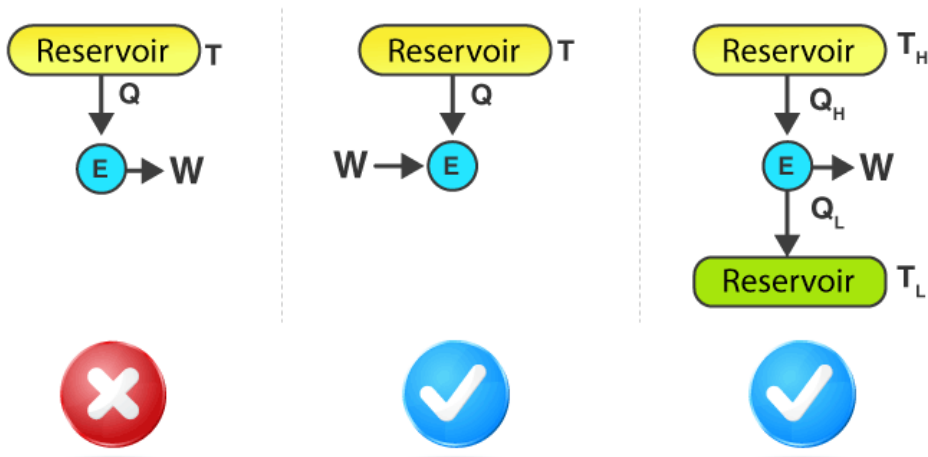


What is the Kelvin Planck Statement?

This is a special case of the second law of thermodynamics. It states that *“It is impossible to construct a device which operates on a cycle and produces no other effect than the transfer of heat from a single body to produce work.”* This means that it is impossible to construct an engine whose sole purpose is to convert the heat from a high-temperature source/reservoir into an equal amount of work.

KELVIN PLANCK STATEMENT

BYJU'S
The Learning App



We know that heat (Q) and Work(W) are the two forms of energy. Both follow the S.I unit Joules, and both are interconvertible. This means work can be converted into heat and vice-versa. Here, work can be fully converted into heat, but heat cannot be fully converted into work. Hence, work is called high-grade energy, and heat is called low-grade energy.

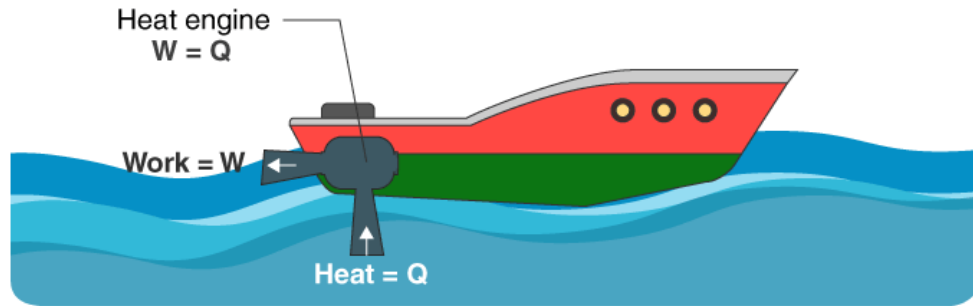
The Kelvin-Planck statement is two different statements given by Lord Kelvin and Planck. They are known as Kelvin's statement and Planck's statement.

Kelvin's statement stated that it is impossible to derive mechanical effect from any matter by cooling it below the highest cooling temperature of the surrounding objects.

Planck's statement states that the total sum of entropies for the reversible system remains constant.

Clubbing both these statements, the Kelvin-Planck statement was derived.

The kelvin-Planck statement, also known as the heat engine statement from the second law of thermodynamics, states that it is impossible to design a device that works on a cycle and produces no other effect other than heat transfer from a single body for the production of work.



This scenario is Impossible

Kelvin-Planck Statement Example

A hypothetical device called the perpetual motion machine of the second kind (PMM2K) was introduced by Wilhelm Ostwald, which would perform work exclusively by absorbing energy as heat from a body.

