Chapter 4. Fundamental Equations[†]

Two key problems in thermodynamics are to relate properties to each other and to develop ways to measure them accurately in the laboratory. For example, we have seen in Chapter 2 that the relationship between the heat capacities at constant volume and at constant pressure for an ideal gas is:

$$C_P^{\mathrm{IG}} = C_V^{\mathrm{IG}} + R$$

It is highly desirable to obtain a general relationship between the two heat capacities,

$$C_V = (\partial \underline{U} / \partial T)_V \text{ and } C_P = (\partial \underline{H} / \partial T)_P \ ,$$

for non-ideal gases, liquids and solids. In the present chapter, we develop a formal approach that allows us to obtain such relationships between thermodynamic derivatives in a systematic fashion.

An important consideration in developing thermodynamic relationships and methods for determining derived thermodynamic functions such as the energy, enthalpy, or entropy, is the preservation of "information content" as one moves from one function to another. In the rest of this chapter, we demonstrate how all these functions, when expressed in terms of their "natural" variables, are essentially equivalent to each other and encompass all available information about equilibrium states of a system. These equivalent, complete descriptions of thermodynamic properties are called *fundamental equations* and are the main topic of the present chapter.

4.1 Thermodynamic Calculus

As already mentioned in Chapter 1, for a given quantity of a one-component system at equilibrium, all properties are completely determined by specifying the values of two additional independent thermodynamic variables. More generally, *n*+2 independent thermodynamic variables, where *n* is the number of components in a system, are needed to fully characterize equilibrium states for multicomponent systems. Common thermodynamic variables used to specify equilibrium

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[†] Draft material from "Statistical Thermodynamics," © (2012), A.Z. Panagiotopoulos

states in such systems are the total volume V, number of moles of each component, $N_1, N_2, \ldots N_\mathrm{n}$, temperature T and pressure P. The total entropy S can also be specified and controlled with some effort, namely by performing reversible processes and using the definition developed in Ch. 3,

$$\Delta S = \int \delta Q^{\mathrm{rev}} / T$$

to measure entropy changes.

It is clear from empirical observations that not all combinations of variables result in a unique specification of the state of thermodynamic systems. This is especially apparent when the possibility of coexistence between phases of different properties is taken into account. For example, at a given temperature and at the saturation pressure in a one-component system, there are infinitely many ways in which two phases can coexist as equilibrium thermodynamic states differing in the relative amounts of the two phases. In other words, specifying the pressure and temperature at vapor-liquid equilibrium of a pure fluid does not uniquely specify the relative amounts of liquid and vapor. Similarly, a given pressure and volume (or density) of a binary mixture can be realized in many different ways for a range of temperatures in a two-phase system. In addition to the issue of the uniqueness of thermodynamic states, certain "privileged" sets of variables are natural for specific properties. Thermodynamic functions expressed in their natural variables contain more complete information than the same properties expressed in other sets of variables. In order to explain why this is the case, let us consider the combined statement of the First and Second Laws for closed systems derived in § 3.4:

$$dU = TdS - PdV \tag{4.1}$$

This expression suggests that the volume and entropy constitute a "good" set of variables for describing the energy U of a closed system. More formally, we write:

$$U = U(S,V) \quad \Rightarrow \quad dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{4.2}$$

The derivatives are identified as:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \tag{4.3}$$

To obtain the full expression for U as a function also of the amount of material in a system in addition to S and V, we need to augment Eq. 4.2 by additional variables, namely the amount of material of each component present in the system. For this purpose, we define an additional partial derivative, written here for a one-component system:

$$\mu \equiv \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{4.4}$$

This derivative defines an important new thermodynamic variable, the *chemical potential* μ of a component. The chemical potential is an intensive variable that has units of specific energy, [J/mol]. Its physical interpretation in classical thermodynamics is somewhat obscure when compared to the two other more intuitively understood first-order derivatives of the energy function given by Eqs. 4.3. However, the chemical potential plays just as fundamental a role in thermodynamics as temperature and pressure.

An example of a relatively simple instrument that measures chemical potentials is the pH meter, which many of us have used in chemistry laboratories. The instrument measures the chemical potential of hydrogen ions, *not* their concentration. Of course, the two are related, with the chemical potential increasing with increasing concentration – but there is a clear distinction. After all, density also increases with pressure, but pressure and density are not usually confused to be the same physical quantity! Another way to develop a physical feeling for the chemical potential is to consider your senses of smell and taste. What exactly is being "measured" when you find that a food tastes sour, or when you smell a fragrance from a flower? One may naively suggest that it is the concentration of the molecules that correlates with the intensity of taste and smell, but in reality it is the chemical potential of the corresponding components that drives the biochemical receptors responsible for these senses. In addition to chemical reactions, diffusion and evaporation are also driven by chemical potential (not concentration) differences. On a hot and humid summer day, sweating does not cool you down because there are no chemical potential differences to drive evaporation, despite the large concentration difference for water between wet skin and air.

Using the newly defined derivative of Eq. 4.4, we can now write a complete differential relationship for the energy as a function of entropy, volume and number of moles, $U = U(S,V,N)$:

$$dU = TdS - PdV + \mu dN \tag{4.5}$$

More generally, for a multicomponent system, one needs $n+2$ variables to fully characterize the state of a system. When the function of interest is the total energy *U*, these variables can be selected to be the total entropy, *S*, volume, *V* and amount of moles for each component present, $\{N\} \equiv N_1, N_2, \ldots N_n$:

$$\boxed{dU = TdS - PdV + \sum_{i=1}^{n} \mu_i dN_i \qquad (4.6)}$$

fundamental equation

The chemical potential μ_i of a component in a mixture is defined from a direct extension of Eq. 4.4,

$$\mu_i \equiv \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}} \tag{4.7}$$

In this equation, $N_{j\neq i}$ indicates that the number of moles of all components other than i are kept constant; more explicitly, $N_1, N_2, \ldots N_{i-1}, N_{i+1}, \ldots N_n$ are constant while N_i varies. Because the chemical potential definition implies an open system to which a component is added, its value depends on the reference state for energy for the corresponding component and thus is not directly measurable, unlike the first two derivatives of Eq. 4.6, temperature and pressure.

