Handbook of

Thermodynamic Potential, Free Energy and Entropy

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Chapter 1

Thermodynamic Potential

A **thermodynamic potential** is a scalar function used to represent the thermodynamic state of a system. The concept of thermodynamic potentials was introduced by Pierre Duhem in 1886. Josiah Willard Gibbs in his papers used the term *fundamental functions*. One main thermodynamic potential which has a physical interpretation is the internal energy, U. It is the energy of configuration of a given system of conservative forces (that is why it is a potential) and only has meaning with respect to a defined set of references (or data). Expressions for all other thermodynamic energy potentials are derivable via Legendre transforms from an expression for U. In thermodynamics, certain forces, such as gravity, are typically disregarded when formulating expressions for potentials. For example, while all the working fluid in a steam engine may have higher energy due to gravity while sitting on top of Mt. Everest than it would at the bottom of the Mariana trench, the gravitational potential energy term in the formula for the internal energy would usually be ignored because *changes* in gravitational potential within the engine during operation would be negligible.

Description and interpretation

Five common thermodynamic potentials are:

Name	Symbol	Formula	Natural variables
Internal energy	U	$\int(TdS - pdV + \sum_i \mu_i dN_i)$	$S,V,\{N_i\}$
Helmholtz free energy	F, A	$U - TS$	$T,V,\{N_i\}$
Enthalpy	H	$U + pV$	$S,p,\{N_i\}$
Gibbs free energy	G	$U + pV - TS$	$T,p,\{N_i\}$
Landau Potential (Grand potential)	Ω, Φ_G	$U - TS - \sum_i \mu_i N_i$	$T,V,\{\mu_i\}$

where T = temperature, S = entropy, p = pressure, V = volume. The Helmholtz free energy is often denoted by the symbol F, but the use of A is preferred by IUPAC. N_i is the number of particles of type i in the system and μ_i is the chemical potential for an i-type particle. For the sake of completeness, the set of all N_i are also included as natural variables, although they are sometimes ignored.

These five common potentials are all energy potentials, but there are also entropy potentials. The thermodynamic square can be used as a tool to recall and derive some of the potentials.

Just as in mechanics, where potential energy is defined as capacity to do work, similarly different potentials have different meanings. Internal energy (U) is the capacity to do work plus the capacity to release heat. Gibbs energy is the capacity to do non-mechanical work. Enthalpy is the capacity to do non-mechanical work plus the capacity to release heat. Helmholtz free energy is the capacity to do work (non-mechanical plus mechanical). From these definitions we can say that ΔU is the energy added to the system, ΔF is the total work done on it, ΔG is the non-mechanical work done on it, and ΔH is the sum of non-mechanical work done on the system and the heat given to it. Thermodynamic potentials are very useful when calculating the equilibrium results of a chemical reaction, or when measuring the properties of materials in a chemical reaction. The chemical reactions usually take place under some simple constraints such as constant pressure and temperature, or constant entropy and volume, and when this is true, there is a corresponding thermodynamic potential which comes into play. Just as in mechanics, the system will tend towards lower values of potential and at equilibrium, under these constraints, the potential will take on an unchanging minimum value. The thermodynamic potentials can also be used to estimate the total amount of energy available from a thermodynamic system under the appropriate constraint.

In particular:

- When the entropy (S) and "external parameters" (e.g. volume) of a closed system are held constant, the internal energy (U) decreases and reaches a minimum value at equilibrium. This follows from the first and second laws of thermodynamics and is called the principle of minimum energy. The following three statements are directly derivable from this principle.
- When the temperature (T) and external parameters of a closed system are held constant, the Helmholtz free energy (F) decreases and reaches a minimum value at equilibrium.
- When the pressure (p) and external parameters of a closed system are held constant, the enthalpy (H) decreases and reaches a minimum value at equilibrium.
- When the temperature (T), pressure (p) and external parameters of a closed system are held constant, the Gibbs free energy (G) decreases and reaches a minimum value at equilibrium.

Natural variables

The variables that are held constant in this process are termed the **natural variables** of that potential. The natural variables are important not only for the above mentioned reason, but also because if a thermodynamic potential can be determined as a function of its natural variables, all of the thermodynamic properties of the system can be found by taking partial derivatives of that potential with respect to its natural variables and this is true for no other combination of variables. Conversely, if a thermodynamic potential is not given as a function of its natural variables, it will not, in general, yield all of the thermodynamic properties of the system.

