

Basic thermodynamics

These notes are an abbreviated form of the first part of the book by Callen (Thermodynamics, Wiley, 1960) which is more lucid than most thermodynamic texts.

1. Description of a thermodynamic system

Thermodynamics is a macroscopic description of the state of a body, we shall focus on thermal properties in the following. We initially consider "simple" systems which are macroscopically homogeneous, isotropic, uncharged, and chemically inert, that are sufficiently large that surface effects can be neglected and that are not acted on by electric or magnetic fields.

For such a system, the volume, V , is the relevant mechanical parameter. The system also has a distinct chemical composition specified by "mole numbers" (the numbers of molecules of each chemical component, divided by Avogadro's number). The mole number, N_k of the k 'th chemical component can be computed as the ratio of its mass to its "molar mass" (the mass of Avogadro's number of molecules). Note that volume and mole numbers are "extensive" quantities and scale with size of the system. You will also often hear about "mole fractions". If we have r chemical components then the mole fraction of the k 'th component is just

$$\frac{N_k}{\sum_{j=1}^r N_j} \quad (1)$$

Macroscopic systems have definite and precise energies, subject to a definite conservation principle. Only differences of energy, rather than absolute values have physical significance. Internal energy is an extensive quantity and is given the symbol U in Callen.

2. Thermodynamic Equilibrium

It is generally observed that isolated systems evolve spontaneously to simple terminal (equilibrium) states. The thermodynamics that we develop here applies to these "equilibrium states" though branches of thermodynamics have been developed to handle non-equilibrium states. We introduce the first postulate of thermodynamics:

Postulate I. There exist particular states – equilibrium states – of simple systems that are characterized completely by the internal energy U , the volume V , and the mole numbers N_k of the chemical components

(Note that as more complicated systems are allowed, the number of parameters describing the system will increase.)

For an equilibrium state, the properties of the system must be independent of the history of the system. In reality, few systems are in true equilibrium – in such a system, for example, all radioactive elements would have completely decayed – but many systems are in metastable equilibrium which is sufficient for our purposes.

3. Walls and constraints

A wall that constrains an extensive parameter of a system to a definite value is said to be "restrictive" wrt that parameter, whereas a wall that allows the parameter to vary freely is "non-restrictive" wrt that parameter. Thus a wall that is impermeable to a chemical species is restrictive for the mole number of that species.

Consider a wall that does not allow the transfer of energy in the form of heat. Such walls are called "adiabatic" while walls which do allow the flow of heat are called "diathermal". If a wall allows the flux of neither work or heat, it is restrictive wrt energy. If a system is enclosed by a wall that is restrictive to energy, volume, and mole numbers, the system is said to be "closed".

There exist walls (adiabatic) with the property that the work done in taking an adiabatically enclosed system between two given states is determined entirely by the initial and final states, independent of all external conditions. The work done is the difference in the internal energy of the two states.

The heat flux to a system in any process (at constant mole number) is simply the difference in internal energy between the final and initial states diminished by the work done in that process. In an infinitesimal quasi-static process (i.e. one that effectively remains in equilibrium at all times), the quasi static heat is therefore given by

$$\bar{d}Q = dU + PdV \quad (2)$$

where the bar indicates an imperfect differential (i.e., it is not the differential of some hypothetical function Q). Remember that the mechanical work done is given by $\bar{d}W = -PdV$.

We shall generally consider closed systems but ones that are composite of two or more simple systems. Constraints that prevent the flow of energy, volume, or matter between the sub-systems are called "internal" constraints. If a closed composite system is in equilibrium wrt certain internal constraints, and if some of these constraints are removed, the system eventually comes into a new equilibrium state.

4. The Entropy Maximum Postulate

From our experience with many physical theories, we might expect that the attainment of equilibrium involves extremising some property of the system. Thus, we expect that the values of the extensive parameters in the equilibrium state are simply those that maximise some function.

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 any internal constraint are those that maximise the entropy over the manifold of constrained equilibrium states

The relation which gives the entropy as a function of the extensive parameters is known as a "fundamental relation". Once the fundamental relation of a particular system is known, all conceivable thermodynamic information about the system can be derived.

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 the energy

Thus, the total entropy of a composite system is

$$S = \sum_{\alpha} S^{\alpha} \quad (3)$$

where $S^\alpha = S^\alpha(U^\alpha, V^\alpha, N_k^\alpha)$. The monotonic property described above is written as:

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} > 0 \quad (4)$$

We shall see that the above derivative is related to the reciprocal of the temperature. The above postulates suggest that the entropy function can be inverted wrt energy so the function

$$S = S(U, V, N_k) \quad (5)$$

can be solved uniquely for U :

$$U = U(S, V, N_k) \quad (6)$$

These two equations are alternative forms of the fundamental relation.

