

1 Laws of thermodynamics

1.1 First and second laws of thermodynamics

Thermodynamics is a science concerning the state of a system when interacting with the surroundings; it is based on two laws of nature, the first and second laws of thermodynamics. The interactions can involve exchanges of any combinations of heat, work, and mass between the system and the surroundings, dictated by the boundary conditions between the system and the surroundings. The first law of thermodynamics describes those interactions, while the second law of thermodynamics governs the evolution of the state inside the system. Consequently, the combination of the first and second laws of thermodynamics provides an integration of the external and internal parts of a system.

A system typically consists of many chemical components. The first law of thermodynamics states that the exchanges of heat, work, and individual components with the surroundings must obey the law of conservation of energy. In the domain of materials science and engineering, the energy of interest is at the atomic and molecular levels. The energies at higher and lower levels such as nuclear energy and the kinetic and potential energies of a rigid body are usually excluded from the discussion of the thermodynamics of materials.

Let us consider a system receiving an amount of heat, dQ , an amount of work, dW , and an amount of each independent component i , dN_i , from the surroundings. Such a system is called an open system in contrast to a closed system when $dN_i = 0$ for all components, i.e. there is no exchange of mass between the system and the surroundings. Other types of systems commonly defined in thermodynamics include adiabatic systems, those without exchange of heat, i.e. $dQ = 0$, and isolated systems, those without exchange of any kind, i.e. $dQ = dW = dN_i = 0$.

The corresponding change of energy in the system, i.e. the internal energy change, dU , is formulated in terms of the first law of thermodynamics as follows,

$$dU = dQ + dW + \sum H_i dN_i \quad 1.1$$

where H_i is the unit energy of component i in the surroundings, and the summation is for all components in the system which can be controlled independently from the surroundings, i.e. the independent components of the system.

It is self-evident that the left-hand side of Eq. 1.1 refers to the change inside the system, while its right-hand side is for the contributions from the surroundings to the

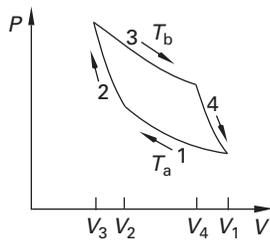


Figure 1.1 Schematic diagram of the Carnot cycle, from [1] with permission from Cambridge University Press.

system. In principle, no matter how the heat and mass are added, or how work is done to the system, as long as their summation is the same the change of the internal energy from the first law of thermodynamics will be the same, indicating that for a closed system the system always reaches the same state. The internal energy is thus a state function in a closed system as it does not depend on how the state is reached.

On the other hand, for the purpose of easy mathematical treatment, a reversible process can be considered for a closed system, in which the initial state of the system can be restored reversibly without any net change in the surroundings. Therefore, the heat transferred and the work done to the system are identical to the heat and work lost by the surroundings and vice versa. The classic example of reversible processes is the Carnot cycle, which is shown in Figure 1.1. It consists of four reversible processes for a closed system. The four reversible processes are compression at constant temperature T_1 (isothermal), compression without heat exchange (adiabatic) ending at T_2 , isothermal expansion at T_2 , and adiabatic expansion ending at T_1 .

The Carnot cycle involves a simple type of mechanical work, either hydrostatic expansion or compression, with the work that the surroundings does to the system represented by

$$dW = -PdV \quad 1.2$$

with P being the external pressure that the surroundings exerts on the system and V the volume of the system. It is now necessary to differentiate the external and internal variables for further discussion, with the former representing variables in the surroundings and the latter representing variables in the system. For the isothermal processes in the Carnot cycle, the entropy change of the system, dS , can be defined as the heat exchange divided by temperature:

$$dS = \frac{dQ}{T} \quad 1.3$$

In addition to processes involving heat, work, and mass exchanges between the system and the surroundings, there can be internal processes taking place inside the system. As the system cannot do work to itself, the criterion for whether an internal process can occur spontaneously must be related to the heat exchange, which is related to the entropy change as shown by Eq. 1.3.

