

AL-Mustaqbal University College

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The Second Stage

Thermodynamics and Heat

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Maxwell's equations and there application

The Maxwell relations are derived from Euler's reciprocity relation. The relations are expressed in partial differential form. The Maxwell relations consists of the characteristic functions: internal energy U, enthalpy H, Helmholtz free energy F, and Gibbs free energy G and thermodynamic parameters: entropy S, pressure P, volume V, and temperature T. Following is the table of Maxwell relations for secondary derivatives:

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

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

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

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

What are Maxwell's relations?

These are the set of thermodynamics equations derived from a symmetry of secondary derivatives and from thermodynamic potentials. These relations are named after James Clerk Maxwell, who was a 19th-century physicist.

Thermodynamic Potentials

Before we continue with Maxwell's relations we will briefly explain all the four thermodynamic potentials which are also known as the characteristic functions that form the base of Maxwell's relations.

Some quantity that is used to represent some thermodynamic state in a system is known as thermodynamic potential. Each thermodynamic potential gives a different measure of the “type” of the energy system. Here we will discuss four types of potentials that help derive the Maxwell thermodynamic relation.

Internal energy- the energy contained in a system is the internal energy of a system. This energy excludes any outside energy that comes due to external forces. It also excludes the kinetic energy of a system as a whole. Internal energy includes only the energy of the system, which is due to the motion, and interactions of the particles that make up the system.

Making use of the first law of thermodynamics, you can seek the differential form of the said internal energy:

$$dU = \delta Q + \delta W$$
$$dU = TdS - PdV$$

Enthalpy- the summation of internal energy and the product of volume and pressure gives enthalpy. The equation of enthalpy represents that the total heat content of a system is always the preferred potential to use when many chemical reactions are under study when such chemical reactions take place at a constant pressure. When the pressure here is constant, the change in the said internal energy is equal to the change in enthalpy of the system. The letter H represents the enthalpy.

$$\mathbf{H = U + PV}$$

You can seek dH with the help of the above stated expression:

$$\mathbf{dH = dU + d(PV) =}$$

$$\mathbf{dU + PdV + VdP}$$

$$\mathbf{dH = TdS - PdV + PdV + VdP}$$

$$\mathbf{dH = TdS + VdP}$$

Helmholtz free energy- Helmholtz free energy is the difference between the internal energy of the system and the product of entropy and temperature. This equation represents the amount of useful work that can be easily obtained from a close system when the temperature and the volume are constant. The letter F in this equation represents the said Helmholtz free energy.

$$\mathbf{F = U - TS}$$

From which you can find the differential form of the said equation above

$$\mathbf{dF = dU - d(TS) = dU - TdS - SdT}$$

Substituting the differential form of the said internal energy ($dU = TdS - PdV$)

$$\mathbf{dF = TdS - PdV - TdS - SdT}$$

$$\mathbf{dF = -PdV - SdT}$$

Gibbs Free Energy - This thermodynamic potential is the last potential that helps to calculate the quantity of work a system can do at constant pressure and temperature. It is a very useful concept while studying phase transitions that happen during such conditions. Gibbs can be defined as the said difference between the enthalpy of a system as well as the product of entropy and temperature of the system. The letter G here given in the equation represents the said Gibbs free energy.

Thus,

$$G = H - TS$$

From which you can find the differential form of the said equation above:

$$dG = dH - d(TS) = dH - Tds - Sdt$$

Now, you need to substitute in the said differential form of the enthalpy ($dH = TdS + VdP$)

$$dG = TdS + VdP - TdS - SdT$$

$$dG = VdP - SdT$$

This Table Summarizes the Differential Forms of the Four Types of Thermodynamic Potentials:

Thermodynamic Potentials	The Derived Derivational Form	The Natural Variables
Internal Energy depicted by U	$dU = TdS - PdV$	S and V
Enthalpy depicted by H	$dH = TdS + VdP$	S and P
Helmholtz Free Energy as depicted by F	$dF = -PdV - SdT$	V and T
Gibbs Free Energy as depicted by Gd	$G = VdP - SdT$	P and T

Thermodynamic cycle Rule

A **thermodynamic cycle** consists of a linked sequence of thermodynamic processes that involve transfer of heat and work into and out of the system, while varying pressure, temperature, and other state variables within the system, and that eventually returns the system to its initial state.^[1] In the process of passing through a cycle, the working fluid (system) may convert heat from a warm source into useful work, and dispose of the remaining heat to a cold sink, thereby acting as a heat engine. Conversely, the cycle may be reversed and use work to move heat from a cold source and transfer it to a warm sink thereby acting as a heat pump. If at every point in the cycle the system is in thermodynamic equilibrium, the cycle is reversible. Whether carried out reversibly or irreversibly, the net entropy change of the system is zero, as entropy is a state function.

During a closed cycle, the system returns to its original thermodynamic state of temperature and pressure. Process quantities (or path quantities), such as heat and work are process dependent. For a cycle for which the system returns to its initial state the first law of thermodynamics applies:

$$\Delta U = E_{in} - E_{out} = 0$$

The above states that there is no change of the internal energy (U) of the system over the cycle. E_{in} represents the total work and heat input during the cycle and E_{out} would be the total work and heat output during the cycle. The repeating nature of the process path allows for continuous operation, making the cycle an important concept in thermodynamics. Thermodynamic cycles are often represented mathematically as quasistatic processes in the modeling of the workings of an actual device