The final postulate is

Postulate IV. The entropy of any system vanishes in the state where $(\partial U/\partial S)_{V,N} = 0$ – that is, at the zero of temperature though this isn't used in the majority of thermodynamics.

5. Intensive Parameters

Consider the equation $U = U(S, V, N_k)$ and compute the first differential

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N_1,\dots} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N_1,\dots} dV + \sum_j \left(\frac{\partial U}{\partial N_j}\right)_{V,N_k,\dots} dN_j \quad (7)$$

The partial derivatives are called intensive parameters and the following notation is conventional

$$\left(\frac{\partial U}{\partial S}\right)_{V,N_1,\dots} = T \quad (8)$$

(the temperature)

$$-\left(\frac{\partial U}{\partial V}\right)_{S,N_1,\dots} = P \quad (9)$$

(the pressure)

$$\left(\frac{\partial U}{\partial N_j}\right)_{V,N_k,\dots} = \mu_j \quad (10)$$

(the chemical potential of the j 'th component)

Thus

$$dU = TdS - PdV + \sum_j \mu_j dN_j \quad (11)$$

In the case of constant mole numbers, we find that

$$\bar{d}Q = TdS \quad (12)$$

Thus a quasi-static heat flux into a system results in an increase in entropy. The temperature, pressure, and chemical potentials are implicitly functions of the extensive parameters (since they are the derivatives of a function of the extensive parameters). Thus

$$T = T(S, V, N_k), \quad P = P(S, V, N_k) \quad (13)$$

etc. Such expressions relating intensive parameters to independent extensive parameters are called "equations of state".

All of the above analysis could have been conducted on $S = S(U, V, N_k)$ and we would end up with a different set of intensive parameters (called the entropic intensive parameters). Which approach is more useful depends on the problem at hand.

6. Thermal equilibrium – temperature

Consider a closed composite system consisting of two simple systems separated by a wall that is rigid and impermeable to matter but which allows the flow of heat. The volumes and mole numbers of the systems are fixed but the energies U^1 and U^2 are free to vary subject to the constraint

$$U^1 + U^2 = \text{constant} \quad (14)$$

At equilibrium, $dS = 0$ and

$$dS = \left(\frac{\partial S^1}{\partial U^1} \right)_{V,N} dU^1 + \left(\frac{\partial S^2}{\partial U^2} \right)_{V,N} dU^2 \quad (15)$$

or

$$dS = \frac{1}{T^1} dU^1 + \frac{1}{T^2} dU^2 \quad (16)$$

But $dU^1 = -dU^2$ so

$$dS = \left(\frac{1}{T^1} - \frac{1}{T^2} \right) dU^1 = 0 \quad (17)$$

so $T^1 = T^2$ – the temperatures are the same.. The analysis can be extended to show that heat flows from regions of high temperature to regions of low temperature.

We adopt the convention that entropy is dimensionless so temperature has the dimensions of energy – though they have different units. Temperature is measured using the absolute Kelvin scale so that ratios of temperatures behave correctly (unlike, say, the Celsius scale)

7. Mechanical equilibrium.

A slightly different analysis can be used for mechanical equilibrium where we consider a closed composite system consisting of two simple systems separated by a moving impermeable diathermal wall. The values of energy and volume of the subsystems may change subject to the closure conditions: $U^1 + U^2 = \text{constant}$ and $V^1 + V^2 = \text{constant}$. Differentiating S and setting $dS = 0$ as we did above we find that

$$dS = \left(\frac{1}{T^1} - \frac{1}{T^2} \right) dU^1 + \left(\frac{P^1}{T^1} - \frac{P^2}{T^2} \right) dV^1 = 0 \quad (18)$$

which has to be true for any value of dU^1 and dV^1 so $T^1 = T^2$ as before and therefore $P^1 = P^2$. In the presence of a movable wall, the pressures are the same when in equilibrium.

8. Chemical equilibrium

Consider the equilibrium state of two simple systems connected by a rigid diathermal wall which is permeable to only one chemical component and impermeable to all others. With the usual closure conditions we find that

$$dS = \left(\frac{1}{T^1} - \frac{1}{T^2} \right) dU^1 + \left(\frac{\mu_1^1}{T^1} - \frac{\mu_1^2}{T^2} \right) dN^1 = 0 \quad (19)$$

which has to be true for any value of dU^1 and dN^1 so $T^1 = T^2$ as before and therefore $\mu_1^1 = \mu_1^2$. It is also straightforward to show that matter tends to flow from regions of high chemical potential to regions of low chemical potential.

