CLASSICAL THERMODYNAMICS — GENERALIZATIONS FOR ANY FLUID

Measurable Quantities:

T, P, V

Thermodynamic Balances:

S, H, U, G (Gibbs Free Energy), A (Helmholz Free Energy)

Example:

$\Delta H = C_p\, \Delta T$

$C_p = (\delta H / \delta T)_p$

Relate measurable quantities to thermodynamic quantities for balances through differential calculus (materials constants like C_p, C_v, μ_{JT}, α_p, κ_T and P, V, T).

The Fundamental Property Relation for *dU* in Simple Systems

Simple System:
-No Gradients
-Reversible
-No fields or walls

$$d(U + E_K + E_P) = dQ + dW_S + dW_{EC} \qquad 6.1$$

$$dU = dQ - PdV \qquad 6.2$$

Emphasizing the neglect of gradients, the reversible differential change between states is

$$dU_{rev} = dQ_{rev} - (PdV)_{rev} \qquad 6.3$$

$$dS = \frac{dQ_{rev}}{T_{sys}} \qquad \Rightarrow T_{sys}dS = dQ_{rev} \quad (T_{sys}\text{-system temperature where } Q \text{ transferred})$$

U(S,V)
H(S,P)

$$\boxed{dU = TdS - PdV} \qquad 6.4 \quad \textbf{❶} \; dU \text{ for a closed simple system.}$$

We have defined enthalpy, $H = U + PV$. Therefore, $dH = dU + PdV + VdP = TdS - PdV + PdV + VdP$,

$$\boxed{dH = TdS + VdP} \quad \text{which shows that } H \text{ is a natural function of } S \text{ and } P \qquad 6.5$$

❶ *dH* for a reversible, closed simple system. Enthalpy is convenient when heat and pressure are manipulated.

Gibbs and Helmholtz Free Energies

$$dU = TdS - PdV$$

define **Helmholtz energy** $A = U - TS$. Therefore, $dA = dU - TdS - SdT = TdS - PdV - TdS - SdT$,

$$dA = -SdT - PdV$$ which shows A is a natural function of T and V 6.6

other frequently used convenience property is **Gibbs energy** $G = U - TS + PV = A + PV = H - TS$. Therefore, $dG = dH - TdS - SdT = TdS + VdP - TdS - SdT$.

$$dG = -SdT + VdP$$ which shows G is a natural function of T and P 6.7

The Gibbs energy is used specifically in phase equilibria problems where temperature and pressure are controlled. We find that for systems constrained by constant T and P, the equilibrium occurs when the derivative of the Gibbs energy is zero ($\Rightarrow$ driving forces sum to zero and Gibbs energy is minimized). Note that $dG = 0$ when T and P are constant ($dT = 0$, $dP = 0$). The Helmholtz and

Often, students' first intuition is to expect that energy is minimized at equilibrium. But some deeper thought shows that equilibrium based purely on energy would eventually reach a state where all atoms are at the minimum of their potential wells with respect to one another. All the world would be a solid block. On the other hand, if entropy was always maximized, molecules would spread apart and everything would be a gas. Interesting phenomena are only possible over a narrow range of conditions (e.g., 298 K) where the spreading generated by entropic driving forces balances the compaction generated by energetic driving forces. A greater appreciation for how this balance occurs should be developed over the next several chapters.

$U(S,V)$
$H(S,P)$
$A(T,V)$
$G(T,p)$

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

$U=H-PV=A+TS$
$A=G-PV=U-ST$
$H=U+PV=G+TS$
$G=H-TS=A+PV$

$-(\partial P/\partial S)_V = (\partial T/\partial V)_S$

$(\partial V/\partial S)_P = (\partial T/\partial P)_S$

$(\partial P/\partial T)_V = (\partial S/\partial V)_T$

$-(\partial V/\partial T)_P = (\partial S/\partial P)_T$

$-S$	**U**	V
H	Thermodynamic Square	**A**
$-p$	**G**	T

Table 6.1 *Fundamental and Auxiliary Property Relations*

	Natural Variables	Legendre Transformation	Transformed Variable Sets
$dU = T\,dS - P\,dV$	$U(S,V)$		---------
$dH = T\,dS + V\,dP$	$H(S,P)$	$H = U + PV$	$\{V,P\}$
$dA = -S\,dT - P\,dV$	$A(T,V)$	$A = U - TS$	$\{S,T\}$
$dG = -S\,dT + V\,dP$	$G(T,P)$	$G = U - TS + PV$	$\{S,T\},\ \{V,P\}$

We have energy $dU = TdS-PdV$, which is not useful since we can't hold S constant very easily so it would be more useful to have a different energy expression that depends on V and T rather than V and S. To obtain this we find the desired varible, $T = (dU/dS)v$. T is the ***conjugate variable*** of S in the dU equation. The Legendre transform of the dU equation is $dA = -SdT-PdV$. This is arrived at from $A = U - TS$ and $dA = dU - TdS - SdT$.