Eq. 4.6 is the single most important equation of this book and is known as the *fundamental equation of thermodynamics* (abbreviated "FE"). It links the key quantities of the First and Second Laws and provides the starting point for understanding equilibrium and stability as well as for deriving thermodynamic relations. S, V and $\{N\}$, the variables in which the function U is expressed in this representation, are all extensive, proportional to system size (mass). The first derivatives, T, P and μ_i's are all intensive, independent of system size. An equivalent representation of the entropy S as a function $S(U, V, N_1, N_2, \ldots N_n)$ can be obtained by rearrangement of the terms of Eq. 4.6:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \sum_{i=1}^{n} \frac{\mu_i}{T} dN_i \tag{4.8}$$

This representation of the fundamental equation is used in statistical mechanics.

<u>Example 4.1</u>[‡]

The fundamental equation for a pure substance is

$$S = \frac{aUV}{N} - \frac{bN^3}{UV}$$

where a and b are positive constants. Obtain the equation of state, P as a function of $\underline{V}$ and T, for this material.

Starting from the FE in the entropy representation (Eq. 4.8), we obtain the pressure and temperature as:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{aV}{N} + \frac{bN^3}{U^2 V} \quad \text{and} \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{aU}{N} + \frac{bN^3}{UV^2} \tag{i}$$

Taking the ratio of the two expressions in (i),

[‡] Adapted from Problem 2.3-5 in Callen, H. B, *Thermodynamics and Introduction to Thermostatistics*, 2nd Ed., Wiley (1985).

$$\frac{P/T}{1/T} = P = \frac{\dfrac{aU}{N}+\dfrac{bN^3}{UV^2}}{\dfrac{aV}{N}+\dfrac{bN^3}{U^2V}} = \frac{\dfrac{aU^2V^2+bN^4}{NUV^2}}{\dfrac{aU^2V^2+bN^4}{NU^2V}} = \frac{U}{V} \Rightarrow U = PV \tag{ii}$$

substituting (ii) into (i),

$$\frac{P}{T} = \frac{aPV}{N} + \frac{bN^3}{PV^3} = aP\underline{V} + \frac{b}{P\underline{V}^3} \Rightarrow P^2\left(\underline{V}^3 - a\underline{V}^4 T\right) = bT \quad \Rightarrow$$

$$\boxed{P = \sqrt{\frac{bT}{\underline{V}^3 - a\underline{V}^4 T}}}$$

4.2 Manipulation of Thermodynamic Derivatives

Deriving relationships between thermodynamic derivatives is the key objective of the present chapter. Manipulations of thermodynamic derivatives can seem quite daunting at times, but can be accomplished systematically with a small number of relatively simple mathematical tools. Thermodynamic functions, after all, are mathematical objects that are subject to the same rules of multivariable calculus as any other functions, even if we frequently do not have explicit, closed-form expressions for them in terms of their independent variables.

In the following, we will consider x, y, z, and w to be mathematical objects with well-behaved functional relationships between them. We will also assume that there are two independent variables in this set and that any two of x, y, z, and w can serve as the independent variables. This assumption is made for simplicity and without loss of generality. The following general mathematical relationships are often useful for manipulating derivatives of functions of many variables – in general – and thermodynamic functions in particular:

<u>Inversion</u>

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\partial y/\partial x\right)_z} \tag{4.9}$$

This relationship is for the underlying *functions* rather than simple algebraic inversion; $x(y,z)$ and $y(x,z)$ that are being differentiated on the two sides of Eq. 4.9 are expressed in terms of different variables (see Example 4.2 for an illustration of this concept).

Commutation

$$\left(\frac{\partial}{\partial x}\right)\left[\left(\frac{\partial z}{\partial y}\right)_x\right]_y = \left(\frac{\partial^2 z}{\partial x \partial y}\right) = \left(\frac{\partial}{\partial y}\right)\left[\left(\frac{\partial z}{\partial x}\right)_y\right]_x \tag{4.10}$$

In other words, mixed second derivatives are independent of the order in which they are taken. This property applied to thermodynamic functions leads to equalities between derivatives known as "Maxwell's relations."

Chain rule

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial w}\right)_z\left(\frac{\partial w}{\partial y}\right)_z \underset{\substack{\text{inversion}\\\text{rule}}}{\equiv} \frac{\left(\partial x/\partial w\right)_z}{\left(\partial y/\partial w\right)_z} \tag{4.11}$$

In Eq. 4.11 we have changed the independent variables from $x(y,z)$ in the left-hand-side to $x(w,z)$ and $y(w,z)$ in the right-hand-side.

Triple-product rule (also known as XYZ-1 rule)

This relationship links three "cyclically permuted" derivatives:

$$\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{4.12}$$

Here, the three functions being differentiated, $x(y,z)$, $y(x,z)$,and $z(x,y)$ express the same underlying relationship in terms of different variables. To prove this equality, let us consider the differential form of the function $x=x(y,z)$:

$$dx=\left(\frac{\partial x}{\partial y}\right)_z dy+\left(\frac{\partial x}{\partial z}\right)_y dz$$

at constant x, this expression becomes:

$$\left(\frac{\partial x}{\partial y}\right)_z dy\big|_x+\left(\frac{\partial x}{\partial z}\right)_y dz\big|_x=0$$

Now let us obtain the derivative $\partial/\partial z\big)_x$ of this relationship:

$$\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x+\left(\frac{\partial x}{\partial z}\right)_y=0 \Rightarrow \left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x=-\left(\frac{\partial x}{\partial z}\right)_y \Rightarrow$$

$$\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y = -1$$

Example 4.2

Demonstrate how the inversion, commutation, chain and triple-product rules apply to the functions:

$x(y,z)=\dfrac{y^2}{z}$; $w=xz$ (variable transformation for the chain rule)