9. The Euler equation

Since the fundamental relation is homogeneous and first order, it is true that, for any λ

$$U(\lambda S, \lambda V, \lambda N_k) = \lambda U(S, V, N_k) \quad (20)$$

Differentiating with respect to λ and setting $\lambda = 1$ (since the equation must be valid for any value of λ) gives

$$U = TS - PV + \sum_j \mu_j N_j \quad (21)$$

Differentiating the above equation gives

$$dU = TdS + SdT - PdV - VdP + \sum_j \mu_j dN_j + \sum_j d\mu_j N_j \quad (22)$$

but we also have (equation 11)

$$dU = TdS - PdV + \sum_j \mu_j dN_j \quad (23)$$

so subtraction gives

$$SdT - VdP + \sum_j d\mu_j N_j = 0 \quad (24)$$

Note that at fixed P and T we get $\sum_j d\mu_j N_j = 0$ which is the "Gibbs-Duhem" relation. For a single component system

$$SdT - VdP + Nd\mu = 0 \quad \text{or} \quad d\mu = -\frac{S}{N}dT + \frac{V}{N}dP \quad (25)$$

Clearly the variation in chemical potential is not independent of the variations of temperature and pressure. Generally, if a fundamental relation is in $t+1$ extensive variables, there are only t independent intensive variables. The number of intensive parameters capable of independent variation is called the

"thermodynamic degrees of freedom" of a given system. A simple system of r components has $r + 1$ thermodynamic degrees of freedom.

It is always possible to express the internal energy as a function of parameters other than S , V , and N – however such a relation is not fundamental and not all thermodynamic properties can be derived from it.

10. Specific heats and other derivatives

Many of the first derivatives of the extensive parameters have important physical significance – in the following, we assume constant mole numbers. For example, the thermal expansion:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (26)$$

The isothermal compressibility:

$$\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (27)$$

The specific heat at constant pressure:

$$C_p = \frac{T}{N} \left(\frac{\partial S}{\partial T} \right)_P \quad (28)$$

The specific heat at constant volume:

$$C_v = \frac{T}{N} \left(\frac{\partial S}{\partial T} \right)_V \quad (29)$$

Later – we shall see there are relationships between these – the so-called Maxwell relations.

11. Reversible and irreversible processes.

Though all real processes are irreversible, there are cases where the increase in entropy may be arbitrarily small. Such processes are called "reversible". They consist of a succession of equilibrium states with no states of larger entropy. A process is said to be irreversible if it is associated with an increase in entropy. Entropy cannot decrease in a closed system.

12. Reformulations of the basic theory – Legendre transforms

The fundamental equation of a thermodynamic system can be written with either the entropy or the energy as the dependent quantity. It is possible to show that the principle of maximum entropy can be replaced by a principle of minimum energy. The entropy maximum principle characterizes the equilibrium state as one having maximum entropy for a given total energy. The energy minimum principle characterizes the state as having minimum energy for a given total entropy. Formally:

Entropy Maximum Principle: The equilibrium value of any unconstrained internal parameter is such as to maximise the entropy for the given value of the total internal energy.

Energy Minimum Principle: The equilibrium value of any unconstrained internal parameter is such as to minimise the energy for the given value of the total entropy.

Reconsider the problem of thermal equilibrium – we considered a closed composite system with an internal rigid impermeable membrane. The fundamental equation in the energy representation is

$$U = U^1(S^1, V^1, N_k^1) + U^2(S^2, V^2, N_k^2) \quad (30)$$

Taking the differential of this gives (since all V and N are fixed):

$$dU = T^1 dS^1 + T^2 dS^2 \quad (31)$$

The energy minimum condition is that $dU = 0$ subject to fixed total entropy ($S^1 + S^2 = \text{constant}$) so

$$dU = (T^1 - T^2) dS^1 = 0 \quad (32)$$

giving us the same condition that $T^1 = T^2$.