Notice that the set of natural variables for the above four potentials are formed from every combination of the T-S and P-V variables, excluding any pairs of conjugate variables. There is no reason to ignore the $\mu_i - N_i$ conjugate pairs, and in fact we may define four additional potentials for each species. Using IUPAC notation in which the brackets contain the natural variables (other than the main four), we have:

Formula	**Natural variables**
$U[\mu_j] = U - \mu_j N_j$	$S, V, \{N_{i\neq j}\}, \mu_j$
$F[\mu_j] = U - TS - \mu_j N_j$	$T, V, \{N_{i\neq j}\}, \mu_j$
$H[\mu_j] = U + pV - \mu_j N_j$	$S, p, \{N_{i\neq j}\}, \mu_j$
$G[\mu_j] = U + pV - TS - \mu_j N_j$	$T, p, \{N_{i\neq j}\}, \mu_j$

If there is only one species, then we are done, but if there are, say two species, then there will be additional potentials such as $U[\mu_1,\mu_2] = U - \mu_1 N_1 - \mu_2 N_2$ and so on. If there are D dimensions to the thermodynamic space, then there are 2^D unique thermodynamic potentials. For the most simple case, a single phase ideal gas, there will be three dimensions, yielding eight thermodynamic potentials.

In statistical mechanics, the relationship between the Helmholtz free energy and the partition function is fundamental, and is used to calculate the thermodynamic properties of matters.

The fundamental equations

The definitions of the thermodynamic potentials may be differentiated and, along with the first and second laws of thermodynamics, a set of differential equations known as the *fundamental equations* follow. By the first law of thermodynamics, any differential change in the internal energy U of a system can be written as the sum of heat flowing into the system and work done by the system on the environment, along with any change due to the addition of new particles to the system:

$$\mathrm{d}U = \delta Q - \delta W + \sum_i \mu_i \,\mathrm{d}N_i$$

where δQ is the infinitesimal heat flow into the system, and δW is the infinitesimal work done by the system, μ_i is the chemical potential of particle type i and N_i is the number of type *i* particles. (Note that neither δ*Q* nor δ*W* are exact differentials. Small changes in these variables are therefore represented with δ rather than *d*.)

By the second law of thermodynamics, we can express the internal energy change in terms of state functions and their differentials. In case of quasistatic changes we have:

$$\begin{aligned}\delta Q &= T\,\mathrm{d}S\\ \delta W &= p\,\mathrm{d}V\end{aligned}$$

where

T is temperature,
S is entropy,
p is pressure,

and *V* is volume, and the equality holds for reversible processes.

This leads to the standard differential form of the internal energy in case of a quasistatic reversible change:

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum_i \mu_i\,\mathrm{d}N_i$$

Since U, S and V are thermodynamic functions of state, the above relation holds also for arbitrary non-reversible changes. If the system has more external variables than just the volume that can change, the fundamental thermodynamic relation generalizes to:

$$dU = T\,dS - \sum_i X_i\,dx_i + \sum_j \mu_j\,dN_j$$

Here the X_i are the generalized forces corresponding to the external variables x_i.

Applying Legendre transforms repeatedly, the following differential relations hold for the four potentials:

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum_i \mu_i\,\mathrm{d}N_i$$

$$\mathrm{d}F = -S\,\mathrm{d}T - p\mathrm{d}V + \sum_i \mu_i\,\mathrm{d}N_i$$

$$\mathrm{d}H = T\,\mathrm{d}S + V\mathrm{d}p + \sum_i \mu_i\,\mathrm{d}N_i$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\mathrm{d}p + \sum_i \mu_i\,\mathrm{d}N_i$$

Note that the infinitesimals on the right hand side of each of the above equations are of the natural variables of the potential on the left hand side. Similar equations can be developed for all of the other thermodynamic potentials of the system. There will be one fundamental equation for each thermodynamic potential, resulting in a total of 2^D fundamental equations.

