

# 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 thermodynamics 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 directly 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.† Happily, 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.

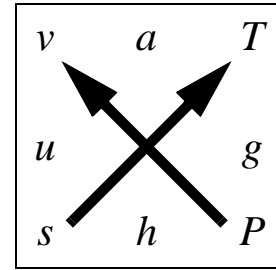
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\* The word “constitutive” means “relating to a particular material or class of materials, possibly further restricted to certain constraints on service conditions.” For example, many materials can be regarded to be elastic under strict conditions 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

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

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

$a$  = Helmholtz free energy  
 $g$  = Gibbs free energy  
 $h$  = enthalpy  
 $u$  = specific internal energy

= natural function of  $v$  and  $T$   
 = natural function of  $T$  and  $P$   
 = natural function of  $P$  and  $s$   
 = natural function of  $s$  and  $v$

$\text{J/kg}$   
 $\text{J/kg}$   
 $\text{J/kg}$   
 $\text{J/kg}$

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,

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

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

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 ( $u, a, h$ , 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,

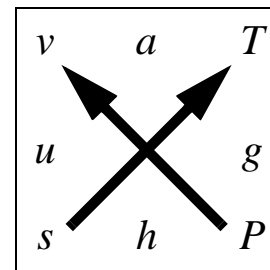
$$s^* = T, \quad T^* = -s, \quad P^* = v, \quad \text{and} \quad v^* = -P. \quad (7)$$

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

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

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**. 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 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\*) 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	$\text{J/m}^3 = \text{N/m}^2$
$K_s$ = bulk modulus at constant entropy	$\text{J/m}^3 = \text{N/m}^2$
$\kappa_T$ = compressibility at constant temperature = $1/K_T$	$\text{m}^3/\text{J}$
$\kappa_s$ = compressibility at constant entropy = $1/K_s$	$\text{m}^3/\text{J}$
$c_v$ = specific heat at constant volume	$\text{J}/(\text{kg}\cdot\text{K})$
$c_p$ = specific heat at constant pressure	$\text{J}/(\text{kg}\cdot\text{K})$
$B_v$ = change in pressure with respect to temperature at constant volume	$\text{J}/(\text{m}^3\cdot\text{K})$
$B_s$ = change in pressure with respect to temperature at constant entropy	$\text{J}/(\text{m}^3\cdot\text{K})$
$\alpha_p$ = volumetric thermal expansion coefficient at constant pressure	$1/\text{K}$
$\gamma$ = 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](#)

$$K_T = -v \left( \frac{\partial P}{\partial v} \right)_T = v \left( \frac{\partial^2 a}{\partial v^2} \right)_T \quad \text{J/m}^3$$

$$K_s = -v \left( \frac{\partial P}{\partial v} \right)_s = v \left( \frac{\partial^2 u}{\partial v^2} \right)_s \quad \text{J/m}^3$$

$$\kappa_T = \frac{1}{K_T} = - \frac{(\partial^2 g / \partial P^2)_T}{v} \quad \text{m}^3/\text{J}$$

$$\kappa_s = \frac{1}{K_s} = - \frac{(\partial^2 h / \partial P^2)_s}{v} \quad \text{m}^3/\text{J}$$

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

$$c_v = T \left( \frac{\partial s}{\partial T} \right)_v = -T \left( \frac{\partial^2 a}{\partial T^2} \right)_v = \frac{T}{(\partial^2 u / \partial s^2)_v} \quad \text{J/(kg}\cdot\text{K)}$$

$$c_p = T \left( \frac{\partial s}{\partial T} \right)_p = -T \left( \frac{\partial^2 g}{\partial T^2} \right)_p = \frac{T}{(\partial^2 h / \partial s^2)_p} \quad \text{J/(kg}\cdot\text{K)}$$

### Thermomechanical (coupling) material properties:

$$\alpha_p = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p = \frac{1}{v} \left( \frac{\partial^2 g}{\partial P \partial T} \right) \quad 1/\text{K}$$

$$B_s = \left( \frac{\partial P}{\partial T} \right)_s = 1 / \left( \frac{\partial^2 h}{\partial s \partial P} \right) \quad \text{J/(m}^3\cdot\text{K)}$$

$$B_v = \left( \frac{\partial P}{\partial T} \right)_v = - \left( \frac{\partial^2 a}{\partial v \partial T} \right) \quad \text{J/(m}^3\cdot\text{K)}$$

$$\gamma = - \frac{v}{T} \left( \frac{\partial T}{\partial v} \right)_s = - \frac{v}{T} \left( \frac{\partial^2 u}{\partial v \partial s} \right) \quad \text{dimensionless}$$