In the energy and entropy representations, the extensive parameters play the roles of independent variables whereas the intensive variables are derived quantities. In practice, it is often easiest to measure the intensive variables (e.g., P and T). This is particularly true for temperature and entropy since no practical instruments exist for the control of entropy whereas control of temperature is commonplace. It therefore becomes advantageous to recast the formalism with intensive parameters replacing extensive parameters as mathematically independent variables. The way this is done is with the use of Legendre transforms. Formally, we are given the fundamental relation of the form

$$Y = Y(X_0, X_1, \dots, X_t). \quad (33)$$

It is desired to find a method where the derivatives:

$$P_k \equiv \frac{\partial Y}{\partial X_k} \quad (34)$$

can be considered as independent variables. A geometrical solution to this problem is given in Callen. The Legendre transform of the fundamental relation is

$$\psi = Y - \sum_k P_k X_k \quad (35)$$

Taking the differential of this gives

$$d\psi = - \sum_k X_k dP_k \quad (36)$$

whence

$$-X_k = \frac{\partial \psi}{\partial P_k} \quad (37)$$

In thermodynamics, the Legendre transformed functions are called "thermodynamic potentials". We consider first the Helmholtz potential, F , (or "free energy") which is a partial Legendre transform of U to replace the entropy with temperature. Thus we go from $U = U(S, V, N_k)$ to

$$F = U - TS \quad (38)$$

where we have used equation (35). The differential is given by

$$dF = -SdT - PdV + \sum_k \mu_k dN_k \quad (39)$$

so now we can see that $F = F(T, V, N_k)$ as desired. The Helmholtz free energy is useful as the fundamental relation for modelling mineral physics data which are taken as a function of volume and temperature.

Another useful potential is the "enthalpy", H , which is a partial Legendre transform of U that replaces the volume by pressure. Remembering that $P = -\partial U/\partial V$, the transform becomes

$$H = U + PV \quad (40)$$

with the differential

$$dH = TdS + VdP + \sum_k \mu_k dN_k \quad (41)$$

whence $H = H(S, P, N_k)$.

A final potential is the "Gibbs Free Energy", G , which is the Legendre transform of U which simultaneously replaces the entropy with temperature and the volume with pressure:

$$G = U - TS + PV \quad (42)$$

with the differential

$$dG = -SdT + VdP + \sum_k \mu_k dN_k \quad (43)$$

whence $G = G(T, P, N_k)$. The Gibbs free energy commonly crops up in phase diagram calculations

The question now arises as to what is the extremum principle for each of these potentials. Callen shows that they are:

Helmholtz free energy minimum principle: The equilibrium value of any unconstrained internal parameter in a system in diathermal contact with a heat reservoir minimizes the Helmholtz free energy at constant temperature (the temperature of the reservoir)

Enthalpy minimum principle: The equilibrium value of any unconstrained internal parameter in a system in contact with a pressure reservoir minimizes the enthalpy at constant pressure (the pressure of the reservoir)

Gibbs free energy minimum principle: The equilibrium value of any unconstrained internal parameter in a system in contact with a temperature and pressure reservoir minimizes the Gibbs free energy at constant temperature and pressure (equal to those of the respective reservoirs)

The general result is now clear:

The equilibrium value of any unconstrained internal parameter in a system in contact with a set of reservoirs (with intensive parameters P_k^r) minimizes the thermodynamic potential $U(P_k)$ at constant P_k (with P_k equal to P_k^r).

The Helmholtz free energy is very convenient in problems where the temperature is held fixed – clearly this reduces the number of variables in the problem. Note: the work delivered in a reversible process by a system in contact with a heat reservoir is equal to the decrease in the Helmholtz potential. For this reason, F is sometimes referred to as the available work at constant temperature – or the Helmholtz free energy.

The enthalpy is convenient when the pressure is held constant. This is often the experimental case so the enthalpy representation can be useful in practice. The enthalpy also acts as a potential for work for systems held at constant pressure. At constant pressure and composition then

$$dH = TdS = \bar{d}Q \quad (44)$$

so heat added to a system at constant pressure and composition appears as an increase in enthalpy.

The Gibbs free energy is most convenient when both temperature and pressure are held constant. G measures the work available in a reversible process from a system at constant T and P which is why it is called the "Gibbs free energy". The Gibbs free energy is closely related to the chemical potential. From the equations for U (21) and G (42) above we find that

$$G = \sum_k \mu_k N_k \quad (45)$$

For a single component system, $\mu = G/N$ which is the molar Gibbs free energy.

