

Brief Thermal Physics Review

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Disclaimer: These are what I am personally making for my review, so I make no guarantee this is helpful, complete, or anything. Please tell me if anything is false on it or should be added. Good luck!

1 Kittel & Kroemer: Chapter 1 and 2

Derives statistical mechanics from the fundamental assumption. The assumption is: *Every particular state of a system is occupied with equal probability.* The number of available states with a given energy implies the maximum entropy principle.

- Accessible states: $g(N, U)$
- For multiple systems put together: $g = g_1 \cdot \dots \cdot g_n$
- Entropy: $S = k_B \sigma = k_B \log g$
- Temperature: $\tau = k_B T = (\partial U / \partial \sigma)_{N, V}$

2 Callen: Chapter 1

Goes over the very basics and tries to build an intuitive relationship between energy and entropy and other extensive parameters.

- **Postulate I.** *There exist particular states (called equilibrium states) of simple systems that, macroscopically, are characterized completely by internal energy U , the volume V , and the mole numbers N .*
- **Postulate II.** *There exists a function (called the entropy S) of the extensive parameters of any composite system, defined for all equilibrium states and having the following property: The values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.*
- **Postulate III.** *The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous and differentiable and is a monotonically increasing function of energy.*
- **Postulate IV.** *The entropy of any system vanishes in the state of zero temperature.*

Work and Heat: $dU = dQ + dW_M = TdS - PdV$

3 Callen: Chapter 2

Intensive parameters are those given by the partial derivatives of the fundamental relation. They are defined by the following:

$$\begin{array}{ll}
(\partial U/\partial S)_{V,N} \equiv T & (\partial S/\partial U)_{V,N} \equiv 1/T \\
(\partial U/\partial V)_{S,N} \equiv -P & (\partial S/\partial V)_{U,N} \equiv -P/T \\
(\partial U/\partial N)_{S,V} \equiv \mu & (\partial S/\partial N)_{U,V} \equiv \mu/T
\end{array}$$

$$dU = TdS - PdV + \mu dN \quad (1)$$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN \quad (2)$$

The chapter also goes over the conditions for equilibrium with heat flow, mechanical equilibrium, and equilibrium with matter flow. These are rather straightforward to derive, so they are omitted. (*Note: Stoichiometry is important when dealing with chemical equilibrium.*)

4 Callen: Chapter 3

Goes over Euler and Gibbs-Duhem relation then summarizes information about the fundamental relation. The chapter then covers ideal gases, Van der Waals fluid, radiation, and the rubber band. The last section goes over the preferred derivatives briefly (α, c_p, κ_T).

- Euler Relation: $U = TS - PV + \mu N$
- Gibbs-Duhem Relation: relations among the derivatives of U. The one for single-component system is $0 = SdT - VdP + Nd\mu$
- The fundamental relation contains all information about a thermodynamic system.
- Two equations of state [such as T,P] can determine the fundamental relation with an unknown constant using the Gibbs-Duhem relation.
- NOTE: The potentials given by Legendre Transformations are not fundamental relations!

5 Callen: Chapter 4

Covers possible processes, quasi-static processes, reversible processes, maximum work theorem, Carnot cycle, refrigeration, and Otto cycle.

- A process is possible if and only if $\Delta S \geq 0$ and the laws of mechanics are obeyed.
- Quasi-Static Process: idealized process where each state can be represented with the fundamental relation as an equilibrium state.
- There is a relaxation time τ between equilibrium states, which is the limit for a process to be *quasi-static*. (Usually related to the speed of sound.)
- Reversible Process: $\delta S_{Total} = 0$ *Note: Subsystems must still maximize entropy.*
- Maximum Work Theorem: reversible process with work extracted from the heat transferred between subsystems
- See *Figure 4.6* on page 115 for diagrams of engine, refrigerator, and heat pump.

Carnot Cycle:¹ A hot reservoir and cold reservoir are put into contact with a reversible work source. The following cycle is done:

¹I suggest googling this and reading wikipedia or another source.

