University of Al-Mustaqbal
College of Science
Department of Medical Physics

Thermodynamics and Heat

Second stage

Thermal machines

Lecture Seven

Name of lecturer

Asst .prof .Dr Rusul Abdul Ameer

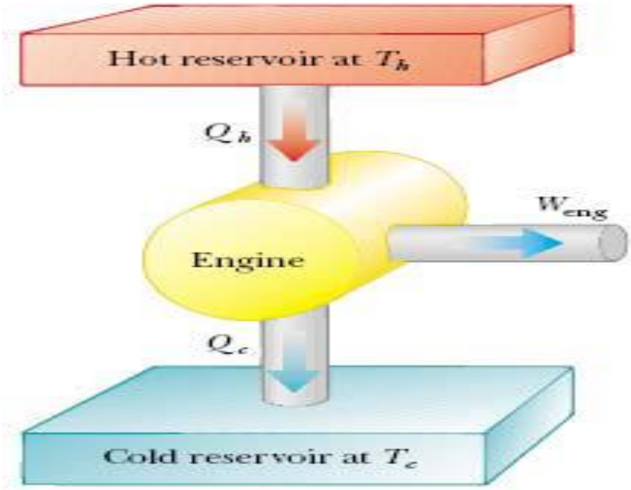
Thermal machines

The thermal machine is a sentence that takes energy in the form of heat and gives part of this energy in the form of work, using a medium. This is done periodically.

Steam engine where the medium is water vapor, and the cycle is as follows:

1. boiling water
2. the steam extend then motor piston moves
3. Re-cool and condense the vapor and return to the steam boiler

The thermal machine can be represented as follows:



Heat Engine:

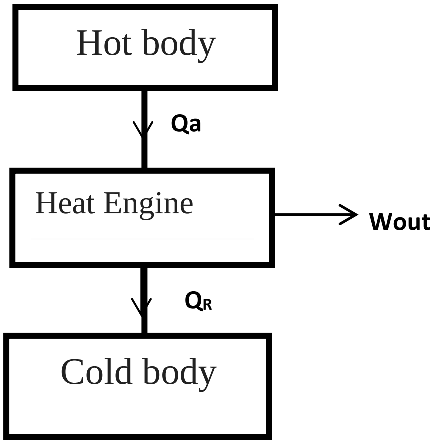
A thermodynamic system that works in a cycle and produces a work when the heat is added to it from the hot body, expelled from the hot body and partially expelled from the heat to the cold body. The thermal motor performance is expressed in thermal efficiency (η).

$$\eta = \frac{Wout}{Qh} = \frac{Qh - Qc}{Qh} \qquad \eta = 1 - \frac{Q_c}{Qh}$$

Q_h= The amount of heat added to the engine by the hot body.

Q_c = Amount of heat discharged from the engine to the cold body.

W_{out} = the work produced by the thermal engine.



Heat pumps:

Heat pumps are defined as transferring heat from the cold source to the hot source by taking mechanical action from the outside.

Figure blew shows the thermal pump, which is a thermodynamic system operating in the role and transfer heat from the cold body to the hot body. To accomplish this, the heat pump takes up a work from the surrounding medium.

The performance of the thermal pump is expressed by the Coefficient of Performance

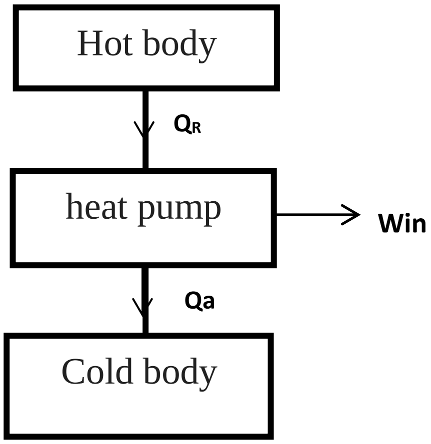
$$\textbf{C.O.P} = \frac{Qc}{Win} = \frac{Qc}{Q_h - Qc}$$

Where :

Q_c = Amount of heat absorbed by the heat pump from the cold body.

Q_h = Amount of heat expelled by the heat pump to the hot body.

W_{in}= The work required for the heat pump



Example: Household fridge, air conditioner

Carnot cycle

Carnot's cycle in physics and thermodynamics is one of the most famous dynamic reflex courses named after the French engineer Sadi Carnot (1796-1832).

Carnot's cycle is a theoretical thermocouple cycle that has a significant reflection in thermodynamics as it gives the maximum to get the work through a thermal cycle between two different degrees of heat. Through the Carnot cycle, the thermal efficiency of a particular machine can be calculated. That is, it gives us the part of the total thermal that we put into the machine to get them to work.

Through periodic reflections (Carnot cycle) the heat can be converted into a work because the amount of transformation in the state functions (internal energy - the entropy) is equal to zero.