Start with is $dA = -SdT-PdV$, that depends on V and T. Use P as the conjugate variable to V. Define $G = A + PV$, and $dG = dA + VdP + PdV = -SdT+VdP$ and $G = PV - ST$.

Legendre Transformations

How does a Legendre transform work?

The key idea is to use the product rule. If (x, y) is a conjugate pair of variables, then $d(xy) = x\,dy + y\,dx$ relates the variation dy in quantity y to the variation dx in quantity x.

eg. 1) $\dot{x}p$ has the same units as L and H

eg. 2) PV and TS have the same units as $U, H, F,$ and G

https://www.aapt.org/docdirectory/meetingpresentations/SM14/Mungan-Poster.pdf   Accessed 3/2/15

Mathematical details

Consider a function of two independent variables, call it $f(x, y)$. Its differential is

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \,. \tag{1}$$

Defining $u \equiv (\partial f/\partial x)_y$ and $w \equiv (\partial f/\partial y)_x$, Eq. (1) can be rewritten as

$$df = u\,dx + w\,dy \,. \tag{2}$$

We call u and x a *conjugate* pair of variables, and likewise w and y. We can recognize our original variables x and y of the function f because the right-hand side of Eq. (2) is written in terms of differentials of those two variables.

Proceeding, use the product rule (or equivalently, integration by parts) to compute the differential

$$d(wy) = y\,dw + w\,dy \tag{3}$$

and subtract this equation from Eq. (2) to get

$$dg = u\,dx - y\,dw \tag{4}$$

where I have introduced the *Legendre-transformed* function $\boxed{g \equiv f - wy}$. Since we are taking differentials of x and w, we can take those two quantities as the independent variables of the new function, $g(x, w)$.

To summarize, we have done a Legendre transformation from an original function $f(x, y)$ to a new function $g(x, w)$ by switching from variable y to its conjugate variable w. Of course, one could instead switch x to u to obtain $h(u, y)$ or one could switch both independent variables to get $k(u, w)$. We see therefore that for two variables, there are 4 possible variants on the function. To make contact with thermodynamics, we might call these various functions the *potentials*. If instead we have 3 independent variables, there are 8 different potentials, or in general there are 2^n potentials for a function of n independent variables, since each variable can be represented by either member of a conjugate pair.

Example 2: Legendre transform from internal energy U to enthalpy H

Suppose we have a system (such as a fixed quantity of gas) for which we have chosen the independent variables to be the entropy S and volume V. Then according to the thermodynamic identity,

$$dU = T\,dS - P\,dV \tag{8}$$

where the temperature T and pressure P are therefore the variables conjugate to the entropy and volume, respectively. We wish to transform from $U(S,V)$ to a new thermodynamic potential $H(S,P)$. We again construct a table of equivalences:

$$f \equiv U \quad \text{(the original function)}$$

$$x \equiv S \quad \text{(the variable we are not switching)}$$

$$u \equiv \left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{(the conjugate of the unswitched variable)}$$

$$y \equiv V \quad \text{(the variable to be switched)}$$

$$w \equiv \left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial U}{\partial V}\right)_S = -P \quad \text{(the conjugate of the switched variable)}$$

where the partial derivatives of U were calculated from Eq. (8). The transformed function is

$$g \equiv f - wy = (U) - (-P)(V) = U + PV \equiv H(S,P). \tag{9}$$

In accord with Eq. (4), its differential is

$$dH = T\,dS + V\,dP. \tag{10}$$

Formulas for the Gibbs free energy $G(T,P)$ and the Helmholtz free energy $F(T,V)$ can be similarly obtained.

Recall that the Gibbs phase rule specifies for a pure single-phase fluid that any state variable is a function of any two other state variables. For convenience, we could write internal energy in terms of $\{P,T\}$, $\{V,T\}$ or any other combination. In fact, we have already seen that the internal energy is a natural function of $\{S,V\}$:

$$dU = T\,dS - P\,dV$$

In real processes, this form is not the easiest to apply since $\{V,T\}$ and $\{P,T\}$ are more often manipulated than $\{S,V\}$. Therefore, what we seek is something of the form:

$$dU = f(P,\ V,\ T,\ C_P,\ C_V)\,dV + g(P,\ V,\ T,\ C_P, C_V)\,dT \qquad\qquad 6.8$$

subset we frequently choose to use as the controlled variables. Therefore, if we know the changes of any two of these variables, we will be able to determine changes in any of the others, including U, H, A, and G. Let's say we want to know how U changes with any two properties which we will denote symbolically as x and y. We express this mathematically as:

$$dU = (\partial U/\partial x)_y\,dx + (\partial U/\partial y)_x\,dy \qquad\qquad 6.9$$

where x and y are any two other variables from our set of properties. We also could write

$$dT = (\partial T/\partial x)_y\,dx + (\partial T/\partial y)_x\,dy \qquad\qquad 6.10$$

where x and y are any properties except T. The structure of the mathematics provides a method to

