this case, we are talking about vertical edges. The arrows are also symmetric about the vertical. Therefore a positive sign is used in the Maxwell relation.

$\frac{\partial v}{\partial T}$  involves variables  $v$  and  $T$ , which are on a horizontal edge

$\frac{\partial s}{\partial P}$  uses the corresponding “mirror-image” variables on the other horizontal edge

In this case, we are talking about horizontal edges, but the arrows are symmetric about the vertical. Therefore a negative sign is used in the Maxwell relation.

**IMPORTANT:** what is being held constant in the derivative matters. Maxwell relations involve only state variables (corners of the thermodynamic square). Moreover, not only are the major players in the derivative following edge symmetry, but the thing being held constant is too. For example

$$\left(\frac{\partial v}{\partial s}\right)_P = \left(\frac{\partial T}{\partial P}\right)_s, \quad \text{but} \quad \left(\frac{\partial v}{\partial s}\right)_P \neq \left(\frac{\partial T}{\partial P}\right)_v \tag{8}$$

In thermodynamics, partial derivatives are almost always of the form  $(\partial A/\partial B)_C$ , which quantifies how some variable “A” changes in response to changes of “B” during processes that hold “C” fixed. Changing the constraint (i.e., changing the thing held constant) will change the meaning of the partial derivative. A partial derivative  $\partial A/\partial B$  that fails to indicate what is being held constant is meaningless. There are 336 ways to form derivatives of the form  $(\partial A/\partial B)_C$  using the eight thermodynamics variables ( $P, v, s, T, u, a, h, g$ ). Of these, some will have reasonably intuitive physical meanings. As a rule, derivatives that involve only corner state variables ( $P, v, s, T$ ) can be readily interpreted physically, and are most likely to be measured in the lab and tabulated in handbooks. We call these **material properties** (they are functions of the thermodynamic state, not constants). For example, the derivative  $(\partial v/\partial T)_P$  represents the volume change produced in a gas if the temperature is increased while holding the pressure constant. Similarly,  $(\partial P/\partial v)_T$  is the local slope of a pressure-volume curve measured under isothermal conditions. Of the 336 possible derivatives, the ones that involve energies often lack apparent meaning. For example,  $(\partial s/\partial h)_a$  is bizarre and incomprehensible. We need a way to transform the derivatives involving energies into expressions that involve more easily interpreted elements. “**Distilling**” is the process of converting any derivative into a form involving only state variables ( $P, v, s, T$ ) and material property derivatives (which are meaningful and often tabulated in handbooks). Simplifying the distilling process is the goal of this document.

## Thermostatic material properties:

The state variables ( $P, v, s, T$ ) are regarded as easily measurable or easily controllable in the lab. In any process, only two state variables can be independently controlled at any time. Standard experiments will vary one state variable while holding a second state variable constant (thus controlling exactly two variables). The resulting variation of the other two state variables is recorded. Suppose, for example, that an experiment is conducted in which the volume is varied under thermally insulated (AKA, adiabatic, constant entropy, isentropic<sup>\*</sup>) conditions. Then the data record how the dependent state variables (pressure and temperature) change in response to this adiabatic volume change. The isentropic bulk modulus (a material property) is determined from the adiabatic pressure-volume curve. The adiabatic temperature-volume curve leads to a lesser-known material property called the Grüneisen parameter. You can perform different experiments that vary different state variables, holding different state variables constant. In every case, the slopes of the response functions are proportional to material properties. Properties that can be measured in this way are listed below:

$K_T$ = Bulk modulus at constant temperature	$J/m^3 = N/m^2$
$K_s$ = bulk modulus at constant entropy	$J/m^3 = N/m^2$
$\kappa_T$ = compressibility at constant temperature = $1/K_T$	$m^3/J$
$\kappa_s$ = compressibility at constant entropy = $1/K_s$	$m^3/J$
$c_v$ = specific heat at constant volume	$J/(kg \cdot K)$
$c_p$ = specific heat at constant pressure	$J/(kg \cdot K)$
$B_v$ = change in pressure with respect to temperature at constant volume	$J/(m^3 \cdot K)$
$B_s$ = change in pressure with respect to temperature at constant entropy	$J/(m^3 \cdot K)$
$\alpha_p$ = volumetric thermal expansion coefficient at constant pressure	$1/K$
$\gamma$ = the Grüneisen parameter	dimensionless

Material properties are defined equal to (or proportional to) the derivative of one state variable ( $P, v, s, T$ ) with respect to a second state variable, holding a third state variable constant. In light of the relationships listed in Eq. (5), only three of the above ten material properties are independent — all of the others can be computed from them. A goal of this document is to show you how to perform these conversions between properties. Specifically, if you have a handbook that lists three properties but you really want a different property, then you can compute it. Material properties are sometimes defined in terms of second derivatives of the energies with respect to their natural variables. For example, since the isentropic bulk modulus is defined to be proportional to the slope of the *isentropic* pressure-volume curve, we know it is proportional to  $(\partial P / \partial v)_s$ , which (using the first expression in Eq. 5a) is equivalent to  $-(\partial^2 u / \partial v^2)_s$ . Each energy is expressible as a function of its two natural variables. Any function of two variables has exactly three independent second-partial derivatives. Therefore natural groupings of three independent material properties correspond to the second-partial derivatives of an energy. Since there are four energies ( $u, a, h, g$ ), material property triplets found in handbooks usually correspond to second-partials of one of the energy functions.

\* In general, adiabatic means “no heat flow is permitted into our out from the system,” while isentropic means “no entropy is generated.” For general materials, these terms mean different things because, even under adiabatic conditions, it is still possible to generate entropy via irreversible material dissipation (which is like internal heating from friction, as opposed to external heating supplied directly from an outside source). This effect can be modeled only by permitting the energy function to depend on *more* than just two state variables — it must additionally depend on other “internal state variables.” Even without material dissipative mechanisms, you can still generate entropy under adiabatic conditions by applying the load dynamically. This document covers only classical thermostatics in which material dissipation is zero and loads are applied very slowly. In this case, adiabatic and isentropic are synonymous.

Material properties are *proportional to* (not always identical to) derivatives of one state variable holding a third state variable constant. The proportionality factors are introduced merely as a convenience. For example, the derivatives that define material properties often contain negative signs to ensure that the definition will be positive for most materials. Material property definitions involving differentials of specific volume  $\partial v$  usually contain a normalizing factor of the specific volume itself, which alters the meaning slightly from being an increment in volume to an increment in volumetric strain, defined  $\varepsilon_v \equiv \ln(v/v_o)^*$ . Here,  $v_o$  is any constant reference volume; which goes away in differential form (i.e.,  $d\varepsilon_v = dv/v$  is independent of  $v_o$ ). With this logarithmic definition of volumetric strain, the expression  $(\partial v)/v$  is equivalent to  $\partial\varepsilon_v$ . Material property definitions involving the differential of entropy  $\partial s$  are likewise usually multiplied by  $T$  because  $Tds$  is the heat increment (for reversible processes). This said, the mathematical definitions of the above thermodynamic properties are listed below, categorized according to whether they characterize mechanical effects, thermal effects, or thermo-mechanical coupling effects.

**Mechanical material properties (pressure-volume relationships):**

units

$K_T = -v\left(\frac{\partial P}{\partial v}\right)_T$	$= v\left(\frac{\partial^2 a}{\partial v^2}\right)_T$	J/m <sup>3</sup>
$K_S = -v\left(\frac{\partial P}{\partial v}\right)_s$	$= v\left(\frac{\partial^2 u}{\partial v^2}\right)_s$	J/m <sup>3</sup>
$\kappa_T = \frac{1}{K_T}$	$= -\frac{(\partial^2 g/\partial P^2)_T}{v}$	m <sup>3</sup> /J
$\kappa_S = \frac{1}{K_S}$	$= -\frac{(\partial^2 h/\partial P^2)_s}{v}$	m <sup>3</sup> /J

**Thermal material properties (temperature-entropy relationships):**

$c_v = T\left(\frac{\partial s}{\partial T}\right)_v$	$= -T\left(\frac{\partial^2 a}{\partial T^2}\right)_v = \frac{T}{(\partial^2 u/\partial s^2)_v}$	J/(kg•K)
$c_p = T\left(\frac{\partial s}{\partial T}\right)_p$	$= -T\left(\frac{\partial^2 g}{\partial T^2}\right)_p = \frac{T}{(\partial^2 h/\partial s^2)_p}$	J/(kg•K)

**Thermomechanical (coupling) material properties:**

$\alpha_p = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$	$= \frac{1}{v}\left(\frac{\partial^2 g}{\partial P\partial T}\right)$	1/K
$B_s = \left(\frac{\partial P}{\partial T}\right)_s$	$= 1/\left(\frac{\partial^2 h}{\partial s\partial P}\right)$	J/(m <sup>3</sup> •K)
$B_v = \left(\frac{\partial P}{\partial T}\right)_v$	$= -\left(\frac{\partial^2 a}{\partial v\partial T}\right)$	J/(m <sup>3</sup> •K)
$\gamma = -\frac{v}{T}\left(\frac{\partial T}{\partial v}\right)_s$	$= -\frac{v}{T}\left(\frac{\partial^2 u}{\partial v\partial s}\right)$	dimensionless

\* For small volume changes,  $v \approx v_o$  and therefore  $\varepsilon = \ln(v/v_o) \approx \frac{v-v_o}{v_o} \approx \frac{v-v_o}{v}$ . Thus, the logarithmic strain reduces to engineering strain in this case. The logarithmic strain is ideal for generalization to large volume changes because it goes to  $+\infty$  at full expansion and  $-\infty$  at full compression (zero volume). Engineering strain does not obey this nice property.