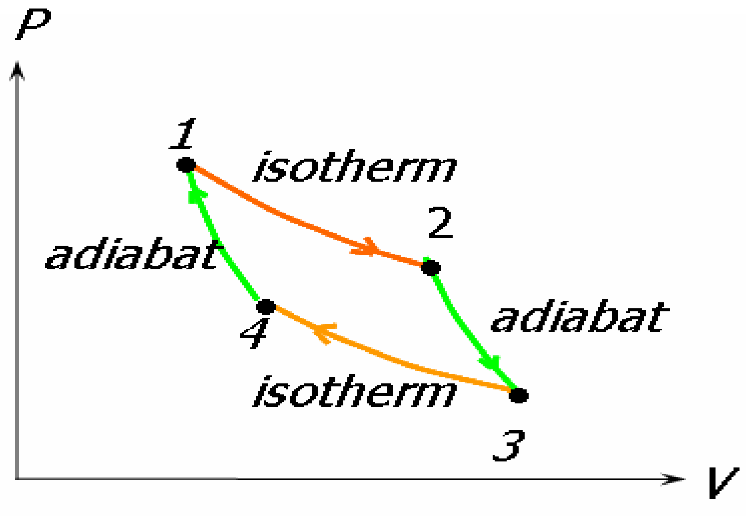
This cycle includes four steps that are reflective:

- 1 The process of extend by temperature stability.

2 - The process of extension adipatic.

- 3 compression by of temperature stability.

4 - The process of compression adipatic .



1- Process No. (1)

The gas expands at a When temperature is confirmed at high temperature of V_1 to V_2 and therefore performs a work .The heat escapes from the hot reservoir to the gas.

2 - Process No. (2)

The cylinder is isolated and the gas is allowed to expand adipatic from V_2 to V_3 (q = 0) and its temperature drops from T_2 to T_1 and the gas performs a work .

Since the gas is isolated, there is no heat exchange between it and the tank.

3 - process No. (3)

When the temperature is confirmed, the volume of the gas is reduced from V_3 to V_1 and thus the ocean performs a work at the expense of the gas and therefore a quantity of heat is transferred from the gas to the tank.

4- Process No. (4)

The gas is compressed backwards (in a large process) from V_4 to V_1 and the piston performs a work on the gas during the compression process.

Since steps 2 and 4 are numerically equal and different by signal , therefore they are equal and cancel each other and thus the work done at the cycle is:

$$W = W1 + W3$$

$$W2 = - Cv\ dT$$

$$W4 = Cv\ dT$$

$$W2 + W4 = - Cv\ dT + Cv\ dT = 0$$

$$\Delta E = q + W$$

$$- q = W$$

$$- q = - P\ dV$$

$$W1 = n\ RT \ln V2 / V1$$

$$W3 = n\ RT \ln V2 / V1$$

Questions

1. What is the primary function of a thermal machine?

a) To convert chemical energy into mechanical energy
b) To convert heat energy into work
c) To transfer heat from a cold source to a hot source
d) To store thermal energy
e) To heat a cold body without work output

2. What is the coefficient of performance (C.O.P) of a heat pump defined as?

a) The ratio of heat absorbed by the heat pump to the heat discharged by it
b) The ratio of work done by the pump to the heat absorbed
c) The ratio of heat absorbed from the cold body to the work input
d) The ratio of work input to the heat discharged to the hot body
e) The ratio of heat discharged to the work input

3. In the Carnot cycle, which of the following processes is characterized by an adiabatic expansion where no heat is exchanged?

a) Process 1 b) Process 2 c) Process 3 d) Process 4 e) None of the above

4. In a heat engine, which of the following represents the heat added from the hot body?

a) Qh b) Qc c) Wout d) Win e) Cv

5. During the Carnot cycle, the work produced is the result of the heat difference between which two bodies?

a) Two hot bodies
b) Two cold bodies
c) A hot body and a cold body
d) A hot body and the engine itself
e) A cold body and the surrounding environment

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Thermodynamics and Heat

Second stage

Maxwell's equations and Thermodynamic Potentials

Lecture Eight

Name of lecturer

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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:

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

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

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

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

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.

$$H = U + PV$$

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

$$dH = dU + d(PV) =$$

$$dU + PdV + VdP$$

$$dH = TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP$$

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.

$$F = U - TS$$

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

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

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

$$dF = TdS - PdV - TdS - SdT$$

$$dF = -PdV - SdT$$

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:

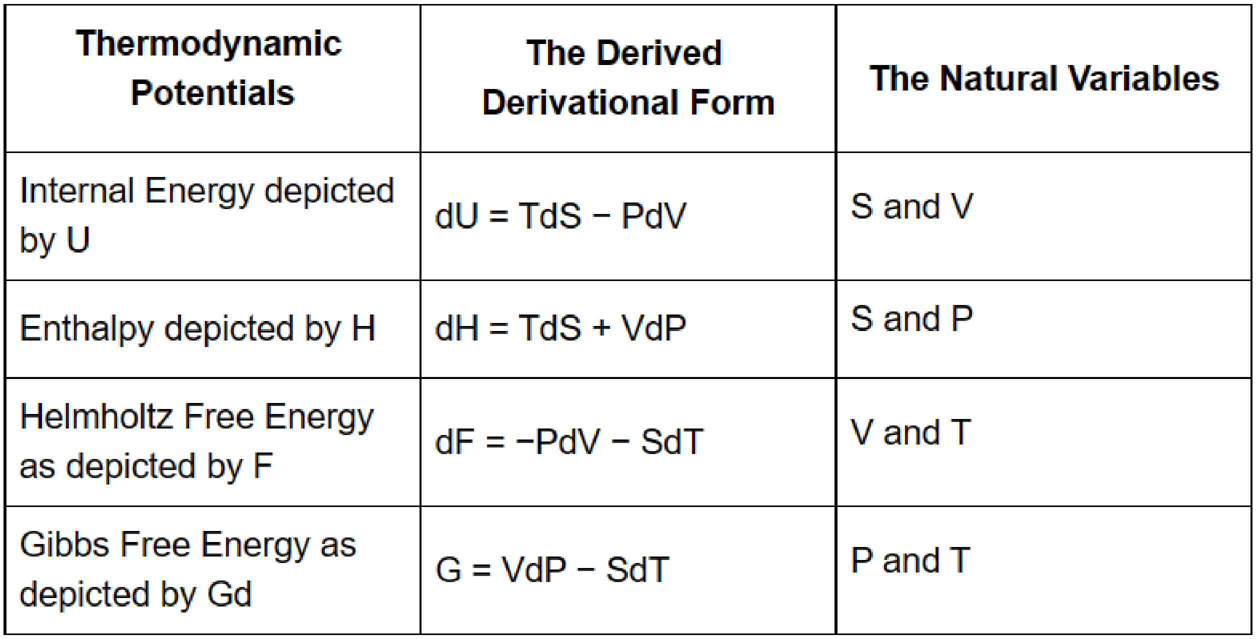
$$dG = dH - d(TS) = dH - TdS - SdT$$

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 reversible 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

Questions

1. Which thermodynamic potential represents the total heat content of a system at constant pressure?

a) Internal energy b) Helmholtz free energy c) Gibbs free energy
d) Enthalpy e) Temperature

Answer: d) Enthalpy

2. The differential form of internal energy (dU) is given by:

a) TdS + PdV b) TdS – PdV c) -PdV + VdP
d) TdS + VdP e) -PdV + SdT

Answer: b) TdS - PdV

3. What does Helmholtz free energy (F) represent in a system?

a) Heat released in a system at constant temperature
b) Work that can be obtained from a system at constant volume and temperature
c) Energy stored in a system d) Total heat content of a system
e) Energy released in a system at constant pressure

Answer: b) Work that can be obtained from a system at constant volume and temperature

4. Which thermodynamic potential is useful for studying phase transitions at constant pressure and temperature?
a) Enthalpy b) Helmholtz free energy c) Gibbs free energy
d) Internal energy e) Temperature

Answer: c) Gibbs free energy

5. What is the formula for Gibbs free energy (G)?
a) $G = U - TS$ b) $G = H - TS$ c) $G = H + TS$
d) $G = U + PV$ e) $G = TS - U$

Answer: b) $G = H - TS$

6. In a thermodynamic cycle, what is the net change in internal energy (ΔU)?
a) Zero b) positive c) Negative d) Undefine e) Equal to the work done

Answer: a) Zero

7. What is the Maxwell relation derived from the Helmholtz free energy?
a) $(\partial S/\partial V)_T = (\partial P/\partial T)_V$ b) $(\partial T/\partial V)_S = (\partial P/\partial S)_V$ c) $(\partial P/\partial T)_S = (\partial V/\partial T)_P$
d) $(\partial S/\partial T)_P = -(\partial V/\partial P)_T$ e) $(\partial T/\partial S)_P = -(\partial V/\partial P)_T$

Answer: d) $(\partial S/\partial T)_P = -(\partial V/\partial P)_T$

8. What is the differential form of the Gibbs free energy (dG)?
a) $dG = VdP - SdT$
b) $dG = TdS + PdV$
c) $dG = -PdV + SdT$
d) $dG = VdP + SdT$
e) $dG = -VdP - TdS$

Answer: a) $dG = VdP - SdT$

9. A thermodynamic cycle in which the system returns to its initial state after completing the cycle is known as:
a) Reversible cycle b) Irreversible cycle c) Heat engine
d) Heat pump e) Ideal cycle

Answer: a) Reversible cycle

10. The change in internal energy (ΔU) over a thermodynamic cycle is:
a) Equal to the heat added to the system b) Equal to the work done by the system
c) Zero d) Equal to the total work done in the cycle
e) The sum of all the heat inputs

Answer: c) Zero

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Thermodynamics and Heat

Second stage

Fundamentals of Phase Transitions

Lecture Nine

Name of lecturer

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Fundamentals of Phase Transitions

Phase transition is when a substance changes from a solid, liquid, or gas state to a different state. Every element and substance can transition from one phase to another at a specific combination of temperature and pressure.

Phase Changes

Each substance has three phases it can change into; solid, liquid, or gas . Every substance is in one of these three phases at certain temperatures. The temperature and pressure at which the substance will change is very dependent on the intermolecular forces that are acting on the molecules and atoms of the substance(2). There can be two phases coexisting in a single container at the same time. This typically happens when the substance is transitioning from one phase to another. This is called a two-phase state(4). In the example of ice melting, while the ice is melting, there is both solid water and liquid water in the cup.