Working of Heat Engine:

For the operation of the heat engine, the working fluid has to continuously exchange heat between the heat sink/reservoir with low temperature Q_L and the heat source/reservoir with high temperature Q_H

The prime parameter involved here is efficiency.

The **efficiency of a heat engine** is “The amount of useful work obtained(output) for a given amount of input”

In general, efficiency tells the heat transfer process. It is the ratio of “how much you get out” to “how much you put in”

Efficiency

$$\begin{aligned}\eta &= \frac{-W}{-Q_H} \\ &= \frac{Q_L - Q_H}{Q_L} \\ &= 1 - \frac{Q_L}{Q_H}\end{aligned}$$

In the absence of a heat sink, that is:

$$Q_L = 0$$

Then efficiency

$$\eta = 1 - \frac{0}{Q_H} = 1$$

This implies that efficiency is 100%. Which is not true according to the second law of thermodynamics. Thus, no heat engine is 100% efficient.

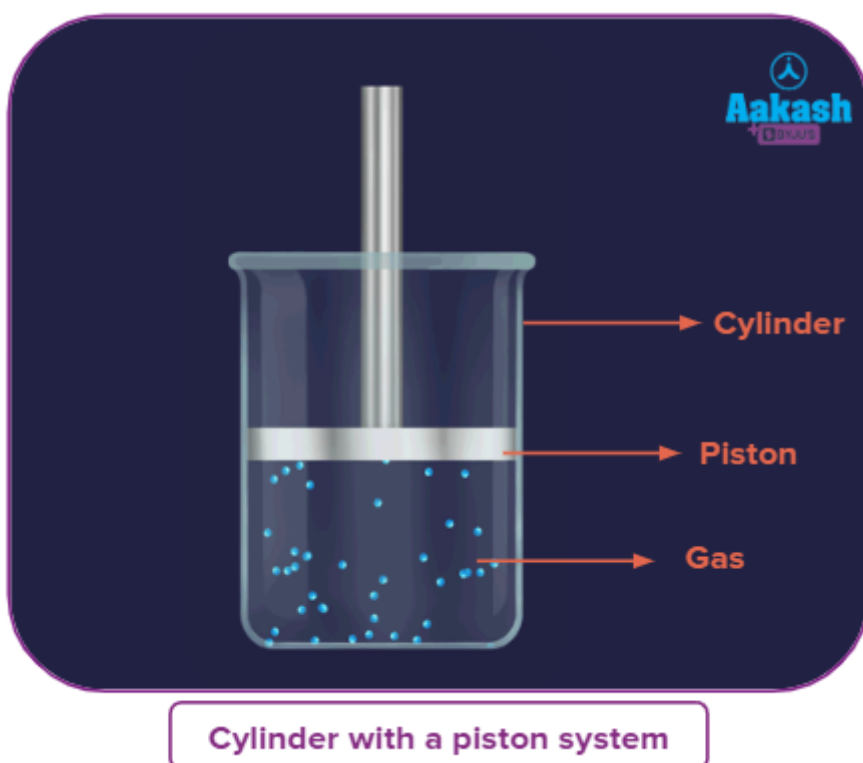
of work being done on the system? We can easily say that it is not possible in most cases. Let's learn more about the type of processes and what kind of processes are found in nature and in the aspects of thermodynamics that are reversible and irreversible.

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What is a Reversible Process?

A thermodynamic process (initial state \rightarrow final state) is said to be a reversible process if the process can be reversed in such a way that both the system and the surroundings return to their initial states, without any net change in the universe.

Let's assume there is some amount of gas in a cylinder-piston system.



The piston is assumed to be massless and frictionless and for now, the piston is also stationary.