13. Maxwell's relations

These relations come from looking at mixed second derivatives. Consider the case for fixed composition then:

$$\left(\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right)_S \right)_V = \left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right)_V \right)_S \quad (46)$$

Thus using equations (8) and (9), we have

$$-\left(\frac{\partial P}{\partial S} \right)_V = \left(\frac{\partial T}{\partial V} \right)_S \quad (47)$$

Using the Helmholtz free energy

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V} \right)_T \right)_V = \left(\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T} \right)_V \right)_T \quad (48)$$

but from (39) at constant composition $(\partial F/\partial V)_T = -P$ and $(\partial F/\partial T)_V = -S$ so

$$\left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T \quad (49)$$

Using the enthalpy gives

$$\left(\frac{\partial}{\partial S} \left(\frac{\partial H}{\partial P} \right)_S \right)_P = \left(\frac{\partial}{\partial P} \left(\frac{\partial H}{\partial S} \right)_P \right)_S \quad (50)$$

but from (41) at constant composition $(\partial H/\partial P)_S = V$ and $(\partial H/\partial S)_P = T$ so

$$\left(\frac{\partial V}{\partial S} \right)_P = \left(\frac{\partial T}{\partial P} \right)_S \quad (51)$$

Using the Gibbs free energy

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right)_P = \left(\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right)_T \quad (52)$$

but from (43) at constant composition $(\partial G/\partial P)_T = V$ and $(\partial G/\partial T)_P = -S$ so

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \quad (53)$$

(47), (49), (51), and (53) are the usual Maxwell relations for a constant composition. Though, of course, compositional relations can also be derived (see Callen).

14. Relations between macrostates and microstates

This section derives some results from statistical physics which we shall need later on in the course.

The essential concept is that, for any given macrostate, at the microscopic scale, the system can be in a large number of different configurations and is constantly flipping from one to another. Each of these configurations is called a microstate.

The statistical weight of a macrostate, denoted by $\Omega(E, V, N)$, is the number of microstates comprising that macrostate with specified V, N and having energy in the small energy interval E to $E + \delta E$. We shall subsequently choose δE sufficiently small that there is only one discrete energy level in the energy interval. Note that all such microstates that satisfy the constraints on E, V, N are considered equally likely to occur.

The equilibrium state is the one of maximum probability and thus corresponds to the state of maximum statistical weight. Entropy is related to the statistical weight through the definition

$$S(E, V, N) = k \ln \Omega(E, V, N) \quad (54)$$

so entropy is also maximized in the equilibrium state. Consider a system in a heat bath. The system possesses a discrete set of microstates with energy E_r . We choose δE to be smaller than the energy spacing between microstates so the energy interval contains only one energy level – but many different microstates. The probability, p_r that the energy will be E_r is proportional to the number of microstates compatible with this energy. Suppose the heat bath has energy E_0 then the states of the heat bath having an energy in the interval $E_0 - E_r$ to $E_0 - E_r + \delta E$ is

$$p_r = \text{const} \times \Omega(E_0 - E_r) = \frac{\Omega(E_0 - E_r)}{\sum_r \Omega(E_0 - E_r)} \quad (55)$$

Given equation (54), we can write p_r as

$$p_r = \text{const} \times \exp[S(E_0 - E_r)/k] \quad (56)$$

where S is the entropy of the heat bath. Expanding the argument of the exponential in a Taylor series gives

$$\frac{1}{k} S(E_0 - E_r) = \frac{S(E_0)}{k} - \frac{E_r}{kT} + \dots \quad (57)$$

where we have used the fact that $\partial S/\partial E = 1/T$ (where T is the temperature of the heat bath). The neglect of higher order terms in the expansion is justified because they represent change in temperature of the heat bath due to exchange of heat with the system. By the definition of a heat bath, these are negligible. Substitution of (57) into (56) and including all constant terms into the pre-exponential gives

$$p_r = \frac{1}{Z} e^{-E_r/kT} \quad \text{with} \quad Z = \sum_r e^{-E_r/kT} \quad (58)$$

which we shall use later in the course. Z is called the partition function. It is also possible to show that

$$S = -k \sum_r p_r \ln p_r \quad (59)$$

For an isolated system with energy in the interval E to $E + \delta E$ there are Ω different microstates with energy E_r in the interval. The probability of finding the system in one of those states, p_r , is $1/\Omega$. Assuming all allowable microstates are equally likely and using the fact that $\sum_r p_r = 1$, we immediately recover equation (54) from equation (59).

If we now substitute equation (58) into equation (59) we find that

$$S = k \ln Z + \frac{\sum_r p_r E_r}{T} \quad (60)$$

where $\sum_r p_r E_r$ is the mean energy of the system, E . Comparing with the definition of the Helmholtz free energy: $F = E - TS$, we find that

$$F = -kT \ln Z \quad (61)$$

which is a very important relationship between the macroscopic Helmholtz free energy and the microscopic partition function.

15. Change in notation

In the notes following, we divide all extensive quantities (U, S, V) by mass and typically use the symbol E for energy per unit mass. Note that now $1/V = \rho$, the density.