

Chapter 1

Thermodynamics: An overview

1.1 Introduction

Thermodynamics deals with the thermal properties of macroscopic systems by determining the relationship between different thermodynamic parameters of the system without considering the internal structure of matter and interaction among the constituent atoms and molecules. A brief description of useful thermodynamic relations is given below.

1.2 Thermodynamic systems

Any macroscopic material body could be considered as a thermodynamic system. Macroscopic system means a system composed of atoms or molecules of the order of one Avogadro number ($N_A \approx 6.022 \times 10^{23}$) per mole. The examples of thermodynamic system could be a wire under tension, a liquid film, a gas in a cylinder, radiation, a solid material such as magnetic material, dielectrics, and many others. The thermodynamic systems should have a boundary which separates the systems from the surroundings. Consider a drop of liquid as a thermodynamic system. The surface of the liquid is the boundary between the liquid and air. In the language of thermodynamics, the boundary is considered as a wall. The nature of the wall classifies the thermodynamic system in different categories. (i) If the wall is such that **energy** or **matter** (atoms or molecules) cannot be exchanged between the system and its surroundings, then the system is called **isolated**. Total energy E , and total number of particles N are conserved for this system. (ii) The wall is such that only **energy** could be exchanged between the system and the surroundings. If the system is in thermal contact with a heat bath in the surroundings, heat energy will be exchanged however total number of particles will remain constant. This system is known as **closed** system. (iii) If the wall is porous, then, beside **energy**, **matter** (atoms or molecules) can also be exchanged between the system and the surroundings. If the system is in contact with a heat bath as well as with a particle reservoir, heat energy and number of particles both will be exchanged. Neither energy nor number of particles is conserved in this system. The system is called an

open system.

1.3 Thermodynamic or macroscopic state

The thermodynamic state or “macroscopic state” of a thermodynamic system is defined by the thermodynamic state parameters. Thermodynamic state parameters are measurable macroscopic physical quantities of a system. Consider a gas in a cylinder. Measurable physical quantities are the pressure (P), temperature (T) and the volume (V) of the gas. These physical quantities are called **thermodynamic parameters** or **thermodynamic variables**. The thermodynamic variables are *macroscopic* in nature. They are divided in two categories, *intensive* and *extensive* parameters. In thermodynamic equilibrium, the intensive parameter has the same value everywhere in the system. Pressure is an example of intensive parameter. It is same everywhere in the gas at equilibrium. On the other hand, the value of the extensive variable changes with the size of the system. For example, volume is an extensive parameter. Every intensive parameter has a corresponding independent extensive parameter. They form a conjugate pair of thermodynamic variables. Since they are independent of each other, one could be changed without effecting the other. Keeping the pressure constant the volume of the gas can be changed and vice versa. A partial list of conjugate thermodynamic parameters are given in Table 1.1. For

System	Intensive parameter	Extensive parameter
Wire	Tension (τ)	Length (L)
Liquid film	Surface tension (γ)	Surface area (A)
Fluid	Pressure (P)	Volume (V)
Magnetic material	Magnetic field (B)	Magnetization (M)
Dielectrics	Electric field (E)	Electric polarization (\mathbf{p})

Table 1.1: A partial list of intensive and extensive conjugate parameters for different thermodynamic systems.

each system, there always exists one more pair of conjugate intensive and extensive parameters. They are temperature (T) and entropy (S). Temperature is the other intensive parameter and entropy is the corresponding conjugate extensive parameter.

1.4 Thermodynamic equilibrium

The state parameters are always defined or measured only at thermodynamic equilibrium. The equilibrium in thermodynamics means that the thermodynamic state does not change with time. Such a situation must correspond to absence of any thermodynamic force as equilibrium in mechanics corresponds to absence of any external force. Thermodynamic forces arise from the gradient of thermodynamic parameters. Thus a system in thermodynamic equilibrium must not have any gradient of any thermodynamic parameter such as pressure, temperature, density, etc.

The **mechanical equilibrium** corresponds to zero pressure gradient within the system. Similarly, the thermal equilibrium corresponds to zero temperature gradient and the chemical equilibrium corresponds to zero concentration gradient, and so on. A system which satisfies all possible equilibrium conditions is said to be in *thermodynamic equilibrium*.