These expressions show how each material property is related to second derivatives of energy potentials. The physically meaningful (practical) definitions, which are cited first, would be used to set up laboratory experiments to measure the properties. The volumetric expansion coefficient  $\alpha_p$  is the increment in volumetric strain [ $d\varepsilon_v = (dv)/v$ ] induced per unit change in temperature, measured while holding the pressure constant. Similarly, since “ $dv/v$ ” equals the increment  $d\varepsilon_v$  in volumetric strain, the isothermal bulk modulus  $K_T$  is the slope of the pressure vs. strain curve that is measured under constant temperature conditions. The definition of  $K_T$  uses a negative because, for most materials, an increase in volume usually corresponds to a decrease in pressure, making  $K_T > 0$ . For a reversible process, heat flow is proportional to the entropy production. Consequently, any derivative that holds  $s$  constant may be regarded as a measurement taken under quasistatic insulated conditions. For example,  $K_s$  is the (negative) slope of the pressure-strain curve that is measured without permitting heat to flow into or away from the system. For reversible thermoelasticity, the increment of heat (per unit mass) added to a system equals  $T\Delta s$ ; therefore, the specific heats ( $c_v$  and  $c_p$ ) can be regarded as the amount of heat needed to induce a unit change in temperature in a unit mass — the result depends on whether the heat is added at constant volume or at constant pressure, which is why there are two specific heats.

## Distilling derivatives

The goal of this document is to outline a “never-fail” procedure for you to convert any partial derivative of the form  $(\partial A/\partial B)_C$  into an expression that involves only state variables and material properties. If you encounter a derivative  $(\partial A/\partial B)_C$  in which one of the letters of the alphabet ( $A$ ,  $B$ , or  $C$ ) is repeated, then you would apply one of the following

$$\left(\frac{\partial A}{\partial A}\right)_C = 1 \qquad \left(\frac{\partial A}{\partial B}\right)_A = 0 \qquad \left(\frac{\partial A}{\partial B}\right)_B = \infty \qquad (9)$$

You will never see all three letters in a derivative repeated. Specifically,  $(\partial A/\partial A)_A$  is meaningless.

Most of the time, you won’t be so lucky to have the same variable appearing twice in a derivative, so simplification is more arduous. Recall that all of the material property definitions involve the derivative of one state variable with respect to a second state variable, holding a third state variable constant. In other words, none of the material property derivatives explicitly involves an energy ( $u$ ,  $a$ ,  $g$ ,  $h$ ). Consequently, the first task is to eliminate energies from a partial derivative. Given a derivative of the form  $(\partial A/\partial B)_C$ , suppose that “ $A$ ” is an energy. If the independent variables ( $B$  and  $C$ ) happen to be the same as the energy’s natural variables, then you can simply apply Eq. (6), and you’re done. Equation (6) holds only when differentiating with respect to one of the energy’s natural state variables, holding the *other* natural variable constant. Suppose that the natural variables associated with an energy  $e$  (i.e., either  $a$ ,  $g$ ,  $h$  or  $u$ ) are  $x$  and  $y$ , and you wish to simplify a derivative of the form  $(\partial e/\partial p)_q$ , where  $p$  and/or  $q$  are *not* natural variables for that energy. In this case, you would use the chain rule so that you can implicitly introduce the natural variable function  $e = e(x, y)$ . Specifically

$$\left(\frac{\partial e}{\partial p}\right)_q = \left(\frac{\partial e}{\partial x}\right)_y \left(\frac{\partial x}{\partial p}\right)_q + \left(\frac{\partial e}{\partial y}\right)_x \left(\frac{\partial y}{\partial p}\right)_q \qquad (10)$$

Now that we have derivatives involving natural variables, Eq. (6) may be used to write

$$\left(\frac{\partial e}{\partial p}\right)_q = x^* \left(\frac{\partial x}{\partial p}\right)_q + y^* \left(\frac{\partial y}{\partial p}\right)_q \qquad (11)$$

This process has eliminated the energy  $e$  from being explicitly present. If  $p$  and  $q$  are state variables, then the remaining derivatives in this expression can be equated to material properties (or the derivatives can be simplified using Eq. 9 if two variables happen to match each other), and you will have succeeded in fully distilling your original derivative into a form involving readily measurable quanti-

ties. On the other hand, if  $p$  and/or  $q$  is an energy, then more work remains. For each of the remaining derivatives, you must use multivariable calculus to recast them into a form that puts the energy in the “numerator”, at which point you can apply a version of Eq. (11) for each energy you wish to remove. Given a generic partial derivative of the form  $(\partial A/\partial B)_C$  two key calculus identities are used at this stage. To change things so that “ $B$ ” (instead of “ $A$ ”) is differentiated, use

$$\boxed{\left(\frac{\partial A}{\partial B}\right)_C = \frac{1}{(\partial B/\partial A)_C}} \quad (12)$$

To change things so that “ $C$ ” (instead of “ $A$ ”) is differentiated, use

$$\boxed{\left(\frac{\partial A}{\partial B}\right)_C = -\frac{(\partial C/\partial B)_A}{(\partial C/\partial A)_B}} \quad \text{(cyclic identity)} \quad (13)$$

**Sidebar:** The presence of the negative sign in Eq. 13 might be confusing to readers who are rusty in multivariable calculus. After all, for ordinary single variable calculus, “everyone” knows that  $\frac{dy}{dx} = \frac{dz/dx}{dz/dy}$ . There is no negative in this equation, so why is there one in Eq. 13? The answer revolves around what is being held constant in derivatives. Suppose that  $y$  is a function of a second variable  $\alpha$  so that  $y = y(x, \alpha)$ . It is definitely true that  $\left(\frac{\partial y}{\partial x}\right)_\alpha = \frac{(\partial z/\partial x)_\alpha}{(\partial z/\partial y)_\alpha}$ . This equation has no negative sign because  $\alpha$  is held constant in *all* derivatives, so this formula is effectively making a statement about a world in which  $\alpha$  is always constant in every derivative (so your favorite formulas from single-variable calculus still apply). Contrast this result with Eq. 13, which has *different* things held constant in all three derivatives. To get Eq. 13, you first note that the very act of writing  $(\partial A/\partial B)_C$  implies that, at least in some local neighborhood,  $A = A(B, C)$ . Imagine locally inverting this relationship to obtain  $C = C(A, B)$  so that  $dC = \left(\frac{\partial C}{\partial A}\right)_B dA + \left(\frac{\partial C}{\partial B}\right)_A dB$ . In a world where  $C$  is constant, we know that  $dC = 0$  and this incremental equation may be solved for  $dA/dB$  to give the right-hand-side of Eq. 13, negative sign and all. To emphasize that the result applies when  $C$  is held constant, you must note that  $\frac{dA}{dB}$  is really  $\left(\frac{\partial A}{\partial B}\right)_C$ .

To reiterate, if an energy is the thing being differentiated, your first task is always to apply Eq. (11) to *get rid of it!* If the remaining derivatives involve no energies, then you are done because they must be expressible in terms of material properties and/or state variables. Otherwise, if you still have partial derivatives involving energies, then you need to use Eq (12) or (13) to move those energies so that they become the things being differentiated, after which Eq. (11) can be applied to eliminate them. Always follow the sequence (first eliminate from “numerator”, then “denominator”, then the “held constant” part) to produce an expression that involves only measurable quantities (material state variables and material properties). Deviating from the sequence will get you nowhere.

The derivative distilling process is essentially recursive. To expedite this stage of the work, we have provided computer-generated recursion tables that show you which partial derivative identities [Eqs. 9, 11, 12 or 13] you need to use. The recursion tables provide formulas for every possible derivative of the form  $(\partial A/\partial B)_C$  that can be made using the eight thermodynamics variables ( $P, v, T, s, u, a, g, h$ ).

## Instructions for using the recursion tables:

In the tables to follow, any three-character symbol of the form “**ABC**” is a short-hand notation for  $(\partial A/\partial B)_C$ , which is the derivative of  $A$  with respect to  $B$  holding  $C$  constant.

The three-column computer-generated recursion table (spanning pages 9 and 10) permits you to reformulate any thermodynamic derivative of the form  $(\partial A/\partial B)_C$  so that it is ultimately phrased only in terms of state variables and material property derivatives (i.e., in terms of “measurable things”). The first step is to recursively apply this three-column table until it provides no further simplification. Then the “**Material property recursion table**” on page 11 is applied to express the result in terms of whatever set of material properties you have available in a handbook.