For the function x in the original representation, $x=x(y,z)$:

$$\left(\partial x/\partial y\right)_z=2y/z$$

To test the inversion rule, we obtain the function in the representation $y=y(x,z)$:

$$x=\frac{y^2}{z} \;\Rightarrow\; y^2=xz \;\Rightarrow\; y=\pm\sqrt{xz} \;\Rightarrow\; \left(\frac{\partial y}{\partial x}\right)_z=\pm\frac{\sqrt{z}}{2\sqrt{x}}$$

Now we need to eliminate x:

$$\pm\frac{\sqrt{z}}{2\sqrt{x}}=\pm\frac{\sqrt{z}}{2\sqrt{y^2/z}}=\frac{z}{2y}=\frac{1}{\left(\partial x/\partial y\right)_z} \quad \therefore \quad \left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{(\partial x/\partial y)_z}$$

For the commutation rule (independence on the order of differentiation), we have

$$\left(\frac{\partial^2 x}{\partial y\partial z}\right)=\frac{\partial}{\partial z}\left(\frac{2y}{z}\right)_y=\frac{\partial}{\partial y}\left(-\frac{y^2}{z^2}\right)_z=-\frac{2y}{z^2}$$

For the chain rule, the new variable is defined as $w=xz$. Then:

$$x=\frac{w}{z}\Rightarrow\left(\partial x/\partial w\right)_z=\frac{1}{z}$$

$$w=xz=\frac{y^2}{\cancel{z}}\cancel{z}\Rightarrow y=\pm\sqrt{w}\Rightarrow\left(\partial y/\partial w\right)_z=\pm\frac{1}{2\sqrt{w}}$$

So that

$$\frac{\left(\partial x/\partial w\right)_z}{\left(\partial y/\partial w\right)_z}=\frac{1/z}{\pm 1/2\sqrt{w}}=\frac{2y}{z}=\left(\partial x/\partial y\right)_z$$

For the triple-product rule we obtain:

$$\left.\begin{array}{r}
x=\dfrac{y^2}{z}\Rightarrow\left(\dfrac{\partial x}{\partial y}\right)_z=2y/z\\[2ex]
y=\pm\sqrt{xz}\Rightarrow\left(\dfrac{\partial y}{\partial z}\right)_x=\pm\dfrac{\sqrt{x}}{2\sqrt{z}}=\dfrac{y}{2z}\\[2ex]
z=\dfrac{y^2}{x}\Rightarrow\left(\dfrac{\partial z}{\partial x}\right)_y=-\dfrac{y^2}{x^2}=-\dfrac{z^2}{y^2}
\end{array}\right\}\Rightarrow\left(\dfrac{\partial x}{\partial y}\right)_z\left(\dfrac{\partial y}{\partial z}\right)_x\left(\dfrac{\partial z}{\partial x}\right)_y=-\dfrac{2y}{z}\dfrac{y}{2z}\dfrac{z^2}{y^2}=-1$$

One could have substituted variables other than y and z in the expressions for the three "cyclic" derivatives with identical results.

4.3 Euler's Theorem for Homogeneous Functions

Thermodynamic functions and derivatives have special properties resulting from the fact that they are either extensive (proportional to the size of the system) or intensive (independent of the size of the system). Mathematically, functions that satisfy the relationship

$$f(\lambda x) = \lambda f(x) \quad \text{for any } x$$

are called *homogeneous* of degree one. Functions can be homogeneous of degree one with respect to some, but not all the variables – for example, a function that is homogeneous of degree one with respect to variables $x_1, x_2, \ldots, x_i$ and homogenous of degree zero with respect to variables $y_1, y_2, \ldots, y_j$ has the property:

$$\begin{array}{c} f(\lambda x_1,\ldots\lambda x_i,y_1,\ldots y_j) \;=\; \lambda f(x_1,\ldots x_i,y_1,\ldots y_j) \\ \text{for any } x_1,\ldots x_i,y_1,\ldots y_j \end{array} \tag{4.13}$$

Extensive thermodynamic functions are homogeneous of degree one with respect to their extensive variables, and homogeneous of degree zero with respect to their intensive variables.

Euler's theorem for homogeneous functions provides a link between such functions and their derivatives, as follows:

$$f(x_1,\ldots x_i,y_1,\ldots y_j) \;=\; x_1\left(\frac{\partial f}{\partial x_1}\right)+x_2\left(\frac{\partial f}{\partial x_2}\right)+\ldots+x_i\left(\frac{\partial f}{\partial x_i}\right) \tag{4.14}$$

The proof of this theorem is as follows.

$$\frac{\partial f(\lambda x_1,\ldots\lambda x_i,y_1,\ldots)}{\partial\lambda} = \frac{\partial\left[\lambda f(x_1,\ldots x_i,y_1,\ldots)\right]}{\partial\lambda} = f(x_1,\ldots x_i,y_1,\ldots)$$

$$= \frac{\partial f(\lambda x_1,\ldots\lambda x_i,y_1,\ldots)}{\partial(\lambda x_1)}\frac{\partial(\lambda x_1)}{\partial\lambda} + \ldots + \frac{\partial f(\lambda x_1,\ldots\lambda x_i,y_1,\ldots)}{\partial(\lambda x_i)}\frac{\partial(\lambda x_i)}{\partial\lambda} =$$

$$= \frac{\partial f(x_1,\ldots x_i,y_1,\ldots)}{\partial x_1}x_1 + \ldots + \frac{\partial f(x_1,\ldots x_i,y_1,\ldots)}{\partial x_i}x_i$$

Application of Euler's theorem to $U(S,V,N_1,N_2,\ldots,N_n)$, a homogeneous function of degree one with respect to all its variables, gives:

$$U = S\left(\frac{\partial U}{\partial S}\right)_{V,\{N\}} + V\left(\frac{\partial U}{\partial V}\right)_{S,\{N\}} + \sum_{i=1}^{n} N_i\left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}} \Rightarrow$$

$$\boxed{U = TS - PV + \sum_{i=1}^{n}\mu_i N_i \qquad (4.15)}$$

Euler-integrated FE

This Euler-integrated form of the fundamental equation is sometimes confusing, as it superficially appears to suggest that U is a function of twice as many variables as previously (T *and* S, P *and* V, μ_i *and* N_i). This is incorrect; despite appearances to the contrary, the same variable set as before, $(S,V,N_1,N_2,\ldots,N_n)$, is being used, with temperature, pressure and chemical potentials that appear in the equation also being functions of the same variables: $T(S,V,N_1,N_2,\ldots,N_n)$, $P(S,V,N_1,N_2,\ldots,N_n)$, and $\mu_i(S,V,N_1,N_2,\ldots,N_n)$.