Consider an isolated system with two partial systems. Initially each of them are in equilibrium at different temperatures. Temperature at all points of each system are the same. They are now taken into thermal contact. The systems only exchange of heat and there is no exchange of matter among each other. Heat would flow from the system of higher temperature to the system of lower temperature until uniform temperature is attained throughout the combined system. The system is then in **thermal equilibrium**. Experience shows, all systems which are in thermal equilibrium with a given system are also in thermal equilibrium with each other. This principle defines the temperature of a thermodynamic system and known as *zeroth law of thermodynamics*. Hence systems which are in thermal equilibrium with each other have a common intensive property, *i.e.*, temperature.

Suppose the system is a mixture of several different chemical components. When the composition of the system remain fixed and definite, the system is said to be in **chemical equilibrium**. Generally, chemical equilibrium takes a long time to achieve. Sometimes the system appears to be in chemical equilibrium, having fixed amount of components but the chemical reaction may continue with an extremely slow reaction rate.

1.5 Thermodynamic equation of state

To specify a thermodynamic state, the values of three thermodynamics parameters, say (X, Y, Z) , are to be specified. The functional relationship among the thermodynamic parameters of a system in equilibrium is called the *equation of state*. If the equilibrium state parameters are (X, Y, Z) , the equation of state takes the form $f(X, Y, Z) = 0$.

For a fluid system, the state parameters are pressure P , volume V and temperature T . The equation of state in general is given by $f(P, V, T) = 0$. If the fluid is an ideal gas the equation reduces to

$$PV - RT = 0 \quad (1.1)$$

where $R \approx 8.31 \text{ J/mole.K}$ is the universal gas constant.

For a magnetic system, the state parameters are external magnetic field B , total magnetization M and temperature T . The equation of state would be given by

$f(B, M, T) = 0$. If the magnet is ideal paramagnet the equation reduces to

$$\frac{M}{B} - \frac{C}{T} = 0 \quad (1.2)$$

where C is the material dependent Curie constant.

1.6 Laws of thermodynamic

The First law: The first law is essentially a law of conservation of energy in thermodynamics. It says that the change in the internal energy dE for an arbitrary infinitesimal change of state (*reversible or irreversible*) is given by the sum of work done dW and heat exchange dQ with the surroundings and can be written as

$$\text{First law : } dE = dQ + dW \quad (1.3)$$

where dQ and dW are inexact differentials and dE is an exact differential. For a reversible process, the heat exchange is given by $dQ = CdT$, C is the specific heat (either at constant volume V or at constant pressure P) of the system and the work is given by $dW = -XdY$, X is an intensive parameter of the system and Y is the conjugate extensive parameter of the system. There are sign convention for work and heat exchange. Heat is positive if it is added to the system and heat is negative if it is taken away from the system. Positive work means that the surroundings do work onto the system whereas negative work means the system does work onto the surroundings. In other words, any form of energy exchange is positive if it is added to the system and it is negative if it is subtracted from the system. The form of first law is listed for a few systems in Table.1.2.

Intensive parameter (X)	Extensive parameter (Y)	First law
Tension in a wire (τ)	Length of the wire (L)	$dE = dQ + \tau dL$
Surface tension (γ)	Surface area (A)	$dE = dQ + \gamma dA$
Electric potential (ϕ)	Electric charge (q)	$dE = dQ + \phi dq$
Chemical potential (μ)	Number of particles (N)	$dE = dQ + \mu dN$
Pressure (P)	Volume (V)	$dE = dQ - PdV$
Electric field (E)	Dielectric polarization (p)	$dE = dQ + Edp$
Magnetic field (B)	Magnetization (M)	$dE = dQ + BdM$

Table 1.2: A partial list of intensive and extensive conjugate variables for different thermodynamic systems and the corresponding form of first law.

For a fluid system, dW is positive if the change in volume dV is negative whereas it is positive if the change in volume dV is positive. In case of a magnetic system, the work done is taken as $dW = BdM$ incorporating the energy stored in the vacuum field. If the field energy is excluded the form of the first law would be $dE =$

$dq - MbB$. This is discussed in many texts such as Statistical Physics by F. Mandl, Elementary Statistical Physics by C. Kittel, and Introduction to Thermodynamics and thermostatics by H. B. Callen.