**A worst-case scenario.** Recall that distilling derivatives requires using identities and thermodynamic relationships to re-write a derivative into a form that involves no explicit presence of energies. Therefore, the most difficult derivative to distill would be the partial derivative of an energy with respect to an energy, holding an energy constant. Suppose, for example, you wish to express the derivative  $(\partial a/\partial g)_h$  in terms of state variables and material properties. First write this derivative in our shorthand notation as “**agh**”. The first table tells you that “**agh**” equals “**-s Tgh -P vgh**”, which translates into more conventional notation as  $(\partial a/\partial g)_h = -s(\partial T/\partial g)_h - P(\partial v/\partial g)_h$ . This entry is simply applying Eq. (11) to eliminate the Helmholtz free energy “ $a$ ” from being explicitly present. Your new expression still involves some *different* energies ( $g$  and  $h$ ) in the derivatives **Tgh** and **vgh**, so you must go back to the table and look *them* up. You will find that the table cites entries that apply Eq. (12) to move the energy  $g$  so that it becomes the thing being differentiated. Again applying the table leads to yet another application of Eq. (11), this time to remove the Gibbs function “ $g$ ” from being explicitly present. At this stage, you will have derivatives involving the enthalpy  $h$  held constant. Looking up these derivatives in the table gives entries that apply Eq. (13) to move  $h$  so that it becomes the thing differentiated. Applying the table one last time gives entries that apply Eq. (11), after which the three-column computer-generated table produces no further changes. By back substitution, you will have succeeded in expressing the original derivative in terms of state variables and “primitive” material property derivatives.

## Example 1

Suppose that you wish to distill the derivative of the Helmholtz free energy with respect to entropy holding pressure constant,  $(\partial a/\partial s)_P$ . In other words, suppose that you desire to express this derivative in terms of measured material properties and the thermodynamic state. This derivative,  $(\partial a/\partial s)_P$ , is denoted “**asP**” in our notation. The first table (starting on page 9) says

$$\begin{aligned}\mathbf{asP} &= \mathbf{-s TsP -P vsP} \\ \mathbf{T sP} &= \mathbf{T sP} \\ \mathbf{v sP} &= \mathbf{v sP}\end{aligned}$$

The first table provides no alteration of either **TsP** or **vsP**. Hence, they are “primitive” material derivatives, and they may be looked up in the second table on page 11, which says that

$$\begin{aligned}\mathbf{T sP} &= T/c_p \\ \mathbf{v sP} &= 1/B_s\end{aligned}$$

Thus, by back substitution,

$$\left(\frac{\partial a}{\partial s}\right)_P = -\frac{sT}{c_p} - \frac{P}{B_s} \tag{14}$$

With this, we have achieved our goal of expressing the original derivative in terms of state variables ( $s$ ,  $T$ , and  $P$ ) and material properties ( $c_p$  and  $B_s$ ).



aag = 1  
 aah = 1  
 aaP = 1  
 aas = 1  
 aaT = 1  
 aau = 1  
 aav = 1  
 aga = 0  
 agg = Infinity  
 agh = -s Tgh -P vgh  
 agP = -s TgP -P vgP  
 ags = -s Tgs -P vgs  
 agT = -P vgT  
 agu = -s Tgu -P vgu  
 agv = -s Tgv  
 aha = 0  
 ahg = -s Thg -P vhg  
 ahh = Infinity  
 ahP = -s ThP -P vhP  
 ahs = -s Ths -P vhs  
 ahT = -P vhT  
 ahu = -s Thu -P vhu  
 ahv = -s Thv  
 aPa = 0  
 aPg = -s TPg -P vPg  
 aPh = -s TPh -P vPh  
 aPP = Infinity  
 aPs = -s TPs -P vPs  
 aPT = -P vPT  
 aPu = -s TPu -P vPu  
 aPv = -s TPv  
 asa = 0  
 asg = -s Tsg -P vsg  
 ash = -s Tsh -P vsh  
 asP = -s TsP -P vsP  
 ass = Infinity  
 asT = -P vsT  
 asu = -s Tsu -P vsu  
 asv = -s Tsv  
 aTa = 0  
 aTg = -s -P vTg  
 aTh = -s -P vTh  
 aTP = -s -P vTP  
 aTs = -s -P vTs  
 aTT = Infinity  
 aTu = -s -P vTu  
 aTv = -s  
 aua = 0  
 aug = -s Tug -P vug  
 auh = -s Tuh -P vuh  
 auP = -s TuP -P vuP  
 aus = -s Tus -P vus  
 auT = -P vuT  
 auu = Infinity  
 auv = -s Tuv  
 ava = 0  
 avg = -s Tvg -P  
 avh = -s Tvh -P  
 avP = -s TvP -P  
 avs = -s Tvs -P  
 avT = -P  
 avu = -s Tvu -P  
 avv = Infinity  
 gaa = Infinity  
 gag = 0  
 gah = -s Tah +v Pah  
 gaP = -s TaP  
 gas = -s Tas +v Pas  
 gaT = v PaT  
 gau = -s Tau +v Pau  
 gav = -s Tav +v Pav  
 gga = 1  
 ggh = 1  
 ggP = 1  
 ggs = 1  
 ggT = 1  
 ggu = 1  
 ggv = 1  
 gha = -s Tha +v Pha  
 ghg = 0  
 ghh = Infinity  
 ghP = -s ThP  
 ghs = -s Ths +v Phs  
 gHT = v PhT

ghu = -s Thu +v Phu  
 ghv = -s Thv +v Phv  
 gPa = -s TPa +v  
 gPg = 0  
 gPh = -s TPh +v  
 gPP = Infinity  
 gPs = -s TPs +v  
 gPT = v  
 gPu = -s TPu +v  
 gPv = -s TPv +v  
 gsa = -s Tsa +v Psa  
 gsg = 0  
 gsh = -s Tsh +v Psh  
 gsP = -s TsP  
 gss = Infinity  
 gsT = v PsT  
 gsu = -s Tsu +v Psu  
 gsv = -s Tsv +v Psv  
 gTa = -s +v PTa  
 gTg = 0  
 gTh = -s +v PTh  
 gTP = -s  
 gTs = -s +v PTs  
 gTT = Infinity  
 gTu = -s +v PTu  
 gTv = -s +v PTv  
 gua = -s Tua +v Pua  
 gug = 0  
 guh = -s Tuh +v Puh  
 guP = -s TuP  
 gus = -s Tus +v Pus  
 guT = v PuT  
 guu = Infinity  
 guv = -s Tuv +v Puv  
 gva = -s Tva +v Pva  
 gvg = 0  
 gvh = -s Tvh +v Pvh  
 gvP = -s TvP  
 gvs = -s Tvs +v Pvs  
 gvT = v PvT  
 gvu = -s Tvu +v Pvuv  
 gvv = Infinity  
 haa = Infinity  
 hag = T sag +v Pag  
 hah = 0  
 haP = T saP  
 has = v Pas  
 haT = T saT +v PaT  
 hau = T sau +v Pau  
 hav = T sav +v Pav  
 hga = T sga +v Pga  
 hgg = Infinity  
 hgh = 0  
 hgP = T sgP  
 hgs = v Pgs  
 hgT = T sgT +v PgT  
 hgu = T sgu +v Pgu  
 hgv = T sgv +v Pgv  
 hha = 1  
 hhg = 1  
 hhP = 1  
 hhs = 1  
 hhT = 1  
 hhu = 1  
 hhv = 1  
 hPa = T sPa +v  
 hPg = T sPg +v  
 hPh = 0  
 hPP = Infinity  
 hPs = v  
 hPT = T sPT +v  
 hPu = T sPu +v  
 hPv = T sPv +v  
 hsa = T +v Psa  
 hsg = T +v Psg  
 hsh = 0  
 hSP = T  
 hss = Infinity  
 hsT = T +v PsT  
 hsu = T +v Psu  
 hsv = T +v Psv  
 hTa = T sTa +v PTa  
 hTg = T sTg +v PTg  
 hTh = 0

hTP = T sTP  
 hTs = v PTs  
 hTT = Infinity  
 hTu = T sTu +v PTu  
 hTv = T sTv +v PTv  
 hua = T sua +v Pua  
 hug = T sug +v Pug  
 huh = 0  
 huP = T suP  
 hus = v Pus  
 huT = T suT +v PuT  
 huu = Infinity  
 huv = T suv +v Puv  
 hva = T sva +v Pva  
 hvg = T svg +v Pvg  
 hvh = 0  
 hvP = T svP  
 hvs = v Pvs  
 hvT = T svT +v PvT  
 hvu = T svu +v Pvuv  
 hvv = Infinity  
 Paa = Infinity  
 Pag = 1 / aPg  
 Pah = 1 / aPh  
 PaP = 0  
 Pas = 1 / aPs  
 PaT = 1 / aPT  
 Pau = 1 / aPu  
 Pav = 1 / aPv  
 Pga = 1 / gPa  
 Pgg = Infinity  
 Pgh = 1 / gPh  
 PGP = 0  
 Pgs = 1 / gPs  
 PGt = 1 / gPT  
 Pgu = 1 / gPu  
 Pgv = 1 / gPv  
 Pha = 1 / hPa  
 Phg = 1 / hPg  
 Phh = Infinity  
 PhP = 0  
 Phs = 1 / hPs  
 PhT = 1 / hPT  
 Phu = 1 / hPu  
 Phv = 1 / hPv  
 PPa = 1  
 PPg = 1  
 PPh = 1  
 PPs = 1  
 PPT = 1  
 PPu = 1  
 PPv = 1  
 Psa = - asP / aPs  
 Psg = - gsP / gPs  
 Psh = - hsP / hPs  
 PsP = 0  
 Pss = Infinity  
 PsT = 1 / sPT  
 Psu = - usP / uPs  
 Psv = Psv  
 PTa = - aTP / aPT  
 PTg = - gTP / gPT  
 PTh = - hTP / hPT  
 PTP = 0  
 PTs = 1 / TPs  
 PTT = Infinity  
 PTu = - uTP / uPT  
 PTv = PTv  
 Pua = 1 / uPa  
 Pug = 1 / uPg  
 Puh = 1 / uPh  
 PuP = 0  
 Pus = 1 / uPs  
 PuT = 1 / uPT  
 Puv = Infinity  
 Puv = 1 / uPv  
 Pva = - avP / aPv  
 Pvg = - gvP / gPv  
 Pvh = - hvP / hPv  
 Pvp = 0  
 Pvs = Pvs  
 PvT = PvT  
 Pvuv = - uvP / uPv  
 Pvv = Infinity

