GLOSSARY OF CONCEPTS FROM CLASSICAL THERMODYNAMICS
Branton Campbell, Physics 360
(updated 13 Feb 2023)

System – A thermodynamic *system* is a macroscopic quantity of physical matter comprising a statistically large number of microscopic entities (particles such as electrons, atoms or molecules) that can be distinguished from other systems.

Open System – a system that can exchange either matter or energy to the outside
Closed System – a system that can exchange energy but not matter to the outside
Isolated System – a system that can't exchange matter or energy to the outside

Property – We will refer to any physical macroscopic tensor quantity (e.g. scalar, vector, etc.) that can be defined for a system as a thermodynamic *property* of the system. These can be quantified with numerical values in a standard system of physical units.

Extensive Property – A property whose value increases linearly with the size of the system is said to be *additive* or *extensive* Examples, some of which will be defined below, include volume (V), internal energy (U), entropy (S), heat capacity (C_P or C_V), mole number (N), particle number ($\widetilde{N}$), total mass (M).

Intensive Property -- A property whose value is independent of sample size is said to be *intensive*. Examples, which will be defined below, include pressure (P), temperature (T) and chemical potential (μ).

Simple System – A system defined by only three extensive variables is called a simple system. Three is the smallest possible number of independent extensive variables that a system can have. They are mole number (N), volume (V), and either internal energy (U) or entropy (S).

Rational Property – An intensive property that has been defined as the ratio of two extensive properties can be referred to as *rational*. Common examples include *specific*, *volumetric*, *molar*, and *particular* ratios and densities. An extensive property (such as entropy S, internal energy U, or heat capacity C) divided by the total system mass (M) yields the corresponding *specific* intensivie property; an extensive property divided by the total volume (V) yields the corresponding *volumetric* intensive property; an extensive property divided by the total mole number (N) yields the corresponding *molar* intensive property; an extensive property divided by the total particle number ($\widetilde{N}$) yields the corresponding *particular* intensive property. Thus, molar heat capacity, particular heat capacity, specific heat capacity, and volumetric heat capacity are all related but still different. The tilde ãccent distinguishes particular ratios, the carot âccent distinguishes specific ratios, and the breve ăccent distinguishes volumetric ratios. While we probably won't encounter many of these quantities, we establish this convention in order to avoid ambiguity. On right side of table, employ common symbols for commonly encountered quantities, and use tilde when numerator or denominator is $\widetilde{N}$, or no accent otherwise.

Symbols to be used for various intensive property ratios and densities

	S	U	C	V	M	$\tilde{N}$	N
Molar	$s = \dfrac{S}{N}$	$u = \dfrac{U}{N}$	$c = \dfrac{C}{N}$	$v = \dfrac{V}{N}$	$m = \dfrac{M}{N}$	$N_A = \dfrac{\tilde{N}}{N}$	1
Particular	$\tilde{s} = \dfrac{S}{\tilde{N}}$	$\tilde{u} = \dfrac{U}{\tilde{N}}$	$\tilde{c} = \dfrac{C}{\tilde{N}}$	$\dfrac{1}{\tilde{n}} = \dfrac{V}{\tilde{N}}$	$\tilde{m} = \dfrac{M}{\tilde{N}}$	1	$\dfrac{1}{N_A} = \dfrac{N}{\tilde{N}}$
Specific	$\hat{s} = \dfrac{S}{M}$	$\hat{u} = \dfrac{U}{M}$	$\hat{c} = \dfrac{C}{M}$	$\dfrac{1}{\rho} = \dfrac{V}{M}$	1	$\dfrac{1}{\tilde{m}} = \dfrac{\tilde{N}}{M}$	$\dfrac{1}{m} = \dfrac{N}{M}$
Volumetric	$\check{s} = \dfrac{S}{V}$	$\check{u} = \dfrac{U}{V}$	$\check{c} = \dfrac{C}{V}$	1	$\rho = \dfrac{M}{V}$	$\tilde{n} = \dfrac{\tilde{N}}{V}$	$n = \dfrac{N}{V}$

Irreducible System – A system in which the properties are uniform and isotropic throughout is said to be *irreducible*. It is convenient to break a complex system (e.g. a deep column of a compressible liquid influenced by gravity, or a charged fluid in an external electric field) up into smaller (even infitesimal) systems that are irreducible.

Equilibrium States -- A irreducible system whose properties all have well-defined, time-independent, and history-independent values is said to be in an *equilibrium state* or a state of thermodynamic equillibrium. Callen's 1st postulate assumes the existence of such equilibrium states.