1. Isothermal expansion
2. Isentropic (reversible adiabatic) expansion
3. Isothermal compression
4. Adiabatic reversible compression

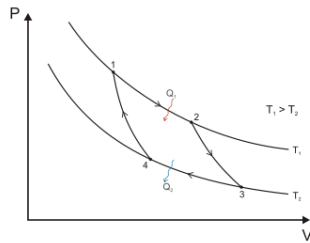


Figure 1: Carnot Cycle Pressure-Volume Plot

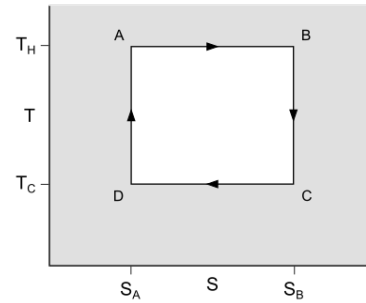


Figure 2: Carnot Cycle Temperature-Entropy Plot

Otto Cycle: Idealized cycle of a typical spark ignition piston engine often used in automobile engines. The following image sums it up:

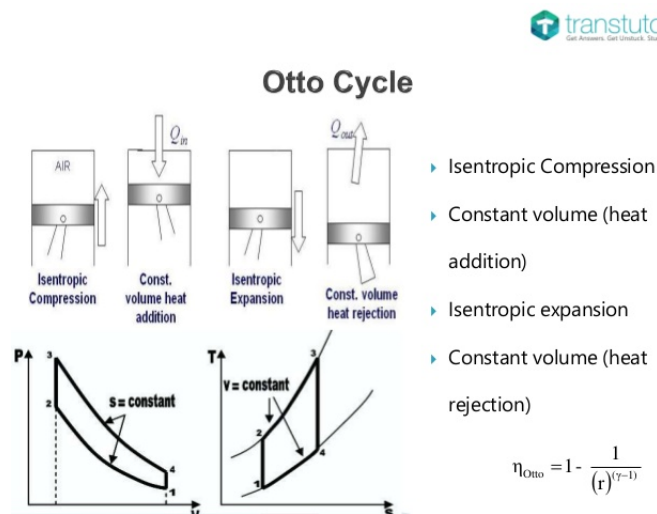


Figure 3: Otto Cycle Summary

6 Callen: Chapter 5

Covers the Energy Minimum Principle, Legendre Transformations, and the resulting potentials. These are developed because experimentation usually finds the intensive parameters easier to measure. The book also briefly goes over Massieu Functions (Legendre Transformations of the entropy), but this was not covered in class.

Energy Minimum Principle: The Entropy Maximum Principle implies a corollary principle for the minimization of internal energy in a system.

Legendre Transformations: The process replaces a number of the function's variables with the partial derivatives in those variables.

Helmholtz Potential or Free Energy $F \equiv U - TS \implies dF = -SdT - PdV + \mu_1dN_1 + \mu_2dN_2 + \dots$	
$U = U(S, V, N_1, N_2, \dots)$ $T = \partial U / \partial S$ $F = U - TS$ Elimination of U and S $F = F(T, V, N_1, N_2, \dots)$	$F = F(T, V, N_1, N_2, \dots)$ $-S = \partial F / \partial T$ $U = F + TS$ Elimination of F and T $U = U(S, V, N_1, N_2, \dots)$
Enthalpy $H \equiv U + PV \implies dH = TdS + VdP + \mu_1dN_1 + \mu_2dN_2 + \dots$	
$U = U(S, V, N_1, N_2, \dots)$ $-P = \partial U / \partial V$ $H = U + PV$ Elimination of U and V $H = H(S, P, N_1, N_2, \dots)$	$H = H(S, P, N_1, N_2, \dots)$ $V = \partial H / \partial P$ $U = H - PV$ Elimination of H and P $U = U(S, V, N_1, N_2, \dots)$
Gibbs Potential or Free Energy $G \equiv U - TS + PV \implies dG = -SdT + VdP + \mu_1dN_1 + \mu_2dN_2 + \dots$	
$U = U(S, V, N_1, N_2, \dots)$ $T = \partial U / \partial S$ $-P = \partial U / \partial V$ $G = U - TS + PV$ Elimination of U, V, and S $G = G(T, P, N_1, N_2, \dots)$	$G = G(T, P, N_1, N_2, \dots)$ $-S = \partial G / \partial T$ $V = \partial G / \partial P$ $U = G + TS - PV$ Elimination of G, P, and T $U = U(S, V, N_1, N_2, \dots)$

