

# الجامعة التكنولوجية

## قسم الهندسة الكيميائية

### المرحلة الثالثة

ثرموداينمك

م.د. شروق طالب

# Introduction to Chemical Engineering Thermodynamics

For  
Chemical Process Engineering Branch

and  
Petroleum Refinery Eng. and Gas Technology  
Branch

College : Chemical Engineering

Class : Third Year

Lecture : Dr. Shurooq Talib Remedhan

1. Introduction

2. Background

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## "References"

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- (6) Rayner Joel, "Basic Engineering Thermodynamics in SI units", Printed in Great Britain, 1971.

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1. The first part of the paper is devoted to the study of the properties of the function  $f(x)$  defined by the equation  $f(x) = \int_0^x f(t) dt$ .

2. In the second part, we shall consider the problem of the existence and uniqueness of the solution of the initial value problem  $y' = f(x, y)$ ,  $y(x_0) = y_0$ .

3. The third part of the paper is devoted to the study of the properties of the function  $f(x)$  defined by the equation  $f(x) = \int_0^x f(t) dt$ .

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4. In the fourth part, we shall consider the problem of the existence and uniqueness of the solution of the initial value problem  $y' = f(x, y)$ ,  $y(x_0) = y_0$ .

5. The fifth part of the paper is devoted to the study of the properties of the function  $f(x)$  defined by the equation  $f(x) = \int_0^x f(t) dt$ .

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# Chapter One

## 1<sup>st</sup> Law and Other basic Concepts

The first law of thermodynamics in general deals with law of conservation of energy and may be stated as when energy disappears in one form it appears simultaneously in other forms.

So "first law" for a process applied both to system and surrounding in general as:

$$\Delta(\text{Energy of system}) + \Delta(\text{Energy of surroundings}) = 0$$

where:

Energy in the system in the form of :-

"U, E<sub>K</sub>, E<sub>P</sub>"

Energy in the surroundings in the form of :-

"Q & W"

W : is (+ve) when done by system.  
(-ve) when done on system.

Q : is (+ve) when transferred from surrounding to system.

(-ve) when transferred from system to surroundings.

Mathematical equations for first law for: U

1)  $\Delta U + m \cdot \frac{\Delta U^2}{2} + m \cdot \Delta Z = Q - W$  "open system"

2)  $\Delta U = Q - W$  "closed system"

W: work is "shaft work";  $W_s$  and work when "fluid flow changes its volume" from initial to final volume as :-

$$W = P \cdot (V_2 - V_1) \quad \text{Constant Pressure.}$$

The heat supplied at constant pressure can be measured as the change in another thermodynamic property of the system which call the "enthalpy". Is denoted by H and is perhaps the most widely used of all thermodynamic functions. It is defined as:

$$H = U + P \cdot V$$

and  $\Delta H = \Delta U + \Delta(P \cdot V)$

U: the internal energy of the system.

P: the absolute pressure.

V: the volume of the system.

## ② The Steady-State Flow Process:

For more important industrially are processes which involve the steady-state flow of a fluid through equipment. For such processes the more general first Law expression must be used.

$$\Delta U + \frac{\Delta U^2}{2} + g \cdot \Delta Z = Q - W$$

$$\therefore W = W_s + P_2 \cdot V_2 - P_1 \cdot V_1$$

$$\therefore \Delta U + \frac{\Delta U^2}{2} + g \cdot \Delta Z = Q - W_s - P_2 \cdot V_2 + P_1 \cdot V_1$$

$$\therefore \Delta H = \Delta U + \Delta(P \cdot V)$$

$$\therefore \Delta H + \frac{\Delta U^2}{2} + g \cdot \Delta Z = Q - W_s$$

for many of the applications considered in thermodynamics, the kinetic and potential energy terms are very small compared with the others and may be neglected. In this case:

$$\Delta H = Q - W_s$$

When no shaft work is accomplished, it reduces to:

$$\Delta H = Q$$

$$\therefore H_2 - H_1 = Q$$



### Example (1):

In a steady flow system, a substance flows at the rate of (4 Kg). It enters at a pressure of  $620 \text{ kN/m}^2$ , a velocity of  $300 \text{ m/s}$ , internal energy  $2100 \text{ kJ/Kg}$  and specific  $0.37 \text{ m}^3/\text{kg}$ . It leaves the system at a pressure of  $130 \text{ kN/m}^2$ , a velocity of  $150 \text{ m/s}$ , internal energy  $1500 \text{ kJ/kg}$  and specific volume  $1.2 \text{ m}^3/\text{kg}$ . During its passage through the system the substance has a loss by heat transfer of  $30 \text{ kJ/Kg}$  to the surroundings. Determine the work of the system, stating whether it is from or to the system. Neglect any change in potential energy.

$$\Delta U + \frac{\Delta U^2}{2} + \cancel{\Delta Z \cdot g} = Q - W_s - \Delta(P \cdot V)$$

$$\begin{aligned} \therefore W_s &= Q - \left[ \Delta U + \frac{\Delta U^2}{2} \right] - (P_2 \cdot V_2 - P_1 \cdot V_1) \\ &= 30 - \left[ (1500 - 2100) + \frac{(150^2 - 300^2)}{2 \times 1000} \right] \\ &\quad - (130 \times 1.2 - 620 \times 0.37) \end{aligned}$$

$$= 676.75 \text{ kJ/Kg}$$

$$= 676.75 \text{ kJ/Kg} \times 4 \text{ Kg}$$

$$= 2707 \text{ kJ} \quad \text{is "positive"}$$

Example (9): A steam turbine using steam at (1368 Kpa) and (645 K) and discharge saturated steam at (137 Kpa) is used to generate work for certain chemical plant. the turbine acts adiabatically and the feed and discharge velocities may be considered equal. Determine the theoretical work developed by the turbine if it uses (1650 Kg) steam. From the steam tables, enthalpy of superheated steam at (1368 Kpa and 645 K) is 3200 KJ/Kg and enthalpy of saturated steam at (137 Kpa) is 2690 KJ/Kg.

Solution:  $\Delta H + \frac{\Delta U^2}{2} + g \cdot \Delta Z = Q - W_s$

$Q = 0$  " the process is adiabatic "

$\Delta Z = 0$  " the same level "

$\Delta U = 0$  " the velocities are equal "

$\therefore \Delta H = -W_s$

or  $W_s = -(H_2 - H_1)$   
 $= -(2690 - 3200)$   
 $= 510 \text{ KJ/Kg}$

$= 510 \frac{\text{KJ}}{\text{Kg}} \times 1650 \text{ Kg}$   
 $= \text{KJ}$

## » The Heat Capacity

It is customary to define a heat capacity ( $C$ ) in terms of the heat required to produce a temperature change when the system is constrained to a specified path:

$$C \equiv \left( \frac{\partial Q}{\partial T} \right)_{\text{path}}$$

Paths of constant volume:  $p \cdot dv = 0$

$$\therefore dW = 0$$

$$\therefore dU = dQ_v$$

The constant volume heat capacity " $C_v$ " is now expressed as:

$$C_v = \left( \frac{\partial U}{\partial T} \right)_v$$

For constant pressure:  $dU = Q - W = Q - p \cdot dv$

$$dH = dQ_p$$

and the constant pressure heat capacity " $C_p$ " becomes

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p$$

The internal energy and enthalpy changes can be expressed as:

$$[\Delta U = \int C_v \cdot dT]_v$$

$$[\Delta h = \int C_p \cdot dT]_p$$

Example (3): Water at (368 K) is pumped from a storage tank at the rate of ( $25 \text{ m}^3$ ). The motor for the pump supplies work at the rate of ( $0.214 \text{ KJ/s}$ ). The water passes through a heat exchanger, where it gives up heat at the rate of ( $100.8 \text{ KJ}$ ) and is delivered to a second storage tank at an elevation of (2m) above the first tank. What is the temperature of the water delivered to the second storage tank? Assume that the enthalpy of water is zero at (273 K) and the specific heat of water is constant at ( $4.2 \text{ KJ/Kg.K}$ ).

Solution: mass of water  $\leq \rho \times V$   
 $\leq 1 \frac{\text{Kg}}{\text{m}^3} \times 25 \text{ m}^3 \leq 25 \text{ Kg}$

$$\Delta E_p \leq m \times g \times \Delta Z \quad \text{KJ/s} \quad \text{KJ/Kg}$$

$$\leq 20 \times 9.8 \times 10^{-3} \leq 0.1962 \text{ KJ/Kg}$$

$$Q \leq -100.8 \text{ KJ/Kg}$$

$$W_s \leq -0.214 \text{ KJ/Kg}$$

$$\Delta E_k \leq 0 \quad \text{"no change in the Kinetic energy of water"}$$

$$\Delta H + \Delta E_p + \Delta E_k^0 = Q - W_s$$

$$\Delta H = Q - W_s - \Delta E_p$$

$$\leq -100.8 + 0.214 - 0.1962$$

$$\leq -100.78 \text{ KJ/Kg}$$

$$H_2 - H_1 \leq -100.78 \text{ KJ/Kg}$$

$$\begin{aligned} H_1 &= c_p (T_1 - T_0) \\ &= 4.2 \times (368 - 273) \\ &= 399 \text{ KJ/Kg} \end{aligned}$$

$$\begin{aligned} H_2 &= H_1 - 100.78 \text{ KJ/Kg} \\ &= 399 - 100.78 \\ &= 298.22 \text{ KJ/Kg} \end{aligned}$$

$$H_2 = c_p \times (T_2 - T_0)$$

$T_2$ : temperature of water at the second tank, U

$$298.22 = 4.2 \times (T_2 - 273)$$

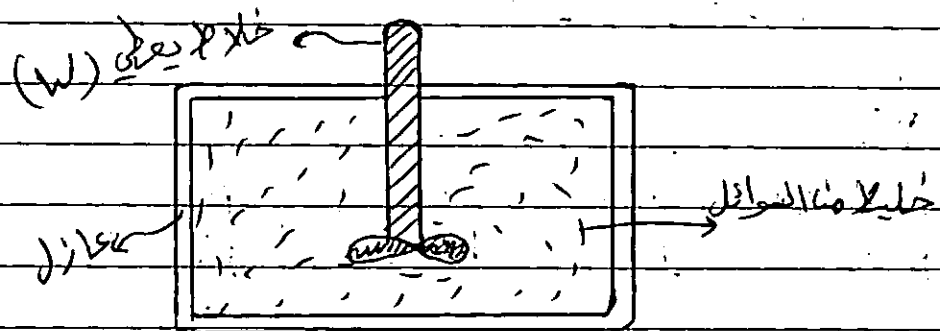
$$\Rightarrow T_2 = 344.0 \text{ K}$$

## Joule's Experiments :

الطاقة الحرارية

To understanding of heat and its relation to work, by James Joule (1818 - 1889).

In the most famous series of measurements, he placed known amount of water, oil, and mercury in an insulated container and agitated the fluid with a rotating stirrer.



The amounts of work done on the fluid by the stirrer were accurately measured, and the temperature changes of the fluid were carefully noted. He found for each fluid that a fixed amount of work was required per unit mass for energy degree of temperature rise caused by the stirring and the original temperature of the fluid.

$$W = Q$$

الشغل = الحرارة

Thus Joule was able to show conclusively that quantitative relationship exists between work and heat and, therefore, that heat is a form of energy.

## The Phase Rule

For any system at equilibrium, the number of independent variables that must be fixed to establish its intensive state is given by the phase rule of "Willard Gibbs" in 1875.

The form applicable to non-reacting systems:

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

where:

$\Pi$  : number of phases

$N$  : number of chemical species

$F$  : Called the degree of freedom of system.

The intensive state of a system at equilibrium is established when its temperature, pressure and the composition of all phases are fixed.

A phase is a homogeneous region of matter. A gas or a mixture of gases, a liquid or a liquid solution, and a crystalline solid are examples of phases.

## ○ State and Path Functions:

Any quantity whose value depends only on the initial and final state (i.e. initial and final temperature, pressure, composition, etc) and not on the path that is followed to reach the final state is called "the state function" such as changes in internal energy, enthalpy, and entropy ( $\Delta U$ ,  $\Delta H$  and  $\Delta S$ ) so that:-

$$\Delta U = U_2 - U_1$$

$$\Delta H = H_2 - H_1$$

$$\Delta S = S_2 - S_1$$

regardless of the path. ~~(this will be same)~~

On the other hand, quantities such as heat ( $Q$ ) and work ( $W$ ) depended on how the process takes place, i.e. depend on the initial and final states of the system and on the path, hence they are known as "Path functions".

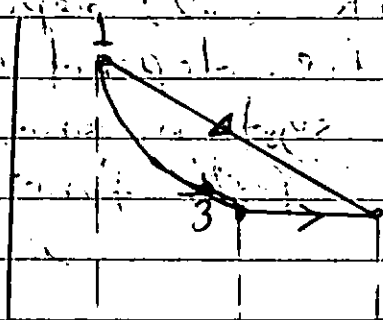
~~(this will be different)~~

Another difference between state and path functions is that a state function represents a property of a system and always has a value, whereas work and heat appear only when changes are carried out in a system by a process which requires time.



## The Reversible Process:

A process is reversible when its direction can be reversed at any point by an infinitesimal change in external conditions. A process which moves a system from A to state B is said to be reversible if the work and heat effects realized from the process are sufficient to restore the system to its original state (state A). Actually, that is considering a cycle  $A \rightarrow B \rightarrow A$  consisting of two reversible steps which when completed leaves no changes in either the system or surroundings. It represents a limiting case which can be approached by an actual process, and it is the only type of process for which work can be calculated. Fig (1-1) realize that path are actually a succession of equilibrium states through which the system passes.



Path 1-2:  $W = \int P_1 dV$  (not a straight line)

Path 1-3-2:  $W = W_{1-3} + W_{3-2}$

First, calculate the reversible work and correct it by means of an efficiency. Defined as a ratio involving actual work and reversible work.

- "Irreversible Process" is the process accompanied by dissipative effect. All real process are practically irreversible and the reversible one is the ideal case and can not be realized but it can be estimated mathematically.

- The actual work input or output for the process can be estimated from that of the reversible one by using the efficiency ( $\eta$ ) according to the following equations:

$$\eta = \frac{\text{actual work output from the process}}{\text{work output from reversible process}}$$

$$\hookrightarrow \frac{W_{act}}{W_{rev}} \times 100$$

This equation when the work done by the system ( $W$  is +ve).

- and  $\eta = \frac{\text{work input for a reversible process}}{\text{actual work input for the process}}$

$$\hookrightarrow \frac{W_{rev.}}{W_{act.}} \times 100$$

when the work done on the system ( $W$  is -ve).



○ Process: It is the operation or a series of operations done on the system to change it from one state to another. The most common thermodynamic processes are:

a) Isothermal: The process carried out under constant temperature.

b) Isobaric: The process carried out under constant pressure.

○ c) Isometric or Isochoric: The process carried out under constant volume.

d) Adiabatic or Isentropic: The process in which no heat is transferred between the system and its surroundings. It is achieved under one of the following circumstances:

1) The system is perfectly insulated.

2) Heat is very small compared to other terms in energy equation and may be neglected.

3) The process takes place so fast that there is no time for heat to be transferred.

Polytropic: It is the general case without specific conditions.

Equations for PVT relationships of an ideal gas under following changes:

i) Reversible Isometric (constant volume) change:

$$V_1 = V_2$$

$$dW = p \cdot dV = 0$$

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}$$

$$dU = dQ = n \cdot C_V \cdot dT$$

$$dH = n \cdot C_P \cdot dT$$

ii) Reversible Isobaric (constant pressure) change:

$$P_1 = P_2$$

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}$$

$$dU = n \cdot C_V \cdot dT$$

$$dH = dQ = n \cdot C_P \cdot dT$$

$$W = Q - \Delta U$$

or

$$W = P \cdot \Delta V$$

$$\Delta U = Q - W$$

$$\Delta H = \Delta U + P \cdot dV$$

iii) Isothermal (Constant Temperature) change:

$$T_1 = T_2$$

$$P_1 V_1 = P_2 V_2$$

$$\Delta U = 0$$

$$\Delta H = 0$$

$$Q = W = n R T \ln \frac{V_2}{V_1}$$

$$Q = W = n R T \ln \frac{P_1}{P_2}$$

iv) Reversible Adiabatic change:

$$Q = 0$$

$$\Delta U = -W$$

$$\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}}$$

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

$$\Delta H = \Delta U + P \Delta V$$

$$W = n \cdot (P_1 V_1 - P_2 V_2) \quad (1)$$

$$(\gamma - 1)$$

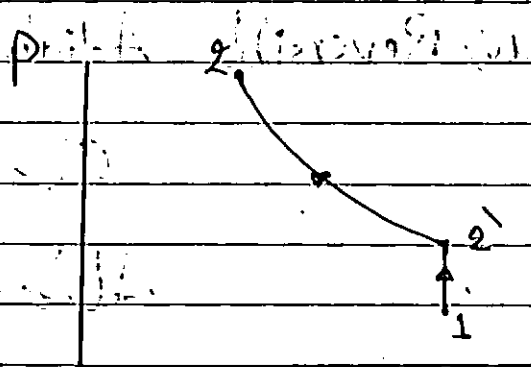
$$W = \frac{n \cdot R \cdot T_1}{(\gamma - 1)} \left[ 1 - \left( \frac{P_2}{P_1} \right)^{\frac{\gamma - 1}{\gamma}} \right]$$

### Example 8

One Kilogram mole of nitrogen undergoes a process in which it is heated, from initial state of (2.026 bar) and (277.4 K) at constant volume to a pressure such that when it is compressed reversibly at constant temperature, its final pressure and temperature are (8.104 bar) and (388.5 K). Calculate  $Q$ ,  $W$ ,  $\Delta U$ , and  $\Delta H$  for the processes assuming  $N_2$  to be an ideal gas.

### Solution:

Since  $1 \rightarrow 2'$  is a constant volume step.



$$\therefore \frac{P_1 \cdot V_1}{T_1} = \frac{P_2' \cdot V_1}{T_2'}$$

$$P_2' = \frac{P_1 \cdot T_2'}{T_1} = \frac{2.026 \times 388.5}{277.4} = 2.8 \text{ bar}$$

$$Q_1 = \Delta U_1 = n \cdot C_V (T_2' - T_1)$$

$$= 1 \times 20934 \frac{\text{J}}{\text{kmole} \cdot ^\circ\text{C}} \times (115.5 - 4.4)^\circ\text{C}$$

$$= 2325767.4 \text{ J}$$

$$\Delta H_1 = n \cdot c_p \cdot (T_2' - T_1)$$

$$= 1 \cdot 29307.6 (115.5 - 4.4)$$

$$= 3256074.3 \text{ J}$$

$$W = 0$$

Since  $2' \rightarrow 2$  isothermal step,

$$T_2' = T_2, \quad \Delta U_2 = 0, \quad \Delta H_2 = 0$$

$$Q_2 = W_2 = n \cdot R \cdot T \cdot \ln \frac{P_1}{P_2}$$

$$= 1 \cdot 8314 \cdot 388.5 \cdot \ln \frac{2.8}{8.104}$$

$$= -3415680.9 \text{ J}$$

$$W = W_1 + W_2$$

$$= -3415680.9 \text{ J}$$

$$Q = Q_1 + Q_2$$

$$\Delta U = \Delta U_1 + \Delta U_2$$

$$= 2325767.4 \text{ J}$$

$$\Delta H = \Delta H_1 + \Delta H_2$$

$$= 3256074.3 \text{ J}$$

$$Q = 2325767.4 - 3415680.9$$

$$= -1089913.5 \text{ J}$$





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## Tutorial Sheet No. (1).