4.4 Legendre Transformations

Even though it is possible in principle to control the variables (S,V,N) experimentally, it is much more common to perform experiments under constant-temperature or constant-pressure conditions, rather than at constant volume or entropy. For example, constant-temperature conditions are closely approximated when a system is immersed in a temperature-controlled bath. Constant-pressure conditions are imposed when a system is open to the atmosphere. Variables such as T and P appear as the first derivatives of the fundamental equation $U(S,V,N)$. Unfortunately, while it is certainly possible to obtain functions such as $U(T,P,N)$, the information content of such functions is not equivalent to that of the fundamental equation $U(S,V,N)$ – this is because of the integration constants that will need to be introduced if one wants to go from $U(T,P,N)$ to $U(S,V,N)$, as illustrated in Example 4.3.

In Chapter 2, we have already introduced an additional thermodynamic function, the enthalpy $H = U + PV$. Here, we will show that this and other similar "derived" thermodynamic functions are more than just convenient combinations of terms. They represent *fundamental equations* that play the same key role in thermodynamics as the energy U, but are expressed in variables other than (S,V,N).

In mathematical terms, for a function $f(x)$ of a single variable x, we would like to obtain a new function $g(\xi)$, with the same information content as the original function, but expressed in a new variable $\xi = df/dx$, the first derivative of the original function. Equivalence of information content implies that the original function can be recovered from the transformed one without any ambiguity in the form of integration constants. It turns out that this can be done through a mathematical operation known as a *Legendre transformation*. For a function of one variable, the transformed function is obtained as $g(\xi) = f - x\xi$, which has the following properties:

$$\begin{aligned} df &= \xi dx \\ dg &= df - xd\xi - \xi dx = -xd\xi \end{aligned} \tag{4.16}$$

In the new function (referred to as the "transform" of the original function), the role of variables and derivatives has been exchanged: the derivative of the original function is the variable of the new function and the variable of the original function is *minus* the derivative of the transform. One can recover the original function by simply applying the Legendre transformation one more time:

$$\begin{aligned} dg &= -xd\xi \\ f &= g + x\xi \end{aligned} \tag{4.17}$$

Example 4.3

Consider the function:

$f(x) = x^2 + 2$

Construct the function $f(w)$ and show that it cannot be used to fully determine $f(x)$. Also obtain the Legendre transform of this function, $g(w)$ and show how it can be used to reconstruct the original function $f(x)$.

The derivative of $f(x)$ is:

$$\xi = \frac{df}{dx} = 2x$$

The function $f(\xi)$ can be obtained by substituting $x = \xi/2$ in $f(x)$:

$$f(\xi)=\frac{\xi^2}{4}+2 \qquad \text{(i)}$$

Given $f(\xi)$, we can attempt to determine $f(x)$ from:

$$\frac{dx}{df}=\frac{1}{\xi} \;\Rightarrow\; x=\int\frac{1}{\xi}df=\int\frac{df}{\pm 2\sqrt{f-2}}=\pm\sqrt{f-2}+c \;\Rightarrow\; f=\left(x-c\right)^2+2 \qquad \text{(ii)}$$

An unknown integration constant c appears in expression (ii), so we have shown that $f(x)$ cannot be fully recovered from $f(\xi)$.

The Legendre transform $g(\xi)$ of $f(x)$ is:

$$g(\xi)=f-x\xi=\frac{\xi^2}{4}+2-\frac{\xi}{2}\xi \;\Rightarrow\; g(\xi)=-\frac{\xi^2}{4}+2 \qquad \text{(iii)}$$

From Eq. 4.17, the variable x can be obtained from (iii) from differentiation:

$$x=-\frac{dg}{d\xi}=\frac{\xi}{2} \qquad \text{(iv)}$$

Now the function $f(x)$ can be obtained from $g(\xi)$ using Eq. 4.17 again:

$$f=g+x\xi=-\frac{\xi^2}{4}+2+\frac{\xi}{2}w=\frac{\xi^2}{4}+2 \;\Rightarrow\; f=x^2+2 \qquad \text{QED}$$

<u>Example 4.4</u>

Consider the function $f(x)=x^3+1$ in the interval [−1,1]. Construct its first Legendre transformation $g(\xi)$ and plot $f(x)$ and $g(\xi)$, marking the points corresponding to x=−0.7, x=0, and x=0.7 on the graph of $g(\xi)$.

Using the definition of Legendre transforms:

$$\frac{df}{dx}=\xi \;\Rightarrow\; \xi=3x^2 \;\Rightarrow\; x=\pm\sqrt{\frac{\xi}{3}}$$

$$g(\xi)=f-x\xi=\pm\left(\frac{\xi}{3}\right)^{3/2}+1\mp\,\xi\sqrt{\frac{\xi}{3}}=\frac{\pm\xi^{3/2}}{3\sqrt{3}}+1\mp\frac{\xi^{3/2}}{\sqrt{3}}\Rightarrow\boxed{g(\xi)=\mp\frac{2\xi^{3/2}}{3\sqrt{3}}+1}$$

The Legendre transform of $g(\xi)$ is:

$$\frac{dg}{d\xi}=\mp\sqrt{\frac{\xi}{3}}=-x$$

$$g-\xi\frac{dg}{d\xi} = \mp\frac{2\xi^{3/2}}{3\sqrt{3}}+1\pm\xi\sqrt{\frac{\xi}{3}} = \frac{\pm\xi^{3/2}}{3\sqrt{3}}+1 = \left(\pm\sqrt{\frac{\xi}{3}}\right)^3+1 = x^3+1 = f(x)$$

Plots of the original and transformed functions are shown in Fig. 4.1. Arrows mark the three points of interest (note that $\xi=3x^2$, so the ξ coordinate corresponding to $x=\pm0.7$ is $\xi=3\cdot0.7^2=1.47$.