Grand-Canonical Potential	
$U[T, \mu] \equiv U - TS - \mu N \implies dU = -SdT - PdV - Nd\mu$	
$U = U(S, V, N_1, N_2, \dots)$ $T = \partial U / \partial S$ $\mu = \partial U / \partial N$ $U[T, \mu] = U - TS - \mu N$ Elimination of U, N, and S $U = U(T, P, \mu)$	$U = U(T, P, \mu)$ $-S = \partial U[T, \mu] / \partial T$ $-N = \partial U[T, \mu] / \partial \mu$ $U = U[T, \mu] + TS + \mu N$ Elimination of G, P, and T $U = U(S, V, N)$

7 Processes in Systems

Table 1: Types of Processes

Name	Meaning	Notes
Adiabatic	$\Delta N, \Delta Q = 0$	
Isobaric	$\Delta P = 0$	
Isochoric	$\Delta V = 0$	
Isothermal	$\Delta T = 0$	
Isentropic	$\Delta N, \Delta Q = 0$	Also reversible
Isenthalpic	$\Delta H = 0$	

Thermal Physics Through the Final

8 Main Potentials

Know these and when to use them. See Callen chapter 5 on Legendre Transformations.

General Minimum Principle for Legendre Transforms: The equilibrium value of any unconstrained internal parameter in a system in contact with a set of reservoirs (with intensive parameters P_1^r, P_2^r, \dots) minimizes the thermodynamic potential $U[P_1, P_2, \dots]$ at constant P_1, P_2, \dots equal to the reservoir values of that parameter.

Table 2: Four Main Potentials

Name	Symbol	Independent Variables	When?
Energy	U	S, V, N	
Helmholtz	F	T, V, N	Const. T
Enthalpy	H	S, P, N	Const. P
Gibbs	G	T, P, N	Const. T, P

9 Energy Minimum Principles

Callen: Chapter 6

- Know when to use each potential

One of the primary advantages of Legendre Transformations is the elimination of extensive parameters based on the system setup.

Table 3: Energy Minimum For Legendre Transforms

Name	Reservoir	Minimized Cond.	Usage
Helmholtz	T_r	$T_{sys} = T_r$	Many systems can be approximated as being in contact with the temperature reservoir of its surroundings.
Enthalpy	P_r	$P_{sys} = P_r$	Most systems have the atmospheric pressure as a reservoir but also ambient temperature, so the Gibbs is more useful in general.
Gibbs	P_r, T_r	$P_{sys} = P_r, T_{sys} = T_r$	This is the situation of most experiments in contact with the atmosphere.

10 Canonical Formalism

Kittel & Kroemer: Chapter 3

- Thermal reservoir
- Weighting of states
- When to use Canonical Formalism
- How to make partition function
- How to use partition function to get expectation values

10.1 Summary of Chapter

Consists of lots of definitions and derivations of thermal we learned in Callen.

Boltzmann Factor: $e^{-\epsilon/\tau}$ gives the relative probability of a given configuration with energy ϵ .

Partition Function (Z): The sum of boltzmann factors for all states s of a system, which allows the calculation of the absolute probability of a given configuration being occupied.

$$Z(\tau) = \sum_{all} e^{-\epsilon_s/\tau} \implies \mathbb{P}(\epsilon_s) = \frac{e^{-\epsilon_s/\tau}}{Z}$$

Convenient relations with partition function:

$$U = -\tau^2 \frac{\partial(F/\tau)}{\partial\tau} = \tau^2 \frac{\partial(\log Z)}{\partial\tau}$$

$$F = -\tau \log Z$$

Expectation Values: These are calculated in the normal way for probability mass functions. The interesting aspect is that these expectation values can be correlated with the macroscopic extensive variables observed.

$$\mathbb{E}(X) = \sum_{all} X_n \mathbb{P}(X_n)$$

11 Ideal Gas & Radiation in Canonical Formalism

Kittel & Kroemer: Chapter 4

- How to derive from Canonical Formalism
- "Basic" radiation flux laws

11.1 Ideal Gas

This is a gas of non-interacting atoms in the classical regime, which corresponds to high temperature and low particle density. The derivation uses Boltzmann factors with the energy of a particle being given by "particle in a box" equation with quantum numbers neglecting spin and structural properties. It assumes that the particles' orbitals do not match, so the particles are *not* identical.