- 2) 1) Heat is transferred to (10 Kg) of air which is initially at (100 KPa) and (300 K) until its temperature reaches (600 K). Determine the change in internal energy, the change in enthalpy, the heat supplied, and the work done in the following Processes :

- a) Constant volume process
- b) Constant pressure process

Assume that air is an ideal gas for which  $PV = nRT$ , where "n" is the number of moles of the gas and  $R = 8.314 \text{ KJ/Kmol} \cdot \text{K}$ . Take  $c_p = 29.099 \text{ KJ/Kmol} \cdot \text{K}$ ,  $c_v = 20.785 \text{ KJ/Kmol} \cdot \text{K}$  and molecular weight of air = 29.

- 3) 2) Compute the horse power developed by a turbine from the data given below:

	$P [\text{N/m}^2]$	$T [^\circ\text{C}]$	$U [\text{m}^2/\text{s}]$	$d [\text{cm}]$	$z [\text{m}]$
Inlet	$20.68 \times 10^5$	426.6	4.57	10.16	3.048
outlet	$0.35 \times 10^5$	93.3	—	20.32	datum level

Assume no heat losses, and from steam table:

$$\begin{aligned} v_1 &= 0.153 \text{ m}^3/\text{kg} & ; & \quad H_1 = 788.5 \text{ Kcal/Kg} \\ v_2 &= 4.88 \text{ m}^3/\text{kg} & \quad H_2 &= 637.77 \text{ Kcal/Kg} \end{aligned}$$

3) A system consisting of some fluid is stirred in a tank. The work done on the system by the stirrer is of the order of (2 H.P.). Heat generated because of stirring is dissipated through surroundings. If this heat transfer is (835 Kcal/hr) determine the change in internal energy.

4) A body of mass (10 Kg) is allowed to fall from a height of (42.7m) into a bucket containing water at the same temperature of body. Find  $Q$ ,  $W$ ,  $\Delta E_k$ ,  $\Delta U$  and  $\Delta E_p$  for the following conditions:-

- i) Body about to enter the water.
- ii) Body comes to rest in the water.
- iii) After enough heat transfer so that body and water are at the same initial temperature.

5) (1.5 Kg) of liquid  $C_{10}H_8$  is burned completely in a constant volume bomb in the atmosphere of oxygen. The reactant are at (1 atm) and (20°C) and product are cooled to (20°C). During this operation (5000 J) is transferred to surroundings. Assuming  $CO_2$  to be an ideal gas and volume of liquid  $C_{10}H_8$  to be same as liquid  $H_2O$  formed. Calculate  $Q$ ,  $W$ ,  $\Delta U$  and  $\Delta H$ ; What will be  $Q$ ,  $W$ ,  $\Delta U$ ,  $\Delta H$  if reaction is carried out at constant pressure instead of constant volume and initial and final temperatures are same?

## Chapter Two

### Volumetric Properties of Pure Fluids

A pure fluid is an equilibrium state when two intensive variables are fixed and all properties are uniform throughout. The PVT behavior of a fluid is usually displayed on a PV diagram on which constant temperature curves.

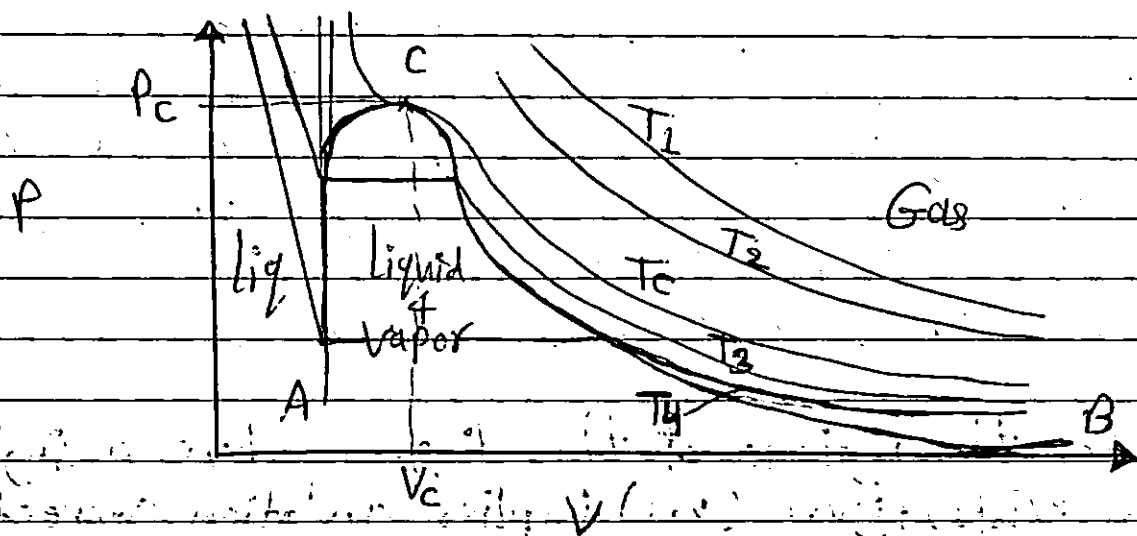


Figure (2.1): P V diagram for a pure fluid

Figure 2.1 is a function of pressure and volume, it shows the variation in molar volume with pressure at various constant temperatures. The lines labeled  $T_1$  and  $T_2$  are isotherms at temperatures greater than the critical. The lines labeled  $T_3$  and  $T_4$  are for lower temperatures and consist of three distinct sections.

The horizontal sections represent the phase change between vapor and liquid. Points along the horizontal lines represent all possible mixture of vapor and liquid in equilibrium, ranging from 100 percent liquid

at the left end to 100 percent vapor at the right end. Curve labeled ACB, the left half of which (from A to C) represents saturated liquid, and the right half (from C to B) saturated vapor. The area under ACB is the two phase region, while the areas to the left and right are the liquid and gas regions. The liquid region are very steep, because liquid volumes change little with large changes in pressure. The horizontal segments of the isotherms in the two phase region become progressively shorter at higher temperatures, reduced to a point at (C). Here the liquid and vapor phases cannot be distinguished from one another, because their properties are the same.

For the regions of the diagram where a single phase exists, figure (2.1) implies a relation connecting  $P, V, T$  which may be expressed by the functional equation:

$$f(P, V, T) = 0$$

If  $V$  is considered a function of  $T$  and  $P$ , then

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

and

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

For liquids they are related to two commonly tabulated properties:

1) The volume expansivity  $\beta \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$

2) The isothermal compressibility

$$K \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

Combination of two equations provides the general eq.

$$dV = \beta \cdot dT - K \cdot dP$$

For real liquids  $\beta$  and  $K$  are weak functions of temperature and pressure. Then this eq can be integrated to give:

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

Example: Express the volume expansivity and the isothermal compressibility as function of density ( $\rho$ ) and its partial derivatives. For water at (50°C) and (1 bar),  $K = 44.18 \times 10^{-6} \text{ bar}^{-1}$ . To what pressure must water be compressed at (50°C) to change its density by (1 percent)? Assume that  $K$  is independent of  $P$ .

Solution: For liquid

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

$$\rho = \frac{m}{V}$$

$$\ln \frac{(m/\rho_2)}{(m/\rho_1)} = \beta(T_2 - T_1) - K(P_2 - P_1)$$

Isothermal

$$P_2 = P_1 + \frac{1}{100} (\alpha P_1)$$

$$\leq 1 + 0.01 \left( \frac{44.18}{1.01} \right) \cdot \frac{1}{1.01} = 1.01$$

$$\ln \frac{1}{1.01} = -44.18 \times 10^{-6} \cdot (P_2 - 1)$$

$$-9.95 \times 10^{-3} = -44.18 \times 10^{-6} \cdot P_2 + 44.18 \times 10^{-6}$$

$$P_2 = 226.22 \text{ bar}$$

## Equations of state

Often (PVT) data are fitted to algebraic equations called equations of state. Many such equations of varying degrees of complexity have been proposed, and while a few have some basis in molecular theory, all are used empirically.

## Virial Equation

The virial equation expressing the compressibility factor ( $Z$ ) as a power series in density, or reciprocal volume, can be derived from statistical mechanics.

Virial equation	$Z = \frac{P.V}{R.T} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots$
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- The parameters  $B$  and  $C$  are called second and third coefficients, and are functions only of temperature. This equation finds its greatest use at low to moderate pressures.

This suggests expression can be represented by a power series in  $P$

Virial also  
 Virial also

$$Z = \frac{P.V}{R.T} = 1 + B'P + C'P^2 + D'P^3 + \dots$$

where

$$B' = \frac{B}{R.T}$$

$$C' = \frac{C - B^2}{(R.T)^2}$$

$$D' = \frac{D - 3.B.C + 2.B^3}{(R.T)^3}$$

In addition may use the approximate relation  $B' = B / R.T$  to express the equation for  $Z$  in terms of the coefficient  $B$

at low to moderate pressure < 15 bar	$Z = \frac{P.V}{R.T} = 1 + \frac{P.B}{R.T}$	Virial also
	$Z = \frac{P.V}{R.T} = 1 + \frac{B}{V}$	Virial also



This equation satisfactorily represents the PVT behavior of most vapors at subcritical temperatures up to a pressure of about 15 bar.

For pressures above the range of applicability above, but below about 50 bar, the virial equation truncated to three terms usually provides excellent results.

For pressure  
(15-50) bar

$$Z = \frac{P \cdot V}{R \cdot T} = 1 + \frac{B}{V} + \frac{C}{V^2}$$

Example: Calculate "Z" and "V" for ethane at (50°C) and (12 bar) by the truncated virial equation with two terms and with three terms, the experimental values of virial coefficients:

$$B = -156.7 \text{ cm}^3/\text{mol}$$

$$C = 9650 \text{ cm}^6/\text{mol}^2$$

Solution:

$$Z = \frac{P \cdot V}{R \cdot T} = 1 + \frac{B \cdot P}{R \cdot T} \quad \text{"Two Terms"}$$

$$\Rightarrow V = \frac{R \cdot T}{P} + B$$

$$= \frac{83.14 \text{ cm}^3/\text{bar} \cdot \text{mol} \cdot \text{K} \cdot (50 + 273) \text{ K}}{12 \text{ bar}} - 156.7 \text{ cm}^3/\text{mol}$$

$$= 12 \text{ bar}$$

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

$$\& Z = \frac{P \cdot V}{R \cdot T} = \frac{V}{\frac{R \cdot T}{P}}$$

$$Z = \frac{P.V}{R.T} = 1 + \frac{B}{V} + \frac{C}{V^2} \quad \text{"Three Terms"}$$

Initial  $V_0 = \frac{R.T}{P} = \frac{83.14 \times (50 + 273.15)}{12} = 2239 \text{ cm}^3/\text{mole}$

$$V_{i+1} = \frac{R.T}{P} \left[ 1 + \frac{B}{V_i} + \frac{C}{V_i^2} \right]$$

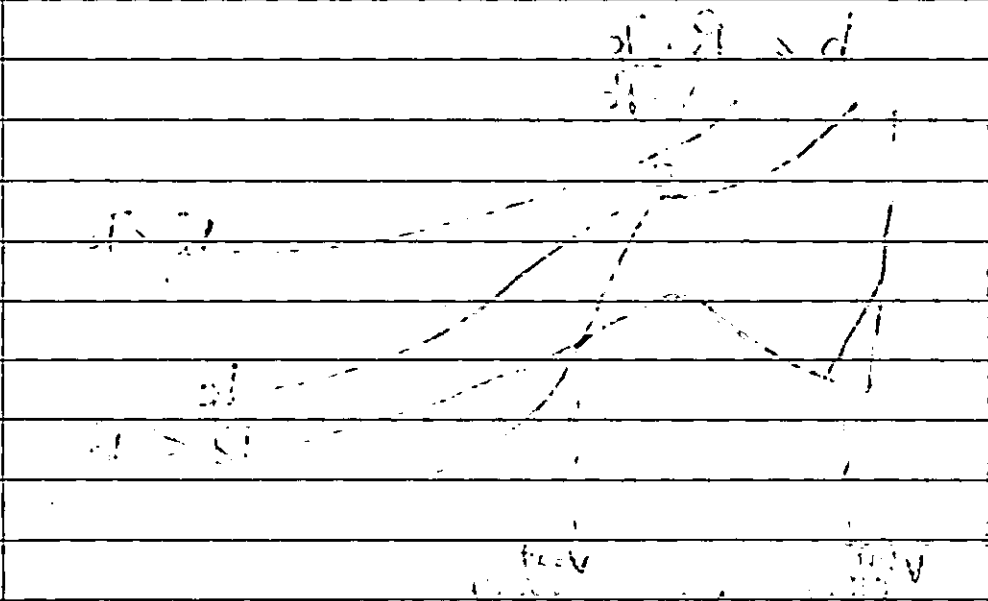
Substitute the value of  $V_i = V_0$  at all

$V_i$	$V_{i+1}$
$V_0 = 2239$	2087
2087	2075
2075	2075

Trial & error Method

$$Z = \frac{P.V}{R.T} = \frac{12 \times 2075}{83.14 \times 323.15}$$

at 50°C



## Cubic equations of state:

For an accurate description of the PVT behavior of fluid over wide ranges of temperature and pressure, an equation of state more comprehensive than the Virial equation is required. Such an equation must be sufficiently general to apply to liquid and gases and vapors.

The first general cubic equation of state was proposed by The van der Waals Equation:

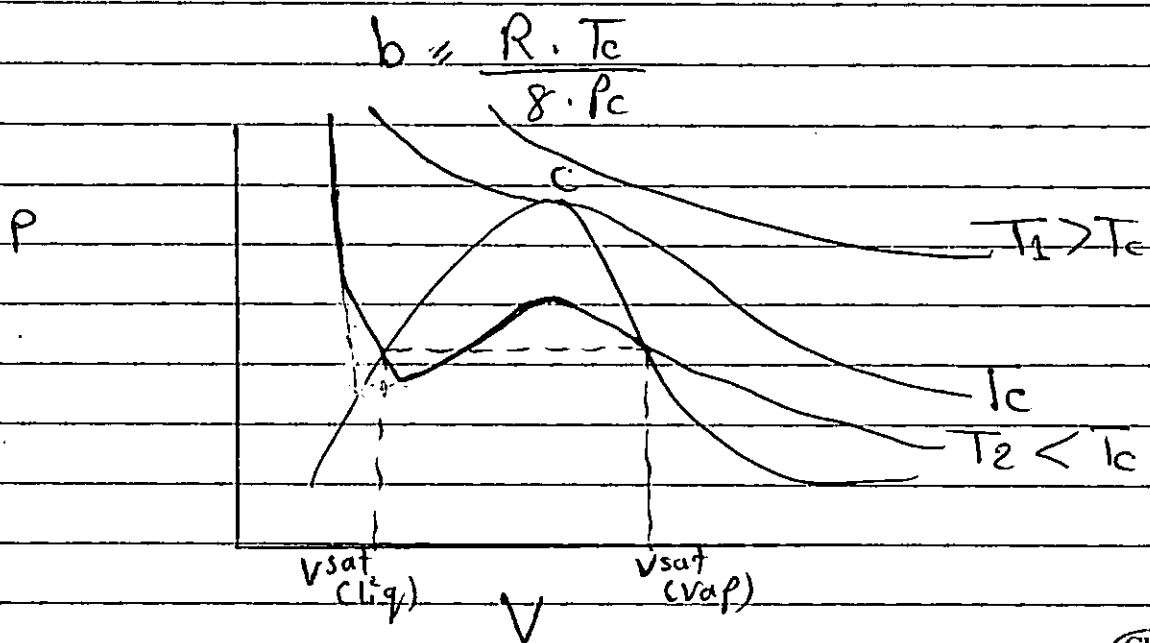
$$P = \frac{R \cdot T}{V - b} - \frac{a}{V^2}$$

where:

$a$  &  $b$  are positive constants, when they are zero, the ideal gas equation is recovered.

$$a = \frac{27 \cdot R^2 \cdot T_c^2}{64 \cdot P_c}$$

$$b = \frac{R \cdot T_c}{8 \cdot P_c}$$



## Redlich-Kwong Equation:

The Redlich-Kwong equation of state may be regarded as a modified "van der Waals equation", and therefore the same rather general physical interpretation may be assigned to its parameters:

$$P = \frac{R \cdot T}{V-b} - \frac{a}{T^{1/2} \cdot V \cdot (V+b)}$$

\* also Redlich-Kwong

This equation like the van der Waals equation, the two parameters may be evaluated from the critical temperature and pressure. The following schemes are usually effective for the Redlich/Kwong equation:-

### 1) Vapor Volumes

The equation above was multiplied through by  $(V-b)/P$  to give:

$$V-b = \frac{R \cdot T}{P} - \frac{a(V-b)}{T^{1/2} \cdot P \cdot V \cdot (V+b)}$$

for iteration, write:

Redlich-Kwong  
also

$$V_{i+1} = \frac{R \cdot T}{P} + b - \frac{a(V_i-b)}{T^{1/2} \cdot P \cdot V_i \cdot (V_i+b)}$$

\*

For initial value;

$$V_i = V_0 = \frac{R \cdot T}{P}$$

## 2) Liquid volumes

Equation of (Redlich/Kwong) was put into an iteration scheme results:

Redlich-Kwong  
جولان مع  $a$  و  $b$

$$V_{j+1} = \frac{1}{C} \left( V_j^3 - \frac{R \cdot T}{P} V_j^2 - \frac{a \cdot b}{P \cdot T^{1/2}} \right) *$$

For an initial value, take  $V_0 = b$  \*

The constants in an equation of cubic state suitable estimates from the critical constants " $T_c$ " and " $P_c$ " and most to be elimination of " $V_c$ " to relating " $a$ " and " $b$ ".

$$a = \frac{0.42748 \cdot R^2 \cdot T_c^{2.5}}{P_c}$$

$$b = \frac{0.08664 \cdot R \cdot T_c}{P_c}$$

$$C = b^2 + \frac{b \cdot R \cdot T}{P} - \frac{a}{P \cdot T^{1/2}}$$

where: A list of values of  $T_c$  &  $P_c$  are available into appendix B, from book "Smith".