! Isothermal compressibility.

$$\kappa_T \equiv \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T \qquad 6.42$$

! Isobaric coefficient of thermal expansion.

$$\alpha_P \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{-1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \qquad 6.43$$

A similar commonly used property is the **Joule-Thomson coefficient** defined by

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_H \qquad 6.44$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$$

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

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\dfrac{\partial y}{\partial x}\right)_z}$$

6.11

$$\left(\frac{\partial x}{\partial y}\right)_x = 0 \quad \text{and} \quad \left(\frac{\partial x}{\partial y}\right)_y = \infty$$

6.12

$$\left(\frac{\partial x}{\partial x}\right)_y = 1$$

6.13

$$\left(\frac{\partial x}{\partial y}\right)_F = \left(\frac{\partial x}{\partial z}\right)_F \left(\frac{\partial z}{\partial y}\right)_F$$

6.16 ❗ Chain rule inter-
posing a variable.

$$\left(\frac{\partial F}{\partial w}\right)_z = \left(\frac{\partial F}{\partial x}\right)_y \left(\frac{\partial x}{\partial w}\right)_z + \left(\frac{\partial F}{\partial y}\right)_x \left(\frac{\partial y}{\partial w}\right)_z$$

6.17 ❗ The expansion
rule.

Triple Product Rule

Suppose $F = F(x,y)$, then

$$dF = (\partial F/\partial x)_y \, dx + (\partial F/\partial y)_x \, dy \qquad\qquad 6.14$$

Consider what happens when $dF = 0$ (i.e., at constant F). Then,

$$0 = \left(\frac{\partial F}{\partial x}\right)_y\left(\frac{\partial x}{\partial y}\right)_F + \left(\frac{\partial F}{\partial y}\right)_x \Rightarrow \left(\frac{\partial x}{\partial y}\right)_F = \frac{-\left(\dfrac{\partial F}{\partial y}\right)_x}{\left(\dfrac{\partial F}{\partial x}\right)_y} = \frac{-\left(\dfrac{\partial x}{\partial F}\right)_y}{\left(\dfrac{\partial y}{\partial F}\right)_x} \text{ or}$$

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_F\left(\frac{\partial y}{\partial F}\right)_x\left(\frac{\partial F}{\partial x}\right)_y = -1} \qquad\qquad 6.15 \quad \text{❗ Triple product rule.}$$

$$U = U(S,V) \Rightarrow dU = (\partial U/\partial S)_V \, dS + (\partial U/\partial V)_S \, dV \qquad 6.18$$

Developing the ability to express any state variable in terms of any other two variables from the set $\{P, T, V, S\}$ as we have just done is very important. But the equation looks a little formidable. However, the fundamental property relationship says:

$$dU = TdS - PdV \qquad 6.19$$

Comparison of the above equations shows that:

$$T = (\partial U/\partial S)_V \quad \text{and} \quad -P = (\partial U/\partial V)_S \qquad 6.20$$

This means that the derivatives in Eqn. 6.18 are really properties that are familiar to us. Likewise, we can learn something about formidable-looking derivatives from enthalpy:

$$H = H(S,P) \Rightarrow dH = (\partial H/\partial S)_P dS + (\partial H/\partial P)_S \, dP \qquad 6.21$$

But the result of the fundamental property relationship is:

$$dH = TdS + VdP$$

Comparison shows that:

$$T = (\partial H/\partial S)_P \quad \text{and} \quad V = (\partial H/\partial P)_S$$

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy$$

For an exact differential, differentiating with respect to x we can define some function M:

$$M \equiv (\partial F/\partial x)_y = M(x,y) \tag{6.22}$$

Similarly differentiating with respect to y:

$$N \equiv (\partial F/\partial y)_x = N(x,y) \tag{6.23}$$

Taking the second derivative and recalling from multivariable calculus that the order of differentiation should not matter,

$$\frac{\partial^2 F(x,y)}{\partial x \partial y} = \frac{\partial}{\partial x}\left(\left(\frac{\partial F(x,y)}{\partial y}\right)_x\right)_y = \frac{\partial}{\partial y}\left(\left(\frac{\partial F(x,y)}{\partial x}\right)_y\right)_x = \frac{\partial^2 F(x,y)}{\partial y \partial x} \tag{6.24}$$

$$\left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial M}{\partial y}\right)_x \tag{6.25}$$

❗ Euler's reciprocity relation.