Energy:

$$U = \frac{3}{2}N\tau = \frac{3}{2}Nk_B T$$

Ideal Gas Law:

$$pV = N\tau = Nk_B T$$

Summary of derivation:

1	$f(\epsilon) = \lambda e^{-\epsilon/\tau}$	Occupancy of an orbital in the classical limit.
2	$\lambda = \frac{N}{\sum e^{-\epsilon/\tau}}$	Given N, this equation determines λ in the limit.
3	$\epsilon_n = \frac{\hbar^2}{2M} \left(\frac{\pi n}{V^{1/3}} \right)^2$	Energy of free particle orbital of quantum number n in cube of volume V.
4	$\sum_n e^{-\epsilon_n/\tau} = \frac{\pi}{2} \int dn n^2 e^{-\epsilon/\tau}$	Transformation from sum to integral.
5	$\lambda = \frac{N}{n_Q V}$	Result of integration after substitution into (2).
6	$n_Q = (M\tau/2\pi\hbar^2)^{3/2}$	Definition of quantum concentration.
7	$\mu = \tau \log(n/n_Q)$	Expression for chemical potential.
8	$F = \int dN \mu(N, \tau, V) = N\tau [\log(n/n_Q) - 1]$	Helmholtz Potential is found in terms of known values.
9	$p = -(\partial F/\partial V)_{\tau, N} = N\tau/V$	And the final expression for the pressure is found.

Table 4: Derivation of Ideal Gas Law

11.2 Radiation

Describes the electromagnetic spectrum within a cavity in thermal equilibrium. A state with s photons has energy $\epsilon_s = s\hbar\omega$. The results are known as the Planck Distribution and the Stefan-Boltzmann Law. These results are similar to the results for phonons (see Debye theory) and electrical noise.

Partition Function: The expression of energy above is plugged in to get

$$Z = \sum_{s=0}^{\infty} e^{-s\hbar\omega/\tau}$$

Which has a form that lends itself to the substitution $x \equiv \exp -\hbar\omega/\tau$. The sum of x^s is $1/(1-x)$, so

$$Z = \frac{1}{1 - e^{-\hbar\omega/\tau}}$$

Planck Distribution Function: thermal average number of photons in a single mode of frequency ω . The result is

$$\langle s \rangle = \frac{1}{e^{\hbar\omega/\tau} - 1}$$

Thermal Average Occupancy: Calculated in the normal way to give

$$\langle \epsilon \rangle = \langle s \rangle \hbar\omega = \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1}$$

Stefan-Boltzmann Law of Radiation: Important part of this result is the τ^4 proportionality. The energy density is

$$\frac{U}{V} = \frac{\pi^2}{15\hbar^3 c^3} \tau^4$$

which can be manipulated to give the way it is normally written.

$$J_v = \sigma_B T^4 \quad \sigma_B \equiv \frac{\pi^2 k_B^2}{60\hbar^3 c^2}$$

Planck Radiation Law: Spectral density u_ω is the energy per unit volume per unit frequency range. Rewriting the distribution in terms of frequency gives this density as

$$u_\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/\tau} - 1}$$

12 Maxwell Relations & Derivative Reduction

Callen: Chapter 7

- Know steps for reducing derivatives
- Know derivative relationships and signs
- Given square on exam
- Know these are cross derivatives

There is a process to change the derivatives to a preferred set. This is mainly useful for reporting results and preferred derivatives being tabulated previously.

The Mnemonic Diagram This is constructed by labeling the sides with the four common potentials (F, G, H, U) in alphabetical order clockwise around the diagram. The corners are labeled with the intensive parameters (T, P) on the right top-to-bottom and the extensive parameters (V, S) on the left corners top-to-bottom. Two arrows are then added to point across each diagonal to the top. The sign of the derivative is indicated by the arrow, with an arrow pointing towards the natural variable implying a positive sign. The usage of it is indicated on the next figure.