Example: A molar volume of gaseous ammonia that is contained in vessel is ( $1021.2 \text{ cm}^3/\text{mole}$ ) immersed in a constant temperature bath at ( $65^\circ\text{C}$ ). Calculate the pressure of the gas by the Redlich-Kwong equation, when  $T_c = 405.6 \text{ K}$  and  $P_c = 112.8 \text{ bar}$ .

$$a = \frac{0.42748 \cdot R^2 \cdot T_c^{2.5}}{P_c}$$

and

$$b = \frac{0.08664 \cdot R \cdot T_c}{P_c}$$

Solution:

$$a = \frac{0.42748 \cdot (83.14)^2 \cdot (405.6)^{2.5}}{112.8}$$

$$= 8.679 \times 10^7 \text{ bar} \cdot \text{cm}^6 \cdot \text{K}^{1/2}$$

$$b = \frac{0.08664 \cdot (83.14) \cdot (405.6)}{112.8}$$

$$= 25.9 \text{ cm}^3$$

$$P = \frac{R \cdot T}{V - b} - \frac{a}{T^{1/2} \cdot V(V + b)}$$

$$= \frac{(83.14) \cdot (338.15)}{1021.2 - 25.9} - \frac{8.679 \times 10^7}{(338.15)^{1/2} \cdot (1021.2) \cdot (1021.2 + 25.9)}$$

$$= 23.83 \text{ bar}$$

P.D.P

Example: Calculate the molar volumes of saturated vapour and saturated liquid at (60°C) and (13.76 bar) by the Redlich/Kwong equation at these conditions:  $T_c = 416.3 \text{ K}$  and  $P_c = 66.8 \text{ bar}$ , when,

$$a = \frac{0.42748 \cdot R^2 \cdot T_c^{2.5}}{P_c}$$

and

$$b = \frac{0.08664 \cdot R \cdot T_c}{P_c}$$

Solution:

$$a = 1.56414 \times 10^8 \text{ cm}^6 \cdot \text{bar} \cdot \text{mol}^{-2} \cdot \text{K}^{-1/2}$$

$$b = 44.891 \text{ cm}^3 / \text{mol}$$

$$V_j = V_0 = \frac{R \cdot T}{P}$$

$$= 2512.94 \text{ cm}^3 / \text{mol}$$

$$V_{j+1} = b + \frac{R \cdot T}{P} - \left[ \frac{a}{T^{1/2} \cdot P} \cdot \frac{1}{V_j} \cdot \frac{(V_j - b)}{(V_j + b)} \right] \quad \begin{matrix} a = 1.56414 \times 10^8 \\ P = 13.76 \end{matrix}$$

$$= \frac{44.891 + 83.14 \cdot (60 + 273.15)}{13.76} - \left[ \frac{1.56414}{(60 + 273.15)^{1/2} \cdot 13.76 \text{ bar}} \right]$$

$$\times \frac{1}{V_j} \times \left[ \frac{V_j - 44.891}{V_j + 44.891} \right]$$

$$= 2057.83 - \frac{662784}{V_j} \left( \frac{V_j - 44.891}{V_j + 44.891} \right)$$

Continues by trail and error on the value:

The molar volume of  $V \approx 1712 \text{ cm}^3/\text{mole}$   
saturated vapor

المعادلة  
المعروفة

$$V_{i+1} = \frac{1}{C} \left( V_i^3 - \frac{R \cdot T}{P} \cdot V_i^2 - \frac{a \cdot b}{P \cdot T^{1/2}} \right)$$

$$C = b^2 + \frac{b \cdot R \cdot T}{P} - \frac{a}{P \cdot T^{1/2}}$$

$$C = -530405 \text{ cm}^6/\text{mole}^2$$

Iteration starts with  $V_i = V_0 = b = 44.891 \text{ cm}^3/\text{mol}$

$$V_{i+1} = \frac{1}{-530405} \left( V_i^3 - 2012.94 \cdot V_i^2 - 2.795 \times 10^7 \right)$$

Continues to convergence on the value

$$\hookrightarrow V \approx 71.34 \text{ cm}^3/\text{mol}$$



#### 4. Generalized correlations for gases and for liquids:

Generalized correlations find widespread use. Most popular are correlations of the kind developed by Pitzer for the compressibility factor  $Z$  and for the second virial coefficient  $B$ .

##### Pitzer Correlations for the Compressibility Factor

The correlation for " $Z$ " takes the form:

$$Z = Z^0 + W_1 Z^1$$

where:

$Z^0$  and  $Z^1$  are functions of both  $[T_r \text{ and } P_r]$ .

and:

$$T_r = T / T_c$$

$$P_r = P / P_c$$

$W_1$  is the centric factor depend on  $[T_c, P_c, \text{ and } V_c]$ .

5. Equation of state that represent " $Z$ " above is said to be generalized because of their general applicability to all gases.

A disadvantage of the generalized compressibility factor correlation is its graphical nature, Thus figures in "chapter three" may be used for quick estimates of  $Z^0$  and  $Z^1$  verses  $P_r$  and  $T_r$ .

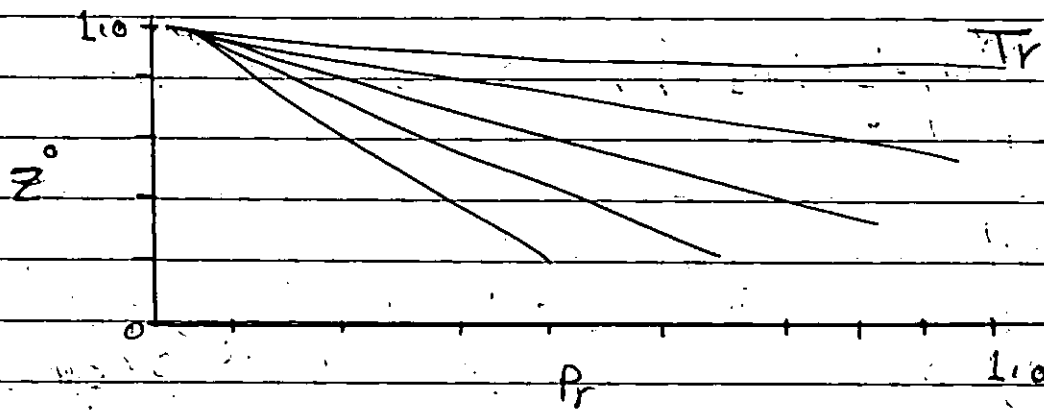


Figure 1: shows estimated of  $(Z^0)$  vs  $(P_r + Tr)$

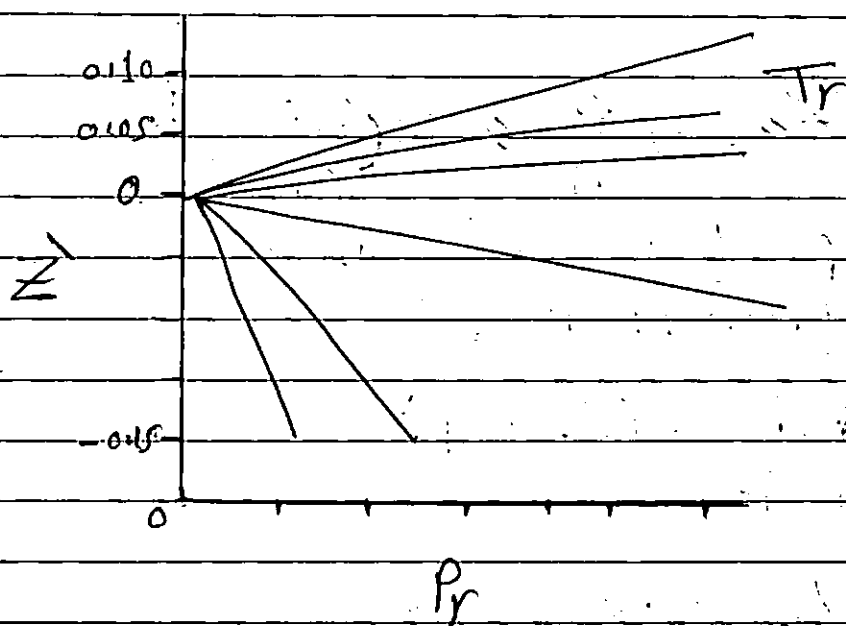


Figure 2: shows estimated of  $(Z^1)$  vs.  $(P_r + Tr)$

## Pitzer Correlations for the Second Virial Coefficient :

The tabular nature of the generalized compressibility factor correlation is a disadvantage, but the complexity of the functions  $Z^0$  and  $Z^1$  precludes their accurate representation by simple equations. The basis for this is virial equation with two terms, the simplest form is :

$$Z \leq 1 + \frac{B \cdot P}{R \cdot T} \leq 1 + \left( \frac{B \cdot P_c}{R \cdot T_c} \right) \frac{P_r}{T_r}$$

Thus, Pitzer proposed a second correlation, which yields values for  $[B \cdot P_c / R \cdot T_c]$  :

$$\frac{B \cdot P_c}{R \cdot T_c} \leq B^0 + w \cdot B^1$$

Together, these two equations become :

$$Z \leq 1 + B^0 \frac{P_r}{T_r} + w \cdot B^1 \cdot \frac{P_r}{T_r}$$

Comparison of this equation with generalized compressibility factor :

$$Z \leq Z^0 + w \cdot Z^1$$

Provides the following identifications :

and

$$\begin{aligned} Z^0 &\leq 1 + B^0 \cdot \frac{P_r}{T_r} \\ Z^1 &\leq B^1 \cdot \frac{P_r}{T_r} \end{aligned}$$

Second virial coefficients are functions of temperature only, and similarly  $B^0$  and  $B^1$  are functions of reduced temperature only. They are represented by the following equations:

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

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

المعاملات الثانية للvirial هي دوال لدرجة الحرارة فقط، وبالمثل  $B^0$  و  $B^1$  هما دوال لدرجة الحرارة المخفضة فقط. يتم تمثيلها بالمعادلات التالية:

### 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.

In addition, generalized equations are available for the estimation of molar volumes of "saturated liquids". The simplest equation, proposed by "Rackett",

$$V^{\text{sat}} = V_c \cdot Z_c (1 - T_r)^{0.2857}$$

The data required are the critical constants, given in (App. B) from Smith, thermodynamic books.

Lydersen and Hougen developed correlation for estimation of liquid volumes. It provides a correlation

- of reduced density ( $\rho_r$ ) as a function of reduced temperature and pressure. By definition,

$$\rho_r = \frac{\rho}{\rho_c} = \frac{V_c}{V}$$

where  $\rho_c$  is the density at the critical point.

A better procedure is to make use of a single known liquid volume by the identity,

$$V_2 = V_1 \cdot \frac{\rho_{r1}}{\rho_{r2}}$$

where:

$V_2$ , required volume

$V_1$ , known volume

$\rho_{r1}$  and  $\rho_{r2}$ , reduced densities read from figure (3.17)

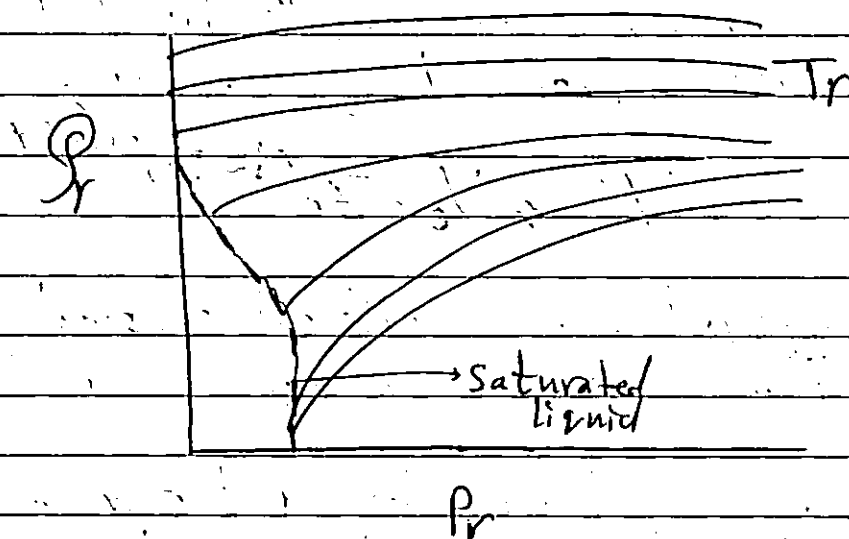


Figure (3.17), Smith 6<sup>th</sup> edition: Generalized density for liquids

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

- The ideal gas equation.
- The generalized compressibility factor correlation.
- The generalized virial-coefficient correlation.

Solution: a) ideal gas  $Z = 1$

$$V = \frac{R \cdot T}{P} = \frac{0.08314 \times 510}{25} = 1.691 \text{ m}^3/\text{kmol}$$

b)  $Z = Z^0 + w \cdot Z^1$

Taking values of  $T_c$  and  $P_c$  from App. B,

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

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

Interpolation in tables [E1 and E2] from App. E,

$$Z^0 = 0.865 \quad Z^1 = 0.038$$

From App. B1,  $w = 0.2$

$$\therefore Z = 0.865 + (0.2 \times 0.038) \\ = 0.873$$

and

$$V = \frac{Z \cdot R \cdot T}{P} = \frac{0.873 \times 0.08314 \times 510}{25} = 1.4807 \text{ m}^3/\text{kmol}$$

$$c) Z \approx 1 + \left( \frac{B \cdot P_c}{R \cdot T_c} \right) \cdot \frac{P_r}{T_r}$$

$$\left( \frac{B \cdot P_c}{R \cdot T_c} \right) \approx B^0 + \omega \cdot B^1$$

$\therefore B^0 \approx -0.232$  and  $B^1 \approx 0.059$   
calculated from equations of it.

$$\therefore \left( \frac{B \cdot P_c}{R \cdot T_c} \right) \approx -0.232 + (0.2 \times 0.059) \approx -0.22$$

$$\therefore Z \approx 1 + \left( -0.22 \times \frac{0.659}{1.2} \right) \approx$$

$$\therefore 0.879$$

$$V \approx \frac{Z \cdot R \cdot T}{P} \approx \frac{0.879 \times 0.08314 \times 510}{25} \approx 1.4891 \text{ m}^3/\text{Kmol}$$

- Example: For ammonia at 310K, estimate the molar volume of:
- The saturated liquid.
  - The liquid at 100 bar.

Solution: Saturated liquid, apply "Rackett eq"

$$V^{\text{sat}} = V_c \cdot Z_c^{(1-T_r)^{0.2857}}$$

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

and  $V_c = 0.107247 \text{ m}^3/\text{Kmol}$ ,  $Z_c = 0.249$   
 "From App. B).

$$\therefore V^{\text{sat}} = 0.107247 \cdot (0.249)^{(1-0.7641)^{0.2857}}$$

$$= 0.02833 \text{ m}^3/\text{Kmol}$$

b) Liquid volume at reduced conditions,

$$V_2 = V_1 \cdot \frac{P_{r1}}{P_{r2}}$$

$$T_r = 0.764 \quad \& \quad P_r = \frac{P}{P_c} = \frac{100}{112.8} = 0.887$$

From figure (3.17), we have  $P_r = 2.38$

$$\therefore P_r = \frac{P}{P_c} = \frac{V_c}{V}$$

$$\therefore V = \frac{V_c}{P_r} = \frac{72.5}{2.38} = 30.5 \text{ cm}^3/\text{mol} \quad \text{"This is Known liquid volume - state"}$$



For saturated liquid at 310K,  $T_r = 0.764$   
find from fig. (3.17)  $P_{r1} = 2.34$

$$\approx V_2 \approx V_{state} \cdot \left( \frac{P_{r1}}{P_{r2}} \right)$$

$$\approx 30.5 \times \left( \frac{2.34}{2.38} \right)$$

$$\approx 30.65 \text{ cm}^3/\text{mol}$$

# Tutorial Sheet

No. 2

Q1: Five kilograms of liquid carbon tetrachloride undergo a mechanically reversible isobaric change of state at (1 bar) during which the temperature changes from (0 to 20) °C. Determine  $\Delta V$ ,  $W$ ,  $Q$ ,  $\Delta H^\dagger$  and  $\Delta U^\dagger$ . The following properties for liquid carbon tetrachloride at (1 bar and 0°C) may be assumed independent of temperature:  $B = 1.2 \times 10^{-3} \text{ K}$ ,  $c_p = 0.84 \text{ KJ/Kg} \cdot \text{K}$ . The density at (0°C) and 1 bar is (1590 Kg/m<sup>3</sup>).

Q2: An ideal gas,  $c_p = (7/2)R$  and  $c_v = (5/2)R$ , undergoes the following mechanically reversible changes in a series of nonflow processes:

a) From an initial state of (40°C) and (150 KPa), it is compressed adiabatically to (600 KPa).

b) It is then cooled to (40°C) at a constant pressure of (600 KPa).

c) Finally, the gas is expanded isothermally to its original state.

Calculate  $Q$ ,  $W$ ,  $\Delta U$  and  $\Delta H$  for each of the three processes and for the cycle.

Repeat these calculations for the same changes accomplished irreversibly with an efficiency for each process of (80 percent) compared with reversible process.

Q3: Calculate (Z) and (V) for methanol vapor at (200°C) and (10 bar) by the following equations:

a) The truncated virial equation with three terms with the following values of coefficients:

$$B = -219 \text{ cm}^3/\text{mol}; \quad C = -17300 \text{ cm}^6/\text{mol}^2$$

b) The truncated virial equation with two terms, with a value of B from the generalized correlation of Pitzer second coefficient,  $\omega = 0.564$ .

c) The Redlich/Kwong equation, with estimates of (a) and (b) from eq:

$$a = 0.42748 \cdot R^2 \cdot T_c^{2.5} / P_c$$

$$b = 0.08664 \cdot R \cdot T_c / P_c$$

$$T_c = 512.6 \text{ K}; \quad B^0 = 0.422 / T_r^{1.6}$$

$$P_c = 81.0 \text{ bar}; \quad B^1 = 0.139 - 0.172 / T_r^{4.2}$$

Q4: Determine Z and V for steam at (250°C) and (2000 KPa) by the following:

a) The truncated virial eq with three terms when the experiments values of virial coefficients:

$$B = -152.5 \text{ cm}^3/\text{mol}; \quad C = -5800 \text{ cm}^6/\text{mol}^2$$

b) The truncated virial equation with two terms, value of B is  $-152.5 \text{ cm}^3/\text{mol}$ .

Q5: One Kilo mol  $\text{CO}_2$  occupies a value of  $0.381 \text{ m}^3$  at  $313 \text{ K}$ . Compare the pressure given by:

- Ideal gas equation
- Van der Waals equation

Take constants to be:  $a = 0.365 \text{ N.m}^4/\text{mol}^2$  and  $b = 4.28 \times 10^{-5} \text{ m}^3/\text{mol}$ .

Q6: Calculate the compressibility factor and molar volume for methanol vapor at  $(500 \text{ K})$  and  $(10 \text{ bar})$  by using the following equations. Experimental values of virial coefficients are,  $B = -2.19 \times 10^{-4} \text{ m}^3/\text{mol}$ ;  $C = -1.73 \times 10^{-8} \text{ m}^6/\text{mol}^2$ . The critical temp and pressure are  $512.6 \text{ K}$  and  $81 \text{ bar}$ .

- Truncated form of virial equation, three term.
- Redlich - Kwong equation.

Q7: Calculate  $Z$  and  $V$  for ethylene at  $298.15 \text{ K}$  ( $25^\circ\text{C}$ ) and  $(12 \text{ bar})$  by generalized Pitzer correlation of virial equation. The critical temperature and pressure are  $282.3 \text{ K}$  and  $50.4 \text{ bar}$ ,  $\omega = 0.087$ .

$$B_0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B_1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

Q8: Calculate the molar volume of saturated liquid by the Redlich/Kwong equation and compare result with values found by suitable generalized correlation proposed by Rackett, for the propane at 313.15 K and  $p^{sat} = 13.71$  bar;  $T_c = 369.8$  K and  $p_c = 42.48$  bar,  $V_c = 200 \frac{\text{cm}^3}{\text{mol}}$ ,  $Z_c = 0.276$ .

## Chapter Three

### The Second Law of thermodynamics

The second law of thermodynamics is just generalisation of our experiences with spontaneous process and can be stated in a number of ways:

- 1- Heat cannot by itself pass from a cold to a hot body.
- 2- All spontaneous processes are, to some extent, irreversible and are accompanied by a degradation of energy.
- 3- Every system, when left to itself, will on the average change toward a system of maximum probability.
- 4- Kelvin-Planck statement. It is impossible to construct an engine that operating continuously, will produce no effect other than the transfer of heat from a single thermal reservoir at a uniform temperature and the performance of an equal amount of work.
- 5- Clausius statement. It is impossible to construct a heat pump that operating continuously, will produce no effect other than the transfer of heat from a lower temperature body to a higher temperature body.

## 1. Heat Engines and the Carnot Cycle

A heat engine is a device, considered a closed system operating in a cyclic manner, which is supplied with heat and performs work. Because heat cannot be completely converted into work, a portion of the input heat must be rejected to a low temperature reservoir (ambient air or cooling water). There is at least one input and one outflow of heat associated with the device. Any cyclic process can form the basis of a heat engine.

From the study of heat engines, devices or machines that produce work from heat in a cyclic process. An example is a steam power plant in which the working fluid (steam) periodically returns to its original state.

A power plant the cycle (in its simplest form) consists of following steps:

- Liquid water at ambient temperature is pumped into a boiler at high pressure.
- Heat from a fuel (heat of combustion of a fuel or heat) is transferred in the boiler to the water, converting it to high-temperature steam at the boiler pressure.
- Energy is transferred as shaft work from the steam to the surroundings by a device such as a turbine, in which the steam expands to reduced pressure and temperature.

Exhaust steam from the turbine is condensed by transfer of heat to the surroundings, producing liquid water for return to the boiler, thus completing the cycle.

Essential to all heat-engine cycles are absorption of heat into the system at a high temperature, rejection of heat to the surroundings at a lower temperature and production of work. In operation, the working fluid of a heat engine absorbs heat  $|Q_H|$  from a hot reservoir, produces a net amount of work  $|W|$ , discards heat  $|Q_C|$  to a cold reservoir, and returns to its initial state. The first law therefore reduces to:

$$|W| = |Q_H| - |Q_C|$$

The thermal efficiency of the engine is defined as:

$$\gamma \equiv \frac{\text{net work output}}{\text{heat absorbed}}$$

$$\therefore \gamma = \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|}$$

or

$$\boxed{\gamma = 1 - \frac{|Q_C|}{|Q_H|}} \quad \text{for Heat Engine}$$

The actual meaning of the "heat engine" is a thermodynamic system which operating in cycle receives a net amount of heat and delivers a net amount of work.



Diagrammatically the principle of heat engines is shown in figure:-

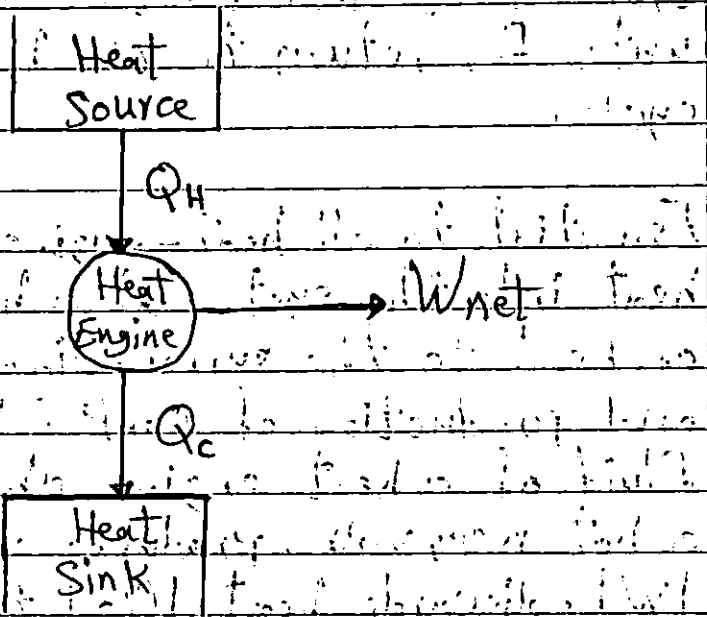


Figure : Principle of Heat Engine

The actual meaning of "Heat pump" is also thermodynamic system which operating in a cycle removes heat from the low temperature body to high temperature body by the application of external energy in the form of work on the pump.

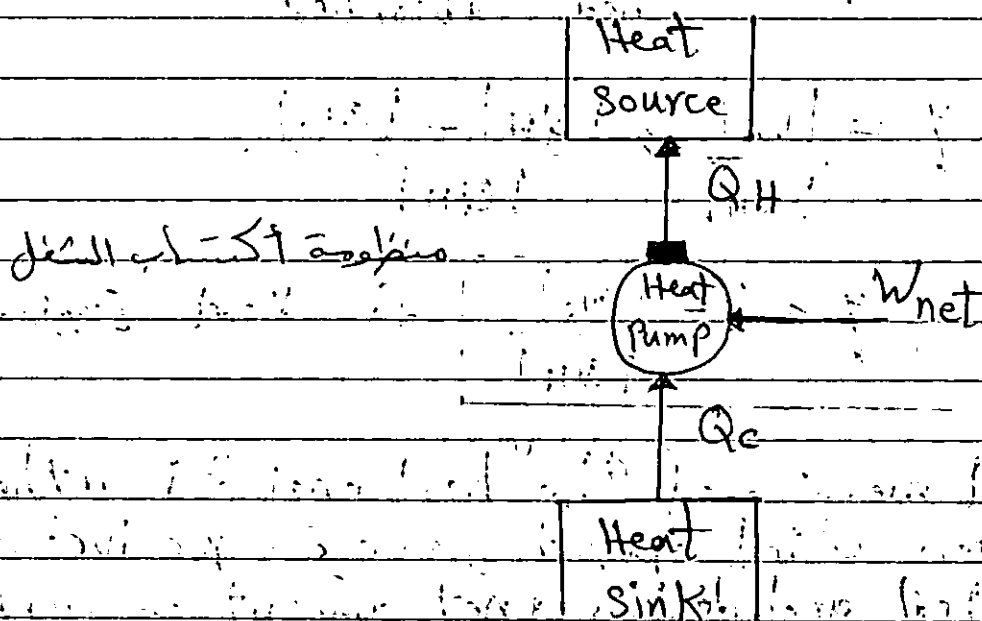


Figure : Principle of Heat pump.

1) The performance of heat pump is indicated by C.O.P. defined as

$$\text{C.O.P. for heat pump} = \frac{Q_H}{W_{\text{net}}}$$

$$\therefore |W| = |Q_H| - |Q_C|$$

$$\therefore \boxed{\text{C.O.P.} = \frac{|Q_H|}{|Q_H| - |Q_C|}} = \frac{|Q_H|}{|Q_H| - |Q_C|}$$

2) The thermal efficiency of 100% is not possible of heat engines, its depend on the degree of reversibility of operation. A heat engine operating in a completely reversible manner is very special and is called "Carnot engine".

A Carnot engine operates between two heat reservoirs in such a way that all heat absorbed at the constant temperature of the hot reservoir and all heat rejected at the constant temperature of the cold reservoir. Any reversible engine operating between two heat reservoirs is a Carnot engine, an engine operating on a different cycle must necessarily transfer heat across temperature differences and therefore cannot be reversible.

Since a Carnot engine is reversible, it may be operated in reverse; the Carnot cycle is then traversed in the opposite direction, and it becomes a reversible refrigeration cycle for which the quantities  $|Q_H|$ ,  $|Q_C|$ , and

$|W|$  are the same as for the engine cycle but are reversed in direction

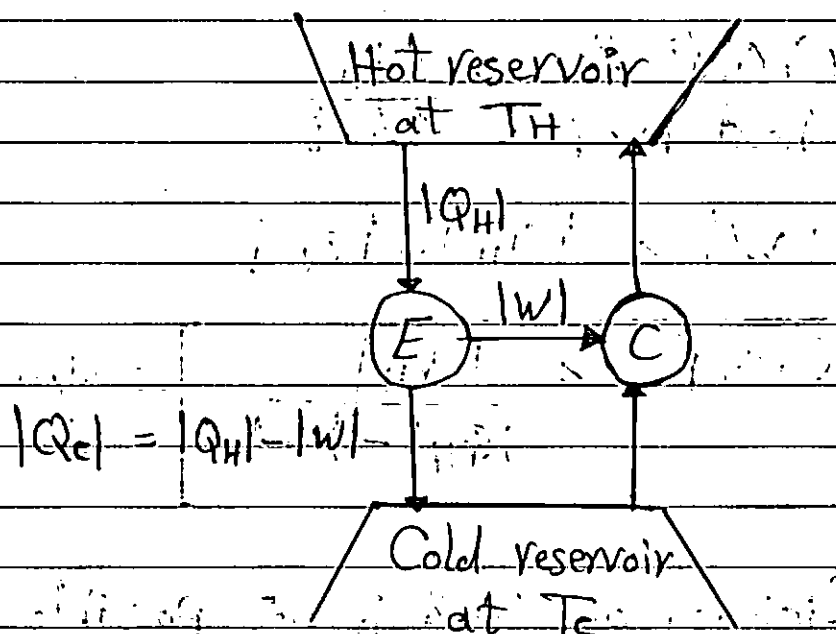


Figure 1: Engine "E" operating a Carnot refrigerator "C."

The four steps that make up a Carnot cycle are performed in the following order:

- 1) A system initially in thermal equilibrium with a cold reservoir at  $T_C$ , and undergoes a reversible adiabatic process that causes its temperature to rise to that of a hot reservoir at  $T_H$ .
- 2) The system maintains contact with the hot reservoir at  $T_H$ , and undergoes a reversible isothermal process during which heat  $|Q_H|$  is absorbed from the hot reservoir.
- 3) The system undergoes a reversible adiabatic process in the opposite direction of step 1 that brings its

temperature back to that of the cold reservoir at  $T_c$ .

4) The system maintaining contact with the reservoir at  $T_c$ , and undergoes a reversible isothermal process in the opposite direction of step 2 that returns it to its initial state with rejection of heat  $|Q_c|$  to the cold reservoir.

For two given reservoirs no engine can have a higher thermal efficiency than a Carnot engine.

### Carnot Cycle for Ideal Gas:

A Carnot engine is shown by a P-V diagram in figure:

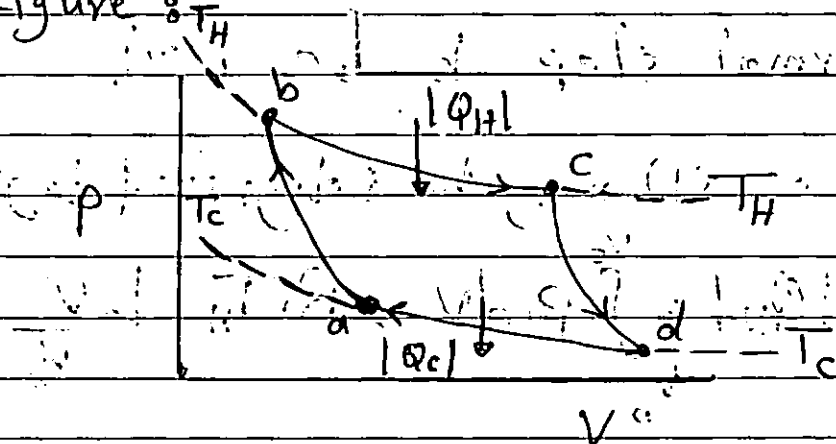


Figure: P-V diagram showing Carnot cycle for an ideal gas.

It consists of four reversible steps:

1)  $a \rightarrow b$  Adiabatic compression until the temperature rises from  $T_c$  to  $T_H$ .

2.)  $b \rightarrow c$  Isothermal expansion to arbitrary point  $c$  with absorption of heat  $|Q_H|$ .

3.)  $c \rightarrow d$  Adiabatic expansion until the temperature decreases to  $T_c$ .

4.)  $d \rightarrow a$  Isothermal compression to the initial state with rejection of heat  $|Q_c|$ .

For any reversible process with an ideal gas as the system, the first law is given by:

$$\Delta U = Q - W$$

$$dQ = C_V dT + P dV \quad \text{(eq. 1)}$$

For the isothermal step  $b \rightarrow c$  with

$P = \frac{R \cdot T_H}{V}$ , eq. (1) may be integrated to give:

$$\therefore |Q_H| = \int_{V_b}^{V_c} P dV = R \cdot T_H \ln \frac{V_c}{V_b}$$

Similarly, for the isothermal step  $d \rightarrow a$  with

$$P = \frac{R \cdot T_c}{V}, \quad Q_{ab} = R \cdot T_c \ln \frac{V_a}{V_d}$$

$$|Q_c| = R \cdot T_c \ln \frac{V_d}{V_a}$$

Therefore  $\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C} \cdot \frac{\ln(V_C/V_b)}{\ln(V_d/V_a)} \dots \text{eq (2)}$

For an adiabatic process  $dQ = 0$ , eq (1) is written.

$$-C_V \cdot dT = P \cdot dV = \frac{R \cdot T}{V} \cdot dV$$

or 
$$-\frac{C_V}{R} \cdot \frac{dT}{T} = \frac{dV}{V}$$

For step  $a \rightarrow b$ , integration gives

$$\int_{T_C}^{T_H} \frac{C_V}{R} \cdot \frac{dT}{T} = \ln \frac{V_a}{V_b}$$

Similarly, for step  $c \rightarrow d$ ,

$$\int_{T_C}^{T_H} \frac{C_V}{R} \cdot \frac{dT}{T} = \ln \frac{V_d}{V_c}$$

Since the left-hand sides of these two eqs are the same,

$$\therefore \ln \frac{V_a}{V_b} = \ln \frac{V_d}{V_c}$$

This may also be written:

$$\ln \frac{V_c}{V_b} = \ln \frac{V_d}{V_a}$$

Eq. (2) now becomes:

$$\boxed{\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C}}$$

For Carnot cycle; ideal gas

and  $\eta = 1 - \frac{|Q_c|}{|Q_H|}$

(2)  $\eta = 1 - \frac{T_c}{T_H}$

$$\eta = 1 - \frac{T_c}{T_H}$$

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or  $\frac{|W|}{|Q_H|} = \frac{T_H - T_c}{T_H}$

$$\frac{|W|}{|Q_H|} = \frac{T_H - T_c}{T_H}$$

Example:

Cubes of ice are manufactured from water initially at 273 K. Assume that surroundings are at 300 K and heat at 300 K is 753,710 J. Compute the minimum work required.

Solution:

$$\frac{|W|}{|Q_H|} = \frac{T_H - T_c}{T_H}$$

$$|W_{\min}| = \left[ \frac{300 - 273}{300} \right] \times 753,710 \text{ J}$$

$$= 678,330.9 \text{ J}$$

$$\frac{|W|}{|Q_H|} = \frac{T_H - T_c}{T_H}$$

$$\frac{|W|}{|Q_H|} = \frac{T_H - T_c}{T_H}$$

Example: A central power plant rated at 800000 Kw, generated steam at 585 K and discards heat to a river at 295 K. If the thermal efficiency of the plant is 70 percent of the maximum possible value, how much heat is discarded to the river at rated power?

Solution: Max. thermal eff. (Carnot's eff.)

$$\eta = 1 - \frac{T_c}{T_H}$$

Taken  $T_H$  : steam generation Temp.

$T_c$  : river Temp.

$$\eta_{\text{max theoretical}} = 1 - \frac{295}{585} = 0.4957$$

Actual thermal efficiency:

$$\eta_{\text{act}} = 0.7 \times 0.4957 = 0.3470$$

By definition

$$\eta = \frac{W}{|Q_H|}$$

$$\therefore W = |Q_H| - |Q_c| \Rightarrow |Q_H| = W + |Q_c|$$

$$\therefore \eta = \frac{W}{W + |Q_c|} \Rightarrow |Q_c| = \left( \frac{1 - \eta}{\eta} \right) * W$$

$$\therefore |Q_c| = \left( \frac{1 - 0.347}{0.347} \right) * 800000$$

$$= 1505500 \text{ Kw or (KJ/sec).}$$



Example :- One Kilogram of water is heated in a heat pump from a temperature of 294 K to boiling point of 373 K and completely vaporized. The latent heat of vaporisation = 1960 KJ/Kg. Determine

- The <sup>minimum</sup> amount of work required.
- The heat transferred is unavailable for transformation to work at a temperature 294 K.

solution :- The work required will be minimum for an ideal Carnot heat engine

$$\begin{aligned} \text{C.O.P. "heat pump"} &= \frac{|Q_H|}{|W|} = \frac{T_H}{T_H - T_C} \\ &= \frac{373}{373 - 294} = 4.72 \end{aligned}$$

$$\begin{aligned} \text{a) } |W| &= \frac{|Q_H|}{\text{C.O.P.}} = \frac{1960 \frac{\text{KJ}}{\text{kg}} \times 1 \text{ kg}}{4.72} \\ &= 415.25 \text{ KJ} \end{aligned}$$

$$\text{b) } |W| = |Q_H| - |Q_C|$$

$$|Q_C| = |Q_H| - |W|$$

$$= 1960 \text{ KJ} - 415.25$$

$$= 1544.75 \text{ KJ}$$

Entropy: It is the most important thermodynamic property, which serves as a measure of the unavailability or degradation of energy.

The entropy of a system is affected only by the nature of the matter under consideration and the state in which it exists. It is not affected by the external position of the body or its motion relative to other bodies.

The entropy of the system is increased by the addition of heat through any mechanism or from source.

The increase in entropy accompanying the addition of a given amount of heat to a system with lowering the temperature at which the heat is added, and it leads to a great degradation of energy than at a higher temperature.

In addition, in order to complete the definition of entropy, the nature of the process should also be specified. The change in entropy (a state function) is dependent only on the initial and final states and not on the path. So, the amount of heat transferred to measure the increase in entropy through the term  $Q/T$  is the degradation of higher forms of energy into heat, which is possible only in a reversible process. Therefore be measured as  $Q_R/T$ , where  $Q_R$  is the heat transferred when the process is occurring reversibly.

To summarise, the definition of entropy requires

the following specifications:

- 1) The amount of heat transferred.
- 2) The temperature level at which the transfer occurs.
- 3) The nature of the process, whether reversible or irreversible.

To comply with these requirements, define entropy change in a process as

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

The entropy change of any system undergoing a reversible process, and integrated gives

$$\Delta S = \int \frac{dQ_R}{T}$$

When a process is reversible and adiabatic ( $dQ_R = 0$ ), hence  $dS = 0$ .

The entropy of the system remains constant ( $\Delta S = 0$ ) and the process is said to be "isentropic".

The mathematical statement of the second law is that every process proceeds in such a direction the total entropy change  $\Delta S_{tot}$  associated with it is always positive, the process is possible.