The equations of state

We can use the above equations to derive some differential definitions of some thermodynamic parameters. If we define Φ to stand for any of the thermodynamic potentials, then the above equations are of the form:

$$\mathrm{d}\Phi = \sum_i x_i\,\mathrm{d}y_i$$

where x_i and y_i are conjugate pairs, and the y_i are the natural variables of the potential Φ. From the chain rule it follows that:

$$x_j = \left(\frac{\partial\Phi}{\partial y_j}\right)_{\{y_{i\neq j}\}}$$

Where $\{y_{i\neq j}\}$ is the set of all natural variables of Φ except y_j. This yields expressions for various thermodynamic parameters in terms of the derivatives of the potentials with respect to their natural variables. These equations are known as **equations of state** since they specify parameters of the thermodynamic state. If we restrict ourselves to the potentials U,F,H and G, then we have:

$$\begin{aligned}
+T &= \left(\frac{\partial U}{\partial S}\right)_{V,\{N_i\}} = \left(\frac{\partial H}{\partial S}\right)_{p,\{N_i\}} \\
-p &= \left(\frac{\partial U}{\partial V}\right)_{S,\{N_i\}} = \left(\frac{\partial F}{\partial V}\right)_{T,\{N_i\}} \\
+V &= \left(\frac{\partial H}{\partial p}\right)_{S,\{N_i\}} = \left(\frac{\partial G}{\partial p}\right)_{T,\{N_i\}} \\
-S &= \left(\frac{\partial G}{\partial T}\right)_{p,\{N_i\}} = \left(\frac{\partial F}{\partial T}\right)_{V,\{N_i\}}
\end{aligned}$$

$$\mu_j = \left(\frac{\partial \phi}{\partial N_j}\right)_{X,Y,\{N_{i\neq j}\}}$$

where, in the last equation, φ is any of the thermodynamic potentials U, F, H, G and $X, Y, \{N_{j\neq i}\}$are the set of natural variables for that potential, excluding N_i. If we use all potentials, then we will have more equations of state such as

$$-N_j = \left(\frac{\partial U[\mu_j]}{\partial \mu_j}\right)_{S,V,\{N_{i\neq j}\}}$$

and so on. In all, there will be *D* equations for each potential resulting in a total of $D\ 2^D$ equations of state. If the *D* equations of state for a particular potential are known, then the fundamental equation for that potential can be determined. This means that all thermodynamic information about the system will be known, and that the fundamental equations for any other potential can be found, along with the corresponding equations of state.

Maxwell relations

Maxwell's relations are a set of equations in thermodynamics which are derivable from the definitions of the thermodynamic potentials. The Maxwell relations are statements of equality among the second derivatives of the thermodynamic potentials. They follow directly from the fact that the order of differentiation of an analytic function of two variables is irrelevant. If Φ is a thermodynamic potential and x_i and x_j are two different natural variables for that potential, then the Maxwell relation for that potential and those variables is:

$$\frac{\partial}{\partial x_j}\left(\frac{\partial \Phi}{\partial x_i}\right) = \frac{\partial}{\partial x_i}\left(\frac{\partial \Phi}{\partial x_j}\right)$$

where the partial derivatives are taken with all other natural variables held constant. It is seen that for every thermodynamic potential there are $n\left(n-1\right)/2$possible Maxwell relations where *n* is the number of natural variables for that potential.

These relations are named for the nineteenth-century physicist James Clerk Maxwell.

The four most common Maxwell relations

The four most common Maxwell relations are the equalities of the second derivatives of each of the four thermodynamic potentials, with respect to their thermal natural variable (temperature *T* or entropy *S*) and their mechanical natural variable (pressure *P* or volume *V*):

$$\begin{aligned}
\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V &&= \frac{\partial^2 U}{\partial S \partial V} \\
\left(\frac{\partial T}{\partial P}\right)_S &= +\left(\frac{\partial V}{\partial S}\right)_P &&= \frac{\partial^2 H}{\partial S \partial P} \\
+\left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V &&= -\frac{\partial^2 A}{\partial T \partial V} \\
-\left(\frac{\partial S}{\partial P}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_P &&= \frac{\partial^2 G}{\partial T \partial P}
\end{aligned}$$

where the potentials as functions of their natural thermal and mechanical variables are:

$U(S,V)$- The internal energy
$H(S,P)$- The Enthalpy
$A(T,V)$- The Helmholtz free energy
$G(T,P)$- The Gibbs free energy

Derivation of the Maxwell relations

Derivation of the Maxwell relations can be deduced from the differential forms of the thermodynamic potentials:

$$\begin{aligned}
dU &= TdS - pdV \\
dH &= TdS + Vdp \\
dA &= -SdT - pdV \\
dG &= -SdT + Vdp
\end{aligned}$$

These equations resemble total differentials of the form

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

And indeed, it can be shown that for any equation of the form

$$dz = M dx + N dy$$

that

$$M = \left(\frac{\partial z}{\partial x}\right)_y, \quad N = \left(\frac{\partial z}{\partial y}\right)_x$$

Consider, as an example, the equation $dH = TdS + Vdp$. We can now immediately see that

$$T = \left(\frac{\partial H}{\partial S}\right)_p, \quad V = \left(\frac{\partial H}{\partial p}\right)_S$$

Since we also know that for functions with continuous second derivatives, the mixed partial derivatives are identical (Symmetry of second derivatives), that is, that

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

we therefore can see that

$$\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right)_p = \frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)_S$$

and therefore that

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

Each of the four Maxwell relationships given above follows similarly from one of the Gibbs equations

Extended derivation of the Maxwell relations

Maxwell relations are based on simple partial differentiation rules.

