

Thermodynamic Potential and Relation with Thermodynamical Variables

The thermodynamic state of a system may be described by certain thermodynamical variables like pressure p , volume V , temperature T and entropy S . Out of these variables, any two of them are considered to be independent and by determining these two, others may be known. They are said to be the functions of independent variables. Among these variables certain relations exist. For example, the change in internal energy dU may be expressed in terms of the thermodynamical variables, as $dU = TdS - pdV$. This is obtained by combining the first and second law of thermodynamics. For the complete information of thermodynamic system, more relations are required.

These relations are mathematically simplified by introducing some functions of thermodynamical variables. These functions are known as the *thermodynamic potentials* or *thermodynamic functions*. There are four thermodynamic potential.

1. Internal energy	U	
2. Enthalpy	H	$H = U + pV$
3. Helmholtz free energy	F	$F = U - TS$
4. Gibbs free energy	G	$G = U - TS + pV$

Significance. A mechanical process would proceed in such a direction so as to acquire minimum potential energy. The behaviour of thermodynamical potential are similar to potential energy in mechanics. For example,

1. In adiabatic-isobaric process H tends to be minimum.
2. In isothermal-isochoric process F tends to be minimum.
3. In isothermal-isobaric process G tends to be minimum.

Since the four functions U , H , F and G play the same role in thermodynamics as played by potential energy in mechanics, they are called thermodynamic potential.

They may be defined and explained as follows:

Internal Energy

The matter is made up of a large number of atoms or molecules. At temperature above absolute zero, they are in a state of constant motion and hence each one of them has kinetic energy. The total kinetic energies of all molecules is known as internal kinetic energy. Also due to interactions among the atoms or molecules each of them possesses potential energy. The total energy stored in the system due to interactions is called total internal potential energy. The sum of total internal kinetic and potential energies of all molecules constitutes the internal energy of the system, denoted by U .

Internal energy is a function of state, i.e., its differential is exact and can be expressed as the algebraic sum of two inexact differential. Thus the internal energy function is independent of path. According to the first and second law of thermodynamics the internal energy of a system is defined by

$$dU = TdS - pdV \quad (38)$$

At constant volume, $dV = 0$, thus $TdS = \delta Q = dU$, i.e., for an isochoric process change in internal energy of thermodynamic system is equal to the heat given to the system. Therefore, heat capacity at constant pressure is

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$$C_v = \left(\frac{\partial Q}{\partial T} \right)_v = \left(\frac{\partial U}{\partial T} \right)_v$$

This equation defines the dependence of U on independent variables S and V . Therefore, the entropy and volume make up the natural pair for internal energy and we can write, $U = U(S, V)$

Further, it easily follows from eq. (38) that temperature and pressure of a system of constant volume and entropy are given by

$$T = \left(\frac{\partial U}{\partial S} \right)_v \quad \text{and} \quad p = - \left(\frac{\partial U}{\partial V} \right)_s \quad (39)$$

This means that once U is known for the system under certain consideration, we can obtain complete information about its thermal properties.

Since internal energy is exact differential, we can show easily

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right)_v \right]_s = \left[\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right)_s \right]_v$$

Using eq. (39) we get
$$\left(\frac{\partial T}{\partial V} \right)_s = - \left(\frac{\partial p}{\partial S} \right)_v \quad (40)$$

which implies that *the increase of temperature per unit increase of volume at constant entropy is equal to the decrease of pressure per unit increase of entropy when the volume is kept constant.* This is same equation obtained earlier, known as **Maxwell's third thermodynamical relation.**

Enthalpy

Enthalpy is a function of state. We denote it by H . For any adiabatic changes, a system at constant pressure is defined solely by the enthalpy. Therefore, the function H is known as the **thermodynamic potential at constant pressure and heat.** The enthalpy (from eq. (31)) of an isolated system remains constant in reversible processes and decreases in irreversible processes, i.e., $dH \leq 0$. In Joule-Thomson expansion, it remains constant. It is mathematically defined as

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

Being a combination of functions of state, H is also a property of state of a system and hence it is an exact differential.

Differentiating this equation and using eq. (6.38), we get

$$\begin{aligned} dH &= dU + d(pV) = TdS - pdV + pdV + Vdp \\ dH &= TdS + Vdp \end{aligned} \quad (41)$$

At constant pressure, $dp = 0$, thus $dH = TdS = \delta Q$, i.e., for an isobaric process change in enthalpy of thermodynamic system is equal to the heat given to the system. Therefore, heat capacity at constant pressure is

$$C_p = \left(\frac{\partial Q}{\partial T} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p$$

This explain the name **heat function.** Moreover the entropy and pressure make up the natural pair for enthalpy and we can write, $H = H(S, p)$

From eq. (6.41) that temperature and volume of a system of constant pressure and entropy are given by

$$T = \left(\frac{\partial H}{\partial S} \right)_p \quad \text{and} \quad V = \left(\frac{\partial H}{\partial p} \right)_s \quad (42)$$

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This means that once H is known for the system under certain consideration, we can obtain complete information about its thermal properties.

