

MME 2009

Metallurgical

Thermodynamics

Introduction: Basic definitions, concepts
and relations in Thermodynamics

What is **Thermodynamics**?

The science dealing with energy transformations involving *heat* and *mechanical work*, and the interactions between energy and matter

Example - Masses falling in gravitational field, combustion, refrigeration, metal extraction, etc.

Chemical and Physical experimental findings have been organized into laws and principles of thermodynamics that describe nature

Laws and principles of thermodynamics are developed into theorems of engineering relevance which are used to control matter

Matter, which is the subject of thermodynamic analysis is called a *system*

Main aim of applied thermodynamics is the determination of the effect of the environment on the equilibrium state of a given system by a series of established relationships

Thermodynamics addresses two types of problems:

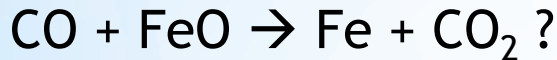
1- Computation of energy difference between two physical conditions

Example- Between coal + oxygen and combustion products

Between gases at different densities

2- Determination of spontaneous direction of a process

Example- Can the top gas from an iron blast furnace containing CO be recycled to reduce more iron oxide?



Will H₂O start to boil at 0.8 atm and 98 °C ?

Problems outside the scope of thermodynamics:

- Determination of the rate of a possible process
- Determination of microscopic mechanisms involved in transformations

Four Fundamental Laws of Thermodynamics

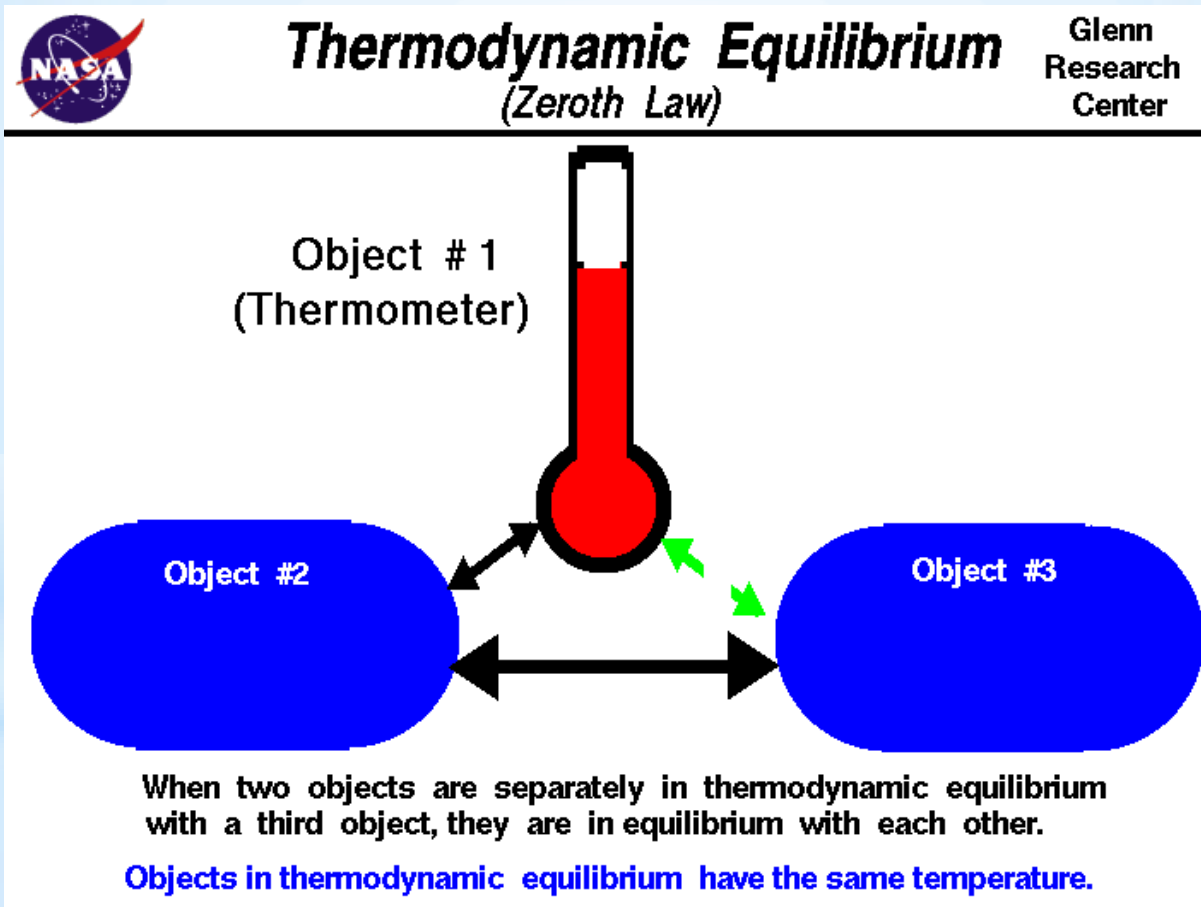
First Law - Energy cannot be created or destroyed. It spontaneously transforms to other form of energy when disappears

Second Law - Entropy or disorderness of the universe increases with irreversable spontaneous processes

Zeroth Law - If two systems A and C are each in thermodynamic equilibrium with a third system B, then A and C are in thermodynamic equilibrium with each other
i.e. temperature satisfies a transitive property

Third Law - The entropy or disorderness of a perfect crystal, at absolute zero Kelvin, is exactly equal to zero
Absolute zero means that atoms are in a state of minimum energy, they can only accept energy, and cannot transmit energy

Zeroth law of thermodynamics defines temperature:
If two bodies are in thermal equilibrium with a third body, they are in thermal equilibrium with each other and hence their temperatures are equal



The first law of thermodynamics defines energy

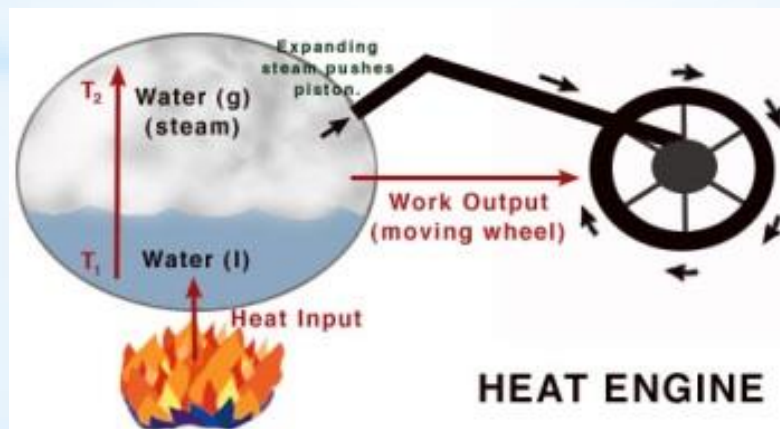
Although energy has many forms, the total quantity of energy is constant. When energy disappears in one form, it appears simultaneously in other forms

Hence

$$\Delta U + \Delta E_K + \Delta E_P = Q - W$$

Heat and work are forms of energy that are transformed into other forms of energy. If friction is eliminated, work is efficiently transformed to potential, kinetic, electrical and heat energy by a conversion ratio of upto 100%