1.2 Law of thermodynamics and equilibrium conditions

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It is a known fact that heat will spontaneously transfer from a higher temperature (T_2) region to a lower temperature (T_1) region inside a system if heat conduction is allowed, and this process is irreversible because heat cannot be conducted from a low temperature region to a high temperature region spontaneously. Equation 1.3 indicates that for the same amount of heat change, the entropy change at T_1 is higher than that at T_2 , and the heat conduction thus results in a positive entropy change in the system, i.e.

$$\Delta S = -\frac{dQ}{T_2} + \frac{dQ}{T_1} = \frac{dQ}{T_2 T_1} (T_2 - T_1) > 0 \quad 1.4$$

Consequently, the second law of thermodynamics is obtained, which states that for an internal process to take place spontaneously, or irreversibly, this internal process (ip) must have positive entropy production, which can be written in differential form as follows:

$$d_{ip}S > 0 \quad 1.5$$

From the definition of entropy change shown by Eq. 1.3, the amount of heat produced by this irreversible internal process can be calculated as follows:

$$d_{ip}Q = T d_{ip}S \quad 1.6$$

Let us represent this internal process by $d\zeta$ and define the driving force for the internal process by D . The work done by this internal process is thus $Dd\zeta$, which is released as heat, i.e.

$$Dd\zeta = d_{ip}Q = T d_{ip}S \quad 1.7$$

An irreversible process thus must have a positive driving force in order for it to take place spontaneously.

1.2 Combined law of thermodynamics and equilibrium conditions

For a system with an irreversible internal process taking place, the entropy change in the system consists of three parts: the heat exchange with the surroundings, defined by Eq. 1.3, the entropy production due to the internal process, represented by Eq. 1.5, and the entropy of mass exchange with the surroundings. The total entropy change of the system can thus be written as follows:

$$dS = \frac{dQ}{T} + d_{ip}S + \sum S_i dN_i \quad 1.8$$

where S_i is the unit entropy of component i in the surroundings, often called the partial entropy of component i , which will be further discussed in Chapter 2.

Combining Eq. 1.7 and Eq. 1.8 and re-arranging, one obtains

$$dQ = TdS - Dd\zeta - \sum TS_i dN_i \quad 1.9$$

Inserting Eq. 1.2 and Eq. 1.9 into Eq. 1.1 yields the combined law of thermodynamics from the first and second laws of thermodynamics,

$$dU = TdS - PdV + \sum (H_i - TS_i)dN_i - Dd\zeta \quad 1.10$$

The internal energy of the system is thus a function of the variables S , V , N_i and ζ of the system, which are called natural variables of the internal energy, i.e. $U(S, V, N_i, \zeta)$. The other variables are dependent variables and can be represented by partial derivatives of the internal energy with respect to their respective natural variables with other natural variables kept constant, as shown below:

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, N_i, \zeta} \quad 1.11$$

$$-P = \left(\frac{\partial U}{\partial V} \right)_{S, N_i, \zeta} \quad 1.12$$

$$\mu_i = H_i - TS_i = \left(\frac{\partial U}{\partial N_i} \right)_{S, V, N_{j \neq i}, \zeta} = U_i \quad 1.13$$

$$-D = \left(\frac{\partial U}{\partial \zeta} \right)_{S, V, N_i} \quad 1.14$$

In Eq. 1.13, a new variable, μ_i , is introduced. This is called the chemical potential and is defined as the internal energy change with respect to the addition of the component i when the entropy, volume, and the amount of other components of the system are kept constant. It may be worth pointing out that for a system at equilibrium, i.e. $d_{ip}S = 0$, and with constant entropy, $dS = 0$, if the system exchanges mass with the surroundings, $dN_i \neq 0$, then it must also exchange heat with the surroundings at the same time in order to keep the entropy invariant as demonstrated by Eq. 1.8.

The pairs of natural variables and their corresponding partial derivatives are called conjugate variables, i.e. S and T , V and $-P$, N_i and μ_i , and ζ and $-D$. There are minus signs in front of P and D as the increase of volume and the progress of the internal process decrease the internal energy of the system. The importance of this conjugate relation will be evident when various forms of combined thermodynamic laws and various types of phase diagrams are introduced.

The last pair of conjugate variables, ζ and $-D$, is worthy of further discussion. Based on the second law of thermodynamics, i.e. Eq. 1.5, no internal processes take place spontaneously if there is no entropy production, i.e. $D \leq 0$ or $d\zeta = 0$ and $D > 0$. With $D \leq 0$, there is no driver for any internal processes, and the system is in a full equilibrium state. The last term in Eq. 1.10 drops off, and ζ becomes a dependent variable of the system and can be calculated from the equilibrium conditions. With $d\zeta = 0$ and $D > 0$, the system is under a constrained equilibrium or freezing-in condition when the internal process is constrained not to take place, and ζ remains an independent variable of the system.

These two cases represent the two branches of thermodynamics: equilibrium, i.e. reversible, thermodynamics and irreversible thermodynamics. It is clear from the above

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discussions that these two branches are identical if the internal energy is not only a function of S , V , and N_i , but is also a function of any internal process variable ζ . This means that one should be able to evaluate the internal energy of a system for any freezing-in equilibrium conditions in addition to the full equilibrium conditions. In the rest of the book, freezing-in equilibrium and full equilibrium are not differentiated unless specified.

As the mechanical work under hydrostatic pressure is very important in experiments, let us define a new quantity called the enthalpy as follows:

$$H = U + PV \quad 1.15$$

Its differential form can be obtained from Eq. 1.1 as

$$dH = dU + d(PV) = dQ + VdP + \sum H_i dN_i \quad 1.16$$

There are two significant consequences of the above equation. First, for a closed system under constant pressure, i.e. $dN_i = dP = 0$, one has $dH = dQ$. This implies that the enthalpy change in a system is equal to the heat exchange between the system and the surroundings of the system, which is why enthalpy and heat are often used interchangeably in the literature. Second, for an adiabatic system under constant pressure, i.e. $dQ = dP = 0$, Eq. 1.16 can be re-arranged to the following equation:

$$H_i = \left(\frac{\partial H}{\partial N_i} \right)_{N_{j \neq i}, dQ=dP=0} \quad 1.17$$

The quantity H_i is thus the partial enthalpy of component i and will be further discussed in Chapter 2. The chemical potential of component i defined in Eq. 1.13 is thus related to the partial enthalpy and partial entropy of the component.

To further define the equilibrium conditions of a system, consider a homogeneous system in a state of internal equilibrium, i.e. no spontaneous internal processes are possible with $Dd\zeta = 0$ and Eq. 1.10 becomes

$$dU = TdS - PdV + \sum \mu_i dN_i = \sum Y_i dX_i \quad 1.18$$

where X represents S , V , N_i , and Y represents their conjugate variables T , $-P$, μ_i . The state of the system with c independent components is completely determined by $c + 2$ variables, i.e. S , V , and N_i with i ranging from 1 to c .

To simplify the situation, let us limit the discussion to an isolated equilibrium system, i.e. $dU = 0$, and conduct a virtual internal experiment inside the system by moving an infinitesimal amount of X_i , dX_i , with other X_j kept constant, from one region of the system to another region of the system as schematically shown in Figure 1.2.

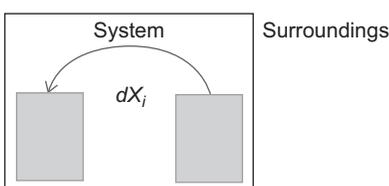


Figure 1.2 Virtual experiment for a system at equilibrium.

As the system is homogeneous and at equilibrium, $-dX'_i = dX''_i = dX_i$. The total change of the internal energy for this internal process is the combination of the changes in the two regions, i.e.

$$dU = dU' + dU'' = Y'_i dX'_i + Y''_i dX''_i = (-Y'_i + Y''_i) dX_i = 0 \quad 1.19$$

Therefore, $Y'_i = Y''_i$ for T , $-P$, and μ_i , indicating that T , $-P$, and μ_i are homogeneous in the system, respectively, and are thus named as potentials of the system. Furthermore, these potentials are independent of the size of the system and are often referred to as intensive variables in the literature. On the other hand, all X , i.e. S , V , and N_i , are proportional to the size of the system and can be normalized with respect to the size of the system, usually in terms of the total number of moles,

$$N = \sum N_i \quad 1.20$$

They are thus called molar quantities and are often referred to as extensive variables, and the respective normalized variables are molar entropy, molar volume, and mole fractions, defined as follows:

$$S_m = \frac{S}{N} \quad 1.21$$

$$V_m = \frac{V}{N} \quad 1.22$$

$$x_i = \frac{N_i}{N} \quad 1.23$$

Consider a small subsystem in this homogeneous system at equilibrium and let the subsystem grow in size. The entropy, volume, and mass enclosed in the subsystem increase as follows:

$$dS = S_m dN \quad 1.24$$

$$dV = V_m dN \quad 1.25$$

$$dN_i = x_i dN \quad 1.26$$

The corresponding change in the internal energy of the subsystem becomes

$$dU = TdS - PdV + \sum \mu_i dN_i = \left(TS_m - PV_m + \sum \mu_i x_i \right) dN = U_m dN \quad 1.27$$

By integration one obtains the integral form of the internal energy as

$$U = \left(TS_m - PV_m + \sum \mu_i x_i \right) N = U_m N = TS - PV + \sum \mu_i N_i \quad 1.28$$

Similarly, the molar enthalpy can be defined as follows:

$$H = U + PV = U_m N + PV_m N = (U_m + PV_m) N = H_m N \quad 1.29$$

In the case when a potential is not homogeneous in a system, the system will not be in a state of equilibrium. Let us consider the same virtual experiment as shown in Figure 1.2 for an isolated system that is not in equilibrium, i.e. by moving an infinitesimal amount of X_i , dX_i , with other X_j kept constant, from one region of the system to another region of the system with the two regions having different potentials. The total internal energy change is equal to zero as the virtual experiment has $dU = 0$. Similarly, each region can be considered to be homogeneous by itself, and one has $-dX'_i = dX''_i = dX_i$. The total internal energy change in the system is thus the sum of that for these two regions plus the entropy production due to the internal process with $d\zeta = dX_i$, i.e.

$$dU = dU' + dU'' + Dd\zeta = Y'_i dX'_i + Y''_i dX''_i + Dd\zeta = (-Y'_i + Y''_i) dX_i + Dd\zeta = 0 \quad 1.30$$

Consequently, one obtains the following:

$$D = Y'_i - Y''_i \quad 1.31$$

The driving force thus represents the difference of the potential at the two regions, and the internal process acts to eliminate inhomogeneity of the potential by means of heat transfer from high temperature regions to low temperature regions, or volume shrinkage of low pressure regions (high $-P$) and volume expansion of high pressure regions (low $-P$), and/or the transport of components from high chemical potential regions to low chemical potential regions.

1.3 Stability at equilibrium and property anomaly

As shown by Eq. 1.19, potentials are homogenous for a homogeneous system in a state of internal equilibrium. To study the stability of the equilibrium state, one considers the entropy production due to a fluctuation of a molar quantity as an internal process. Based on the second law of thermodynamics, the driving force, as the first derivative of the entropy production with respect to the internal process, is zero for such a fluctuation at equilibrium, i.e. $D = 0$, and the entropy of production thus depends on the second derivative. It can be written as follows in terms of Taylor expansion:

$$Td_{ip}S = \frac{\partial_{ip}S}{\partial\zeta} d\zeta + \frac{1}{2} \frac{\partial_{ip}^2 S}{\partial\zeta^2} (d\zeta)^2 = Dd\zeta - \frac{1}{2} D_2 (d\zeta)^2 \quad 1.32$$

with $D_2 = -\partial_{ip}^2 S / \partial\zeta^2$. When $\partial_{ip}^2 S / \partial\zeta^2 < 0$ or $D_2 > 0$ along with $D = 0$, the fluctuation does not produce positive entropy of production and thus cannot develop further. The equilibrium state of the system is therefore stable against the fluctuation. On the other hand, when $\partial_{ip}^2 S / \partial\zeta^2 > 0$ or $D_2 < 0$ along with $D = 0$, the fluctuation creates positive entropy of production and can continue to grow. The equilibrium state of the system is therefore unstable against the fluctuation. In connection with Eq. 1.8, one can realize that for a system at stable equilibrium without heat and mass