This means, the inside and outside pressure are the same, or we can say that the system is in equilibrium i.e., $P_{\text{ext}} = P_{\text{int}}(\text{gas})$

Now let's say if we compress this gas from its initial volume V_1 to a final volume V_2 . This process can be done in two different ways. Let's look at the first one.

Reversible compression of a Gas

Here, we put grains of sand on top of the piston and thereby increase the external pressure on the gas. Notice that the piston is going down and the gas is getting compressed. The movement of the piston is barely visible to our naked eye, let's zoom in and view this compression.



Let the very tiny extra pressure due to this grain that assists the compression to be denoted as dp . This infinitesimally small increase in pressure is due to the extra force acting due to the grain of sand of mass dm . Of course, you know that this extra force will be:

$$\text{Force} = dm \times g \quad (\text{since, } F = m \times a).$$

dm is the mass of each tiny sand grain

g is the acceleration due to gravity

And we know the pressure is force/area. So,

$$dp = \frac{dm \times g}{A}$$

Where, A is the cross-sectional area of the piston.

To continue with the compression, we need to keep adding more sand particles and the addition of each new particle can be considered as a new step in the compression process. After each step, the piston moves down slightly, and the gas system responds by increasing its own internal pressure due to compression and coming to equilibrium with its surroundings or we can say that after every step (after the addition of every grain of sand), the external pressure becomes equal to the internal pressure of the gas.

$$P_{int} = P_{ext}$$

Where P_{int} is the internal pressure of the gas.

One important thing to note here is that, since the system is in equilibrium, it can now move in either direction after each step depending on the external conditions, right?

What does it mean is that we could reverse the process direction at any point in time by reversing the driving force behind it? Like, if we remove one sand particle after a step, the gas would expand by a small amount instead of getting compressed, thereby going back to the volume from our previous step.

So, a thermodynamic process is said to be a reversible process if the process can be turned back in such a way that both the system and the surroundings return to their original states, with no other change anywhere else in the universe. In our case also, if the sand grains are added and removed, the volume change will be of the same amount both in cases of compression and expansion respectively without changing the universe conditions.

So, let's think in this way if 30 J of work is done on the system from the surrounding to compress the gas then if the process is reversible, then the same amount of work will be done by gas on surrounding while expansion.

As we all know, there are no such things as reversible processes in reality. Reversible processes can thus be simply characterised as idealizations or models of real processes based on which the system or device's boundaries are to be specified. They assist us in determining the maximum efficiency a system can deliver under ideal operating conditions, as well as the target design that can be established.

Examples of Reversible Processes

- Compression and extension of springs
- Infinitesimally slow isothermal compression or expansion of gases
- Melting of Ice to water and Cooling of water to Ice
- Movement of objects without experiencing friction from surface
- Infinitesimally slow adiabatic compression or expansion of gases

What is an Irreversible Process?

An irreversible process can be defined as a process in which the system and the surroundings do not return to their initial state once the process is started. In other words, in an irreversible process, if the system and surroundings return to their original state after taking certain paths, there will be some net change which occurred in the universe. Consider the case of a vehicle engine that has travelled a distance using gasoline in the amount of 'x'. The fuel burns to generate energy to the engine, converting itself to smoke and heat energy in the process. We will never be able to recover the energy lost by the fuel, nor will we ever be able to return to its original state.

The irreversibility of a process is caused by a number of reasons, including:

1. Friction is the process of converting the energy of the fuel into heat energy.
2. The unregulated expansion of the fluid prevents the fuel from returning to its original form. The reversal of heat transfer through a finite temperature is not feasible because the forward process is spontaneous in this scenario.
3. Intermixing two different substances can't be separated since the intermixing process is spontaneous in nature, and the opposite isn't possible.

As a result, depending on their ability to return to their original form from their final state, certain processes are reversible while others are irreversible in nature.

Illustration for an irreversible process

Considers an ideal gas enclosed in a cylinder at 10 atm. At any point in time, there are two forces acting on the piston.