This simple observation is sometimes called Euler's reciprocity relation.[3] To apply the reciprocity relation, recall the total differential of enthalpy considering $H = H(S,P)$:

$$dH = (\partial H/\partial S)_P dS + (\partial H/\partial P)_S\, dP = TdS + VdP \tag{6.26}$$

Considering second derivatives:

$$\frac{\partial^2 H}{\partial S \partial P} = \frac{\partial^2 H}{\partial P \partial S} = \left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)_S\right]_P = \left[\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_P\right]_S \tag{6.27}$$

$$\Rightarrow \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S \tag{6.28}$$

Maxwell's Relations

$$dU = TdS - PdV \;\;\Rightarrow\;\; -(\partial P/\partial S)_V = (\partial T/\partial V)_S \qquad\qquad 6.29$$

$$dH = TdS + VdP \;\;\Rightarrow\;\; (\partial V/\partial S)_P = (\partial T/\partial P)_S \qquad\qquad 6.30$$

$$dA = -SdT - PdV \;\Rightarrow\; (\partial P/\partial T)_V = (\partial S/\partial V)_T \qquad\qquad 6.31$$

$$dG = -SdT + VdP \;\Rightarrow\; -(\partial V/\partial T)_P = (\partial S/\partial P)_T \qquad\qquad 6.32$$

$-(\partial P/\partial S)_V = (\partial T/\partial V)_S$

$(\partial V/\partial S)_P = (\partial T/\partial P)_S$

$(\partial P/\partial T)_V = (\partial S/\partial V)_T$

$-(\partial V/\partial T)_P = (\partial S/\partial P)_T$

$-S$

U

V

H

Thermodynamic Square

A

$-p$

G

T

Example 6.1 Pressure dependence of H

Derive the relation for $\left(\frac{\partial H}{\partial P}\right)_T$ and evaluate the derivative for: a) water at 20°C where

$\left(\frac{\partial V}{\partial T}\right)_P = 2.07\times10^{-4}$ cm³/g-K and $\left(\frac{\partial V}{\partial P}\right)_T = -4.9\times10^{-5}$ cm³/g-bar, $\rho = 0.998$ g/cm³; b) an ideal gas.

Solution: First, consider the general relation $dH = TdS + VdP$. Applying the expansion rule,

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

by a Maxwell relation, the entropy derivative may be replaced

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V \qquad\qquad 6.33$$

which is valid for any fluid.

(a) Plugging in values for liquid water,

$$\left(\frac{\partial H}{\partial P}\right)_T = -293.15(2.07 \times 10^{-4}\text{cm}^3/\text{g-K}) + 1.002$$

$$= -0.061 + 1.002$$

Therefore, within 6% at room temperature, $\left(\frac{\partial H}{\partial P}\right)_T \approx V$ for liquid water as used in Eqn. 2.42 on page 59 and Example 2.6 on page 60.

(b) For an ideal gas, we need to evaluate $(\partial V/\partial T)_P$. Applying the relation to $V = RT/P$, $(\partial V/\partial T)_P = R/P$. Inserting into Eqn. 6.33, enthalpy is independent of pressure for an ideal gas.

$$\left(\frac{\partial H}{\partial P}\right)_T = -\frac{TR}{P} + V = -V + V = 0 \qquad\qquad \text{(ig) 6.34}$$

A non-ideal gas will have a different partial derivative, and the enthalpy will depend on pressure as we will show in Chapter 8.

Example 6.2 Entropy change with respect to T at constant P

Evaluate $(\partial S/\partial T)_P$ in terms of C_P, C_V, T, P, V, and their derivatives.

Solution: C_P is the temperature derivative of H at constant P. Let us start with the fundamental relation for enthalpy and then apply the expansion rule. Recall, $dH = TdS + VdP$. Applying the expansion rule, Eqn. 6.17, we find,

$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P + V\left(\frac{\partial P}{\partial T}\right)_P \qquad 6.35$$

Applying the basic identity of Eqn. 6.12 to the second term on the right-hand side, since P appears in the derivative and as a constraint the term is zero,

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

But the definition of the left-hand side is given by Eqn. 2.36: $C_P \equiv (\partial H/\partial T)_P$. Therefore, $(\partial S/\partial T)_P = C_P/T$, which we have seen before as Eqn. 4.31, and we have found that the constant-pressure heat capacity is related to the constant-pressure derivative of entropy with respect to temperature. An analogous analysis of U at constant V results in a relation between the constant-volume heat capacity and the derivative of entropy with respect to temperature at constant V. That is, Eqn. 4.30,

$$(\partial S/\partial T)_V = C_V/T$$

From the definitions of C_p and C_v and the chain rule:

$$dS\,(T,\,V) = C_V/T\ dT + (\partial P/\partial T)_V\ dV \qquad\qquad 6.38$$

$$dS\,(V,\,P) = C_P(\partial T/\partial V)_P/T\ dV + C_V(\partial T/\partial P)_V/T\ dP \qquad\qquad 6.39$$

$$dH\,(T,\,P) = C_P\ dT + [V - T(\partial V/\partial T)_P]\ dP \qquad\qquad 6.40$$

A summary
of useful relations.

$$dU\,(T,\,V) = C_V\ dT + [T(\partial P/\partial T)_V - P]\ dV \qquad\qquad 6.41$$

One may wonder, "What is so important about the variables C_P, C_V, P, V, T, and their derivatives?" The answer is that these properties are **experimentally measureable**. Engineers have developed **equations of state** written in terms of these fundamental properties. Briefly, an equation of state provides the link between P, V, and T. So, we can solve for all the derivatives by knowing an equation for $P = P(V,T)$ and add up all the changes. Properties like H, U, and S are not considered mea-