Combined form first and second law of thermodynamics,

$TdS = dU + PdV$ (Eq.1)

U,S,V are state functions. Let,

$U = U(x,y)$
$S = S(x,y)$
$V = V(x,y)$

$$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy$$
$$dS = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy$$
$$dV = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy$$

Substitute them in Eq.1 and one gets,

$$T\left(\frac{\partial S}{\partial x}\right)_y dx + T\left(\frac{\partial S}{\partial y}\right)_x dy = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy + P\left(\frac{\partial V}{\partial x}\right)_y dx + P\left(\frac{\partial V}{\partial y}\right)_x dy$$

And also written as,

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T\left(\frac{\partial S}{\partial x}\right)_y dx + T\left(\frac{\partial S}{\partial y}\right)_x dy - P\left(\frac{\partial V}{\partial x}\right)_y dx - P\left(\frac{\partial V}{\partial y}\right)_x dy$$

comparing the coefficient of dx and dy, one gets

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y$$
$$\left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x$$

Differentiating above equations by y,x respectively

$$\left(\frac{\partial^2 U}{\partial y \partial x}\right) = \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T\left(\frac{\partial^2 S}{\partial y \partial x}\right) - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P\left(\frac{\partial^2 V}{\partial y \partial x}\right)$$

(Eq.2)

and

$$\left(\frac{\partial^2 U}{\partial x \partial y}\right) = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T\left(\frac{\partial^2 S}{\partial x \partial y}\right) - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P\left(\frac{\partial^2 V}{\partial x \partial y}\right)$$

(Eq.3)

U,S and V are exact differentials, therefore,

$$\left(\frac{\partial^2 U}{\partial y \partial x}\right) = \left(\frac{\partial^2 U}{\partial x \partial y}\right)$$

$$\left(\frac{\partial^2 S}{\partial y \partial x}\right) = \left(\frac{\partial^2 S}{\partial x \partial y}\right) : \left(\frac{\partial^2 V}{\partial y \partial x}\right) = \left(\frac{\partial^2 V}{\partial x \partial y}\right)$$

Subtract eqn(2) and (3) and one gets

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x$$

Note: The above is called the general expression for Maxwell's thermodynamical relation.

Maxwell's first relation

Allow x = S and y = V and one gets

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

Maxwell's second relation

Allow x = T and y = V and one gets

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

Maxwell's third relation

Allow x = S and y = P and one gets

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

Maxwell's fourth relation

Allow x = T and y = P and one gets

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

Maxwell's fifth relation

Allow x = P and y = V

$$\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial S}{\partial V}\right)_P - \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial S}{\partial P}\right)_V = 1$$

Maxwell's sixth relation

Allow x = T and y = S and one gets

$$\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1$$

General Maxwell relationships

The above are by no means the only Maxwell relationships. When other work terms involving other natural variables besides the volume work are considered or when the number of particles is included as a natural variable, other Maxwell relations become apparent. For example, if we have a single-component gas, then the number of particles *N* is also a natural variable of the above four thermodynamic potentials. The Maxwell relationship for the enthalpy with respect to pressure and particle number would then be:

$$\left(\frac{\partial \mu}{\partial p}\right)_{S,N} = \left(\frac{\partial V}{\partial N}\right)_{S,p} = \frac{\partial^2 H}{\partial p \partial N}$$

where μ is the chemical potential. In addition, there are other thermodynamic potentials besides the four that are commonly used, and each of these potentials will yield a set of Maxwell relations.

Each equation can be re-expressed using the relationship

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

which are sometimes also known as Maxwell relations.

Euler integrals

Again, define x_i and y_i to be conjugate pairs, and the y_i to be the natural variables of the internal energy. Since all of the natural variables of the internal energy *U* are extensive quantities

$$U(\{\alpha y_i\}) = \alpha U(\{y_i\})$$

it follows from Euler's homogeneous function theorem that the internal energy can be written as: