CL 3003 CHEMICAL ENGINEERING THERMODYNAMICS

MONSOON 2018

Lecture – 1 : Course Introduction and Overview

Department of Chemical Engineering
BIT Mesra, Ranchi, Jharkhand-835215

Course Instructor: **Dr. Anand Bharti**

Assistant Professor

Department of Chemical Engineering

Birla Institute of Technology Mesra, Ranchi

www.anandbharti.co.in

- Ph.D. in Chemical Engineering from IIT Guwahati (2013-2017).
- Industrial Experience: Indian Oil Corporation Limited (5 Yrs. +)

➢ **Areas of Interest:**

Separation Processes

Thermodynamics

Molecular Simulation

Optimization

Process Design.

WHAT IS CHEMICAL ENGINEERING?

Chemical engineering is all about changing **raw materials** into **useful products** we use everyday on an **industrial scale** in a **safe and cost effective way**.

Chemical engineers are concerned with **PROCESSES** and **PRODUCTS**.

Processes:

- ✓ Making chemicals and pharmaceuticals
- ✓ Processing polymers and foodstuffs
- ✓ Energy generation
- ✓ Wastewater treatment
- ✓ Environmental clean-up

Process Design:

- ✓ Inventing a new process
- ✓ Designing the equipment for a process
- ✓ Operating a process
- ✓ Improving a process

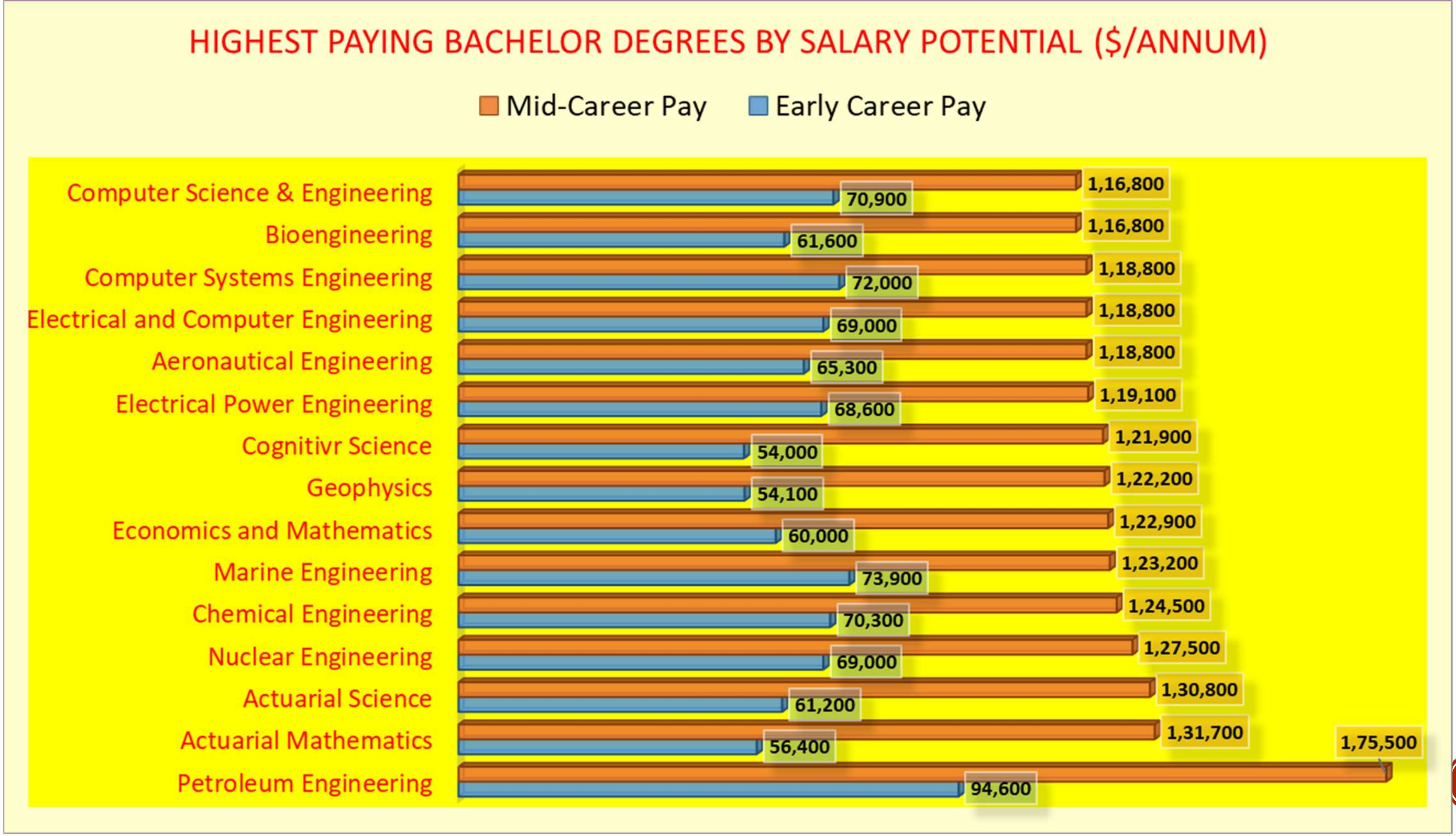
Products:

- ✓ Chemicals - petrol, ammonia, methanol
- ✓ Polymers - polythene, PVC, synthetic fibres
- ✓ Consumer products - shampoo
- ✓ Foodstuffs - ice cream, chocolate, beer
- ✓ Pharmaceuticals - paracetamol, penicillin

Product Design:

- ✓ Choosing a product for an application
- ✓ Designing the product
- ✓ Improving the product

WHY STUDY CHEMICAL ENGINEERING?



HIGHEST PAYING BACHELOR DEGREES BY SALARY POTENTIAL ($/ANNUM)

CHEMICAL ENGINEERS THAT SHAPED OUR WORLD

GEORGE E DAVIS

- ‘Founding Father’ of Chemical Engineering.
- Coined the term ‘Chemical Engineering’.
- Delivered first chemical engineering course at the University of Manchester in 1887 in the form of 12 lectures covering various aspects of industrial chemical practice.

CARL BOSCH

- Haber-Bosch process was developed by industrial chemist Fritz Haber, and scaled up by chemical engineer Carl Bosch.
- It takes nitrogen from the air and converts it to ammonia.
- This work made it possible to produce **synthetic fertilizers** and thus produce enough food for the Earth's growing population. Without it, we would only be able to produce two-thirds the amount of food we do today.
- **Nobel Prize in Chemistry 1931** "in recognition of their contributions to the invention and development of chemical high pressure methods"

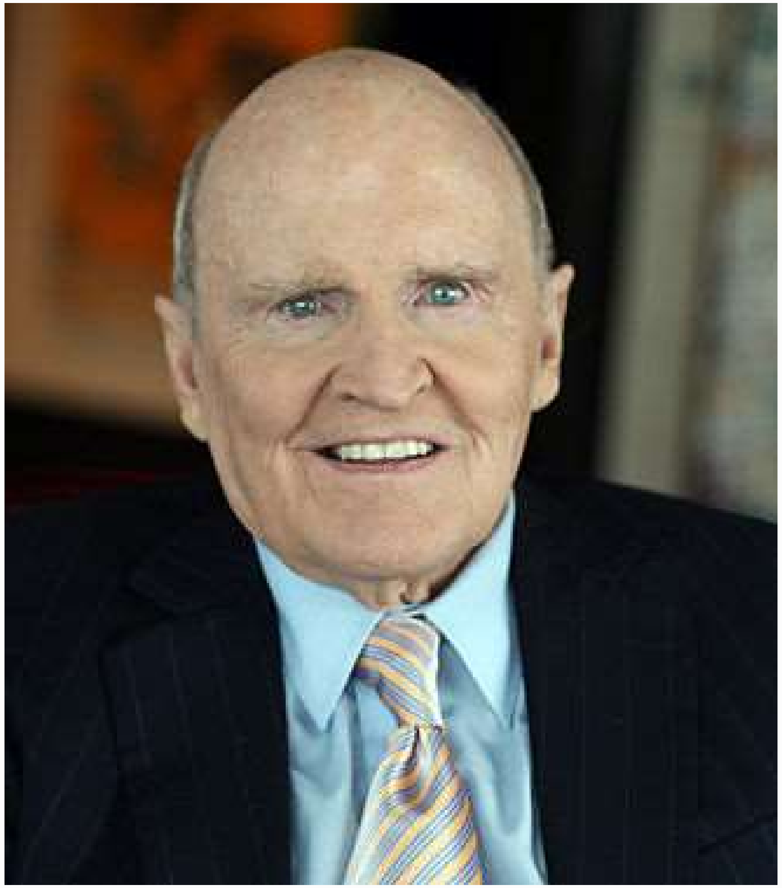
MARGARET HUTCHINSON ROUSSEAU

- First women to receive a chemical engineering doctorate from MIT.
- Margaret developed the process of deep-tank fermentation which enabled large-scale production of **penicillin**.
- Mass production of penicillin was a key moment in history; not only for the billions of lives it saved (and still saves today) but for the chemical engineering involved.

JOHN H. PERRY

- Perry's is the go to **handbook for chemical engineers**. Edited its first edition – published in 1934.
- John went on to edit two more editions of Perry's, until his son, Robert H. Perry, took over the family tradition for the fourth edition in 1963, until his death.
- John was a physical chemist and chemical engineer and was known for his development of improved catalysts for sulfuric acid production.
- However, it is his book that truly shaped the world and has been the **key source of knowledge for chemical engineers** for over 70 years.

JACK WELCH

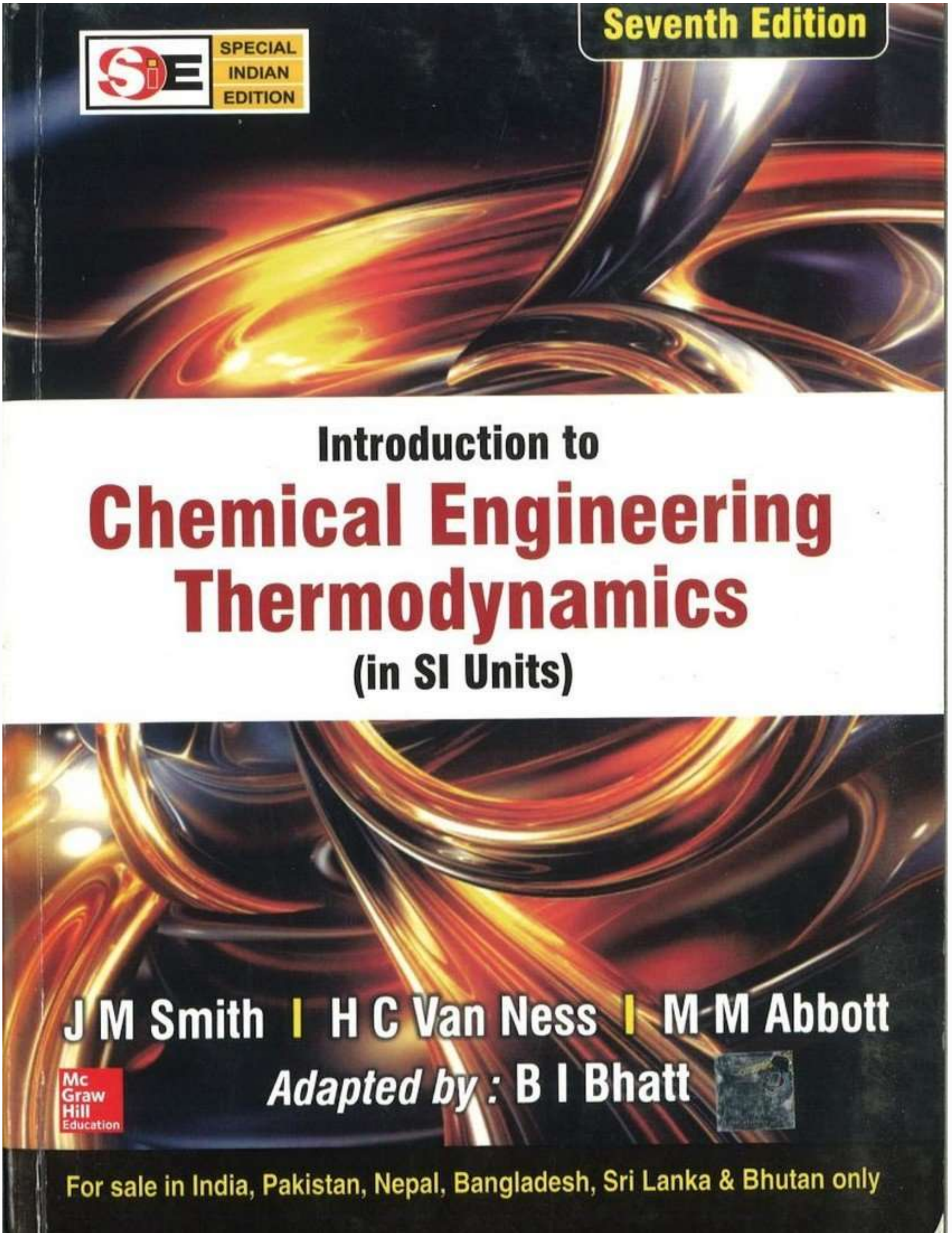


- Masters and PhD in chemical engineering from University of Illinois at Urbana-Champaign.
- Chairman and CEO of **General Electric** between 1981 and 2001.
- During his tenure at GE, the company's value rose 4,000%.

ANDREW GROVE

- Ph.D. in chemical engineering from the University of California, Berkeley in 1963.
- After completing his Ph.D., worked for Fairchild Semiconductor, hired by and working under Gordon Moore.
- When Moore and Noyce left Fairchild to start **Intel**, Grove was Intel's third employee, the first person to be hired by company founders Gordon Moore and Robert Noyce.
- President: 1979 - 1997 and CEO: 1987 - 1998.
- Chairman of the board of Intel Corporation from 1997 to 2005.
- **"Man of the Year (1997)", for being "the person most responsible for the amazing growth in the power and the innovative potential of microchips."**

THANKS



Seventh Edition

SIE SPECIAL INDIAN EDITION

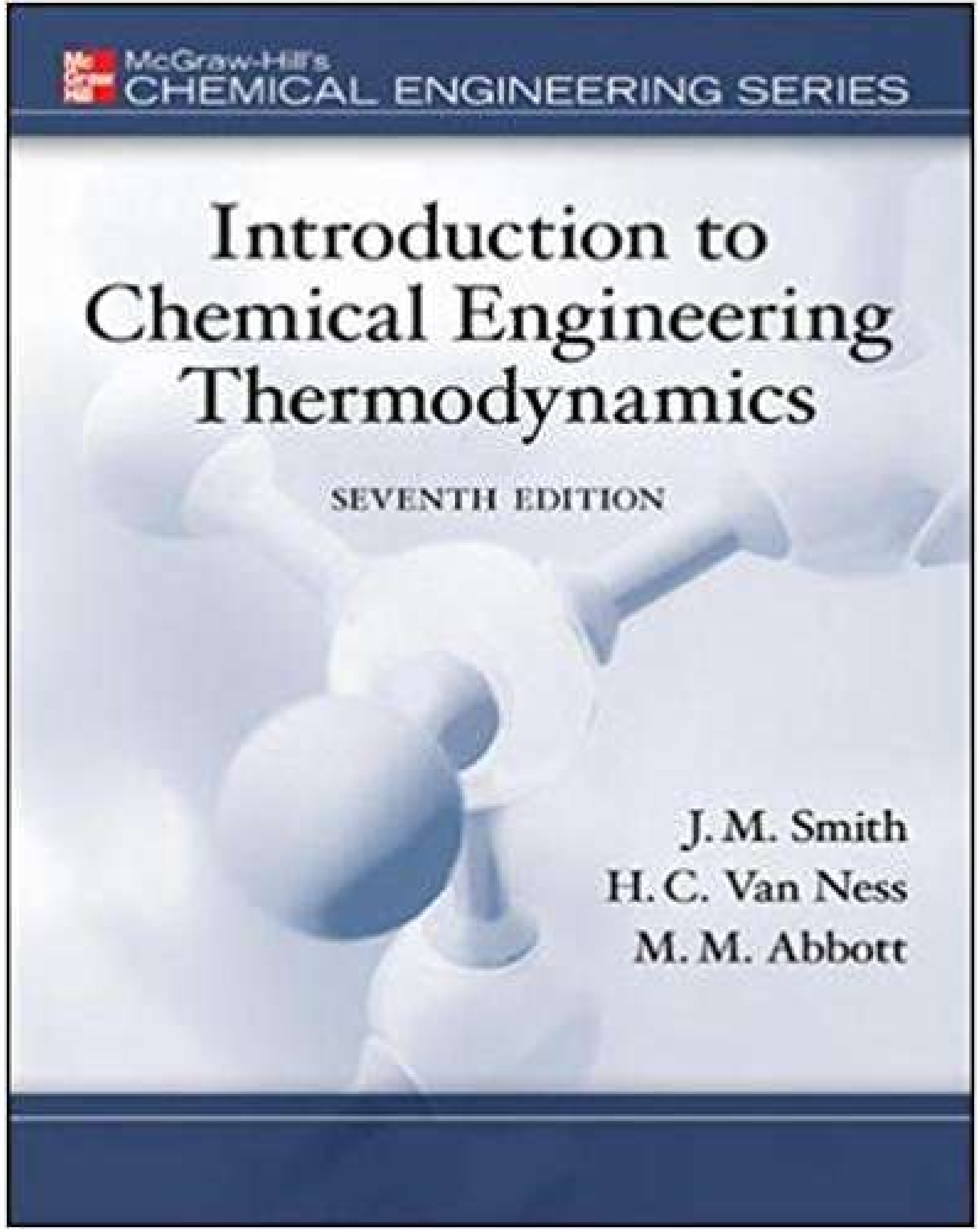
Introduction to
Chemical Engineering
Thermodynamics
(in SI Units)

J M Smith | H C Van Ness | M M Abbott

Mc Graw Hill Education

Adapted by : B I Bhatt

For sale in India, Pakistan, Nepal, Bangladesh, Sri Lanka & Bhutan only



McGraw-Hill's
CHEMICAL ENGINEERING SERIES

Introduction to
Chemical Engineering
Thermodynamics

SEVENTH EDITION

J. M. Smith
H. C. Van Ness
M. M. Abbott

CL 3003 CHEMICAL ENGINEERING THERMODYNAMICS

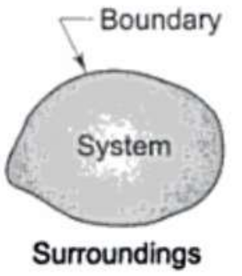
MONSOON 2018

Lecture – 2 : PRELIMINARY CONCEPTS (THE LANGUAGE OF THERMO)

Department of Chemical Engineering
BIT Mesra, Ranchi, Jharkhand-835215

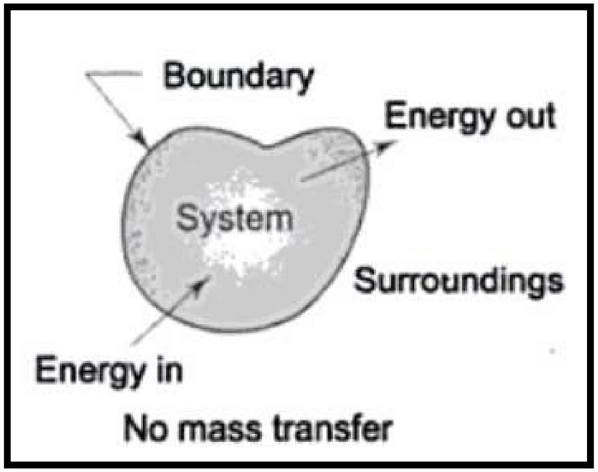
THERMODYNAMIC SYSTEM

- ✓ A ***thermodynamic system*** is defined as a quantity of matter or a region in space on which we focus our attention for thermodynamic analysis.
- ✓ Everything external to the system is called the ***surroundings*** or the environment.
- ✓ A system and its surroundings together comprise a ***universe***.
- ✓ The system is separated from the surroundings by the ***system boundary***.
- ✓ The boundary enclosing the system may be ***real or imaginary***.
- ✓ The system boundary may be **rigid** ***or may change its shape*** as well as size during a given process.

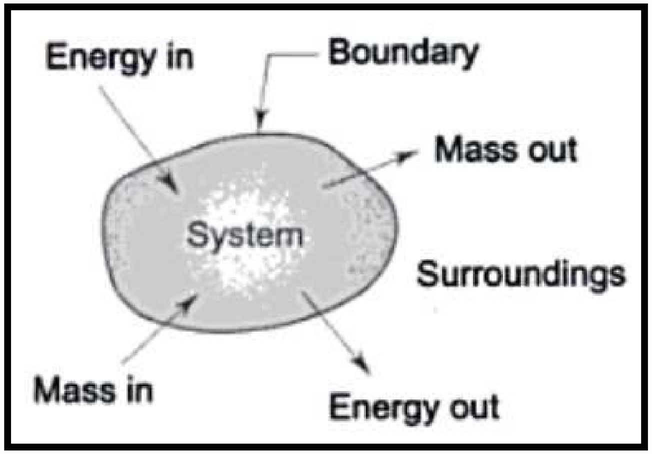


A thermodynamic system

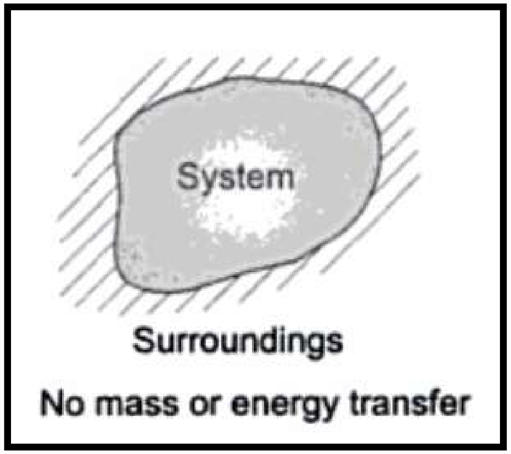
TYPES OF THERMODYNAMIC SYSTEM



Closed System



Open System



Isolated System

PHASE, HOMOGENEOUS AND HETEROGENEOUS SYSTEM

- ✓A quantity of matter homogeneous throughout in chemical composition and physical structure is called a ***phase***.
- ✓A system consisting of a single phase is called a ***homogeneous system***.
- ✓A system consisting of more than one phase is known as a ***heterogeneous system***.

THERMODYNAMIC PROPERTIES

- ✓Every system has certain characteristics by which its physical condition may be described. Such characteristics are called ***properties of the system***.
- ✓These are all ***macroscopic*** in nature.
- ✓When all the properties of a system have definite values, the system is said to exist at a definite ***state***.
- ✓Properties are the ***coordinates*** to describe the state of a system.

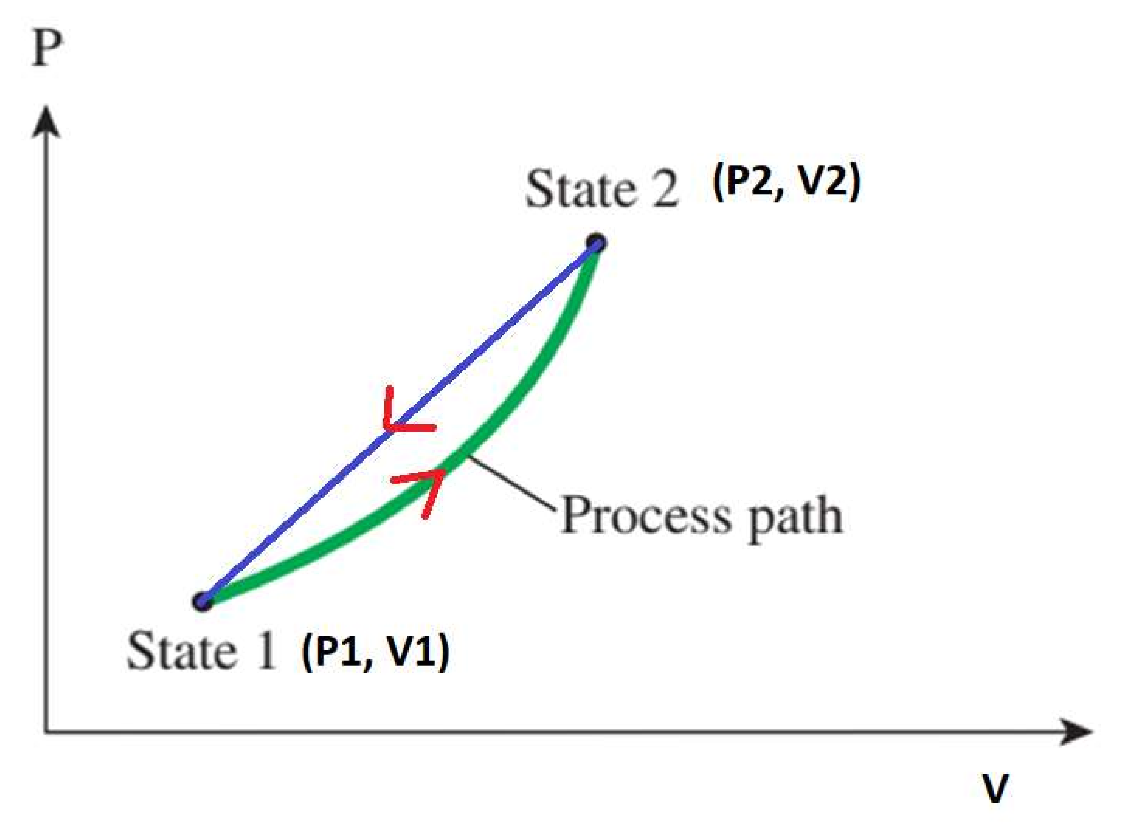
INTENSIVE AND EXTENSIVE PROPERTIES

- ✓***Intensive properties*** are those that are **independent of the mass of the system**.
  - ✓Example of Intensive properties: Temperature, Pressure, Density.
- ✓***Extensive properties*** are those that are **dependent on the mass of the system.**
  - ✓Example of Extensive properties: Mass, Volume.
- ✓***Extensive properties*** per unit mass are Intensive properties.
  - ✓Example: Specific volume, Specific energy.

STATE, PROCESS, CYCLE

- ✓Any operation in which one or more of the properties of a system changes is called a ***change of state***.
- ✓The succession of states passed through during a change of state is called the ***path*** of the change of state.
- ✓When the path is completely specified, the change of state is called a ***process***.
- ✓A thermodynamic ***cycle*** is defined as a series of state changes such that the final state is identical with the initial state.

STATE, PROCESS, CYCLE



1 -> 2 Process
2 -> 1 Process
1->2->1 Cycle

VARIOUS THERMODYNAMIC PROCESSES

- ✓**Isothermal Process**: ***Temperature*** of the system remains ***constant***.

- ✓**Isobaric Process**: ***Pressure*** remains constant.

- ✓**Isochoric Process**: ***Volume*** remains constant.

- ✓**Adiabatic Process**: ***No heat transfer*** occurs across the system boundary.

GIBBS PHASE RULE (FOR NON-REACTIVE SYSTEM)

$$F = C - P + 2$$

Where,

F = Number of degree of freedom, C= Number of components, P = Number of co-existing phases.

The phase rule determines the ***number of independent variables*** that must be specified to establish the intensive state of any system at equilibrium.

GIBBS PHASE RULE (FOR NON-REACTIVE SYSTEM)

- ✓The intensive state of a system at equilibrium is established when its temperature, pressure, and the compositions of all phases are fixed.
- ✓These are therefore, regarded as phase-rule variables; but they are not all independent.
- ✓The degrees of freedom derivable from the phase rule gives the number of variables which must be specified to fix all other remaining phase-rule variables. Thus, F means the number of intensive properties (such as temperature or pressure), which are independent of other intensive variables.

GIBBS PHASE RULE (FOR NON-REACTIVE SYSTEM)

- ✓For example, for a pure component gaseous system, phase rule yields two degrees of freedom. This implies that if one specifies temperature and pressure, all other intensive properties are then uniquely determined from these two variables.
- ✓Similarly for a biphasic system of a pure component – say water and steam – there is only one degree of freedom, i.e., either temperature or pressure may be specified to fix all other intensive properties of the system.

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Lecture – 3 : Basic Concepts

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Thermodynamics can be studied through two different approaches:

(a) Macroscopic Approach, and
(b) Microscopic Approach.

The Macroscopic approach has the following features:

- The structure of the matter is not considered.
- A few variables are used to describe the state of the matter under consideration.
- The values of these variables are measurable following the available techniques of experimental physics.
- Does not require knowledge of behaviour of individual molecules.
- We disregard the atomic nature of a substance and view it as a continuous homogeneous matter, that is, a continuum.

The microscopic approach can be summarized as:

- A Knowledge of the molecular structure of matter under consideration is essential.
- A Large number of variables are needed for a complete specification of the state of the matter.

- Macroscopic experiments provide no insight into why substances exhibit observed property values.
- classical thermodynamics is the part of thermodynamics that emerged during the nineteenth century before everyone was fully convinced about the reality of atoms. we can do classical thermodynamics even if we don't believe in atoms. Towards the end of the nineteenth century, when most scientists accepted that atoms were real, there emerged the version of thermodynamics called statistical thermodynamics, which sought to account for the bulk properties of matter in terms of its constituent atoms.

The 'statistical' part of the name comes from the fact that in the ~~disussion~~ discussion of bulk properties we don't need to think about the behaviour of individual atoms but we do need to think about the average behaviour of atoms.

Work and Heat: Transfer of Energy Between the System and the Surroundings

In a closed system, the transfer of energy between the Surroundings and the system can only be accomplished by heat or by work.

Heat is the transfer of energy by a temperature gradient, whereas all other forms of energy transfer in a closed system occur via work. We generally associate work with something useful being done by (or to) the system.

Work:

There are many forms of work, for example, mechanical (expansion/compression, rotating shaft), electrical and magnetic.

The most common case of work in engineering thermodynamics is when a force causes a displacement in the boundary of a system. In the case of expansion, the system needs to push the surroundings out of the way to increase the boundary; in this process, the system expends energy. Thus, the System exchanges energy with the surroundings in the form of work.

The work, W, can be described mathematically by the line integral of the external force, F_E, with respect to the direction of displacement, dx:

$$W = \int \vec{F}_E \cdot d\vec{x} \xrightarrow{} (1)$$

↳ ~~component of force acting along the line of displacement.~~

In contrast to thermodynamic properties, the work on a system depends not only on the initial state, 1 and the final state, 2, but also on the specific path that it takes. Whenever we calculate the work, we must account for the real path that the system takes.

Sign convention:

→ Work is positive when energy is transferred from the surroundings to the system. or work is positive when it is done on the system.

→ Work is negative when energy is transferred from the system to the surroundings. or ~~the~~ work is negative when it is done by the system.

The work which accompanies a change in volume of a fluid is often encountered in thermodynamics. A common example is the compression or expansion of a fluid in a cylinder resulting from the movement of a piston. The force exerted by the piston on the fluid is equal to the product of the piston area and the pressure of the fluid. The displacement of the piston is equal to the total volume change of the fluid divided by the area of the piston. Thus, Eqⁿ. (1) becomes-

$$W = \cancel{-\int P_E A\, d\left(\frac{V}{A}\right)} - \int P_E A\left(\frac{dV}{A}\right)$$

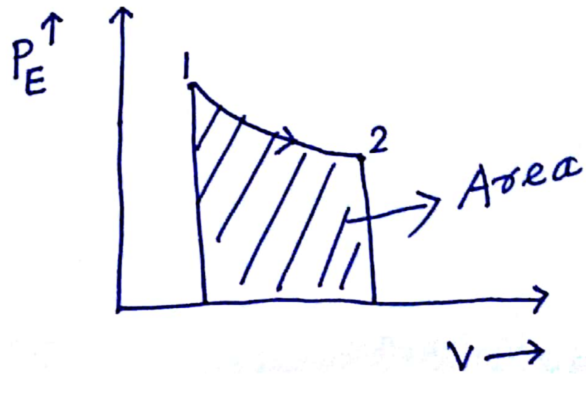
*** PV - work**

$$\boxed{W = -\int P_E\, dV} \longrightarrow (2)$$

$\hookrightarrow$ External pressure to the surface.

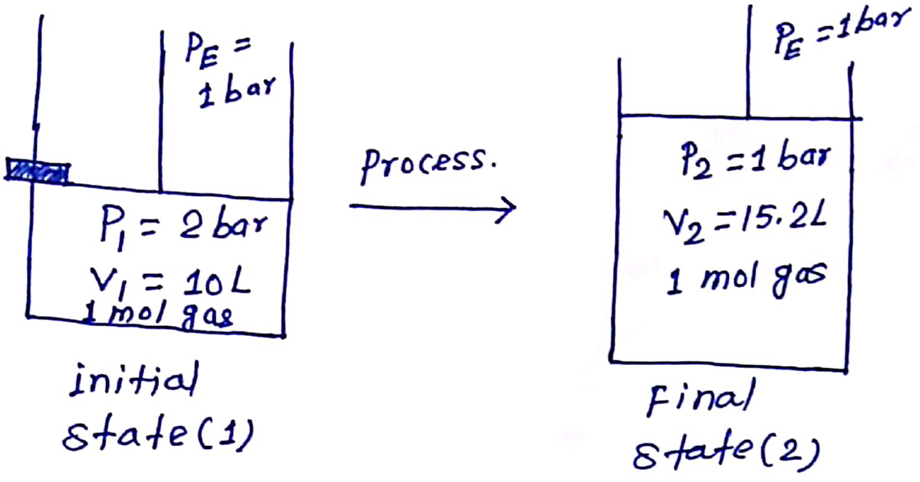
The minus sign in these equations are made necessary by the sign convention adopted for work. ~~when the piston moves into the cylinder so as to compress the fluid, the applied force and its displacement are in the same direction; the work is therefore positive.~~

PV-diagram



Area under the curve gives the work done.

Example 1: Consider a system which contains 1 mole of gas and is at 2 bar having a volume of 10L.



The expansion process is initiated by releasing the latch. The gas in the cylinder expands untill the pressure of the gas matches the pressure of the surroundings. The final volume is 15.2L. Calculate work done by the system during this process.

Solution: Work done ~~by the system is~~ can be calculated by applying eqⁿ. (2),

$$W = -\int_{V_1}^{V_2} P_E \, dV$$

Since External pressure is constant,

$$W = -P_E \int_{V_1}^{V_2} dV = -P_E \left[V_2 - V_1\right]$$

$$= -(1\,bar)\frac{(10^5\,pa)}{(1\,bar)}(15.2-10)L\left[\frac{10^{-3}\,m^3}{L}\right]$$

$$\underline{W = -520\,J}$$

In this case, the value of work is negative since the system loses energy to the surroundings as a result of this process

State functions and Path functions :

The values of thermodynamic properties donot depend on the process (i.e., path) through which the system arrived at its state.; they depend only on the state itself. Thus, the change in a given property between states 1 and 2 will be the same for any process that starts at state 1 and ends at state 2.

This aspect of thermodynamic properties is very useful in solving problems;. We will devise hypothetical paths between thermodynamic states so that we can use data that are readily available. ~~for~~ more easily performing computation. Since properties depend only on the state itself, they are often termed state functions.

On the other hand, there are quantities that we will be interested in, such as heat and work, that depend on path. These are referred to as path functions. When calculating values for these quantities, we must use the real path the system takes during the process.

Thermodynamic Equilibrium:

For a system to be in a state of thermodynamic equilibrium it should simultaneously satisfy the criteria for-

thermal equilibrium,
mechanical equilibrium,
chemical equilibrium.

Thermal equilibrium:
No temp. gradient.

Mechanical equilibrium:
No pressure gradient.

chemical equilibrium:
No chemical potential gradient.

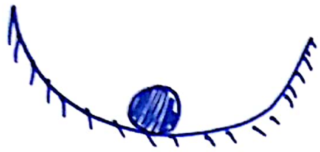
In a state of equilibrium, the system has no tendency to undergo any further change.

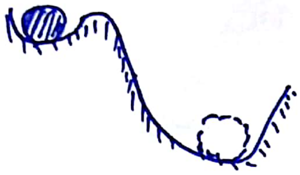
Equilibrium is a concept associated with the absence of any tendency for further change on a macroscopic level.

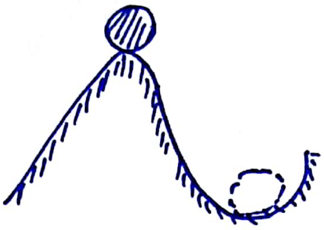
The tendency to change occurs due to the presence of driving forces. Thus, equilibrium implies the absence of driving forces.

In a state of equilibrium, thermodynamic properties of a system have unique values.

States of Equilibrium:


(a)
(stable)


(b)
(Metastable)


(c)
(unstable)

consider a sphere resting at the bottom of a spherical bowl as shown in fig.(a). If the sphere is disturbed it will settle into the original state, however larger the disturbance may be. this state of equilibrium, in which the system returns to its original state even if it is subjected to large disturbances is called stable equilibrium. In thermodynamics, we mostly interested in stable equilibrium states.

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Lecture – 4 : Reversible & Irreversible Processes

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Reversible and Irreversible Processes:

A process is reversible if, after the process occurs, the system can be returned to its original state without any net effect on the surroundings.
This result occurs only when the driving force is infinitesimally small.
To accomplish a reversible process we must be able to reverse the direction of the process ~~an~~ at any point and go the other way by changing the driving force by an infinitesimal amount. For a process to be reversible, there can be no friction.
If a gas undergoes an expansion process, we must be able to turn the process around at any point and compress it merely by changing the force on the piston by an infinitesimal amount.

Reversible processes are never completely realized in real life. These processes represent an idealization. They represent a limiting case, that is, a process that is perfectly executed.

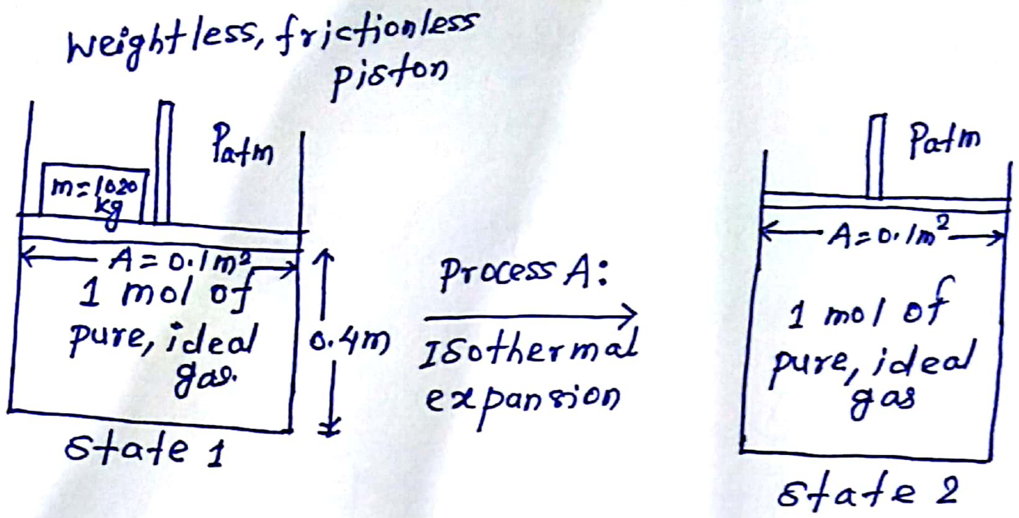
However, in engineering these types of idealization are often useful. For example, it is useful to know how much work we could get out of a system if a process could be executed reversibly. This value tells us the best that we could possibly do. We can then compare how well we really do, and see if it is worth focusing our efforts on improving the process.

Real processes are not reversible. They have friction and are carried out with finite driving forces. Such processes are irreversible processes. In an irreversible process, if the system is returned to its original state, the surroundings must be altered. The work obtained in an irreversible process is always less than that obtained in the idealization of a reversible proces.

A reversible process

- is frictionless.
- is never more than differentially removed from equilibrium.
- traverses a succession of equilibrium states.
- is driven by forces whose imbalance is differential in magnitude.
- Can be reversed at any point by a differential change in external conditions.
- when reversed, retraces its forward path, and restores the initial state of system and surroundings.

Example to explain reversible process:



Schematic of an isothermal expansion process (Process A)

The system conteins 1 mole of pure ideal gas. A 1020-kg mass sits on the piston. The surroundings are at atmospheric pressure. The molar volume in state 1 can be found from the area ($0.1 m^2$) and the height ($0.4 m$);

$$v_1 = \left(\frac{AZ}{n}\right)_1 = 0.04\ m^3/mol.$$

Since the piston is originally at rest, the pressure inside the piston can be found by a force balance:

$$P_1 = \frac{mg}{A} + P_{atm} = \left(\frac{1020\times 10}{0.1}\right)\times\frac{1}{10^5} + 1$$

$$= 1.01 + 1 = 2.0\ \text{bar}.$$

Process 'A' is initiated by removing the 1020-kg mass. The pressure of the piston is now greater than that exerted by the surroundings, and the gas within the piston expands.

The expansion process continues untill once again the pressures equilibrate. The piston then comes to rest in state '2' where the pressure is given by:

$$P_2 = P_{atm} = 1 \text{ bar.}$$

The ideal gas law can be applied to this isothermal process to give:

$$Pv = RT = \text{const.}$$

The volume of state '2' is then given by:

$$v_2 = \frac{P_1 v_1}{P_2} = \frac{2 \times 0.04}{1} = 0.08 \frac{m^3}{mol.}$$

To find the work, we apply.

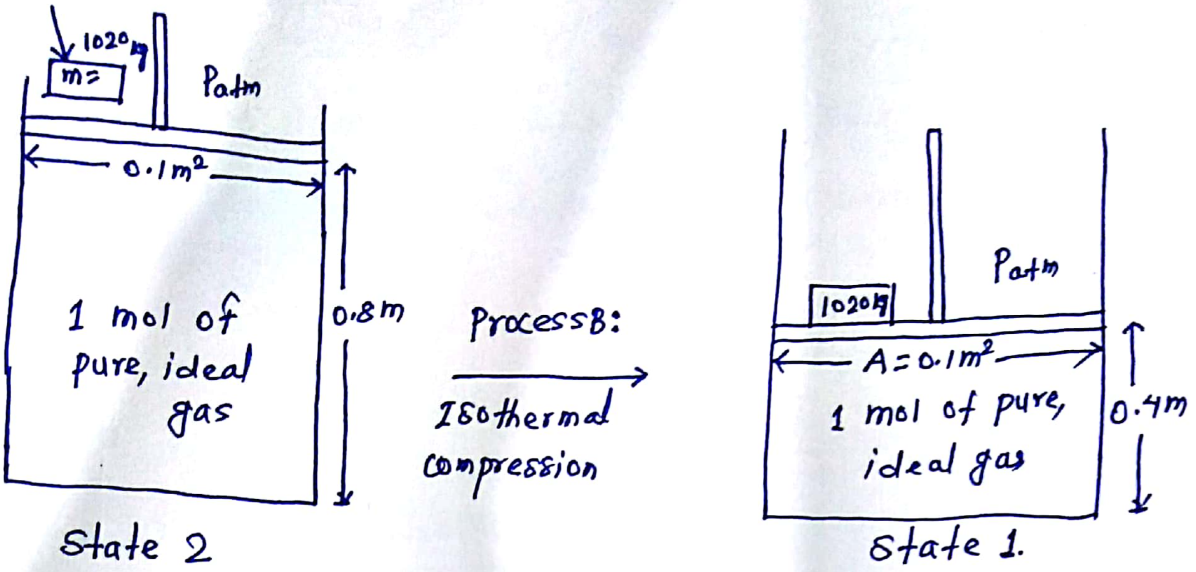
$$W = -\int_{v_1}^{v_2} P_E dv = -P_{atm}\int_{v_1}^{v_2} dv$$

$$= (-1 \text{ bar})(v_2 - v_1) = (-1 \text{bar})(0.08 - 0.04)\frac{m^3}{mol}$$

$$= -10^5 \times 4 \times 10^{-2} \frac{J}{mol} = -4000 \frac{J}{mol.}$$

$\downarrow$

(-) sign indicates we get 4 KJ of work out of the system from this expansion process.



We next want to calculate the work needed to compress the gas from state 2 back to state 1. We drop the 1020-kg mass back on the piston. The external pressure now exceeds the ~~go~~ pressure of the gas initiating the compression process. The piston goes down untill the pressures equilibrate, at state 1. In this case, the external pressure consists of contributions from both the block and the atmosphere.

The work in this case is-

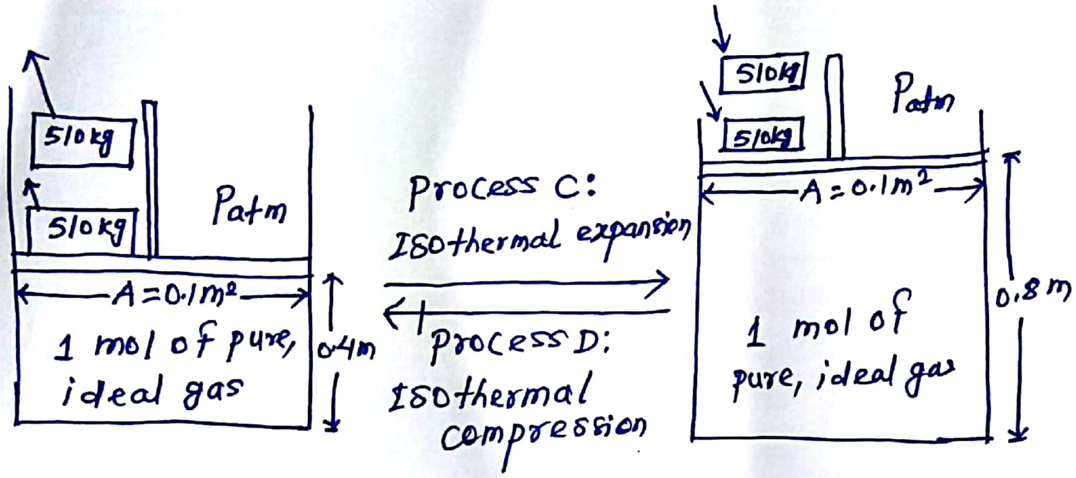
$$W = -\int_{V_2}^{V_1} \left(\frac{mg}{A} + P_{atm}\right) dV$$

$$= -\left(\frac{1020\times10}{0.1}\times\frac{1}{\cancel{10^5}} + 10^5\right)(V_1 - V_2)$$

$$= \cancel{2(0.04-0.08) = 0.08}. = 8000\,\frac{J}{mol}.$$

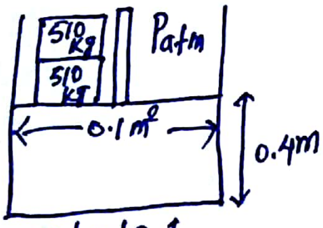
⇒ Comparing process 'A' and process 'B', we see it costs us more work to compress the piston back to state 1 than we got from expanding it to state 2.

The net difference in work (8000 − 4000 = 4000 J) in going from state 1 to state 2 and back to state 1 results in a "net effect on the surrounding."



Next we again consider expansion from state 1 to 2 (process C) and compression from state 2 to 1 (process D), but now we use two 510-kg masses instead of one larger 1020-kg mass.

The expansion is carried out as follows:



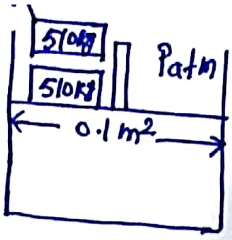
State 1

In state 1, pressure inside the piston is.

$$P_1 = P_{atm} + \frac{mg}{A} = (1\,bar) + \left(\frac{1020\,kg \times 10\,m/s^2}{0.1\,m^2}\right) \times \frac{1\,bar}{10^5\,pa}$$

$$= 2\,bar$$

$$V_1 = 0.04\,m^3.$$



State 1'

The system is brought from state 1 to state 1' by removing one 510-kg mass.

In state 1', pressure inside the piston is-

$$P_1' = P_{atm} + \frac{510 \times 10}{0.1} \times \frac{1}{10^5} = 1.51 \text{ bar.}$$

Since, the process is isothermal, volume at state 1' is,

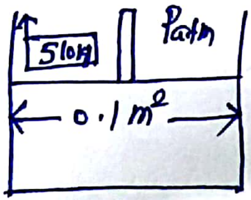
$$V_1' = \frac{P_1 V_1}{P_1'} = \frac{(2 \text{ bar})(0.04 m^3)}{(1.51 \text{ bar})} = 0.053 m^3.$$

work done by the system in going from state 1 to state 1' is.

$$W = -\int_{V_1}^{V_1'} P_E \, dV = (-1.51 \times 10^5 \text{ pa})(V_1' - V_1) m^3$$

$$= -1.51 \times 10^5 \times (0.053 - 0.04)$$

$$\underline{W = -1963 J}$$



state2

The system is brought from state 1' to state 2 by removing second 510-kg mass.

In state 2, pressure inside the piston is

$$P_2 = P_{atm} = 1 \text{ bar.}$$

$$V_2 = \frac{P_1' V_1'}{P_2} = \frac{1.51 \times 0.053}{1} = 0.08 m^3.$$

work done by the system in going from state 1' to state 2 is

$$W = -\int_{V_1'}^{V_2} P_E \, dV = -1 \times 10^5 \times (V_2 - V_1')$$

$$= -10^5 \times (0.08 - 0.053) = -2700 J.$$

Thus, total work $= -1963 - 2700 = \underline{-4663 J}$

→ Process 'c' is "better" than process 'A' as it allows us to extract more work from the system.

The compression process is the opposite of the expansion. with the system in state 2, a 510-kg block is placed on the piston until it compresses to the intermediate state, followed by placement of the second block. The work is:

$$W = -\int_{V_2}^{V_1} P_E dV = -\left[\left(P_{atm} + \frac{mg/2}{A}\right)\int_{V_2}^{V_{int}} dV + \left(P_{atm} + \frac{mg}{A}\right)\int_{V_{int}}^{V_1} dV\right]$$

$\underline{W = +6654 \text{ J}}$

In analogy to the expansion process, process D is "better" than process 'B' in that it costs us less work to compress the system back to state 1. when we have to put work into a system, we want it to be as small as possible. However, it still costs us more work to compress from state 2 to state 1 than we get out of the expansion, so these processes are still irreversible.

we did better in both expansion and compression processes when we divided the 1020-kg mass into two parts. Presumably, we would do better by dividing it into four parts, and even better by dividing it into eight parts and so on. If we want to do the best possible, we can divide the 1020-kg mass into many "differential" units and take them off one at a time for expansion or place them on one at a time for compression. At each differential step, the system pressure is no more than $\partial mg/A$ different than the external pressure. Thus, to a close approximation:

$$\underset{\text{system pressure.}}{\underset{\downarrow}{P}} = P_E$$

To find the work, we integrate over the external pressure. However, since the external pressure is equal to the system pressure, we get:

$$W = -\int_{V_1}^{V_2} P_E dV = -\int_{V_1}^{V_2} P dV = -\int_{V_1}^{V_2} \frac{P_1 V_1}{V} dV = -P_1 V_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$= -2\times10^5 \times 0.04 \times \ln\left(\frac{0.08}{0.04}\right)$$

$$= \underline{\underline{-5545\ J}}.$$

Similarly, the work of compression is:

$$W = -\int_{V_2}^{V_1} P_E dV = -\int_{V_2}^{V_1} P dV = -\int_{V_2}^{V_1} \frac{P_1 V_1}{V} dV = -P_1 V_1 \ln\left(\frac{V_1}{V_2}\right)$$

$$= \underline{\underline{5545\ J}}.$$

Hence, we can go from state 1 to 2 and back to state 1 without a net effect on the surroundings. Thus, these processes are reversible. In a reversible process, we are never more than slightly out of equilibrium. At any point during the expansion, we could turn the process around the other way and compress the piston by adding differential masses instead of removing them. Moreover, we get more work out of the reversible expansion than the irreversible expansions. Similarly, the reversible compression costs us less work than the irreversible processes.

* Only in a reversible process, we can substitute the system pressure for the external pressure.

CL 3003 CHEMICAL ENGINEERING THERMODYNAMICS

MONSOON 2018

Lecture – 5 : Reversible/Irreversible Processes and 1st Law of Thermodynamics

Department of Chemical Engineering
BIT Mesra, Ranchi, Jharkhand-835215

Comparison of work done between Expansion process & compression process

	Expansion	Compression
Case-I Single block of mass 1020 Kg	−4000 J	+8000 J
Case-II 02 blocks each of mass ~~255~~ 510 kg (Total mass = 1020 kg)	−4663 J	+6677 J
Case-III 04 blocks each of mass 255 kg (Total mass = 1020 kg)	−5079 J	+6068 J
Case-IV 08 blocks each of mass 127.5 Kg (Total mass = 1020 Kg)	−5306 J	+5813 J

As we increase the number of blocks, keeping total mass constant, Expansion work increases while work required to compress the system decreases.

Pressure profiles in different cases:
(Expansion)

Case I : 2 bar → 1 bar

ase II : 2 bar → 1.51 bar → 1.0 bar

se III :

$$\begin{tikzcd}
2\text{ bar} \arrow[r] & 1.77\text{ bar} \arrow[r] & 1.51\text{ bar} \arrow[d] \\
 & 1.0\text{ bar} & 1.26\text{ bar} \arrow[l]
\end{tikzcd}$$

ase IV :

$$\begin{tikzcd}
2\text{ bar} \arrow[r] & 1.89\text{ bar} \arrow[r] & 1.77\text{ bar} \arrow[d] \\
 & 1.51\text{ bar} \arrow[d] & 1.64\text{ bar} \arrow[l] \\
 & 1.38\text{ bar} \arrow[r] & 1.26\text{ bar} \arrow[d] \\
 & 1.0\text{ bar} & 1.13\text{ bar} \arrow[l]
\end{tikzcd}$$

In case of compression, values will remain same while arrow sign will reverse.

The first Law of thermodynamics:

The first law of thermodynamics states that while energy can be changed from one form to another, the total quantity of Energy, E, in the universe is constant. This statement can be quantitatively expressed as follows:

$$\Delta E_{univ} = 0.$$

However, it is very inconvenient to consider the entire universe every time we need to do a calculation. As we have seen, we can break down the universe into the region in which we are interested (the system) and the rest of the universe (the surroundings). The system is separated from the surroundings by its boundary. We can now restate the first law by saying that "the energy change of the system must be equal to the energy transferred across its boundaries from the surroundings."

Energy can be transferred by heat, Q, by work, W, and in the case of open systems, by the energy associated with the mass that flows into and out of the system. In essence, the first law then lets us be accountants of the energy in the system.

There are two modes in which energy may be stored in a system:

(a) Macroscopic energy mode.
(b) Microscopic energy mode.

The macroscopic energy mode includes the macroscopic kinetic energy and potential energy of a system.

The macroscopic kinetic energy, E_K, is the energy associated with the bulk (macroscopic) motion of the system as a whole. The macroscopic potential energy, E_p, is the energy associated with the bulk (macroscopic) position of the system in a potential field.

The microscopic energy mode refers to the energy stored in the molecular and atomic level of the system, which is called the molecular internal energy or simply internal energy, denoted by the symbol 'U'.

The internal energy is the energy associated with the motion, position and chemical-bonding configuration of the individual molecules of the substances with in the system.

If 'ϵ' represents the energy of one molecule, then

$$\epsilon = \epsilon_{trans} + \epsilon_{rot} + \epsilon_{vib} + \epsilon_{electronic} + \epsilon_{nuclear} + \ldots$$

If 'N' is the total number of molecules in the system, then the total internal energy,

$$U = N\epsilon$$

other forms of energy which can also be possessed by a system are magnetic energy, electrical energy, Surfale energy. In the absence of these forms, the total energy 'E' of a system is given by-

$$E = \underbrace{E_K + E_P}_{\text{Macro}} + \underbrace{U}_{\text{micro}}$$

In the absence of motion & gravity / ~~or neg~~

$$E = U$$

Internal energy is an important form of energy for chemical engineering applications. Internal energy encompasses all forms of molecular energy, including the kinetic and potential energies of the molecules themselves.

There are two general components of internal energy - molecular potential energy and molecular kinetic energy.

Molecular potential energy can be either intermolecular (between different molecules) and intramolecular (with in the same molecule).

Like macroscopic kinetic energy, by molecular kinetic energy we mean motion; in this case, the motion of the individual molecules in a system. The type of motion depends on the phase the species are in. In the gas phase, for example, the molecules are flying around at significant speeds. This motion is referred to as translational motion because the individual molecules are going somewhere - that is, translating - even though the bulk of the gas may not be. Additionally, diatomic and polyatomic molecules can vibrate and rotate, which provide additional modes of molecular kinetic energy - vibrational and rotational motion. In contrast, solids donot have translational motion; their main mode of molecular kinetic energy is in the form of vibrations.

consider next a phase change, such as the sublimation of a solid into a vapor. The solid is held together by bonds between the molecules. often the bonding in a solid results from electrostatic attraction of the molecules, that is, molecular potential energy.

On the other hand, the molecules in the vapor are much farther away from one another and have little or no attraction. Thus, the vapor phase is representative of higher internal energy relative to the solid at the same temperature To sublime, the molecular energy of the attraction of the bonds must be overcome, that is, energy must be added to the system, resulting in higher internal energy.

CL 3003 CHEMICAL ENGINEERING THERMODYNAMICS

MONSOON 2018

Lecture – 6 : 1st Law of Thermodynamics

Department of Chemical Engineering
BIT Mesra, Ranchi, Jharkhand-835215

The first law of thermodynamics for closed systems.

[Energy balances for closed systems]

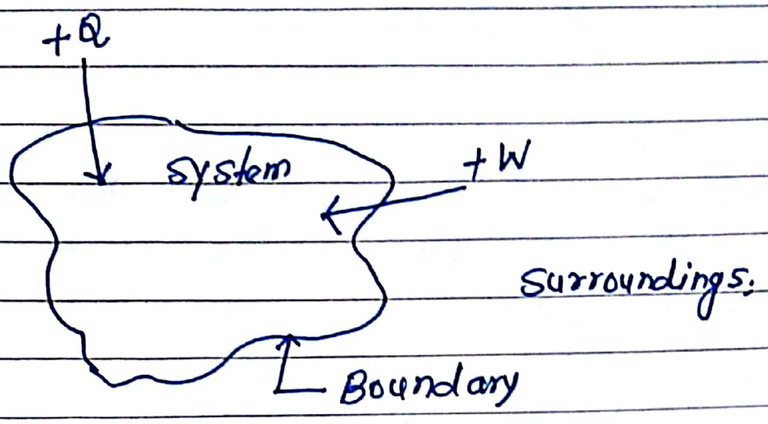


Figure shows a schematic of a closed system that undergoes a process from initial state 1 to final state 2. Since mass cannot enter or leave a closed system, the changes in the energy within the system are equal to the energy transferred from the surroundings by either heat or work.

Writing down the first law in quantitative terms, we get-

$$\left\{\begin{array}{c}\text{change in}\\ \text{energy in}\\ \text{system}\end{array}\right\} = \left\{\begin{array}{c}\text{energy transferred}\\ \text{from surroundings}\\ \text{to system}\end{array}\right\}$$

$$\underbrace{\Delta E_K + \Delta E_p + \Delta U^t}_{\text{property : depends only on state 1\&2}} = \underbrace{Q + W}_{\text{depends on path}}$$

; where U^t is the total internal energy of the system.

We often neglect macroscopic kinetic and potential energy.

So,

$$\boxed{\Delta U^t = Q + W}$$

* Heat and work refer to the amount of energy transferred. Hence, it would be wrong to write them ΔQ or ΔW. we reserve the 'Δ' for state function that depends just on the initial and final state of the system.

The first law can also be written in differential form for each differential step in time during the process. Numerical solutions are obtained by integration of the resulting differential energy balance. Common forms of energy balance over a differential element can be written by analogy to the equations just presented.

$$\boxed{dU^t + dE_K + dE_p = \delta Q + \delta W}$$

or, neglecting kinetic and potential energy,

$$\boxed{dU^t = \delta Q + \delta W}$$

We use the exact differential 'd' with the energy terms to indicate that they depend only on the final states; in contrast, we use the inexact differential 'δ' with heat and work to remind us that we must keep track of the path when we integrate to get these quantities.

The differential of a state function represents an infinitesimal change in its value. Integration of such a differential results in a finite difference between two of its values, e.g.,

$$\int_{P_1}^{P_2} dP = P_2 - P_1 = \Delta P \quad \text{and} \quad \int_{V_1}^{V_2} dV = V_2 - V_1 = \Delta V$$

The differentials of heat and work are not changes, but are infinitesimal amounts. When integrated, these differentials give not finite changes, but finite amounts. Thus,

$$\int \delta Q = Q \quad \text{and} \quad \int \delta W = W.$$

* $U^t = mU$ or nU

where 'U' represent the internal energy of a unit amount of material, either a unit mass or a mole. Thés is specific or molar properties, and they are intensive, independent of the quantity of material actually present.

For a closed system of 'n' moles,

$$\boxed{\begin{array}{c} \Delta(nU) = n\Delta U = Q + W \\ \hline d(nU) = n\,dU = \delta Q + \delta W \end{array}}$$

The above Equation is the ultimate source of all property relations that connect the internal energy to measurable quantities.

Constant - V and constant - P processes:

For 'n' moles of a homogeneous fluid contained in a closed system the energy balance is:

$$d(nU) = dQ + dW \longrightarrow (1)$$

The work for a mechanically reversible, closed system process is given by

$$dW = -Pd(nV) \longrightarrow (2)$$

These two equations combine to form

$$d(nU) = dQ - Pd(nV) \longrightarrow (3)$$

This energy balance is general for 'n' moles of homogeneous fluid in a closed system undergoing a mechanically reversible process.

Constant - volume process:

If the process occurs at constant total volume, the work is zero.
Thus, Eq^n. (3), reduces to-

$$dQ = d(nU) \longrightarrow (4)$$

or,

$$Q = n\Delta U \longrightarrow (5)$$

Thus, the heat transferred in a mechanically reversible, constant-volume, ~~cons~~ closed-system process equals the internal-energy change of the system.

Constant-Pressure Process:

From Eq^n. (3),

$$dQ = d(nU) + Pd(nV)$$

$$= d(nU) + d(nPV)$$

$$= d[nU + nPV]$$

$$= d[n(U + PV)]$$

$$\boxed{H\,(\text{Enthalpy}) = U + PV} \longrightarrow (6)$$

$$\boxed{dQ = d(nH)} \longrightarrow (7)$$

Integration yields,

$$\boxed{Q = n\Delta H} \longrightarrow (8)$$

Thus, the heat transferred in a mechanically reversible, constant-pressure, closed-system process equals the enthalpy change of the system.

Because U, P and V are all state functions, 'H' defined by eq^n. (6) is also a state function.

The differential form of Eqn. (6) is:

$$dH = dU + d(PV) \longrightarrow (9)$$

upon integration,

$$\Delta H = \Delta U + \Delta(PV) \longrightarrow (10).$$

Heat capacity

Heat capacity at constant volume: [illegible]

The constant-volume heat capacity of a substance is defined as.

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \longrightarrow (11)$$

Although this definition makes no reference to any process, it relates in an especially simple way to a constant-volume process in a closed system, for which Eqn. (11) may be written:

$$dU = C_V\, dT \longrightarrow (12)$$

Integration yields:

$$\Delta U = \int_{T_1}^{T_2} C_V dT \longrightarrow (13)$$

This result with Eqⁿ. (5) for a mechanically reversible, constant-volume process gives:

$$Q = n\Delta U = n\int_{T_1}^{T_2} C_V dT \longrightarrow (14)$$

Heat capacity at constant pressure

The constant-pressure heat capacity is defined as.

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \longrightarrow (15)$$

$$dH = C_P dT \longrightarrow (16)$$

$$\text{or,} \quad \Delta H = \int_{T_1}^{T_2} C_P dT \longrightarrow (17)$$

For a reversible, constant-P process Eqⁿ. (17) may be combined with Eqⁿ. (8),

$$Q = n\Delta H = n\int_{T_1}^{T_2} C_P dT \longrightarrow (18)$$

Implied Property Relations for an ideal gas:

- The equation of state:

$$PV = RT \quad \text{(ideal gas)} \longrightarrow (19)$$

- Internal energy is a function of temperature only:

$$U = U(T) \quad \text{(ideal gas)} \longrightarrow (20)$$

The definition of heat capacity at constant volume, leads for an ideal gas to the conclusion that C_V is a function of temperature only:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{dU(T)}{dT} = C_V(T) \longrightarrow (21)$$

The defining equation for enthalpy applied to an ideal gas, leads to the conclusion that 'H' also is a function of temperature only:

$$H = U + PV = U(T) + RT = H(T) \longrightarrow (22)$$

The heat capacity at constant pressure C_p, like C_V, is a function of temperature only:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P = \frac{dH(T)}{dT} = C_p(T) \longrightarrow (23)$$

A useful relation between C_p and C_V for an ideal gas comes from differentiation of Eqn. (22):

$$C_p = \frac{dU}{dT} + R = C_V + R$$

$$C_p - C_V = R \longrightarrow (24)$$

* This equation does not imply that C_p and C_V are themselves constant for an ideal gas, but only that they vary with temperature in such a way that their difference is equal to R.

For any change of state of an ideal gas, (regardless of the kind of process)

$$dU = C_V dT \longrightarrow (25)$$

or

$$\Delta U = \int C_V dT \longrightarrow (26)$$

$$dH = C_p dT \longrightarrow (27)$$

or

$$\Delta H = \int C_p dT \longrightarrow (28)$$

Equations for process calculations for ideal gases:

Process calculations provide work and heat quantities.

The work of a reversible closed-system process is given by (for a unit mass or a mole):

$$dW = -PdV$$

For an ideal gas in any closed-system process, the first Law written for a unit mass or a mole,

$$dQ + dW = C_V dT$$

$$\text{or, } dQ - PdV = C_V dT$$

$$\text{or, } dQ = PdV + C_V dT$$

$$\text{or, } \boxed{dQ = RT\frac{dV}{V} + C_V dT} \longrightarrow (29)$$

$$\& \quad \boxed{dW = -RT\frac{dV}{V}} \longrightarrow (30)$$

With $C_p - C_V = R$ eq^n. (29) & eq^n. (30) becomes-

$$dQ = RT\frac{dV}{V} + (C_p - R)dT$$

$$dQ = RT\frac{dV}{V} + C_p dT - RdT$$

$$\text{with, } \cancel{V} = \frac{RT}{\cancel{P}} \qquad PV = RT$$

$$pdV + Vdp = RdT$$

$$dq = \frac{RT\,dV}{(RT/p)} + C_p dT - R dT$$

$$= P dV + C_p dT - R dT$$

$$= C_p dT - V dp$$

$$\boxed{dq = C_p dT - RT\frac{dP}{P}} \longrightarrow (31)$$

$$dW = -P dV$$

$$= -(\cancel{Vdt}\ R dT - V dp)$$

$$= -R dT + V dp$$

$$\boxed{dW = -R dT + RT\frac{dp}{p}} \longrightarrow (32)$$

* These equations may be applied for ideal gases to various Kinds of processes. The assumptions implicit in their derivation are that the system is closed and the process is reversible.

Isothermal process: (T = const.)

By Eqs. (26) and (28),

$$\Delta U = \Delta H = 0$$

By Eqs. (29) and (31),

$$Q = RT \ln \frac{V_2}{V_1} = -RT \ln \frac{P_2}{P_1}$$

By Eqs. (30) and (32),

$$W = -RT \ln \frac{V_2}{V_1} = RT \ln \frac{P_2}{P_1}$$

From 1st law of thermodynamics,

$$Q + W = \Delta U = 0$$
$$\Rightarrow Q = -W$$

Therefore,

$$\boxed{Q = -W = RT \ln \frac{V_2}{V_1} = -RT \ln \frac{P_2}{P_1}} \rightarrow (33)$$

Isobaric process: ($P =$ constant)

By Eqs. (26) and (28),

$$\Delta U = \int C_V dT \quad \text{and} \quad \Delta H = \int C_P dT$$

By Eqs. (31) and (32),

$$Q = \int C_P dT \quad \text{and} \quad W = -R(T_2 - T_1)$$

Note that $Q = \Delta H$,

therefore,

$$\boxed{Q = \Delta H = \int C_P dT} \longrightarrow (34)$$

Isochoric (constant-V) Process:

Eqs. (26) and (28) again apply:

$$\Delta U = \int C_V dT \quad \text{and} \quad \Delta H = \int C_P dT$$

$W = -\int P dV = 0$ and $Q + W = \Delta U$ gives

$$\boxed{Q = \Delta U = \int C_V dT} \longrightarrow (35)$$

(Lecture-7)

Adiabatic process (constant heat capacities)

An adiabatic process is one for which there is no heat transfer between the system and its surroundings; i.e. $dQ = 0$.

- Reversible
- Adiabatic compression or expansion
- ideal gas

$$\boxed{pV^{\gamma} = \text{const}; \quad TV^{\gamma-1} = \text{const}; \quad p^{1-\gamma}T^{\gamma} = \text{const}.} \rightarrow (36)$$

where, $\boxed{\gamma = \dfrac{C_P}{C_V}} \xrightarrow[(37)]{}$

For ideal gases, the work of any adiabatic-system process is given by:

$$dW + \underbrace{dQ}_{0} = dU$$

$$\Rightarrow dW = dU = C_V dT$$

for constant C_V, $W = \Delta U = C_V \Delta T \rightarrow (38)$

$$\gamma = \frac{C_P}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V}$$

Thus, $W = \dfrac{R\Delta T}{\gamma - 1}$

$$\Rightarrow \gamma - 1 = \frac{R}{C_V}$$

$$C_V = \frac{R}{\gamma - 1}$$

since, $RT_1 = P_1V_1$ and $RT_2 = P_2V_2$,

$$W = \frac{RT_2 - RT_1}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1} \longrightarrow (39)$$

Eqⁿs. (38) and (39) are general for adiabatic compression and expansion processes in a closed system, whether reversible or not.

(since V_2 is usually unknown).

Elimination of V_2 from eqⁿ. (39) using eqⁿ. (36)

$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

$$\Rightarrow \quad V_2^{\gamma} = V_1^{\gamma}\frac{P_1}{P_2}$$

$$V_2 = V_1\left(\frac{P_1}{P_2}\right)^{1/\gamma}$$

$$W = \frac{P_2V_2 - P_1V_1}{\gamma - 1} = \frac{P_1V_1}{\gamma - 1}\left[\frac{P_2V_2}{P_1V_1} - 1\right]$$

$$= \frac{P_1V_1}{\gamma - 1}\left[\frac{P_2}{P_1}\left(\frac{P_1}{P_2}\right)^{1/\gamma} - 1\right]$$

$$= \frac{P_1V_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right]$$

$$W = \frac{P_1V_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right] = \frac{RT_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right] \longrightarrow (40)$$

The same result is obtained when the relation between P and V given by Eqn. (36) is used for the integration, $W = -\int P dV$.

+ Eqn. (40) is valid only for ideal gases with constant heat capacities in adiabatic, reversible, closed-system processes.

For monoatomic gases,

$$\gamma = 1.67$$

Diatomic gases,

$$\gamma = 1.4$$

Simple polyatomic gases (CO_2, SO_2, NH_3, CH_4)

$$\gamma = 1.3$$

Polytropic process:

polytropic process suggests a model of some verstatility. With δ a constant, it is defined as a process represented by the empirical equation:

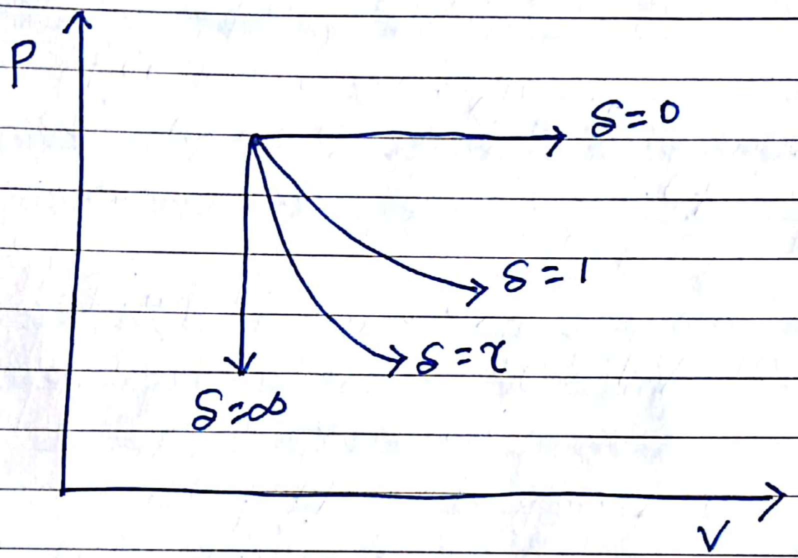
$$PV^{\delta} = \text{constant} \longrightarrow (41)$$

For an ideal gas,

$$\left.\begin{aligned} TV^{\delta-1} &= \text{const.} \\ P^{1-\delta}\,T^{\delta} &= \text{const.} \end{aligned}\right\} \longrightarrow (42)$$

Eq^n. analogous to Eq^n. (40), can be written by replacing 'γ' by δ:

$$W = \frac{RT_1}{\delta-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\delta-1}{\delta}} - 1\right] \longrightarrow (43)$$



Paths of polytropic processes characterized by specific value of 'δ'.

- Isobaric process, $\delta=0$.
- Isothermal process: $\delta=1$.
- Adiabatic process: $\delta=\gamma$.
- Isochoric process;

$$PV^\delta = \text{const.}$$

$$P\delta V^{\delta-1}\frac{dV}{dP} + V^\delta = 0$$

$$\Rightarrow \delta P V^{\delta-1}\frac{dV}{dP} = -V^\delta$$

$$\Rightarrow \frac{dV}{dP} = -\frac{V}{P\delta}\text{; for const. } V,\ \delta = \pm\infty.$$

Irreversible process.

All equations developed above have been derived for reversible, closed-system processes for ideal gases. However, those equations which give property changes- dU, dH, ΔH, ΔU - are valid for ideal gases regardless of the process. They apply equally to reversible and irreversible processes in closed system.

The work of an irreversible process is calculated by a two-step procedure.

First, W is determined for a reversible process that accomplishes the same change of state as the actual irreversible process.

Second, this result is multiplied or divided by an efficiency to give the actual work. If the process produces work, the absolute value for the reversible process is too large and must be multiplied by an efficiency. If the process requires work, the value for the reversible process is too small and must be divided by an efficiency.

Lecture-8

Mass and Energy balances for open systems:

- The laws of mass and energy conservation apply to all processes, to open as well as to closed systems.
- Indeed, the open system includes the closed system as a special case.

Measures of flow:

open systems are characterized by flowing streams; there are four common measures of flow:

- Mass flowrate, $\dot{m}$
- Molar flowrate, $\dot{n}$
- Volumetric flowrate, q
- Velocity, u

Measures of quantity per unit of time.

The measures of flow are interrelated:

$$\underbrace{\dot{m} = M\dot{n}}_{M:\ \text{Molar mass.}} \quad \text{and} \quad \underbrace{q = uA}_{A:\ \text{cross-sectional area}}$$

Importantly, mass and molar flowrates relate to velocity:

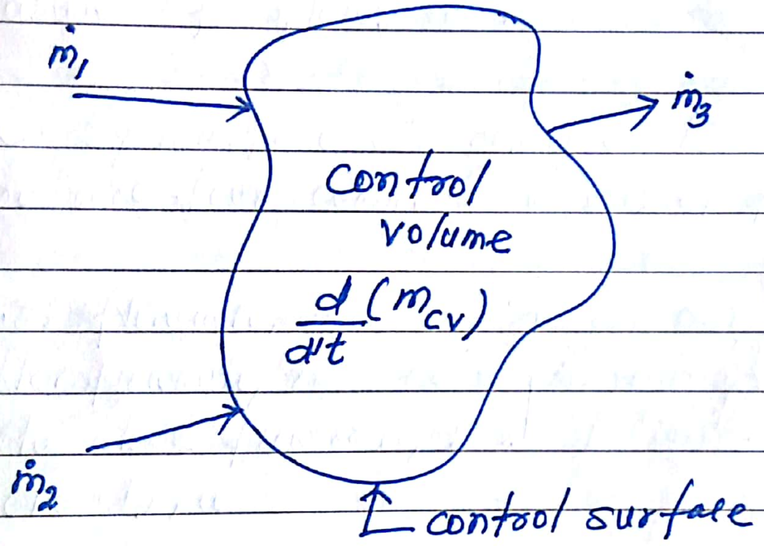
$$\dot{m} = uA\rho \longrightarrow (1)$$

$$\dot{n} = uA\rho \longrightarrow (2)$$

where, ρ, is specific or molar density.

Mass Balance for open systems

The region of space identified for analysis of open systems is called a control volume; it is separated from its surroundings by a control surface. The fluid with in the control volume is the thermodynamic system for which mass and energy balances are written.



Two streams with flow rates $\dot{m}_1$ and $\dot{m}_2$ are shown directed into the control volume, and one stream with flowrate $\dot{m}_3$ is directed out.

Because mass is conserved, the rate of change of mass within the control volume, $d(m_{cv})/dt$, equals the net rate of flow of mass into the control.

Mathematically,

$$\dot{m}_1 + \dot{m}_2 = \dot{m}_3 + \frac{d}{dt}(m_{cv})$$

$$\Rightarrow \frac{d(m_{cv})}{dt} + \underbrace{\dot{m}_3 - \dot{m}_1 - \dot{m}_2}_{\Delta \dot{m}} = 0$$

$\Delta \dot{m}$ = Difference between exit and entrance flows.

$$\boxed{\frac{d}{dt}(m_{cv}) + \Delta\dot{m} = 0} \longrightarrow (3)$$

using eq^n. (1),

$$\boxed{\frac{d}{dt}(m_{cv}) + \Delta(\rho u A) = 0} \longrightarrow (4)$$

In this form the mass-balance equation is often called the continuity equation.

The flow process characterized as steady state is an important special case for which conditions within the control volume do not change with time. The control volume then contains a constant mass of fluid, and the accumulation term of eq^n. (4) is zero, reducing eq^n. (4) to-

$$\Delta(\rho u A) = 0 \longrightarrow (5)$$

The term "steady state" does not necessarily imply that flowrates are constant, merely that the inflow of mass is exactly matched by the outflow of mass.

When there is but a single entrance and a single exit stream, the mass flowrate $\dot{m}$ is the same for both stream; then,

$$\rho_2 u_2 A_2 - \rho_1 u_1 A_1 =$$

or,

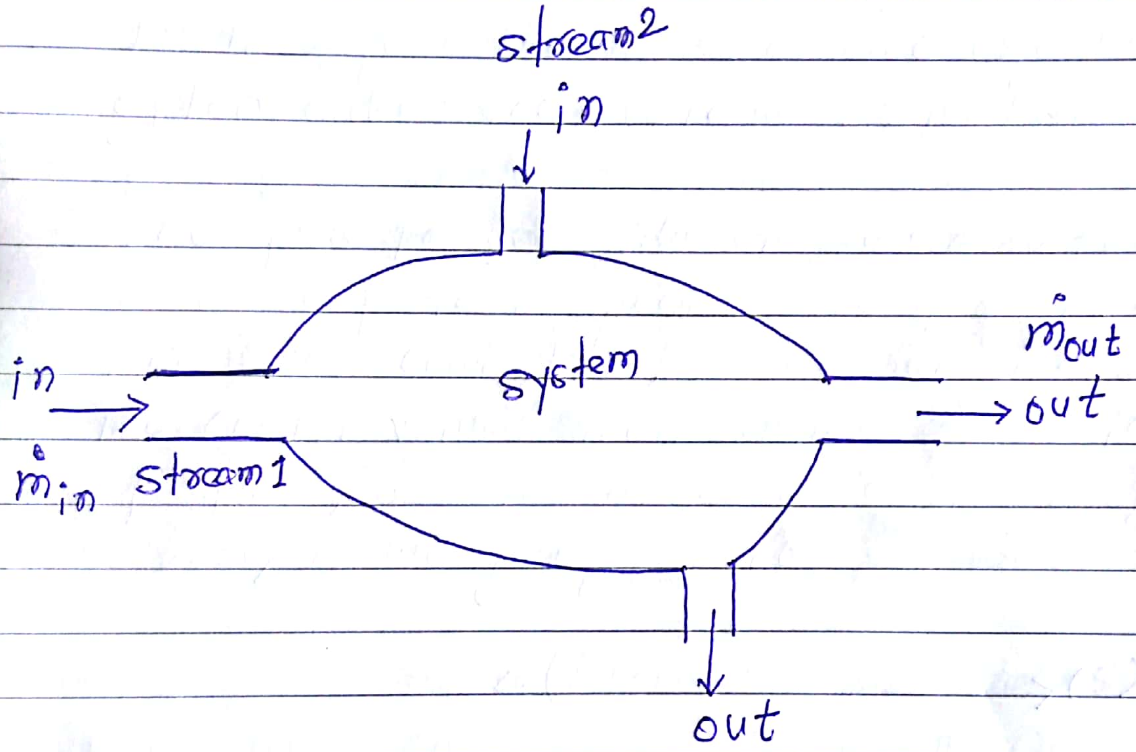
$$\dot{m} = \text{const.} = \rho_2 u_2 A_2 = \rho_1 u_1 A_1 \longrightarrow (6)$$

Because specific volume is the reciprocal of density,

$$\dot{m} = \frac{u_1 A_1}{V_1} = \frac{u_2 A_2}{V_2} = \frac{uA}{V} \longrightarrow (7)$$

Lecture-9

The general Energy Balance:



The energy balance for an open system contains all the terms associated with an energy balance for a closed system, but we must also account for the energy change in the system associated with the stream flowing into and out of the system.

Let's look at the contribution to the energy balance from the inlet stream labeled stream 1. compared to the closed-system analysis, there are two additional ways in which energy can be transferred from the surroundings.

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Lecture-9

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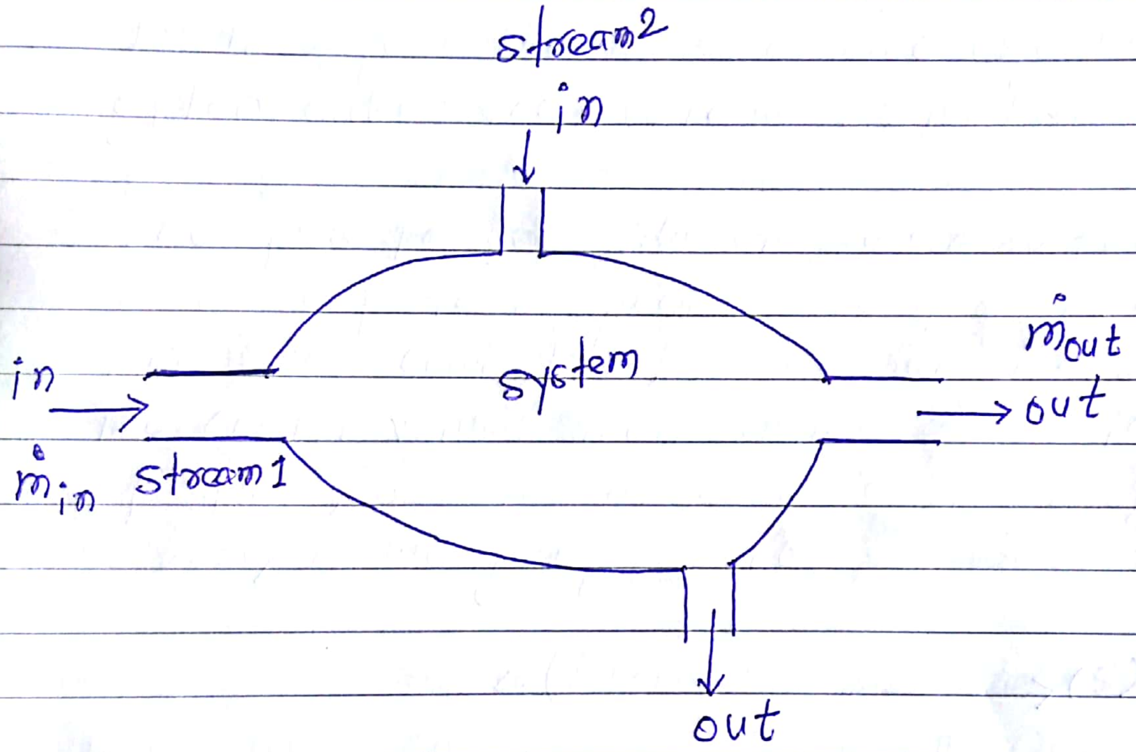

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Let's look at the contribution to the energy balance from the inlet stream labeled stream 1. Compared to the closed-system analysis, there are two additional ways in which energy can be transferred from the surroundings.

First, the molecules flowing into the system carry their own energy; typically the most important form of energy is the specific internal energy, $\hat{u}_{in}$, but the flowing streams can also have (macroscopic) kinetic energy, $(\hat{e}_K)_{in}$, and potential energy, $(\hat{e}_P)_{in}$, associated with them.

Second, the inlet stream adds energy into the system by supplying work, the so-called flow work. Flow work is the work the inlet fluid must do on the system to displace fluid within the system so that it can enter. Flow work of any inlet stream is given by the term

$$(P\hat{v})_{in}.$$

Similarly, flow work of any outlet stream is given by:

$$-(P\hat{v})_{out}$$

We can write the total energy transfer due to work in the system in terms of shaft work, W_s and flow work, as follows:

$$\dot{W} = \dot{W}_{shaft} + \dot{W}_{flow}$$

$$= \left[\dot{W}_s + \sum_{in} \dot{m}_{in}(P\hat{v})_{in} + \sum_{out} \dot{m}_{out}(-P\hat{v})_{out}\right]$$

$\longrightarrow$ (8)

The shaft work is representative of the useful work that is obtained from the system. The flow work does not provide a source of power; it is merely the "cost" of pushing fluid into or out of the open system.

We can now include the ways in which energy can exchange between the system and surroundings in our energy balance for open systems. In the general case of many streams in and many streams out, we must sum over all the in and out streams.

First, we consider a system at steady-state; that is, there is no accumulation of energy or mass in the system with time.

The energy balance is written as (on a rate basis):

$$0 = \underbrace{\sum_{in} \dot{m}_{in}\left(\hat{u}+\frac{1}{2}v^2+gz\right)_{in}}_{\text{Energy flowing into the system with the inlet streams}} - \underbrace{\sum_{out} \dot{m}_{out}\left(\hat{u}+\frac{1}{2}v^2+gz\right)_{out}}_{\text{Energy flowing out of the system with the outlet streams}}$$

$$+\dot{Q}+\left[\dot{W}_s+\underbrace{\sum_{in}\dot{m}_{in}(P\hat{v})_{in}}_{\text{flow work from the inlet stream}}+\underbrace{\sum_{out}\dot{m}_{out}(-P\hat{v})_{out}}_{\text{flow work from the outlet streams}}\right]$$

$$\longrightarrow (9)$$

Rearranging, we get:

$$0 = \sum_{in}\dot{m}_{in}\left[(\hat{u}+P\hat{v})+\frac{1}{2}v^2+gz\right]_{in} - \sum_{out}\dot{m}_{out}\left[(\hat{u}+P\hat{v})+\frac{1}{2}v^2+gz\right]_{out}$$

$$+\dot{Q}+\dot{W}_s$$

$$\longrightarrow (10)$$

In summary, the steady-state energy balances can be written:

$$0 = \sum_{in} \dot{m}_{in}\left(\hat{h}+\frac{1}{2}v^2+gz\right)_{in} - \sum_{out} \dot{m}_{out}\left(\hat{h}+\frac{1}{2}v^2+gz\right)_{out} + \dot{Q} + \dot{W}_s$$

$\longrightarrow$ (11)

In cases where we can neglect (macroscopic) kinetic and potential energy, the steady-state energy balance becomes:

$$0 = \sum_{in} \dot{m}_{in}\hat{h}_{in} - \sum_{out} \dot{m}_{out}\hat{h}_{out} + \dot{Q} + \dot{W}_s$$

$\longrightarrow$ (12)

Transient Energy Balance

Another useful form of the energy balance for open systems is for unsteady-state conditions. Unsteady-state is important, for example, in start-up as the equipment "warms up".

$$\left(\frac{dU}{dt}+\frac{dE_k}{dt}+\frac{dE_p}{dt}\right)_{sys} = \sum_{in} \dot{m}_{in}\left(\hat{h}+\frac{1}{2}v^2+gz\right)_{in}$$

$$-\sum_{out} \dot{m}_{out}\left(\hat{h}+\frac{1}{2}v^2+gz\right)_{out} + \dot{Q} + \dot{W}_s$$

$\longrightarrow$ (13)

In cases where we can neglect (macroscopic) kinetic and potential energy, the unsteady-state energy balance becomes:

$$\left(\frac{dU}{dt}\right)_{sys} = \sum_{in} \dot{m}_{in} \hat{h}_{in} - \sum_{out} \dot{m}_{out} \hat{h}_{out} + \dot{Q} + \dot{W}_s \longrightarrow (14)$$

In Equations (13) and (14), the left-hand side represents accumulation of energy within the system. There is no flow work associated with this term; hence, the appropriate property is U. On the other hand, the first two terms on the right-hand side account for energy flowing in and out of the system, respectively. These terms must account for both the internal energy and flow work of the flowing streams.

Example 1: Steam enters a turbine with a mass flow rate of 10 kg/s. The inlet pressure is 100 bar and the inlet temperature is 500°C. The outlet contains saturated steam at 1 bar. At steady-state, calculate the power (in kW) generated by the turbine

Solution: The steady-state energy balance is given by Eqn. (12),

$$0 = \sum_{in} \dot{m}_{in} \hat{h}_{in} - \sum_{out} \dot{m}_{out} \hat{h}_{out} + \dot{Q} + \dot{W}_s$$

For a turbine, there is one stream in and one stream. Moreover, heat dissipation is negligible, since $\dot{Q} << \dot{W}_s$. If we label the inlet stream "1" and the outlet stream "2", Equation becomes -

$$0 = \dot{m}_1 \hat{h}_1 - \dot{m}_2 \hat{h}_2 + \dot{W}_s$$

Scanned by CamScanner

At steady-state, the mass balance can be written as:

$$\dot{m}_1 = \dot{m}_2 = \dot{m}$$

Thus,

$$\dot{W}_s = \dot{m}(\hat{h}_2 - \hat{h}_1)$$

$$\hat{h}_2 = 2675.5 \ \frac{kJ}{kg}$$

$$\hat{h}_1 = 3373.6 \ \frac{kJ}{kg}$$

So,

$$\dot{W}_s = [10 \ kg/s][2675.5 - 3373.6] \frac{kJ}{kg}$$

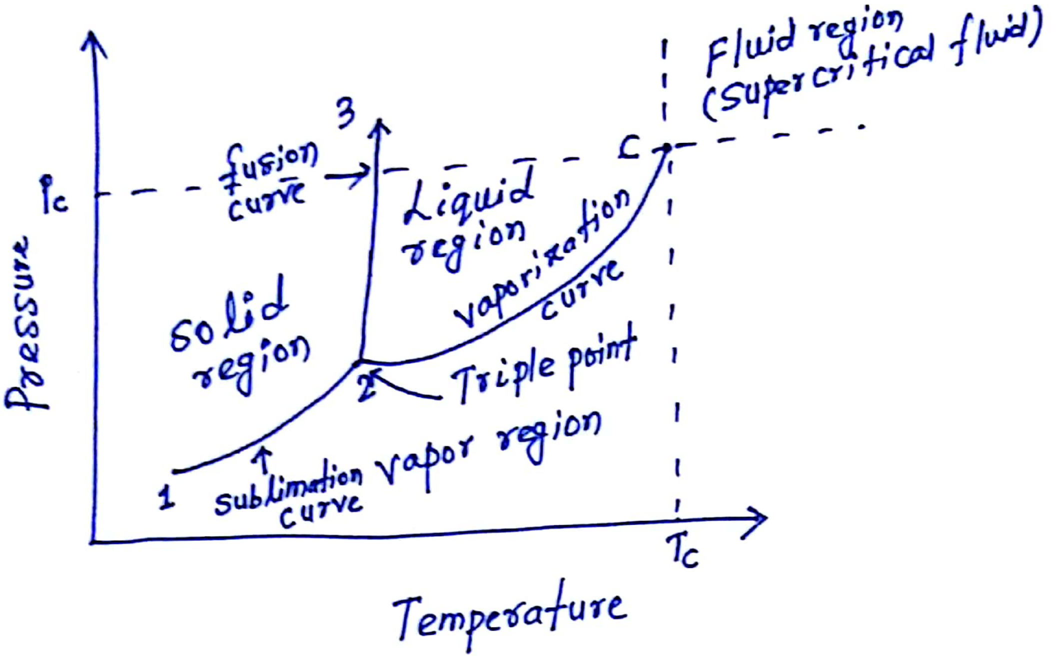
$$= -6981 \ kW$$

Thus, this turbine generates approximately 7 MW of power.

Note the negative sign, which indicates that we are getting useful work from the system.

Lecture-10

volumetric properties of pure fluids
(PVT behaviour)



PT- diagram for a pure substance

Lines 1-2 and 2-C represent for a pure substance conditions of pressure and temperature at which solid and liquid phases exist in equilibrium with a vapor phase. These vapor pressure vs. temperature lines characterize solid/vapor (1-2) and liquid/vapor (2-C) equilibrium relationships. The solid/liquid equilibrium relationship is represented by line 2-3. The three lines display conditions of 'p' and 'T' at which two phases may coexist, and divide the diagram into single-phase regions. Line 1-2, the sublimation curve, separates the solid and gas regions; line 2-3, the fusion curve, separates the solid and liquid regions; line 2-C, the vaporization curve, separates the liquid and gas regions.

point 'c' is known as the critical point; its coordinate "P_c" and "T_c" are the highest pressure and highest temperature at which a pure chemical species is observered to exist in vapor/liquid equilibrium.

The three lines meet at the triple point, where the three phases coexist in equilibrium.

* According to the phase rule, the triple point is invariant (F=0). If the system exists along any of the two-phase lines, it is univariant (F=1), whereas in the single-phase regions it is divariant (F=2).

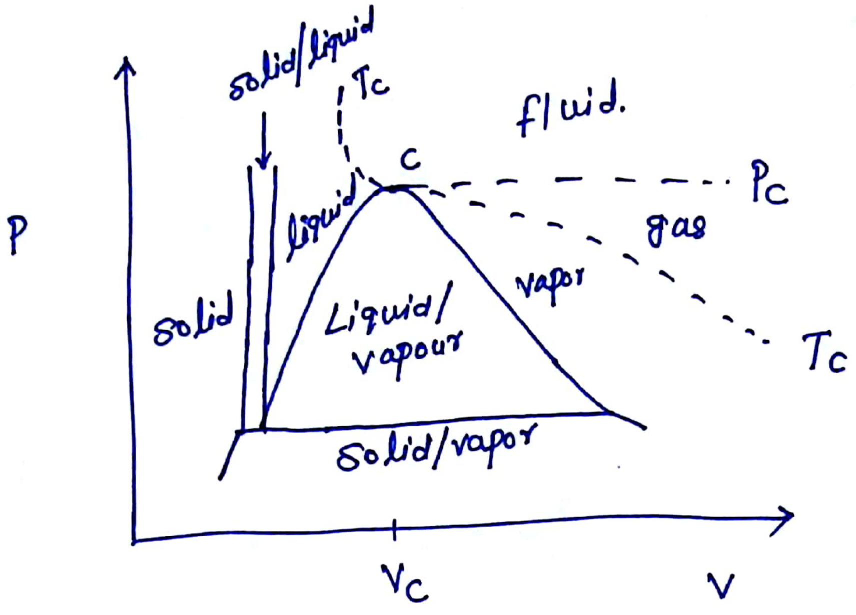
* water in an open flask is obviously a liquid in contact through a meniscus with air. If the flask is sealed and the air is pumped out, water vaporizes to replace the air, and H_2O fills the flask. The liquid water resides at the bottom of the flask because its density is much greater than that of water vapor, and the two phases are in equilibrium at conditions represented by a point on curve 2-c. The properties of liquid and vapor are very different. However, if the temperature is raised so that the equilibrium state progresses upward along curve 2-C, the properties of the two phases become more and more nearly alike; at point 'c' they become identical and the meniscus disappears.

* The gas region is sometimes divided into two parts, as indicated by the dotted vertical line. A gas to the left of this line, which can be condensed either by compression at constant temperature or by cooling at constant pressure is called a vapour. A fluid existing at a temperature greater than T_C is said to be supercritical. An example is atmospheric air.

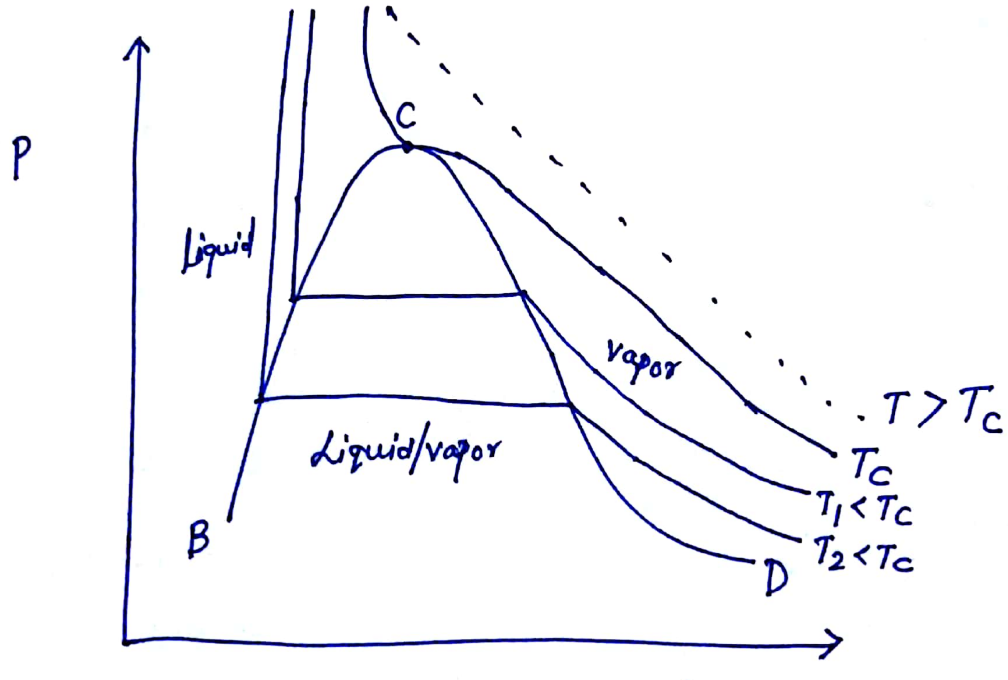
* A phase is generally considered a liquid if vaporization results from pressure reduction at constant temperature.

  A phase is considered a gas if condensation results from temperature reduction at constant pressure. Since neither process can be initiated in the region beyond the dashed lines, it is called the fluid region.

Pv - diagram



PT- diagram doesn't provide any information about volume; it merely displays the phase boundaries on a PT- diagram. On a PV-diagram, these boundaries in turn become regions where two phases - solid/liquid, solid/vapor and liquid/vapor - coexist in equilibrium.



Liquid, liquid/vapor, vapor regions with isotherms

The lines labeled T_1 and T_2 are for subcritical temperatures, and consist of three segments. The horizontal segment of each isotherm represents all possible mixtures of liquid and vapor in equilibrium, ranging from 100% liquid at the left end to 100% vapor at the right end. The locus of these end points is the dome-shaped curve labeled BCD, the left half of which (B to C) represents single-phase liquids at their vaporization (boiling) temperatures, and the right half (C to D), single-phase vapors at their condensation temperatures. Liquids and vapors represented by BCD are said to be saturated, and coexisting phases are connected by the horizontal segment of the isotherm at the saturation pressure specific to the isotherm.

The two-phase liquid/vapor region lies under dome BCD; the subcooled-liquid region lies to the left of the saturated-liquid curve BC, and the superheated-vapor region lies to right of the saturated-vapor curve CD. Isotherms in the subcooled-liquid region are very steep, because liquid volumes change little with large changes in pressure. The horizontal segment of the isotherms in the two-phase region become progressively shorter at higher temperatures, being ultimately reduced to a point at C.

Subcooled liquid and Saturated liquid

Consider a piston-cylinder device containing liquid water at 20°c and 1 atm pressure. Under these conditions, water exists in the liquid phase, and it is called a compressed liquid or a subcooled liquid., meaning that it is not about to vaporize. As heat is transferred, the temperature keeps rising untill it reaches 100°c. At this point water is still a liquid, but any heat addition will cause some of the liquid to vaporize. That is, a phase-change process from liquid to vapor is about to take place. A liquid that is about is vaporize is called a saturated liquid.

Saturated vapor and Superheated vapor

Once boiling starts, the temperature stops rising until. the liquid is completely vaporized. During a boiling process, the only change we will observe is a large increase in the volume and a steady decline in the liquid level as a result of more liquid turnig to vapor. As we continue transferring heat, the vaporization process continues untill the last drop of liquid is vaporized. At this point, the entire cylinder is filled with vapor. ~~that~~ Any heat loss from this vapor will cause some of the vapor to condense. A vapor that is about to condense is called a saturated vapor.

one the phase-change process is completed, we are back to a single-phase region (this time vapor), and further transfer of heat results in an increase in both the temperature and the specific volume. Let us say, the temperature of the vapor is 300°c and if we transfer some heat from the vapor; the temperature may drop somewhat but no condensation will take place as long as the temperature remains above 100°c (for p = 1 atm). A vapor that is not about to condense is called a <u>superheated vapor.</u>

Steam Table

		Saturation pressure ↑	specific vol (cm^3/g)		Internal Energy (KJ/kg)		Enthalpy (KJ/kg)		Entropy (KJ/kg)	
t	T	P	sat. Liq.	sat. vap.	sat. Liq.	sat. vap.	sat. Liq.	sat. vap.	sat. Liq.	sat. vap.
°c	K	kpa								
100	373.15	101.33	1.044	1673.0	419	2506.5	419.1	2676.0	1.3069	7.355

* At a given pressure, the temperature at which a pure substance changes phase is called the <u>saturation temperature.</u>

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E.g. At a pressure of 101.325 kpa, T_{sat} is 99.97°C.

At a temperature of 99.97°C, P_{sat} is 101.325 kpa.

The subscript 'f' is used to denote properties of a saturated liquid, and the subscript 'g' to denote the properties of a saturated vapor. These symbols are commonly used in thermodynamics Another subscript commonly used is 'fg', which denotes the difference between the saturated vapor and saturated liquid values of the same property.

For example,

v_f = specific volume of saturated liquid

v_g = specific volume of saturated vapor.

v_{fg} = difference between v_g and v_f

i.e. $v_{fg} = v_g - v_f$.

Example.: A rigid tank contains 50 kg of saturated liquid water at 90°C. Determine the pressure in the tank and the volume of the tank.

Solution: Rigid tank contains saturated liquid water at 90°C. Therefore, from steam tables, saturation pressure at 90°C is:

$$P_{sat @ 90°C} = 70.11 \text{ kpa}.$$

The specific volume of the saturated liquid at 90°C is: $v_{f @ 90°C} = 1.036 \text{ cm}^3/\text{g}$.

Then the total volume of the tank $= (50 \text{ kg})\left(1.036 \frac{\text{cm}^3}{\text{g}}\right)$

$= \underline{0.0518 \text{ m}^3}$.

Saturated liquid-vapor mixture

During a vaporization process, a substance exists as part liquid and part vapor. That is, it is a mixture of saturated liquid and saturated vapor. To analyze the mixture properly, we need to know the proportions of the liquid and vapor phases in the mixture. This is done by defining a new property called the quality (x):

$$x = \frac{m_{vapor}}{m_{total}}$$

where, $m_{total} = m_{liquid} + m_{vapor}$

$$= m_f + m_g$$

Its value is between 0 and 1.

For saturated liquid, $x = 0$.

For saturated vapor, $x = 1$.

Consider a tank that contains a saturated liquid-vapor mixture. The volume occupied by saturated liquid is V_f, and the volume occupied by saturated ~~vola~~ vapor is V_g. The total volume is the sum of the two:

$$V = V_f + V_g$$

Since, $V = mv$

$$\downarrow$$

$$m_t v_{avg} = m_f v_f + m_g v_g$$

Since, $m_t = m_f + m_g$

$$\Rightarrow \quad m_t v_{avg} = (m_t - m_g) v_f + m_g v_g$$

Dividing by m_t,

$$v_{avg} = (1 - x) v_f + x v_g$$

$$= v_f - x v_f + x v_g$$

$$= v_f + x(v_g - v_f)$$

$$\boxed{v_{avg} = v_f + x v_{fg}}$$

Similarly, $u_{avg} = u_f + x u_{fg}$ (kJ/kg)

$h_{avg} = h_f + x h_{fg}$ (kJ/kg)

<u>Example</u>: A rigid tank contains 10 kg of water at 90°C. If 8 kg of water is in the liquid form and the rest is in the vapor form, determine (a) the pressure in the tank, and (b) the volume of the tank.

Solution : At 90°C, saturation pressure is-

$P_{sat} @ 90°C = 70.11$ kpa.

At 90°C, $v_f = 0.001036 \; m^3/kg$

$v_g = 2.3613 \; m^3/kg$.

Thus, total volume of the tank,

$V = V_f + V_g$

$= m_f v_f + m_g v_g$

$= (8 kg)(0.001036 \; m^3/kg) + (2 kg)(2.3613 \; m^3/kg)$

$= \underline{\underline{4.74 \; m^3}}$.

Single-phase Region

For the regions of the phase diagram where a single phase exists, a relation connecting P, V, and T can be written. Expressed analytically, as $f(P,V,T)=0$, such a relation is Known as a PVT equation of state. It relates pressure, molar or specific volume, and temperature for a pure homogeneous fluid in equilibrium states. The simplest equation of state is ideal-gas equation of state.

An equation of state may be solved for any one of the three quantities P, V or T as a function of the other two. For example, if 'V' is considered a function of 'T' and 'P', then $V=V(T,P)$, and

$$dV=\left(\frac{\partial V}{\partial T}\right)_P dT+\left(\frac{\partial V}{\partial P}\right)_T dP \longrightarrow (1)$$

The partial derivatives in this equation have definite physical meanings, and are related to two properties, commonly tabulated for liquids, and defined as follows:

- volume expansivity:

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \longrightarrow (2)$$

- Isothermal compressibility:

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \longrightarrow (3)$$

Eq^n. (1), (2) and (3), gives.

$$\frac{dV}{V} = \beta dT - \kappa dp \longrightarrow (4)$$

If 'β' and 'κ' are weak functions of temp. and pressure.

$$\ln \frac{V_2}{V_1} = \beta(T_2 - T_1) - \kappa(P_2 - P_1) \longrightarrow (5)$$

Example: For liquid acetone at 20°C and 1 bar,

$\beta = 1.487 \times 10^{-3}\ {}^\circ C^{-1}$; $\kappa = 62 \times 10^{-6}\ bar^{-1}$; $V = 1.287\ \frac{cm^3}{g}$

For acetone, find the

(a) value of $(\partial P/\partial T)_V$ at 20°C and 1 bar.

(b) pressure generated by heating at constant 'V' from 20°C and 1 bar to 30°C.

(c) change in volume for a change from 20°C and 1 bar to 0°C and 10 bar.

Solution :- (a) From equation (4), at constant volume,

$dV=0$

i.e. $\beta dT - K dp = 0$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{K} = \frac{1.487\times10^{-3}}{62\times10^{-6}} = \underline{\underline{24 \text{ bar } {}^\circ C^{-1}}}$$

(b) If 'β' and 'K' are assumed constant in the 10°C temperature interval, then at constant volume. from eq^n (4),

$$\Delta P = \frac{\beta}{K}\Delta T = 24(10) = 240 \text{ bar}$$

and, $P_2 = P_1 + \Delta P = 1 + 240 = \underline{\underline{241 \text{ bar.}}}$

(c) From eq^n. (5),

$$\ln\frac{V_2}{V_1} = (1.487\times10^{-3})(-20) - (62\times10^{-6})(9)$$

$$= -0.0303$$

$$\frac{V_2}{V_1} = 0.9702$$

and $V_2 = (0.9702)(1.287)$

$$= \underline{\underline{1.249 \text{ cm}^3/\text{g}}}$$

Then, $\Delta V = V_2 - V_1 = 1.249 - 1.287$

$$= \underline{\underline{-0.038 \text{ cm}^3/\text{g}}}$$

Virial Equations of state

~~The two forms of the virial expansion~~

Expressing 'PV' for an isotherm by a power series in P:

$$PV = a + bP + cP^2 + \ldots\ldots \longrightarrow (1)$$

If $b = aB'$, $c = aC'$, etc. then,

$$PV = a(1 + B'P + C'P^2 + D'P^3 + \ldots) \longrightarrow (2)$$

where a, B', C', etc. are constants for a given temperature and a given chemical species.

* In principle, the right side of Eq. (2) is an infinite series. However, in practice a finite number of terms is used. In fact, PVT data show that at low pressures truncation after two terms often provides satisfactory results.

* parameters B', C' etc are species dependent and functions of temperature, but parameter 'a' is found by experiment to be the same function of temperature for all chemical species.

* The virial equation of state has a sound theoretical foundation; it can be derived from first principles using statistical mechanics.

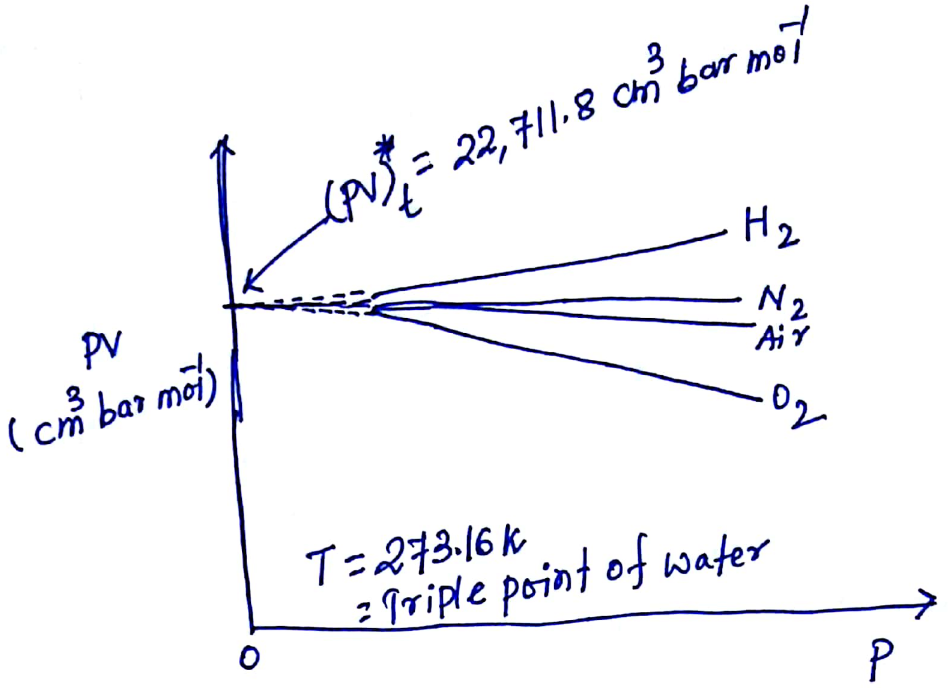


Figure shows a plot of PV vs. P for four gases at the triple-point temperature of water. The limiting value of PV as P→0 is the same for all of the gases.

In this limit, eqⁿ. (2) becomes – (denoted by the asterisk)

$$(PV)^* = a = f(T) \longrightarrow (3)$$

The simplest function is defined as

$$\underline{(PV)^* = a = RT} \longrightarrow (4)$$

[directly proportional to 'T', with 'R' as the proportionality constant]

Assign the value of 273.16 to the temperature,

$$(PV)^*_t = \underset{\substack{\downarrow \\ \text{universal gas constant}}}{R} \times 273.16 \longrightarrow (5)$$

its numerical value is determined by means of Eqn.(5) from experimental PVT data:

$$R = \frac{(PV)^*_t}{273.16\,K} \longrightarrow (6)$$

Because PVT data cannot in fact be taken at zero pressure, data taken at finite pressures are extrapolated to the zero-pressure state. The accepted value of $(PV)^*_t$ is 22,711.8 bar cm^3 mol^{-1}, leading to the following value of R:

$$R = \frac{22{,}711.8\ cm^3\ bar\ mol^{-1}}{273.16\,K}$$

$$\boxed{R = 83.1447\ cm^3\ bar\ mol^{-1}\ K^{-1}}$$

A useful auxiliary thermodynamic property is defined by the equation:

$$Z = \frac{V_{real}}{V_{ideal}}$$

$$\text{since, } V_{idea} = \frac{RT}{P}$$

$$\text{Thus, } Z = \frac{V_{real}}{(RT/P)}$$

$$\boxed{Z = \frac{PV_r}{RT}} \longrightarrow (7)$$

This dimensionless ratio is called the compressibility factor.

with this definition and with $a = RT$, Eq^n.(2) becomes:

$$✓ \boxed{Z = 1 + B'P + C'P^2 + D'P^3 + \dots} \longrightarrow (8)$$

An alternate expression for 'z' is also in common use:

$$✓ \boxed{Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots} \longrightarrow (9)$$

Both of these equations are known as virial expansions, and the parameters B', C', D', etc. and B, C, D, etc. are called virial coefficients. Parameters B' and B are second virial coefficients; C' and C are third virial coefficients etc. For a given gas the virial coefficients are functions of temperature only.

The two sets of coefficients in Eqs.(8) and (9) are related as follows:

$$B' = \frac{B}{RT} \longrightarrow (10a)$$

$$C' = \frac{C - B^2}{(RT)^2} \longrightarrow (10b)$$

$$D' = \frac{D - 3BC + 2B^3}{(RT)^3} \longrightarrow (10c)$$

{To derive these relations, we set $Z = PV/RT$ in eq^n(9), and solve for P. This allows elimination of 'P' on the right of eq^n.(8). The resulting equation reduces to a power series in $1/V$ which may be compared term by term with Eq.(9) to yield the given relations.

Many other equations of state have been proposed for gases, but the virial equations are the only ones firmly based on statistical mechanics, which provides physical significance to the virial coefficients. Thus, the term B/V arises on account of interactions between pairs of molecules; the C/V^2 term, on account of three-body interactions; etc.

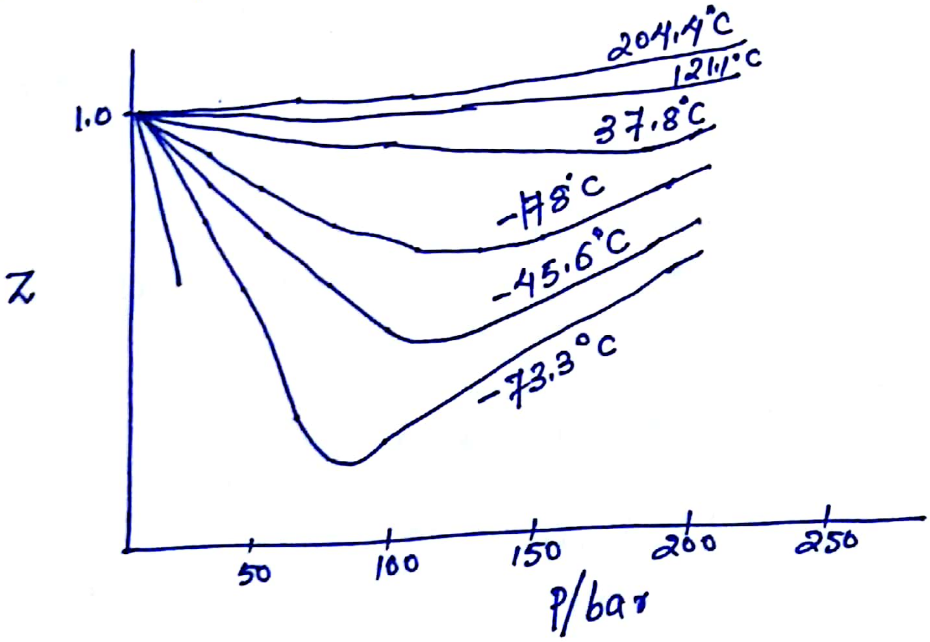
Because the terms B/V, C/V^2 etc. of the virial expansion arise on account of molecular interactions, the virial coefficients B, C, etc., would be zero when no such interactions to exist, and the virial expansion would reduce to

$$Z = 1 \quad \text{or} \quad pV = RT$$

Molecular interactions do in fact exist, and influence the observed behavior of real gases. As pressure is reduced at constant temperature, V increases and the contributions of the terms, B/V, $C/V^2 \ldots$, decrease. For $p \to 0$, Z approaches unity, not because of any change in the virial coefficients, but because V becomes infinite. Thus, in the limit as $p \to 0$, the equation of state reduces to the same simple form as for the hypothetical case of $B = C = \ldots = 0$; i.e. $Z \to 1$ or $pV \to RT$.

Application of the virial Equations

The two forms of the virial expansion given by Eqs. (8) and (9) are infinite series. For engineering purposes their use is practical only where convergence is very rapid, that is, where two or three terms suffice for reasonably close approximations to the values of the series. This is realized for gases and vapors at low to moderate pressures.



compressibility-factor graph for methane

Figure shows a compressibility-factor graph for methane. Values of the compressibility factor 'z' are plotted vs. pressure for various constant temperatures. All isotherms originate at the value z=1 for P=0, and the isotherms are nearly straight lines at low pressures.

Thus the tangent to an isotherm at $p=0$ is a good approximation of the isotherm from $p \to 0$ to some finite pressure. Differentiation of Eqn. (8) for a given temperature gives

$$\left(\frac{\partial Z}{\partial P}\right)_T = B' + 2C'P + 3D'P^2 + \cdots$$

from which $\left(\frac{\partial Z}{\partial P}\right)_{T;\,P=0} = B'$

Thus, the equation of the tangent line is

$$Z = 1 + B'P,$$

a result also given by truncating Eq. (8) to two terms.

A more common form of this equation results from substitution for B' by Eq. (10a):

Moderate pressures (upto ~ 15 bar)

$$\boxed{Z = \frac{PV}{RT} = 1 + \frac{BP}{RT}} \longrightarrow (11)$$

This equation expresses a direct proportionality between 'Z' and 'P', and is often applied to vapors at subcritical temperatures up to their saturation pressures.

Equation (9) as well may be truncated to two terms for application at low pressures:

$$\boxed{Z = \frac{PV}{RT} = 1 + \frac{B}{V}} \longrightarrow (12)$$

Eq^n. (11) is more convenient in application and is normally at least as accurate as Eq^n. (12). Thus, when the virial equation is truncated to two terms, Eq^n. (11) is preferred.

The second virial coefficient 'B' is substance dependent and a function of temperature. Experimental values are available for a number of gases. Moreover, estimation of second virial coefficients is possible where no data are available (will be discussed in next classes).

For pressures above the range of applicability of Eq^n. (11) but below the critical pressure, the virial equation truncated to three terms often provides excellent results. In this case Eq^n. (9) is far superior to Eq^n. (8). Thus when the virial equation is truncated to three terms, the appropriate form is.

(From 15 to 50 bar)

$$\boxed{Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2}} \longrightarrow (13)$$

This equation can be solved directly for pressure, but is cubic in volume. Solution for 'V' is readily accomplished by an iterative scheme.

values of 'C', depend on the gas and on temperature. However, much less is known about third virial coefficients than about second virial coefficients. Because virial coefficients beyond the third are rarely known and because the virial expansion with more than three terms becomes unwieldy, its use is uncommon.

Example: Reported values for the virial coefficients of isopropanol vapor at 200°c are:

$$B = -388 \text{ cm}^3/\text{mol}$$

$$C = -26000 \text{ cm}^6/\text{mol}^2$$

calculate V and Z for isopropanol vapor at 200°c and 10 bar by (a) the ideal-gas equation

(b) $Z = \frac{PV}{RT} = 1 + \frac{BP}{RT}$

(c) $Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2}$

Solution : $T = 473.15 \text{ K}$, $R = 83.14 \text{ cm}^3 \text{ bar mol}^{-1} \text{K}^{-1}$.

(a) For an ideal gas, $Z=1$, and

$$V = \frac{RT}{P} = \frac{(83.14\ cm^3\ bar\ mol^{-1}\ K^{-1})(473.15K)}{(10\ bar)}$$

$$\underline{\underline{V = 3934\ cm^3\ mol^{-1}}}$$

(b) $$\frac{PV}{RT} = 1 + \frac{BP}{RT}$$

$$\Rightarrow V = \frac{RT}{P} + B$$

$$= 3934 - 388$$

$$\underline{\underline{V = 3546\ cm^3\ mol^{-1}}}$$

Thus, $$Z = \frac{PV}{RT} = \frac{(10 bar)(3546\ cm^3\ mol^{-1})}{(83.14\ cm^3\ bar\ mol^{-1} K^{-1})(473.15K)}$$

$$\underline{\underline{Z = 0.9014}}$$

(c) $$\frac{PV}{RT} = \left(1 + \frac{B}{V} + \frac{C}{V^2}\right)$$

$$\Rightarrow V = \frac{RT}{P}\left[1 + \frac{B}{V} + \frac{C}{V^2}\right]$$

For iteration; $$V_{i+1} = \frac{RT}{P}\left[1 + \frac{B}{V_i} + \frac{C}{V_i^2}\right]$$

For 1st iteration, $i=0$, and

$$V_1 = \frac{RT}{P}\left[1 + \frac{B}{V_0} + \frac{C}{V_0^2}\right]$$ where $V_0 = 3934$.

$$V_1 = 3934\left[1 - \frac{388}{3934} - \frac{26,000}{(3934)^2}\right] = 3539 \text{ cm}^3/\text{mol.}$$

$$V_2 = 3934\left[1 - \frac{388}{3539} - \frac{26,000}{(3539)^2}\right] = 3495 \text{ cm}^3/\text{mol.}$$

$$V_3 = 3934\left[1 - \frac{388}{3495} - \frac{26,000}{(3495)^2}\right] = 3488 \text{ cm}^3/\text{mol.}$$

$$V_4 = 3934\left[1 - \frac{388}{3488} - \frac{26,000}{(3488)^2}\right] = 3488 \text{ cm}^3/\text{mol}$$

Thus, $\underline{\underline{V = 3488}}$ cm^3/mol.

and $Z = \dfrac{PV}{RT} = \dfrac{10 \times 3488}{83.14 \times 473.15} = 0.8866.$

$$\underline{\underline{Z = 0.8866}}$$

cubic Equations of state

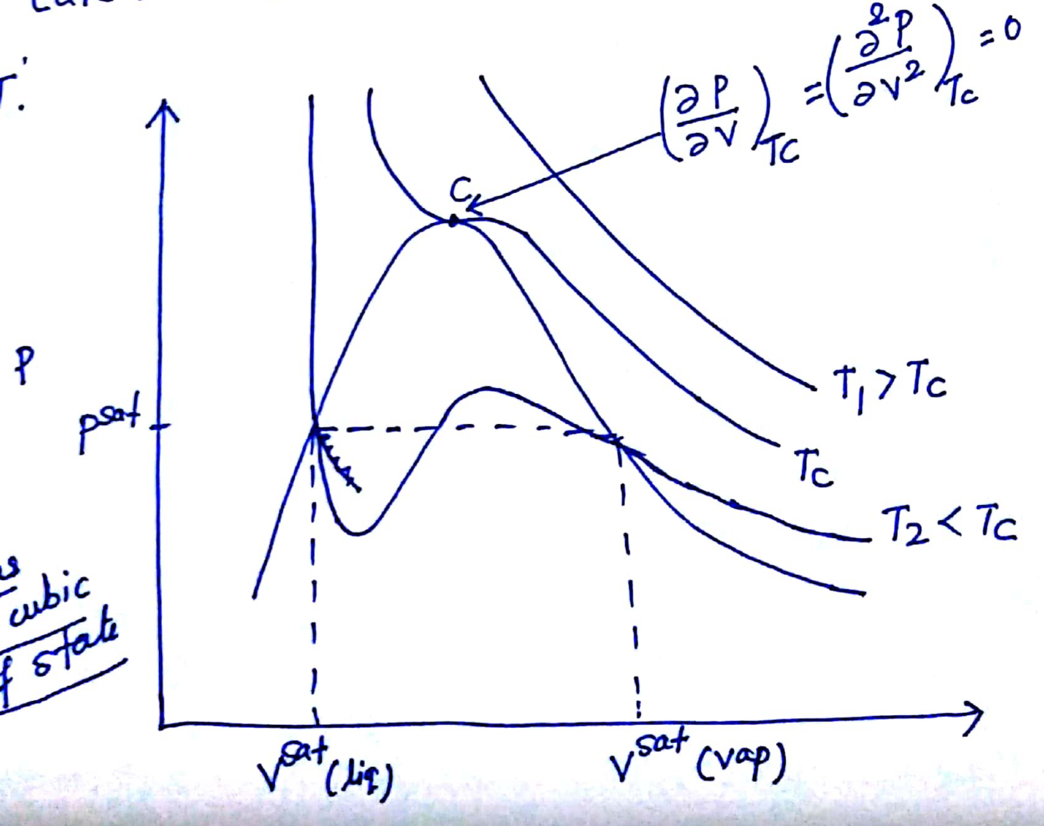
- simplest equations capable of representing both liquid and vapor behavior.
- polynomial equations that are cubic in molar volume.

The Van der Waals Equation of state

The first practical cubic equation of state was proposed by Van der waals in 1873:

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \longrightarrow (1)$$

Here, ''a and 'b' are positive constants; when they are zero, the ideal-gas equation is recovered. Given values of 'a' and 'b' for a particular fluid, one can calculate 'p' as a function of 'V' for various values of 'T'.



Isotherms as given by a cubic equation of state

The above figure is a schematic PV diagram showing three isotherms. For the isotherms $T_1 > T_c$, pressure is a monotonically decreasing function with increasing molar volume. The critical isotherm contains the horizontal inflection at 'C' characteristic of the critical point.

For the isotherm $T_2 < T_c$, the pressure decreases rapidly in the subcooled-liquid region with increasing V; after crossing the saturated-liquid line, it goes through a minimum, rises to a maximum, and then decreases, crossing the saturated-vapor line and continuing downward into the superheated-vapor region.

Experimental isotherms do not exhibit this smooth transition from saturated liquid to saturated vapor; rather they contain a horizontal segment within the two-phase region where saturated liquid and saturated vapor coexist in varying proportions at the saturation pressure.

Cubic equations of state have three volume roots. physically meaningful values of V are always real, positive and greater than constant b.

Inside dome $\longrightarrow \left[\begin{array}{l} \text{Smallest root} \equiv V^{sat}(liq) \\ \text{Largest root} \equiv V^{sat}(vap) \end{array}\right]$ The third root is of no significance.

Above the critical point there is one positive, real root and two roots containing imaginary numbers. only the positive, real root represents a physical value - the volume of the supercritical fluid.

Determination of van der waals parameters:

To use the van der waals equation, the parameters 'a' and 'b' must be determined for a species of interest. The most accurate values are obtained by fitting experimental PVT data. However, for cubic equations of state, suitable estimates are usually found from values for the critical constants T_c and P_c. Because the critical isotherm exhibits a horizontal inflection at the critical point, we may impose the mathematical conditions:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial V}\right)_{T_c} = 0 \longrightarrow (2)$$

Thus, at the critical point we have:

$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} \longrightarrow (3)$$

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 = \frac{-RT_c}{(V_c-b)^2} + \frac{2a}{V_c^3} \longrightarrow (4)$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 = \frac{2RT_c}{(V_c-b)^3} - \frac{6a}{V_c^4} \longrightarrow (5)$$

Multiply Eq^n. (4) by 2 and Eq^n. (5) by $(V_c - b)$ and add them together, we get:

$$\frac{4a}{V_c^3} - \frac{6a(V_c-b)}{V_c^4} = 0$$

$$\Rightarrow \frac{2a}{V_c^3} = \frac{3a(V_c-b)}{V_c^4}$$

$$\Rightarrow 2V_c = 3V_c - 3b$$

$$\boxed{V_c = 3b} \longrightarrow (6)$$

Using eq^n. (6) in eq^n. (4),

$$\frac{2a}{V_c^3} = \frac{RT_c}{(3b-b)^2} = \frac{RT_c}{4b^2}$$

$$\Rightarrow \frac{2a}{(3b)^3} = \frac{RT_c}{4b^2}$$

$$\Rightarrow \frac{2a}{27b^3} = \frac{RT_c}{4b^2} \Rightarrow a = \frac{27}{8}RT_c b = \frac{27}{8}RT_c\left(\frac{V_c}{3}\right)$$

$$\boxed{a = \frac{9}{8}RT_cV_c} \rightarrow (7)$$

$$\Rightarrow \cancel{\boxed{a = \frac{9}{8}RT_c b}} \quad \cancel{\rightarrow (7)}$$

Using ~~(7)~~ & (6), in (3),

$$P_c = \frac{RT_c}{3b-b} - \frac{9}{8}\frac{RT_c b}{V_c^2}$$

$$= \frac{RT_c}{2b} - \frac{9RT_c b}{8V_c^2} = \frac{RT_c}{2b} - \frac{9RT_c b}{8(9b^2)}$$

$$= \frac{RT_c}{2b} - \frac{RT_c}{8b} = \frac{4RT_c - RT_c}{8b} = \frac{3RT_c}{8b}$$

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$$\cancel{\boxed{b = \frac{3}{8}\frac{RT_c}{P_c}} \longrightarrow (8)}$$

using eqⁿ (7) in (3),

$$P_c = \frac{RT_c}{V_c - b} - \frac{9}{8}\frac{RT_c \cancel{V_c}}{V_c^{\cancel{2}}}$$

$$= \frac{RT_c}{3b-b} - \frac{9}{8}\frac{RT_c}{V_c}$$

$$= \frac{RT_c}{2b} - \frac{9}{8}\frac{RT_c}{V_c}$$

$$= \frac{RT_c}{2b} - \frac{9}{8}\frac{RT_c}{(3b)} = \frac{RT_c}{2b} - \frac{3RT_c}{8b}$$

$$= \frac{4RT_c - 3RT_c}{8b} = \frac{RT_c}{8b}$$

$$\boxed{b = \frac{RT_c}{8P_c}} \longrightarrow (8)$$

From, (7), $a = \frac{9}{8} RT_c (3b)$

$$= \frac{27}{8} RT_c \left(\frac{RT_c}{8P_c}\right)$$

$$\therefore \boxed{a = \frac{27}{64}\frac{(RT_c)^2}{P_c}} \longrightarrow (9)$$

We now have an equation of state for which we only need critical property data to solve for the parameters.

we can calculate the compressibility factor at the critical point,

$$Z_c = \frac{P_c V_c}{R T_c} = \frac{P_c}{R T_c}(3b) = \frac{3 \cancel{P_c}}{\cancel{R T_c}} \times \frac{1}{8} \frac{\cancel{R T_c}}{\cancel{P_c}}$$

$$Z_c = \frac{3}{8} = 0.375$$

$$\boxed{Z_c = 0.375} \longrightarrow (10)$$

i.e. a single value for Z_c applicable alike to all substances.

Experimental values for the compressibility factor at the critical point are around 0.29 for simple species and usually less for complex species. Thus, the value predicted by the van der Waals equation is considerably high-indicating its limitations in predicting PVT behavior.

(Lecture-14/15)

A Generic Cubic Equation of State

Since the introduction of the van der Waals equation, Several hundred cubic equations of state have been proposed. All are special cases of the equation:

$$\boxed{P = \frac{RT}{(V-b)} - \frac{\theta(V-\eta)}{(V-b)(V^2+\kappa V+\lambda)}} \longrightarrow (1)$$

Here, b, θ, η, κ and λ are parameters which in general depend on temperature and (for mixtures) composition. Although this equation appears to possess great flexibility, it has inherent limitations because of its cubic form. It reduces to the van der Waals equation when $\eta = b$, $\theta = a$, and $\kappa = \lambda = 0$.

An important class of cubic equations results from the preceding equation with the assignments:

$$\eta = b; \quad \theta = a(T); \quad \kappa = (\epsilon+\sigma)b; \quad \lambda = \epsilon\sigma b^2 \longrightarrow (2)$$

For a given equation, ϵ and σ are pure numbers, the same for all substances, whereas parameters $a(T)$ and b are substance dependent.

$$P = \frac{RT}{(V-b)} - \frac{a(T)\cancel{(V-b)}}{\cancel{(V-b)}[V^2+(\epsilon+\sigma)bV+\epsilon\sigma b^2]}$$

$$= \frac{RT}{(V-b)} - \frac{a(T)}{(V^2+\epsilon bV+\sigma bV+\epsilon\sigma b^2)}$$

$$= \frac{RT}{V-b} - \frac{a(T)}{V(V+\epsilon b)+\sigma b(V+\epsilon b)}$$

$$\boxed{P = \frac{RT}{(V-b)} - \frac{a(T)}{(V+\epsilon b)(V+\sigma b)}}$$

$\longrightarrow (3)$

It is thus transformed into an expression general enough to serve as a generic cubic equation of state, which reduces to all others of interest here upon assignment of appropriate parameters.

$$\boxed{a(T) = \Psi \frac{\alpha(T_r) R^2 T_c^2}{P_c}} \longrightarrow (4)$$

Here $\alpha(T_r)$ is an empirical expression, specific to a particular equation of state.

$$\boxed{b = \Omega \frac{R T_c}{P_c}} \longrightarrow (5)$$

In these equations, 'Ω' and 'Ψ' are pure numbers, independent of substance and determined for a particular equation of state from the values assigned to 'ϵ' and 'σ'.

Vapor and Vapor-Like Roots of the Generic Cubic Equation of state:

(Largest root)

Multiply Eq^n. (3) through by $\frac{V-b}{RT}$. Thus,

$$\frac{P(V-b)}{RT} = \cancel{\frac{RT}{V-b}} \times \cancel{\frac{V-b}{RT}} - \frac{V-b}{RT}\,\frac{a(T)}{(V+\epsilon b)(V+\sigma b)}$$

$$\Rightarrow \frac{PV}{RT} - \frac{Pb}{RT} = 1 - \frac{V-b}{RT}\,\frac{a(T)}{(V+\epsilon b)(V+\sigma b)}$$

$$\Rightarrow \frac{PV}{RT} = 1 + \frac{Pb}{RT} - \frac{V-b}{RT}\,\frac{a(T)}{(V+\epsilon b)(V+\sigma b)}$$

$$\Rightarrow \boxed{V = \frac{RT}{P} + b - \frac{a(T)}{P}\,\frac{(V-b)}{(V+\epsilon b)(V+\sigma b)}} \longrightarrow (6)$$

* solution for 'V' is found by iteration.

* An initial estimate for 'V' is the ideal-gas value RT/P.

* For iteration, this value is substituted on the right side of Eq. (6). The resulting value of 'V' on the left is then returned to the right side, and the process continues untill the change in 'V' is suitably small.

An equation for 'z' equivalent to Eq. (6) is obtained by substituting $V = ZRT/P$.

Thus,

$$\frac{ZRT}{P} = \frac{RT}{P} + b - \frac{a(T)}{P} \frac{\left(\frac{ZRT}{P} - b\right)}{\left(\frac{ZRT}{P} + \epsilon b\right)\left(\frac{ZRT}{P} + \sigma b\right)}$$

Defining two dimensionless quantities,

$$\boxed{\beta = \frac{bP}{RT}} \xrightarrow{} (7) \quad \text{and} \quad \boxed{q = \frac{a(T)}{bRT}} \xrightarrow{} (8)$$

Therefore,

$$z = 1 + \frac{bP}{RT} - \frac{a(T)}{\cancel{P}} \cdot \frac{\cancel{P}}{RT} \cdot \frac{\cancel{RT/P}\left(z - bP/RT\right)}{\cancel{RT/P}\left(z + \epsilon \frac{bP}{RT}\right) \frac{RT}{P}\left(z + \sigma \frac{bP}{RT}\right)}$$

$$z = 1 + \beta - \underbrace{\frac{a(T)}{RT} \cdot \frac{P}{RT}}_{(q\beta)} \cdot \frac{(z - \beta)}{(z + \epsilon\beta)(z + \sigma\beta)}$$

$$\boxed{z = 1 + \beta - q\beta \frac{(z - \beta)}{(z + \epsilon\beta)(z + \sigma\beta)}} \xrightarrow{} (9)$$

- Iterative solution of Eq. (9) starts with the value of $z = 1$ substituted on the right side. The calculated value of 'z' is returned to the right side and the process continues to convergence.
- The final value of 'z' yields the volume root through $V = zRT/P$.

Liquid and Liquid-Like Roots of the Generic cubic Equation of state:

From Eq^n. (6),

$$V = \frac{RT}{P} + b - \frac{a(T)}{P}\frac{(V-b)}{(V+\epsilon b)(V+\sigma b)}$$

$$\Rightarrow \left(V - \frac{RT}{P} - b\right) = -\frac{a(T)}{P}\frac{(V-b)}{(V+\epsilon b)(V+\sigma b)}$$

$$\Rightarrow \left(V - \frac{RT}{P} - b\right)\frac{P(V+\epsilon b)(V+\sigma b)}{a(T)} = -V+b$$

$$\Rightarrow V = b - \left(V - \frac{RT}{P} - b\right)\frac{P}{a(T)}(V+\epsilon b)(V+\sigma b)$$

$$= b - \left(\frac{PV-RT-Pb}{\cancel{P}}\right)\frac{\cancel{P}}{a(T)}(V+\epsilon b)(V+\sigma b)$$

This equation with a starting value of $V=b$ on the right side converges upon iteration to a Liquid or Liquid-like root.

$$\boxed{V = b + (V+\epsilon b)(V+\sigma b)\left(\frac{RT+bP-PV}{a(T)}\right)} \longrightarrow (10)$$

substituting, $V = \frac{ZRT}{P}$ in Eq^n. (10),

$$\frac{ZRT}{P} = b + \left(\frac{ZRT}{P} + \epsilon b\right)\left(\frac{ZRT}{P} + \sigma b\right)\left(\frac{RT+bP-\cancel{P}ZRT}{a(T)}\right)$$

$$\Rightarrow Z = \frac{Pb}{RT} + \cancel{\frac{RT}{P}}\left(Z + \frac{\epsilon bP}{RT}\right)\frac{RT}{P}\left(Z + \sigma\frac{bP}{RT}\right)RT\left(\frac{1+\frac{bP}{RT}-Z}{a(T)}\right)$$

$$= \beta + \cancel{\frac{RT}{P}}\cdot\frac{RT}{P}\cdot\frac{RT}{a(T)}(Z+\epsilon\beta)(Z+\sigma\beta)(1+\beta-Z)$$

$$\boxed{Z = \beta + (Z+\epsilon\beta)(Z+\sigma\beta)\left(\frac{1+\beta-Z}{q\beta}\right)} \longrightarrow (11)$$

* For iteration a starting value of $Z=\beta$ is substituted on the right side. once 'Z' is known, the volume is

$$V = \frac{ZRT}{P}.$$

Parameter Assignments for Equations of state

Eq. of state	$\alpha(T_r)$	σ	ϵ	Ω	Ψ	Z_c
vdW(1873)	1	0	0	$1/8$	$27/64$	$3/8$
RK(1949)	$T_r^{-1/2}$	1	0	0.08664	0.42748	$1/3$
SRK(1972)	α_{SRK}	1	0	0.08664	0.42748	$1/3$
PR(1976)	α_{PR}	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07780	0.45724	0.30740

$$\alpha_{SRK}(T_r;\omega) = \left[1 + m\left(1 - T_r^{1/2}\right)\right]^2$$

$$\hookrightarrow (0.480 + 1.574\omega - 0.176\omega^2)$$

$$\alpha_{PR}(T_r;\omega) = \left[1 + m\left(1 - T_r^{1/2}\right)\right]^2$$

$$\hookrightarrow (0.37464 + 1.54226\omega - 0.26992\omega^2)$$

RK ≡ Redlich/Kwong

SRK ≡ Soave/Redlich/Kwong

PR ≡ Peng-Robinson.

Example : 3.9 (from Smith)

Given that the vapor pressure of n-butane at 350K is 9.4573 bar. Find the molar volumes of

(a) Saturated vapor, and

(b) Saturated-liquid n-butane at these conditions

using, 1.) vdW; 2.) RK; 3). SRK & 4). PR EoS.

$R = 83.14 \text{ cm}^3 \text{ bar mol}^{-1} K^{-1}$

Solution: For n-butance, $T_c = 425.1$ K

$P_c = 37.96$ bar.

$$\text{Thus,} \quad T_r = \frac{T}{T_c} = \frac{350}{425.1} = 0.8233$$

$$P_r = \frac{P}{P_c} = \frac{9.4573}{37.96} = 0.2491$$

(a) For Saturated vapor:

The generalized cubic EoS is given by -

$$Z = 1 + \beta - q\beta \frac{(Z-\beta)}{(Z+\epsilon\beta)(Z+\sigma\beta)}$$

$$\text{where,} \quad \beta = \frac{bP}{RT} \quad \& \quad q = \frac{a(T)}{bRT}$$

$$\text{and} \quad a(T) = \Psi \frac{\alpha(T_r) R^2 T_c^2}{P_c}$$

$$\& \quad b = \Omega \frac{R T_c}{P_c}.$$

1). For vdW EOS:

$$a(T) = \frac{27}{64}\frac{(1)(83.14)^2(425.1)^2}{(37.96)}$$

$$\therefore a(T) = 13882249 \text{ cm}^6 \text{ bar mol}^{-2}$$

$$b = \frac{1}{8} \times \frac{83.14 \times 425.1}{37.96}$$

$$\therefore b = 116.3818 \text{ cm}^3 \text{ mol}^{-1}$$

So, $$\beta = \frac{bP}{RT} = \frac{(116.3818 \text{ cm}^3 \text{ mol}^{-1})(9.4573 \text{ bar})}{(83.14 \text{ cm}^3 \text{ bar mol}^{-1} \text{K}^{-1})(350 \text{ K})}$$

$$\therefore \beta = 0.0378.$$

$$q = \frac{a(T)}{bRT} = \frac{13882249 \text{ cm}^{\cancel{6}} \text{ } \cancel{\text{bar}} \text{ } \cancel{\text{mol}^{-2}}}{(116.3818 \text{ } \cancel{\text{cm}^3} \text{ } \cancel{\text{mol}^{-1}})(83.14 \text{ } \cancel{\text{cm}^3} \text{ } \cancel{\text{bar}} \text{ } \cancel{\text{mol}^{-1}} \cancel{\text{K}^{-1}})(350 \cancel{\text{K}})}$$

$$\therefore q = 4.0992$$

So, the above eqn. reduces to-

$$Z = 1 + 0.0378 - (4.0992)(0.0378)\frac{(Z - 0.0378)}{Z^2}$$

$$Z = 1.0378 - 0.1549\frac{(Z - 0.0378)}{Z^2}$$

Starting the iteration with an initial value of $Z = 1$,

$$Z_1 = 1.0378 - 0.1549\frac{(1 - 0.0378)}{1^2} = 0.8888$$

$$Z_2 = 1.0378 - 0.1549\frac{(0.8888 - 0.0378)}{0.8888^2} = 0.8709$$

$Z_3 = 0.8677$; $Z_4 = 0.8671$; $Z_5 = 0.8669$; $\boxed{Z_6 = 0.8669}$

Thus, ~~Z~~ $$V = \frac{ZRT}{P} = \frac{0.8669 \times 83.14 \times 350}{9.4573} = \boxed{2667 \text{ cm}^3/\text{mol}}$$

2). For RK EOS:

$a(T) = 15502897 \text{ cm}^6 \text{ bar mol}^{-2}$

$b = 80.6665 \text{ cm}^3 \text{ mol}^{-1}$

$\beta = 0.0262$

$q = 6.6045$

Thus, $Z = 1.0262 - 0.1730 \dfrac{(Z-0.0262)}{Z(Z+0.0262)}$

So, starting with $Z=1$

$Z_1 = 0.8620$; $Z_2 = 0.8373$; $Z_3 = 0.8321$; $Z_4 = 0.8310$; $Z_5 = 0.8307$

$\boxed{Z_6 = 0.8307}$

$\therefore \boxed{V = 2556 \text{ cm}^3 \text{ mol}^{-1}}$

3). <u>For SRK EOS:</u>

$a(T) = 16206231 \text{ cm}^6 \text{ bar mol}^{-2}$; $\alpha = 1.1512$

$b = 80.6665 \text{ cm}^3 \text{ mol}^{-1}$

$\beta = 0.0262$

$q = 6.9042$

Thus, $Z = 1.0262 - 0.1809 \dfrac{(Z-0.0262)}{Z(Z+0.0262)}$

Now, $Z_1 = 0.8545$; $Z_2 = 0.8271$; $Z_3 = 0.8209$;

$Z_4 = 0.8195$; $Z_5 = 0.8191$; $\boxed{Z_6 = 0.8190}$

$\therefore \boxed{V = 2520 \text{ cm}^3/\text{mol}}$

4.) **For PR EoS:**

$\alpha = 1.1284$

$a(T) = 16977875 \text{ cm}^6 \text{ bar mol}^{-2}$

$b = 72.4360 \text{ cm}^3/\text{mol}$

$\beta = 0.0235$

$q = 8.0547$

Thus,

$$Z = 1.0235 - 0.1893 \frac{(Z-0.0235)}{(Z-0.0097)(Z+0.0567)}$$

$Z_1 = 0.8469$; $Z_2 = .8175$; $Z_3 = 0.8107$; $Z_4 = 0.8090$;

$Z_5 = 0.8086$; $Z_6 = 0.8085$; $\boxed{Z_7 = 0.8085}$

$$\boxed{V = 2488 \text{ cm}^3/\text{mol}}$$

(Lecture-14/15)

A Generic Cubic Equation of State

Since the introduction of the van der Waals equation, several hundred cubic equations of state have been proposed. All are special cases of the equation:

$$\boxed{P = \frac{RT}{(V-b)} - \frac{\theta(V-\eta)}{(V-b)(V^2+\kappa V+\lambda)}} \longrightarrow (1)$$

Here, b, θ, η, κ and λ are parameters which in general depend on temperature and (for mixtures) composition. Although this equation appears to possess great flexibility, it has inherent limitations because of its cubic form. It reduces to the van der Waals equation when $\eta = b$, $\theta = a$, and $\kappa = \lambda = 0$.

An important class of cubic equations results from the preceding equation with the assignments:

$$\eta = b; \quad \theta = a(T); \quad \kappa = (\epsilon+\sigma)b \quad ; \lambda = \epsilon\sigma b^2 \longrightarrow (2)$$

For a given equation, ϵ and σ are pure numbers, the same for all substances, whereas parameters $a(T)$ and b are substance dependent.

$$P = \frac{RT}{(V-b)} - \frac{a(T)\cancel{(V-b)}}{\cancel{(V-b)}[V^2+(\epsilon+\sigma)bV+\epsilon\sigma b^2]}$$

$$= \frac{RT}{(V-b)} - \frac{a(T)}{(V^2+\epsilon bV+\sigma bV+\epsilon\sigma b^2)}$$

$$= \frac{RT}{V-b} - \frac{a(T)}{V(V+\epsilon b)+\sigma b(V+\epsilon b)}$$

$$\boxed{P = \frac{RT}{(V-b)} - \frac{a(T)}{(V+\epsilon b)(V+\sigma b)}} \longrightarrow (3)$$

It is thus transformed into an expression general enough to serve as a generic cubic equation of state, which reduces to all others of interest here upon assignment of appropriate parameters.

$$\boxed{a(T) = \Psi \frac{\alpha(T_r) R^2 T_c^2}{P_c}} \longrightarrow (4)$$

Here $\alpha(T_r)$ is an empirical expression, specific to a particular equation of state.

$$\boxed{b = \Omega \frac{R T_c}{P_c}} \longrightarrow (5)$$

In these equations, 'Ω' and 'ψ' are pure numbers, independent of substance and determined for a particular equation of state from the values assigned to 'ϵ' and 'σ'.

Vapor and Vapor-Like Roots of the Generic Cubic Equation of state:
(Largest root)

Multiply Eq^n. (3) through by $\frac{V-b}{RT}$. Thus,

$$P\frac{(V-b)}{RT} = \cancel{\frac{RT}{V-b}} \times \cancel{\frac{V-b}{RT}} - \frac{V-b}{RT}\frac{a(T)}{(V+\epsilon b)(V+\sigma b)}$$

$$\Rightarrow \frac{PV}{RT} - \frac{Pb}{RT} = 1 - \frac{V-b}{RT}\frac{a(T)}{(V+\epsilon b)(V+\sigma b)}$$

$$\Rightarrow \frac{PV}{RT} = 1 + \frac{Pb}{RT} - \frac{V-b}{RT}\frac{a(T)}{(V+\epsilon b)(V+\sigma b)}$$

$$\Rightarrow \boxed{V = \frac{RT}{P} + b - \frac{a(T)}{P}\frac{(V-b)}{(V+\epsilon b)(V+\sigma b)}} \rightarrow (6)$$

* Solution for 'V' is found by iteration.

* An initial ~~estimated~~ estimate for 'V' is the ideal-gas value RT/P.

* For iteration, this value is substituted on the right side of Eq. (6). The resulting value of 'V' on the left is then returned to the right side, and the process continues until the change in 'V' is suitably small.

An equation for 'z' equivalent to Eq. (6) is obtained by substituting $V = ZRT/P$.

Thus,

$$\frac{ZRT}{P} = \frac{RT}{P} + b - \frac{a(T)}{P} \frac{\left(\frac{ZRT}{P} - b\right)}{\left(\frac{ZRT}{P} + \epsilon b\right)\left(\frac{ZRT}{P} + \sigma b\right)}$$

Defining two dimensionless quantities,

$$\boxed{\beta = \frac{bP}{RT}} \xrightarrow{} (7) \quad \text{and} \quad \boxed{q = \frac{a(T)}{bRT}} \xrightarrow{} (8)$$

Therefore,

$$Z = 1 + \frac{bP}{RT} - \frac{a(T)}{\cancel{P}} \cdot \frac{\cancel{P}}{RT} \cdot \frac{\cancel{RT/P}\left(Z - bP/RT\right)}{\cancel{RT/P}\left(Z + \epsilon \frac{bP}{RT}\right)\frac{RT}{P}\left(Z + \sigma \frac{bP}{RT}\right)}$$

$$Z = 1 + \beta - \underbrace{\frac{a(T)}{RT} \cdot \frac{P}{RT}}_{(q\beta)} \cdot \frac{(Z - \beta)}{(Z + \epsilon\beta)(Z + \sigma\beta)}$$

$$\boxed{Z = 1 + \beta - q\beta \frac{(Z - \beta)}{(Z + \epsilon\beta)(Z + \sigma\beta)}} \xrightarrow{} (9)$$

* Iterative solution of Eq. (9) starts with the value of $Z = 1$ substituted on the right side. The calculated value of 'Z' is returned to the right side and the process continues to convergence.

* The final value of 'Z' yields the volume root through $V = ZRT/P$.

Liquid and Liquid-Like Roots of the Generic cubic Equation of state:

From Eq^n. (6),

$$V = \frac{RT}{P} + b - \frac{a(T)}{P}\frac{(V-b)}{(V+\epsilon b)(V+\sigma b)}$$

$$\Rightarrow \left(V - \frac{RT}{P} - b\right) = -\frac{a(T)}{P}\frac{(V-b)}{(V+\epsilon b)(V+\sigma b)}$$

$$\Rightarrow \left(V - \frac{RT}{P} - b\right)\frac{P(V+\epsilon b)(V+\sigma b)}{a(T)} = -V + b$$

$$\Rightarrow V = b - \left(V - \frac{RT}{P} - b\right)\frac{P}{a(T)}(V+\epsilon b)(V+\sigma b)$$

$$= b - \left(\frac{PV - RT - Pb}{P}\right)\frac{\cancel{P}}{a(T)}(V+\epsilon b)(V+\sigma b)$$

This equation with a starting value of $V=b$ on the right side converges upon iteration to a Liquid or Liquid-Like root.

$$\boxed{V = b + (V+\epsilon b)(V+\sigma b)\left(\frac{RT+bP-PV}{a(T)}\right)} \longrightarrow (10)$$

substituting, $V = \frac{ZRT}{P}$ in Eq^n. (10),

$$\frac{ZRT}{P} = b + \left(\frac{ZRT}{P} + \epsilon b\right)\left(\frac{ZRT}{P} + \sigma b\right)\left(\frac{RT + bP - \cancel{P}ZRT}{a(T)}\right)$$

$$\Rightarrow Z = \frac{Pb}{RT} + \frac{\cancel{RT}}{\cancel{P}}\left(Z + \frac{\epsilon bP}{RT}\right)\frac{RT}{P}\left(Z + \sigma\frac{bP}{RT}\right)RT\left(\frac{1 + \frac{bP}{RT} - Z}{a(T)}\right)$$

$$= \beta + \frac{\cancel{RT}}{\cancel{P}}\cdot\frac{RT}{P}\cdot\frac{RT}{a(T)}(Z+\epsilon\beta)(Z+\sigma\beta)(1+\beta-Z)$$

$$\boxed{Z = \beta + (Z+\epsilon\beta)(Z+\sigma\beta)\left(\frac{1+\beta-Z}{q\beta}\right)} \longrightarrow (11)$$

* For iteration a starting value of $Z=\beta$ is substituted on the right side. once 'Z' is known, the volume is

$$V = \frac{ZRT}{P}.$$

Parameter Assignments for Equations of state

Eq. of state	$\alpha(T_r)$	σ	ϵ	Ω	Ψ	Z_c
VdW(1873)	1	0	0	1/8	27/64	3/8
RK(1949)	$T_r^{-1/2}$	1	0	0.08664	0.42748	1/3
SRK(1972)	α_{SRK}	1	0	0.08664	0.42748	1/3
PR(1976)	α_{PR}	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07780	0.45724	0.30740

$$\alpha_{SRK}(T_r;\omega) = [1+m(1-T_r^{1/2})]^2$$

$$\hookrightarrow (0.480+1.574\omega-0.176\omega^2)$$

$$\alpha_{PR}(T_r;\omega) = [1+m(1-T_r^{1/2})]^2$$

$$\hookrightarrow (0.37464+1.54226\omega-0.26992\omega^2)$$

RK ≡ Redlich/Kwong

SRK ≡ Soave/Redlich/Kwong

PR ≡ Peng-Robinson.

Example : 3.9 (from Smith)

Given that the vapor pressure of n-butane at 350 K is 9.4573 bar. Find the molar volumes of

(a) Saturated vapor, and

(b) Saturated-liquid n-butane at these conditions

using. 1.) vdW; 2.) RK; 3). SRK & 4). PR EoS.

$R = 83.14 \text{ cm}^3 \text{ bar mol}^{-1} \text{ K}^{-1}$

Solution: For n-butance, $T_c = 425.1$ K

$P_c = 37.96$ bar.

Thus, $T_r = \frac{T}{T_c} = \frac{350}{425.1} = 0.8233$

$P_r = \frac{P}{P_c} = \frac{9.4573}{37.96} = 0.2491$

(a) For Saturated vapor:

The generalized cubic EoS is given by-

$$Z = 1 + \beta - q\beta \frac{(Z-\beta)}{(Z+\epsilon\beta)(Z+\sigma\beta)}$$

where, $\beta = \frac{bP}{RT}$ & $q = \frac{a(T)}{bRT}$

and $a(T) = \Psi \frac{\alpha(T_r) R^2 T_c^2}{P_c}$

& $b = \Omega \frac{R T_c}{P_c}$.

1). For VdW EOS:

$$a(T) = \frac{27}{64}\,\frac{(1)(83.14)^2(425.1)^2}{(37.96)}$$

$$\therefore\ a(T) = 13882249\ \text{cm}^6\,\text{bar}\,\text{mol}^{-2}$$

$$b = \frac{1}{8}\times\frac{83.14\times 425.1}{37.96}$$

$$\therefore\ b = 116.3818\ \text{cm}^3\,\text{mol}^{-1}$$

$$\text{So,}\quad \beta = \frac{bP}{RT} = \frac{(116.3818\ \text{cm}^3\,\text{mol}^{-1})(9.4573\ \text{bar})}{(83.14\ \text{cm}^3\,\text{bar}\,\text{mol}^{-1}\,\text{K}^{-1})(350\ \text{K})}$$

$$\therefore\ \beta = 0.0378.$$

$$q = \frac{a(T)}{bRT} = \frac{13882249\ \cancel{\text{cm}^6}\ \cancel{\text{bar}}\ \cancel{\text{mol}^{-2}}}{(116.3818\ \cancel{\text{cm}^3}\,\cancel{\text{mol}^{-1}})(83.14\ \cancel{\text{cm}^3}\,\cancel{\text{bar}}\,\cancel{\text{mol}^{-1}}\,\cancel{\text{K}^{-1}})(350\cancel{\text{K}})}$$

$$\therefore\ q = 4.0992$$

So, the above eq^n. reduces to-

$$Z = 1 + 0.0378 - (4.0992)(0.0378)\frac{(Z-0.0378)}{Z^2}$$

$$Z = 1.0378 - 0.1549\frac{(Z-0.0378)}{Z^2}$$

Starting the iteration with an initial value of $Z = 1$,

$$Z_1 = 1.0378 - 0.1549\frac{(1-0.0378)}{1^2} = 0.8888$$

$$Z_2 = 1.0378 - 0.1549\frac{(0.8888-0.0378)}{0.8888^2} = 0.8709$$

$$Z_3 = 0.8677;\ Z_4 = 0.8671;\ Z_5 = 0.8669;\ \boxed{Z_6 = 0.8669}$$

$$\text{Thus,}\ \cancel{Z_6}\ V = \frac{ZRT}{P} = \frac{0.8669\times 83.14\times 350}{9.4573} = \boxed{2667\ \text{cm}^3/\text{mol}}$$

2). For RK EOS:

$a(T) = 15502897 \ cm^6 \ bar \ mol^{-2}$

$b = 80.6665 \ cm^3 \ mol^{-1}$

$\beta = 0.0262$

$q = 6.6045$

Thus,
$$Z = 1.0262 - 0.1730 \frac{(Z - 0.0262)}{Z(Z + 0.0262)}$$

So, starting with $Z = 1$

$Z_1 = 0.8620$; $Z_2 = 0.8373$; $Z_3 = 0.8321$; $Z_4 = 0.8310$; $Z_5 = 0.8307$

$\boxed{Z_6 = 0.8307}$

$\therefore \boxed{V = 2556 \ cm^3 \ mol^{-1}}$

3). For SRK EOS:

$a(T) = 16206231 \ cm^6 \ bar \ mol^{-2}$; $\alpha = 1.1512$

$b = 80.6665 \ cm^3 \ mol^{-1}$

$\beta = 0.0262$

$q = 6.9042$

Thus,
$$Z = 1.0262 - 0.1809 \frac{(Z - 0.0262)}{Z(Z + 0.0262)}$$

Now, $Z_1 = 0.8545$; $Z_2 = 0.8271$; $Z_3 = 0.8209$;

$Z_4 = 0.8195$; $Z_5 = 0.8191$; $\boxed{Z_6 = 0.8190}$

$\therefore \boxed{V = 2520 \ cm^3/mol}$

4.) For PR EoS:

$\alpha = 1.1284$

$a(T) = 16977875 \text{ cm}^6 \text{ bar mol}^{-2}$

$b = 72.4360 \text{ cm}^3/\text{mol}$

$\beta = 0.0235$

$q = 8.0547$

Thus,

$$Z = 1.0235 - 0.1893 \frac{(Z-0.0235)}{(Z-0.0097)(Z+0.0567)}$$

$Z_1 = 0.8469$; $Z_2 = .8175$; $Z_3 = 0.8107$; $Z_4 = 0.8090$;

$Z_5 = 0.8086$; $Z_6 = 0.8085$; $\boxed{Z_7 = 0.8085}$

$$\boxed{V = 2488 \text{ cm}^3/\text{mol}}$$

(Lecture-16)

Theorem of corresponding states

Experimental observation shows that compressibility factor for different fluids exhibit similar behaviour when correlated as a function of reduced temperature T_r and reduced pressure P_r; by definition,

$$T_r = \frac{T}{T_c} \quad \text{and} \quad P_r = \frac{P}{P_c}$$

These dimensionless thermodynamic co-ordinates provide the basis for the simplest form of the theorem of corresponding states:

"All fluids, when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor, and all deviate from ideal-gas behavior to about the same degree."

corresponding-states correlations of 'z' based on this theorem are called two-parameter correlation, because they require use of the two reducing parameters 'T_c' and 'P'. Although these correlations are very nearly exact for the simple fluids (argon, krypton and xenon) systematic deviations are observed for more complex fluids.

Appreciable improvement results from introduction of a third corresponding-states parameter (in addition to T_c and P_c), characteristic of molecular structure; the most popular such parameter is the acentric factor ω, introduced by K.S. pitzer and coworkers (1955).

$$\boxed{\omega = -1 - \log (P_r^{sat})_{T_r = 0.7}} \longrightarrow (1)$$

Therefore, 'ω' can be determined for any fluid from T_c, P_c and a single vapor-pressure measurement made at $T_r = 0.7$.

Three-parameter theorem of corresponding states:

All fluids having the same value of 'ω', when compared at the same 'T_r' and 'P_r', have about the same value of 'Z', and all deviate from ideal-gas behaviour to about the same degree.

Generalized correlations for gases

Generalized correlations find widespread use. Most popular are correlations of the kind developed by pitzer and coworkers for the compressibility factor 'z' and for the second virial coefficient 'B'.

pitzer correlations for the compressibility factor:

The correlation for 'z' is:

$$\boxed{z = z^0 + \omega z'} \longrightarrow (2)$$

where z^0 and z' are functions of both 'T_r' and 'P_r'.

[values of z^0 and z' as functions of 'T_r' and 'P_r' are given in Appendix E as Tables E.1 through E.4]

pitzer correlations for the second virial coefficient:

[Tabular nature of the generalized compressibility factor correlation is a disadvantage]

The simplest form of the virial equation:

$$z = 1 + B'P = 1 + \frac{BP}{RT} \longrightarrow (3)$$

$$P = P_c P_r \text{ and } T = T_c T_r$$

$$z = 1 + \frac{B P_c P_r}{R T_c T_r} = 1 + \hat{B} \frac{P_r}{T_r} \longrightarrow (4)$$

where $\hat{B}$ is a reduced second virial coefficient,

$$\hat{B} = \frac{BP_c}{RT_c} \longrightarrow (5)$$

Pitzer and coworkers proposed a correlation,

$$\hat{B} = B^0 + \omega B^1 \longrightarrow (6)$$

Thus, eq^n. (4) and (6), gives-

$$Z = 1 + (B^0 + \omega B^1)\frac{P_r}{T_r}$$

$$Z = 1 + B^0\frac{P_r}{T_r} + \omega B^1\frac{P_r}{T_r} \longrightarrow (7)$$

Comparison with eq^n. (2), gives-

$$\boxed{Z^0 = 1 + B^0\frac{P_r}{T_r}} \longrightarrow (8)$$

$$\boxed{Z^1 = B^1\frac{P_r}{T_r}} \longrightarrow (9)$$

where,

$$\boxed{B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}} \longrightarrow (10)$$

$$\boxed{B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}} \longrightarrow (11)$$

Example : Determine the molar volume of n-butane at 510 K and 25 bar by each of the following:

(a) The ideal-gas equation.

(b) Eqⁿ. (4), Eqⁿ. (8) – Eqⁿ. (11).

Experimental value = 1480.7 cm^3/mol.

Solution : (a) $V = \frac{RT}{P} = \frac{83.14 \times 510}{25} = 1696.1\ cm^3/mol.$

(b) $T_c = 425.1\,K\ ;\ P_c = 37.96\ bar.$

$$T_r = \frac{T}{T_c} = \frac{510}{425.1} = 1.2$$

$$P_r = \frac{P}{P_c} = \frac{25}{37.96} = 0.659$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = 0.083 - \frac{0.422}{(1.2)^{1.6}}$$

$$B^0 = -.232$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = 0.139 - \frac{0.172}{1.2^{4.2}}$$

$$B^1 = 0.059$$

Thus, $\hat{B} = B^0 + \omega B^1 = -0.232 + (0.2)(0.059)$

$$\hat{B} = -0.220$$

$$\therefore Z = 1 - 0.22 \times \frac{0.659}{1.2} = \underline{\underline{0.879.}}$$

& $v = \frac{ZRT}{P} = \frac{0.879 \times 83.14 \times 510}{25} = 1491\ cm^3/mol.$

Generalized correlations for liquids

Although the molar volumes of liquids can be calculated by means of generalized cubic equations of state, the results are often not of High accuracy. Generalized equations are available for the estimation of molar volumes of saturated liquids. The simplest equation, proposed by Rackett is,

$$V^{sat} = V_c Z_c^{(1-T_r)^{2/7}}$$

An alternate form is:

$$Z^{sat} = \frac{P_r}{T_r} Z_c^{[1+(1-T_r)^{2/7}]}$$

Example : For ammonia at 310 K, estimate the density of the saturated liquid. Exp. = 29.14 cm³/mol.

sol^n For ammonia, $T_c = 405.7$ K.

$$T_r = \frac{T}{T_c} = \frac{310}{405.7} = 0.7641$$

$$V_c = 72.5 \text{ cm}^3/\text{mol}; \; Z_c = 0.242$$

$$V^{sat} = (72.5)(0.242)^{[(1-0.7641)^{2/7}]}$$

$$V^{sat} = 28.35 \text{ cm}^3/\text{mol}.$$