saa = Infinity  
 sag = 1 / asg  
 sah = 1 / ash  
 saP = 1 / asP  
 sas = 0  
 saT = 1 / asT  
 sau = 1 / asu  
 sav = 1 / asv  
 sga = 1 / gsa  
 sgg = Infinity  
 sgh = 1 / gsh  
 sgp = 1 / gsP  
 sgs = 0  
 sgt = 1 / gsT  
 sgu = 1 / gsu  
 sgv = 1 / gsv  
 sha = 1 / hsa  
 shg = 1 / hsg  
 shh = Infinity  
 shP = 1 / hsP  
 shs = 0  
 shT = 1 / hsT  
 shu = 1 / hsu  
 shv = 1 / hsv  
 sPa = - aPs / asP  
 sPg = - gPs / gsP  
 sPh = - hPs / hsP  
 sPP = Infinity  
 sPs = 0  
 sPT = sPT  
 sPu = - uPs / usP  
 sPv = 1 / Psv  
 ssa = 1  
 ssg = 1  
 ssh = 1  
 ssP = 1  
 sst = 1  
 ssu = 1  
 ssv = 1  
 sTa = - aTs / asT  
 sTg = - gTs / gsT  
 sTh = - hTs / hsT  
 sTP = sTP  
 sTs = 0  
 sTT = Infinity  
 sTu = - uTs / usT  
 sTv = sTv  
 sua = 1 / usa  
 sug = 1 / usg  
 suh = 1 / ush  
 suP = 1 / usP  
 sus = 0  
 suT = 1 / usT  
 suu = Infinity  
 suv = 1 / usv  
 sva = - avS / asv  
 svg = - gvs / gsv  
 svh = - hvs / hsv  
 svP = 1 / vsP  
 svS = 0  
 svT = svT  
 svu = - uvs / usv  
 svv = Infinity  
 Taa = Infinity  
 Tag = 1 / aTg  
 Tah = 1 / aTh  
 TaP = 1 / aTP  
 Tas = 1 / aTs  
 TaT = 0  
 Tau = 1 / aTu  
 Tav = 1 / aTv  
 Tga = 1 / gTa  
 Tgg = Infinity  
 Tgh = 1 / gTh  
 TgP = 1 / gTP  
 Tgs = 1 / gTs  
 TgT = 0  
 Tgu = 1 / gTu  
 Tgv = 1 / gTv  
 Tha = 1 / hTa  
 Thg = 1 / hTg  
 Thh = Infinity  
 ThP = 1 / hTP  
 Ths = 1 / hTs

ThT = 0  
 Thu = 1 / hTu  
 Thv = 1 / hTv  
 TPa = - aPT / aTP  
 TPg = - gPT / gTP  
 TPh = - hPT / hTP  
 TPP = Infinity  
 TPs = TPs  
 TPT = 0  
 TPu = - uPT / uTP  
 TPv = 1 / PTv  
 Tsa = - asT / aTs  
 Tsg = - gsT / gTs  
 Tsh = - hsT / hTs  
 TsP = TsP  
 Tss = Infinity  
 TsT = 0  
 Tsu = - usT / uTs  
 Tsv = Tsv  
 TTA = 1  
 TTg = 1  
 TTh = 1  
 TTP = 1  
 TTs = 1  
 TTu = 1  
 TTv = 1  
 Tua = 1 / uTa  
 Tug = 1 / uTg  
 Tuh = 1 / uTh  
 TuP = 1 / uTP  
 Tus = 1 / uTs  
 TuT = 0  
 Tuu = Infinity  
 Tuv = 1 / uTv  
 Tva = - avT / aTv  
 Tvg = - gvT / gTv  
 Tvh = - hvT / hTv  
 TvP = 1 / vTP  
 Tvs = Tvs  
 TvT = 0  
 Tvu = - uvT / uTv  
 Tvv = Infinity  
 uaa = Infinity  
 uag =T sag -P vag  
 uah =T sah -P vah  
 uaP =T saP -P vaP  
 uas = -P vas  
 uaT =T saT -P vaT  
 uau = 0  
 uav =T sav  
 uga =T sga -P vga  
 ugg = Infinity  
 ugh =T sgh -P vgh  
 ugp =T sgp -P vgp  
 ugs = -P vgs  
 ugt =T sgt -P vgt  
 ugu = 0  
 ugv =T sgv  
 uha =T sha -P vha  
 uhg =T shg -P vhg  
 uhh = Infinity  
 uhp =T shP -P vhp  
 uhs = -P vhs  
 uhT =T shT -P vht  
 uhu = 0  
 uhv =T shv  
 uPa =T sPa -P vPa  
 uPg =T sPg -P vPg  
 uPh =T sPh -P vPh  
 uPP = Infinity  
 uPs = -P vPs  
 uPT =T sPT -P vPT  
 uPu = 0  
 uPv =T sPv  
 usa =T -P vsa  
 usg =T -P vsg  
 ush =T -P vsh  
 usP =T -P vsP  
 uss = Infinity  
 usT =T -P vsT  
 usu = 0  
 usv =T  
 uTa =T sTa -P vTa  
 uTg =T sTg -P vTg

uTh =T sTh -P vTh  
 uTP =T sTP -P vTP  
 uTs = -P vTs  
 uTT = Infinity  
 uTu = 0  
 uTv =T sTv  
 uua = 1  
 uug = 1  
 uuh = 1  
 uup = 1  
 uus = 1  
 uut = 1  
 uuv = 1  
 uva =T sva -P  
 uvg =T svg -P  
 uvh =T svh -P  
 uvP =T svP -P  
 uvs = -P  
 uvT =T svT -P  
 uvu = 0  
 uvv = Infinity  
 vaa = Infinity  
 vag = 1 / avg  
 vah = 1 / avh  
 vaP = 1 / avP  
 vas = 1 / avs  
 vaT = 1 / avT  
 vau = 1 / avu  
 vav = 0  
 vga = 1 / gva  
 vgg = Infinity  
 vgh = 1 / gvh  
 vgp = 1 / gvp  
 vgs = 1 / gvs  
 vgt = 1 / gvt  
 vgu = 1 / gvu  
 vgv = 0  
 vha = 1 / hva  
 vhg = 1 / hvg  
 vhh = Infinity  
 vhp = 1 / hvp  
 vhs = 1 / hvs  
 vht = 1 / hvT  
 vhu = 1 / hvu  
 vhv = 0  
 vPa = - aPv / avP  
 vPg = - gPv / gvP  
 vPh = - hPv / hvP  
 vPP = Infinity  
 vPs = vPs  
 vPT = vPT  
 vPu = - uPv / uvP  
 vPv = 0  
 vsa = - asv / avs  
 vsg = - gsv / gvs  
 vsh = - hsv / hvs  
 vsP = vsP  
 vss = Infinity  
 vsT = 1 / svT  
 vsu = - usv / uvs  
 vsv = 0  
 vTa = - aTv / avT  
 vTg = - gTv / gvT  
 vTh = - hTv / hvT  
 vTP = vTP  
 vTs = 1 / Tvs  
 vTT = Infinity  
 vTu = - uTv / uvT  
 vTv = 0  
 vua = 1 / uva  
 vug = 1 / uvg  
 vuh = 1 / uvh  
 vuP = 1 / uvP  
 vus = 1 / uvs  
 vuT = 1 / uvT  
 vuu = Infinity  
 vuv = 0  
 vva = 1  
 vvg = 1  
 vvh = 1  
 vvp = 1  
 vvs = 1  
 vvt = 1  
 vvu = 1