13 Grand-Canonical Formalism

Kittel & Kroemer: Chapter 5

- Know the Gibbs Sum & Gibbs Factor
- Use thermal, chemical reservoir
- Construct Grand-Canonical partition function and compute expectation values

The Grand-Canonical Formalism is used to describe the states of a system in equilibrium with a thermal and chemical reservoir. The same arguments from the Canonical Formalism carries over.

Gibbs Factor: Gives the relative probability of a state s with occupation N_s and energy ϵ_s by

$$\exp [(N_s \mu - \epsilon_s) / \tau]$$

Gibbs Sum: (OR Grand-Canonical Partition Function) sums all of the Gibbs Factor so one can calculate the absolute probability of a given state.

$$\mathcal{Z} = \sum_{all} \exp [(N_s \mu - \epsilon_s) / \tau]$$

This gives the probability as

$$\mathbb{P}(x) = \frac{e^{(N_x \mu - \epsilon_x) / \tau}}{\sum_{all} e^{(N_s \mu - \epsilon_s) / \tau}}$$

The expectation values are calculated in the usual way.

Absolute Activity: Sometimes useful to use this lambda notation.

$$\lambda \equiv e^{\mu / \tau}$$

14 Fermi-Dirac & Bose-Einstein Distributions

Kittel & Kroemer: Chapter 6

- How to construct from Grand Canonical Formalism
- Will be given distribution, energy function, Fermi energy, etc. if needed

NOTE: Both distributions tend towards the same result in the high τ limit. This describes an "ideal gas", and it is the **Classical Distribution Function:**

$$f(\epsilon) \approx e^{(\mu - \epsilon) / \tau} = \lambda e^{-\epsilon / \tau}$$

14.1 Fermi-Dirac Distribution

Describes the distribution of fermions over energy states in a system. Fermions are 1/2 integer spin and obey Pauli Exclusion Principle (Either 0 or 1 particle occupying each state). The expectation value of the "Thermal Average Occupancy" $\langle N(\epsilon) \rangle$ in the Grand-Canonical Formalism gives the **Fermi-Dirac Distribution:**

$$\langle N(\epsilon) \rangle = f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon - \mu) / \tau} + 1}$$

Fermi Level: μ in this equation is often referred to by this name in Solid State Physics.

Fermi Energy: ϵ_F is the highest occupied energy value at $\tau = 0$

14.2 Bose-Einstein Distribution

Describes the distribution of bosons over energy states in a system. Bosons have integer spin and can occupy the same state without limit. The "Thermal Average Occupancy" $\langle N(\epsilon) \rangle$ in the Grand-Canonical Formalism for bosons gives the **Bose-Einstein Distribution**:

$$\langle N(\epsilon) \rangle = f_{BE}(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/\tau} - 1}$$

15 Degenerate Gas

Kittel & Kroemer: Chapter 7

- Using Fermi-Dirac Distribution in the low temperature limit
- How to use zero temperature Fermi-Dirac Distribution to find expectation values

Whenever $n \geq n_Q$ the gas is said to be in the quantum regime, which occurs at high density or low temperature. This is when there are more particles than available states at a given temperature. This is often called a **degenerate gas**³. The applications of this theory include:

- conduction electrons in metals⁴
- white dwarf stars
- liquid ³He
- nuclear matter
- phonons in solids

I do not like Kittel's treatment very much, but Dr. Townsley gave good notes in lecture. I highly recommend learning about Bose-Einstein condensates from the book or elsewhere since the class did not get to it. This concept is a big deal in some areas of physics (like Cooper pairs in Type I Superconductors).

Fermi Energy: This concept is revisited in this context. The energy of the highest filled orbital in the ground state of a free particle gas of fermions (will be given to us on exam) is

$$\epsilon_F = \frac{\hbar^2}{2M} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

Which can be used to find the total kinetic energy in the ground state as

$$U_0 = \frac{3}{5} N \epsilon_F$$

Fermi Temperature: $\tau_F = \epsilon_F$

Fermi Occupancy: n_F is the value of n in the expression of ϵ_F

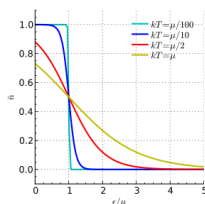


Figure 6: Behavior of Fermi-Dirac distribution at different temperatures.