## Entropy changes of an Ideal Gas

By the first law for one mole or unit mass of fluid:

$$dU = dQ - dW$$

For a reversible process, this equation becomes:

$$dU = dQ_R - p.dV$$

By the definition of enthalpy,

$$H = U + pV$$

whence

$$dH = dU + p.dV + V.dp$$

Substitution for  $dU$  gives:

$$dH = dQ_R - p.dV + p.dV + V.dp$$

$$dQ_R = dH - V.dp$$

For an ideal gas,  $dH = c_p^ig . dT$  and  $V = R.T/p$

$$dQ_R = c_p^ig . dT - \frac{R.T}{p} . dp$$

(T) is a variable

or

$$\frac{dQ_R}{T} = c_p^ig . \frac{dT}{T} - R . \frac{dp}{p}$$

$$dS = c_p^ig . \frac{dT}{T} - R . \frac{dp}{p}$$

Integration from an initial state at condition  $T_1$  and  $P_1$  to a final state at conditions  $T_2$  and  $P_2$  gives:

$$\Delta S = \int_{T_1}^{T_2} c_p^{ig} \cdot \frac{dT}{T} - R \cdot \ln \frac{P_2}{P_1}$$

$$c_{p_{ms}}^{ig} = \frac{\int_{T_1}^{T_2} c_p^{ig} \cdot dT / T}{\ln(T_2 / T_1)}$$

"ms": denotes a mean value specific to entropy calculations.

$$\frac{c_{p_{ms}}^{ig}}{R} = A + B \cdot T_{lm} + T_{am} \cdot T_{lm} \left[ \frac{C + D}{(T_1 \cdot T_2)^2} \right]$$

where:

$T_{am}$ : is the arithmetic mean temperature

$T_{lm}$ : is the logarithmic mean temperature

$$T_{am} = \frac{T_1 + T_2}{2}$$

$$T_{lm} = \frac{T_2 - T_1}{\ln(T_2 / T_1)}$$

Solving the integration  $\int_{T_1}^{T_2} c_p^{ig} \cdot \frac{dT}{T} = c_{p_{ms}}^{ig} \cdot \ln \frac{T_2}{T_1}$

Then

$$\Delta S = c_{p_{ms}}^{ig} \cdot \ln \frac{T_2}{T_1} - R \cdot \ln \frac{P_2}{P_1}$$

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And the process that  $\Delta S_{tot} \rightarrow 0$ , approaching zero is become reversible.

No process is possible for which  $\Delta S_{tot}$  is negative.

Hence, the general equations:

$$\Delta S_{tot} \geq 0$$

$\Delta S_{tot} (+) \Rightarrow$  possible

$\Delta S_{tot} (0) \Rightarrow$  reversible

$\Delta S_{tot} (-) \Rightarrow$  impossible

For Carnot Engine:

$$\frac{|Q_H|}{T_H} = \frac{|Q_C|}{T_C} \Rightarrow \frac{Q_H}{T_H} = - \frac{Q_C}{T_C}$$

$$\text{or } \frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0$$

The heat quantities refer to the engine (heat reservoirs), the value of  $Q_H$  is positive and  $Q_C$  is negative. The equivalent equation written without absolute value signs. Thus for a complete cycle of a Carnot engine, the quantities  $Q/T$  associated with the absorption rejection of heat by working fluid of engine sum zero.

For the entire cycle,  $\frac{dQ_H}{T_H} + \frac{dQ_C}{T_C} = 0$

Integration gives the sum of all quantities  $\frac{dQ}{T}$

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

$\oint$ : The circle in the integral sign that integration over a complete cycle

$Q_R$ : the subscript "R" indicates that equation is valid only for reversible cycles

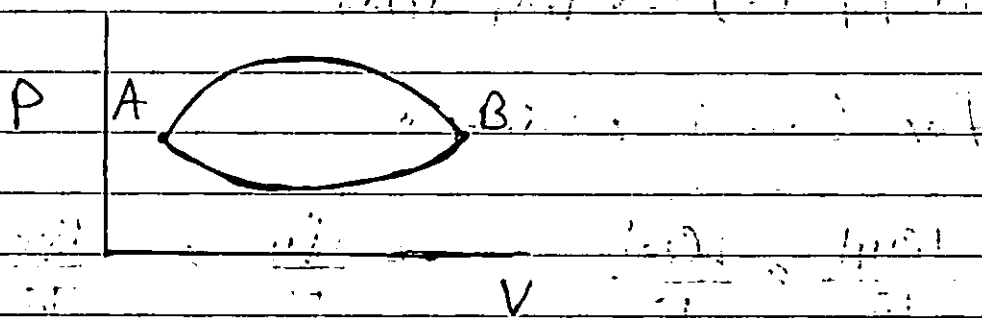


Figure: Two reversible paths joining equilibrium states A and B.

## 6/ Liquid Entropy (S) to be raised to unit mass of vapor

Consider unit mass of a liquid which will ultimately be raised to unit mass of vapor at constant pressure. For the unit mass of liquid,

$$\therefore dQ = c_{p_l} dT \quad \text{--- (1)}$$

where:

$c_{p_l}$  = Specific heat capacity of the liquid at constant pressure.

Dividing eq (1) throughout by  $T$ , then,

$$\frac{dQ}{T} = c_{p_l} \frac{dT}{T}$$

Since  $ds = \frac{dQ}{T}$

$\therefore$  For this case,  $ds = c_{p_l} \frac{dT}{T}$

Integrating this equation from initial state (1) to final state (2)

$$\int_{S_1}^{S_2} ds = c_{p_l} \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\boxed{[S_2 - S_1] = c_{p_l} \cdot \ln \frac{T_2}{T_1}}$$

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Example: (0.3 Kg) of air at (350 K N/m<sup>2</sup>) and (35 °C) receives heat at constant volume until its pressure becomes (700 K N/m<sup>2</sup>). Determine the change of entropy during each process.  
Take  $c_p = 1.006 \text{ KJ/Kg} \cdot \text{K}$ ,  $c_v = 0.717 \text{ KJ/Kg} \cdot \text{K}$ .

Solution:  $R = c_p - c_v$

$$= 1.006 - 0.717$$

$$= 0.289 \text{ KJ/Kg} \cdot \text{K}$$

$$P_2/T_2 = P_1/T_1$$

$$\therefore T_2 = T_1 \times \frac{P_2}{P_1}$$

$$= 308 \text{ K} \times \frac{700}{350}$$

$$T_2 = 616 \text{ K}$$

$$\Delta S = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

$$= 1.006 \ln \frac{616}{308} - 0.289 \ln \frac{700}{350}$$

$$= 0.496 \text{ KJ/Kg} \cdot \text{K}$$

$$\Delta S = 0.496 \times 0.3 \text{ Kg}$$

$$= 0.1488 \text{ KJ/K}$$

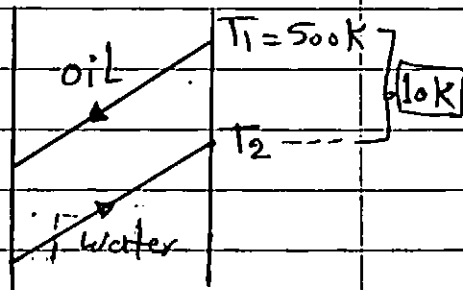
Note: assume air as ideal gas and  $c_p^{\text{ig}} = c_p$  for air; So, R constant was calculated in order to get the units required (KJ/Kg · K).

Example: Oil at 500 K is to be cooled at 5000 kg in a counter current exchanger using cold water available at 295 K. A temperature approach of 10 K is to be maintained at both ends of the exchanger. The specific heats of oil and water are respectively 3.2 and 4.2 kJ/kg.K. Determine the total entropy change in the process.

Solution: The mass of water can be determined by an enthalpy balance.

$$m_{\text{water}} \times c_p (T_2 - T_1) = 5000 \text{ kg} \times c_p (T_1 - T_2)$$

The inlet and exit temperature of oil are 500 K and 305 K.



The inlet and exit temperature of the water are 295 K and 490 K.

$$\therefore m \times 4.2 \times (490 - 295) = 5000 \times 3.2 (500 - 305)$$

$$m_{\text{water}} = 3809.5 \text{ kg}$$

$$\Delta S = m \cdot c_p \cdot \ln \frac{T_2}{T_1} = R \cdot \ln \frac{P_2}{P_1} \quad \text{Constant Pressure}$$

$$\Delta S_{\text{oil}} = 5000 \times 3.2 \times \ln \frac{305}{500} = -7908.7 \text{ kJ/K}$$

$$\Delta S_{\text{water}} = 3809.5 \times 4.2 \times \ln \frac{490}{295} = 8118.8 \text{ kJ/K}$$

$$(\Delta S)_{\text{tot}} = 8118.8 - 7908.7 = 210.1 \text{ kJ/K} \quad \text{"Positive"}$$

Example: Methane gas at 550 K and 5 bar undergoes a reversible adiabatic expansion to 1 bar. Assuming methane an ideal gas at these conditions, what is its final temperature?

Solution: For this process,  $\Delta S = 0$  "adiabatic"

$$\frac{C_{p,m}^{ig}}{R} \ln \frac{T_2}{T_1} = \ln \frac{P_2}{P_1}$$

$$= \ln \frac{1}{5} = -1.6094$$

Since  $C_{p,m}^{ig}$  depends on  $T_2$ , we arrange this equation for iteration solution,

$$\ln \frac{T_2}{T_1} = \frac{-1.6094}{C_{p,m}^{ig}/R}$$

$$T_2 = T_1 \exp \left( \frac{-1.6094}{C_{p,m}^{ig}/R} \right) \quad \text{--- (a)}$$

$(C_{p,m}^{ig}/R)$  is given by eq. above with constants from table (4.1) in hand book.

$$\frac{C_{p,m}^{ig}}{R} = 1.702 + 9.081 \times 10^{-3} T_{2m} - 2.164 \times 10^{-6} T_{2m}^2 \quad \text{--- (b)}$$

$$T_{2m} = \frac{550 + T_2}{2}$$

$$T_{2m} = \frac{550 - T_2}{2}$$

$$\ln (550/T_2)$$

with initial value  $T_2 < 550 \Rightarrow$  final value  $T_2 = 411.34 \text{ K}$

## Tutorial Sheet No. (3)

Q1: A particular power plant operates with a heat source reservoir at  $300^\circ\text{C}$  and a heat sink reservoir at  $25^\circ\text{C}$ . It has a thermal efficiency equal to 60 percent of the Carnot engine thermal efficiency for the same temperature.

- What is the thermal efficiency of the plant?
- To what temperature must the heat source reservoir be raised to increase the thermal efficiency of the plant to 40 percent?

Q2: A rigid vessel of  $0.05\text{m}^3$  volume contains an ideal gas,  $C_V = (5/2)R$  at  $500\text{K}$  and  $1\text{bar}$ .

- If heat in the amount of  $12,000\text{J}$  is transferred to the gas, determine its entropy change.
- If the vessel is fitted with a stirrer that is rotated by a shaft so that work in the amount of  $12,000\text{J}$  is done on the gas, what is the entropy change of the gas if the process is adiabatic? what is  $\Delta S_{\text{tot}}$ ? what is the irreversible feature of the process?

Q3: For an ideal gas with constant heat capacities show that:

- For a temperature increase from  $T_1$  to  $T_2$ ,  $\Delta S$  of the gas is greater when the change occurs at constant pressure than when it occurs at constant volume.

b) For a pressure change from  $P_1$  to  $P_2$ , the sign of  $\Delta S$  of an isothermal change is opposite that for a constant volume change.

Q4: One mole of an ideal gas,  $c_p = (7/2)R$  and  $c_v = (5/2)R$ , is compressed adiabatically in a piston/cylinder device from 1 bar and  $40^\circ\text{C}$  to 4 bar. The process is irreversible and requires 30 percent more work than a reversible adiabatic compression from the same initial state to the same final pressure. What is the entropy change of the gas?

Q5: If heat in the amount of  $5.275 \times 10^5 \text{ KJ}$  is added to 13.61 kgmol of methane initially at  $210^\circ\text{C}$  in a steady flow process at approximately atmospheric pressure, what is its entropy change?

Q6: A device with no moving parts is claimed to provide a steady stream of chilled air at  $(-20^\circ\text{C})$  and (1 bar). The feed to the device is "compressed air" at  $25^\circ\text{C}$  and 4 bar. In addition to the stream of chilled air, a second stream of air flows at an equal mass rate from the device at  $70^\circ\text{C}$  and 1 bar. Are these claims in violation of the second law? Assume that air is an ideal gas for which  $c_p = (7/2)R$ .

Q7: A steel casting [ $c_p = 0.5 \text{ KJ/Kg.K}$ ] weighing (40 kg) and at a temperature of  $(450^\circ\text{C})$  is quenched in (150 kg) of oil [ $c_p = 2.5 \text{ KJ/Kg.K}$ ] at  $(25^\circ\text{C})$ . If there are no heat losses, what is the change in entropy of  
a) the castings, b) the oil, c) both considered together.

## Chapter Four Thermodynamic Properties of Fluids

### Introduction

It is well known that a gaseous material approach ideal behaviour at low pressure and high temperature so that the PVT relations of gases are given with satisfactory accuracy by the ideal gas law. Alternatively the assumption of ideal gas behaviour may cause errors as great as at high pressure in the absence of experimental data.

This chapter deals with the use of the corresponding states principle to estimate the values of thermodynamic properties such as enthalpy and entropy changes in addition to  $\Delta U$  and  $\Delta G$  for real behaviour when experimental PVT data are lacking.

Our initial purpose in this chapter is to develop from the first and second laws the fundamental property relations which the mathematical structure of thermodynamics. We then discuss the diagrams and tables by which both measured and calculated property values are presented for convenient use. Then developed generalized correlations which allow estimates of property values.

$$2T - U = P$$

$$2T - U = 0$$

## Relationships Among Thermodynamic Properties for Homogeneous Phase :

The first law for "a closed system" of  $n$  moles is given by :

$$d(nU) = dQ - dW$$

for the special case of a "reversible process",

$$d(nU) = dQ_{\text{rev}} - dW_{\text{rev}}$$

$$\therefore dW_{\text{rev}} = P \cdot d(nV)$$

$$\text{and } dQ_{\text{rev}} = T \cdot d(nS)$$

These three equations combine to give :

$$d(nU) = T \cdot d(nS) - P \cdot d(nV)$$

All of the primary thermodynamic properties [ $P$ ,  $V$ ,  $T$ ,  $U$ , and  $S$ ] are included in this equation above.

The enthalpy was defined as

$$H = U + PV$$

Additional properties also defined, (Helmholtz energy)

$$A = U - TS$$

and (Gibbs energy)

$$G = H - TS$$

Upon multiplication by  $(n)$ ,  $nH = nU + P(nV)$

Differentiation gives:

$$d(nH) = d(nU) + P \cdot d(nV) + (nV) \cdot dP$$

When  $d(nU)$  is replaced by equation above, this reduced to:

$$d(nH) = T \cdot d(nS) - P \cdot d(nV) + P \cdot d(nV) + (nV) \cdot dP$$

$$\therefore d(nH) = T \cdot d(nS) + (nV) \cdot dP$$

Similarly, find:  $d(nA) = d(nU) - T \cdot d(nS) - (nS) \cdot dT$

Eliminating  $d(nU)$ , get:

$$d(nA) = T \cdot d(nS) - P \cdot d(nV) - T \cdot d(nS) - (nS) \cdot dT$$

$$d(nA) = -P \cdot d(nV) - (nS) \cdot dT$$

In analogous, gives

$$d(nG) = d(nH) - T \cdot d(nS) - (nS) \cdot dT$$

$d(nH)$  was replaced to give:

$$d(nG) = T \cdot d(nS) + (nV) \cdot dP - T \cdot d(nS) - (nS) \cdot dT$$

$$\therefore d(nG) = (nV) \cdot dP - (nS) \cdot dT$$



For immediate application of these equations is to one mole (or to a unit mass) of homogeneous fluid of constant composition. They simplify to:

$$dU = T \cdot dS - P \cdot dV$$

$$dH = T \cdot dS + V \cdot dP$$

$$dA = -P \cdot dV - S \cdot dT$$

$$dG = V \cdot dP - S \cdot dT$$

The PVT behavior of a fluid in the [ideal gas state] is expressed by the equations:

$$P V^ig = R \cdot T$$

$$\text{and } \left( \frac{\partial V^ig}{\partial T} \right)_P = \frac{R}{P}$$

$$dH^ig = c_p^ig \cdot dT$$

$$dS^ig = c_p^ig \cdot \frac{dT}{T} - \frac{R}{P} \cdot dP$$

where:

$V^ig$  is the molar volume of an ideal gas at temperature  $T$  and pressure  $P$ .

These equations merely results derived for ideal gas.

For liquid: not near the critical point, the volume itself is small, as are both  $\beta$  and  $K$  (i.e.) volume expansivity and isothermal compressibility, are usually applied only to liquids.

Thus at most conditions pressure has little effect on the entropy, enthalpy and internal energy of liquids and its independent of  $P$ , that is  $K$  is zero.

$$K \equiv (-) \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

and 
$$\beta \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

The corresponding derivative for enthalpy and entropy of liquids:

$$dH = c_p \cdot dT + V(1 - \beta \cdot T) \cdot dP$$

and

$$dS = c_p \cdot \frac{dT}{T} - \beta \cdot V \cdot dP$$

Integration of these equations with arithmetic average is satisfactory. The integrated forms result:

$$\Delta H = c_p^{\text{ave}} (T_2 - T_1) + V^{\text{ave}} (1 - \beta^{\text{ave}} \cdot T_2) (P_2 - P_1)$$

$$\Delta S = c_p^{\text{ave}} \ln \frac{T_2}{T_1} - \beta^{\text{ave}} \cdot V^{\text{ave}} (P_2 - P_1)$$

where,

$\beta$  and  $V$  are weak functions of pressure of liquid.

Example: Determine the enthalpy and entropy changes for liquid water for a change state from [1 bar and 25°C] to [1000 bar and 50°C]. The following data for water are available.

T (°C)	P (bar)	C <sub>p</sub> (J/mol.K)	V (cm <sup>3</sup> /mol)	β (K <sup>-1</sup> )
25	1	75.305	18.075	256 × 10 <sup>-6</sup>
25	1000	—	17.358	366 × 10 <sup>-6</sup>
50	1	75.314	18.240	458 × 10 <sup>-6</sup>
50	1000	—	17.535	568 × 10 <sup>-6</sup>

Solution:

For P = 1 bar

$$C_p^{ave} = \frac{75.305 + 75.314}{2} = 75.310 \text{ J/mol.K}$$

and for

$$T = 50^\circ\text{C}$$

$$V^{ave} = \frac{18.240 + 17.535}{2} = 17.888 \text{ cm}^3/\text{mol}$$

$$\beta^{ave} = \frac{(458 + 568) \times 10^{-6}}{2} \text{ K}^{-1} = 513 \times 10^{-6}$$

$$\Delta H = C_p^{ave} (T_2 - T_1) + V^{ave} (1 - \beta^{ave} T_2) (P_2 - P_1)$$

$$= 75.310 (323.15 - 298.15) + 17.888 \left[ 1 - (513 \times 10^{-6}) (323.15) \right]$$

$$\times (1000 - 1) \times \frac{100 \text{ cm}^3 \times \text{bar}}{1 \text{ J}}$$

$$= 1883 + 1491$$

$$= 3374 \text{ J/mol}$$

$$\Delta S = c_p^{\text{ave}} \ln \frac{T_2}{T_1} - \beta^{\text{ave}} V^{\text{ave}} (P_2 - P_1)$$

$$= 75.31 \ln \frac{323.15}{298.15} - (5.13 \times 10^{-6}) (17.888) (1000 - 1)$$

$$= 6.06 - 0.92$$

$$= 5.14 \text{ J/mol.K}$$

## Residual Properties:

A general definition for residual properties:

$$M^R = M - M^{\text{ig}}$$

where

$M$  is any properties such as  $G, V, H$ ,

for example

$$G^R = G - G^{\text{ig}}$$

$$V^R = V - V^{\text{ig}}$$

$$S^R = S - S^{\text{ig}}$$

Then

$$H = H_0^{\text{ig}} + c_{p,mh}^{\text{ig}} (T - T_0) + H^R$$

and

$$S = S_0^{\text{ig}} + c_{p,ms}^{\text{ig}} \ln \frac{T}{T_0} - R \ln \frac{P}{P_0} + S^R$$

These  $H$  and  $S$  are found from the corresponding ideal-gas and residual properties by simple addition.

when the property in the actual and ideal gas values at the same temperature and pressure.