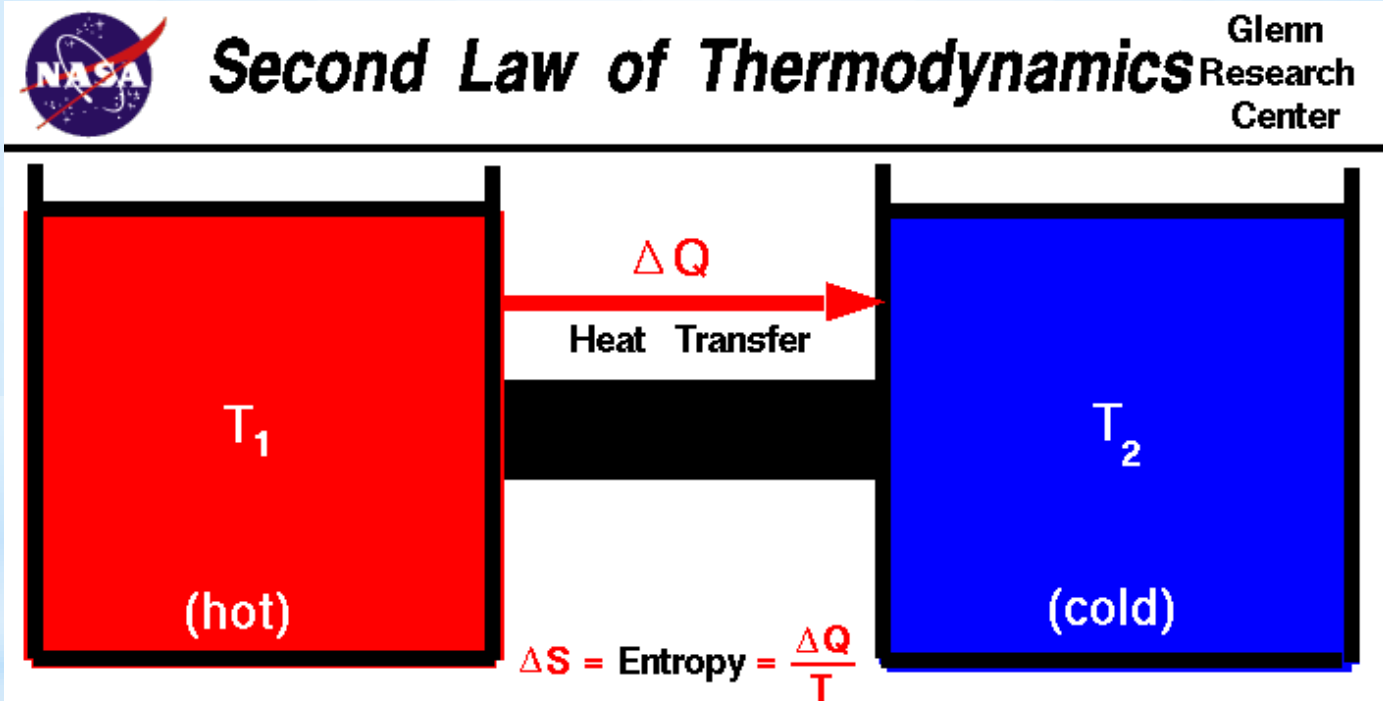
Heat on the other hand is readily lost to the surroundings and its conversion into work, mechanical or electrical energy does not exceed 40% efficiency because the flow of heat always takes place from the hotter to the cooler body and never in the reverse direction



The second law of thermodynamics defines entropy

The second law of thermodynamics states that the entropy of the universe increases for spontaneous processes, and the entropy of the universe does not change for reversible processes

As a result of all spontaneous processes, the entropy of the universe increases



There exists a useful thermodynamic variable called entropy (S). A natural process that starts in one equilibrium state and ends in another will go in the direction that causes the entropy of the system plus the environment to increase for an irreversible process and to remain constant for a reversible process.

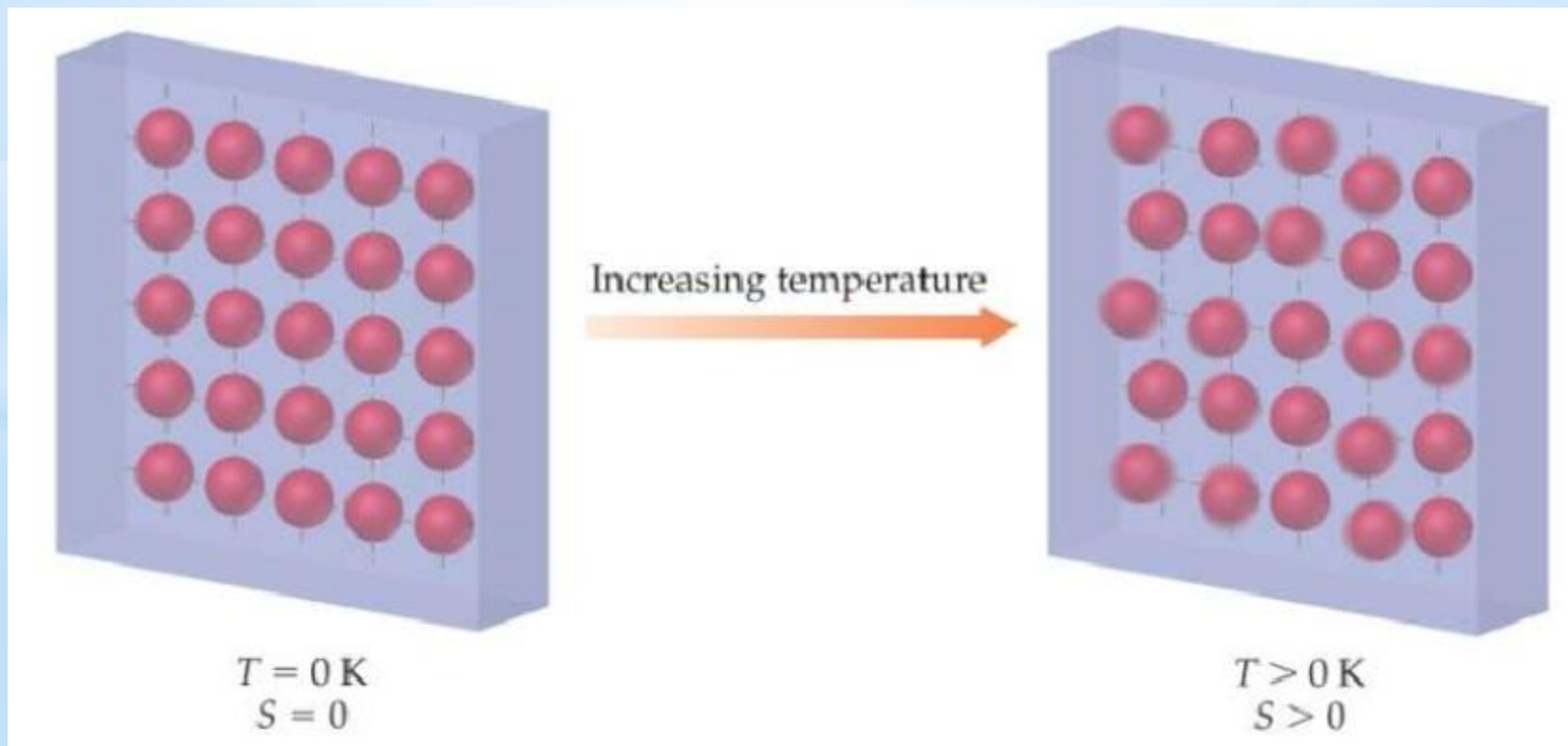
$$S_f = S_i \text{ (reversible)}$$

$$S_f > S_i \text{ (irreversible)}$$

Third law of thermodynamics gives numerical value to entropy:
Only substance having a perfectly ordered state with zero entropy is a perfect crystal at absolute zero

These extreme conditions can never be met, therefore all substances have some entropy or randomness

From an entropy standpoint, reactions tend to progress towards the formation of gases from liquids and solids and also tend towards forming more molecules from fewer by decomposition, thereby being capable of an even greater disordered condition



