Extensive thermodynamic potentials (single component)

name	independent variables	differential form	integrated form
entropy	$S(E,V,N)$	$dS = \dfrac{1}{T}dE + \dfrac{P}{T}dV - \dfrac{\mu}{T}dN$	$S = \dfrac{E}{T} + \dfrac{PV}{T} - \dfrac{\mu N}{T}$
energy	$E(S,V,N)$	$dE = TdS - PdV + \mu dN$	$E = TS - PV + \mu N$
enthalpy	$H(S,P,N)$	$dH = TdS + VdP + \mu dN$	$\begin{aligned} H &= E + PV \\ &= TS + \mu N \end{aligned}$
Helmholtz free energy	$A(T,V,N)$	$dA = -SdT - PdV + \mu dN$	$\begin{aligned} A &= E - TS \\ &= -PV + \mu N \end{aligned}$
Gibbs free energy	$G(T,P,N)$	$dG = -SdT + VdP + \mu dN$	$\begin{aligned} G &= E + PV - TS \\ &= A + PV \\ &= H - TS \\ &= \mu N \end{aligned}$

Intensive thermodynamic potentials (single component)

name	independent variables	differential form	integrated relations
entropy per-particle	$s(e,v)$	$ds = \dfrac{1}{T}de + \dfrac{P}{T}dv$	$\dfrac{\mu}{T} = -s + \dfrac{e}{T} + \dfrac{Pv}{T}$
energy per-particle	$e(s,v)$	$de = Tds - Pdv$	$\mu = e - Ts + Pv$
enthalpy per-particle	$h(s,P)$	$dh = Tds + vdP$	$\begin{aligned} h &= e + Pv \\ \mu &= h - Ts \end{aligned}$
Helmholtz free energy per-particle	$a(T,v)$	$da = -sdT - Pdv$	$\begin{aligned} a &= e - Ts \\ \mu &= a + Pv \end{aligned}$
Gibbs free energy per-particle	$g(T,P)$	$dg = -sdT + vdP$	$\begin{aligned} g &= e + Pv - Ts \\ &= a + Pv \\ &= h - Ts \\ \mu &= g \end{aligned}$

Measurable quantities

name	definition	name	definition
pressure	P	temperature	T
volume	V	heat of phase change	ΔH
constant-volume heat capacity	$C_V = \left(\dfrac{dE}{dT}\right)_V$	isothermal compressibility	$\kappa_T = -\dfrac{1}{V}\left(\dfrac{dV}{dP}\right)_T = -\left(\dfrac{d\ln V}{dP}\right)_T$
constant-pressure heat capacity	$C_P = \left(\dfrac{dH}{dT}\right)_P$	thermal expansivity	$\alpha_P = \dfrac{1}{V}\left(\dfrac{dV}{dT}\right)_P = \left(\dfrac{d\ln V}{dT}\right)_P$

Thermodynamic calculus manipulations

name	applies to...	functional form	example
inversion	anything	$\left(\dfrac{dX}{dY}\right)_Z = 1\Big/\left(\dfrac{dY}{dX}\right)_Z$	$\left(\dfrac{dP}{dS}\right)_T = 1\Big/\left(\dfrac{dS}{dP}\right)_T$
triple product rule	anything	$\left(\dfrac{dX}{dY}\right)_Z\left(\dfrac{dZ}{dX}\right)_Y\left(\dfrac{dY}{dZ}\right)_X = -1$	$\left(\dfrac{dP}{dT}\right)_S = -\left(\dfrac{dS}{dT}\right)_P\Big/\left(\dfrac{dS}{dP}\right)_T$
Maxwell's relations	potential second derivatives	$\left(\dfrac{d^2F}{dXdY}\right) = \left(\dfrac{d^2F}{dYdX}\right) \rightarrow \left(\dfrac{dA}{dX}\right)_Y = \left(\dfrac{dB}{dY}\right)_X$	$\left(\dfrac{dS}{dP}\right)_T = -\left(\dfrac{dV}{dT}\right)_P$
addition of variable	anything	$\left(\dfrac{dX}{dY}\right)_Z = \left(\dfrac{dX}{dW}\right)_Z\Big/\left(\dfrac{dY}{dW}\right)_Z$	$\left(\dfrac{dH}{dS}\right)_P = \left(\dfrac{dH}{dT}\right)_P\Big/\left(\dfrac{dS}{dT}\right)_P = T$
potential transformation	potentials	$\dfrac{d(F_1/X)}{dX} = -\dfrac{F_2}{X^2}$	$\dfrac{d(A/T)}{dT} = -\dfrac{E}{T^2}$
nonnatural derivative	anything	$A(X,Y) \rightarrow \left(\dfrac{dA}{dY}\right)_Z = \left(\dfrac{dA}{dX}\right)_Y\left(\dfrac{dX}{dY}\right)_Z + \left(\dfrac{dA}{dY}\right)_X$	$\left(\dfrac{dE}{dV}\right)_P = \left(\dfrac{dE}{dS}\right)_V\left(\dfrac{dS}{dV}\right)_P + \left(\dfrac{dE}{dV}\right)_S = T\left(\dfrac{dS}{dV}\right)_P - P$

Note: Sometimes the notation U is used instead of E to indicate the thermodynamic internal energy.