## Material property recursion table

	<b>Helmholtz (v, T)</b> $K_T, c_v, B_v$	<b>Gibbs (T,P)</b> $\kappa_T, c_p, \alpha_p$	<b>Enthalpy (s,P)</b> $\kappa_s, c_p, B_s$	<b>Energy (v,s)</b> $K_s, c_v, \gamma$
P <sub>s</sub> T=	PvT/svT	1/sPT	-TsP/TPs	Psv-Pvs*Tsv/ Tvs
Psv=	PTv/sTv	1/sPv	-vsP/vPs	$\gamma T/v = -\left(\frac{\partial^2 u}{\partial v \partial s}\right)$
PTs=	PTv-PvT*sTv/svT	-sTP/sPT	1/TPs	Pvs/Tvs
PTv=	$B_v = -\left(\frac{\partial^2 a}{\partial v \partial T}\right)$	-vTP/vPT	1/TPv	Psv/Tsv
Pvs=	PvT-PTv*sTv/sTv	1/vPs	1/vPs	$-K_s/v = \left(\frac{\partial^2 u}{\partial v^2}\right)_s$
PvT=	$-K_T/v = -\left(\frac{\partial^2 a}{\partial v^2}\right)_T$	1/vPT	1/vPT	Pvs-Psv*Tvs/ Tsv
sPT=	svT/PvT	$-v\alpha_p = -\left(\frac{\partial^2 g}{\partial T \partial P}\right)$	-TPs/TsP	1/PsT
sPv=	sTv/PTv	sPT-sTP*vPT/vTP	-vPs/vsP	1/Psv
sTP=	sTv-svT*PTv/PvT	$c_p/T = -\left(\frac{\partial^2 g}{\partial T^2}\right)_P$	1/TsP	1/TsP
sTv=	$c_v/T = -\left(\frac{\partial^2 a}{\partial T^2}\right)_v$	sTP-sPT*vTP/vPT	1/Tsv	1/Tsv
svP=	svT-sTv*PvT/PTv	sTP/vTP	1/vsP	-Pvs/Psv
svT=	$B_v = -\left(\frac{\partial^2 a}{\partial v \partial T}\right)$	sPT/vPT	1/vsT	-Tvs/Tsv
TPs=	1/PTs	-sPT/sTP	$1/B_s = \left(\frac{\partial h}{\partial s \partial P}\right)$	Tvs/Pvs
TPv=	1/PTv	-vPT/vTP	TPs-TsP*vPs/vsP	Tsv/Psv
TsP=	1/sTP	1/sTP	$T/c_p = \left(\frac{\partial^2 h}{\partial s^2}\right)_P$	Tsv-Tvs*Psv/ Pvs
Tsv=	1/sTv	1/sTv	TsP-TPs*vsP/vPs	$T/c_v = \left(\frac{\partial^2 u}{\partial s^2}\right)_v$
TvP=	-PvT/PTv	1/vTP	TsP/vsP	Tvs-Tsv*Pvs/ Psv
Tvs=	-svT/sTv	1/vTs	TPs/vPs	$-\gamma T/v = \left(\frac{\partial^2 u}{\partial s \partial v}\right)$
vPs=	1/Pvs	vPT-vTP*sPT/sTP	$-v\kappa_s = \left(\frac{\partial^2 h}{\partial P^2}\right)_s$	1/Pvs
vPT=	1/PvT	$-v\kappa_T = \left(\frac{\partial^2 g}{\partial P^2}\right)_T$	vPs-vsP*TPs/TsP	1/PvT
vsP=	1/svP	vTP/sTP	$1/B_s = \left(\frac{\partial h}{\partial P \partial s}\right)$	-Psv/Pvs
vsT=	1/svT	vPT/sPT	vsP-vPs*TPs/TPs	-Tsv/Tvs
vTP=	-PTv/PvT	$v\alpha_p = \left(\frac{\partial^2 g}{\partial P \partial T}\right)$	vsP/TsP	1/TvP
vTs=	-sTv/svT	vTP-vPT*sTP/sPT	vPs/TPs	1/Tvs

u = internal energy

a = Helmholtz free energy

g = Gibbs free energy

h = enthalpy

v = specific volume

T = temperature

s = entropy

P = pressure

Remember these relationships:

$$\kappa_T = 1/K_T$$

$$\kappa_s = 1/K_s$$

## Example 2

Suppose you wish to distill the derivative of the temperature with respect to internal energy, holding volume constant,  $(\partial T/\partial u)_v$ , or **Tuv** in our table notation. The first table (starting on page 9) says

$$\begin{aligned} \mathbf{Tuv} &= 1 / \mathbf{uTv} \\ \mathbf{uTv} &= T \mathbf{sTv} \\ \mathbf{sTv} &= \mathbf{sTv} \end{aligned}$$

Back substitution gives

$$\mathbf{Tuv} = 1 / (T \mathbf{sTv})$$

The line “**sTv=sTv**” triggers moving to the material property table on page 11, which lists

$$\mathbf{sTv} = c_v/T.$$

Thus, back substitution gives the final result:

$$\left(\frac{\partial T}{\partial u}\right)_v = \frac{1}{c_v} \quad (15)$$

## Example 3

Suppose you wish to distill the derivative of the temperature with respect to internal energy, holding enthalpy constant,  $(\partial T/\partial u)_h$ , or **Tuh** in our table notation. The first table (starting on page 9) says

$$\mathbf{Tuh} = 1/\mathbf{uTh}.$$

Using the table again gives

$$\mathbf{uTh} = T \mathbf{sTh} - P \mathbf{vTh}.$$

Using the table again gives

$$\mathbf{sTh} = - \mathbf{hTs} / \mathbf{hsT}$$

and

$$\mathbf{vTh} = - \mathbf{hTv} / \mathbf{hvT}.$$

One more time gives...

$$\mathbf{hTs} = \mathbf{v} \mathbf{PTs}, \quad \mathbf{hsT} = T + \mathbf{v} \mathbf{PsT}, \quad \mathbf{hTv} = T \mathbf{sTv} + \mathbf{v} \mathbf{PTv}, \quad \text{and} \quad \mathbf{hvT} = T \mathbf{svT} + \mathbf{v} \mathbf{PvT}$$

The first table now gives no further simplification because all energies ( $u$  and  $h$ ) have been removed from all derivatives. Back substitution gives

$$\mathbf{Tuh} = 1/(-T \mathbf{v} \mathbf{PTs} / (T + \mathbf{v} \mathbf{PsT}) + P (T \mathbf{sTv} + \mathbf{v} \mathbf{PTv}) / (T \mathbf{svT} + \mathbf{v} \mathbf{PvT}))$$

This result is rather ugly because the starting derivative, **Tuh**, involved two energies. Nevertheless, by using the first table, we have converted to a form that involves no energies. Using the second table, each of the “energy-free derivatives” may be expressed in terms of material properties. For example,

$$\mathbf{PTs} = 1/TPs = B_s.$$

Similarly applying the table on page 11 for the remaining “energy-free” derivatives leads to the final expression of  $(\partial T/\partial u)_h$  in terms of state variables and properties.

## Relationships between properties

Recall that the result in Eq. (14) was expressed in terms of the material properties  $c_p$  and  $B_s$ . The specific heat at constant pressure might be available from some materials handbooks, but other handbooks are likely to list values for  $c_v$  instead. The isentropic thermal stress coefficient  $B_s$  is a quirky material property that is not likely to be listed in *any* handbooks. Even though we have defined a total of ten material properties in this document, only three are independent. Materials handbooks will tabulate three properties, and it will be your job to compute other (dependent) properties as needed.

How do you assign values to the material properties  $c_p$  and  $B_s$ , that appear in Eq. (14) if you have a handbook that tabulates only the isothermal bulk modulus  $K_T$ , the specific heat at constant volume  $c_v$  and the *linear* expansion coefficient  $\alpha_p^{\text{linear}}$ ? The answer is

$$c_p = c_v + 9vT(\alpha_p^{\text{linear}})^2 K_T \quad (16)$$

$$B_s = 3\alpha_p^{\text{linear}} K_T + \frac{c_v}{vT3\alpha_p^{\text{linear}}}. \quad (17)$$

The process used to derive such formulas is the subject of this section.

More often than not, the three properties listed in your favorite handbook will all belong to one of the four groupings in the material property recursion table. If, for example, your handbook lists values for the expansion coefficient  $\alpha_p$ , the constant pressure specific heat  $c_p$ , and the isothermal compressibility  $\kappa_T$ , then your handbook supports the Gibbs group of properties (second column in the property recursion table). If you seek the value for a property in a different column, then you need to equate the entry for that property to the entry in the Gibbs column of the property recursion table. Thereafter, you *stay in the Gibbs column*, recursively simplifying until your non-Gibbs property is expressed in terms of the Gibbs properties available in your handbook.

Suppose, for example, you seek the value of  $c_v$ , expressed in terms of Gibbs properties. First go to the material property recursion table and locate any expression involving  $c_v$ . Then equate it to the expression in the Gibbs column. For example, the property recursion table says

$$sTv = c_v/T \quad \text{in the Helmholtz column} \quad (18)$$

$$sTv = sTP - sPT + vTP/vPT \quad \text{in the Gibbs column.} \quad (19)$$

*Staying in the Gibbs column* (because Gibbs properties are presumed to be available), the property table tells us

$$sTP = c_p/T \quad (20)$$

$$sPT = -v\alpha_p \quad (21)$$

$$vTP = v\alpha_p \quad (22)$$

$$vPT = -vK_T. \quad (23)$$

Back substituting these four results into Eq. (19) gives

$$sTv = \frac{c_p}{T} - \frac{v\alpha_p^2}{\kappa_T} \quad \text{from the Gibbs column.} \quad (24)$$

Equating this result with Eq. (18) and solving for  $c_v$  gives

$$\boxed{c_v = c_p - \frac{Tv\alpha_p^2}{\kappa_T}} \quad \text{J/kg}\cdot\text{K} \quad (25)$$

**NOTE:** specific heat has been defined in this document to equal the amount of heat needed to induce a unit temperature change in a *unit mass*. Similarly, the specific volume is the volume *per unit mass*. For a finite volume  $V$  of mass  $M$ ,  $v = V/M$ , so you might see the above result expressed as

$$c_v = c_p - \frac{TV\alpha_p^2}{M\kappa_T}. \quad (26)$$

**CAUTION:** Many books define specific heat to be the amount of heat needed to induce a unit temperature increase in a unit *mole* of material, not a unit mass as we have done. Let  $x$  be one of our “per unit mass” properties. Let an asterisk denote the analogous “molar” (per unit mole) property. Then  $x^* = x(M/N)$ , where  $N$  is the number of moles and  $M$  is the mass. Multiplying both sides of Eq. (26) by  $M/N$  converts the specific heats *per unit mass* to specific heats *per unit mole*, and the last term that involved division by  $M$  changes to division by  $N$ . Hence, Eq. (26) might appear in some textbooks as

$$c_v^* = c_p^* - \frac{TV\alpha_p^2}{N\kappa_T}, \quad \text{J/mol}\cdot\text{K} \quad (27)$$

where, as mentioned, an asterisk denotes the “per mole” version of the property. The key is to pay very close attention to how your reference books define a material property. You might need slight adjustments like these to use the handbook properties. Checking units is essential.