An equation of
state links the
P, V, T properties
of a fluid.

$$\kappa_T \equiv \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T \qquad 6.42$$

$$\alpha_P \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{-1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \qquad 6.43$$

A similar commonly used property is the **Joule-Thomson coefficient** defined by

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_H \qquad 6.44$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$$

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

Isothermal compressibility.

$$\kappa_T \equiv \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T$$

Isobaric coefficient of thermal expansion.

$$\alpha_P \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{-1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P$$

A similar commonly used property is the **Joule-Thomson coefficient** defined by

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_H$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad\qquad C_V = T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

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

$$dS\,(T,\,V) = C_V/T\ dT + (\partial P/\partial T)_V\ dV$$

$$dS\,(V,\,P) = C_P(\partial T/\partial V)_P/T\ dV + C_V(\partial T/\partial P)_V/T\ dP$$

$$dH\,(T,\,P) = C_P\ dT + [V - T(\partial V/\partial T)_P]\ dP$$

$$dU\,(T,\,V) = C_V\ dT + [T(\partial P/\partial T)_V - P]\ dV$$

-S	U	V
H		A
-P	G	T

Example 6.3 Entropy as a function of T and P

Derive a general relation for entropy changes of any fluid with respect to temperature and pressure in terms of C_P, C_V, P, V, T, and their derivatives.

Solution: First, since we choose T, P to be the controlled variables, applying Eqn. 6.14

$$dS = (\partial S/\partial T)_P \, dT + (\partial S/\partial P)_T \, dP \qquad\qquad 6.36$$

but $(\partial S/\partial T)_P = C_P/T$ as derived above, and Maxwell's relations show that

$$(\partial S/\partial P)_T = -(\partial V/\partial T)_P$$

$$\Rightarrow dS \, (T, P) = C_P/T \; dT - (\partial V/\partial T)_P \; dP \qquad\qquad 6.37$$

This useful expression is ready for application, given an equation of state which describes $V(T,P)$.

Example 6.4 Entropy change for an ideal gas

A gas is being compressed from ambient conditions to a high pressure. Devise a model equation for computing $\Delta S(T,P)$. Assume the ideal gas equation of state.

Solution: We begin with the temperature effect at (constant) low pressure. By Eqn. 6.37,

$$dS)_P{}^{ig} = C_P^{ig}\ dT/T \tag{ig}$$

Having accounted for the temperature effect at constant pressure, the next step is to account for the pressure effect at constant temperature. The derivative $(\partial V/\partial T)_P$ is required.

$$V = RT/P \implies (\partial V/\partial T)_P = R/P \tag{ig}$$

Putting it all together,

$$dS = \frac{C_P^{ig}}{T}dT - \frac{R}{P}dP = C_P^{ig}d\ln T - R\ln P \tag{ig}$$

Assuming C_P^{ig} is independent of T and integrating,

$$\Delta S = C_P^{ig}\ \ln(T_2/T_1) - R\ln(P_2/P_1) \tag{ig}$$

Example 6.5 Entropy change for a simple nonideal gas

A gas is compressed from ambient conditions to a high pressure. Devise a model equation for computing $\Delta S(T,P)$ with the equation of state: $V = RT/P + (a + bT)$, where a and b are constants.

Solution: Substituting the new equation of state and following the previous example,

$$(\partial V/\partial T)_P = R/P + b$$

We can still apply C_P^{ig} because we could be careful to calculate temperature effects at low P before calculating the pressure effect. Inserting into Eqn. 6.37,

$$dS = \frac{C_P^{ig}}{T}dT - \frac{R}{P}dP - bdP = C_P^{ig}\,d\ln T - R\ln P - bdP$$

Assuming C_P^{ig} is independent of T and integrating,

$$\Delta S = C_P^{ig}\ln(T_2/T_1) - R\ln(P_2/P_1) - b\Delta P \tag{*}$$

Example 6.6 Accounting for T and V impacts on energy

Derive an expression for $\left(\dfrac{\partial U}{\partial V}\right)_T$ in terms of measurable properties. (a) Evaluate for the ideal gas.

(b) Evaluate for the van der Waals equation of state, $P = RT/(V-b) - a/V$.

Solution: Beginning with the fundamental relation for dU,

$$dU = TdS - PdV$$

Applying the expansion rule

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\left(\frac{\partial V}{\partial V}\right)_T \qquad 6.45$$

Using a Maxwell relation and a basic identity

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad 6.46$$

(a) For an ideal gas, $P = RT/V$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}; \quad \left(\frac{\partial U}{\partial V}\right)_T^{ig} = \frac{RT}{V} - P = 0 \qquad \text{(ig)}$$

Thus, internal energy of an ideal gas does not depend on volume (or pressure) at a given T.