State Variable – The intensive and extensive properties of a system are well defined for any equilibrium state, and are therefore called *state variables* when used to uniquely identify a state. Because an equilibrium state is time-independent, the value of a state variable cannot depend on the system's history (i.e. how it reached that state). It generally takes several independent state variables to define the state of a system – at least three (U, V, N) in the simplest cases.

Internal Energy -- Any kinetic and potential energy attributed to the detailed momenta and positions of the microscopic constituents of a system, not including any energy contributions that can be attributed to macroscopic variables (e.g. macroscopic motion, interaction with external fields, etc), comprise the *internal energy*. This is where we sweep all of the energy terms that are too complicated to keep track of.

System Boundaries – A boundary that prevents heat from being transferred in or out of a system is called *adiabatic*, whereas a boundary that permits heat transfer is called *diathermal*. Two systems that share a diathermal boundary are said to be in thermal contact. A boundary that prevents work-energy from being transferred in or out of a system is called *rigid* or *immovable*, whereas a boundary that permits work-energy transfer is called *movable*. Two systems that share a movable boundary are said to be in mechanical contact. A boundary that prevents mass from being transferred in or out of a system is called *impermeable*, whereas a boundary that allows mass transfer is called *permeable*. Two systems that share a permeable boundary are said to be in chemical contact.

Mutual Thermal Equilibrium -- Two systems in thermal contact that experience zero net heat-energy transfer are said to be in *mutual thermal equilibrium*. Two systems in mechanical contact that experience zero net work-energy transfer are said to be in mutual mechanical equilibrium. Two systems in chemical contact that experience zero net mass transfer are said to be in mutual chemical equilibrium. For convenience, we often drop the word "mutual". Two objects in thermal equilibrium have the same temperature. Two objects in mechanical equilibrium have the same pressure. Two objects in chemical equilibrium have the same chemical potential.

Heat and Work -- *Heat* (ΔQ) is internal energy transferred into a system (from another system) via random kinetic collisions of the microscopic constituents at the boundary. We say that $\Delta Q > 0$ when heat energy flows into a system, causing U to increase, and $\Delta Q < 0$ when heat energy flows out of a system causing U to decrease. *Work* (ΔW) is the internal energy transferred into a system (from another system) due to a change in macroscopic volume. We say that $\Delta W > 0$ when the system is worked upon by an external force causing U to increase, or $\Delta W < 0$ when the system does work against an external force causing U to decrease.

Reservoir – Suppose that we place our system in some combination of thermal, mechanical, chemical or other contact with a large external system. If the external system is much larger than our system, the state of the external system will be approximately unaffected by the ensuing equillibration. In such a case, we refer to the external system as a *reservoir*. Being in equilibrium with a reservoir allows us to effectively constrain one or more of the intensive variables of our system. Thermal contact with a reservoir, for example, constrains the temperature of our system.

Internal Constraints – are mechanisms for creating a non-homogeneous configuration in the intensive variables of a system. Examples might be a partition that pushes all of the gas in a cylinder over to one side or that separates two different species of gas, a vibrating wall that creates a pressure wave, or an external gravitational field that creates a linearly-varying density.

Homogeneous Function – A function of the extensive variables of a system that is also extensive itself is said to be *homogeneous* to first-order, meaning that $S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$, where λ is a parameter that simply scales the size of the system.

Additive Function – A function of the extensive variables of a system is *additive* over its subsystems if $S(U, V, N) = \sum_i S_i(U_i, V_i, N_i)$, where $U = \sum_i U_i$, $V = \sum_i V_i$, and $N = \sum_i N_i$. An additive function of the extensive system variables must also be homogeneous to first order, and hence extensive itself.

Entropy -- Let Callen's postulates II-IV define the thermodynamic property called entropy.
- 2nd postulate : The entropy S is a function of the extensive variables of any composite system, defined for all equilibrium states, such that in the absence of an internal constraint, the extensive variables take the values that maximize this function over the manifold of internally-constrained equilibrium states.
- 3rd postulate: The entropy S of a system is additive over its subsystems (and therefore homogeneous to first order in its extensive system variables), and is also a differentiable (and therefore continuous) and monotonically-increasing function of the internal energy (U). This further implies that U is a differentiable and and monotonically-increasing function of S.

- 4th postulate: The entropy S goes to zero in the limit that $\partial U/\partial S$ goes to zero. Or more generally, if the ground state is degenerate as in some quantum systems, S goes to a non-zero constant value. We will later define $\partial U/\partial S$ to be temperature.