The Second law: The second law tells us about the direction of a natural process in an isolated system. The entropy $dS = \delta Q/T$ is the amount of heat reversibly exchanged with the surroundings at temperature T . For an isolated system, $\delta Q = 0$. Therefore, in an isolated system the entropy is constant in thermodynamic equilibrium and it has an extremum because $dS = 0$. It is found that in every situation this extremum is a maximum. All irreversible processes in isolated systems which lead to equilibrium are then governed by an increase in entropy and the equilibrium will be reached only when the entropy will assume its maximum value. This is the second law of thermodynamics. Thus, for an isolated system at equilibrium it can be stated as

$$\text{Second law : } dS = 0, \quad S = S_{max} \quad (1.4)$$

and for irreversible processes $dS > 0$. In irreversible processes, the system looks for a new equilibrium state and during this process the entropy increases until it reaches its maximum value. Note that, entropy could be negative if there is heat exchange with the surroundings *i.e.*, the system is not an isolated system.

The Third law: The third law of thermodynamics deals with the entropy of a system as the absolute temperature tends to zero. It states that the entropy of every system at absolute zero can always be taken equal to zero,

$$\text{Third law : } \lim_{T \rightarrow 0} S = 0. \quad (1.5)$$

The zero temperature entropy is then independent of any other properties like volume or pressure of the system. It is generally believed that the ground state at $T = 0$ is a single non-degenerate state. It is therefore convenient to choose this non-degenerate state at $T = 0$ as the standard initial state in the definition of entropy and one could set the entropy of the standard state equal to zero.

1.7 Thermodynamic state functions

The parameters required to define the thermodynamic state or “macroscopic state” of a system depends on at what macroscopic condition or under what external interaction the equilibrium of the system is achieved. Interaction of a system with the surroundings depends on the boundary which separates the system from the surrounding. Depending upon the nature of the boundary thermodynamic systems are classified as isolated, closed and open systems. The state parameters and the state functions corresponding these systems at equilibrium are described below. In the following, we will be considering the fluid and magnetic systems only.

1.7.1 Fluid system

Depending on the nature of the thermodynamic system such as isolated, closed or open, different thermodynamic state functions or potentials are found suitable to define the equilibrium situation of a system. Let us start with the first law of thermodynamics whose differential form in a reversible change of state is given by

$$dE = TdS - PdV + \mu dN \quad (1.6)$$

where beside heat exchange and mechanical work done, work done due to the exchange of particles is also considered.

1.7.1.1 Entropy as thermodynamic potential

Consider an isolated system with fixed volume. Thus, the thermodynamic state is given by (E, N, V) . The entropy S becomes the state function for such a system and the differential form is given by

$$TdS = dE + PdV - \mu dN \quad (1.7)$$

The thermodynamic parameters such as temperature T , pressure P and chemical potential can be obtained as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N}, \quad P = T \left(\frac{\partial S}{\partial V} \right)_{E,N}, \quad \mu = -T \left(\frac{\partial S}{\partial N} \right)_{E,V} \quad (1.8)$$

By the second law of thermodynamics, an isolated system during a spontaneous change reaches an equilibrium state characterized by maximum entropy or as $S = S_{\max}$.

1.7.1.2 Enthalpy as thermodynamic potential

Consider an isolated system at constant pressure. Process at constant pressure are of special interest in chemistry since most of the chemical reactions occur under constant atmospheric pressure. The thermodynamic state is defined by (S, N, P) . The enthalpy H of the system becomes the state function and it is defined as

$$H = E + PV \quad \text{or} \quad dH = TdS + VdP + \mu dN \quad (1.9)$$

Knowing the enthalpy $H = H(S, P, N)$, the state variables can be calculated as

$$T = \left(\frac{\partial H}{\partial S} \right)_{P,N}, \quad V = \left(\frac{\partial H}{\partial P} \right)_{S,N}, \quad \mu = \left(\frac{\partial H}{\partial N} \right)_{S,P} \quad (1.10)$$

Since in an isolated-isobaric system, $\delta Q = 0$ and P is constant, then $d(E + PV) = dH = 0$. Therefore, in a spontaneous process of an adiabatic-isobaric system, the equilibrium corresponds to the minimum of the enthalpy $H = H_{\min}$.