\* Note, 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 definitions 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 definitions do 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

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

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 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

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

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

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



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 quantities. 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 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

$$\begin{aligned}\mathbf{asp} &= \mathbf{-s TsP -P vsP} \\ \mathbf{Tsp} &= \mathbf{Tsp} \\ \mathbf{vsp} &= \mathbf{vsp}\end{aligned}$$

Note that 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

$$\begin{aligned}\mathbf{Tsp} &= T/c_p \\ \mathbf{vsp} &= 1/B_s\end{aligned}$$

Thus, by back substitution,

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

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 Pvu  
 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 Pvu  
 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 / TPps  
 PTT = Infinity  
 PTu = - uTP / uPT  
 PTv = PTv  
 Pua = 1 / uPa  
 Pug = 1 / uPg  
 Puh = 1 / uPh  
 PuP = 0  
 Pus = 1 / uPs  
 PuT = 1 / uPT  
 Puu = Infinity  
 Puv = 1 / uPv  
 Pva = - avP / aPv  
 Pvg = - gvP / gPv  
 Pvh = - hvP / hPv  
 Pvp = 0  
 Pvs = Pvs  
 PvT = PvT  
 Pvu = - 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

	Helmholtz (v, T) $K_T, c_v, B_v$	Gibbs (T, P) $\kappa_T, c_p, \alpha_p$	Enthalpy (s, P) $\kappa_s, c_p, B_s$	Energy (v, s) $K_s, c_v, \gamma$
P <sub>sT</sub> =	PvT/svT	1/sPT	-TsP/TPs	Psv-Pvs*Tsv/Tvs
P <sub>sv</sub> =	PTv/sTv	1/sPv	-vsP/vPs	$\gamma T/v = -\left(\frac{\partial^2 u}{\partial v \partial s}\right)$
PT <sub>s</sub> =	PTv-PvT*sTv/svT	-sTP/sPT	1/TPs	Pvs/Tvs
PT <sub>v</sub> =	$B_v = -\left(\frac{\partial^2 a}{\partial v \partial T}\right)$	-vTP/vPT	1/TPv	Psv/Tsv
P <sub>vs</sub> =	PvT-PTv*sTv/sTv	1/vPs	1/vPs	$-K_s/v = \left(\frac{\partial^2 u}{\partial v^2}\right)_s$
P <sub>vT</sub> =	$-K_T/v = -\left(\frac{\partial^2 a}{\partial v^2}\right)_T$	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
sP <sub>v</sub> =	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
sT <sub>v</sub> =	$c_v/T = -\left(\frac{\partial^2 a}{\partial T^2}\right)_v$	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
TP <sub>s</sub> =	1/PTs	-sPT/sTP	$1/B_s = \left(\frac{\partial h}{\partial s \partial P}\right)$	Tvs/Pvs
TP <sub>v</sub> =	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
Ts <sub>v</sub> =	1/sTv	1/sTv	TsP-TPs*vPs/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
Tv <sub>s</sub> =	-svT/sTv	1/vTs	TPs/vPs	$-\gamma T/v = \left(\frac{\partial^2 u}{\partial s \partial v}\right)$
vP <sub>s</sub> =	1/Pvs	vPT-vTP*sPT/sTP	$-vK_s = \left(\frac{\partial^2 h}{\partial P^2}\right)_s$	1/Pvs
vPT=	1/PvT	$-vK_T = \left(\frac{\partial^2 g}{\partial P^2}\right)_T$	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*TsP/TPs	-Tsv/Tvs
vTP=	-PTv/PvT	$v\alpha_p = \left(\frac{\partial^2 g}{\partial P \partial T}\right)$	vsP/TsP	1/TvP
vT <sub>s</sub> =	-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

Note:

$$\kappa_T = 1/K_T$$

$$\kappa_s = 1/K_s$$

## Example 2

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

$$\mathbf{Tuv} = 1 / \mathbf{uTv}$$

$$\mathbf{uTv} = T \mathbf{sTv}$$

$$\mathbf{sTv} = \mathbf{sTv}$$

Back substitution gives

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

Moving now to the material property table on page 11, note that

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

Thus,

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

## Example 3

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

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

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

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

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

$$\mathbf{hTs} = \mathbf{v PTs},$$

$$\mathbf{hsT} = T + \mathbf{v PsT},$$

$$\mathbf{hTv} = T \mathbf{sTv} + \mathbf{v PTv},$$

$$\mathbf{hvT} = T \mathbf{svT} + \mathbf{v PvT}$$

We can stop using the first table at this point because all energies ( $u$  and  $h$ ) have been removed from all derivatives. Back substitution gives