In statistical mechanics, the entropy will take on more intuitive meaning: a measure of the degeneracy of the system (i.e. the number of equivalent ways to configure the microscopic variables without changing the macroscopic variables) or the amount of information needed to describe the system.

Fundamental Relation – The expression of the entropy of a system in terms of a complete set of independent extensive state variables is called a *fundamental relation* (FR). As an example, the Sackur-Tetrode equation is a well-known fundamental relation for a monatomic idea gas. The FR contains everything there is to know about a thermodynamic system, which means that one can use it to compute expressions for all other thermodynamic system properties. Thermodynamic theory is not just about knowing the numerical value of the entropy, but rather about being able to express it in terms of the right variables. For example, an expression for the function $S(U, V, N)$ is an FR, while an expression for the function $S(T, V, N)$ is not. Note that any algebraic rearrangement of an FR is still an FR, so long as the variables appearing in the FR don't change.

Equation of State -- An equation relating two or more state variables of a system is called a *state relation* or an *equation of state*. Such a relation is well defined for any equilibrium state, independent of the history of the system. Consider that a first partial derivative of the energy (or entropy) provides a useful equation of state. The expression, $PV = NRT$, is a well-known equation of state for an ideal gas, which is obtained by taking first derivatives of the Sackur-Tetrode equation. Given a sufficiently complete list of state relations, one can reconstruct the fundamental relation to within an unknown integration constant.

Thermodynamic Laws -- If two systems with different values for the intensive state variables are brought into thermal contact, and possibly other types of contact (e.g. mechanical or chemical), so that the composite system undergoes a process resulting in equilibrium with respect to the affected intensive variables (e.g. temperature, pressure or chemical potential), what will be the final state of the composite system? The laws of thermodynamics have been formulated to allow us to answer this type of question.

Zeroth Law of Thermodynamics -- If system A is in thermal equilibrium with system B, and system B is in thermal equilibrium with system C, then system A is also in thermal equilibrium with system C. The same would hold for other types of thermodynamic equilibria (e.g. mechanical or chemical).

First Law of Thermodynamics -- The first law is often stated as $\Delta U = Q + W$ for a process occurring in a closed system, though one could also generalize it to include other mechanisms of energy transfer. This law merely recognizes that the internal energy of a system can be converted into other forms of energy and that total energy is strictly conserved.

Second Law of Thermodynamics -- One could argue that the existence of an entropy function with the properties specified by Callen's 2nd and 3rd postulates yields all other popular formulations of the second law as corollaries. These postulates embody a fairly technical statement of the 2nd law. Given the sublety of the thermodynamic definition of entropy, it's not hard to see why there a variety of more intuitive but seemingly disparate formulations. Here are a few examples.

(a) The total entropy of an isolated system can never decrease.
(b) The combined total entropy of a system and its environment (i.e. any other systems, including reservoirs, that it is in contact with) can never decrease.
(c) Heat cannot sponteously flow from a region of low temperature to a region of high temperature.
(d) A change in the entropy of a system obeys $dQ \leq TdS$, where equality only holds for a reversible process. Thus an irreversible process cannot be simultaneously adiabatic and isentropic.
(e) A system in a non-equilibrium state will evolve towards the equilibrium state consistent with the system constraints (because the equilibrium state maximizes the entropy).
(f) No heat engine can have the sole effect of converting heat energy into work – some heat energy must be wasted by transferring it to a lower-temperature entity.

Third Law of Thermodynamics -- Equivalent to Callen's 4th postulate: the entropy of a system approaches a constant value as temperature approaches zero. If the ground state of the system is non-degenerate, this value is zero.

Differential Fundamental Relation: When we isolate the internal energy on the left-hand side of the fundamental relation, we say that we are working with its *energetic representation*. For a simple system, the energetic *differential fundamental relation* is

$$dU(S,V,N) = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN = TdS - PdV + \mu dN,$$

which defines several important first derivatives.

Temperature $\quad T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$, the propensity to transfer heat away

Pressure $\quad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$, the propensity for volume to increase

Chemical Potential $\quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$, the propensity to transfer mass away

When we instead isolate the entropy on the left-hand side of the fundamental relation, we say that we are working with its *entropic representation*. For a simple system, the entropic *differential fundamental relation* is

$$dS(U,V,N) = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN,$$

which effectively defines the same first derivatives.