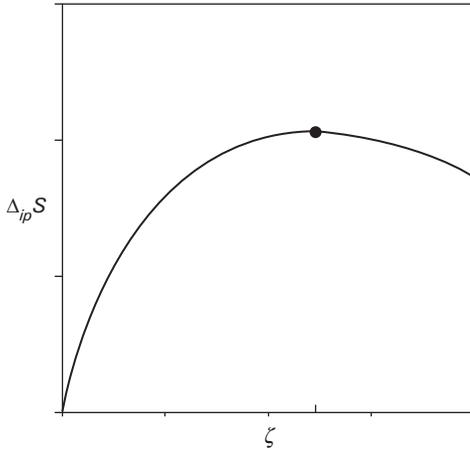


Figure 1.3 Schematic diagram showing maximum entropy, from [1] with permission from Cambridge University Press.

exchange with the surroundings, its entropy is at its maximum and there are no other internal processes which could produce any more entropy. This is schematically shown in Figure 1.3.

Using Eq. 1.10, Eq. 1.18, and Eq. 1.32, the combined law of thermodynamics can be written as

$$dU = \sum Y_i dX_i - Dd\zeta + \frac{1}{2}D_2(d\zeta)^2 \quad 1.33$$

Let us carry out the same virtual internal experiment as in Section 1.2, i.e. moving an infinitesimal amount of X_i in an isolated homogenous system with the other X_j kept constant, i.e. $dU = 0$ and $D = 0$. The internal energy change due to this internal process is

$$dU = \frac{1}{2}D_2 \left\{ (dX'_i)^2 + (dX''_i)^2 \right\} \quad 1.34$$

For a homogeneous system in a state of stable equilibrium with $(dX'_i)^2 = (dX''_i)^2 = (dX_i)^2$, this internal process must result in an increase of internal energy, $dU > 0$, and thus gives

$$D_2 = 2 \left(\frac{\partial^2 U}{\partial X_i^2} \right)_{X_j} = 2 \left(\frac{\partial Y_i}{\partial X_i} \right)_{X_j} > 0 \quad 1.35$$

Equation 1.35 shows that for a system to be stable, any pair of conjugate variables must change in the same direction when other independent molar quantities are kept constant. For the conjugate variables discussed so far, this means that for a stable system, the addition of entropy increases with temperature if $\partial T / \partial S > 0$, the volume decreases with pressure or increases with the negative of pressure if $\partial(-P) / \partial V > 0$, and the chemical

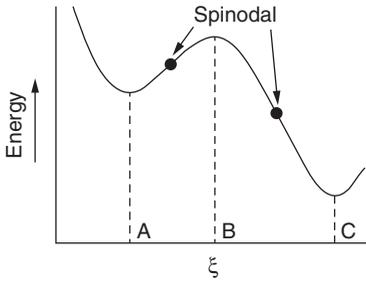


Figure 1.4 Schematic diagram showing the metastable (A), unstable (B), and stable (C) equilibrium states.

potential of a component increases with the amount of the component, i.e. $\partial\mu_i/\partial N_i > 0$, where the derivatives are taken with all other molar quantities kept constant. The limit of stability is reached when Eq. 1.35 becomes zero, i.e.

$$D_2 = 2 \left(\frac{\partial Y_i}{\partial X_i} \right)_{X_j} = 0 \quad 1.36$$

Figure 1.4 shows schematically the energy as a function of configuration including three states: unstable, stable, and metastable. Both the stable and metastable states have positive curvatures due to $D_2 > 0$, while the unstable state has a negative curvature due to $D_2 < 0$. There is an inflection point, at which $D_2 = 0$, for a state between a stable or metastable state with $D_2 > 0$ and an unstable state with $D_2 < 0$. These two inflection points, called spinodal, represent the limit of stability. The states between the two inflection points are unstable, and the other states are either stable or metastable. The two inflection points can move apart from or close to each other depending on the change of external conditions, i.e. the natural variables. One extreme situation is when these two inflection points merge into one point, and the instability occurs only at this particular point. It is evident that then all three states, stable, metastable, and unstable, also merge into one point. This point is called the critical or consolute point, beyond which the instability no longer exists.