(b) For the van der Waals equation,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}; \quad \left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V-b} - \left(\frac{RT}{V-b} - \frac{a}{V^2}\right) = \frac{a}{V^2} \qquad \text{(ig)}$$

Example 6.7 The relation between Helmholtz energy and internal energy

Express the following in terms of U, H, S, G, and their derivatives: $(\partial(A/RT)/\partial T)_V$

Solution: Applying the product rule,

$$\left(\frac{\partial(A/RT)}{\partial T}\right)_V = \frac{1}{RT}\left(\frac{\partial A}{\partial T}\right)_V - \frac{A}{RT^2}$$

Applying Eqn. 6.6 and the definition of A,

$$\left(\frac{\partial(A/RT)}{\partial T}\right)_V = \frac{-S}{RT} - \frac{(U-TS)}{RT^2} = \frac{-U}{RT^2}$$

Rearranging, and introducing a common definition $\beta \equiv 1/kT$,

$$\frac{U}{RT} = \left(-\frac{T\partial(A/RT)}{\partial T}\right)_V = \left(\frac{\beta\,\partial(A/RT)}{\partial\beta}\right)_V \qquad 6.47$$

The significance of Eqn. 6.47 is that one can easily transform from Helmholtz energy to internal energy and vice versa by integrating or differentiating. This is especially easy when the temperature dependence is expressed as a polynomial.

Hints on Manipulating Partial Derivatives

1. Learn to recognize $\left(\frac{\partial S}{\partial T}\right)_P$ and $\left(\frac{\partial S}{\partial T}\right)_V$ as being related to C_P and C_V, respectively.

2. If a derivative involves entropy, enthalpy, or Helmholtz or Gibbs energy being held constant, e.g., $\left(\frac{\partial T}{\partial P}\right)_H$, bring it inside the parenthesis using the triple product relation (Eqn. 6.15). Then apply the expansion rule (Eqn. 6.17) to eliminate immeasurable quantities. The expansion rule is very useful when F of that equation is a fundamental property.

3. When a derivative involves $\{T, S, P, V\}$ only, look to apply a Maxwell relation.

4. When nothing else seems to work, apply the Jacobian method.[4] The Jacobian method will always result in derivatives with the desired independent variables.

Example 6.9 Volumetric dependence of C_V for ideal gas

Determine how C_V depends on volume (or pressure) by deriving an expression for $(\partial C_V/\partial V)_T$. Evaluate the expression for an ideal gas.

Solution: Following hint #1 and applying Eqn. 4.30:

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

By the chain rule:

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

Changing the order of differentiation:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\frac{\partial}{\partial T}\left[\left(\frac{\partial S}{\partial T}\right)_T\right]_V = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

For an ideal gas, $P = RT/V$, we have $\left(\frac{\partial P}{\partial T}\right)_V$ in Example 6.6:

$$\frac{\partial}{\partial T}\left[\left(\frac{\partial P}{\partial T}\right)_V\right]_V = \frac{\partial}{\partial T}\left(\frac{R}{V}\right)_V = 0 \qquad \text{(ig) 6.51}$$

Thus, heat capacity of an ideal gas does not depend on volume (or pressure) at a fixed temperature. (We will reevaluate this derivative in Chapter 7 for a real fluid.)

Example 6.10 Application of the triple product relation

Evaluate $(\partial S/\partial V)_A$ in terms of C_P, C_V, T, P, and V. Your answer may include absolute values of S if it is not a derivative constraint or within a derivative term.

Solution: This problem illustrates a typical situation where the triple product rule is helpful because the Helmholtz energy is held constant (hint #2). It is easiest to express changes in the Helmholtz energies as changes in other variables. Applying the triple product rule:

$$(\partial S/\partial V)_A = -(\partial A/\partial V)_S / (\partial A/\partial S)_V$$

Applying the expansion rule twice, $dA = -PdV - SdT \Rightarrow (\partial A/\partial V)_S = -P - S(\partial T/\partial V)_S$ and $(\partial A/\partial S)_V = 0 - S(\partial T/\partial S)_V$. Recalling Eqn. 4.30 and converting to measurable derivatives:

$$\Rightarrow \left(\frac{\partial T}{\partial S}\right) = \frac{T}{C_V} \text{ and } (\partial T/\partial V)_S = \left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T = -\frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_V$$

Substituting:

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_A = \frac{-PC_V}{ST} + \left(\frac{\partial P}{\partial T}\right)_V$$

Example 6.11 Master equation for an ideal gas

Derive a master equation for calculating changes in U for an ideal gas in terms of $\{V, T\}$.

Solution:

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

Applying results of the previous examples:

$$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P \right] dV \qquad 6.52$$

Notice that this expression is more complicated than the fundamental property relation in terms of $\{S, V\}$. As we noted earlier, this is why $\{S, V\}$ are the natural variables for dU, rather than $\{T, V\}$ or any other combination. For an ideal gas, we can use the results of Example 6.6 to find:

$$dU^{ig} = C_V^{ig} dT \qquad \text{(ig) } 6.53$$

Example 6.12 Relating C_P to C_V

Derive a general formula to relate C_P and C_V.