- Throttling of a gas from a small hole
- Heat transfer from one object to another
- Diffusion/effusion of gasses

Difference Between Reversible and Irreversible Process

Reversible Process	Irreversible Process
Reversible processes are ideal processes	Irreversible processes are real processes
Reversible process is a slow process	Irreversible process is a fast process
Reversible process can be reversed without affecting the universe	Irreversible process cannot be reversed without affecting the universe
In a reversible process, infinite changes occur in the system.	In an irreversible process, finite changes occur in the system.
Reversible process takes infinite time for the completion	Irreversible process takes a finite time for the completion
In the case of a reversible process, there is always an equilibrium condition establishment between the initial state and the final state of a system	In case of an irreversible process, the initial state and the final state of a system is never in the equilibrium. The equilibrium is only achieved at the end of the process.
In the case of a reversible process, $P_{\text{int}} = P_{\text{ext}}$ throughout the process.	In the case of an irreversible process, $P_{\text{int}} \neq P_{\text{ext}}$ during the process. Internal pressure is only equal to external pressure when the equilibrium is achieved that is at the end of the process.
Examples: Compression and extension of springs, Infinitesimally slow isothermal compression or expansion of gases, Movement of objects without experiencing friction from surface Infinitesimally slow adiabatic compression or expansion of gases	Examples: Movement of objects with experiencing friction from the surface, Throttling of a gas from a small hole, Heat transfer from one object to another, Diffusion/effusion of gasses

What is the Clausius Inequality?

To understand what the Clausius Inequality is, one must first look at a [thermodynamic system](#), which exchanges heat with its environment. The Clausius Inequality relates the change in [entropy](#) of this thermodynamic system to the heat supplied to the system. Therefore, the Inequality implies a reduction in entropy in the system during the thermodynamic cycle.

In this article, you will learn the Clausius Inequality equation, its derivation, and its applicability to [thermodynamic cycles](#).

Clausius Inequality Equation

The Clausius Inequality equation highlights the difference between a reversible process and an irreversible process. Therefore, it shows that for an irreversible process, the ratio of the [heat](#) entering a thermodynamic system at any point (dQ), to the temperature at the point of heat entry (T) will remain less than or equal to zero for a cycle. Moreover, this ratio represents the change in [entropy](#) (dS) of the system.

$$dS > \frac{dQ}{T}$$

$$\oint \frac{dQ}{T} < 0$$

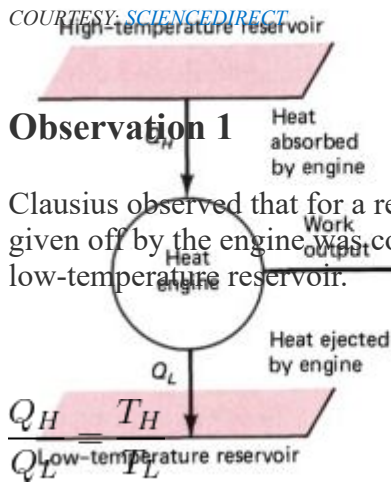
However, for a reversible process ([Carnot](#) or ideal cycle), there is no net change in entropy for a complete cycle. Thus, we express the Clausius Inequality equation for this scenario as follows:

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

$$\oint \frac{dQ}{T} = 0$$

Derivation of Clausius Inequality

The derivation of Clausius Inequality stems from observations of reversible and irreversible processes of a heat engine made by Rudolf Clausius. These processes entail the flow of heat from a high-temperature reservoir into an engine to enable it to work. Then, some of this [heat](#) ejects into the environment, which constitutes a low-temperature reservoir. Moreover, he recorded the heat coming into the engine (Q_H), and the heat leaving the engine into the environment (Q_L). Also, Clausius recorded the absolute temperature of the high-temperature reservoir (T_H), and the absolute temperature of the low temperature reservoir (T_L).