The transform is multivalued – two values of the function $g(\xi)$ exist for any given ξ. This is the price we have to pay for ensuring that the reverse transform is unique. In addition, the transformed function has a "cusp" at $\xi=0$, with a discontinuous first derivative. Multivalued functions arise naturally in thermodynamics when a system can exist in multiple phases; cusps are also present in thermodynamic functions for systems with multiple phases.

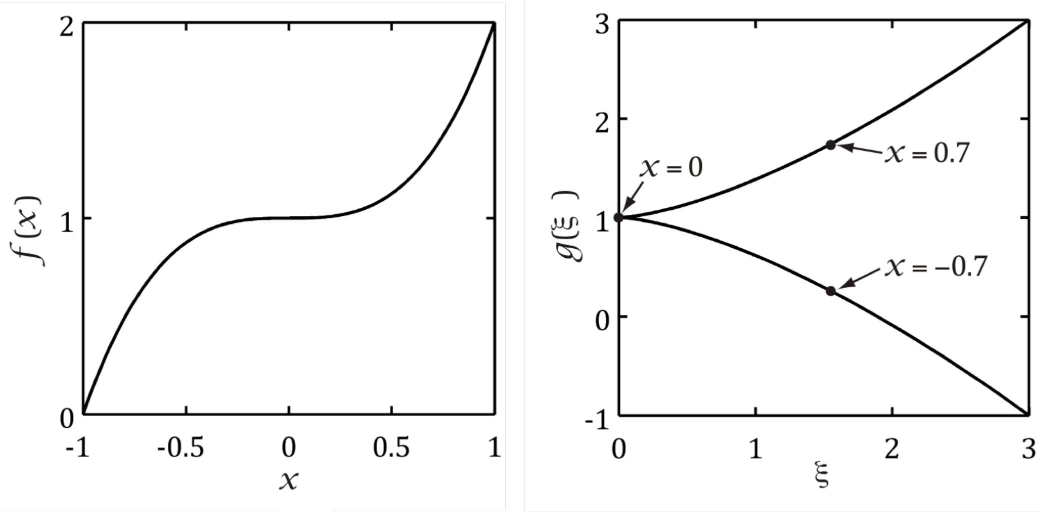

Figure 4.1 A one-dimensional function and its transform.

For functions of many variables, the Legendre transform procedure can be applied sequentially, giving the first, second and higher-order transforms. Formally, we consider a general function of *l* variables, as a *basis function* $y^{(0)}$, where "basis" means simply the starting point of the transform:

$$y^{(0)}(x_1,x_2,\cdots,x_k,x_{k+1},\cdots x_l) \tag{4.18}$$

The first and second derivatives of the basis function are defined as:

$$\xi_i \equiv y_i^{(0)} = \left(\frac{\partial y^{(0)}}{\partial x_i}\right)_{x_{j[i]}} \quad \text{and} \quad y_{ij}^{(0)} = \frac{\partial^2 y^{(0)}}{\partial x_i \partial x_j} = \frac{\partial}{\partial x_i}\left(\left(\frac{\partial y^{(0)}}{\partial x_j}\right)_{x_{i[j]}}\right)_{x_{j[i]}} \tag{4.19}$$

Thus, the differential form of $y^{(0)}$ is:

$$dy^{(0)} = \xi_1 x_1 + \xi_2 x_2 + \cdots + \xi_k x_k + \xi_{k+1} x_{k+1} + \cdots \xi_l x_l \tag{4.20}$$

The k-th transform of $y^{(0)}$ is denoted as $y^{(k)}$ and is obtained from:

$$y^{(k)}(\xi_1,\xi_2,\cdots,\xi_k,x_{k+1},\cdots x_l) = y^{(0)} - x_1\xi_1 - x_2\xi_2 - \cdots - x_k\xi_k \tag{4.21}$$

The k-th transform is a function of a new set of variables, $(\xi_1,\xi_2,\cdots,\xi_k,x_{k+1},\cdots x_l)$. Its differential form is

$$dy^{(k)} = -x_1 d\xi_1 - x_2 d\xi_2 - \cdots - x_k d\xi_k + \xi_{k+1} dx_{k+1} + \cdots + \xi_l dx_l \tag{4.22}$$

A common basis function for thermodynamics is the fundamental equation in the energy representation, $U(S,V,N_1,N_2,\ldots,N_n)$. Additional thermodynamic functions, such as H, are simply transforms of the fundamental equation U that preserve its information content. Note that different Legendre transforms result if the order of variables of the original function is changed, for instance to $U(V,S,N_1,N_2,\ldots,N_n)$.

$$\begin{gathered}\text{Fundamental equation: } y^{(0)} = U(S,V,N_1,N_2,\cdots,N_n) \\ dU = TdS - PdV + \sum_{i=1}^{n}\mu_i dN_i\end{gathered} \tag{4.5}$$

The first Legendre transformation of $U(S,V,N_1,N_2,\cdots,N_n)$ gives a new thermodynamic function, the *Helmholtz free energy A*:

$$\begin{gathered}\text{Fundamental equation: } y^{(1)} = A(T,V,N_1,N_2,\cdots,N_n) \\ A = U - TS \quad ; \quad dA = -SdT - PdV + \sum_{i=1}^{n}\mu_i dN_i\end{gathered} \tag{4.23}$$

The second transform of U, gives another fundamental equation, the *Gibbs free energy G*, named after American scientist Josiah Willard Gibbs (1839-1903):

$$\begin{gathered}\text{Fundamental equation: } y^{(2)} = G(T,P,N_1,N_2,\cdots,N_n) \\ G = U - TS + PV = A + PV \quad ; \quad dG = -SdT + VdP + \sum_{i=1}^{n}\mu_i dN_i\end{gathered} \tag{4.24}$$

Table 4.1 Fundamental equations (thermodynamic potential functions) for one-component systems.

Function	Internal energy U	Helmholtz energy A	Enthalpy H	Gibbs free energy G
Variables	$S \quad V \quad N$	$T \quad V \quad N$	$S \quad P \quad N$	$T \quad P \quad N$
Differential	$dU = TdS - PdV + \mu dN$	$dA = -SdT - PdV + \mu dN$	$dH = TdS + VdP + \mu dN$	$dG = -SdT + VdP + \mu dN$
Integral	$U = TS - PV + \mu N$	$A = -PV + \mu N$	$H = TS + \mu N$	$G = \mu N$
First derivatives	$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \quad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$ $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$	$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} \quad P = -\left(\frac{\partial A}{\partial V}\right)_{T,N}$ $\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}$	$T = \left(\frac{\partial H}{\partial S}\right)_{P,N} \quad V = \left(\frac{\partial H}{\partial P}\right)_{S,N}$ $\mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}$	$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$ $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = \underline{G}$
A second derivative	$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N} = \left(\frac{\partial T}{\partial S}\right)_{V,N} = \frac{T}{NC_V}$	$-\left(\frac{\partial^2 A}{\partial T^2}\right)_{V,N} = \left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{NC_V}{T}$	$\left(\frac{\partial^2 H}{\partial S^2}\right)_{P,N} = \left(\frac{\partial T}{\partial S}\right)_{P,N} = \frac{T}{NC_P}$	$-\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N} = \left(\frac{\partial S}{\partial T}\right)_{P,N} = \frac{NC_P}{T}$
Maxwell's rule	$-\left(\frac{\partial P}{\partial S}\right)_{V,N} = \left(\frac{\partial T}{\partial V}\right)_{S,N}$	$-\left(\frac{\partial P}{\partial T}\right)_{V,N} = -\left(\frac{\partial S}{\partial V}\right)_{T,N}$	$\left(\frac{\partial V}{\partial S}\right)_{P,N} = \left(\frac{\partial T}{\partial P}\right)_{S,N}$	$-\left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{P,N}$

Reordering the variables to $U(S,V,N_1,N_2,\cdots,N_n)$ gives the enthalpy H, first introduced in deriving First Law balances for open systems as the first Legendre transform $y^{(1)}$:

$$\text{Fundamental equation: } y^{(1)} = H(S,P,N_1,N_2,\cdots,N_n)$$
$$H = U + PV \quad ; \quad dH = TdS + VdP + \sum_{i=1}^{n} \mu_i dN_i \tag{4.25}$$

The Legendre transforms of U are also known as *thermodynamic potentials.* Table 4.1 (p. 14) summarizes the information on variables and derivatives for the four thermodynamic potentials we have discussed thus far, for the case of a one-component system for simplicity. The table also lists a second derivative for each transform and an example Maxwell's relationship between second derivatives.

The Euler-integrated form of each of the fundamental equations expresses them as sum of terms, each term being an extensive variable of the transform multiplied by the corresponding derivative. The results are summarized in Table 4.1 and are consistent with the Legendre transformations above. For example, for the Gibbs free energy G,

$$G = \mu N = U - TS + PV = H - TS = A + PV \tag{4.26}$$

An important consequence of the integral relationship for G in the special case of a one-component system is that the molar Gibbs free energy is, in this case, equal to the chemical potential:

$$\text{for one-component systems only: } \underline{G} = \mu \tag{4.27}$$

Additional transformations, not listed in the table, are possible as well. For example, one could order the variables as $U(N_1,N_2,\cdots,N_n,S,V)$ and perform a single transform to obtain a function of $(\mu_1,N_2,\cdots,N_n,S,V)$. The resulting function is also a valid fundamental equation, even if it is not frequently used in practice.

The final comment here is that the last transform, $y^{(n+2)}$, yields a function of only intensive variables, T, P and all the chemical potentials. By Euler integration we obtain that the resulting "function" is identically zero, a result known as the *Gibbs-Duhem relationship*:

Gibbs-Duhem relationship

$$\boxed{-SdT + VdP - \sum_{i=1}^{n} N_i d\mu_i = 0 \qquad (4.28)}$$

4.5 Derivative Relationships

As already stated, two key objectives of classical thermodynamics are to obtain relationships between properties, and to develop techniques to measure them. Obtaining thermodynamic relationships helps bring forward “hidden” connections between seemingly unrelated quantities and facilitates the measurement and validation of physical property data.

The Legendre transformation facilitates developing relationships between thermodynamic derivatives. For example, the following relationships exist between second derivatives of a transform and its basis function:

$$y_{11}^{(1)} = -\frac{1}{y_{11}^{(0)}} \tag{4.29}$$

$$y_{1i}^{(1)} = \frac{y_{1i}^{(0)}}{y_{11}^{(0)}} \quad i \neq 1 \tag{4.30}$$

$$y_{ij}^{(1)} = y_{ij}^{(0)} - \frac{y_{1i}^{(0)} y_{1j}^{(0)}}{y_{11}^{(0)}} \quad i,j \neq 1 \tag{4.31}$$

For proofs of these relationships, as well as more complex general relationships between derivatives of the k-th transform and those of the basis function, see Beegle, Modell and Reid, *AIChE J.*, **20**: 1194-200 (1974) and Kumar and Reid, *AIChE J.*, **32**: 1224-6 (1986).