There are six ways a substance can change between these three phases; melting, freezing, evaporating, condensing, sublimination, and deposition. These processes are reversible and each transfers between phases differently:

- **Melting**: The transition from the solid to the liquid phase
- **Freezing**: The transition from the liquid phase to the solid phase
- **Evaporating**: The transition from the liquid phase to the gas phase
- **Condensing**: The transition from the gas phase to the liquid phase
- **Sublimination**: The transition from the solid phase to the gas phase
- **Deposition**: The transition from the gas phase to the solid phase

How Phase Transition works

There are two variables to consider when looking at phase transition, pressure (P) and temperature (T). For the gas state, The relationship between temperature and pressure is defined by the equations below:

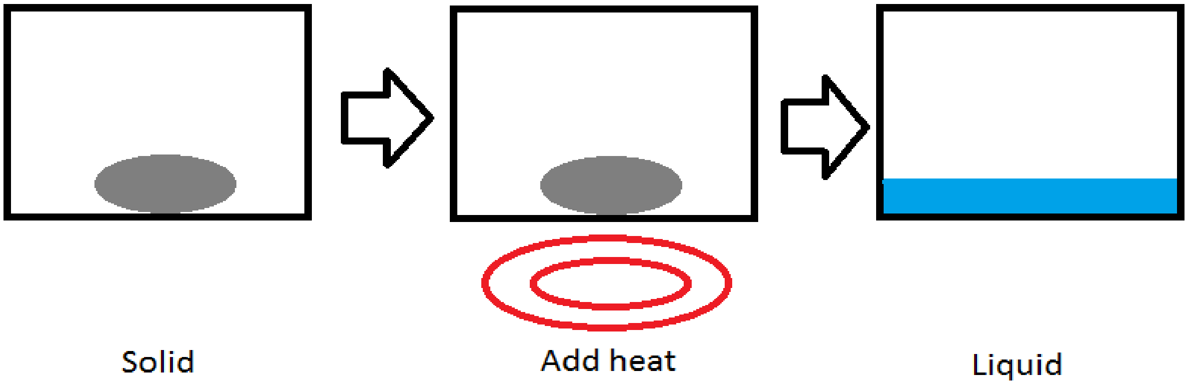
Ideal Gas Law: $PV=nRT$

Where V is volume, R is the gas constant, and n is the number of moles of gas.

The ideal gas law assumes that no intermolecular forces are affecting the gas in any way, while the van der Waals equation includes two constants, a and b, that account for any intermolecular forces acting on the molecules of the gas.

Temperature

Temperature can change the phase of a substance. One common example is putting water in a freezer to change it into ice. In the picture above, we have a solid substance in a container. When we put it on a heat source, like a burner, heat is transferred to the substance increasing the kinetic energy of the molecules in the substance. The temperature increases until the substance reaches its melting point . As more and more heat is transferred beyond the melting point, the substance begins to melt and become a liquid(3). This type of phase change is called an isobaric process because the pressure of the system stays at a constant level.



Melting point (T_f)

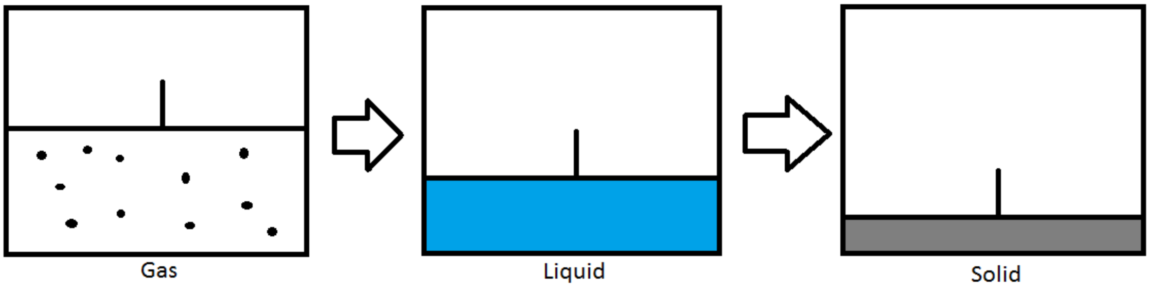
Each substance has a melting point. The melting point is the temperature that a solid will become a liquid. At different pressures, different temperatures are required to melt a substance. Each pure element on the periodic table has a normal melting point, the temperature that the element will become liquid when the pressure is 1 atmosphere(2).

Boiling Point (T_b)

Each substance also has a boiling point. The boiling point is the temperature that a liquid will evaporate into a gas. The boiling point will change based on the temperature and pressure. Just like the melting point, each pure element has a normal boiling point at 1 atmosphere.

