The Thermodynamic Potentials

We have established the four laws of Thermodynamics, defined the Entropy and now re-established the 2\textsuperscript{nd} Law as the Clausius Inequality. Additionally, we developed a series of additional Thermodynamic State Functions, H(S,P), A(T,V) and G(T,P) that can contain more useful expressions of the thermodynamic laws than either U(S,V) or S(U,V). Now we mine these functions to understand how various systems come to equilibrium and to establish additional statements of the 2\textsuperscript{nd} Law. In the process we will gain some insight into their physical "meaning".

First, to review, the Entropy, when defined according to:

\[ dS = \frac{\delta Q_{rev}}{T} \]

can be used to write the Internal Energy as a function of S and V, U(S,V).

\[ dU = \delta Q + \delta W = T \, dS - P \, dV \]

This can be inverted to write the Entropy as a function of U and V, S(U,V).

\[ dS = \left( \frac{1}{T} \right) \, dU + \left( \frac{P}{T} \right) \, dV \]

As such, the entropy S(U,V) is a fundamental equation in that it "contains all thermodynamic information."

By the same token, the internal energy, written as U(S,V), is also fundamental. And this can be Legendre Transformed into equally fundamental state functions.

\[ H(S,P) = U + PV \quad \text{Enthalpy} \]

\[ A(T,V) = U - TS \quad \text{Helmholtz Energy} \]

\[ G(T,P) = U - TS + PV \quad \text{Gibbs Energy} \]

Now, we manipulate the differentials of each of these state functions. As an example, consider H(S,P):
\[ \text{dH} = \text{d}(U + PV) \]
\[ = \text{d}U + \text{d}(PV) \]
\[ = \text{d}U + P \text{dV} + V \text{dP} \]
\[ = (T \text{dS} - P \text{dV}) + P \text{dV} + V \text{dP} \quad \text{b/c} \quad \text{dU} = T \text{dS} - P \text{dV} \]
\[ = T \text{dS} + V \text{dP} \]

But, as a function of S and P, dH can be written as:
\[ \text{dH} = \left( \frac{\partial H}{\partial S} \right)_P \text{dS} + \left( \frac{\partial H}{\partial P} \right)_S \text{dP} \]

This means the following thermodynamic derivatives can be identified as:
\[ \left( \frac{\partial H}{\partial S} \right)_P = T \quad \text{and} \quad \left( \frac{\partial H}{\partial P} \right)_S = V \]

In this manner, we manipulate the differentials of each of the above state functions:

\[ \frac{\text{dH}}{\text{dS}} = T \text{dS} + V \text{dP} \]
\[ \frac{\text{dU}}{\text{dU}} = T \text{dS} - P \text{dV} \]
\[ = \left( \frac{\partial U}{\partial S} \right)_V \text{dS} + \left( \frac{\partial U}{\partial V} \right)_S \text{dV} \]
\[ \frac{\text{dA}}{\text{dT}} = -S \text{dT} - P \text{dV} \]
\[ = \left( \frac{\partial A}{\partial T} \right)_V \text{dT} + \left( \frac{\partial A}{\partial V} \right)_T \text{dV} \]
\[ \frac{\text{dG}}{\text{dG}} = -S \text{dT} + V \text{dP} \]
\[ = \left( \frac{\partial G}{\partial T} \right)_P \text{dT} + \left( \frac{\partial G}{\partial P} \right)_T \text{dP} \]

Using these relationships we obtain the following identities:
\[ \left( \frac{\partial U}{\partial S} \right)_V = T \quad \text{and} \quad \left( \frac{\partial U}{\partial V} \right)_S = -P \]
\[
\left(\frac{\partial H}{\partial S}\right)_p = T \quad \text{and} \quad \left(\frac{\partial H}{\partial P}\right)_S = V
\]
\[
\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \text{and} \quad \left(\frac{\partial A}{\partial V}\right)_T = -P
\]
\[
\left(\frac{\partial G}{\partial T}\right)_p = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P}\right)_T = V
\]

A summary of the differentials of all of our state functions is provided in the appendix below.

With this housekeeping out of the way, we now consider how to determine the state of a system at equilibrium. Determining a system's equilibrium configuration is in fact the fundamental problem of thermodynamics. This will be of particular interest when we begin to consider chemical problems.

Let us suppose that two simple systems are contained within a closed cylinder, separated from each other by an internal piston. Assume that the cylinder walls and the piston are rigid, impermeable to matter, and adiabatic and that the position of the piston is firmly fixed. Each of the systems is closed. If we now free the piston, it will, in general, seek some new position. Similarly, if the adiabatic coating is stripped from the piston so that heat can flow between the two systems, there will be a redistribution of energy between the two systems. Again, if holes are punched in the piston, there will be a redistribution of matter (and also of energy) between the two systems.

Thus, the removal of a constraint in each case results in the onset of some spontaneous process, and when the systems finally settle into new equilibrium states they do so with the new values of the parameters \(U^{(1)}\), \(V^{(1)}\), \(N_1^{(1)}\), ..., and \(U^{(2)}\), \(V^{(2)}\), \(N_1^{(2)}\), .... The basic problem of thermodynamics is the calculation of the equilibrium values of these parameters.