Conjugate Variables – Given the internal energy of a system as a function of its other extensive state variables, the first partial derivative with respect to any extensive variable yields an intensive variable such that the resulting external/internal variable pair have a special relationship. We refer to them as *conjugate variables* or *conjugate partners*. For example, entropy and temperature are a conjugate pair, as are volume and pressure, and also particle number and chemical potential.

Process -- A *process* is the state-space trajectory traversed by a system during a change of state. This trajectory may pass through both equilibrium and non-equilibrium states along the way; but we will assume that it begins and ends in equilibrium states.

Process Variable – parameters that can be used to define the evolution of a process. In addition to the intensive and extensive state variables of the system, these include the mechanical work done (W) and heat exchanged (Q). Process variables that are not state variables are allowed to be history dependent.

Process Relation – an equation relating two or more process variables of a specific process. It defines a trajectory through state space. Examples that apply to an ideal gas include $PV^\gamma = constant$ for quasi-static adiabatic expansion, and $PV = constant$ for isolated free expansion (which is adiabatic but irreversible).

Fixed-Variable Process -- a process that holds one or more process variables constant. Such processes are useful as thought experiments, and are also common in practice. Examples include isothermal ($\Delta T = 0$), adiabatic or isocaloric ($\Delta Q = 0$), isoenergetic or isolated ($\Delta U = 0$), isentropic ($\Delta S = 0$), isobaric ($\Delta P = 0$), isovolumetric or isochoric or isometric ($\Delta V = 0$), isenthalpic ($\Delta H = 0$), and constant-chemical-potential ($\Delta \mu = 0$) processes.

Equilibrium Process or Quasi-static Process -- A process that consists entirely of equilibrium states is called an *equilibrium* process. It can be viewed as a sequence of infitesimal and infinitely-slow steps, hence-the name *quasi-static*. Real processes are never truly equilibrium processes, as even small finite jumps throw the system out of equilibrium. But if the steps are sufficiently small and slow to allow equilibration after each step, then a quasi-static approximation can be quite accurate. For an incremental equilibrium process, the differential form of the fundamental relation ($dU = TdS - PdV + \mu dN$) allows us to express an incremental change in the internal energy in terms of the incremental state variables.

Reversible Process – When a process keeps the global entropy (system plus environment) constant, we say that it is *reversible* because it is then possible to return to the original state without violating the 2nd law. To be reversible, a process must also be quasi-static, though not all quasi-static processes are reversible. For a reversible process, the differential heat transferred to the system is computed as $dQ = TdS$, while the differential work done on the system is computed as $dW = -PdV$. Thus, heat and work can be computed as integrals over state variables along a specific trajectory in state space. Unlike the change in internal energy, which depends only on the endpoint states, heat and work are path dependent. The slow expansion of a thermally-isolated ideal-gas system under the influence of an external pressure control is a common example of a reversible process.

Irreversible Process -- If a process is not reversible, it causes the total entropy of the system and its environment to increase, and we say that the process is *irreversible*. In fact, the total entropy increase (ΔS) quantifies the degree of irreversibility. To run it backwards would violate the 2nd law. When an equilibrium process is irreversible, we can still use define the differential FR. But we must understand that $dQ < TdS$ and $-dW < PdV$ are strict inequalities arising from the 2nd law. The quasi-static free expansion of an isolated gas system ($dU = TdS - PdV = dQ = dW = 0$) is a common example of an irreversible process. See that it obeys the inequalities.

Non-Equilibrium States – If the properties of the system are changing at a finite rate (even if the change is very slow), then the system is in a *non-equilibrium state*. The simplest way to create a non-equilibrium state is to temporarily apply internal constraints and them suddenly remove them again, upon which the

system will slosh around through non-equillibrium states as it returns to equilibrium. A uniform *metastable* state, which lies in a local rather a global energy minimum (e.g. a supersaturated solution like carbonated water, or a room-temperature diamond crystal), is also a non-equilibrium state, and must overcome local energy barriers to achieve equilibrium. If the rate of the transformation towards equilibrium is very slow, we sometimes pretend that a metastable state is an equilibrium state. When we refer to a "state" without qualifiers, we are refer to an equilibrium state.

Non-Equlibrium Process – If a process traverses states that are not equilibrium states, then we call it a *non-equilibrium process*. A non-equilibrium process cannot be reversible – it always increases the global entropy. Typically, a discrete jump in a state variable will throw the system out of equilibrium, initiating a non-equilibrium process that evolves the system towards a new equilibrium state. For a non-equilibrium process, the differential form of the fundamental relation is not applicable because state variables are only defined for equilibrium states. Thus, the total heat transferred (ΔQ) and work done (ΔW) cannot be defined in terms of integrated state variables, and will not be straightforward to calculate. The energy difference (ΔU), however, still depends only on the endpoint states, not the path taken.