Brief History of Thermodynamics

10 AD - People in ancient Alexandria were reported to build early steam engines

10 AD - Middle ages

Countless attempts to convert energy from a heat source to mechanical work without the benefit of a cleanly formulized theory

1650 - World's first modern engine built by Otto von Guericke

1656 - R. Boyle built World's first air pump

1697 - World's first steam engine built by T. Savery in 1697

1660

Pressure-Volume relationship of a gas at constant temperature determined experimentally by R. Boyle

$$P \propto \frac{1}{V}$$

1777

Watt built the modern steam engine

1783

Caloric theory by Lavoisier - the temperature of a substance was considered to be determined by the quantity of caloric gas it contained

1787

Volume-Temperature relationship of a gas at constant pressure determined experimentally by J. A. C. Charles

$$V \propto T \quad PV = RT$$

$$\frac{PV}{T} = \frac{P_0V_0}{T_0} = R$$

1799

Caloric theory discredited by Rumford and H. Davy - melted two blocks of ice by rubbing them together in vacuum



Brief History of Thermodynamics

1824 - Heat, power and engine efficiency related by S. Carnot in 1824

1840

Relationship between heat and work established by J. Joule in 1840:

Work performed in adiabatically contained water increased the temperature of water

$$W = Q$$

1 calorie = the quantity of heat required to increase the of 1 gram of water from 14.5 to 15.5 °C

1847 - Hermann von Helmholtz publishes his theory of energy conservation

1848

William Thomson postulates an absolute zero of temperature and uses the word “Thermodynamics”

1850

Entropy and the second law introduced by R. Clausius as the heat turned into waste

1871

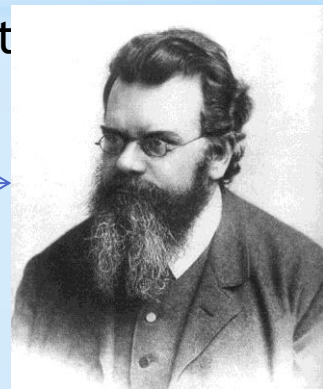
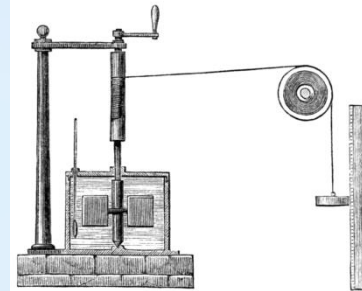
J.C. Maxwell formulated a new branch of thermodynamics called Statistical Thermodynamics

1875

Entropy and molecular motion connected by L. Boltzmann $S = k \log W$

1876

Gibbs energy, enthalpy and phase rule presented by J. Williard Gibbs

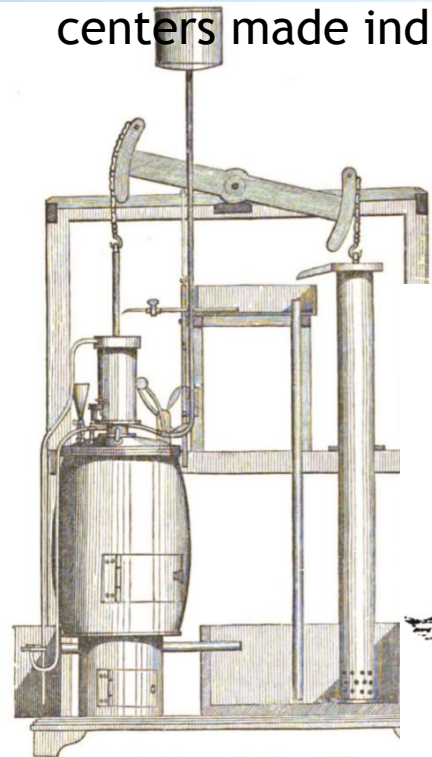


Practical applications of thermodynamics

Invention of steam engine transformed the world in a way similar to the invention of networked computers in the late 20th century, in fact more remarkably

Steam power replaced animal power throughout much of the world and enabled rapid development of broad economic segments: mining, manufacturing, land and sea transportation

Large scale population movements started as opportunities in urban manufacturing centers made industrial work more appealing than agricultural work



• Fig. IV.—Watt's model in Glasgow College.

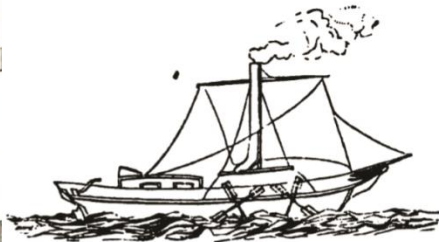


Fig. VI.—The "Comet," 1811-12.

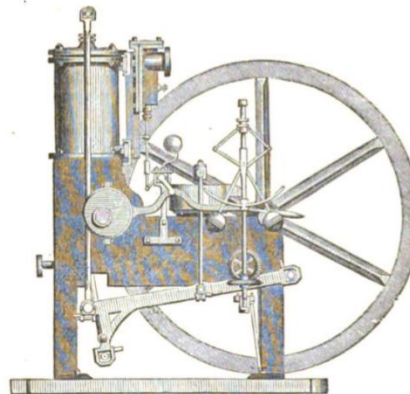


Fig. VII.—Engine of the "Comet," 1811-12.

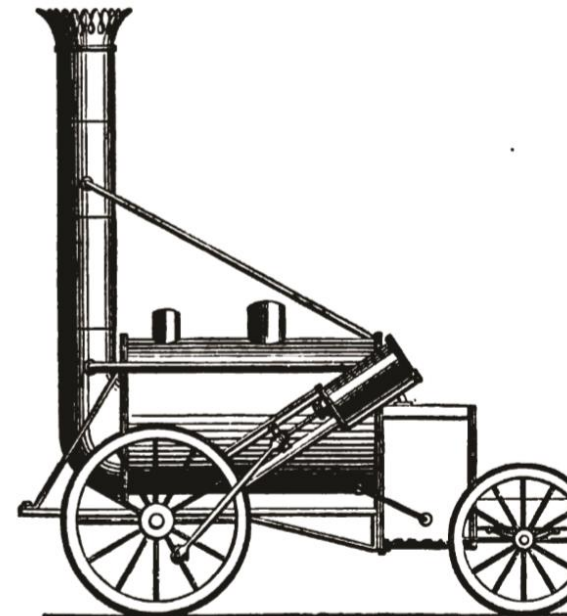


Fig. VIII.—The "Rocket," 1829.

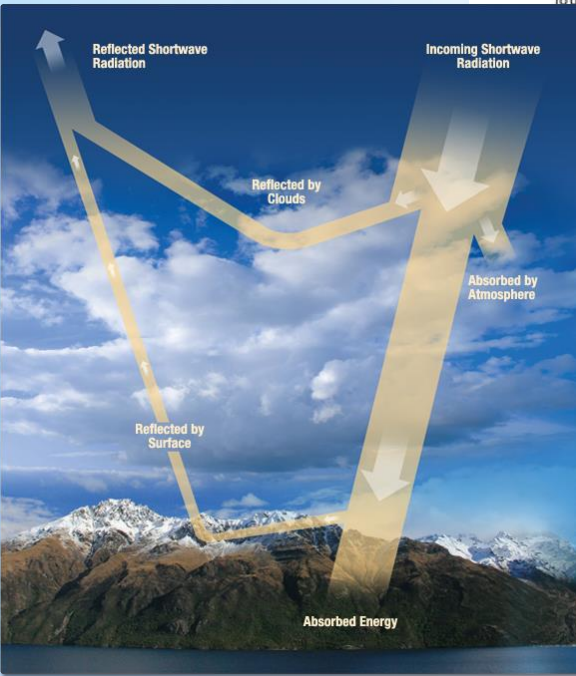
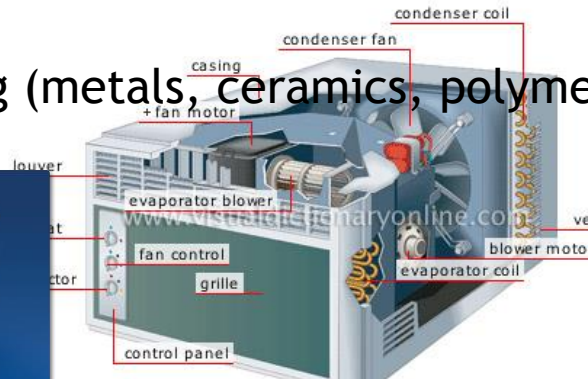
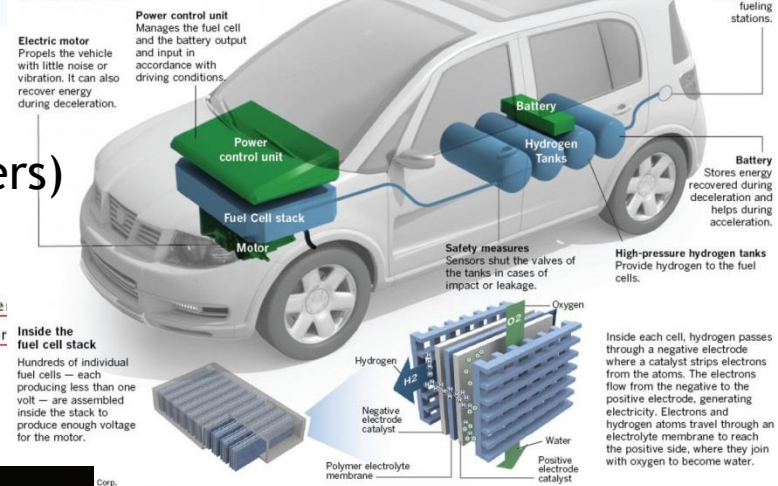
Modern fields of thermodynamic study

- Gasoline and Diesel engines
- Fuel cells
- Power plants
- Weather
- Space exploration and Astronomy
- Chemical rocket engines
- Heating, refrigeration, and air conditioning
- Cooking
- Materials processing (metals, ceramics, polymers)



How fuel cell cars work

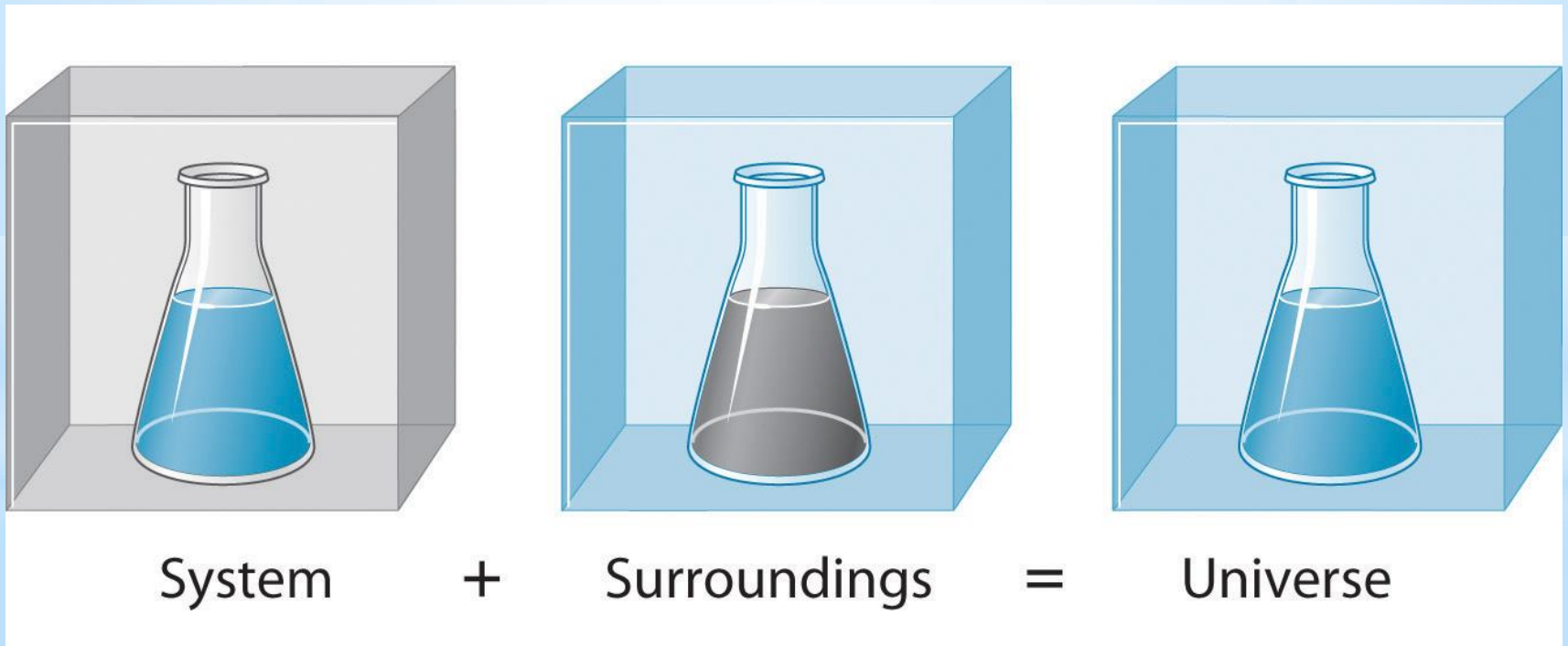
A fuel cell is a clean and efficient power plant that makes electricity through a chemical reaction between hydrogen and oxygen.



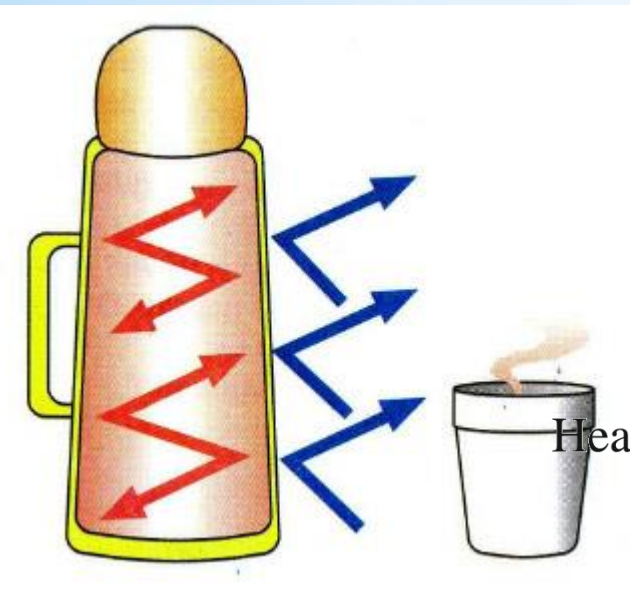
Basic Definitions

System: Part of the universe conceptually separated from the rest

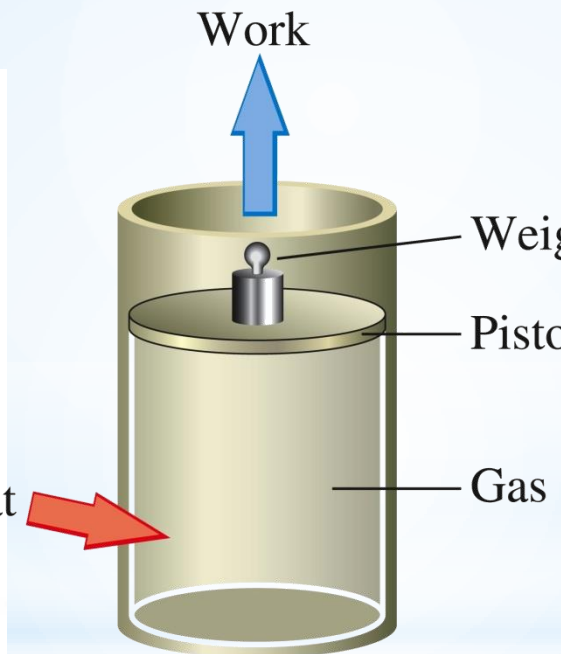
Surroundings: All that remains outside what has arbitrarily been chosen as the system