Observation 1

Clausius observed that for a reversible heat engine, the ratio of heat absorbed by the engine to that given off by the engine was consistently equal to the ratio of the high-temperature reservoir and low-temperature reservoir.

$$\frac{Q_H}{T_H} = \frac{Q_L}{T_L}$$

$$\frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

(1)

Observation 2

For an irreversible process, Clausius found that the relationship was not the same as in his first observation. Rather, the ratio of heat to absolute temperature increased in the direction of natural heat flow as seen in the second equation.

$$\frac{Q_H}{T_H} < \frac{Q_L}{T_L}$$

$$\frac{Q_H}{T_H} - \frac{Q_L}{T_L} < 0$$

(2)

Practically, because the heat exchange process involves both reversible and irreversible components, both equations combine to become a general one for all cycles.

$$\frac{Q_H}{T_H} - \frac{Q_L}{T_L} \leq 0$$

(3)

Finally, integrating the third equation over a cycle gives the Clausius Inequality equation for both reversible and irreversible cycles.

$$\oint \frac{dQ}{T} \leq 0$$

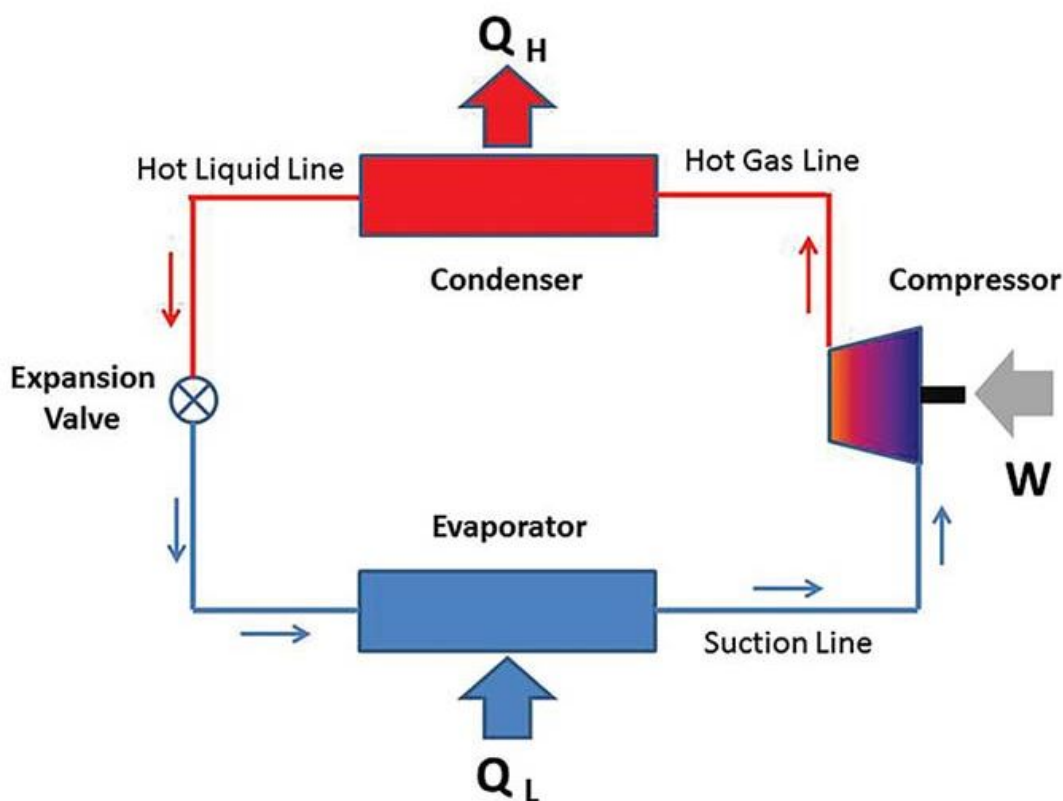
Applicability to Thermodynamic Cycles

The Clausius Inequality gives a mathematical explanation of the second law of thermodynamics. Hence, its application is evident in certain devices that operate in [thermodynamic cycles](#). Also, it is one of the first theorems that clearly addresses the concept of entropy. In addition, it shows the proportional relationship between entropy and energy flow.