³Otherwise called "zero-temperature gas", "ground state", or simply "fermi gas".

⁴This is most familiar to people most likely. I work in this area so am a bit biased towards this application.

Derivation from class: The energy of an un-bound electron in a "box" is

$$\epsilon_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2$$

We want the Average Occupancy $\langle N \rangle$. This is given by the sum of the Fermi-Dirac Distribution over all energies. This sum can be turned into an integral if the gaps between energy values is small enough, and a factor of two is added for the spin multiplicity.

$$\langle N \rangle = \int_{all} f_{FD}(\epsilon) d\epsilon = 2 \int_0^\infty \int_0^\infty \int_0^\infty f_{FD}(\epsilon) dn_x dn_y dn_z$$

One can note that the value of ϵ only depends on the magnitude of n , which lends itself to a conversion into pseudo-spherical coordinates in phase space $dn_x dn_y dn_z \rightarrow n^2 \sin\theta dn d\theta d\phi$. The quantum numbers are only positive, so the limits of integration correspond to the first octant. This is summarized below.

$$\left. \begin{array}{l} 0 \leq n_x \\ 0 \leq n_y \\ 0 \leq n_z \end{array} \right\} \implies \left. \begin{array}{l} 0 \leq n \\ 0 \leq \theta \leq \pi/2 \\ 0 \leq \phi \leq \pi/2 \end{array} \right\}$$

The figure above shows how the Fermi-Dirac Distribution approaches the behavior of a step function at zero temperature. This can be written as

$$f_{FD} = \begin{cases} 1, n < n_F \\ 0, n > n_F \end{cases}$$

Which makes the integral

$$\langle N \rangle = 2 \int_0^{n_F} \int_0^{\pi/2} \int_0^{\pi/2} f_{FD}(\epsilon) n^2 \sin\theta dn d\theta d\phi = \frac{\pi}{3} n_F^3 = N$$

This can be solved for $n_F = (3N/\pi)^{1/3}$ and put into the ϵ_F to get it in terms of N, V .

$$\epsilon_F = \frac{\hbar^2}{2M} (3\pi^2)^{2/3} \left(\frac{N}{V} \right)^{2/3}$$

Now, to get the expectation value for the energy $\langle U \rangle$, a similar procedure is followed.

$$\langle U \rangle = 2 \int_0^\infty \int_0^\infty \int_0^\infty \epsilon(n) f_{FD}(\epsilon) dn_x dn_y dn_z$$

Using the same change of coordinates

$$\langle U \rangle = 2 \int_0^{n_F} \int_0^{\pi/2} \int_0^{\pi/2} \epsilon(n) f_{FD}(\epsilon) n^2 \sin\theta dn d\theta d\phi = \frac{\pi^3 \hbar^2}{10mL^2} n_F^5$$

Which becomes the final result

$$U = \frac{3}{5} N \epsilon_F$$

Math Appendix

A Partial Derivative Relations

If you, like myself, find the derivative reduction process confusing, then I recommend reading the section in Appendix A of Callen called "Some Relations Involving Partial Derivatives." I summarize with the most useful relations below.

Begin with general function $\psi(x, y, z)$, and you can use the following relations between the partial derivatives:

$$\left(\frac{\partial y}{\partial x}\right)_{\psi, z} = \frac{-\left(\frac{\partial \psi}{\partial x}\right)_{y, z}}{\left(\frac{\partial \psi}{\partial y}\right)_{x, z}}$$

With similar expressions for the partials in the other derivatives. This is used to bring variable (usually S) out of the constants.

$$\left(\frac{\partial x}{\partial y}\right)_{\psi, z} = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_{\psi, z}}$$

This one is the most elementary looking, and it is usually used to bring S or V to the numerator.

$$\left(\frac{\partial y}{\partial x}\right)_{\psi, z} = \frac{\left(\frac{\partial y}{\partial u}\right)_{\psi, z}}{\left(\frac{\partial x}{\partial u}\right)_{\psi, z}}$$

Can be used to put T into the derivatives when using the standard set of derivatives.