The residual volume:  $V^R = V - \frac{R \cdot T}{P}$

Since  $V_{act} = \frac{Z \cdot R \cdot T}{P}$ , the residual volume and

the compressibility factor are related:

$$V^R = \frac{R \cdot T}{P} (Z - 1)$$

This is direct connection with experiment that makes residual properties essential to the practical application of thermodynamics.

Example: Calculate the enthalpy and entropy of saturated isobutane vapor at (360 K) from the following information:  $H^R = -2,841.3 \text{ J/mole}$  and  $S^R = -5.734 \text{ J/mole} \cdot \text{K}$

1) The vapor pressure of isobutane at 360 is 15.41 bar.

2) Set  $H_o^{ig} = 18,115.0 \text{ J/mole}$  and  $S_o^{ig} = 295.976 \text{ J/mole} \cdot \text{K}$

for the ideal gas reference state at 300 K and 1 bar.

3) The ideal gas heat capacity of isobutane vapor in the temperature range of interest is given by:

$$\frac{C_{p,m}^{ig}}{R} = A + B \cdot T_{km}$$

$$A = 1.7765$$

$$B = 33.037 \times 10^{-3}$$

$$\frac{C_{p,m}^{ig}}{R} = A + B \cdot T_{km}$$

A & B as the same values.

Solution:  $T_{am} = \frac{T_1 + T_2}{2} = \frac{300 + 360}{2} = 330 \text{ K}$

$T_{2m} = \frac{T_2 - T_1}{\ln(T_2/T_1)} = \frac{(360 - 300)}{\ln(360/300)} = 329.09 \text{ K}$

$\frac{C_{p_{mh}}}{R} = 1.7765 + 33.037 \times 10^{-3} \times 330$

$= 12.679$

and

$\frac{C_{p_{ms}}}{R} = 1.7765 + 33.037 \times 10^{-3} \times 329.09$

$= 12.649$

$H = H_0^{ig} + C_{p_{mh}}^{ig} (T - T_0) + H^R$

$= 18,115.0 + (12.679)(8.314)(360 - 300) - 2,841.3$

$= 21,598.5 \text{ J/mol}$

and

$S = S_0^{ig} + C_{p_{ms}}^{ig} \ln \frac{T}{T_0} - R \ln \frac{P}{P_0} + S^R$

$= 295.976 + (12.649)(8.314) \ln \frac{360}{300} - 8.314 \times$

$\ln \frac{15.41}{1} = 5.734$

$= 286.676 \text{ J/mol.K}$

The accurate calculation of thermodynamic Properties for construction of a table or diagram is an exacting task. Moreover, data are frequently incomplete, and are extended by interpolation and extrapolation.

## Two-Phase Systems :

The PT diagram shows curves representing phase boundaries for a pure substance. A phase transition at constant temperature and pressure occurs when these curves are crossed and caused a property change. Thus the molar or specific volume of a saturated liquid is very different from that for saturated vapor at the same  $T$  and  $P$ , this is true for internal energy, enthalpy and entropy.

If a differential amount of liquid is caused to evaporate at constant temperature and pressure,  $dG=0$ , and this requires the molar Gibbs energy of the vapour to be identical with that of the liquid. More general for two phases  $\alpha$  and  $\beta$  of a pure species at equilibrium,

$$G^{\alpha} = G^{\beta}$$

where ;

$G^{\alpha}$  and  $G^{\beta}$  : are the molar Gibbs energies of the individual phases.

The equations that holds throughout this change from liquid to vapor are :

## Clapeyron Equation :

If temperature of a two-phase system is changed, then the pressure must also change in accord with the relation between vapor pressure and temperature.

For the particularly important case of phase transition from liquid (L) to vapor (V), it is written:

$$\frac{dp^{\text{sat}}}{dT} = \frac{\Delta H^{L,V}}{T \cdot \Delta V^{L,V}}$$

"Clapeyron of Vaporization"  
"مع الانتقال"

And

$$\frac{dp^{\text{sat}}}{dT} = \frac{\Delta S^{L,V}}{\Delta V^{L,V}}$$

"بدلالة الإنتروبي"

Antoine Equation:

Which is more satisfactory for general use, has the form:

$$\ln p^{\text{sat}} = A - \frac{B}{(T+C)}$$

A principle advantage of this equation is that values of the constants (A, B and C) are readily available for many species.

Riedel Equation:

The accurate representation of vapor pressure data over a wide temperature range requires an equation of greater complexity as:

$$\ln p^{\text{sat}} = A - \frac{B}{T} + D \cdot \ln T + F \cdot T^6$$

Where:

A, B, D and F are constants.



When a system consists of saturated-liquid and saturated vapor phases coexisting in equilibrium, the total value of any extensive property of the two phases system is the sum of the total properties of the phases. For the volume this relation is as follows:

$$n \cdot V = n^L \cdot V^L + n^V \cdot V^V$$

where:

$V$  is the system volume on a molar basis and total number of moles is

$$n = n^L + n^V$$

$$V = x^L \cdot V^L + x^V \cdot V^V$$

where:

$x^L$  and  $x^V$  represent the fractions of the total system that are liquid and vapor.

Since  $x^L = 1 - x^V$

$$V = (1 - x^V) \cdot V^L + x^V \cdot V^V$$

Analogous equations can be written for the other extensive thermodynamic properties. All of these relations summarized by equation:

$$M = (1 - x^V) \cdot M^L + x^V \cdot M^V$$

where:

$M$  represents  $V, U, H, S, \dots$  etc.

$x^V$  is called "quality".

## ○ Important Terms Relating Steam Formation :

### - Sensible heat of water ( $h_{f1}$ ) :

It is defined as the quantity of heat absorbed by (1 Kg) of water when it is heated from  $[0^{\circ}\text{C}]$  "freezing point" to boiling point. This type of heat is denoted by letter ( $h_{f1}$ ) and its value can be directly read from the steam tables.

○ Note. The value of specific heat of water may be taken as  $(4.18 \text{ KJ/Kg} \cdot \text{K})$  at low pressure but at high pressure it is different from this value.

### - Latent heat or hidden heat ( $h_{fg}$ ) :

It is the amount of heat required to convert water at a given temperature and pressure into steam at the same temperature and pressure. It is expressed by the symbol ( $h_{fg}$ ) and its value is available from steam tables. The value of latent heat is not constant and varies according to pressure variation.

### - Dryness fraction ( $x$ ) :

The term dryness fraction is related with wet steam. It is defined as the ratio of the mass of actual dry steam to the mass of steam containing it. It is usually expressed by the symbol ' $x$ '.

$$x = \frac{m_s}{m_s + m_w}$$

If  $m_s$  = mass of dry steam  
 $m_w$  = mass of liquid water particles in suspension in the steam.

Thus if in (1 Kg) of wet steam (0.9) Kg is the dry steam and (0.1 Kg) water particles then  $x = 0.9$ .

- Total heat or enthalpy of wet steam ( $h$ ):

It is defined as the quantity of heat required to convert (1 Kg) of water at (0°C) into wet steam at constant pressure. It is the sum of total heat of water and the latent heat and this sum is also called enthalpy.

$$h = h_L + x \cdot h_{Lg}$$

If steam is dry and saturated, then  $x = 1$  and

$$h_g = h_L + h_{Lg}$$

- Superheated steam:

When steam is heated after it has become dry and saturated, it is called superheated steam and the process of heating is called superheating, that is always carried out at constant pressure. "Heat of superheat" can be calculated by using the specific heat of superheated steam at constant pressure ( $c_{pg}$ ), then the total heat of superheated steam is given by:

$$h_{sup} = h_L + h_{Lg} + c_{pg}(T_{sup} - T_s)$$

$$\begin{matrix} \text{sensible} & \text{latent} & \text{super} \\ m \cdot c_{pw} \cdot \Delta T & + x \cdot h_{Lg} & + m \cdot c_{pg} \cdot \Delta T \end{matrix} \quad \text{Class}$$

## Thermodynamic Properties of steam and steam tables:

In engineering problem, for any fluid which is used as working fluid, the six basic thermodynamic properties required are:  $P$  (Pressure),  $T$  (temperature),  $V$  (Volume),  $U$  (Internal energy),  $h$  (Enthalpy) and  $s$  (Entropy).

These properties must be known at different pressure for analysing the thermodynamic cycles used for work producing devices.

The values of these properties are determined theoretically or experimentally and are tabulated in the form of tables which are known as "steam tables". The properties of wet steam are then computed from such tabulated data. Also, the values were available for superheated steam. It may be noted that steam has only one saturation temperature at each pressure.

Following are the thermodynamic properties of steam which are tabulated in the form of table:

- $P$  : Absolute pressure (bar or  $\text{KPa}$ ).
- $t_s$  : Saturated temperature ( $^{\circ}\text{C}$ ).
- $h_l$  : Enthalpy of saturated liquid ( $\text{KJ/Kg}$ ).
- $h_{fg}$  : Enthalpy of latent heat of vaporization ( $\text{KJ/Kg}$ ).
- $h_g$  : Enthalpy of saturated vapor (steam) ( $\text{KJ/Kg}$ ).
- $s_l$  : Entropy of saturated liquid ( $\text{KJ/Kg.K}$ ).
- $s_{fg}$  : Entropy of vaporization ( $\text{KJ/Kg.K}$ ).
- $s_g$  : Entropy of saturated vapor ( $\text{KJ/Kg.K}$ ).
- $v_l$  : specific volume of saturated liquid ( $\text{m}^3/\text{Kg}$ ).
- $v_g$  : specific volume of saturated vapor (steam) ( $\text{m}^3/\text{Kg}$ ).

Also,  $h_{lg} = h_g - h_l$  change of enthalpy during evaporation.

$S_{lg} = S_g - S_l$  change of entropy

$V_{lg} = V_g - V_l$  change of volume

The above mentioned properties at different conditions are tabulated in the form of tables as under:

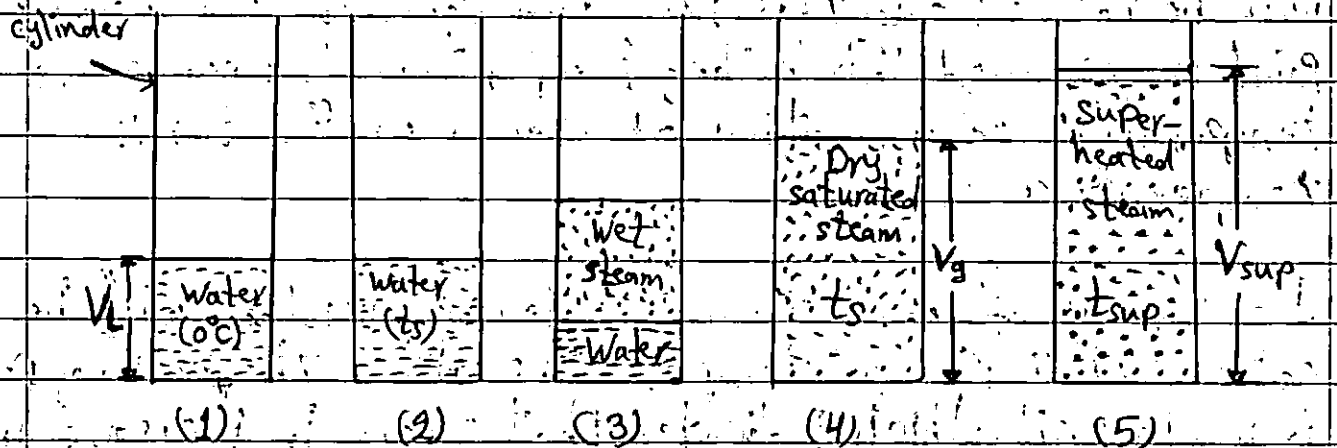
Press. P (bar)	Temp. T (°C)	specific enthalpy (KJ/kg)			specific entropy (KJ/kg.k)			specific volume (m³/kg)	
		$h_l$	$h_{lg}$	$h_g$	$S_l$	$S_{lg}$	$S_g$	$V_l$	$V_g$
1	99.6	417.5	2257.9	2675.4	1.302	6.057	7.359	0.0010	1.693
50	263.9	1154.9	1639.7	2794.2	2.920	3.052	5.973	0.00128	0.0039
100	311.1	1488.0	1319.7	2727.7	3.360	2.259	5.619	0.00145	0.01811

Values are given at intervals close enough so that linear interpolation is satisfactory.

$$\frac{X - X_1}{X_2 - X_1} = \frac{Y - Y_1}{Y_2 - Y_1}$$

## Formation of Steam:

The Process of formation of steam is discussed in detail in the following steps:



$t_s$  = Saturated temperature

$t_{sup}$  = Temperature of superheated steam

$V_L$  = Volume of liquid "water"

$V_g$  = Volume of dry and saturated steam

$V_{sup}$  = Volume of superheated steam

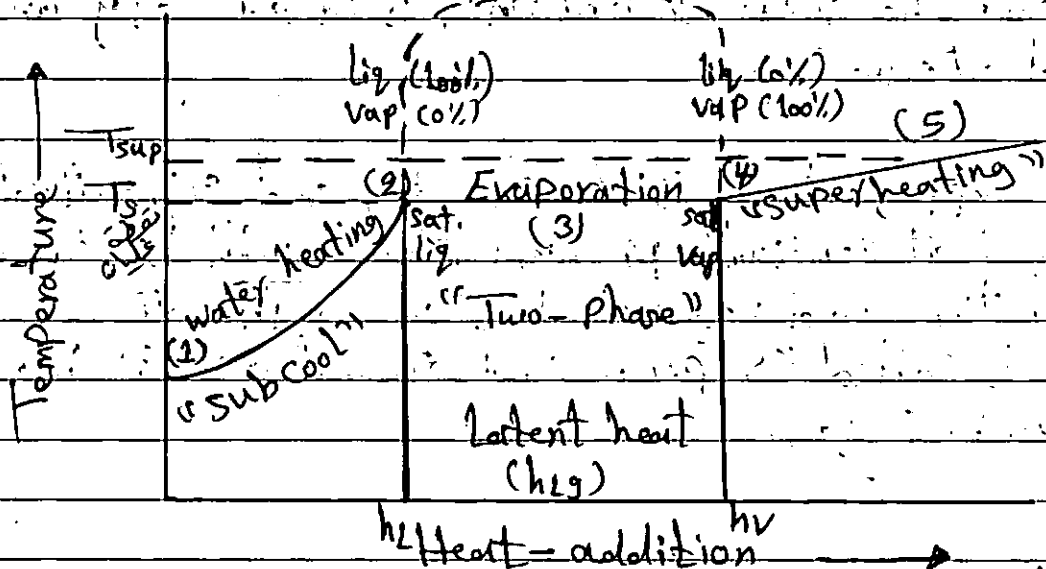


Figure: Graphical representation of formation of steam.

1) Consider a cylinder, for the sake of simplicity, there be 1 Kg of water at  $0^{\circ}\text{C}$  with volume  $V_1 \text{ m}^3$ .

2) If the heat is imparted to water, a rise in temperature will be noticed and this rise will continue till boiling point is reached. This boiling temperature is known as the temperature of formation of steam or "saturated temperature".

3) If supply of heat to water is continued it will be noticed that rise of temperature after the boiling point is reached nil, but indicates that there is increase in volume is possible as steam formation occurs. The heat being supplied does not show any rise of temperature but changes water into vapor state (steam) and is known as "latent heat or hidden heat". So long as the steam is in contact with water, it is called "wet steam".

4) And if heating of steam is further progressed such that all the water particles associated with steam are evaporated, the steam so obtained is called "dry and saturated steam".

5) Again, if supply of heat to the dry and saturated steam is continued at constant pressure there will be increase in temperature and volume of steam. The steam so obtained is called "superheated steam" and it behaves like a perfect gas.

Example: Steam at  $(1.4 \text{ MN/m}^2)$  and of dryness fraction is  $(0.7)$  is throttled to  $(0.1 \text{ MN/m}^2)$ . Determine the dryness fraction of the steam after throttle.

Solution:  $X_1 = 0.7$  The steam is wet

∴ throttling process ∴  $h_1 = h_2$

$$(h_{f1} + X_1 h_{fg1}) = (h_{f2} + X_2 h_{fg2})$$

From saturated steam table in App. (c) find,

$$h_{f1} = 830.1 \text{ kJ/kg}, h_{fg1} = 1957.7 \text{ kJ/kg}$$

$$h_{f2} = 428.8 \text{ kJ/kg}, h_{fg2} = 2250.8 \text{ kJ/kg}$$

$$830.1 + (0.7 \times 1957.7) = 428.8 + (X_2 \times 2250.8)$$

∴  $X_2 = 0.787$  (dryness fraction) after throttle



Example: Superheated steam originally at  $P_1$  and  $T_1$  expands through a nozzle to an exhaust pressure  $P_2$ . Assuming the process is reversible and adiabatic and that equilibrium is attained, determine the state of the steam at the exit of the nozzle for the following conditions:

a)  $P_1 = 1000 \text{ KPa}$ ,  $T_1 = 260^\circ \text{C}$  and  $P_2 = 200 \text{ KPa}$

b)  $P_1 = 150 \text{ Psia}$ ,  $T_1 = 500^\circ \text{F}$  and  $P_2 = 30 \text{ Psia}$

Solution: Since the process is reversible and adiabatic

$$\therefore \Delta S = 0 \implies S_2 = S_1$$

a) The initial state of the steam is as follows:

$$\left. \begin{array}{l} T_1 = 260^\circ \text{C} \\ P_1 = 1000 \text{ KPa} \end{array} \right\} \xrightarrow{\text{superheated steam}} \begin{array}{l} H_1 = 2965.2 \text{ KJ/kg} \\ S_1 = 6.9680 \text{ KJ/kg}\cdot\text{K} \end{array}$$

The final state,

$$P_2 = 200 \text{ KPa} \quad \text{and} \quad \therefore S_2 = S_1 = 6.9680 \text{ KJ/kg}\cdot\text{K}$$

\* Since the entropy of "saturated vapor in table" at  $P_2 = 200 \text{ KPa}$  is "greater" than  $S_2 = 6.9680 \text{ KJ/kg}\cdot\text{K}$ ,

$\therefore$  the final state is in "two phase region", then

# Problem Sheet No. (4)

6.7

6.17

6.21

6.22

6.23

6.24

6.25

6.27

6.28

6.30

6.32

6.35

6.36



$$1.6609 \leq 0.3682 \times (1 - x^V) + 1.6995 \times x^V$$

$$0.10295 \times x^V \leq 0.9705$$

$$H_2 \leq (0.10295 \times 218.9) + 0.9705 \times 11.6411$$

$$h_{\text{out}}/A \text{ (Btu)} \leq 113.62 \text{ (Btu/lbm)} \times \text{Area}$$

$$V \times \text{Area} \times \rho \times \Delta T \leq Q$$

$$h_{\text{out}}/A \times \text{Area} \times \rho \times \Delta T \leq Q$$

$$h_{\text{out}} \leq Q / (\rho \times \Delta T)$$

2. The first part of the problem is to find the heat transfer rate (Q) from the hot fluid to the cold fluid.

The heat transfer rate (Q) can be calculated using the following equation:

$$Q = U \times A \times \Delta T_{\text{LM}}$$

$$Q = U \times A \times \Delta T_{\text{LM}} = 100 \times 10 \times 10 = 10,000 \text{ Btu/hr}$$