The thermal expansion coefficient is another example of a “differently defined” property. In this document, we defined the *volumetric* thermal expansion coefficient  $\alpha_p$  to be the *volumetric* strain resulting from a unit temperature change, holding pressure constant. Many books will instead tabulate the *linear* expansion coefficient  $\alpha_p^{\text{linear}}$ , which is the *length* strain per unit temperature change at constant pressure. Consider a cube with dimensions  $L_o \times L_o \times L_o$  that is then heated under constant pressure so that it expands to new cube dimensions  $L \times L \times L$ . The *volumetric* strain is the log of the volume ratio

$$\epsilon_v = \ln \frac{V}{V_o} = \ln \frac{L^3}{L_o^3} = 3 \ln \frac{L}{L_o}. \quad (28)$$

The *linear* strain is the log of the length ratio

$$\epsilon_{\text{lin}} = \ln \frac{L}{L_o}. \quad (29)$$

Therefore,

$$\epsilon_v = 3\epsilon_{\text{lin}}. \quad (30)$$

In other words, a given linear strain will produce a volumetric strain that’s three times as large if the same linear strain occurs in all three spatial directions. Therefore, if you have a handbook that lists the linear expansion coefficient, you can convert it to the *volumetric* expansion coefficient by tripling:

$$\alpha_p = 3\alpha_p^{\text{linear}} \quad 1/\text{K} \quad (31)$$

Some other useful property relationships can be readily deduced from the property recursion table. The compressibilities  $\kappa_T$  and  $\kappa_s$  are not as popular as the bulk moduli  $K_T$  and  $K_s$ . How are these related? This question is again answered by finding  $\kappa_T$  and  $K_s$  in the property recursion table and performing cross-correlations. That table says

$$v_{PT} = -v\kappa_T \quad \text{in the Gibbs column} \quad (32)$$

$$\nu_{PT} = 1/P\nu_T \quad \text{in the Helmholtz column} \quad (33)$$

Staying in the Helmholtz column the table says

$$P\nu_T = -K_T/\nu. \quad (34)$$

Thus, by back substitution, the above three equations imply

$$\boxed{\kappa_T = \frac{1}{K_T}} \quad (35)$$

Similarly,

$$\boxed{\kappa_s = \frac{1}{K_s}} \quad (36)$$

Another less-common material property is the thermal pressure coefficient  $B_\nu$ . According to its definition, this parameter measures the pressure increase induced by a unit temperature change performed under constant volume conditions. How is  $B_\nu$  related to more commonly available properties? The property table says

$$P_{T\nu} = B_\nu \quad \text{in the Helmholtz column} \quad (37)$$

$$P_{T\nu} = -\nu_{TP}/\nu_{PT} \quad \text{in the Gibbs column} \quad (38)$$

Staying in the Gibbs column, the table says

$$\nu_{TP} = \nu\alpha_p \quad \text{in the Gibbs column} \quad (39)$$

$$\nu_{PT} = -\nu\kappa_T \quad \text{in the Gibbs column} \quad (40)$$

Back substituting these relationships leads to the formula

$$B_\nu = \frac{\alpha_p}{\kappa_T}, \quad (41)$$

or

$$B_\nu = K_T\alpha_p. \quad (42)$$

In other words, the thermal pressure coefficient is simply the volumetric expansion property times the isothermal bulk modulus. This makes a lot of sense because, under a unit temperature change, you can imagine letting a sample first expand at constant pressure (producing a strain  $\alpha_p$ ), and then recompressing isothermally (so that the temperature change will be the same) back to the original volume. The pressure required to do this is the isothermal bulk modulus times the strain, as indicated in Eq. (42). Going back to the original volume is needed because the  $B_\nu$  is defined to be the pressure change *holding volume constant*.

The Grüneisen parameter might be new to you. This material property and the other “energetic” properties (i.e., those listed in the “energy” column of the property table) are often used in acoustics. The energetic properties are important in acoustic wave motion because sound waves travel so fast that there is not sufficient time for heat to conduct away from the system (i.e., entropy is constant\*). Two different property sets (enthalpic and energetic) both have entropy as a natural variable. Then

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\* Acoustic waves are *low amplitude* waves. Hence, even though they are dynamic, they disturb the material only very slightly and the associated entropy production is negligible. High amplitude (shock) waves, on the other hand, produce considerable entropy even though they are adiabatic.

why are *energetic* properties more commonly used in acoustics? The answer is that volume is treated as the independent variable in most wave mechanics codes. In other words, most material models take the volume change as input and predict the pressure change as output. Thus, the controlled state variables are the *internal energy's* natural variables,  $v$  and  $s$ . Getting back to the meaning of the Grüneisen parameter  $\gamma$ , note that the property table tells us that

$$P_{sv} = \gamma T/v \quad \text{in the (internal) energy column} \quad (43)$$

$$P_{sv} = P_{Tv}/s_{Tv} \quad \text{in the Helmholtz column} \quad (44)$$

Staying in the Helmholtz column, the property table says

$$P_{Tv} = B_v \quad \text{in the Helmholtz column} \quad (45)$$

$$s_{Tv} = c_v/T \quad \text{in the Helmholtz column} \quad (46)$$

Thus, these equations imply

$$\boxed{\gamma = \frac{v B_v}{c_v}}, \quad \text{dimensionless} \quad (47)$$

or, noting that  $v = 1/\rho$ , where  $\rho$  is the mass density, and also using Eq. (42),

$$\boxed{\gamma = \frac{K_T \alpha_p}{\rho c_v}}. \quad \text{dimensionless} \quad (48)$$

Note from the property table that

$$\gamma = -\frac{v}{T} \left( \frac{\partial T}{\partial v} \right)_s = \frac{\rho}{T} \left( \frac{\partial T}{\partial \rho} \right)_s = \left( \frac{\partial [\ln(T/T_0)]}{\partial [\ln(\rho/\rho_0)]} \right)_s, \quad (49)$$

where  $\rho$  is the mass density, while  $T_0$  and  $\rho_0$  are reference values (at the beginning of an experiment or at a standard state). The Grüneisen parameter quantifies sensitivity of temperature to volume changes under isentropic conditions. The fact that the Grüneisen parameter is defined in terms of logarithms suggests that, for real materials, the isentropic temperature-density relationship tends to be a straight line on log-log scales. If the relationship is not a straight line, it merely means that the Grüneisen parameter (i.e., the local slope in this log-log plot) isn't a constant. The value of the Grüneisen parameter is typically in the neighborhood of 1.0.

Using the recursion property table, you can prove the following mixed property relationships:

$$\frac{K_s}{K_T} = \frac{c_p}{c_v} \quad (\text{mnemonic: subscripts alphabetical in each ratio}) \quad (50)$$

$$\frac{B_v}{B_s} = 1 - \frac{K_T}{K_s} \quad (51)$$

$$B_v = K_T \alpha_p \quad (52)$$

$$B_s = \frac{\rho c_p}{T \alpha_p}. \quad (53)$$

For quick reference, the following page summarizes formulas that allow you to compute all ten material properties if you have a handbook citing three properties.



**Given Helmholtz properties  $K_T, c_v, B_v$ :**

$K_T$ = Bulk modulus at constant temperature	$\text{J/m}^3$
$c_v$ = specific heat at constant volume	$\text{J/kg}\cdot\text{K}$
$B_v$ = change in pressure with respect to temperature at constant volume	$\text{J/m}^3\cdot\text{K}$

**The other (non-Helmholtz) properties are found by**

$$\begin{aligned}
 K_s &= K_T + \frac{B_v^2 T}{\rho c_v} & \kappa_T &= \frac{1}{K_T} & \kappa_s &= 1/K_s & \frac{K_s}{K_T} &= 1 + \frac{B_v^2 T}{\rho c_v K_T} \\
 c_p &= c_v \left( \frac{K_s}{K_T} \right) & \alpha_p &= \frac{B_v}{K_T} & B_s &= \frac{\rho c_p}{T \alpha_p} & \gamma &= \frac{B_v}{\rho c_v}
 \end{aligned}$$

**Given Gibbs properties  $\kappa_T, c_p, \alpha_p$ :**

$\kappa_T$ = compressibility at constant temperature = $1/K_T$	$\text{m}^3/\text{J}$
$c_p$ = specific heat at constant pressure	$\text{J/kg}\cdot\text{K}$
$\alpha_p$ = volumetric thermal expansion coefficient at constant pressure	$1/\text{K}$