1.7.1.3 Helmholtz free energy as thermodynamic potential

Consider a closed system of fixed volume V in contact with a heat bath at constant temperature T . The system is interacting with the heat bath through heat exchange only. The thermodynamic state is defined by (N, V, T) . The Helmholtz free energy (or potential) becomes the state function here and it is defined as

$$F = E - TS \quad \text{or} \quad dF = -SdT - PdV + \mu dN \quad (1.11)$$

Knowing $F = F(N, V, T)$, the state variables S , P and μ can be determined as

$$-S = \left(\frac{\partial F}{\partial T} \right)_{V,N}, \quad -P = \left(\frac{\partial F}{\partial V} \right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} \quad (1.12)$$

For an isothermal system which does not perform work (mechanically isolated), $d(E - TS) = dF = 0$. Thus in a spontaneous process, the system always looks for a minimum of Helmholtz potential until the $F = F_{min}$ is reached and an equilibrium is achieved.

1.7.1.4 Gibbs free energy as thermodynamic potential

Consider a closed system at fixed pressure P in contact with a heat bath at constant temperature T . The system is interacting with the heat bath through heat exchange only. The thermodynamic state is defined by (N, P, T) . The Gibbs potential (or free energy) becomes the state function here and it is defined as

$$G = E - TS + PV = F + PV \quad \text{or} \quad dG = -SdT + VdP + \mu dN \quad (1.13)$$

The thermodynamic variables can be obtained in terms of $G(N, P, T)$ as

$$-S = \left(\frac{\partial G}{\partial T} \right)_{P,N}, \quad V = \left(\frac{\partial G}{\partial P} \right)_{T,N}, \quad \mu = \left(\frac{\partial G}{\partial N} \right)_{T,P} \quad (1.14)$$

For a closed system at constant temperature and pressure, the equilibrium corresponds to minimum of Gibbs potential. In a spontaneous process in an isothermal isobaric system $G = G_{min}$ is always achieved at equilibrium.

1.7.1.5 Grand potential as state function

Consider an open system at constant volume V . The system is attached to a heat bath at temperature T as well as with a particle reservoir at constant chemical potential μ . System exchanges heat with heat bath and exchanges particle with the particle reservoir. The thermodynamic state is defined by (μ, V, T) . The grand potential Φ becomes the state function here and it is defined as

$$\Phi = E - TS - \mu N = F - \mu N = -PV \quad \text{or} \quad d\Phi = -SdT - PdV - Nd\mu \quad (1.15)$$

The thermodynamic state variables are then obtained in terms of $\Phi(\mu, V, T)$ as

$$-S = \left(\frac{\partial \Phi}{\partial T} \right)_{V, \mu}, \quad -P = \left(\frac{\partial \Phi}{\partial V} \right)_{T, \mu}, \quad -N = \left(\frac{\partial \Phi}{\partial \mu} \right)_{T, V} \quad (1.16)$$

For a system of fixed volume at constant temperature and chemical potential, $d(E - TS - \mu N) = d\Phi = 0$. Thus, for spontaneous processes in an isothermal system with constant chemical potential and fixed volume the equilibrium correspond to $\Phi = \Phi_{min}$.

1.7.1.6 Maxwell relations for a fluid system:

A number of relations between the thermodynamic state variables can be obtained since the thermodynamic potentials E, H, F and G (also Φ) are state functions and have exact differentials. The relations given below

$$\begin{aligned} \left(\frac{\partial T}{\partial V} \right)_S &= - \left(\frac{\partial P}{\partial S} \right)_V, & \left(\frac{\partial T}{\partial P} \right)_S &= \left(\frac{\partial V}{\partial S} \right)_P \\ \left(\frac{\partial S}{\partial V} \right)_T &= \left(\frac{\partial P}{\partial T} \right)_V, & - \left(\frac{\partial S}{\partial P} \right)_T &= \left(\frac{\partial V}{\partial T} \right)_P \end{aligned} \quad (1.17)$$

1.7.1.7 Response functions for fluid systems

Response functions can be obtained as the second derivatives of thermodynamic state functions.