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

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,

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

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

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

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

*Staying in the Gibbs column* (because it is Gibbs properties that are presumably 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 to denote the analogous “molar” (per unit mole) property. Then  $x^* = x \frac{M}{N}$ , where  $N$  is the number of moles and  $M$  is the mass. Multiplying both sides of Eq. (26) by  $\frac{M}{N}$  converts the specific heats per unit mass to specific heats *per unit mole* and the last term involving division by  $M$  changes to division by  $N$ . Hence, Eq. (26) might appear in some textbooks as

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

The lesson is that you must pay very close attention to how your reference books define a material property. You might be required to make slight adjustments to your conversion formulas in order to use the handbook properties. Checking units is essential.

Another example of a “differently defined” property is the thermal expansion coefficient. 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 that is initially with dimensions  $L_o \times L_o \times L_o$  and then heated under constant pressure so that it expands to new cube dimensions  $L \times L \times L$ . The *volumetric* strain is

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

The *linear* strain is

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

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. Therefore, if you have a handbook that lists the linear expansion coefficient, you can convert it to the *volumetric* expansion coefficient by tripling:

$\alpha_p = 3\alpha_p^{\text{linear}}$

1/K (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, 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 table says

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

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

Staying in the Gibbs's 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 definition of  $B_\nu$  is 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 “internal 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.

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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, then 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 parameters 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 and  $T_0$  and  $\rho_0$  are reference values (at the beginning of an experiment or at a standard state). The Gruneisen parameter essentially quantifies how temperature changes with volume under isentropic conditions. The fact that the Gruneisen parameter is defined in terms of logarithms means suggests that 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 Gruneisen parameter isn't a constant. A typical value for the Gruneisen parameter is 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.

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

$K_T$	= Bulk modulus at constant temperature	J/m <sup>3</sup>
$c_v$	= specific heat at constant volume	J/kg•K
$B_v$	= change in pressure with respect to temperature at constant volume	J/m <sup>3</sup> •K

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

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

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

$\kappa_T$	= compressibility at constant temperature = $1/K_T$	m <sup>3</sup> /J
$c_p$	= specific heat at constant pressure	J/kg•K
$\alpha_p$	= volumetric thermal expansion coefficient at constant pressure	1/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 = $1/K_s$	m <sup>3</sup> /J
$c_p$	= specific heat at constant pressure	J/kg•K
$B_s$	= change in pressure with respect to temperature at constant entropy	J/m <sup>3</sup> •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	J/m <sup>3</sup>
$c_v$	= specific heat at constant volume	J/kg•K
$\gamma$	= the Grüneisen parameter	dimensionless

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

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

## 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, and 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 under heating in constant volume conditions, which (because the heating increment is, for reversible thermoelasticity,  $Tds$ ) 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 the relationship between shear stress and shear strain (as well as yield, fracture, etc.) is referred to as the “constitutive model.” This is an unfortunate corruption of terminology because it implicitly assumes that deviatoric (shear) response can be decoupled from isotropic (pressure-volume-temperature) response. However, 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 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, 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

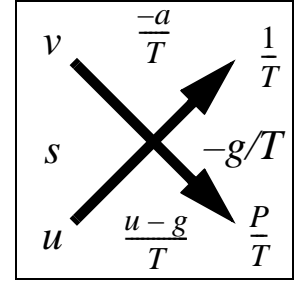
$$\left(\frac{\partial h}{\partial P}\right)_s = v(P, s) \quad \text{and} \quad \left(\frac{\partial h}{\partial s}\right)_P = T(P, s)$$

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). However, you must express the result in terms of natural variables in order 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 is an independent variable. Therefore, a *different* thermodynamic square applies as shown.



You would seek  $s(u, v)$  as a fundamental potential whenever two independent equations [measured or theoretical] are available involving  $(P, T, u, v)$ . When these are the independent variables, the two equations are called “entropic equations of state” (not because entropy appears anywhere but because these variables imply that it is the entropic fundamental potential that is most relevant). In this case, solve the system for  $P$  and  $T$  as functions of  $u$  and  $v$ . Then integrate

$$\left(\frac{\partial s}{\partial u}\right)_v = \frac{1}{T(u, v)} \quad \text{and} \quad \left(\frac{\partial s}{\partial v}\right)_u = \frac{P(u, v)}{T(u, v)} \quad (54)$$

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

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

$$Pv = RT \quad \text{and} \quad u = cRT. \quad (\text{ideal gas}) \quad (55)$$

Here,  $c$  is a 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. (54) gives

$$\left(\frac{\partial s}{\partial u}\right)_v = \frac{cR}{u} \quad \text{and} \quad \left(\frac{\partial s}{\partial v}\right)_u = \frac{R}{v}. \quad (\text{ideal gas}) \quad (56)$$