For pure components, a major simplification of thermodynamic relationships is possible relative to the general multicomponent case, because composition is not an independent variable. Extensive properties can then be normalized by the amount of mass (moles) in a system to obtain intensive properties. Thermodynamic derivatives at constant number of moles can be taken either on a total or on a molar basis, for example:

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = \left(\frac{\partial (N\underline{U})}{\partial (N\underline{S})}\right)_{N\underline{V},N} = \left(\frac{\partial \underline{U}}{\partial \underline{S}}\right)_{\underline{V}} = T \tag{4.32}$$

N was eliminated in the last derivative of this expression because intensive properties do not depend on the size of the system, so that N is no longer a relevant constraint. The differential forms of the fundamental equations in one-component systems for the intensive thermodynamic functions $\underline{U}$, $\underline{A}$, $\underline{G}$, and $\underline{H}$, are as follows:

$$\boxed{\begin{aligned} d\underline{U} &= Td\underline{S} - Pd\underline{V} \\ d\underline{A} &= -\underline{S}dT - Pd\underline{V} \\ d\underline{H} &= Td\underline{S} + \underline{V}dP \\ d\underline{G} &= -\underline{S}dT + \underline{V}dP \end{aligned} \qquad (4.33)}$$

intensive FEs for one-component systems

First derivatives of these functions with respect to their natural variables are obtained directly, either from Table 4.1 or from Eqs. 4.33. An example of such a first derivative is given above in Eq. 4.32 – temperature is clearly an experimentally measurable quantity. Other examples include:

$$\left(\frac{\partial U}{\partial V}\right)_{S,N} = \left(\frac{\partial \underline{U}}{\partial \underline{V}}\right)_{\underline{S}} = -P \quad \text{and} \quad \left(\frac{\partial \underline{H}}{\partial P}\right)_{\underline{S}} = \left(\frac{\partial \underline{G}}{\partial P}\right)_{T} = \underline{V} \qquad (4.34)$$

Some first derivatives of Fundamental Equations with respect to natural variables cannot be measured directly:

$$\left(\frac{\partial \underline{A}}{\partial T}\right)_{\underline{V}} = \left(\frac{\partial \underline{G}}{\partial T}\right)_{P} = -\underline{S} \quad \text{and} \quad \left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu \qquad (4.35)$$

First derivatives of Fundamental Equations with respect to "unnatural" variables or under other constraints can be obtained from the differential expressions of Eq. 4.33. For example, to obtain the volume derivative of the energy at constant temperature in terms of measurable properties, we start from:

$$d\underline{U} = Td\underline{S} - Pd\underline{V}$$

We now take the partial derivative $(\partial/\partial\underline{V})_T$, followed by Maxwell's rule on $\underline{A}$ to obtain:

$$\left(\frac{\partial \underline{U}}{\partial \underline{V}}\right)_{T} = T\left(\frac{\partial \underline{S}}{\partial \underline{V}}\right)_{T} - P = T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P \qquad (4.36)$$

Second derivatives of fundamental equations with respect to their natural variables are important from a theoretical and experimental viewpoint. For example, differentiating A and G twice with respect to temperature, we obtain two important experimentally measurable quantities, the heat capacities defined in Chapter 3:

$$\left(\frac{\partial^2 \underline{A}}{\partial T^2}\right)_{\underline{V}} = -\left(\frac{\partial \underline{S}}{\partial T}\right)_{\underline{V}} = -\frac{1}{T}\left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} = -\frac{C_V}{T} \qquad (4.37)$$

$$\left(\frac{\partial^2 \underline{G}}{\partial T^2}\right)_P = -\left(\frac{\partial \underline{S}}{\partial T}\right)_P = -\frac{1}{T}\left(\frac{\partial \underline{H}}{\partial T}\right)_P = -\frac{C_P}{T} \tag{4.38}$$

The other two second derivatives of $\underline{G}$ with respect to its natural variables are also important experimentally measurable quantities. The cross derivative with respect to temperature and pressure is:

$$\frac{\partial^2 \underline{G}}{\partial T \partial P} = \frac{\partial}{\partial T}\left(\left(\frac{\partial \underline{G}}{\partial P}\right)_T\right)_P = \left(\frac{\partial \underline{V}}{\partial T}\right)_P = \alpha_P \underline{V} \tag{4.39}$$

This derivative is proportional to the *coefficient of thermal expansion*, defined as:

$$\alpha_P \equiv (\partial \underline{V} / \partial T)_P / \underline{V} \tag{4.40}$$

The second derivative with respect to pressure is:

$$\left(\frac{\partial^2 \underline{G}}{\partial P^2}\right)_T = \left(\frac{\partial \underline{V}}{\partial P}\right)_T = -\kappa_T \underline{V} \tag{4.41}$$

This derivative is proportional to the *isothermal compressibility*, which is defined as:

$$\kappa_T \equiv -(\partial \underline{V} / \partial P)_T / \underline{V} \tag{4.42}$$

Mixed second derivatives of fundamental equations with respect to their natural variables can be written in two equivalent ways, using the commutation property (Maxwell's relationships):

$$\frac{\partial^2 \underline{U}}{\partial \underline{S} \partial \underline{V}} = -\left(\frac{\partial P}{\partial \underline{S}}\right)_{\underline{V}} = \left(\frac{\partial T}{\partial \underline{V}}\right)_{\underline{S}} \tag{4.43}$$

$$\frac{\partial^2 \underline{A}}{\partial T \partial \underline{V}} = -\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = -\left(\frac{\partial \underline{S}}{\partial \underline{V}}\right)_T \tag{4.44}$$

$$\frac{\partial^2 \underline{H}}{\partial \underline{S} \partial P} = \left(\frac{\partial T}{\partial P}\right)_{\underline{S}} = \left(\frac{\partial \underline{V}}{\partial \underline{S}}\right)_P \tag{4.45}$$

$$\frac{\partial^2 \underline{G}}{\partial T \partial P} = -\left(\frac{\partial \underline{S}}{\partial P}\right)_T = \left(\frac{\partial \underline{V}}{\partial T}\right)_P \tag{4.46}$$

It is clear from the last three expressions that derivatives of the entropy S with respect to volume or pressure are experimentally measurable, even though the absolute value of entropy itself is not directly obtainable in classical thermodynamics.