Specific heats: Thermal response functions The specific heats C_V and C_P are measures of the heat absorption from a temperature stimulus. The definition of heat capacities are given as by

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V \quad (1.18)$$

and

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_P \quad (1.19)$$

Compressibilities: Mechanical response functions The isothermal and adiabatic compressibilities are defined as

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left(\frac{\partial^2 G}{\partial P^2} \right)_T, \quad (1.20)$$

and

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S = -\frac{1}{V} \left(\frac{\partial^2 H}{\partial P^2} \right)_S \quad (1.21)$$

Coefficient of volume expansion The change of volume generally is made under constant pressure for the solid system. The coefficient of volume expansion α_P is defined as

$$\alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \left(\frac{\partial^2 G}{\partial T \partial P} \right). \quad (1.22)$$

Relations among response functions The response functions are not all independent of one another. They satisfy certain relations among them as given below:

$$\kappa_T(C_P - C_V) = TV\alpha_P^2 \quad \text{and} \quad C_P(\kappa_T - \kappa_S) = TV\alpha_P^2 \quad (1.23)$$

From the above relations it can be shown that $C_P/C_V = \kappa_T/\kappa_S$.

The entropy of a system at any temperature T can be obtain in terms of specific heats as

$$S(T) = \int_0^T \frac{C_V(T)}{T} dT \quad \text{or} \quad S(T) = \int_0^T \frac{C_P(T)}{T} dT \quad (1.24)$$

when the system is heated at constant volume or constant pressure respectively. As a consequence of the third law $S(0) = 0$, the heat capacities C_V or C_P must be zero at $T = 0$ otherwise the above integrals will diverge at the lower limit. Thus as $T \rightarrow 0$,

$$C_V \rightarrow 0 \quad \text{and} \quad C_P \rightarrow 0. \quad (1.25)$$

This is because of the fact that as $T \rightarrow 0$, the system tends to settle down in its ground state. The mean energy of the system then become essentially equal to its ground state energy, and no further reduction of temperature can result in a further reduction of mean energy. Not only the individual heat capacities go to zero but also their difference ($C_P - C_V$) goes to zero as $T \rightarrow 0$. The volume expansion coefficient α_P goes to zero

$$\alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = -\frac{1}{V} \left(\frac{\partial S}{\partial P} \right)_T = 0. \quad (1.26)$$

at $T = 0$. However, the compressibility κ_T , a purely mechanical property, remains well-defined and finite as $T \rightarrow 0$. Thus, following Eq.1.23 one has

$$C_P - C_V = \frac{TV\alpha_P^2}{\kappa_T} \rightarrow 0 \quad (1.27)$$

as $T \rightarrow 0$. This is not in contradiction to the ideal gas result $C_P - C_V = R$ because as $T \rightarrow 0$, the system approaches its ground state and quantum mechanical effects become very important. Hence the classical ideal gas equation $PV = RT$ is no longer valid at $T = 0$.

1.7.2 Magnetic system

Let us start with the first law of thermodynamics whose differential form in a reversible change of state is given by

$$dE = TdS + BdM \quad (1.28)$$

where field energy is taken into account. The other state functions and thermodynamic potentials such as enthalpy $H(N, S, B)$, the Helmholtz free energy $F(N, M, T)$ and the Gibbs free energy $G(N, B, T)$ and their differential change in a reversible change of state are given by

$$\begin{aligned} H(N, S, B) = E - MB & \quad \text{and} \quad dH = TdS - MdB \\ F(N, M, T) = E - TS & \quad \text{and} \quad dF = -SdT + BdM \\ G(N, B, T) = E - TS - MB & \quad \text{and} \quad dG = -SdT - MdB \end{aligned} \quad (1.29)$$

where explicit N dependence is also avoided since we will be mostly discuss magnetic solid. If one wants to take into account of number of particles, there must be another term μdN in all differential forms of the state functions. It can be noticed that the thermodynamic relations of a magnetic system can be obtained from those in fluid system if V is replaced by $-M$ and P is replaced by B .

Note that if the other form of the first law $dE = TdS - MdB$ is used it can be checked that the differential change in Helmholtz free energy would be given by $dF = -SdT - MdB$ same as Gibbs free energy given in Eq.1.29. The Helmholtz free energy becomes $F(B, T)$ function of B and T instead of $F(M, T)$ function of M and T . In many text books, $F(B, T)$ is used as free energy and the reader must take a note that in this situation a different definition of magnetic work and energy is used.