[More generally], given two or more simple systems, they may be considered as constituting a single composite system. The composite system is termed closed if it is surrounded by a wall that is restrictive with respect to the total energy, the total volume, and the total mole numbers of each component of the composite system. The individual simple systems within a closed composite system need not themselves be closed. Thus, in the particular example referred to, the composite system is closed even if the internal piston is free to move or has holes in it. Constraints that prevent the flow of energy, volume, or matter among the simple systems constituting the composite system are known as internal constraints. If a closed composite system is in equilibrium with respect to certain internal constraints and if some of these constraints are then removed, the system eventually comes into a new equilibrium state. That is, certain processes which were previously disallowed be allowed or, in the terminology of mechanics, become virtual
The basic problem of thermodynamics is the determination of the equilibrium state that eventually results after the removal of internal constraints in a closed composite system.

H.B. Callen
Thermodynamics

Castellan approaches the problem of equilibrium in a slightly different manner.

Our aim now is to find out what characteristics distinguish irreversible (real) transformations from reversible (ideal) transformations. We begin by asking what relation exists between the entropy change in a transformation and the irreversible heat flow that accompanies it. At every stage of a reversible transformation, the system departs from equilibrium only infinitesimally. The system is transformed, yet remains effectively at equilibrium throughout a reversible change in state. The condition for reversibility is therefore a condition of equilibrium; from the defining equation for dS, the condition of reversibility is that

\[ T \, dS = \delta Q_{\text{rev}} \]

The condition placed on an irreversible change in state is the Clausius inequality, which we write in the form

\[ T \, dS > \delta Q \]

Irreversible changes are real changes or natural changes or spontaneous changes. We shall refer to changes in the natural direction as spontaneous changes, and the inequality [above] as the condition of spontaneity. The two relations [above] can be combined into

\[ T \, dS \geq \delta Q \]

where it is understood that the equality sign implies a reversible value of \( \delta Q \).

Gilbert W. Castellan
Physical Chemistry, 3rd Ed.

Now to cases that are of interest to us; an isolated system, a system in contact with a temperature reservoir and a system in contact with temperature and pressure reservoirs.

Isolated System

2nd Law Statement

Consider a system surrounded by an adiabatic, rigid and impermeable wall. This wall is restrictive with respect to energy, volume and matter. The system is completely isolated. For any system process \( dU = 0 \) and \( dV = 0 \) along the entire process path.

In this case, we can write:

\[ \delta Q = dU - \delta W = dU + P_{\text{op}} \, dV = 0 \]
So, the Clausius Inequality becomes:

\[ dS \geq \frac{\delta Q}{T} = 0 \]

Or,

\[ \Delta S \geq 0 \]

This means that the entropy tends toward a maximum for the spontaneous processes of an isolated system.

**Equilibrium**

Now allow the system be made up of two subsystems; \( \alpha \) and \( \beta \). Each is separated by an adiabatic, rigid and impermeable wall and is at a specified temperature. The internal constraint of adiabaticity is removed and heat is allowed to flow from one subsystem to another.

If heat flows, it is specified that it will flow in the direction indicated above. Now,

\[ dS \geq 0 \]

Since, \( dS = dS_\alpha + dS_\beta \), we have:

\[ dS_\alpha + dS_\beta \geq 0 \]

This gives,

\[ \frac{\delta Q_\alpha}{T_\alpha} + \frac{\delta Q_\beta}{T_\beta} \geq 0 \]

Since, as specified above, \( \delta Q_\alpha = -\delta Q \) and \( \delta Q_\beta = +\delta Q \), we have:

\[ \delta Q \left( \frac{1}{T_\beta} - \frac{1}{T_\alpha} \right) \geq 0 \]

If heat flows, then \( T_\alpha > T_\beta \). If the system is at equilibrium, then \( T_\alpha = T_\beta \).
**Constant Temperature Processes**

*2nd Law Statement*

Now our system is contained within a rigid diathermal wall and placed in a temperature reservoir. Thus, all internal processes will be isothermal.

Again we start with the Clausius Inequality,

\[ dS \geq \frac{\delta Q}{T} \]

Writing \( \delta Q = dU - \delta W \), we have:

\[ T\, dS \geq dU - \delta W \]

or,

\[ -dU + T\, dS \geq -\delta W \]

Now, since our processes are isothermal:

\[ -dU + T\, dS = -dU + d(TS) = -d(U - TS) = -dA \]

So,

\[ -dA \geq -\delta W \]

Or, finally:

\[ dA \geq \delta W \]

This provides us with an interpretation for the Helmholtz Energy; \( A \) represents the maximum work available as a result of an isothermal process. Thus, \( A \) is sometimes referred to as the “Work Function”.

If \( \delta W = -P_{op}\, dV \), then:

\[ dA \geq -P_{op}\, dV \]

or,

\[ dA \leq P_{op}\, dV \]

Thus, for isothermal, constant volume process:
dA ≤ 0

Or,

\[ \Delta A \leq 0 \]

This means that the Helmholtz Energy tends toward a minimum for spontaneous isothermal, isochoric processes.