Spontaneous Process – a process that occurs spontaneously without external control. A spontaneous process is driven forward by the opportunity to maximize the global entropy (that of the primary system plus any contact reservoirs), and must therefore be irreversible.

Joule's Theorem states that for any two points in state space, there exists an adiabatic (but not necessarily reversible) process connecting the two points which is traversable in at least one direction. For a gas, start with the point of lower entropy and add entropy via irreversible isovolumetric stirring; then finish the task with reversible adiabatic compression or expansion.

Gibbs-Duhem Relation – While reservoir contact can allow one or more of the intensive variables to become indepdendent, it is always necessary to keep at least one independent extensive variable so that the system scale is variable. If all but one intensive state variable become independent, the last one will depend on the others. This is known as the *Gibbs-Duhem relation*, which can be expressed for a simple system as $-SdT + VdP - Nd\mu = 0$. It implies that the chemical potential can be expressed solely as a function of temperature and pressure: $\mu(T, P)$.

Euler Equation -- Because the internal energy is a homogenous function of its extensive variables, the differential form of the energetic fundamental relation can be integrated to obtain a functional relationship between all of the intensive and extensive variables: $U = \int(TdS - PdV + \mu dN) = TS - PV + \mu N$, where U, T, P and μ are all functions of (S, V, N).

Thermodynamic cycles – a sequence of thermodynamic processes that begins and ends at the same state. If the cycle includes non-equilibrium states, we assume that it can be approximated by a quasi-static trajectory over equilibrium states. All state variables, including thermodynamic potentials, experience zero net change over a complete cycle. Thus, $\Delta U = \Delta Q + \Delta W = 0$. For a reversible cycle, $\Delta Q = \oint TdS$ and $\Delta W = -\oint PdV$, which are computed as the areas of loops in state space (the sign matters). For an irreversible cycle, the magnitudes of the heat and work transfers must be smaller than the corresponding loop areas. An irreversible cycle can only be run in one direction; the reverse direction violates the 2nd

law. In a system with only three variables (S, V, N), the simple cycles are rectangular in one of the two-variable planes; these are the Ideal (P, V), Carnot (T,S), Brayton (P,S), Otto (S, V), Stirling (T,V) and Ericsson (P,T) cycles. The Diesel cycle is similar to the Otto cycle, but with isobaric rather than isovolumetric heating. A CW engine cycle in either the $P - V$ or $T - S$ plane converts heat to work and is called a *heat engine*. A heat engine has a limited theoretical *efficiency* $(e < 1)$. A CCW cycle in either plane converts work to heat and is called either a *refrigerator* or a *heat pump* depending on whether we value the heat removed from the low-T reservoir or the heat delivered to the high-T reservoir.

Carnot Engine – functions by extracting heat (Q_h) from a high-temperature (T_h) reservoir and passing part of it (Q_c) to a low-temperature (T_c) reservoir as wasted energy, while converting the difference into mechanical work (W). The efficiency is $\varepsilon = \dfrac{W}{Q_h} = 1 - \dfrac{Q_c}{Q_h} = 1 - \dfrac{T_c}{T_h}$. No heat engine operating between these same temperature reservoirs can have a higher efficiency than the Carnot engine.

Extremum Principles – For an isolated system, an adjustable internal constraint generates a manifold of non-equilibrium states (relative to the state that would exist without the constraint). Such a manifold can be defined in at least two ways: (1) restricted to have a constant global internal energy, or (2) restricted to have a constant global entropy. The constant energy case is physical because energy conservation is always respected – when we release an internal constraint, the system explores a constant energy manifold and finds the state with maximum entropy. This is the *maximum-entropy principle*. Over the manifold of internally-constrained constant entropy states, the global internal energy is minimized by the equilibrium state. This is the *minimum-energy principle*. The constant-entropy case may not be physically realizable in practice, but is still mathematically important.

Natural Variables – Contact with a reservoir effectively constrains one or more of the intensive properties of a system, making them independent rather than dependent variables. Because only one member of each conjugate pair can be independent in the FR, making an intensive variable independent through contact with a reservoir renders its conjugate extensive variable dependent in the FR. Because both the members of a conjugate pair are commonly referred as state variables, we will distinguish the independent state variables of a reservoir-constrained system by calling them *natural* state variables. The natural variables of an isolated simple system are S, V, and N; when in contact with a thermal reservoir, however, the natural variables are T, V, and N. Note that a system must always have at least one extensive natural variable with which to establish the system size.