The second part of the problem is to find the heat transfer coefficient (U). The heat transfer coefficient (U) can be calculated using the following equation:

$$U = Q / (A \times \Delta T_{\text{LM}})$$

$$S_2 = (1 - x^v) \cdot S^L + x^v \cdot S^v$$

$$6.9680 = (1 - x^v) \cdot 1.530 + x^v \cdot 7.1268$$

$$\text{Hence } x^v = 0.9716$$

The mixture is (97.16%) vapor and (2.84%) liquid.

$$H_2 = x^L \cdot H^L + x^v \cdot H^v$$

$$= 0.0284 \cdot 504.7 + 0.9716 \cdot 2706.7$$

$$= 2644.9 \text{ KJ/Kg.}$$

b) The initial state of the steam is as follows:  
(data from steam tables in english units)

$$\left. \begin{array}{l} T_1 = 500^\circ\text{F} \\ P_1 = 150 \text{ Psia} \end{array} \right\} \Rightarrow \begin{array}{l} H_1 = 1274.3 \text{ Btu/lbm} \\ S_1 = 1.6602 \text{ Btu/lbm}\cdot\text{R} \end{array}$$

final state :

$$P_2 = 30 \text{ Psia} \quad , \quad S_2 = S_1 = 1.6602 \text{ Btu/lbm}\cdot\text{R}$$

Since the entropy of "saturated vapor" at  $P_2 = 30 \text{ Psia}$  is greater than  $S_2$ , the final state is in "two phase region".

$$S_2 = (1 - x^v) \cdot S^L + x^v \cdot S^v$$

## Chapter Five

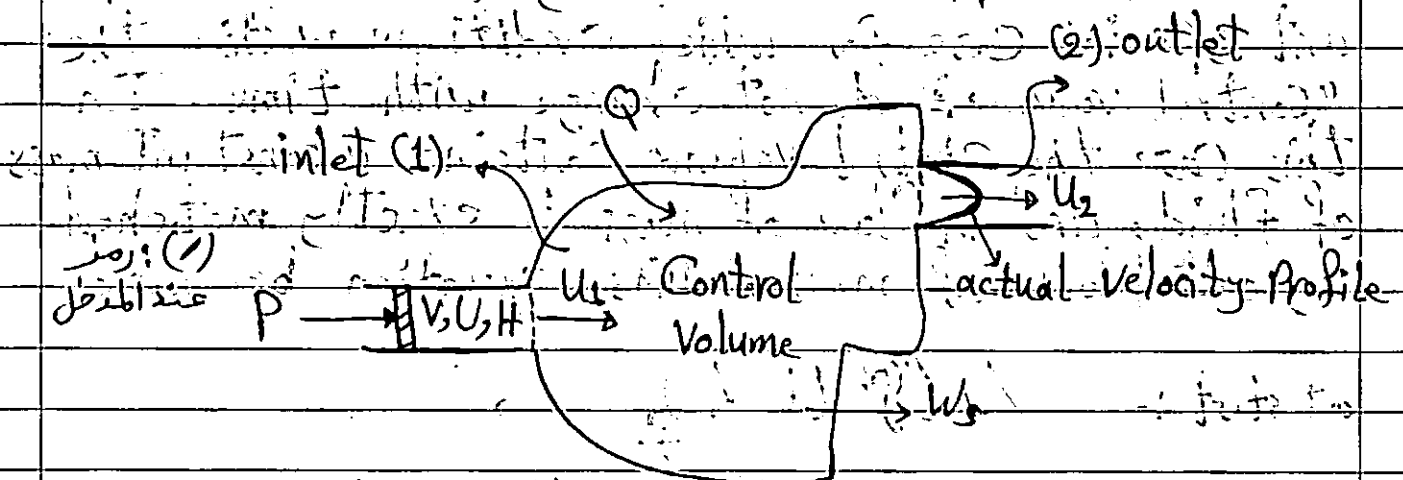
### Applications of Thermodynamics to Flow Process

The thermodynamics of flow is based on mass, energy, and entropy balances, which have been developed in other chapters. The distinction between thermodynamics problems and fluid mechanics problems depends on whether this principle is required for solution. Those problems whose solutions depend only on mass conservation and on the laws of thermodynamics are commonly set apart from the study of fluid mechanics and are treated in courses on thermodynamics.

Flow processes inevitably result from pressure gradients within the fluid. More over temperature, velocity, and even concentration gradients may exist within the flowing fluid.

The equations of balance for open system restricted forms of the mass balance. These equations are the basis for the thermodynamic analysis of processes. When combined with thermodynamic property statements, they allow calculation of process rates and system states.

## Conservation of Mass:



"Control volume with one entrance and one exit"

The principle of "Conservation of mass" for a flow process may be written in words as:

Rate of accumulation of mass within the control volume = { mass flow rate in at entrances } - { mass flow rate out at exits }

$$\frac{dm}{dt} = m_i - m_o$$

where:  $m_i$  = mass flow rate in  $(\rho \cdot u \cdot A)_i$

$m_o$  = mass flow rate out  $(\rho \cdot u \cdot A)_o$

$\rho$ : average fluid density

$u$ : its average velocity

$A$ : the cross-sectional area of the entrance or exit duct.

The mass-conservation equation (also called the continuity equation) is expressed mathematically as:

$$\frac{dm}{dt} + (\rho \cdot u \cdot A)_{\text{exit}} - (\rho \cdot u \cdot A)_{\text{entrance}} = 0$$

Rate of accumulation of energy within the control volume = {rate of energy transport in at entrances} - {rate of energy transport out at exits}

$$+ \left\{ \text{heat flow, } \dot{Q}, \text{ in across the control surface} \right\} = \left\{ \text{net power, } \dot{W}, \text{ out across the control surface} \right\}.$$

Each stream at entrances and exits is:

$$\dot{m} \left( U + \frac{1}{2} u^2 + gZ \right)$$

$$\frac{d(m \cdot U)_{cv}}{dt} + \Delta \left[ \dot{m} \left( U + \frac{1}{2} u^2 + gZ \right) \right]_{fs} = \dot{Q} - \dot{W}$$

"Energy Conservation eq"

The power or work rate ( $\dot{W}$ ) consists of two parts is shaft work rate and associated work with moving the flowing streams into and out of control volume at entrances and exits. The work done by the piston in pushing the unit mass into the control volume is  $P \cdot V$ , and the work rate is  $\dot{m} \cdot (P \cdot V)$ . Thus:-

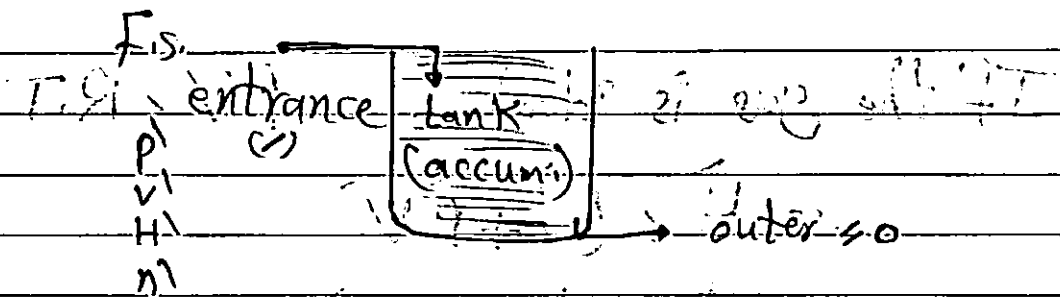
$$\dot{W} = \dot{W}_s + \Delta [ (P \cdot V) \cdot \dot{m} ]_{fs}$$

Combining two equations gives:

$$\frac{d(m \cdot U)_{cv}}{dt} + \Delta \left[ \left( U + P \cdot V + \frac{1}{2} u^2 + gZ \right) \cdot \dot{m} \right]_{fs} = \dot{Q} - \dot{W}_s$$

$$U + P \cdot V = H$$





assume tank is "control volume"

$$\because dW_s \approx 0, \Delta E_p \text{ \& } \Delta E_k \text{ "negligible"}$$

$$\because d(mU)_{\text{tank}} + [(H_1 dm)_{\text{out}} - (H_1 dm)_{\text{in}}] \approx 0$$

integration of equation with

$H_{\text{in}} \approx H$  is constant

$$\therefore \Delta(mU)_{\text{tank}} = H \cdot m' \approx 0$$

(1) is the entrance stream.

$$\Delta(mU)_{\text{tank}} \approx m_2 \cdot U_2 - m_1 \cdot U_1$$

$$\therefore m_2 \cdot U_2 - m_1 \cdot U_1 \approx H \cdot m'$$

$m_1 \approx 0$ : Since the mass in tank initially "zero", at  $(t=0)$

$$\therefore m_2 \approx m' \quad \text{where } m_2 \text{ at } (t=t)$$

$$\therefore m_2 \cdot U_2 \approx m' \cdot H \quad (2) \text{ is the exit stream}$$

$$\therefore \boxed{U_2 \approx H} \quad \text{--- (A)} \quad (1), p, v, T$$

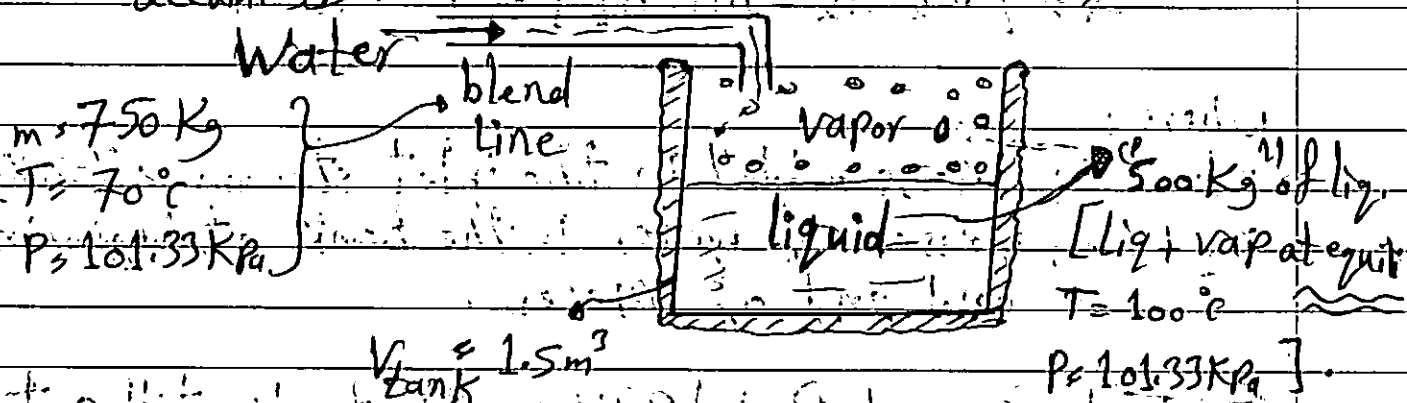
Example: A ( $1.5 \text{ m}^3$ ) tank contains ( $500 \text{ Kg}$ ) of liquid water in equilibrium with pure water vapor which fills the remainder of the tank. The temperature and pressure are ( $100^\circ\text{C}$ ) and ( $101.33 \text{ KPa}$ ). From a water line at a constant temperature of ( $70^\circ\text{C}$ ) and a constant pressure some what above ( $101.33 \text{ KPa}$ ), ( $750 \text{ Kg}$ ) is bled into the tank. If the temperature and pressure in the tank are not to change as a result of the process, how much energy as heat must be transferred to the tank?

Solution:  $W_s \ll 0$ ,  $E_K \Delta E_p \ll 0$

assume the tank as "control volume"

$$\therefore d(m \cdot U)_{cv} + \Delta [H \cdot dm] \ll dQ \quad dW_s$$

accum. is



Since the mass in the tank initially is "zero",  $m_1 \ll 0$  and  $m_2 \ll m$ . Therefore the preceding equation reduces to:

$$d(m \cdot U)_{\text{tank}} = H \cdot dm \ll dQ$$

(✓) : sign at entrance "Control volume"

$$H^L = 293.0 \text{ kJ/kg} \quad \text{"sat. liq. at } 70^\circ\text{C"}$$

entrance

$$H^L = 419.1 \text{ kJ/kg} \quad \text{"sat. liq. at } 100^\circ\text{C"}$$

$$H^V = 2676.0 \text{ kJ/kg} \quad \text{"sat. vap. at } 100^\circ\text{C"}$$

$$v^L = 0.001044 \text{ m}^3/\text{kg} \quad \text{"sat. liq. at } 100^\circ\text{C"}$$

$$v^V = 1.673 \text{ m}^3/\text{kg} \quad \text{"sat. vap. at } 100^\circ\text{C"}$$

$$\therefore \rho = 1/v$$

$$\therefore V = \frac{m}{\rho} \Rightarrow V = m \cdot v$$

$$V_1^V = V_{\text{tank}} - m_1^L \cdot v^L$$

(in the tank)

$$= 1.5 \text{ m}^3 - (500 \text{ kg} \cdot 0.001044 \text{ m}^3/\text{kg})$$

$$= 0.978 \text{ m}^3$$

and

$$m_1^V = \frac{V_1^V}{v^V} = \frac{0.978 \text{ m}^3}{1.673 \text{ m}^3/\text{kg}} = 0.585 \text{ kg}$$

$$m_1 \cdot H_1 = m_1^L \cdot H_1 + m_1^V \cdot H_1$$

(in the tank)

$$= 500 \cdot (419.1) + 0.585 \cdot (2676.0)$$

$$= \underline{(211,115.5 \text{ kJ})}$$

$$m_2 = (m_1^L + m_1^V) + m_{\text{added}}$$

"end process"

$$= 500 + 0.585 + 750$$

$$= 1250.6 \text{ kg}$$

$$\therefore m_2 = m_2^V + m_2^L$$

$$1250.6 = m_2^V + m_2^L \quad \text{--- (1)}$$

- Since  $W_s = 0$  and flow in nozzle is nearly adiabatic, and potential energy changes are negligible, the energy balance equation as given by eqn:

$$dH = -u \cdot du + g \cdot dz + \frac{1}{\rho} \cdot dp$$

The mechanical energy balance takes the form:

$$-V \cdot dp = u \cdot du + df$$

- when  $g \cdot dz = 0$  and if the flow is isentropic, this further reduces to:

$$-V \cdot dp = u \cdot du \quad (\text{Constant } S)$$

When  $df = 0$ , since constant entropy, isentropic flow is achieved. Compressible flow.

The velocity varies with cross-sectional area of the nozzle. The variety of results for compressible fluids (e.g. gases), depends in part on whether the velocity is below or above the speed of sound in the fluid.

- For "subsonic flow" in a converging nozzle, the velocity increases and pressure decreases as the cross-sectional area diminishes.
- In a diverging nozzle with "supersonic flow", the area increase, but still the velocity increases and the pressure decreases.
- The velocity at the throat (minimum cross-sectional area) of converging/diverging nozzle, in which the exit velocity is "supersonic".

at throat (A) is constant, and equation applies is:

$$\rho dU = U \rho \frac{dV}{V}$$

Substituting this expression into equation of reduced mechanical energy balance:

$$-V \cdot dp = U \cdot \left( U \cdot \frac{dV}{V} \right)$$

$$U_{throat}^2 = 1 - V_{throat}^2 \left( \frac{dp}{dV} \right)$$

(\*) Therefore, although  $V =$

Comparison this equation of "velocity for throat" with equation of "velocity for maximum" shows that  $U_{throat}$  is equal to the speed of sound.

\* The relation of velocity to pressure in a nozzle can be given analytically if the fluid behaves as an ideal gas.

When an ideal gas with constant heat capacities, undergoes "isentropic expansion",

we have  $P \cdot V^\gamma = \text{constant}$  (eq. \*)

and  $-V \cdot dp = U \cdot dU$

"Constant S"

With integration:

$$\int_{P_1}^{P_2} V \cdot dp = \int_{U_1}^{U_2} U \cdot dU$$

$$\Rightarrow U^2 = -2 \cdot \int_{P_1}^{P_2} V \cdot dp$$

$$(U_2^2 - U_1^2) = -2 \cdot \int_{P_1}^{P_2} V \cdot dp$$

derivable  
Integration of (eq \*) become:

$$V^{\gamma} dp = -\gamma P V^{\gamma-1} dV$$

$$\frac{1}{V} = \frac{dp}{dV} \cdot \frac{1}{\gamma P}$$

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

Substitute into eq

$$U_2^2 - U_1^2 = 2 \cdot \gamma \int_{P_1}^{P_2} P \frac{dV}{dP} \cdot dP$$

$$W = \int_{P_1}^{P_2} P \cdot dV$$

$$\therefore (U_2^2 - U_1^2) = 2 \cdot \gamma \cdot W$$

For adiabatic process :  $Q = 0$

From 1st law thermodynamic  $\Delta U = Q - W$

$$(U_2^2 - U_1^2) = -2 \gamma \Delta U$$

$$= -2 \gamma (C_V \Delta T)$$

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

$$(U_2^2 - U_1^2) = -2 \gamma R \frac{(T_2 - T_1)}{(\gamma - 1)}$$

$$= 2 \gamma R \frac{(T_1 - T_2)}{(\gamma - 1)}$$

$$\textcircled{11} \quad (\gamma - 1)$$

$$= \frac{2 \gamma (P_1 V_1 - P_2 V_2)}{(\gamma - 1)}$$

$$= \frac{2 \gamma P_1 V_1}{\gamma - 1} \left[ 1 - \frac{P_2 V_2}{P_1 V_1} \right]$$

For "adiabatic Process" :-

$$\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma - 1}$$

and

$$\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{\frac{\gamma - 1}{\gamma}}$$

Reciprocating this eqs :-

$$\frac{T_1}{T_2} = \left( \frac{V_2}{V_1} \right)^{\gamma - 1} \text{ and } \frac{T_1}{T_2} = \left( \frac{P_1}{P_2} \right)^{\frac{\gamma - 1}{\gamma}}$$

From two eqs :-

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

$$(U_2^2 - U_1^2) = \frac{2 \gamma P_1 V_1}{(\gamma - 1)} \left[ 1 - \left( \frac{P_2}{P_1} \right)^{\frac{\gamma - 1}{\gamma}} \right]$$

$$(U_2^2 - U_1^2) = \frac{2 \gamma P_1 V_1}{(\gamma - 1)} \left[ 1 - \left( \frac{P_2}{P_1} \right)^{\frac{\gamma - 1}{\gamma}} \right]$$

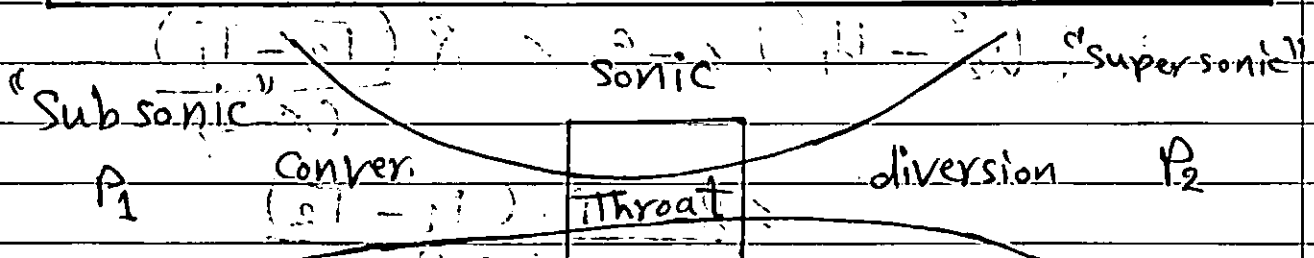


Fig shows the sections of nozzle device

~ Evaluation of the derivative  $(\partial P / \partial V)_s$  for the isentropic expansion of an ideal gas with constant heat capacities from equation that:

$$P \cdot V^\gamma = \text{Constant} \quad \text{--- (1)}$$

$$\because \Delta H + \frac{\Delta U^2}{2} + g \cdot \Delta Z = \overset{\text{horizontal}}{\cancel{Q}} - \overset{\text{isentropic}}{\cancel{W_s}} \quad \text{no shaft work}$$