**Equilibrium**

Now allow the system be made up of two subsystems; \( \alpha \) and \( \beta \). Each is separated by an diathermal, rigid wall and is at a specified pressure. The internal constraint of rigidity is removed and the volume of each subsystem is allowed to change according to the diagram below, if a change occurs.

Now,

\[ dA_\alpha + dA_\beta \leq 0 \]

Since, \( dA = -P \, dV \) for an isothermal process, we have:

\[ -P_\alpha \, dV_\alpha - P_\beta \, dV_\beta \leq 0 \]

If the volume changes of the subsystems occur according to the diagram above, then \( dV_\alpha = + dV \) and \( dV_\beta = - dV \). So:

\[ (P_\beta - P_\alpha) \, dV \leq 0 \]

If the volumes change, then \( P_\alpha > P_\beta \). If the system is at equilibrium, then \( P_\alpha = P_\beta \).
Constant Temperature and Pressure Processes

2nd Law Statement

Finally, we consider a system that is contained within a piston surrounded by a diathermal wall and placed in a temperature reservoir. The piston works against a pressure reservoir. Thus, all internal processes will be isothermal and isobaric.

Again, we start with the Clausius Inequality,

\[ \text{d}S \geq \frac{\delta Q}{T} \]

We now write \( \delta Q = \text{d}U - \delta W \) or \( \delta Q = \text{d}U + P \text{d}V - \delta W_a \). where have split the work into terms representing PV-work and other "available" forms of work, \( \delta W_a \). These other forms of work may be electrical, chemical, gravitational, etc. The Clausius Inequality is now:

\[ T \text{d}S \geq \text{d}U + P \text{d}V - \delta W_a \]

or,

\[ -\text{d}U + T \text{d}S + P \text{d}V \geq -\delta W_a \]

As before, we can write TdS as d(TS) because all processes are isothermal. Similarly, we can write PdV as d(PV) because of the constant pressure constraint. Thus, our terms on the left in the above equation,1 can be written as:

\[ -\text{d}(U + TS - PV) \geq -\delta W_a \]

Invoking the definition of G, we have:

\[ -\text{d}G \geq -\delta W_a \]

or,

\[ \text{d}G \geq \delta W_a \]

This gives us a physical interpretation for the Gibbs Free Energy. \( \Delta G \) represents the maximum non-PV work available during an isothermal, isobaric process.

If no additional work is available, then \( \delta W_a = 0 \) and we have:

\[ -\text{d}G \geq 0 \]

or,
\[ \Delta G \leq 0 \]

This means that the Gibbs Free Energy tends toward a minimum for spontaneous isothermal, isobaric processes.

Changing our viewpoint slightly, we can write this minimization principle as involving both enthalpic and entropic considerations:

\[ G = U + PV - TS = H - TS \]

So,

\[ \Delta G = \Delta H - \Delta (TS) \]

If we have a constant temperature and pressure process, we have:

\[ \Delta G = \Delta H - T \Delta S \]

This means that the requirement for \( \Delta G < 0 \) for a spontaneous, isothermal and isobaric process can be achieved by having \( \Delta H < 0 \) and/or \( \Delta S > 0 \).

Many of our chemical reactions occur open to the atmosphere in a vessel such that the reaction system is in thermal equilibrium with its surroundings. Thus,

\[ \Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T \Delta S_{\text{rxn}} \]

In order that the reaction occur spontaneously:

\[ \Delta G_{\text{rxn}} < 0. \]

If \( \Delta G_{\text{rxn}} = 0 \), then the reaction is at equilibrium.

Most chemical reactions are Exothermic (\( \Delta H_{\text{rxn}} < 0 \)) and are driven forward by their exothermicity; \( \Delta S_{\text{rxn}} \) being relatively unimportant. Historically this led to the mistaken assumption that chemical reactions were driven by heat evolution.

Thermodynamics was not quickly applied to chemistry even though there had long been an interest in the heat liberated during chemical reactions. Lavoisier and Laplace had studied heat output, both in combustion and respiration. Germain Henri Hess (1802-1850) had enunciated a limited form of the law of conservation of energy with his law of heat summation, in which he concluded that the heat liberated in a chemical process is independent of the path by which the process is carried out.

Beginning in 1852 more extensive measurements of heats of reaction were undertaken by Julius Thomsen (1826-1909) in Copenhagen and Marcelin Berthelot in Paris, who considerably refined their equipment and the techniques of thermochemical measurements during the next decade. The Berthelot bomb for measuring heats of
combustion, developed in 1881, is essentially the one used today. For a time these studies were based on the assumption that chemical forces were proportional to the heat evolved during a chemical reaction.

Aaron J. Ihde
The Development of Modern Chemistry

Bertholet and Thomsen codified their initial observations in the Bertholet-Thomsen Principle:

All chemical changes are accompanied by the production of heat and those processes which occur will be ones in which the most heat is produced.

Of course, this Principle could not account for the fact that Endothermic reactions, $\Delta H_{\text{rxn}} > 0$, do occur. So, it was rather short lived and is now mostly of historical interest. Endothermic reactions do occur because they can be driven by a favorable entropy change. We must keep in mind that it is the Gibbs function that determines the spontaneity of chemical reactions.