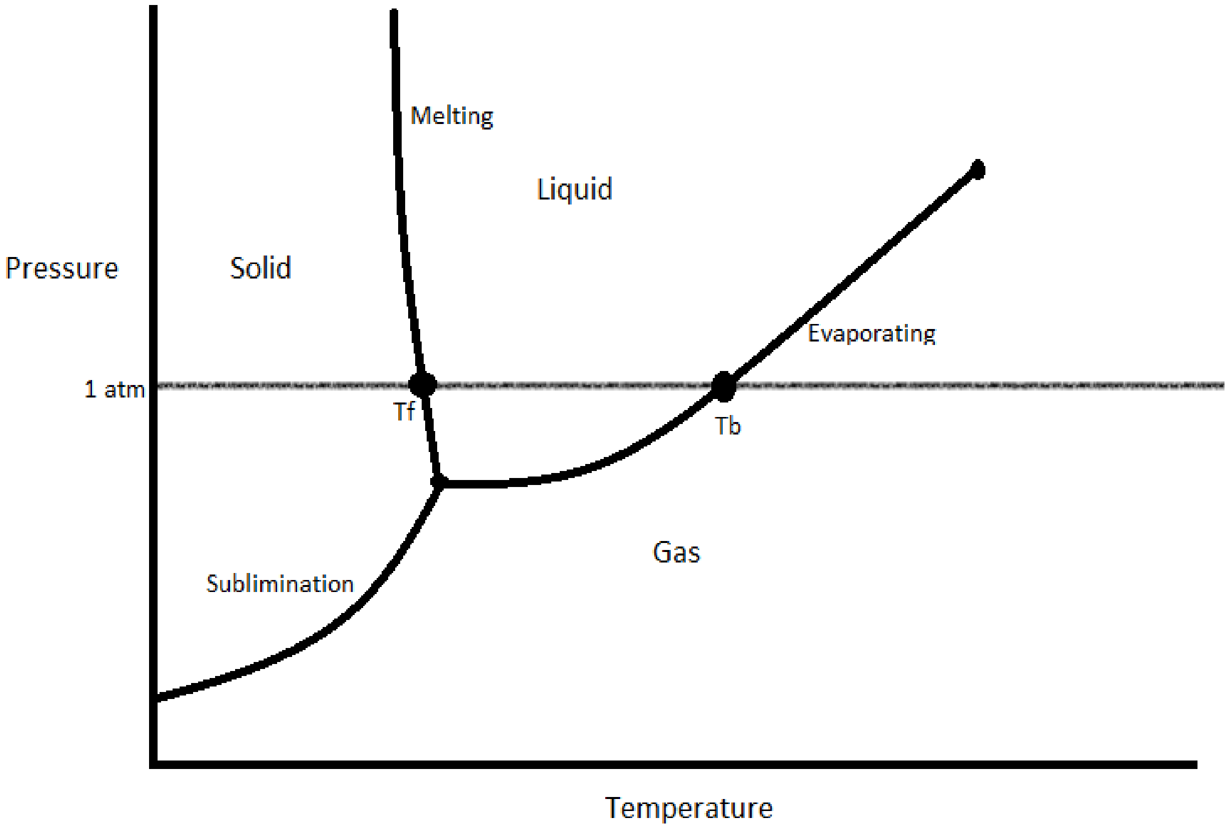
Pressure

Pressure can also be used to change the phase of the substance. In the picture above, we have a container fitted with a piston that seals in a gas. As the piston compresses the gas, the pressure increases. Once the boiling point has been reached, the gas will condense into a liquid. As the piston continues to compress the liquid, the pressure will increase until the melting point has been reached. The liquid will then freeze into a solid. This example is for an isothermal process where the temperature is constant and only the pressure is changing.



A Brief Explanation of a Phase Diagram

Phase transition can be represented with a phase diagram. A phase diagram is a visual representation of how a substance changes phases.



This is an example of a phase diagram. Often, when you are asked about a phase transition, you will need to refer to a phase diagram to answer it. These diagrams usually have the normal boiling point and normal melting point marked on them, and have the pressures on the y-axis and temperatures on the x-axis. The bottom curve marks the temperature and pressure combinations in which the substance will subliminate . The left left marks the temperature and pressure combinations in which the substance will melt . Finally, the right line marks the conditions under which the substance will evaporate.

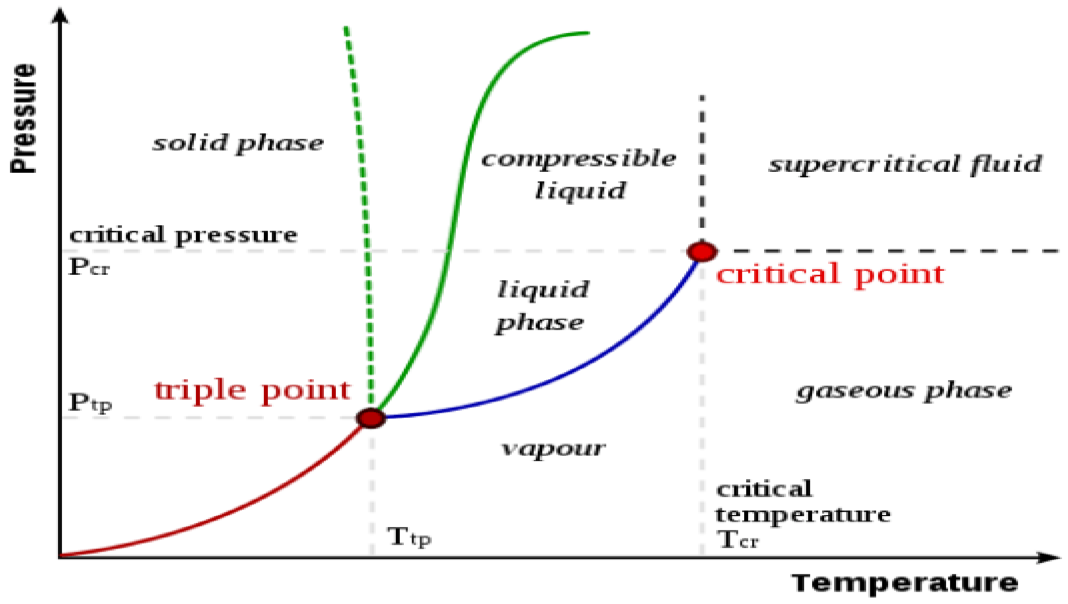
What is the Difference Between First and Second Order Phase Transition