To mathematically define the consolute point, the third derivative needs to be added to Eq. 1.32 because both D and D_2 vanish at this point, i.e.

$$Td_{ip}S = \frac{\partial_{ip}S}{\partial \xi} d\xi + \frac{1}{2} \frac{\partial_{ip}^2 S}{\partial \xi^2} (d\xi)^2 + \frac{1}{6} \frac{\partial_{ip}^3 S}{\partial \xi^3} (d\xi)^3 = Dd\xi - \frac{1}{2} D_2 (d\xi)^2 + \frac{1}{6} D_3 (d\xi)^3 \quad 1.37$$

$$dU = \sum Y_i dX_i - Dd\xi + \frac{1}{2} D_2 (d\xi)^2 - \frac{1}{6} D_3 (d\xi)^3 \quad 1.38$$

At the consolute point, the third derivative also becomes zero, i.e.

$$D_3 = \frac{\partial_{ip}^3 S}{\partial \xi^3} = 0 \quad 1.39$$

Let us further discuss the properties of the system in relation to the critical point. By taking the inverse of the equation for the limit of stability, Eq. 1.36, one obtains

$$\left(\frac{\partial X_i}{\partial Y_i}\right)_{X_j} = +\infty \quad 1.40$$

i.e. all X_i quantities diverge at the critical point. Therefore, when a system approaches the critical point from its stable region, the change of a molar quantity with respect to its conjugate potential varies dramatically and becomes infinite at the critical point, resulting in property anomalies in the system. In the unstable region, the system will thus separate into stable subsystems and become heterogeneous, and the X_i will change discontinuously between subsystems. In the stable region, the change of a molar quantity with respect to its conjugate potential decreases as the system moves away from the critical point and remains positive due to the stability criterion denoted by Eq. 1.35.

However, it is not clear how a molar quantity changes with respect to a non-conjugate potential at the critical point. From the Maxwell relation, one has

$$\left(\frac{\partial Y_i}{\partial X_j}\right)_{X_{k \neq j}} = \frac{\partial^2 U}{\partial X_i \partial X_j} = \left(\frac{\partial Y_j}{\partial X_i}\right)_{X_{k \neq i}} \quad 1.41$$

$$\left(\frac{\partial X_j}{\partial Y_i}\right)_{X_{k \neq j}} = \left(\frac{\partial X_i}{\partial Y_j}\right)_{X_{k \neq i}} \quad 1.42$$

Since all the X_i diverge at the critical point, both derivatives in Eq. 1.42 should also go to infinity at the critical point. To investigate their signs, let us carry out a virtual experiment similar to that used to derive the stability condition (Eq. 1.34 and Eq. 1.35). In this case, two internal processes are needed for moving two molar quantities simultaneously in an isolated system, i.e.

$$dU = -D_{\xi_1} d\xi_1 - D_{\xi_2} d\xi_2 + D_{\xi_1 \xi_2} d\xi_1 d\xi_2 + \frac{1}{2} D_{2\xi_1} (d\xi_1)^2 + \frac{1}{2} D_{2\xi_2} (d\xi_2)^2 \quad 1.43$$

Based on the above discussions, in a stable system at equilibrium with $D_{\xi_1} = D_{\xi_2} = 0$, $D_{2\xi_1} > 0$, and $D_{2\xi_2} > 0$, the sign of $D_{\xi_1 \xi_2}$ cannot be unambiguously determined when keeping the change of internal energy positive, i.e. $dU > 0$. This indicates that the quantities in Eq. 1.41 can be either positive or negative in the stable region and become zero at the critical point. By the same token, the quantities in Eq. 1.42 can be either positive or negative and become either positive or negative infinity at the critical point.

A profound conclusion from this analysis is that in a stable system, even though a molar quantity always changes in the same direction as its conjugate potential, the same molar quantity may change in the opposite direction to a non-conjugate potential, resulting in additional anomalies represented by Eq. 1.40. One example of Eq. 1.42 is the thermal expansion in a closed system, i.e. $dN_i = 0$, as follows

$$\left(\frac{\partial V}{\partial T}\right)_S = \left(\frac{\partial S}{\partial(-P)}\right)_V \quad 1.44$$

The left-hand side of Eq. 1.44 can be understood as follows: with the increase of temperature, the system regulates its pressure in order to keep the entropy from