Now one can obtain all the thermodynamic parameters from the state functions defined in Eqs.1.28 and 1.29 by taking appropriate derivatives as given below

$$\begin{aligned} T &= \left(\frac{\partial E}{\partial S} \right)_M & \text{or} & \quad T = \left(\frac{\partial H}{\partial S} \right)_B, \\ S &= - \left(\frac{\partial F}{\partial T} \right)_M & \text{or} & \quad S = - \left(\frac{\partial G}{\partial T} \right)_B, \\ B &= \left(\frac{\partial E}{\partial M} \right)_S & \text{or} & \quad B = \left(\frac{\partial F}{\partial M} \right)_T, \\ M &= - \left(\frac{\partial H}{\partial B} \right)_S & \text{or} & \quad M = - \left(\frac{\partial G}{\partial B} \right)_T. \end{aligned} \quad (1.30)$$

1.7.2.1 Maxwell relations for a magnetic system:

A number of relations between the thermodynamic state variables can be obtained since the thermodynamic potentials E, H, F and G (also Φ) are state functions and

have exact differentials.

1. Form Internal Energy E :

$$dE = TdS + BdM \quad \Longrightarrow \quad \left(\frac{\partial T}{\partial M}\right)_S = \left(\frac{\partial B}{\partial S}\right)_M$$

2. From enthalpy H :

$$dH = TdS - MdB \quad \Longrightarrow \quad \left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial M}{\partial S}\right)_B$$

3. From Helmholtz potential F :

$$dF = -SdT + BdM \quad \Longrightarrow \quad \left(\frac{\partial S}{\partial M}\right)_T = -\left(\frac{\partial B}{\partial T}\right)_M$$

4. From Gibbs potential G :

$$dG = -SdT - MdB \quad \Longrightarrow \quad \left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B$$

1.7.2.2 Response functions for a magnetic system

Definitions of the thermodynamic response functions will be given here.

Specific heats: The specific heats C_M and C_B are the measures of the heat absorption from a temperature stimulus at constant magnetization and constant external magnetic field respectively. The definition of heat capacities are :

$$C_M = T \left(\frac{\partial S}{\partial T}\right)_M = -T \left(\frac{\partial^2 F}{\partial T^2}\right)_M$$

and

$$C_B = T \left(\frac{\partial S}{\partial T}\right)_B = -T \left(\frac{\partial^2 G}{\partial T^2}\right)_B.$$

Susceptibilities: In case of magnetic systems, instead of isothermal and adiabatic compressibilities one have the isothermal and the adiabatic magnetic susceptibilities

$$\chi_T = \left(\frac{\partial M}{\partial B}\right)_T = -\left(\frac{\partial^2 G}{\partial B^2}\right)_T,$$

and

$$\chi_S = \left(\frac{\partial M}{\partial B}\right)_S = -\left(\frac{\partial^2 H}{\partial B^2}\right)_S$$

where M is the total magnetization and B is the external magnetic field. Note that the normalizing factor of $1/V$ is absent here.

Coefficient α_B : The change of magnetization M with respect to temperature T under constant external magnetic field α_B , is defined as

$$\alpha_B = \left(\frac{\partial M}{\partial T} \right)_B = \left(\frac{\partial^2 G}{\partial T \partial B} \right).$$

1.7.2.3 Relations among response functions:

The response functions are not all independent of one another. It can be shown that

$$C_B/C_M = \chi_T/\chi_S.$$

Two more useful relations among them are

$$\chi_T(C_B - C_M) = T\alpha_B^2 \quad \text{and} \quad C_B(\chi_T - \chi_S) = T\alpha_B^2.$$