Two examples of entropically driven chemical reactions are the reaction of Barium Hydroxide and Ammonium Nitrate and the combustion of Peroxyacetone.

\[
\text{Ba(OH)}_2\cdot8\text{H}_2\text{O}(s) + 2\text{NH}_4\text{NO}_3(s) \rightarrow \text{Ba(NO}_3)_2(\text{aq}) + 2\text{NH}_3(\text{aq}) + 10\text{H}_2\text{O}
\]

\[
2\text{C}_9\text{H}_{18}\text{O}_6(s) + 21\text{O}_2(g) \rightarrow 18\text{CO}_2(g) + 18\text{H}_2\text{O(g)}
\]

The first of these is very endothermic ($\Delta H_{\text{rxn}}^0 = +62.3$ kJ/mol at 298.15K) and can produce temperatures as low as -25°C to -30°C for even small reaction mixtures. This
reaction is entropically driven \( \Delta S_{rxn} = 406 \text{ J/K mol} \) at 298.15K by the large number of aqueous products; these will be much more entropically favored than the relatively ordered solid reactants. This reaction proceeds with \( \Delta G_{rxn}(298.15) = -60.2 \text{ kJ/mol} \). A nice demonstration of the endothermicity of this reaction can be found at http://www.youtube.com/watch?v=9kRS8tY7aJY.

The second reaction, the combustion of Peroxyacetone, is also entropically driven; \( \Delta S_{rxn} > 0 \). This reaction is an example of a heatless explosion; \( \Delta H_{rxn} \approx 0 \). In this case it is the very large number of gaseous products, with their large entropy, that cause the reaction to be spontaneous. A demonstration of this reaction can be found at http://www.youtube.com/watch?v=GGlbzFUsiRM.

We are now in a position to look back and examine why the state functions \( H(S,P) \), \( A(T,V) \) and \( G(T,P) \) were introduced.

In both the energy \([U]\) and entropy \([S]\) representations the extensive parameters play the roles of mathematically independent variables, whereas the intensive parameters \([T \text{ and } P]\) arise as derived concepts. This situation is in direct contrast to the practical situation dictated by convenience in the laboratory. The experimenter frequently finds that the intensive parameters are the more easily measured and controlled and therefore is likely to think of the intensive parameters as operationally independent variables and of the extensive parameters as operationally derived quantities. The extreme instance of this situation is provided by the conjugate variables entropy and temperature; \([U(S,V) \text{ vs. } G(T,P)]\). No practical instruments exist for the measurement and control of entropy, whereas thermometers and thermostats, for the measurement and control of the temperature, are common laboratory equipment.

It is, perhaps, superfluous at this point to stress again that thermodynamics is logically complete and self-contained within either the entropy \([S(U,V)]\) or the energy \([U(S,V)]\) representations and that the introduction of the transformed representations is purely a matter of convenience. This is, admittedly, a convenience without which thermodynamics would be almost unusably awkward, but in principle it is still only a luxury rather than a logical necessity.

H.B. Callen
Thermodynamics

We now turn to one last and very useful consequence of the thermodynamic state functions we have been considering. Each of these potentials \((U, H, A, G)\) represent state functions. As such, integrals over their differentials \((dU, dH, dA, dG)\) are path independent; it does not matter how the change is carried out, only the initial and final states of the system are important for the evaluation of \( \Delta U, \Delta H, \Delta A \) and \( \Delta G \). This means that the differentials are exact.

If a function \( F(x,y) \) is a state function and its differential is exact:

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

\[
= M(x,y) \, dx + N(x,y) \, dy
\]

then its mixed second partial derivatives are equal:
Since and , we have:

Established in 1871 by James Clerk Maxwell, the Maxwell Relations are derived from the fact mixed second partial derivatives of the thermodynamic potentials are equivalent in the manner demonstrated above for .

For example, the differential of the state function can be written as:

As we have already noted:

From the fact that the mixed second partial derivatives of must be equal:
\[
\left( \frac{\partial^2 H}{\partial P \partial S} \right) = \left( \frac{\partial^2 H}{\partial S \partial P} \right)
\]

we can derive a Maxwell Relation by inserting the appropriate first derivatives into each of the above expressions:

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

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

And now we have the Maxwell Relation:

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

Applying this procedure to the four thermodynamic potentials \(U(S,V), H(S,P), A(T,V),\) and \(G(T,P),\) we obtain the four usual Maxwell Relations.

**Internal Energy**

\[
dU = T \, dS - P \, dV
\]

\[
= \left( \frac{\partial U}{\partial S} \right)_V \, dS + \left( \frac{\partial U}{\partial V} \right)_S \, dV
\]

\[
\left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V
\]

**Enthalpy**

\[
dH = T \, dS + V \, dP
\]

\[
= \left( \frac{\partial H}{\partial S} \right)_P \, dS + \left( \frac{\partial H}{\partial P} \right)_S \, dP
\]

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

**Helmholtz Free Energy**

\[
dA = - S \, dT - P \, dV
\]

\[
= \left( \frac{\partial A}{\partial T} \right)_V \, dT + \left( \frac{\partial A}{\partial V} \right)_T \, dV
\]

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

**Gibbs Free Energy**

\[
dG = - S \, dT + V \, dP
\]

\[
= \left( \frac{\partial G}{\partial T} \right)_P \, dT + \left( \frac{\partial G}{\partial P} \right)_T \, dP
\]

\[
- \left( \frac{\partial S}{\partial P} \right)_T = \left( \frac{\partial V}{\partial T} \right)_P
\]
The Maxwell Relations are themselves useful in transforming hard to measure thermodynamic derivatives into those that are much easier to measure.