Thermodynamic Potential –When a system is constrained by contact with a reservoir, the internal energy can be subjected to a Legendre transform with respect to the affected external variables, yielding a new *thermodynamic potential* that depends only on the new natural variables. The thermodynamic potential of an isolated system is the internal energy, which is a natural function of the extensive state variables, including the entropy. However, if we place a system in thermal contact with a reservoir, the new thermodynamic potential will be the Helmholtz potential, $F(T,V,N) = U - \dfrac{\partial U}{\partial S}S = U - TS$, which is a natural function of temperature rather than of entropy. In general terms, we can say that the expression of any thermodynamic potential in terms of its natural state variables is a fundamental relation. It is important to appreciate that any property of a system can be expressed in terms of partial derivatives (possibly n^{th}-order mixed partials) of a thermodynamic potential with respect to its natural state variables.

The table below summarizes the $2^3 = 8$ thermodynamic potentials of a simple 3-variable system, where $dW_{mech} = -PdV$, $dW_{chem} = \mu dN$, and $dW_{all} = dW_{mech} + dW_{chem}$. Observe that reservoir contact simplifies the differential form of the thermodynamic potential by excluding energy transfers associated with the constrained intensive variables – this tends to isolate a specific type of energy transfer. For simple systems: dU includes all forms of energy transfer, dF excludes heat transfer so as to isolate all useful work (mechanical and chemical), dG isolates chemical work, dH isolates heat transfer in a closed system, dL isolates mechanical work, etc.

Generic symbol	Natural variables	Traditional name/symbol	Definition			Differential form		Reversible process with reservoir contact
Φ	(S,V,N)	Internal (U)	U	$=$	$TS - PV + \mu N$	dU	$= TdS - PdV + \mu dN$	$dU = dW_{all} + dQ$
Φ_T	(T,V,N)	Helmholtz (F)	$U - TS$	$=$	$-PV + \mu N$	dF	$= -SdT - PdV + \mu dN$	$dF = dW_{all}$
Φ_P	(S,P,N)	Enthalpy (H)	$U + PV$	$=$	$TS + \mu N$	dH	$= TdS + VdP + \mu dN$	$dH = dW_{chem} + dQ$
$\Phi_{T.P}$	(T,P,N)	Gibbs (G)	$U - TS + PV$	$=$	μN	dG	$= -SdT + VdP + \mu dN$	$dG = dW_{chem}$
Φ_μ	(S,V,μ)		$U - \mu N$	$=$	$TS - PV$	$d\Phi_\mu$	$= TdS - PdV - Nd\mu$	$d\Phi_\mu = dW_{mech} + dQ$
$\Phi_{T,\mu}$	(T,V,μ)	Grand (L)	$U - TS - \mu N$	$=$	$-PV$	dL	$= -SdT - PdV - Nd\mu$	$dL = dW_{mech}$
$\Phi_{P,\mu}$	(S,P,μ)		$U + PV - \mu N$	$=$	TS	$d\Phi_{P,\mu}$	$= TdS + VdP - Nd\mu$	$d\Phi_{P,\mu} = dQ$
$\Phi_{T,P,\mu}$	(T,P,μ)	Total (K)	$U - TS + PV - \mu N$	$=$	0	dK	$= -SdT + VdP - Nd\mu$	$dK = 0$ (always)

Free Energy – The term *free energy* is applied to some thermodynamic potentials in the context of a process that isolates one or more forms of work. These include the Helmholtz, Gibbs and Grand potentials (a.k.a. free energies). If the natural reservoir variables are held constant, a reversible process over the remaining system variables will result in amount of work equal to $\Delta W_\Phi = \Delta \Phi$. Thus, we think of the free energy of a system as the *capacity of the system to do useful work*.