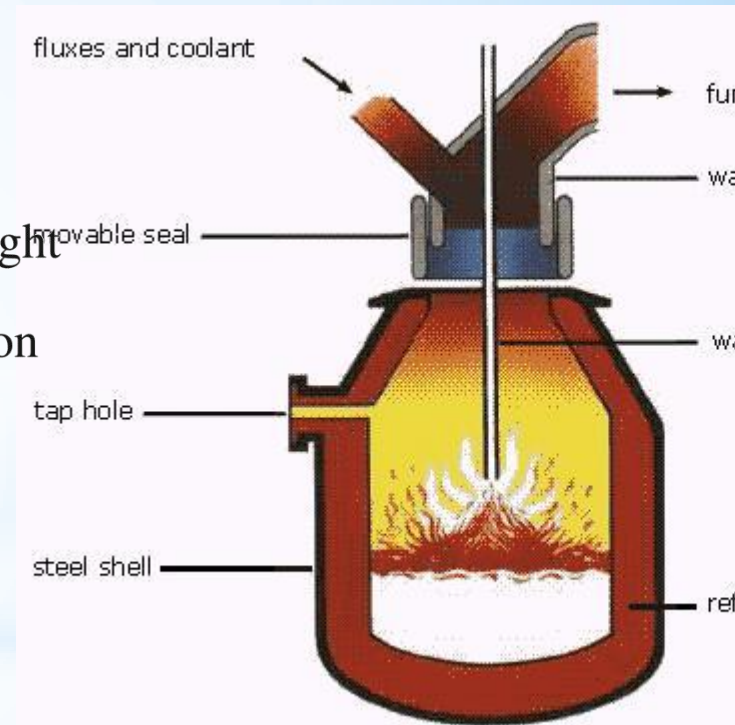
Open system- can exchange both mass and energy with surroundings
Closed system- can exchange only energy with surroundings
Isolated system- no exchange of mass or energy with surroundings



Isolated System



Closed System



Open System

Thermodynamic Equilibrium

A system is said to be in equilibrium when its observable properties do not change with time as long as the external conditions are unaltered

Thermal equilibrium - T constant

Mechanical equilibrium - P constant

Chemical equilibrium - Forward and reverse reaction rates constant

Process - Transformation of a system from one state to another by a change in any one of the thermodynamic properties of the system

Isothermal process - constant temperature

Isobaric process - constant pressure

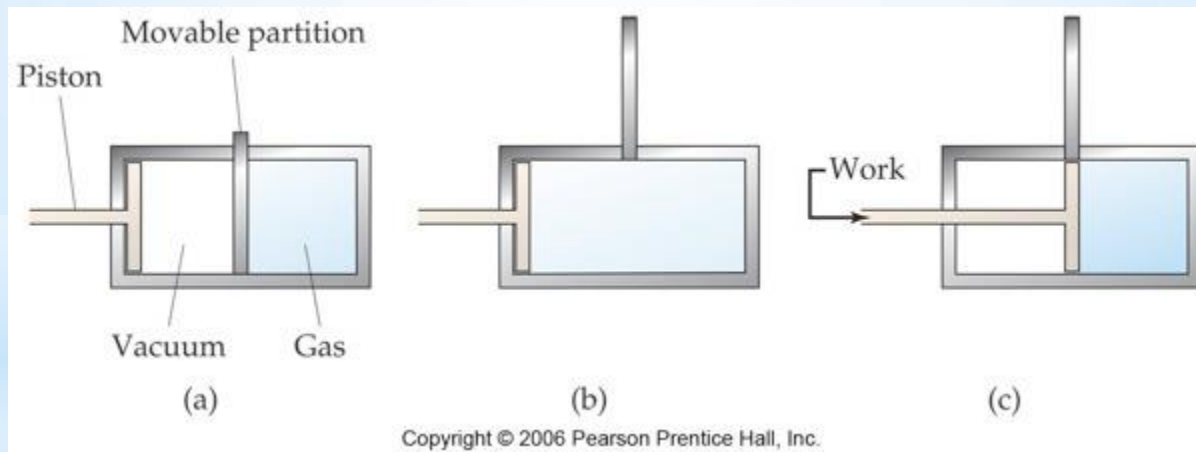
Isochoric process - constant volume

Path - Locus of all the states that the system passes through during the process

Reversible Process

The system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process

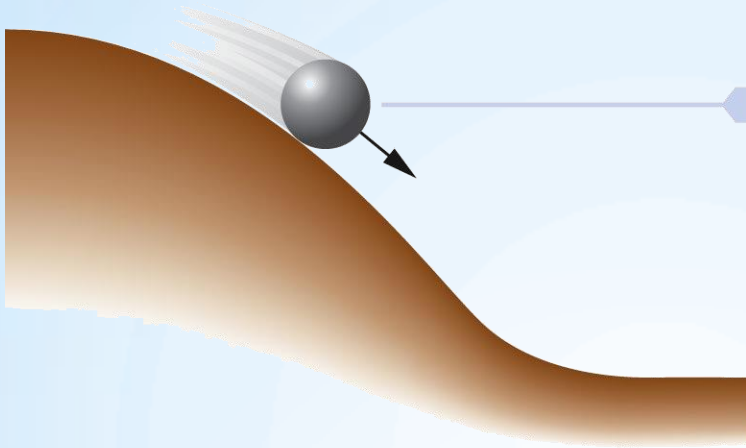
Irreversible processes cannot be undone by exactly reversing the change to the system



Spontaneous Process

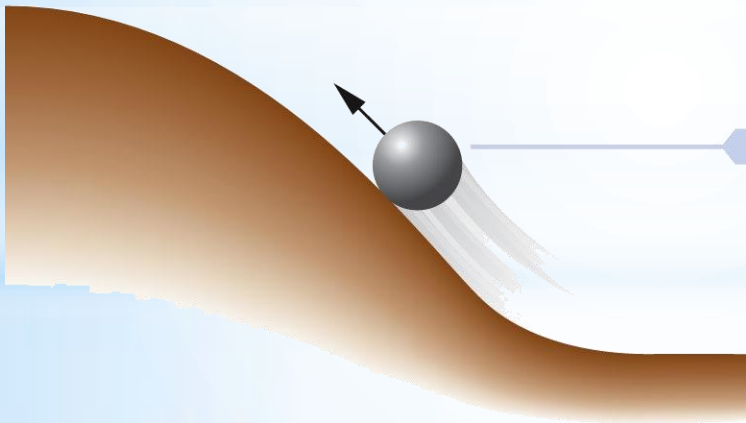
A physical or chemical change that occurs by itself. It does not require any outside force, and it continues until equilibrium is reached.

Spontaneous processes are irreversible



The rolling of a rock downhill is a spontaneous process. The rock eventually comes to equilibrium at the bottom of the hill.

Spontaneous process



The rolling of a rock uphill is a nonspontaneous process.