The **key difference between first and second order phase transition** is that first order phase transitions depend on the first power of the reactant concentration in a rate equation, whereas second order phase transitions depend on the second power of the concentration in the rate equation.

A phase transition is a change of phase of matter, which is a physical process of transition of a state of a medium to a different state of the same medium, which is identified by parameters such as density and volume. Generally, this term is used to describe phases such as solid, liquid, gas, and plasma. The types of phase transitions include melting, boiling, sublimation, vaporization, ionization, deposition, condensation, and recombination.

What is First Order Phase Transition?

First order phase transitions are chemical reactions in which the rate of reaction depends on the molar concentration of one of the reactants involved in the reaction. Therefore, the sum of the powers to which the reactant concentrations are raised in the rate law equation will always be 1. If a single reactant takes part in these reactions, the concentration of that reactant determines the rate of the reaction. But sometimes, there is more than one reactant taking part in these reactions. In such cases, one of these reactants will determine the rate of the reaction.

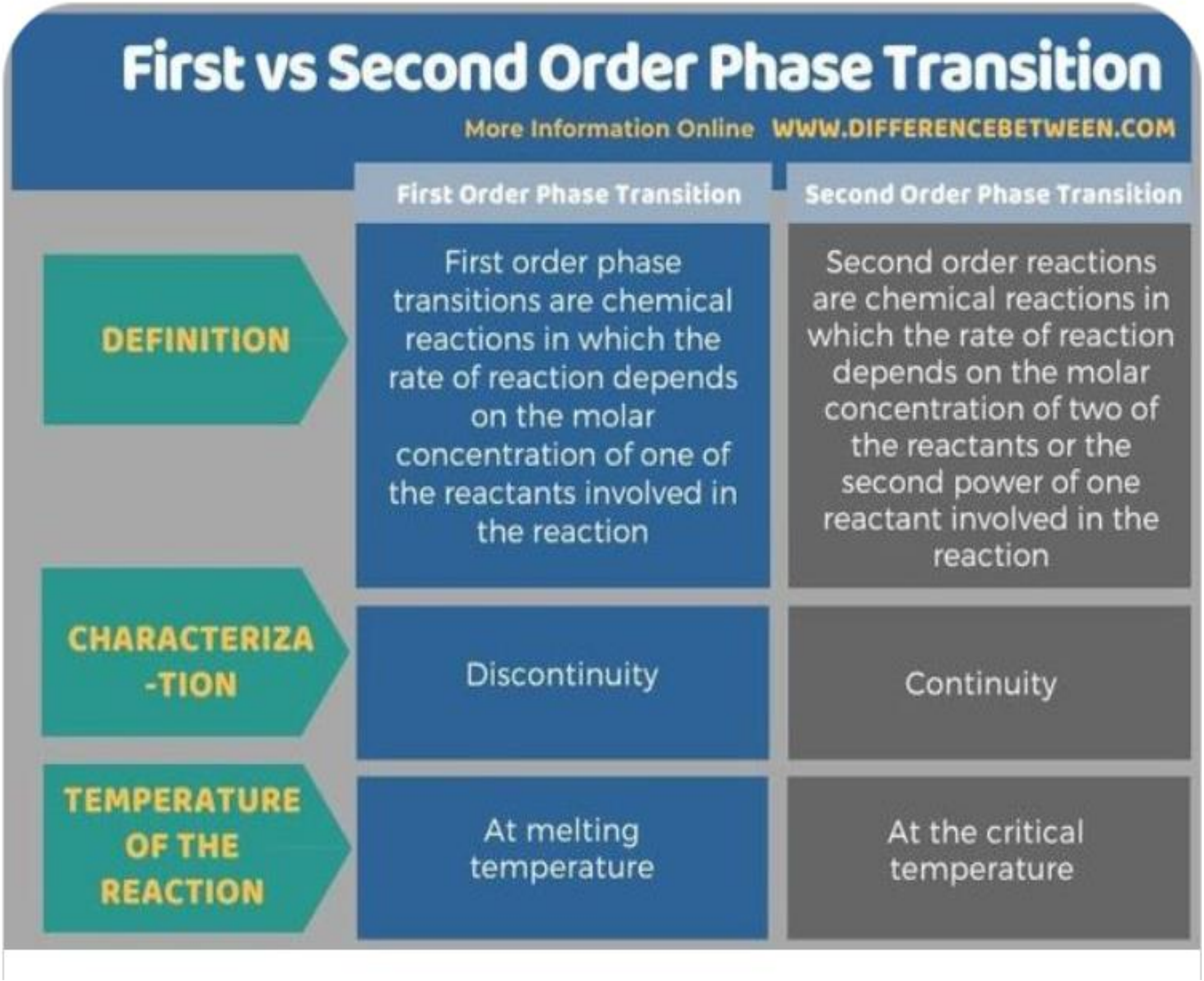


We can characterize a first order phase transition by the discontinuity of thermodynamic variables, including density and entropy. Moreover, this type of transition is usually displayed by changes in volume.

What is Second Order Phase Transition?

Second order phase transitions are chemical reactions in which the rate of reaction depends on the molar concentration of two of the reactants or the second power of one reactant involved in the reaction. Therefore, the sum of the powers to which the reactant concentrations are raised in the rate law equation will always be 2. If there are two reactants, the rate of reaction will depend on the first power of the concentration of each reactant.