As a result, one can confidently state that the transfer of heat will always occur from a hotter body to a cooler body naturally. Therefore, we need to use a device to achieve heat flow from a cooler to a hotter environment.

Refrigerator

A practical ramification of Clausius' observation is the use of a compressor in a [refrigeration system](#). The [compressor](#) drives the refrigerant to take heat out of the cooler refrigerating space into the hotter environment, through the aid of an evaporator and condenser respectively.



COURTESY: [INSULATION OUTLOOK](#)

For a refrigerator, the key parameter is its coefficient of performance (COP). The COP refers to the ratio of the quantity of heat removed from the refrigerating space to the work done by the [compressor](#). If no work is done for the heat to be removed, then the COP for a refrigerator equals infinity. According to Clausius Inequality, this is impossible. Evidently, he is right.

Heat Pump

volume,

$$C_P$$

heat capacity at constant pressure.

Maxwell's relations are a set of equations in [thermodynamics](#) which are derivable from the [symmetry of second derivatives](#) and from the definitions of the [thermodynamic potentials](#). These relations are named for the nineteenth-century physicist [James Clerk Maxwell](#).

Equations

See also: [symmetry of second derivatives](#)

The structure of Maxwell relations is a statement of equality among the second derivatives for continuous functions. It follows directly from the fact that the order of differentiation of an [analytic function](#) of two variables is irrelevant ([Schwarz theorem](#)). In the case of Maxwell relations the function considered is a thermodynamic potential and x_i and x_j are two different [natural variables](#) for that potential, we have

Schwarz's theorem (general)

$$\frac{\partial}{\partial x_j} \left(\frac{\partial \Phi}{\partial x_i} \right) = \frac{\partial}{\partial x_i} \left(\frac{\partial \Phi}{\partial x_j} \right)$$

where the [partial derivatives](#) are taken with all other natural variables held constant. For every thermodynamic potential there are

$$\frac{1}{2}n(n-1)$$

possible Maxwell relations where n is the number of natural variables for that potential.

The four most common Maxwell relations

The four most common Maxwell relations are the equalities of the second derivatives of each of the four thermodynamic potentials, with respect to their thermal natural variable ([temperature](#) T , or [entropy](#) S) and their *mechanical* natural variable ([pressure](#) P , or [volume](#) V):

Maxwell's relations (common)

$$\begin{array}{lll} +\left(\frac{\partial T}{\partial V}\right)_S & = & -\left(\frac{\partial P}{\partial S}\right)_V = \frac{\partial^2 U}{\partial S \partial V} \\ +\left(\frac{\partial T}{\partial P}\right)_S & = & +\left(\frac{\partial V}{\partial S}\right)_P = \frac{\partial^2 H}{\partial S \partial P} \\ +\left(\frac{\partial S}{\partial V}\right)_T & = & +\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\partial^2 F}{\partial T \partial V} \\ -\left(\frac{\partial S}{\partial P}\right)_T & = & +\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial^2 G}{\partial T \partial P} \end{array}$$

where the potentials as functions of their natural thermal and mechanical variables are the [internal energy](#)

$U(S, V)$
, [enthalpy](#)

$H(S, P)$
, [Helmholtz free energy](#)

$F(T, V)$
, and [Gibbs free energy](#)

$G(T, P)$

. The [thermodynamic square](#) can be used as a [mnemonic](#) to recall and derive these relations. The usefulness of these relations lies in their quantifying entropy changes, which are not directly measurable, in terms of measurable quantities like temperature, volume, and pressure.

Each equation can be re-expressed using the relationship

$$\left(\frac{\partial y}{\partial x}\right)_z = 1 / \left(\frac{\partial x}{\partial y}\right)_z$$

which are sometimes also known as Maxwell relations.