Solution: Start with an expression that already contains one of the desired derivatives (e.g., C_V) and introduce the variables necessary to create the second derivative (e.g., C_P). Beginning with Eqn. 6.38,

$$dS = \frac{C_V}{T}dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

and using the expansion rule with T at constant P,

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_V}{T}\overset{1}{\cancel{\left(\frac{\partial T}{\partial T}\right)_P}} + \left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P, \text{ where the left-hand side is } \frac{C_P}{T}.$$

$$C_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$$

Exercise:
Verify that the last term simplifies to R for an ideal gas.

USEFUL DERIVATIVES

Differential Property		Corresponding Maxwell Relation
$dU = TdS - PdV$	$U(S, V)$	$-(\partial P/\partial S)_V = (\partial T/\partial V)_S$
$dH = TdS + VdP$	$H(S, P)$	$(\partial V/\partial S)_P = (\partial T/\partial P)_S$
$dA = -SdT - PdV$	$A(T, V)$	$(\partial P/\partial T)_V = (\partial S/\partial V)_T$
$dG = -SdT + VdP$	$G(T, P)$	$-(\partial V/\partial T)_P = (\partial S/\partial P)_T$

Other useful derivative relations shown in Chapter 6

$$dS\,(T, P) = C_P/T\ dT - (\partial V/\partial T)_P\ dP \qquad 6.37$$

$$dS\,(T, V) = C_V/T\ dT + (\partial P/\partial T)_V\ dV \qquad 6.38$$

$$dS\,(V, P) = C_P(\partial T/\partial V)_P/T\ dV + C_V(\partial T/\partial P)_V/T\ dP \qquad 6.39$$

$$dH\,(T, P) = C_P\ dT + [V - T(\partial V/\partial T)_P]\ dP \qquad 6.40$$

$$dU\,(T, V) = C_V\ dT + [T(\partial P/\partial T)_V - P]\ dV \qquad 6.41$$

Hints for Remembering the Auxiliary Relations

Auxiliary relations can be easily written by memorizing the fundamental relation for dU and the natural variables for the other properties. Note that $\{T,S\}$ and $\{P,V\}$ always appear in pairs, and each pair is a set of conjugate variables. A Legendre transformation performed on internal energy among conjugate variables changes the dependent variable and the sign of the term involving the conjugate variables. For example, to transform P and V, the product PV is added to U, resulting in Eqn. 6.5. To transform T and S, the product TS is subtracted: $A = U - TS$, $dA = dU - TdS - SdT = -SdT - PdV$. The pattern can be easily seen in the "Useful Derivatives" table on the front book end paper. Note that $\{T,S\}$ always appear together, and $\{P,V\}$ always appear together, and the sign changes upon transformation.

Jacobian Method of Derivative Manipulation

change at fixed enthalpy, $\left(\frac{\partial T}{\partial P}\right)_H$, which is written in Jacobian notation as $\left(\frac{\partial T}{\partial P}\right)_H = \frac{\partial(T, H)}{\partial(P, H)}$. Note how the constraint of constant enthalpy is incorporated into the notation. The rules for manipulation of the Jacobian notation are,

1. Jacobian notation represents a determinant of partial derivatives,

$$\frac{\partial(K, L)}{\partial(X, Y)} = \left(\frac{\partial K}{\partial X}\right)_Y \left(\frac{\partial L}{\partial Y}\right)_X - \left(\frac{\partial K}{\partial Y}\right)_X \left(\frac{\partial L}{\partial X}\right)_Y = \begin{vmatrix} \left(\frac{\partial K}{\partial X}\right)_Y & \left(\frac{\partial K}{\partial Y}\right)_X \\ \left(\frac{\partial L}{\partial X}\right)_Y & \left(\frac{\partial L}{\partial Y}\right)_X \end{vmatrix} \qquad 6.54$$

The Jacobian is particularly simple when the numerator and denominator have a common variable,

$$\frac{\partial(K, L)}{\partial(X, L)} = \left(\frac{\partial K}{\partial X}\right)_L \qquad 6.55$$

which is a special case of Eqn. 6.54.