Certain kinds of data are easily measured, whereas others may involve a great investment of time and effort. Thus, for example; we may be engaged in high-pressure experiments in which we need to know how the enthalpy changes with pressure at constant temperature. We need, in other words, the derivative \((\partial H/\partial P)_T\). We could determine the derivative by undertaking a series of calorimetric experiments over a range of pressure values, but calorimetric experiments are difficult and time-consuming. We want to determine the information in the easiest possible way. We have meters to measure temperature, pressure, and volume. We do not have entropy meters, enthalpy meters, free-energy meters, or Helmholtz-energy meters. Variables that are easily measurable include compressibilities, coefficients of thermal expansion, and heat capacities.

J. Phillip Bromberg
Physical Chemistry, 2nd Ed.

The situation is somewhat stronger than Bromberg suggests. It turns out that a very limited number of measured quantities is required to determine almost all the desired derivatives.

In the practical applications of thermodynamics the experimental situation to be analyzed frequently dictates a partial derivative to be evaluated. For instance, we may be concerned with the analysis of the temperature change which is required to maintain the volume of a single-component system constant if the pressure is increased slightly. This temperature change is evidently

\[
dT = \left( \frac{\partial T}{\partial P} \right)_{V,N} dP
\]

and consequently we are interested in an evaluation of the derivative \((\partial T/\partial P)_{V,N}\). ... A general feature of the derivatives that arise in this way is that they are likely to involve constant mole numbers and that they generally involve both intensive and extensive parameters. Of all such derivatives, only three can be independent, and any given derivative can be expressed by an identity in terms of an arbitrarily chosen set of three basic derivatives. This set is conventionally chosen as \(C_p\), \(\alpha\), and \(\kappa\).

H.B. Callen
Thermodynamics

Callen then proceeds with a proof of this last statement, a proof you are welcome to consider by turning to his text.

The manipulation of hard to measure thermodynamic derivatives into those that are more easily measured is known as the reduction of derivatives. At this point we will demonstrate the reduction of derivatives by providing a couple well chosen of examples. It is at this point that we find ourselves returning to all of those cases during the progress of the class in which we indicated that a particular expression would be "proven later". We now provide those proofs. So, sit back, relax and enjoy the examples.
**Thermodynamic Equations of State**

We are familiar with several Equations of State; the Ideal Gas Equation, the van der Waals Equation, etc. Below we derive an Equation of State that is general and applicable for any system.

We previously defined an Equation of State as a relationship between the variables \( P, \ T, \) and \( \tilde{V} \) of the form:

\[
g(P, \tilde{V}, T) = 0
\]

For a general system, we have:

\[
dU = T \, dS - P \, dV
\]

Dividing by \( dV \) and holding \( T \) constant, we have:

\[
\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - P
\]

Applying the Maxwell Relation

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

We obtain:

\[
\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P
\]

This can be rearranged into a more familiar form for an Equation of State, as specified above.

\[
P = T \left( \frac{\partial P}{\partial T} \right)_V - \left( \frac{\partial U}{\partial V} \right)_T
\]

**The Derivative of the Internal Energy wrspt Volume at Const. \( T \)**

We wish to reduce the derivative:

\[
\left( \frac{\partial U}{\partial V} \right)_T
\]

We start with:

\[
U = A + TS
\]

and then form the needed derivative:
\[ \left( \frac{\partial U}{\partial V} \right)_T = \left( \frac{\partial A}{\partial V} \right)_T + T \left( \frac{\partial S}{\partial V} \right)_T \]

Now, we apply an appropriate Maxwell Relation:

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

and get:

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

Finally, we recognize:

\[ \left( \frac{\partial A}{\partial V} \right)_T = -P \quad \text{and} \quad \left( \frac{\partial P}{\partial T} \right)_V = \frac{\alpha}{\kappa} \]

This then gives us:

\[ \left( \frac{\partial U}{\partial V} \right)_T = -P + T \left( \frac{\partial P}{\partial T} \right)_V = -P + \frac{T\alpha}{\kappa} \]

Notice we have converted the need to make \( U \) vs. \( V \) measurements into making measurements of \( \alpha \) and \( \kappa \), which are much easier.

For an Ideal Gas:

\[ P = \frac{RT}{V} \]

So, \[ \left( \frac{\partial P}{\partial T} \right)_V = \frac{R}{V} \]

And, \[ \left( \frac{\partial U}{\partial V} \right)_T = -P + T \left( \frac{R}{V} \right) = -P + P = 0; \] which is Joule's Law.