Degradation – Gaskell refers to an increase in the global entropy during an irreversible process as *degredation* in the sense that the potential of the system to do work is reduced. For system whose intensive reservoir contact variables are natural to thermodynamic potential Φ, let $-\Delta W_\Phi$ be the actual work isolated by Φ during a quasi-static process, and let $-\Delta W_\Phi^{max}$ be the maximum work that would be isolated by Φ if the same process were reversible. We can quantify the degradation as
$\Delta \mathcal{D} \equiv (-\Delta W_\Phi^{max}) - (-\Delta W_\Phi) = \Delta W_\Phi - \Delta W_\Phi^{max} > 0$, which is never negative, and is only zero for a reversible process. This is called the *maximum work theorem*: for all thermodynamic processes between the same initial and final state, the delivery of work is a maximum for a reversible process. When global entropy increases, we know that less than the maximum possible work was done by the process. Practical folk who value work might refer to such a process as a waste, a lost opportunity, or even a "crying shame". Note that when Φ is a free energy (i.e. T is a natural variable), we conveniently have $\Delta W_\Phi^{max} = \Delta \Phi$ and $\Delta \mathcal{D} = \Delta W_\Phi - \Delta \Phi$, so that degradation is directly associated with a free energy decrease that is not balanced by an equal amount of actual work done. Recall that the free expansion of an ideal gas has $\Delta U = \Delta Q = \Delta W = 0$ and $\Delta \mathcal{D} = \Delta W + \int PdV = \int PdV$, which typifies the worst-case scenario: entropy increases without accomplishing any beneficial work at all.

Curvature – The function $f(x,y,z)$ has positive (upward or convex) curvature with respect to x if $(\partial^2 f / \partial x^2)_{y,z} > 0$ and negative (downward or concave) curvature if $(\partial^2 f / \partial x^2)_{y,z} < 0$.

Generalized Extremum Principles – For systems in contact with reservoirs that hold temperature and possibly other intensive variables constant, the maximization of the local entropy of the primary system is not a general principle, nor is the minimization of the local internal energy. However, we can generalize the minimum-energy principle by defining a manifold of internally-constrained states that hold the reservoir-connected intensive variables constant rather than a manifold that holds the local entropy constant. The equilibrium state will then be the state that <u>minimizes the relevant local thermodyanamic potential</u> over the manifold of internally-constrained states whose intensive variables match those of the contacted reservoirs. This concept cuts right to the heart of practical thermodynamics, as it ensures the stability of the equilibrium state. Using the properties of partial derivatives, one can prove the minimum-thermodynamic-potential principle starting from entropy maximation, though the proof is somewhat beyond the scope of our course. One can do something similar with the maximization of generalized Massiu functions (Legendre transforms of the entropy).

LeChatlier's Principle – If the value of an unconstrained state variable p, with initial value p_i, is changed directly by an amount Δp_1, pushing the system out of equilibrium, the responses of other state variables will produce an indirect change Δp_2, such that the new equilibrium value will reflect the following inequality: $p_f - p_i = \Delta p_1 + \Delta p_2 < \Delta p_1$. In other words, the system reacts by sending the variable back in a direction opposite to the original change ($\Delta p_1 \, \Delta p_2 < 0$).

Maxwell Relation – a relationship that equates two mixed second-order mixed partial derivatives of a thermodynamic potential with respect to its natural variables, but is expressed in terms of first-order partial derivatives of first-order conjugate variables. These second derivatives are typically viewed as material properties (e.g. heat capacity, coefficient of thermal expansion, isothermal compressibility). The two partial derivatives in a Maxwell relation each contain a distinct pair of conjugate variables, wherein one variable sits in the numerator and its conjugate variable is held constant, while the variable in the denominator is the conjugate variable held constant on the other side of the relation. So if (A, A') and (B, B') are pairs of conjugate variables for which A' and B' are both first derivatives respect to natural variables of the same thermodynamic potential, $\left(\frac{\partial A'}{\partial B}\right)_A = \left(\frac{\partial B'}{\partial A}\right)_B$ is the corresponding Maxwell relation.

Phase diagram – a diagram over one or more intensive state variables that indicates the regions of stability for each of the thermodynamic phases than can achieved within the ranges illustrated. Independent state variables that are not varied in the diagram are assumed to be constant. Two-dimensional diagrams (e.g. temperature and pressure, or temperature and binary composition) are most common. Diagrams are often drawn to include metastable phases, based on a specific system history; but these aren't real thermodynamic phase diagrams, and cannot be rigorously interpreted.

Phase transition – the transition from one thermodynamic phase to another. This occurs when following a trajectory in state space that crosses a boundary between the regions of stability of two phases.