Since enthalpy is exact differential, we can show easily

$$\left[\frac{\partial}{\partial p} \left(\frac{\partial H}{\partial S} \right) \right]_p = \left[\frac{\partial}{\partial S} \left(\frac{\partial H}{\partial p} \right) \right]_p$$

Using eq. (42), we get
$$\left(\frac{\partial T}{\partial p} \right)_s = \left(\frac{\partial V}{\partial S} \right)_p \quad (09)$$

which implies that *the increase of temperature per unit increase of pressure at constant entropy is equal to the increase of volume per unit increase of entropy when the pressure is kept constant.* This is same equation derived before known as **Maxwell's fourth thermodynamical relation.**

Helmholtz Free Energy

In isothermal processes, for reversible changes the work done by the system is equal to the decrease in this Helmholtz free energy function F . For irreversible changes the work done by the system is less than the decrease in F , i.e., $dF \leq -\delta W$. Being a combination of functions of state, F is a property of state of a system and hence it is an exact differential. It is mathematically defined as

$$F = U - TS \quad (43)$$

It follows from this equation that internal energy $U = F + TS$ is made up of two parts: (a) the free energy F , which is *available* for work in reversible isothermal processes, and (b) the hidden energy TS which is *not available* for useful work. As entropy increases, available energy decreases.

At fixed temperature, a system of constant volume is characterised solely by F and a spontaneous change will occur in the direction in which F decreases, i.e., $dF \leq 0$. Therefore, the function F is known as the **thermodynamic potential at constant volume.**

If we differentiate eq. (6.43) and using eq. (6.38), we get

$$dF = dU - d(TS) = (TdS - pdV) - (TdS + SdT)$$

or,
$$dF = -SdT - pdV \quad (44)$$

This equation defines the dependence of F on independent variations of T and V . These, therefore, make up the natural pair for Helmholtz energy and one can write, $F = F(T, V)$

Further, from eq. (44) that entropy and pressure of a fixed T and V system are given by

$$S = - \left(\frac{\partial F}{\partial T} \right)_V \quad \text{and} \quad p = - \left(\frac{\partial F}{\partial V} \right)_T \quad (45)$$

This means that once F is known for the system under certain consideration, we can obtain complete information about its thermal properties.

Since Helmholtz free energy is exact differential, we can show easily

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

Using eq. (45), we get
$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V \quad (06)$$

which implies that *the increase of entropy per unit increase of volume at constant temperature is equal to the*

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increase of pressure per unit increase of temperature when the volume is kept constant. This is derived once before and is known as **Maxwell's first thermodynamical relation**.

On substituting eq. (45a) in eq. (43), we get the thermodynamic relation in the new form

$$F = U + T \left(\frac{\partial F}{\partial T} \right)_V \quad \text{or,} \quad U = F - T \left(\frac{\partial F}{\partial T} \right)_V \quad (46)$$

Gibbs Free Energy

At constant temperature and pressure system is solely defined by the Gibbs free energy or potential, G . Therefore, the function G is known as the **thermodynamic potential at constant pressure**. A spontaneous change under these conditions will occur in the direction of decreasing G , whereas in a reversible change Gibbs energy will be conserved, i.e. $dG \leq 0$, Mathematically, it can be define as

$$G = F + pV = U - TS + pV = H - TS \quad (47)$$

Since all the quantities occurring in this equation are functions of state, G is also a function of state. That is why we have denoted it as an exact differential.

Differentiate eq. (47) and substituting eq. (38), we get

$$\begin{aligned} dG &= dU - d(TS) + d(pV) = (TdS - pdV) - (TdS + SdT) + (pdV + Vdp) \\ \text{or,} \quad dG &= -SdT + Vdp \end{aligned} \quad (48)$$

This equation specifies the dependence of G on independent variations of T and p . Hence,

$$G = G(T, p)$$

It readily follows from eq. (48) that the thermal properties of such a system are given by

$$S = - \left(\frac{\partial G}{\partial T} \right)_p \quad \text{and} \quad V = \left(\frac{\partial G}{\partial p} \right)_T \quad (49)$$

This means that once G is known for the system under certain consideration, we can obtain complete information about its thermal properties.

Since Helmholtz free energy is exact differential, we can show easily

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

$$\text{Using eq. (49), we get} \quad \left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p \quad (47)$$

which implies that *the increase of entropy per unit increase of pressure at constant temperature is equal to the decrease of volume per unit increase of temperature when the pressure is kept constant*. This is known as **Maxwell's second thermodynamical relation**.

On substituting eq. (49) in eq. (47), we get the thermodynamic relation in the new forms

$$G = F + p \left(\frac{\partial G}{\partial p} \right)_T \quad (50)$$

$$G = H + T \left(\frac{\partial G}{\partial T} \right)_p \quad (51)$$

$$\text{and} \quad G = U + T \left(\frac{\partial G}{\partial T} \right)_p + p \left(\frac{\partial G}{\partial p} \right)_T \quad (52)$$