For a van der Waals Gas:

\[ P = \frac{RT}{V-b} - \frac{a}{V^2} \]

So, \[ \left( \frac{\partial P}{\partial T} \right)_V = \frac{R}{V-b} \]

And, \[ \left( \frac{\partial U}{\partial V} \right)_T = -P + T \left( \frac{R}{V-b} \right) = -\frac{RT}{V-b} + \frac{a}{V^2} + \frac{RT}{V-b} = \frac{a}{V^2} \]

This is a result we have used previously.
Heat Capacity Difference; $C_p - C_v$

Previously, we showed:

$$C_p - C_v = \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_P$$

We can now use our above expression for the derivative of the internal energy wrt $V$ at constant $T$:

$$C_p - C_v = \left[ P + T \left( \frac{\partial p}{\partial T} \right)_V \right] \left( \frac{\partial V}{\partial T} \right)_P$$

Now we use:

$$\left( \frac{\partial p}{\partial T} \right)_V = \frac{\alpha}{\kappa} \quad \text{and} \quad \left( \frac{\partial V}{\partial T} \right)_P = V \alpha$$

to obtain the desired reduction:

$$C_p - C_v = \frac{TV \alpha^2}{\kappa}$$

**Joule-Thomson Coefficient**

To obtain a reduction for the Joule-Thomson Coefficient:

$$\mu_{JT} = \left( \frac{\partial T}{\partial p} \right)_H = -\frac{1}{C_p} \left( \frac{\partial H}{\partial p} \right)_T$$

Here we start with:

$$\left( \frac{\partial H}{\partial p} \right)_T = \frac{\partial}{\partial p} (G + TS) = \left( \frac{\partial G}{\partial p} \right)_T + T \left( \frac{\partial S}{\partial p} \right)_T$$

Applying the Maxwell Relation:

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

we obtain:

$$\left( \frac{\partial H}{\partial p} \right)_T = \left( \frac{\partial G}{\partial p} \right)_T + T \left( \frac{\partial V}{\partial T} \right)_P$$

Recognizing:

$$\left( \frac{\partial G}{\partial p} \right)_T = V \quad \text{and} \quad \left( \frac{\partial V}{\partial T} \right)_P = V \alpha$$
we arrive at the final reduction:
\[
\mu_T = - \frac{1}{c_p} \left( \frac{\partial H}{\partial P} \right)_T = - \frac{1}{c_p} \left[ V - TV \alpha \right] = \frac{V (T \alpha - 1)}{c_p}
\]

These and other important derivatives are given in the following appendicies:

Basic Thermodynamic Equations

First Derivatives of T, P, V, and S

First Derivatives of U, H, A and G

You should notice that the use of the Maxwell Relations is only one piece in the puzzle that is the path from our initial derivative to its final reduced form. Along this path we may also need to use an expression for dU, dS, dH, dA or dG as well as be able to manipulate derivatives generally. To this end, you should review the following three relationships involving partial derivatives:

\[
\left( \frac{\partial x}{\partial y} \right)_z = \frac{1}{\left( \frac{\partial y}{\partial x} \right)_z}
\]

\[
\left( \frac{\partial x}{\partial y} \right)_z = \left( \frac{\partial x}{\partial w} \right)_z \left( \frac{\partial y}{\partial w} \right)_z
\]

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

Let's proceed with another example. I've drawn it from our "First Derivatives of U, H, A and G" handout.

Another Example

I've chosen for this example, almost at random, a derivative of enthalpy:

\[
\left( \frac{\partial H}{\partial V} \right)_T = ?
\]

Now to the reduction of this derivative. Start with:

\[
dH = T \, dS + V \, dP
\]

and form the needed derivative:
\[
\left( \frac{\partial H}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T + V \left( \frac{\partial P}{\partial V} \right)_T
\]

Now apply a Maxwell Relation and invert the last derivative:

\[
\left( \frac{\partial H}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V + V \left( \frac{1}{\partial P} \right)_T
\]

Finally, use our usual transformations to \( \alpha \) and \( \kappa \):

\[
\left( \frac{\partial H}{\partial V} \right)_T = \frac{T\alpha}{\kappa} - \frac{1}{\kappa}
\]

At this point you should peruse the "First Derivatives of U, H, A and G" and "First Derivatives of T, P, V, and S" appendices and imagine how you might carry-out each of the indicated "reductions". Just for fun, you might want to pick out a few and prove the "reductions".
Appendix - Thermodynamic State Functions

Internal Energy

\[ U(S,V) \quad dU = \left( \frac{\partial U}{\partial S} \right)_T dS + \left( \frac{\partial U}{\partial V} \right)_S dV \]
\[ = T \, dS - P \, dV \]

\[ U(T,V) \quad dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \]
\[ = C_v \, dT + \Pi_T \, dV \]

Enthalpy

\[ H(S,P) \quad dH = \left( \frac{\partial H}{\partial S} \right)_P dS + \left( \frac{\partial H}{\partial P} \right)_S dP \]
\[ = T \, dS + V \, dP \]

\[ H(T,P) \quad dH = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP \]
\[ = C_p \, dT - C_p \mu \, dP \]