**The other (non-Gibbs) properties are found by**

$$\begin{aligned}
 K_T &= \frac{1}{\kappa_T} & \kappa_s &= \kappa_T - \frac{T \alpha_p^2}{\rho c_p} & K_s &= \frac{1}{\kappa_s} & \frac{K_T}{K_s} &= 1 - \frac{T \alpha_p^2}{\rho c_p \kappa_T} \\
 c_v &= c_p \left( \frac{K_T}{K_s} \right) & B_v &= K_T \alpha_p & B_s &= \frac{\rho c_p}{\alpha_p T} & \gamma &= \frac{B_v}{\rho c_v}
 \end{aligned}$$

**Given enthalpic properties  $\kappa_s, c_p, B_s$ :**

$\kappa_s$ = compressibility at constant entropy = $1/K_s$	$\text{m}^3/\text{J}$
$c_p$ = specific heat at constant pressure	$\text{J/kg}\cdot\text{K}$
$B_s$ = change in pressure with respect to temperature at constant entropy	$\text{J/m}^3\cdot\text{K}$

**The other (non-enthalpic) properties are found by**

$$\begin{aligned}
 K_s &= \frac{1}{\kappa_s} & \kappa_T &= \kappa_s + \frac{\rho c_p}{T B_s^2} & K_T &= \frac{1}{\kappa_T} & \frac{K_T}{K_s} &= \left[ 1 + \frac{\rho c_p}{T B_s^2 \kappa_s} \right]^{-1} \\
 c_v &= c_p \left( \frac{K_T}{K_s} \right) & \alpha_p &= \frac{\rho c_p}{T B_s} & B_v &= K_T \alpha_p & \gamma &= \frac{B_v}{\rho c_v}
 \end{aligned}$$

**Given energetic (internal energy) properties  $K_s, c_v, \gamma$ :**

$K_s$ = bulk modulus at constant entropy	$\text{J/m}^3$
$c_v$ = specific heat at constant volume	$\text{J/kg}\cdot\text{K}$
$\gamma$ = the Grüneisen parameter	dimensionless

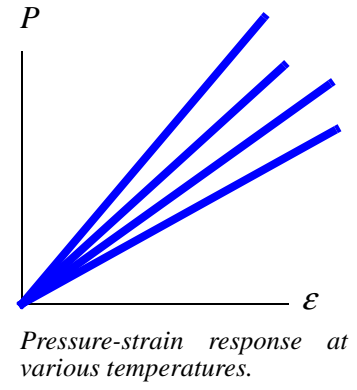
**The other (non-energetic) properties found by**

$$\begin{aligned}
 K_T &= K_s - \rho \gamma^2 T c_v & \kappa_T &= \frac{1}{K_T} & \kappa_s &= \frac{1}{K_s} & \frac{K_s}{K_T} &= \left[ 1 - \frac{\rho \gamma^2 T c_v}{K_s} \right]^{-1} \\
 c_p &= c_v \left( \frac{K_s}{K_T} \right) & B_v &= \rho \gamma c_v & B_s &= \frac{K_s}{\gamma T} & \alpha_p &= \frac{B_v}{K_T}
 \end{aligned}$$

## Thermodynamic consistency and inconsistency

Thermodynamic consistency means that a theoretical model (good or bad) is implemented in such a way that all thermodynamic derivative identities hold. To illustrate the concept, we will consider a contrived example of a model that is thermodynamically inadmissible.

Suppose that laboratory experiments conducted at constant temperature suggest that pressure is a linear function of strain, where (recall strain is defined as  $\epsilon = \ln(v_0/v)$ ). Further suppose that the slope of the pressure-strain plot depends on the temperature at which the experiment is conducted. In other words, the isothermal bulk modulus,



$$K_T = \left( \frac{\partial P}{\partial \epsilon} \right)_T, \quad (54)$$

is a function of temperature, but not a function of strain. If a numerical thermoelasticity model is already available in which the all material properties ( $K_T$ ,  $\alpha_p$ ,  $c_p$ ) are constants, handling a temperature-dependent bulk modulus might seem to be a simple matter of modifying the model to set the value of  $K_T$  according to the current temperature. It might seem that no further code revisions would be required. However, such a model would be thermodynamically inadmissible, as we will now show.

Using Eq. (54), the dependence of the bulk modulus on temperature is quantified by the following mixed partial derivative:

$$\frac{dK_T}{dT} = \frac{\partial^2 P}{\partial \epsilon \partial T} = \frac{\partial^2 P}{\partial T \partial \epsilon} = \left( \frac{\partial B_v}{\partial \epsilon} \right)_T, \quad (55)$$

where

$$B_v = \left( \frac{\partial P}{\partial T} \right)_\epsilon. \quad (56)$$

Noting from the material property table that  $B_v = K_T \alpha_p$ , and recalling that  $K_T$  depends only on temperature in our contrived example, Eq. (55) becomes

$$\frac{dK_T}{dT} = K_T \left( \frac{\partial \alpha_p}{\partial \epsilon} \right)_T. \quad \text{(for this contrived example)} \quad (57)$$

Equivalently,

$$\left( \frac{\partial \alpha_p}{\partial \epsilon} \right)_T = \frac{1}{K_T} \frac{dK_T}{dT}. \quad \text{(for this contrived example)} \quad (58)$$

The right hand side is nonzero by premise. Therefore, the left hand side must be nonzero as well. In other words, *temperature dependence of the bulk modulus requires strain dependence of the thermal expansion coefficient*. Using a constant  $\alpha_p$  would result in a thermodynamically inadmissible model.

The division by  $K_T$  in Eq. (58) might make it seem that  $(\partial \alpha_p / \partial \epsilon)_T$  is negligible, but one must inspect the governing equations, where it can be seen that terms involving strain dependence of  $\alpha_p$  are comparable in order of magnitude to terms involving temperature dependence of  $K_T$ .

## Finding fundamental energy potentials

We have mentioned that  $u(s, v)$  is a fundamental potential function. Determining this function from laboratory data usually entails performing experiments in which state variables (not energies) are controlled. Changes in state variables (not energies) are measured. In other words,  $u(s, v)$  is never measured *directly* — instead, it must be *inferred* from tractable data. You might, for example, measure how pressure  $P$  varies with specific volume  $v$  under insulated conditions. You might additionally have measurements of the temperature history induced by heating in constant volume conditions, which (because the heat increment =  $Tds$  for *reversible* thermoelasticity) is essentially a family of relationships between entropy  $s$  and temperature  $T$  for each fixed volume. These individual laboratory-measured relationships between state variables are called **equations of state (EOS)**. For generalized material models that include shear stress, practitioners often use “EOS” to mean the relationships between pressure, volume, temperature, and entropy, while relationships between shear stress and shear strain (as well as yield, fracture, etc.) are referred to as the “constitutive model.” This is an unfortunate corruption of terminology because it assumes that deviatoric (shear) response can be decoupled from isotropic (pressure-volume-temperature) response. If an *anisotropic* material such as a fiber-reinforced composite is subjected to an isotropic increase in size (with no change in shape), the stress change is *not* isotropic — there is a larger stress required in the fiber direction. We prefer that “EOS” means any relationship between measurable state variables, with no explicit presence of an energy. For inviscid fluids, a fundamental potential function can be found whenever you have two independent EOS equations involving the four state variables ( $P, T, s, v$ ):

Given a system of two independent equations (usually laboratory data), involving the four state variables ( $P, T, s, v$ ), the fundamental potentials are found as follows:

To get  $u(s, v)$ , solve the system for  $T$  and  $P$  as functions of  $s$  and  $v$ . Then integrate

$$\left(\frac{\partial u}{\partial s}\right)_v = T(s, v) \quad \text{and} \quad \left(\frac{\partial u}{\partial v}\right)_s = -P(s, v)$$

To get  $a(v, T)$ , solve the system for  $P$  and  $s$  as functions of  $v$  and  $T$ . Then integrate

$$\left(\frac{\partial a}{\partial v}\right)_T = -P(v, T) \quad \text{and} \quad \left(\frac{\partial a}{\partial T}\right)_v = -s(v, T)$$

To get  $g(T, P)$ , solve the system for  $s$  and  $v$  as functions of  $T$  and  $P$ . Then integrate

$$\left(\frac{\partial g}{\partial T}\right)_P = -s(T, P) \quad \text{and} \quad \left(\frac{\partial g}{\partial P}\right)_T = v(T, P)$$

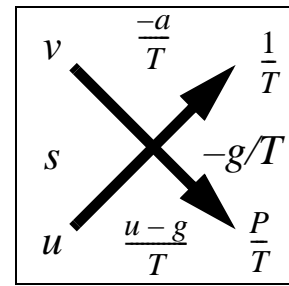
To get  $h(P, s)$ , solve the system for  $v$  and  $T$  as functions of  $P$  and  $s$ . Then integrate

$$\left(\frac{\partial h}{\partial P}\right)_s = v(P, s) \quad \text{and} \quad \left(\frac{\partial h}{\partial s}\right)_P = T(P, s)$$

Keep in mind: when integrating a partial derivative, the integration “constant” is actually a function of the quantity held constant in the partial derivative. Once one of the energy potentials is found, the other energies may be found by using Eq. (4). You must express the result in terms of natural variables for the function to be a fundamental potential.

## The entropic fundamental potential

Recall that  $(\partial u / \partial s)_v = T$ . Therefore, assuming that temperature is always positive\*, the slope of  $u$  plotted as a function of  $s$  (for any fixed value of  $v$ ) is everywhere positive, implying that the relationship is globally invertible for  $s$  as a function of  $u$  (and  $v$ ). Consequently, not only is  $u(s, v)$  a fundamental potential, so is  $s(u, v)$ . When  $s(u, v)$  is a fundamental potential, internal energy becomes a natural independent variable. Therefore, a *different* thermodynamic square applies as shown.