Order parameter – When the physical symmetries of the phases on either side of a phase transition are related (i.e. have a group-subgroup relationship or a common subgroup or supergroup), the changes to the system can be quantified using one or more tensor properties called *order parameters*. Order parameters are normally defined so as to be zero on one side of the transition and non-zero on the other. Examples include the scalar density for a liquid-gas transition, the electric polarization vector of a ferroelectric

transition, the magnetic moment pseudovector for a ferromagnetic transition, or the complex amplitude for a superconducting phase transition. The variation of the order parameter as a function of the intensive state variables is important. If the order parameter (a first derivative of the energy) is discontinuous at the transition, the transition will involve a latent heat, and we say that the transition is of *first order*. If the order parameter is continuous, buts its first derivative (a 2nd derivative of the energy) is discontinuous, the transition has no latent heat, and we say that it is *continuous* or of *second-order*. At a continuous phase transition, the order parameter and other related quantities (e.g. suspectibilities, heat capacity, correlation length, etc) have power-law dependencies on the reduced temperature: $\left(1 - \frac{T}{T_C}\right)^{\beta}$, where β is called a critical exponent.

Quantum Concentration – the concentration (n_Q) at which the average distance between particles is equal to the de Broglie wavelength of the particles. Above this concentration, quantum-statistical effects become important, and the fundamental relation becomes more complicated. Note that the Sackur-Tetrode equation for a ideal gas is only valid for $n < n_Q$.

Latent heat – the heat that must be added to or taken away from a system during a phase transition that occurs without changing the state variables. If heat must be added to the system, we say that the transition is *endothermic*. If heat must be taken away from the system, we say that the transition is *exothermic*. Latent heat is often presented as a specific (per unit mass) quantity.

Critical point – the termination point of a critical line of first-order phase transitions. The discontinuity of the order parameter along the critical line approaches zero at the critical point, where the transition becomes second order.

Triple point -- the point in the $T - P$ phase diagram of an atomic or molecular system where the gaseous, liquid, and solid phases all coexist. Not all systems have such a point. The triple point of H_2O is a common reference for both temperature and pressure measurements.

Lever rule – Consider a region of a binary phase diagram that contains a mixture of two phases, one being rich in atom type A and the other being rich in atom type B. The fraction of atom B in phase α is x_α and the fraction of atom B in phase β is x_β, whereas the overall fraction of atom B in the phase mixture is x_o. The *lever rule* relates the atom fractions in each phase to the phase fractions X_α and X_β: $X_\alpha = \frac{x_o - x_\beta}{x_\alpha - x_\beta}$ and $X_\beta = 1 - X_\alpha$. We can use either specific, volumetric, molar, or particular ratios for these fractions so long as the choice is consistent throughout the equation.

Gibbs phase rule: $F = C - \phi + 2$, where F is the dimensionality of the coexistence region, C is the number of chemical species present, and Φ is the number of coexisting phases. For the liquid-gas transition of water ($\phi = 2, C = 1$), $F = 1$ means that we have a coexistence line. For the triple point of water ($\Phi = 3, C = 1$), $F = 0$ means that we have only a coexistence point.

Clausius, Clausius-Clapeyron, and Antoine equations – The Clapeyron equation relates the slope of the $P - T$ coexistence curve to the molar latent heat (q) and the molar volume change (Δv) according to $\frac{dP}{dT} = \frac{q}{T \Delta v}$. For a liquid-gas transition, we can approximate $\Delta v \approx v_g = RT/P$ in the Claypeyron equation

and then integrate to obtain the Clausius-Clapeyron equation: $\log(P) = \log(P_\infty) - \frac{q/R}{T}$. This describes $P(T)$ along the liquid-gas coexistence line. Antoine's equation, $\log(P) = A - \frac{B}{C+T}$, is a more accurate but purely empirical relationship that works for both liquid-gas and solid-gas coexistence curves; one can add additional terms on the right-hand side to improve its accuracy.

****

I referred to a variety of textbooks and internet sources in compiling this axiomatic glossary of thermal physics. These include but are not limited to those listed below. Most entries are common knowledge and do not require specific citations, except where given. In some cases (e.g. rational variables), I created my own terminology.

- *Thermodynamnics and an Introduction to Thermostatistics* by H. B. Callen
- *Statistical and Thermal Physics* by H. Gould and J. Tobochnik
- *Thermodynamics* by H. J. Kreuzer and I. Tamblyn
- *Introduction to the Thermodynamics of Materials* by D. R. Gaskell
- *An Introduction to Thermal Physics* by D. V. Schoeder
- Concepts in Thermal Physics by S. J. Blundell and K. M. Blundell.
- wikipedia.com, hyperphysics.com, physics.about.com
- http://web.mit.edu/16.unified/www/FALL/thermodynamics/notes