Derivations and memory techniques

Triple product rule

Take, as an example, the function $P(T, V)$, although we could consider any state function. We know that the full differential is given by

$$dP = \left(\frac{dP}{dT}\right)_V dT + \left(\frac{dP}{dV}\right)_T dV$$

Now consider the case in which P is held constant, such that $dP = 0$. Then we can combine the differentials dT and dV *at constant P conditions.*

$$0 = \left(\frac{dP}{dT}\right)_V \left(\frac{dT}{dV}\right)_P + \left(\frac{dP}{dV}\right)_T$$

Rearranging and using the inversion rule gives the triple product rule:

$$\left(\frac{dP}{dT}\right)_V \left(\frac{dV}{dP}\right)_T \left(\frac{dT}{dV}\right)_P = -1$$

How can you remember this? It's simple. Starting with one partial derivative, just rotate the variables by putting the constant one in the numerator, the numerator in the denominator, and the denominator in the constant. Do two rotations and remember the product is -1.

Maxwell's relations

For constant N conditions, as we have discussed here, there is a particularly convenient way to remember all the Maxwell relationships without having to go through all the derivations each time (although you should always be able to do so!). It's called the "magic square". Here is what it looks like:

G	P	H
T		S
A	V	U

To get Maxwell relations from the magic square, you need to do draw arrows that swoop past the thermodynamic potentials along the side edges (not corners). Here is an example:

The arrows indicate that $\left(\frac{dS}{dP}\right)_T = -\left(\frac{dV}{dT}\right)_P$. They both start at the numerator and end at the constant value. The potential they swoop by is G, which is also the potential from which this Maxwell relation is

derived. The negative sign comes from the fact that G is in the top-left quadrant (think of it as negative x and positive y). Maxwell relations about U (E) also have a negative sign, but those for H and A do not.

To remember the order of the magic square, start at the top left hand corner and use the mnemonic "Great people have studied under very able teachers." (No egoism intended.)

Potential transformation

As an example, let's prove $\frac{d(A/T)}{dT} = -\frac{E}{T^2}$. To do this, start with the fact that

$$E = A + TS$$

Now, express S as the derivative of A:

$$E = A - T\left(\frac{dA}{dT}\right)_V$$

Divide both sides by T^2:

$$\frac{E}{T^2} = \frac{A}{T^2} - \frac{1}{T}\left(\frac{dA}{dT}\right)_V$$

Now, the RHS can be expressed as a derivative using the chain rule, giving finally:

$$\frac{E}{T^2} = -\left(\frac{d(A/T)}{dT}\right)_V$$

Nonnatural derivative

What if we know $E(S, V)$, but want to find $\left(\frac{dE}{dV}\right)_P$? Here, P is not one of the natural variables that can be held constant. We start by writing the full differential dE:

$$dE = \left(\frac{dE}{dS}\right)_V dS + \left(\frac{dE}{dV}\right)_S dV$$

Then, we divide through by the desired derivative, taken at constant P:

$$\left(\frac{dE}{dV}\right)_P = \left(\frac{dE}{dS}\right)_V\left(\frac{dS}{dV}\right)_P + \left(\frac{dE}{dV}\right)_S$$

Substituting in some definitions gives,

$$\left(\frac{dE}{dV}\right)_P = T\left(\frac{dS}{dV}\right)_P - P$$

This procedure works with any complete state function, even with nonnatural variables. For example, starting with $E(T, V)$, we could show:

$$\left(\frac{dE}{dV}\right)_P = \left(\frac{dE}{dT}\right)_V \left(\frac{dT}{dV}\right)_P + \left(\frac{dE}{dV}\right)_T$$

Carrying this a little further, to get to measurable variables:

$$\left(\frac{dE}{dV}\right)_P = \frac{C_V}{V\,\alpha_P} + T\left(\frac{dS}{dV}\right)_T - P$$

$$= \frac{C_V}{V\,\alpha_P} - T\left(\frac{dP}{dT}\right)_V - P$$

$$= \frac{C_V}{V\,\alpha_P} + T\left(\frac{dP}{dV}\right)_T \left(\frac{dV}{dT}\right)_P - P$$

$$= \frac{C_V}{V\,\alpha_P} + \frac{T\alpha_P}{\kappa_T} - P$$

Here, another nonnatural derivative was expanded in the first line, a Maxwell relation was used in the second, and the triple product rule was used in the third.