1.8 Thermodynamic stability, positive response function and convexity of free energy

Free energy functions are often found a concave or a convex function of thermodynamic parameters. A function $f(x)$ is called a convex function of x if

$$f\left(\frac{x_1 + x_2}{2}\right) \leq \frac{f(x_1) + f(x_2)}{2} \quad (1.31)$$

for all x_1 and x_2 . That is to say the chord joining the points $f(x_1)$ and $f(x_2)$ lies above or on the curve $f(x)$ for all x in the interval $x_1 < x < x_2$ for a convex function. Similarly, a function $f(x)$ is called a concave function of x if

$$f\left(\frac{x_1 + x_2}{2}\right) \geq \frac{f(x_1) + f(x_2)}{2} \quad (1.32)$$

for all x_1 and x_2 . Thus, for a concave function, the chord joining the points $f(x_1)$ and $f(x_2)$ lies below or on the curve $f(x)$ for all x in the interval $x_1 < x < x_2$. If the function is differentiable and the derivative $f'(x)$ exists, then a tangent to a convex function always lies below the function except at the point of tangency whereas for a concave function it always lies above the function except at the point of tangency. If the second derivative exists, then for a convex function $f''(x) \geq 0$ and for a concave function $f''(x) \leq 0$ for all x .

On the other hand, thermodynamic response functions such as specific heat, compressibility, susceptibility (for ferromagnetic systems) are found to be positive and

the positive values of the response function implies the convexity properties of the free energy functions such as $F = E - TS$ or $G = F + PV$.

The positive response function is a direct consequence of Le Chatelier's principle for stable equilibrium. The principle says, if a system is in thermal equilibrium any small spontaneous fluctuation in the system parameter, the system gives rise to certain processes that tends to restore the system back to equilibrium. Suppose there was a spontaneous temperature fluctuation in which the temperature of the system increases from T to T' . In order to maintain the stability, the system should absorb certain amount of heat ΔQ and as a consequence the specific heat $C = \Delta Q/\Delta T$ must be positive since both ΔQ and ΔT are positive. If there occurs a spontaneous pressure fluctuation, $P \rightarrow P'$ and $P' > P$, then the system will reduce its volume by certain amount ΔV to maintain the stability. As a consequence the compressibility $\kappa = -\Delta V/\Delta P$ is also to be positive since ΔP is positive but ΔV is negative. Thus, for thermally and mechanically stable fluid system, the specific heat and compressibility should be positive for all T . However, for a magnetic system such arguments that the susceptibility χ and specific heat C both are positive cannot be made. It is known that for diamagnetic materials, $\chi < 0$. The ferromagnetic materials on the other hand have positive χ . It can be shown that such systems are described by the Hamiltonian $\mathcal{H} = \mathcal{H}_0 - \vec{B} \cdot \vec{M}$.

The response functions are not all independent. One could show for a fluid system,

$$C_P - C_V = TV\alpha_P^2/\kappa_T \quad \text{and} \quad \kappa_T - \kappa_S = TV\alpha_P^2/C_P \quad (1.33)$$

where $\alpha_P = (\partial V/\partial T)_P/V$, the thermal expansion coefficient and similarly for a magnetic system,

$$C_B - C_M = T\alpha_B^2/\chi_T \quad \text{and} \quad \chi_T - \chi_S = T\alpha_B^2/C_H \quad (1.34)$$

where $\alpha_B = (\partial M/\partial T)_B$. Since, the specific heat and compressibility are positive, it could be shown from the above relations that $C_P \geq C_V$ and $\kappa_T \geq \kappa_S$. The equality holds either at $T = 0$ or at $\alpha = 0$, for example, $\alpha = 0$ for water at $4^\circ C$.

From thermodynamic relations, it is already known that

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\frac{C_P}{T} \quad \text{and} \quad \left(\frac{\partial^2 F}{\partial T^2}\right)_V = -\frac{C_V}{T}. \quad (1.35)$$

Since the specific heats are positive, these second derivatives are negative and as a consequence G and F both are concave functions of temperature T . It is also known that

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_T = -V\kappa_T \quad \text{and} \quad \left(\frac{\partial^2 F}{\partial V^2}\right)_T = \frac{1}{V\kappa_T}. \quad (1.36)$$

Since the compressibility is a positive quantity, G is a concave function of P whereas F is a convex function of V .

It can be shown that $G(T, B)$ is a concave function of both T and H whereas $F(T, M)$ is a concave function of T but a convex function of M for magnetic systems described by the Hamiltonian $\mathcal{H} = \mathcal{H}_0 - \vec{B} \cdot \vec{M}$.