Entropy

\[ S(U,V) \quad dS = \left( \frac{\partial S}{\partial U} \right)_V dU + \left( \frac{\partial S}{\partial V} \right)_U dV \]
\[ = \frac{1}{T} \, dU + \frac{P}{T} \, dV \]

\[ S(T,V) \quad dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV \]
\[ = \frac{C_v}{T} \, dT + \frac{\alpha}{\kappa} \, dV \]

\[ S(T,P) \quad dS = \left( \frac{\partial S}{\partial T} \right)_P dT + \left( \frac{\partial S}{\partial P} \right)_T dP \]
\[ = \frac{C_p}{T} \, dT - V \alpha \, dP \]
Helmholtz Free Energy

\[ A(T,V) \] 
\[ \text{d}A = \left( \frac{\partial A}{\partial T} \right)_V \text{d}T + \left( \frac{\partial A}{\partial V} \right)_T \text{d}V \]
\[ = -S \text{d}T - P \text{d}V \]

Gibb’s Free Energy

\[ G(T,P) \] 
\[ \text{d}G = \left( \frac{\partial G}{\partial T} \right)_P \text{d}T + \left( \frac{\partial G}{\partial P} \right)_T \text{d}P \]
\[ = -S \text{d}T + V \text{d}P \]

*Fundamental thermodynamic relationships. According to Bromberg:

In mechanics a conservative field is one for which a force is derivable from a potential. An analogous situation exists in thermodynamics in which an intensive property is obtained from the various thermodynamic functions, thus \( P = -\left( \frac{\partial U}{\partial V} \right)_S \). Work terms arise from the product of an intensive property with its associated extensive property, for example, \( PdV \). When we compare these work terms with the definition of work, \( Fdx \), the intensive properties such as \( P \) take the form of generalized forces. For this reason, the functions \( U, H, A, \text{and} G \) are often referred to as *potentials*. Heat is also measured by the product of an intensive and an extensive property; in the expression \( TdS \), the term \( T \) is the intensive and \( S \) the extensive property.

... the four potentials \( [U, H, A, G] \) are written in terms of their natural variables \( [^*\text{relationships}] \). The energy \( U \) is a function of the *extensive* properties of the system, \( S \) and \( V \). What we have accomplished in constructing \( H, A, \text{and} G \) from \( U \) is to substitute an intensive property for its associated extensive property. Enthalpy is generated from energy by replacing the extensive property \( V \) by its associated intensive property \( P \). The Helmholtz energy \( A \) is generated by replacing \( S \) by \( T \); and \( G \) is generated by simultaneously replacing \( S \) and \( V \) by \( T \) and \( P \). These can be regarded as analogous to coordinate transformations such as the transformation from cartesian to polar coordinates. Here the transformation involves replacing an extensive property by its associated intensive property. When viewed in this light, the functions \( H, A, \text{and} G \) are simply the energy transformed into a different set of variables. In mathematics, such a transformation is known as a *Legendre transformation*.

*Physical Chemistry, 2nd Ed.*
J. Phillip Bromberg
Appendix - Basic Thermodynamic Equations

\[ C_v = \left( \frac{\partial U}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V = -T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_S \]

\[ C_p = \left( \frac{\partial H}{\partial T} \right)_p = T \left( \frac{\partial S}{\partial T} \right)_p = T \left( \frac{\partial V}{\partial T} \right)_p \left( \frac{\partial P}{\partial T} \right)_S \]

\[ C_p - C_v = \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_p = \frac{\alpha^2 TV}{\kappa} \]

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

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

\[ \gamma = \frac{C_p}{C_v} \]

\[ \mu_T = \left( \frac{\partial T}{\partial P} \right)_H = \frac{V}{C_p} (\alpha T - 1) \]

\[ \eta = \left( \frac{\partial T}{\partial V} \right)_U = -\frac{1}{C_v} \left( \frac{\alpha T}{\kappa} - P \right) \]
Appendix - First Derivatives of $T$, $P$, $V$, and $S$

\[ \left( \frac{\partial T}{\partial P} \right)_V = \frac{\kappa}{\alpha} \quad \left( \frac{\partial T}{\partial P} \right)_S = \frac{\nu \alpha T}{C_p} = \frac{(y-1)\kappa}{y\alpha} \]

\[ \left( \frac{\partial T}{\partial V} \right)_P = \frac{1}{\nu \alpha} \quad \left( \frac{\partial T}{\partial V} \right)_S = -\frac{\nu \alpha T}{C_v \kappa} = -\frac{y-1}{\nu \alpha} \]

\[ \left( \frac{\partial T}{\partial S} \right)_P = \frac{T}{C_p} \quad \left( \frac{\partial T}{\partial S} \right)_V = \frac{T}{C_v} \]

\[ \left( \frac{\partial P}{\partial T} \right)_V = \frac{\alpha}{\kappa} \quad \left( \frac{\partial P}{\partial T} \right)_S = \frac{C_p}{\nu \alpha T} = \frac{y\alpha}{(y-1)\kappa} \]

\[ \left( \frac{\partial P}{\partial V} \right)_T = -\frac{1}{\nu \kappa} \quad \left( \frac{\partial P}{\partial V} \right)_S = -\frac{y}{\nu \kappa} \]