A second phase transition is also known as a continuous phase transition because it is characterized by a divergent susceptibility, a power law decay of correlations near criticality, etc. The theory behind the second order phase transitions was developed by scientists using the Landau theory.



First vs Second Order Phase Transition

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	First Order Phase Transition	Second Order Phase Transition
DEFINITION	First order phase transitions are chemical reactions in which the rate of reaction depends on the molar concentration of one of the reactants involved in the reaction	Second order reactions are chemical reactions in which the rate of reaction depends on the molar concentration of two of the reactants or the second power of one reactant involved in the reaction
CHARACTERIZA-TION	Discontinuity	Continuity
TEMPERATURE OF THE REACTION	At melting temperature	At the critical temperature

Summary – First vs Second Order Phase Transition

First order phase transitions are chemical reactions in which the rate of reaction depends on the molar concentration of one of the reactants involved in the reaction. Second order reactions, on the other hand, are chemical reactions in which the rate of reaction depends on the molar concentration of two of the reactants or the second power of one reactant involved in the reaction. The key difference between first and second order phase transition is that first order phase transitions depend on the first power of the reactant concentration in a rate equation, whereas second order phase transitions depend on the second power of the concentration in the rate equation.

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Thermodynamics and Heat

Second stage

Third Law of Thermodynamics

Lecture Ten

Name of lecturer

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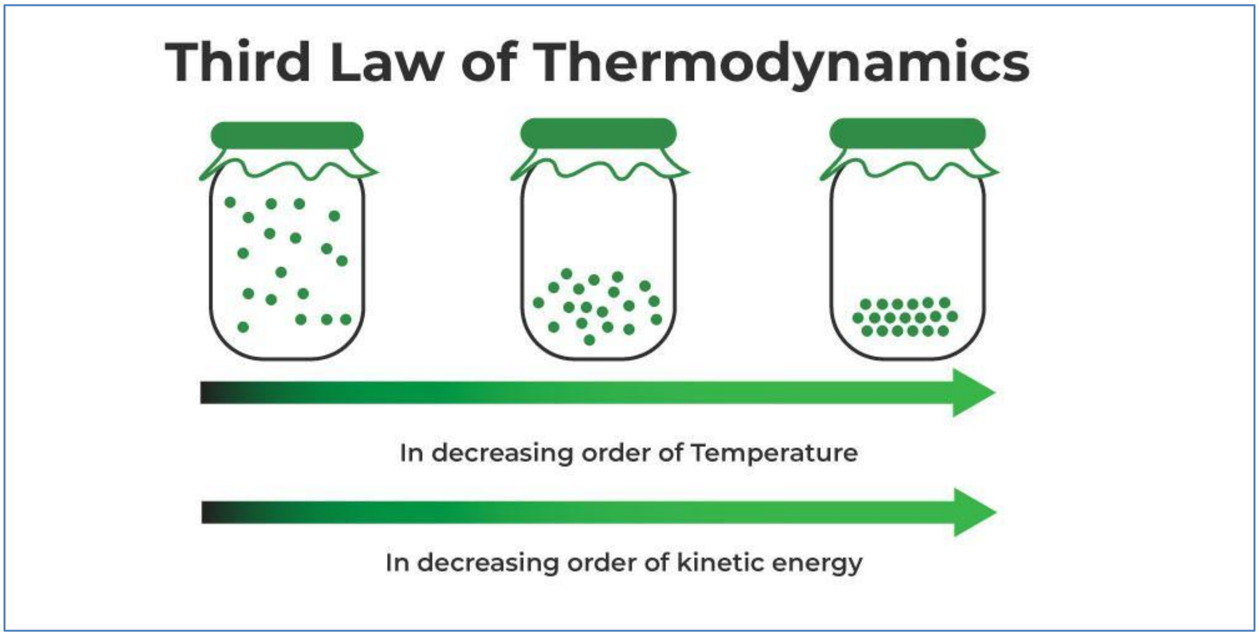
Third Law of Thermodynamics

The third law of thermodynamics states that when the temperature approaches absolute zero, the entropy of a system approaches a constant value. At absolute zero temperature, the entropy of a pure crystalline solid is zero. If the perfect crystal has only one state with minimum energy, this assertion holds true.