Other derivatives can be obtained using the tools described in § 4.2. For example, the Joule-Thompson coefficient, $(\partial T/\partial P)_{\underline{H}}$ is the rate of temperature change with pressure when a fluid flows across a throttling valve, as can be confirmed from a differential First Law balance in an open system at steady state with $\text{đ}Q = \text{đ}W = 0$ (see Eq. 2.18, p. 18). This coefficient can be expressed in terms of equation-of-state derivatives and heat capacities by first invoking the triple-product rule:

$$\left(\frac{\partial T}{\partial P}\right)_{\underline{H}}\left(\frac{\partial \underline{H}}{\partial T}\right)_{P}\left(\frac{\partial P}{\partial \underline{H}}\right)_{T} = -1 \;\Rightarrow\; \left(\frac{\partial T}{\partial P}\right)_{\underline{H}} = -\frac{(\partial \underline{H}/\partial P)_T}{(\partial \underline{H}/\partial T)_P}$$

The denominator is simply C_P; the numerator can be obtained from the differential form of $\underline{H}$,

$$d\underline{H} = Td\underline{S} + \underline{V}dP \quad\Rightarrow\quad \left(\frac{\partial \underline{H}}{\partial P}\right)_T = T\left(\frac{\partial \underline{S}}{\partial P}\right)_T + \underline{V} = -T\left(\frac{\partial \underline{V}}{\partial T}\right)_P + \underline{V}$$

The final result is:

$$\left(\frac{\partial T}{\partial P}\right)_{\underline{H}} = \frac{1}{C_P}\left(T\left(\frac{\partial \underline{V}}{\partial T}\right)_P - \underline{V}\right) \tag{4.47}$$

Example 4.5 Differential expressions for U

Obtain differential expressions for $\underline{U} = \underline{U}(T, \underline{V})$ and $\underline{U} = \underline{U}(T, P)$ in terms of experimentally measurable properties. Note that these expressions are *not* fundamental equations because the natural variables of $\underline{U}$ are $\underline{S}$ and $\underline{V}$.

We seek to construct expressions of the form:

$$d\underline{U} = \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} dT + \left(\frac{\partial \underline{U}}{\partial \underline{V}}\right)_T d\underline{V} \tag{i}$$

$$d\underline{U} = \left(\frac{\partial \underline{U}}{\partial T}\right)_{P} dT + \left(\frac{\partial \underline{U}}{\partial P}\right)_T dP \tag{ii}$$

The temperature derivative $(\partial \underline{U}/\partial T)_{\underline{V}} = C_V$, and the volume derivative $(\partial \underline{U}/\partial \underline{V})_T$, have been obtained in Eq. 4.36, so the desired expression for $\underline{U} = \underline{U}(T, \underline{V})$ is:

$$\boxed{d\underline{U} = C_V dT + \left(T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right) d\underline{V}} \tag{iii}$$

For the derivatives needed for expression (ii), we start again from the fundamental equation for $\underline{U}$ in terms of its natural variables, $d\underline{U}=Td\underline{S}-Pd\underline{V}$. Differentiating with respect to T at constant P gives:

$$\left(\frac{\partial \underline{U}}{\partial T}\right)_P = T\left(\frac{\partial \underline{S}}{\partial T}\right)_P - P\left(\frac{\partial \underline{V}}{\partial T}\right)_P \qquad \text{(iv)}$$

The temperature dependence of the entropy at constant pressure, $(\partial \underline{S}/\partial T)_P$, can be obtained by differentiating $d\underline{H}=Td\underline{S}+\underline{V}dP$:

$$\left(\frac{\partial \underline{H}}{\partial T}\right)_P = C_P = T\left(\frac{\partial \underline{S}}{\partial T}\right)_P$$

After substituting the result into (iv), we get:

$$\left(\frac{\partial \underline{U}}{\partial T}\right)_P = C_P - P\left(\frac{\partial \underline{V}}{\partial T}\right)_P \qquad \text{(v)}$$

The pressure derivative needed for (ii) is:

$$\left(\frac{\partial \underline{U}}{\partial P}\right)_T = T\left(\frac{\partial \underline{S}}{\partial P}\right)_T - P\left(\frac{\partial \underline{V}}{\partial P}\right)_T = -T\left(\frac{\partial \underline{V}}{\partial T}\right)_P - P\left(\frac{\partial \underline{V}}{\partial P}\right)_T \qquad \text{(vi)}$$

We used Maxwell's relationship on $\underline{G}$ to get rid of $\underline{S}$. Substituting (v) and (vi) into (ii) we finally obtain:

$$\boxed{d\underline{U} = \left(C_P - P\left(\frac{\partial \underline{V}}{\partial T}\right)_P\right)dT - \left(T\left(\frac{\partial \underline{V}}{\partial T}\right)_P + P\left(\frac{\partial \underline{V}}{\partial P}\right)_T\right)dP} \qquad \text{(vii)}$$

One observation we can make here is that the functional forms of $\underline{U}$ in "unnatural" variables are more complex than the comparable expressions in its "natural" variables. This is an additional disadvantage – beyond the loss of information content – discouraging the use of functional forms such as $\underline{U}=\underline{U}(T,\underline{V})$ and $\underline{U}=\underline{U}(T,P)$.

Example 4.6 Difference between heat capacities

Calculate the difference between the heat capacities at constant pressure and constant volume, C_P-C_V, for a general thermodynamic system, in terms of P, $\underline{V}$, T and their mutual derivatives.

We use as starting point expression (iii) in Example 4.5:

$$d\underline{U} = C_V dT + \left(T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right)d\underline{V}$$

Differentiating with respect to T at constant P and setting the result equal to expression (v) of Example 4.5, we obtain:

$$\left(\frac{\partial \underline{U}}{\partial T}\right)_P \underset{\text{from (iii)}}{\underbrace{=}} C_V + \left(T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right)\left(\frac{\partial \underline{V}}{\partial T}\right)_P \underset{\text{from (v)}}{\underbrace{=}} C_P - P\left(\frac{\partial \underline{V}}{\partial T}\right)_P \Rightarrow$$

$$\boxed{C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}\left(\frac{\partial \underline{V}}{\partial T}\right)_P}$$

For ideal gases, one can simplify this relationship considerably:

$$(\partial P/\partial T)_{\underline{V}} = R/\underline{V} \quad \text{and} \quad (\partial \underline{V}/\partial T)_P = R/P \quad \Rightarrow \quad C_P - C_V = TR^2/(P\underline{V}) = R$$

Thus, the difference in heat capacities at constant pressure and constant volume for ideal gases is simply the ideal-gas constant R, as already derived in § 2.4.