\[ \left( \frac{\partial P}{\partial S} \right)_T = -\frac{1}{\nu \alpha} \quad \left( \frac{\partial P}{\partial S} \right)_V = \frac{x \alpha T}{C_v \kappa} = \frac{y-1}{\nu \alpha} \]

\[ \left( \frac{\partial V}{\partial T} \right)_P = V \alpha \quad \left( \frac{\partial V}{\partial T} \right)_S = -\frac{C_v \nu \kappa}{\alpha T} = -\frac{\nu \alpha}{y-1} \]

\[ \left( \frac{\partial V}{\partial P} \right)_T = -V \kappa \quad \left( \frac{\partial V}{\partial P} \right)_S = -\frac{\nu \kappa}{y} \]

\[ \left( \frac{\partial V}{\partial S} \right)_T = \frac{\kappa}{\alpha} \quad \left( \frac{\partial V}{\partial S} \right)_P = \frac{\nu \alpha T}{C_p} = \frac{(y-1)\kappa}{y\alpha} \]

\[ \left( \frac{\partial S}{\partial T} \right)_V = \frac{C_v}{T} \quad \left( \frac{\partial S}{\partial T} \right)_P = \frac{C_p}{T} \]

\[ \left( \frac{\partial S}{\partial P} \right)_T = -V \alpha \quad \left( \frac{\partial S}{\partial P} \right)_V = \frac{C_v \nu \kappa}{\alpha T} = \frac{\nu \alpha}{y-1} \]

\[ \left( \frac{\partial S}{\partial V} \right)_P = \frac{C_p}{\nu \alpha T} = \frac{y\alpha}{(y-1)\kappa} \quad \left( \frac{\partial S}{\partial V} \right)_T = \frac{\alpha}{\kappa} \]
### Appendix - First Derivatives of U, H, A and G

<table>
<thead>
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<th>Enthalpy $H$</th>
<th>Helmholtz $A$</th>
<th>Gibbs $G$</th>
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</thead>
<tbody>
<tr>
<td>$\frac{\partial U}{\partial T}_p = C_P - P\alpha$</td>
<td>$\frac{\partial H}{\partial T}_p = C_P$</td>
<td>$\frac{\partial A}{\partial T}_p = -S - PV\alpha$</td>
<td>$\frac{\partial G}{\partial T}_p = -S$</td>
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<tr>
<td>$\frac{\partial U}{\partial T}_V = C_V$</td>
<td>$\frac{\partial H}{\partial T}_V = C_V + \frac{V\alpha}{\kappa}$</td>
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<td>$\frac{\partial G}{\partial T}_V = -S + \frac{V\alpha}{\kappa}$</td>
</tr>
<tr>
<td>$\frac{\partial U}{\partial T}_S = \frac{P\gamma\kappa}{aT}$</td>
<td>$\frac{\partial H}{\partial T}_S = \frac{C_P}{aT}$</td>
<td>$\frac{\partial A}{\partial T}_S = -S + \frac{PV\alpha}{T}$</td>
<td>$\frac{\partial G}{\partial T}_S = -S + \frac{C_P}{aT} + \frac{V\gamma\alpha}{(\gamma-1)\kappa}$</td>
</tr>
<tr>
<td>$\frac{\partial U}{\partial P}_T = -V\alpha + V\kappa\rho$</td>
<td>$\frac{\partial H}{\partial P}_T = V(1 - \alpha T)$</td>
<td>$\frac{\partial A}{\partial P}_T = PV\kappa$</td>
<td>$\frac{\partial G}{\partial P}_T = V$</td>
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<td>$\frac{\partial U}{\partial P}_V = \frac{C_V\kappa}{aT} + \frac{V\alpha}{\gamma - 1}$</td>
<td>$\frac{\partial H}{\partial P}_V = V + \frac{C_V\kappa}{\alpha}$</td>
<td>$\frac{\partial A}{\partial P}_V = -\frac{S\alpha}{\alpha}$</td>
<td>$\frac{\partial G}{\partial P}_V = -\frac{S\alpha}{\alpha} + V$</td>
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<tr>
<td>$\frac{\partial U}{\partial P}_S = \frac{PV\kappa}{\gamma}$</td>
<td>$\frac{\partial H}{\partial P}_S = V$</td>
<td>$\frac{\partial A}{\partial P}_S = -\frac{SV\alpha T + PV\kappa}{C_P} + \frac{PV\kappa}{\gamma} = -\frac{S\alpha (\gamma-1)\rho}{\gamma^2} + V$</td>
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<td>$\frac{\partial U}{\partial V}_T = \frac{aT}{\kappa} - P$</td>
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<td>$\frac{\partial H}{\partial V}_S = -\frac{\gamma}{\kappa}$</td>
<td>$\frac{\partial A}{\partial V}_S = -\frac{S\alpha T - \gamma}{\gamma - 1}$</td>
<td>$\frac{\partial G}{\partial V}_S = -\frac{S\alpha T}{C_P}\frac{\gamma}{\gamma - 1} - P$</td>
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