2. When the order of variables in the numerator or denominator is switched, the sign of the Jacobian changes. Switching the order of variables in both the numerator and denominator results in no sign change due to cancellation. Consider switching the order of variables in the numerator,

$$\frac{\partial(K, L)}{\partial(X, Y)} = -\frac{\partial(L, K)}{\partial(X, Y)} \qquad 6.56$$

3. The Jacobian may be inverted.

$$\frac{\partial(K, L)}{\partial(X, Y)} = \left[\frac{\partial(X, Y)}{\partial(K, L)}\right]^{-1} = \frac{1}{\dfrac{\partial(X, Y)}{\partial(K, L)}} \qquad 6.57$$

4. Additional variables may be interposed. When additional variables are interposed, it is usually convenient to invert one of the Jacobians.

$$\frac{\partial(K, L)}{\partial(X, Y)} = \frac{\partial(K, L)}{\partial(B, C)}\frac{\partial(B, C)}{\partial(X, Y)} = \frac{\dfrac{\partial(K, L)}{\partial(B, C)}}{\dfrac{\partial(X, Y)}{\partial(B, C)}} \qquad 6.58$$

Manipulation of Derivatives

Before manipulating derivatives, the desired independent variables are selected. The selected independent variables will be held constant outside the derivatives in the final formula. The general procedure is to interpose the desired independent variables, rearrange as much as possible to obtain Jacobians with common variables in the numerator and denominator, write the determinant for any Jacobians without common variables; then use Maxwell relations, the expansion rule, and so on, to simplify the answer.

1. If the starting derivative already contains both the desired independent variables, the result of Jacobian manipulation is redundant with the triple product rule. The steps are: 1) write the Jacobian; 2) interpose the independent variables; 3) rearrange to convert to partial derivatives.

    Example: Convert $\left(\frac{\partial T}{\partial P}\right)_H$ to derivatives that use T and P as independent variables.

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{\partial(T, H)}{\partial(P, H)} = \frac{\partial(T, H)}{\partial(T, P)}\frac{\partial(T, P)}{\partial(P, H)} = \frac{\frac{\partial(H, T)}{\partial(P, T)}}{-\frac{\partial(H, P)}{\partial(T, P)}} = \frac{-\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = \frac{-\left(\frac{\partial H}{\partial P}\right)_T}{C_P}$$

    and the numerator can be simplified using the expansion rule as presented in Example 6.1.

2. If the starting derivative has just one of the desired independent variables, the steps are: 1) write the Jacobian; 2) interpose the desired variables; 3) write the determinant for the Jacobian without a common variable; 4) rearrange to convert to partial derivatives.

    Example: Find a relation for the adiabatic compressibility, $\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$ in terms of derivatives using T, P as independent variables.

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

    Now, including a Maxwell relation as we simplify the second term in square brackets, and then combining terms:

$$\left(\frac{\partial V}{\partial P}\right)_S = \left(\frac{\partial V}{\partial P}\right)_T + \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P^2$$

$$\kappa_S = -\frac{1}{V}\left(\left(\frac{\partial V}{\partial P}\right)_T + \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P^2\right) = \kappa_T - \frac{T}{VC_P}\left(\frac{\partial V}{\partial T}\right)_P^2$$

3. If the starting derivative has neither of the desired independent variables, the steps are: 1) write the Jacobian; 2) interpose the desired variables; 3) write the Jacobians as a quotient and write the determinants for both Jacobians; 4) rearrange to convert to partial derivatives.

    Example: Find $\left(\frac{\partial S}{\partial V}\right)_U$ in measurable properties using P and T as independent variables.

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

3. If the starting derivative has neither of the desired independent variables, the steps are:
   1) write the Jacobian; 2) interpose the desired variables; 3) write the Jacobians as a quotient and write the determinants for both Jacobians; 4) rearrange to convert to partial derivatives.

   Example: Find $\left(\dfrac{\partial S}{\partial V}\right)_U$ in measurable properties using P and T as independent variables.

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

Writing the determinants for both Jacobians:

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

Now, using the expansion rule for the derivatives of U, and also introducing Maxwell relations,

$$\frac{-\left(\dfrac{\partial V}{\partial T}\right)_P\left[C_P - P\left(\dfrac{\partial V}{\partial T}\right)_P\right] + \dfrac{C_P}{T}\left[T\left(\dfrac{\partial V}{\partial T}\right)_P + P\left(\dfrac{\partial V}{\partial P}\right)_T\right]}{\left(\dfrac{\partial V}{\partial P}\right)_T\left[C_P - P\left(\dfrac{\partial V}{\partial T}\right)_P\right] + T\left(\dfrac{\partial V}{\partial T}\right)_P^2 + P\left(\dfrac{\partial V}{\partial P}\right)_T\left(\dfrac{\partial V}{\partial T}\right)_P} =$$

$$\frac{P\left(\dfrac{\partial V}{\partial T}\right)_P^2 + C_P\dfrac{P}{T}\left(\dfrac{\partial V}{\partial P}\right)_T}{T\left(\dfrac{\partial V}{\partial T}\right)_P^2 + C_P\left(\dfrac{\partial V}{\partial P}\right)_T} = \frac{P}{T}$$

The result is particularly simple. We could have derived this directly if we had recognized that S and V are the natural variables for U. Therefore, $dU = TdS - P\,dV = 0$, $TdS|_U = -PdV|_U$, $T\left(\dfrac{\partial S}{\partial V}\right)_U = P$, $\left(\dfrac{\partial S}{\partial V}\right)_U = \dfrac{P}{T}$. However, the exercise demonstrates the procedure and power of the Jacobian technique even though the result will usually not simplify to the extent of this example.