Nonspontaneous process

The Concept of State

State - Physical condition of the system as specified by a small set of measurable variables

Microscopic state of the system depends on the masses, velocities, positions, and all modes of motion of all of the constituent particles

In the absence of detailed knowledge, thermodynamics considers the properties of the system which, when determined, define the macroscopic state of the system

Still an enormous amount of information might be required to fix the macroscopic state of the system

Phase Rule introduces a valuable simplification to determine the state of the system such that when a small number of properties are fixed, the values of all the rest are fixed

Commonly for a pure substance, only two properties are independent and all other are dependent variables

Intensive variable - microscopic property of matter (temperature, pressure, composition)

Extensive variable - macroscopic property that depends on the quantity of matter (total volume)

Specific property - the ratio of an extensive property to the mass of the system

Various state properties are related to each other with an equation of state

Example - Ideal gas equation of state $P = \frac{nRT}{V}$

Ideal gas law

For many gases it is possible to write a simple thermal equation of state which accurately describes the relation between pressure, volume, and temperature

Such equations were developed in the 1600s and early 1800s based entirely on macroscopic empirical observation. In the late 1800s, statistical mechanics provided a stronger theoretical foundation for them

Ideal gas law, which is a combination of *Boyle's law*, *Charles' law*, and *Avogadro's law*, is most fundamentally stated as

$$PV = nRT$$

Boyle's Law

If the temperature of a certain quantity of gas is held constant the volume V is inversely proportional to the absolute pressure P

$$V \propto \frac{1}{P}; PV = C$$

Charles' Law

A. At Constant Pressure

If the pressure of a certain quantity of gas is held constant, the volume V is directly proportional to the temperature T during a quasistatic change of state

$$V \propto T; \frac{V}{T} = C$$

B. At Constant Volume

If the volume of a certain quantity of gas is held constant, the pressure P varies directly as the absolute temperature T

$$P \propto T; \frac{P}{T} = C$$

Avogadro's Law

All gases at the same temperature and pressure have the same number of molecules per unit of volume, and it follows that the specific weight is directly proportional to its molecular weight

$$\gamma \propto M$$

Thus, if an ideal gas undergoes a process going from state 1 to state 2:

$$\frac{P_2V_2}{T_2} = \frac{P_1V_1}{T_1} = R$$

$$P = \frac{nRT}{V}$$

Temperature is the absolute temperature K

Here, n is the number of moles. Recall there are

$N = 6.02214179 \times 10^{23}$ molecules in a mole, where N is Avogadro's number

Also R is the *universal gas constant*

From experiment, it is determined to be

$$R = 8.314472 \text{ kJ} / \text{ kmole K}$$

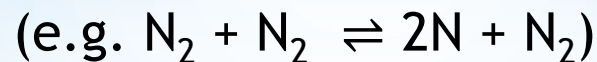
Non-ideal thermal equations of state

The ideal gas law is not a good predictor of the P – V – T behavior of gases when:

The gas has high enough density that molecular interaction forces become large

The molecules occupy a significant portion of the volume

The temperature is high enough to induce molecular dissociation



Equation of State

For a closed system containing a pure substance which does not undergo a chemical change, any two intensive properties can be chosen as the independent variables in order to completely define the state of the system

$I_1, I_2, I_3, \dots \dots \dots I_j$	intensive properties
$I_j = f(I_1, I_2)$	2 independent variables
$E_1, E_2, E_3, \dots \dots \dots E_j$	extensive properties
$E_j = f(I_1, I_2)$	Equation of state

The choice of the 2 independent variables is a matter of convenience
Pressure and Temperature are controlled most practically

Thus $V = V(P, T)$ Equation of state

The points in P-V-T space which represents the equilibrium states of existence of the system lie on a surface

Fixing the values of any two of the three variables fixes the value of the third variable

$$V = V(P, T)$$

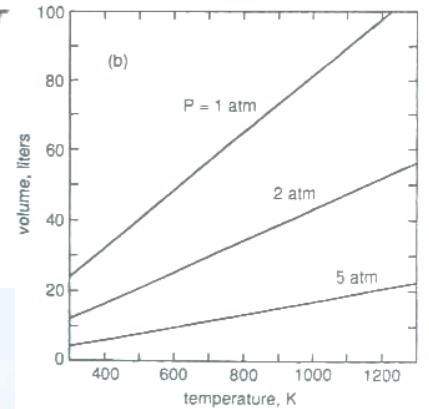
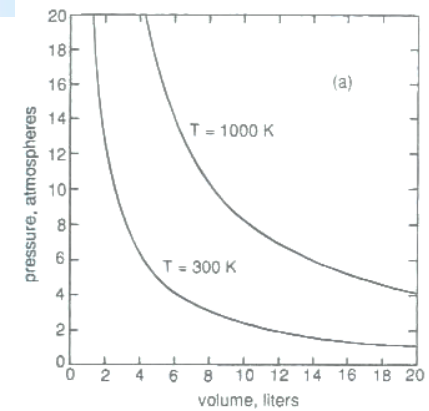
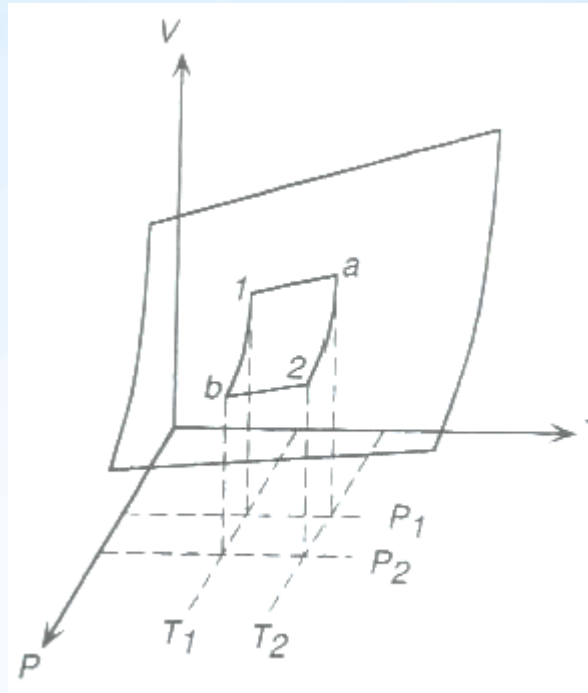


Figure 1.3 (a) The variations, with pressure, of the volume of 1 mole of ideal gas 300 and 1000 K. (b) The variations, with temperature, of the volume of 1 mole of ideal gas at 1, 2, and 5 atm.

Consider a process which moves the gas from state 1 to state 2

$$\Delta V = V_2 - V_1$$

Process could proceed along an infinite number of paths

1-a, b-2 constant P paths

1-b, a-2 constant T paths

For path 1→a→2,

$$\begin{aligned}\Delta V &= V_2 - V_1 \\ &= (V_a - V_1) + (V_2 - V_a)\end{aligned}$$

For constant P path 1→a,

$$(V_a - V_1) = \int_{T_1}^{T_a} \left(\frac{\partial V}{\partial T}\right)_{P_1} dT$$

For constant T path a→2,

$$(V_2 - V_a) = \int_{P_a}^{P_2} \left(\frac{\partial V}{\partial P}\right)_{T_2} dP$$

Thus

$$\Delta V = \int_{T_1}^{T_a} \left(\frac{\partial V}{\partial T}\right)_{P_1} dT + \int_{P_a}^{P_2} \left(\frac{\partial V}{\partial P}\right)_{T_2} dP$$