Integrating the second equation with respect to  $v$  gives

$$s = R \ln v + f(u) \quad (\text{ideal gas}) \quad (57)$$

Because “ $u$ ” was held constant in the partial derivative, the integration “constant” is actually an undetermined function of  $u$ . Differentiating Eq. (57) with respect to  $u$  and substituting the result into the first PDE in Eq. (56) gives

$$\frac{df}{du} = \frac{cR}{u} \quad (58)$$

Solving this ordinary differential equation for  $f(u)$  and substituting the result back into Eq. (57) gives

\* A small community of researchers regard this to be 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. Reaching this state entails a jump discontinuity in temperature from positive to negative so that the material never really passes through zero temperature. 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 make  $T\Delta s$  appear requires changing the direction of the inequality.

$$s = R \ln v + c R \ln u + k \quad (\text{ideal gas}) \quad (59)$$

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

$$s - s_o = R \ln \frac{v}{v_o} + c R \ln \frac{u}{u_o} \quad (\text{ideal gas}) \quad (60)$$

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

$$s - s_o = R \ln \left[ \left( \frac{v}{v_o} \right) \left( \frac{u}{u_o} \right)^c \right] \quad (\text{ideal gas}) \quad (61)$$

The energetic fundamental potential is found by simply solving Eq. (60) for  $u(s, v)$ :

$$u = u_o \left[ \frac{e^{(s-s_o)/R}}{v/v_o} \right]^{1/c} \quad (\text{ideal gas}) \quad (62)$$

As a special case, isentropic ( $s = s_o$ ) behavior implies that  $u v^{1/c} = u_o v_o^{1/c}$ . Noting from Eq. (55) that  $u = c P v$ , this may be written

$$P v^\Gamma = P_o v_o^\Gamma \quad (\text{ideal gas, isentropic}) \quad (63)$$

where

$$\Gamma \equiv 1 + \frac{1}{c} \quad (\text{ideal gas, this CONSTANT parameter is an alternative to "c"}) \quad (64)$$

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,

$$P = - \left( \frac{\partial u}{\partial v} \right)_s = \dots = \frac{u}{c v} = (\Gamma - 1) \frac{u}{v} \quad (\text{ideal gas}) \quad (65)$$

$$T = \left( \frac{\partial u}{\partial s} \right)_v = \dots = \frac{u}{c R} = \left( \frac{\Gamma - 1}{R} \right) u \quad (\text{ideal gas}) \quad (65b)$$

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

$$T = \left( \frac{\Gamma - 1}{R} \right) u \quad P = \frac{R T}{v} \quad (\text{ideal gas}) \quad (66)$$

\* 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  $(\partial s / \partial \underline{\varepsilon})_u = \underline{\sigma} / (\rho T)$ , where  $\underline{\varepsilon}$  is the elastic strain tensor,  $\underline{\sigma}$  is the conjugate stress, and  $\rho$  is the density. In analogy with ideal gases, one might postulate  $s - s_o = \phi[\underline{\varepsilon}] + \psi[u]$ , where the separable potentials would be determined in the laboratory.



$$K_s = \Gamma P \quad c_v = \frac{R}{\Gamma - 1} \quad \gamma = \Gamma - 1 \quad (67)$$

$$K_T = P \quad \frac{K_s}{K_T} = \Gamma \quad \frac{c_p}{c_v} = \Gamma \quad (68)$$

$$c_p = \frac{\Gamma R}{\Gamma - 1} \quad B_v = \frac{P}{T} \quad B_s = \left( \frac{\Gamma}{\Gamma - 1} \right) \frac{P}{T} \quad \alpha_p = \frac{1}{T}, \quad (69)$$

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. (60) and (62) can be easily converted to *molar* form by replacing each “per mass” variable  $x$  by

$$x = nx^*, \quad (70)$$

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. (60) and (62), recalling that  $R = nR_u$ , gives the molar forms for the fundamental potentials:

$$s^* - s_o^* = R_u \ln \frac{v^*}{v_o^*} + cR_u \ln \frac{u^*}{u_o^*} \quad (\text{ideal gas}) \quad (71)$$

$$u^* = u_o^* \left[ \frac{e^{(s^* - s_o^*)/R_u}}{v^*/v_o^*} \right]^{1/c} \quad (\text{ideal gas}) \quad (72)$$

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. The only thing that distinguishes one ideal gas from another is its value of  $n$  (i.e., the number of moles per mass).