In the previous section, we conjectured that two independent equations (presumably lab observations) were available inter-relating  $(P, T, s, v)$ , in which case you could immediately obtain the fundamental potential for internal energy  $u$ . Now suppose that you have two independent equations [measured or theoretical] available involving  $(P, T, u, v)$ . In this case, you should seek  $s(u, v)$  as a fundamental potential. When  $(P, T, u, v)$  are the variables, the two independent equations are called “entropic equations of state” (not because entropy appears anywhere but because these variables imply that it is the entropic fundamental potential is most relevant). In this case, you must solve the system for  $P$  and  $T$  as functions of  $u$  and  $v$ . Then integrate

$$\left(\frac{\partial s}{\partial u}\right)_v = \frac{1}{T(u, v)} \quad \text{and} \quad \left(\frac{\partial s}{\partial v}\right)_u = \frac{P(u, v)}{T(u, v)}. \quad (59)$$

Once  $s(u, v)$  is found, it may (if desired and if tractable) be inverted to obtain the energetic fundamental potential  $u(s, v)$ .

In practice, engineers need a thermodynamically consistent model when only a pressure-volume curve is available. This is one equation involving  $P$  and  $v$ , but finding a fundamental potential requires a second equation. When faced with a dearth of data like this, it is common for the constitutive modeler to simply hypothesize that the internal energy varies in proportion to temperature, where the constant of proportionality is regarded as a material property (to be determined by “tuning” the model as data later become available, although *it would be unethical to tune the model differently for each different experiment*, as getting different values would invalidate the hypothesized equation).

**EXAMPLE: IDEAL GAS.** For an ideal gas, the entropic equations of state are

$$Pv = RT \quad \text{and} \quad u = cRT. \quad (\text{ideal gas}) \quad (60)$$

Here,  $c$  is a material constant and  $R = nR_u$ , where  $n = N/M$  is the number of moles per unit mass and  $R_u$  is the universal gas constant [ $R_u = 8.31 \text{ J}/(\text{mol}\cdot\text{K})$ ]. This is a system of two equations involving  $(P, T, u, v)$ . What is the entropic fundamental potential? Solving the system for  $T$  and  $P$  as functions of  $u$  and  $v$ , and then substituting the result into Eq. (59) gives

$$\left(\frac{\partial s}{\partial u}\right)_v = \frac{cR}{u} \quad \text{and} \quad \left(\frac{\partial s}{\partial v}\right)_u = \frac{R}{v}. \quad (\text{ideal gas}) \quad (61)$$

Integrating the second equation with respect to  $v$  gives

$$s = R \ln v + f(u). \quad (\text{ideal gas}) \quad (62)$$

\* This is sometimes regarded as an assumption rather than immutable truth because [as mentioned in a footnote of **Physics: Part II** by Halliday and Resnick] some materials can be placed into an excited state where the quantum definition of temperature gives negative values. This state is not reached by passing continuously through zero. Instead, temperature jumps from positive to negative via an inversion in the quantum structure. In this state, the other equations of macroscale thermostatics continue to hold if they are properly rephrased to allow for negative temperatures. In particular, the second law inequality needs to have temperature in the *denominator* — multiplying both sides by temperature to get  $T\Delta s$  requires *changing the direction of the inequality*.

Because “ $u$ ” was held constant in the partial derivative, the integration “constant” is actually an undetermined function  $f(u)$ . Differentiating Eq. (62) with respect to  $u$  and substituting the result into the first PDE in Eq. (61) gives

$$\frac{df}{du} = \frac{cR}{u}. \quad (63)$$

Solving this ordinary differential equation for  $f(u)$  and substituting the result back into Eq. (62) gives

$$s = R \ln v + cR \ln u + k, \quad (\text{ideal gas}) \quad (64)$$

where  $k$  is an integration constant. Letting  $(s_o, v_o, u_o)$  denote any known reference state, this result may be written

$$s - s_o = R \ln \frac{v}{v_o} + cR \ln \frac{u}{u_o}. \quad (\text{ideal gas}) \quad (65)$$

Note that, for an ideal gas, the change in entropy is additively separable into individual and uncoupled contributions from volume strain and internal energy\*. Some generalizations of ideal gases Upon simplification, the entropic fundamental potential is

$$s - s_o = R \ln \left[ \left( \frac{v}{v_o} \right) \left( \frac{u}{u_o} \right)^c \right]. \quad (\text{ideal gas}) \quad (66)$$

The energetic fundamental potential is found by simply solving Eq. (65) for  $u(s, v)$ :

$$u = u_o \left[ \frac{e^{(s-s_o)/R}}{v/v_o} \right]^{1/c}. \quad (\text{ideal gas}) \quad (67)$$

As a special case, isentropic ( $s = s_o$ ) behavior implies that  $uv^{1/c} = u_o v_o^{1/c}$ . Noting from Eq. (60) that  $u = cPv$ , this may be written

$$Pv^\Gamma = P_o v_o^\Gamma, \quad (\text{ideal gas, isentropic}) \quad (68)$$

where

$$\Gamma \equiv 1 + \frac{1}{c}. \quad (\text{ideal gas, this CONSTANT parameter is an alternative to “c”}) \quad (69)$$

Hence, for an ideal gas, plotting the pressure-volume isentrope on log-log axes will produce a straight line having slope  $\Gamma$ . If a measured pressure-volume isentrope is *not* a straight line on log-log axes, then you know that the gas will not be well modeled using ideal gas theory.

With the fundamental potentials available, you can use the techniques described in this document to compute any other state variables or material properties of interest. For example, applying Eq. (5), and using an ellipsis (...) to indicate omitted simplification steps,

$$P = -\left( \frac{\partial u}{\partial v} \right)_s = \dots = \frac{u}{cv} = (\Gamma - 1) \frac{u}{v}, \text{ and} \quad (\text{ideal gas}) \quad (70)$$

\* Observations like this (i.e., about the general structure of fundamental potentials for idealized models) are often used as a guide for more realistic theories. For example, the equation  $(\partial s / \partial v)_u = P/T$  generalizes to solids as  $(\partial s / \partial \xi) = \underline{\underline{\sigma}} / (\rho T)$ , where  $\xi$  is the elastic strain tensor,  $\underline{\underline{\sigma}}$  is the conjugate stress, and  $\rho$  is the density. In analogy with ideal gases, one might postulate  $s - s_o = \phi[\xi] + \psi[u]$ , where the separable potentials would be determined in the laboratory.

$$T = \left(\frac{\partial u}{\partial s}\right)_v = \dots = \frac{u}{cR} = \left(\frac{\Gamma-1}{R}\right)u. \quad (\text{ideal gas}) \quad (70b)$$

Applying the definitions on page 5 or the table on page 11, material properties associated with an ideal gas are

$$T = \left(\frac{\Gamma-1}{R}\right)u \quad P = \frac{RT}{v} \quad (\text{ideal gas}) \quad (71)$$

$$K_s = \Gamma P \quad c_v = \frac{R}{\Gamma-1} \quad \gamma = \Gamma - 1 \quad (72)$$

$$K_T = P \quad \frac{K_s}{K_T} = \Gamma \quad \frac{c_p}{c_v} = \Gamma \quad (73)$$

$$c_p = \frac{\Gamma R}{\Gamma-1} \quad B_v = \frac{P}{T} \quad B_s = \left(\frac{\Gamma}{\Gamma-1}\right)\frac{P}{T} \quad \alpha_p = \frac{1}{T}. \quad (74)$$

For the ideal gas, the specific heats are constant, but the other material properties are not constant. Bulk moduli increase linearly with pressure (i.e., the material becomes stiffer with increasing compression). The volumetric expansion property  $\alpha_p$  varies inversely with temperature (i.e., a temperature change at constant pressure induces a much larger change in volumetric strain at low temperatures than it does at high temperatures).

*Molar forms of the ideal gas potentials:* So far, we have used *specific* (per mass) energies. For example,  $u$  has SI units of Joules per kilogram. Fundamental results like Eqs. (65) and (67) can be easily converted to *molar* form by replacing each “per mass” variable  $x$  by

$$x = nx^*, \quad (75)$$

where (as previously mentioned)  $n = N/M$  is the number of moles per unit mass and therefore  $x^*$  is a “per mole” quantity. Making these substitutions in Eqs. (65) and (67), recalling that  $R = nR_u$ , gives the molar forms for the fundamental potentials:

$$s^* - s_o^* = R_u \ln \frac{v^*}{v_o^*} + cR_u \ln \frac{u^*}{u_o^*} \quad (\text{ideal gas}) \quad (76)$$

$$u^* = u_o^* \left[ \frac{e^{(s^* - s_o^*)/R_u}}{v^*/v_o^*} \right]^{1/c}. \quad (\text{ideal gas}) \quad (77)$$

These molar forms involve the universal gas constant  $R_u$  whereas the equivalent specific (mass-based) forms involve the material-specific gas constant  $R = nR_u$ . Different ideal gases have different gas constants  $R$ , but they *all* have the same universal gas constant. This is the primary advantage of the molar form over the “per mass” form. The molar form involves true constants, not parameters that vary from material to material. As far as materials modeling goes, the main thing that distinguishes one ideal gas from another is its value of  $n$  (i.e., the number of moles per mass).