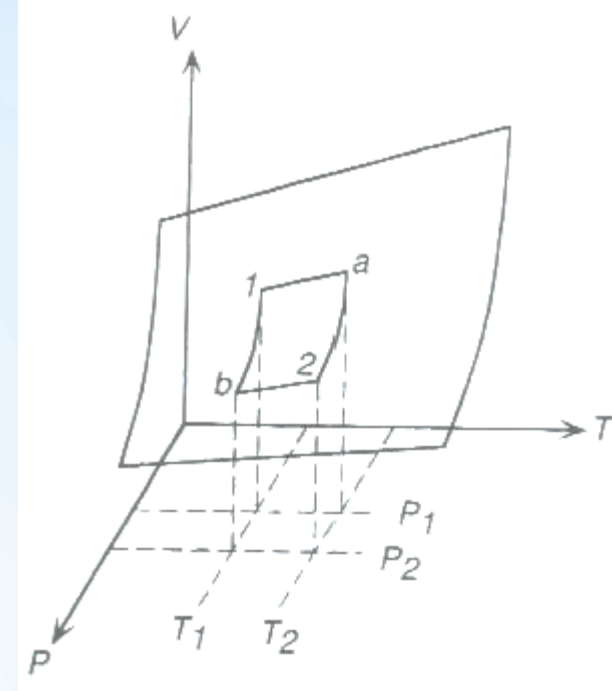
Similarly for path 1→b→2,

$$\Delta V = \int_{P_1}^{P_b} \left(\frac{\partial V}{\partial P}\right)_{T_1} dP + \int_{T_b}^{T_2} \left(\frac{\partial V}{\partial T}\right)_{P_2} dT$$

Above equations are identical and are physical representations of the integration of the complete differential between the limits P_2T_2 and P_1T_1

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

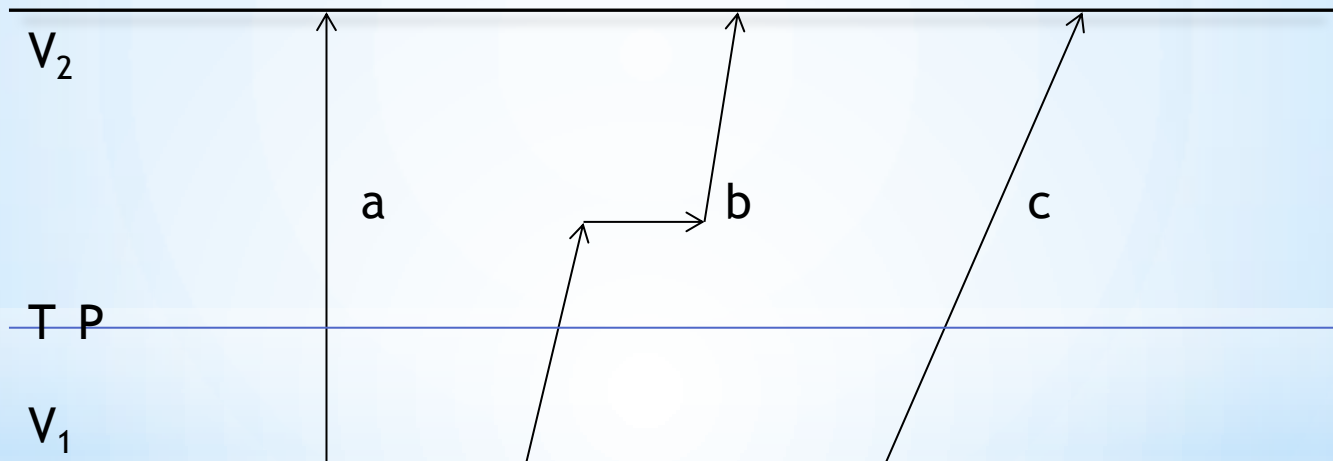
The change in volume depends only on volume at state 1 and volume at state 2 and is independent of the path taken by the gas between states 1 and 2 since V is a *state function*, hence its differential is exact



$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

The change in volume depends only on volume at state 1 and volume at state 2 and is independent of the path taken by the gas between states 1 and 2 since V is a *state function*

State functions have exact differentials



$$\Delta V_a = \Delta V_b = \Delta V_c$$

$$T_a \neq T_b \neq T_c$$

$$P_a \neq P_b \neq P_c$$

Phase: A homogeneous region of matter

Physically separable parts of a mixture containing one or more chemical species

Example - water and ice, oil and water, iron and cementite
alcohol and water?

An abrupt change in properties occurs at the boundary between phases



The state of a pure homogeneous fluid is fixed when two intensive thermodynamic properties are set at definite values

Presence of more phases decreases the number of independent intensive variables that must be fixed to establish the state of a system

$$F = 2 - \pi + N$$

Gibbs' Phase Rule gives the degrees of freedom of the system

The number of phase rule variables which must be arbitrarily specified in order to fix the intensive state of a system at equilibrium is the difference between the total number of phase rule variables and the number of independent equations that can be written connecting these variables

Phase rule variables for a system containing N chemical species and π phases in equilibrium:

Temperature T

Pressure P

$N-1$ mole fractions X for each phase (only $N-1$ because $\sum X_i = 1$)

Total number = $2 + (N - 1)(\pi)$

Phase equilibrium equations that may be written connecting the phase rule variables:

$$\mu^{\alpha}_i = \mu^{\beta}_i = \dots = \mu^{\pi}_i \quad (i = 1, 2, \dots, N)$$

Total number = $(\pi - 1)(N)$

Thus

$$F = 2 + (N - 1)(\pi) - (\pi - 1)(N) = 2 - \pi + N$$

The minimum degrees of freedom for any system is zero
 $F=0$ means the system is invariant and equation becomes

$$F = 2 - \pi + N \quad \longrightarrow \quad \pi = 2 + N$$

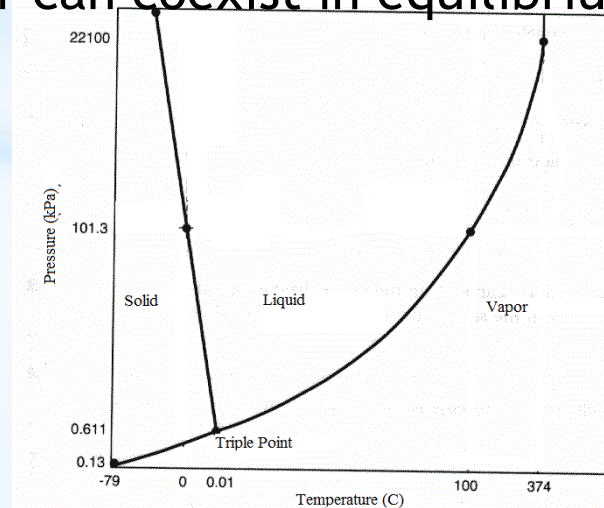
π is the maximum number of phases which can coexist at equilibrium for a system containing N species

Example - $\pi = 3$ for water at the triple point at 0.01°C and 0.0061 bar

Independent control on two variables is not possible for a pure substance with two phases in equilibrium