Derivation

Maxwell relations are based on simple partial differentiation rules, in particular the [total differential of a function](#) and the symmetry of evaluating second order partial derivatives.

Derivation

Derivation of the Maxwell relation can be deduced from the differential forms of the [thermodynamic potentials](#):

The differential form of internal energy U is

$$dU = T dS - P dV$$

This equation resembles [total differentials](#) of the form

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

It can be shown, for any equation of the form,

$$dz = M dx + N dy$$

that

$$M = \left(\frac{\partial z}{\partial x}\right)_y, \quad N = \left(\frac{\partial z}{\partial y}\right)_x$$

Consider, the equation

$$dU = T dS - P dV$$

. We can now immediately see that

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

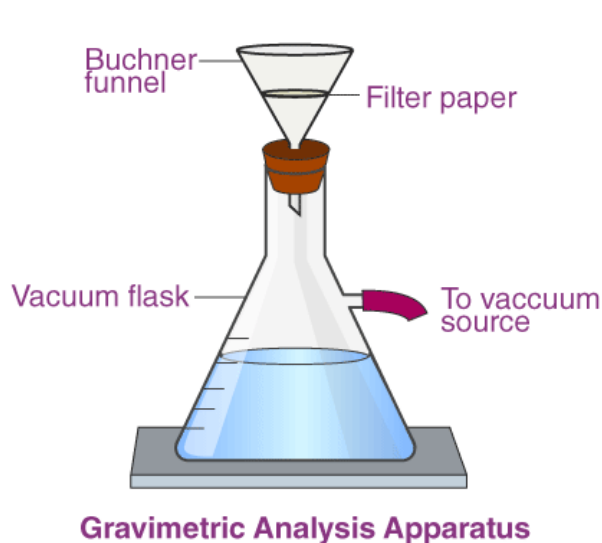
Since we also know that for functions with continuous second derivatives, the mixed partial derivatives are identical ([Symmetry of second derivatives](#)), that is, that

What is Gravimetric Analysis?

Gravimetric analysis is a method in [analytical chemistry](#) to determine the quantity of an analyte based on the mass of a solid. Example: Measuring the solids suspended in the water sample – Once a known volume of water is filtered, the collected solids are weighed.

The principle of Gravimetric Analysis:

The principle behind the gravimetric analysis is that the mass of an ion in a pure compound and can be determined. Later, used to find the mass percent of the same ion in a known quantity of an impure compound.



Gravimetric Analysis Apparatus

Steps followed in the Gravimetric Analysis

1. Preparation of a solution containing a known weight of the sample.
2. Separation of the desired constituent.
3. Weighing the isolated constituent.
4. Computation of the amount of the particular constituent in the sample from the observed weight of the isolated substance.

Types of Gravimetric Analysis

There are 4 fundamental types of gravimetric analysis. Of which, there are 2 common types involving changes in the phase of the analyte to separate it from the rest of a mixture, resulting in a change in mass.

Volatilisation gravimetry

- Volatilisation Gravimetry involves separating components of our mixture by heating or chemically decomposing the sample.

Precipitation gravimetry.

- Precipitation Gravimetry uses a precipitation reaction to separate one or more parts of a solution by incorporating it into a solid.

Electrogravimetry.

- Electrogravimetry is a method used to separate and quantify ions of a substance, usually a metal.

Thermogravimetry.

- Thermogravimetry is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature or as a function of time.

Advantages of Gravimetric Analysis

If the methods are followed carefully, it provides exceedingly precise analysis. It is used to determine the atomic masses of many elements to six-figure accuracy. It provides little room for instrumental error and does not require a series of standards for calculation of an unknown.

Disadvantages of Gravimetric Analysis

It usually provides only for the analysis of a single element, or a limited group of elements, at a time. Comparing modern dynamic flash combustion coupled with gas chromatography with traditional combustion analysis.

Examples of Gravimetric Analysis