Third law of Thermodynamics mathematical expression

As per **statistical mechanics**, the entropy of any system is a function of initial entropy, which is

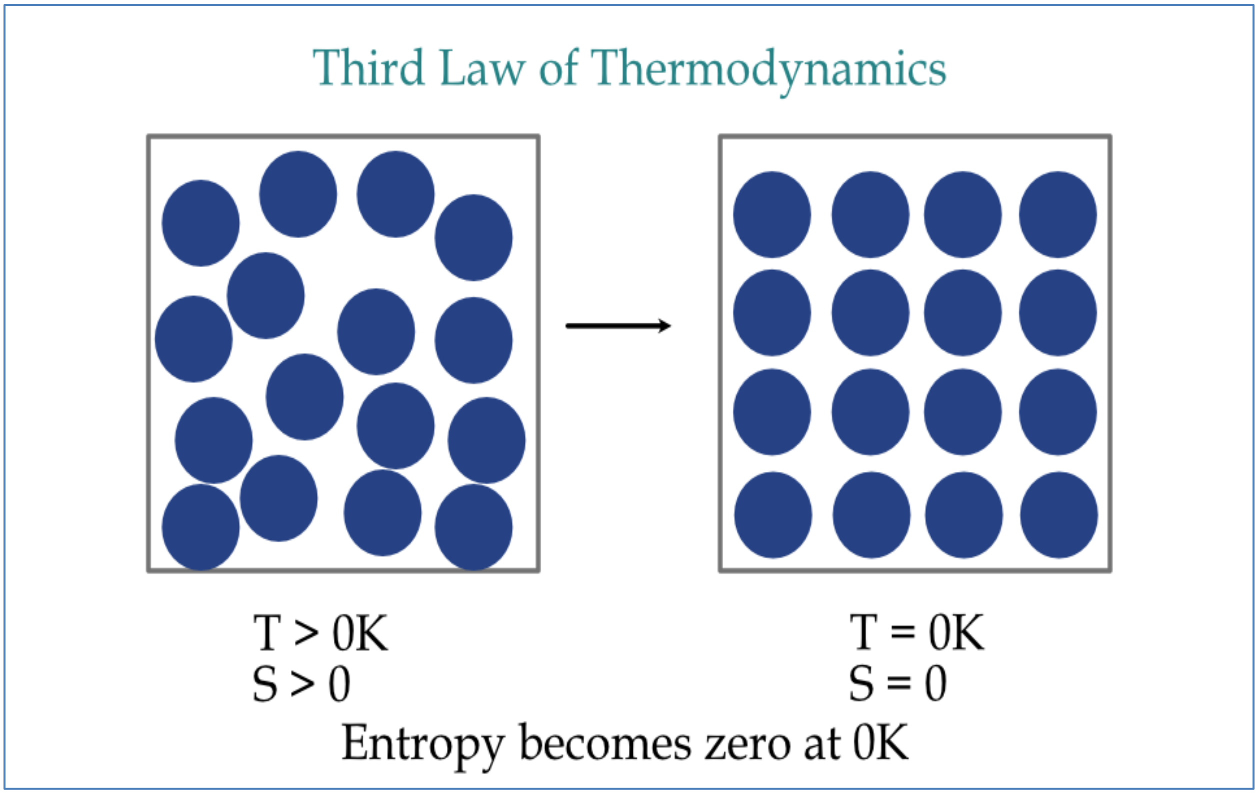
$$S–S0=k_B \ln\Omega$$

where S and S_0 are the entropy and initial entropy of the system and K_b is the Boltzmann constant. Ω is the total number of microstates in the system (the number of ways the system can become ordered).

For a perfect crystal, the number of microstates is 1. And on considering the initial entropy as zero, the entropy of the perfect crystal at absolute zero becomes

$$\mathbf{S = k_B \ln(1) = 0}$$

Thus, the entropy of a perfect crystal becomes zero at absolute zero temperature.



Applications of the Third Law of Thermodynamics

An important application of the third law of thermodynamics is that it helps in the calculation of the absolute entropy of a substance at any temperature ‘T’. These determinations are based on the heat capacity measurements of the substance. For any solid, let S_0 be the entropy at 0 K and S be the entropy at T K, then

$$\mathbf{\Delta S = S - S_0}$$

$\Delta S=\int 0TCpdTT$

According to the third law of thermodynamics, $S_0 = 0$ at 0 K,

$S=\int 0TCpTdT$

The value of this integral can be obtained by plotting the graph of C_p / T versus T and then finding the area of this curve from 0 to T. The simplified expression for the absolute entropy of a solid at temperature T is as follows:

$S=\int 0TCpTdT$

$S=\int 0TCpdlnT$

$= C_p \ln T = 2.303\ C_p \log T$

Here C_p is the heat capacity of the substance at constant pressure and this value is assumed to be constant in the range of 0 to T K.