Example

Steam and liquid water can coexist in equilibrium at 100°C only at 101.33



Examples

Liquid water in equilibrium with its vapor

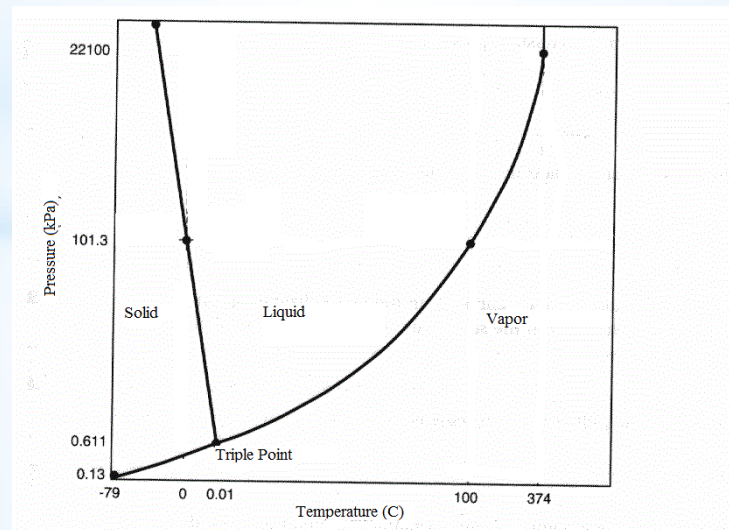
T or P may be specified for a system consisting of water in equilibrium with its vapor

$$F = 2 - 2 + 1 = 1$$

Liquid water in equilibrium with a mixture of water vapor and nitrogen

T and P may be independently varied for a pure system with the addition of an inert gas, but once they are fixed the system described can exist in equilibrium only at a particular composition X

$$F = 2 - 2 + 2 = 2$$



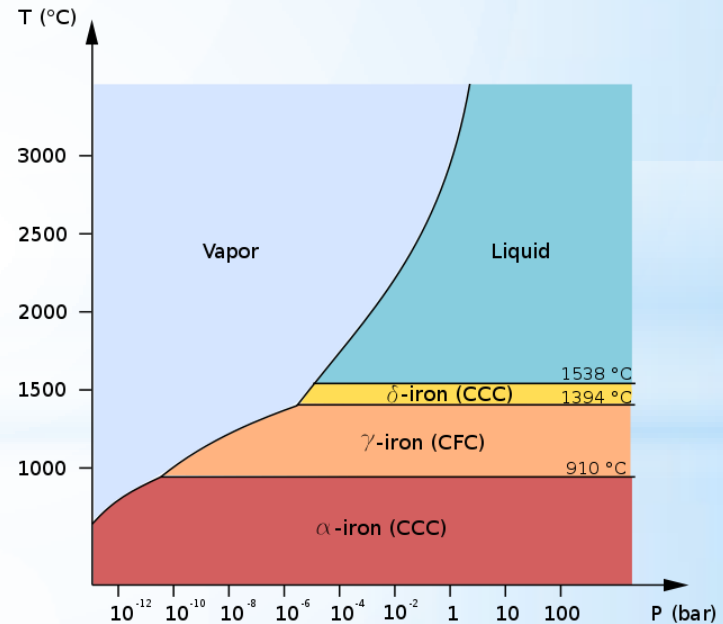
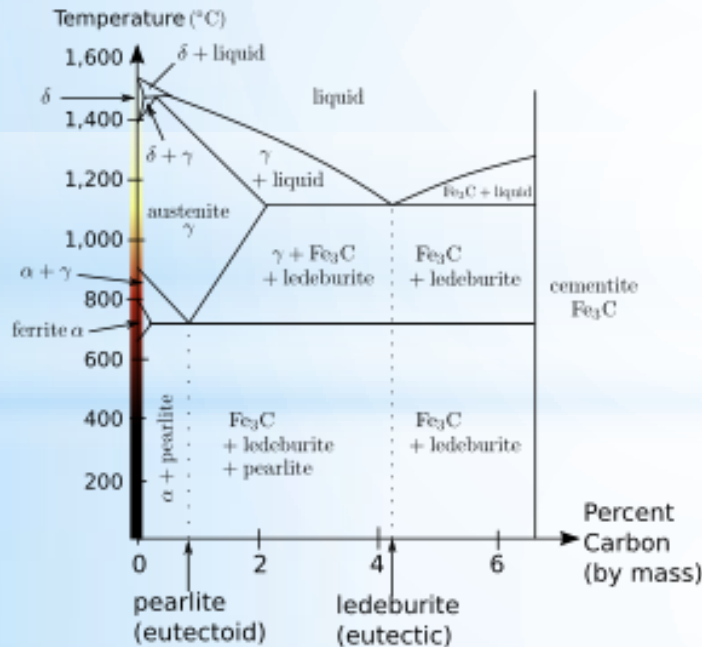
Application of Phase Rule to Metal Phase Diagrams

Vapor pressures of metals and alloys in solid or liquid state are low and any change exerted on the system by the variations in the pressure of the surroundings is negligible

Thus

$$F = 1 - \pi + N$$

Only variable for a solid or liquid metal system of constant composition is temperature



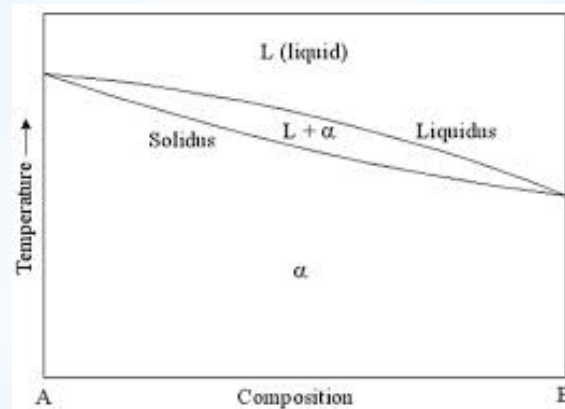
Application of Phase Rule to Binary Phase Diagrams

Phase rule is modified for the special case of two completely miscible metals as:

$$F = 1 - \pi + N = 1 - \pi + 2 = 3 - \pi$$

There exists a single phase at any point in the liquid or solid regions of the binary phase diagrams, hence degrees of freedom $F = 3 - 1 = 2$

The variables temperature and composition are free to change independently



Consider any point on the liquidus line where the solid phase starts to appear
Equilibrium of two phases reduces the degrees of freedom to 1 as

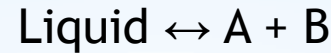
$$F = 3 - 2 = 1$$

Either variable is dependent on the one chosen as convenient

The horizontal line connecting solid and liquid phases in equilibrium is the *tie line*
Two phases existing in equilibrium at a constant temperature are *conjugate phases*
Ratio of the conjugate phases on a tie line is determined according to the *lever rule*

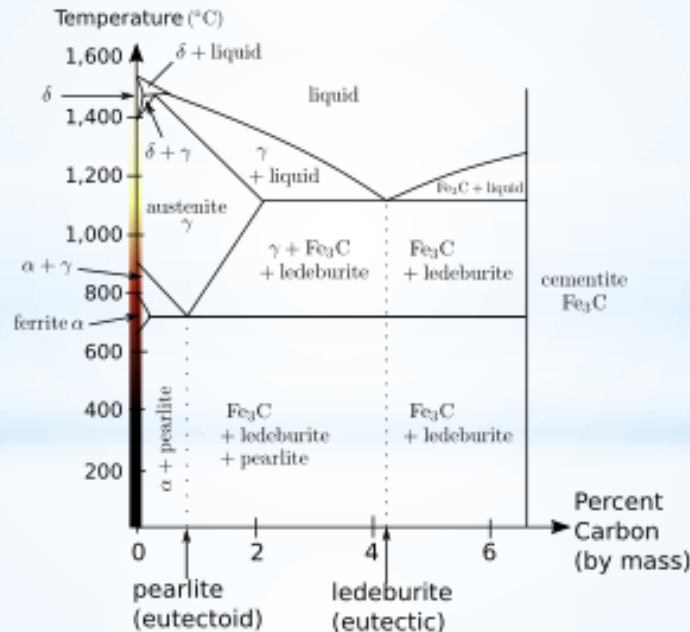
Application of Phase Rule to Eutectic Phase Diagrams

The same principles apply to the two phase regions in a eutectic phase diagram
In contrast, three phases coexist at any point on the eutectic line



so the degrees of freedom reduces to zero

$$F = 3 - \pi = 3 - 3 = 0$$



Three phases can coexist only at the eutectic temperature and eutectic composition
Same principles apply for eutectoid, peritectic and peritectoid reactions