Reduce this eq to:

$$\Delta H + \frac{\Delta U^2}{2} \approx 0$$

$$\because U_{\text{throat}}^2 \approx -V^2 \cdot \left( \frac{\partial P}{\partial V} \right)_s \quad \text{--- (2)}$$

$$\text{and: } (U_2^2 - U_1^2) \approx -2 \cdot \int_{P_1}^{P_2} V \cdot dP \approx \frac{2\gamma}{(\gamma-1)} \frac{P_1 V_1}{\gamma} \left( 1 - \left( \frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \right)$$

derived eq (1):

$$P \cdot \gamma \cdot (V)^{\gamma-1} \cdot dV + -V^\gamma \cdot dP \approx 0$$

dividing on  $(V^\gamma \cdot dV)$ :

$$\frac{P \cdot \gamma \cdot V^{\gamma-1} \cdot dV}{V^\gamma \cdot dV} = \frac{-V^\gamma \cdot dP}{V^\gamma \cdot dV}$$

$$\because \left( \frac{dP}{dV} \right)_s \approx - \frac{P \cdot \gamma}{V} \quad \text{--- (3) for isentropic expansion into nozzle}$$

rearranged eq (2):

$$\frac{U_{\text{throat}}^2}{-V^2} \approx \left( \frac{dP}{dV} \right)_s \quad \text{--- (4)}$$



Substitute eq (3) into eq (4) :-

$$\frac{u_{throat}^2}{\cancel{1/V^2}} = \cancel{1/V} \frac{P_1 \cdot \gamma}{\cancel{V}}$$

$$\therefore u_{throat}^2 \propto P_1 \cdot V \cdot \gamma$$

where conditions at the throat of nozzle are denoted by subscript (2).

$$\therefore u_{throat}^2 \propto \gamma \cdot P_2 \cdot V_2$$

Substituting this value of the "throat velocity" for  $u_2$ , and solving for the pressure ratio with  $[u_1 \neq 0]$  gives :-

$$(\gamma \cdot P_2 \cdot V_2 = 0) \propto \frac{2 \cdot \gamma \cdot P_1 \cdot V_1}{\gamma - 1} \left[ 1 - \left( \frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \right]$$

$$\frac{P_2}{P_1} \left( \frac{V_2}{V_1} \right) \propto \frac{2}{(\gamma-1)} \cdot \left[ 1 - \left( \frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \right] \quad \text{--- (5)}$$

$$\therefore P_1 \cdot V_1^\gamma = P_2 \cdot V_2^\gamma = \text{Constant}$$

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

and

$$\left( \frac{V_2}{V_1} \right) \propto \left( \frac{P_2}{P_1} \right)^{-\frac{1}{\gamma}} \quad \text{--- (6)}$$

Substitut eq (6) into eq (5) :-

$$\frac{P_2}{P_1} \propto \left( \frac{P_2}{P_1} \right)^{-\frac{1}{\gamma}} \propto \frac{2}{(\gamma-1)} \left[ 1 - \left( \frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \right]$$

$$\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} = \frac{2}{(\gamma-1)} \left(1 - \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right)$$

$$= \frac{2}{(\gamma-1)} - \frac{2}{(\gamma-1)} \cdot \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

$$\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \left[1 + \frac{2}{(\gamma-1)}\right] = \frac{2}{(\gamma-1)}$$

$$\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \cdot \left[\frac{\gamma-1+2}{(\gamma-1)}\right] = \frac{2}{(\gamma-1)}$$

$$\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} (\gamma+1) = 2$$

$$\frac{P_2}{P_1} = \left(\frac{2}{(\gamma+1)}\right)^{\frac{\gamma}{\gamma-1}}$$

A general relationship between velocity and cross-sectional area, expressed not in terms of the Properties ( $P, T, V, H$ ) of the fluid but in terms of the speed of sound. We start with the Continuity equation but express the derivative as:

$$\frac{d(u \cdot A)}{V} = 0$$

$$\frac{1}{V} (u \cdot dA + A \cdot du) - u \cdot A \cdot \left(\frac{dV}{V^2}\right) = 0$$

Rearrange:  $\frac{u \cdot dA + A \cdot du}{u \cdot A} = V \cdot \frac{dV}{V^2} \quad \text{--- (7)}$

Then replacing "V" in the numerator on the right hand side by its value from equation for an isentropic process, mechanical energy balance takes the form:

$$-V \cdot dp = u \cdot du \quad (\text{const. } S)$$

$$\therefore V = -u \cdot \frac{du}{dp}$$

equation (7) becomes:

$$\therefore \frac{dA}{A} + \frac{du}{u} = -u \cdot \frac{du}{dp} \cdot \frac{dv}{v^2}$$

$$= \frac{u \cdot du}{-v^2 \cdot (dp/dv)_s}$$

$$= \frac{u \cdot du}{u_{sonic}^2}$$

$$\therefore \frac{dA}{A} = \frac{u \cdot du}{u_{sonic}^2} = \frac{du}{u}$$

$$= \frac{du}{u} \left( \frac{u^2}{u_{sonic}^2} - 1 \right)$$

The ratio of the "actual velocity" to the "speed of sound" is called the "Mach number"; M.

Hence this equation expressed a relation between the cross-sectional area and velocity, and the local Mach number at any axial position in the nozzle; i.e.,

$$\frac{dA}{A} = (M^2 - 1) \cdot \frac{du}{u} \quad \text{---(8)}$$

Depending on whether :

M is greater than 1 (Supersonic) , or  
M is less than 1 (Subsonic).

The cross-sectional area increases or decreases with velocity increase. Equation (8) is applicable to any type of nozzle, as long as the flow is isentropic.

The speed of sound is attained at the throat of a "converging/diverging" nozzle only when the pressure at the throat is low enough that the critical value of  $P_2/P_1$  is reached.

H.W:

1) Show that for ideal gas (flow in pipe) at constant heat capacity :

$$U_2^2 - U_1^2 = -2 \int_{P_1}^{P_2} v dp = \frac{2 \cdot \gamma \cdot P_1 \cdot V_1}{\gamma - 1} \left[ 1 - \left( \frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \right]$$

2) Show that :  $U_{2, \text{throat}}^2 \ll \gamma \cdot P_2 \cdot V_2$

3) Show that :  $\frac{P_2}{P_1} \ll \left( \frac{2}{\gamma+1} \right)^{\frac{\gamma}{\gamma-1}}$

Example (3): A high velocity nozzle is designed to operate with steam at (700 kPa) and (300°C). At the nozzle inlet the velocity is (30 m/sec). Calculate values of the ratio ( $A/A_1$ ) where " $A_1$ " is the cross sectional area of the nozzle inlet for the sections where the pressure is 600, 500, 400, 300 and 200 kPa. Assume that the nozzle operates isentropically.

Solution:  $\therefore m = \frac{u_1 \cdot A_1}{V_1} = \frac{u \cdot A}{V}$

The area ratio required:

$$\therefore \frac{A}{A_1} = \frac{u_1}{u} \cdot \frac{V}{V_1}$$

$$\therefore \Delta H + \frac{\Delta u^2}{2} = 0$$

$$\therefore u^2 = u_1^2 - 2(H - H_1)$$

From the steam tables, initial values for  $S, H, V$ , taken from "super steam table" at  $P = 700 \text{ kPa}$  &  $T = 300^\circ\text{C}$ :

$$S_1 = 7.2997 \text{ kJ/kg}\cdot\text{K}$$

$$H_1 = 3059.8 \times 10^3 \text{ J/kg}$$

$$V_1 = 371.39 \text{ cm}^3/\text{gm}$$

$$\therefore \frac{A}{A_1} = \left(\frac{30}{u}\right) \times \left(\frac{V}{371.39}\right) \quad \text{--- (A)}$$

and

$$u^2 = (30)^2 - 2(H - 3059.8 \times 10^3) \quad \text{--- (B)}$$

Since the expansion process is (isentropic),  $\Delta S = 0$

at  $P = 600 \text{ Kpa}$  and  $S = S_1 = 7.2997 \text{ KJ/Kg.K}$   
 The steam is "super steam" ;  $S > S^v$  at (600 Kpa)

$$H = 3020.4 \times 10^3 \text{ J/Kg}$$

$$V = 418.25 \text{ cm}^3/\text{gm}$$

From eq. (B) :  $u = 282.3 \text{ m/s}$

and From eq. (A) :  $\frac{A}{A_1} = \left( \frac{30}{282.3} \right) \left( \frac{418.25}{371.39} \right)$

$$= 0.120$$

تبقى "S" ثابتة مع تغير الضغط والحرارة لأن العملية إيسنتروبية

Area ratios for other pressures are evaluated the same way, and the results are summarized in the following table.

$P/\text{Kpa}$	$V/\text{cm}^3/\text{gm}$	$u/\text{m/sec}$	$A/A_1$
500	481.26	411.2	0.095
400	571.23	523.0	0.088
300	711.93	633.0	0.091
200	970.04	752.2	0.104

هو أنفل مرفوع، diverging nozzle

Example (4) - Consider again the nozzle of Ex(3), assuming now that steam behaves as an ideal gas. Calculate:

a) The critical pressure ratio and the velocity at the throat.

b) The discharge pressure if a Mach number of 2.0 is required at the nozzle exhaust.

Solution: The ratio of specific heats  $c_p/c_v$  for steam is about 1.3.

$$a) \text{ Throat } \frac{P_2}{P_1} = \left( \frac{2}{\gamma+1} \right)^{\frac{\gamma}{\gamma-1}} = \left( \frac{2}{1.3+1} \right)^{\frac{1.3}{1.3-1}} \\ = 0.55$$

The velocity at the throat, which is equal to the speed of sound.

$$(u_2^2 - u_1^2) = \frac{2 \cdot \gamma \cdot P_1 \cdot V_1}{\gamma-1} \left[ 1 - \left( \frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \right]$$

$$u_{\text{throat}}^2 = (30)^2 + \frac{2 \times 1.3 \times 700000 \times 0.37139}{1.3-1} \left[ 1 - (0.55)^{\frac{1.3-1}{1.3}} \right]$$

$$= 291254$$

$$\therefore u_{\text{throat}} = 539.7 \text{ m/sec.}$$

b) For  $[M=2]$  (based on conditions at the nozzle throat), the discharge velocity is:

$$M^2 = \frac{u^2}{u_{throat}^2} \Rightarrow (2)^2 = \frac{u^2}{(539.7)^2}$$

$$\therefore u_{discharge} \approx 1079.4 \text{ m/sec.}$$

$$u_2^2 - u_1^2 = \frac{\gamma \cdot P_1 \cdot V_1}{\gamma - 1} \left[ 1 - \left( \frac{P_2}{P_1} \right)^{\frac{\gamma - 1}{\gamma}} \right]$$

$$(1079.4)^2 = (30)^2 + \frac{1.3 \times 700000 \times 0.37139}{1.3 - 1} \left[ 1 - \left( \frac{P_2}{P_1} \right)^{\frac{1.3 - 1}{1.3}} \right]$$

$$\left( \frac{P_2}{P_1} \right)^{\frac{1.3 - 1}{1.3}} \approx 0.483$$

$$\frac{P_2}{P_1} \approx 0.0427$$

$$\therefore P_2 \approx 0.0427 \times P_1$$

$$\approx 29.9 \text{ KPa.}$$



[illegible]

## Turbines or Expanders:

The expansion of a gas in a nozzle to produce a high-velocity stream is a process that converts internal energy into kinetic energy. This kinetic energy can in turn be converted into shaft work when the stream is attached to a rotating shaft. Thus a turbine (or expander) consists of alternate sets of nozzle and rotating blades through which gas flows in a steady-state expansion process whose overall effect is the efficient conversion of the internal energy of a high pressure stream into shaft work. The process is represented in figure:-

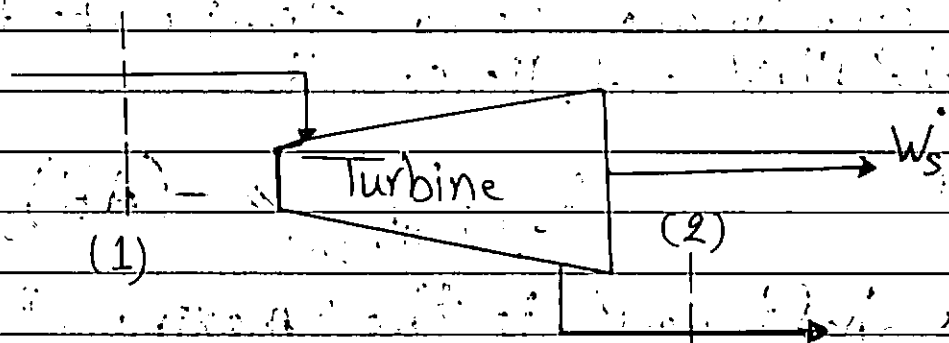


Figure (5.1): Steady-state flow through a turbine or expander.

The energy balance for steady-state flow processes,

$$\dot{m} \cdot \Delta \left[ H + \frac{1}{2} U^2 + g \cdot Z \right] = \dot{Q} - \dot{W}_s$$

However, the potential energy term can be omitted, because there is little change in elevation. And in any designed for turbine, heat transfer is negligible so the inlet and exit pipes velocities relatively low. The equation reduce to:-

$$\dot{W}_s = -\dot{m} \cdot \Delta H$$

and division  
by "m"

$$W_s = -\Delta H$$

The energy equation alone does not allow any calculation to be made. However, if the fluid in the turbine undergoes an expansion process that is reversible as well as adiabatic, then the process is isentropic, and:

$$S_2 = S_1$$

This equation allows us to determine the final state of the fluid and, hence  $H_2$ .

and

$$W_s(\text{isentropic}) = -(\Delta H)_s$$

This shaft work is the "maximum" that can be obtained from an adiabatic turbine with given inlet conditions and given discharge pressure.

Actual turbine produce "less work", because the actual expansion process is (irreversible). Therefore define a turbine efficiency as:

$$\eta = \frac{W_s}{W_s(\text{isentropic})}$$

where  $W_s$  is the actual shaft work.

$$\eta = \frac{\Delta H}{(\Delta H)_s}$$

Values of  $(\eta)$  for turbines in the range (70 to 80)%

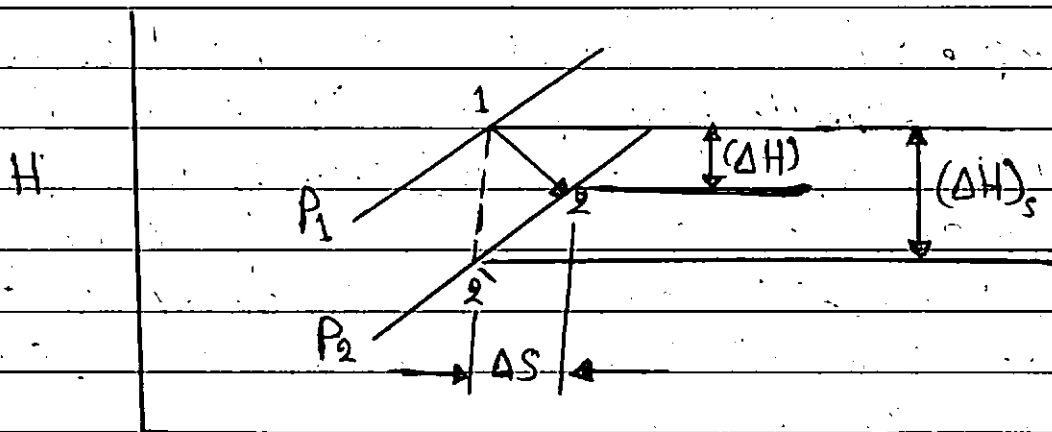


Figure (5.2): Adiabatic expansion process in a turbine or expander.

Figure (5.2) shows an  $H-S$  diagram on which are compared an actual expansion process in a turbine and the reversible process for the same intake conditions and the same discharge pressure. The reversible path is a vertical line of constant entropy from point 1 at the intake pressure  $P_1$  to point 2' at the discharge pressure  $P_2$ . The line representing the actual irreversible process starts also from point 1, but is directed downward and to the right, in the direction of increasing entropy. Since the process is adiabatic, irreversibilities cause an increase in entropy of the fluid. The more irreversible the process, the further this point lies to the right on the  $P_2$  isobar, and the lower the efficiency  $\eta$  of the process.

Example: A steam turbine with rated capacity of 56400 kW operates with steam at inlet conditions of 8600 kPa and 500 °C, and discharges into a condenser at a pressure of 10 kPa. Assuming a turbine efficiency of 75 percent, determine the state of the steam at discharge and the mass rate of flow of the steam.

Solution: At:  $P_1 = 8600 \text{ kPa}$  and  $T_1 = 500 \text{ °C}$

From super steam table  $P_1$ :  $H_1 = 3391.6 \text{ kJ/kg}$   
 $S_1 = 6.6858 \text{ kJ/kg·K}$

$P_2 = 10 \text{ kPa}$ , the expansion is isentropic,

$$S_2 = S_1 = 6.6858$$

Steam with this entropy at 10 kPa is "wet", and

$$S_2 = (1-x) \cdot s^L + x \cdot s^V$$

$$6.6858 = (1-x) \cdot 0.6493 + x \cdot 8.1519$$

$$\therefore x_2 = 0.80467$$

and  $H_2 = (1-x) \cdot H^L + x \cdot H^V$

$$= (1 - 0.80467) \cdot 191.8 + x \cdot 2584.8$$

$$= 2117.4 \text{ kJ/kg}$$

and

$$(\Delta H)_s = H_2 - H_1 = 2117.4 - 3391.6$$

$$(\Delta H)_s = -1274.2 \text{ KJ/kg}$$

$$\Delta H = \gamma \times (\Delta H)_s$$

$$= 0.75 \times (-1274.2)$$

$$= -955.6 \text{ KJ/kg}$$

The actual enthalpy:

$$H_2 = \Delta H + H_1$$

$$= (-955.6) + 3391.6$$

$$= 2436.0 \text{ KJ/kg}$$

Thus the steam in its actual final state is also wet,

$$H_2 = H^L + X_2 (H^V - H^L)$$

$$2436.0 = 191.8 + X_2 (2584.8 - 191.8)$$

$$X_2 = 0.93782$$

Finally,  $S_2 = S^L + X_2 (S^V - S^L)$

$$= 0.6493 + 0.93782 (8.1511 - 0.6493)$$

$$= 7.6864 \text{ KJ/kg} \cdot \text{K}$$

The steam rate (m):

$$W_s = -m \cdot \Delta H$$

$$56400 \frac{\text{KJ}}{\text{sec}} = -m (2436.0 - 3391.6)$$

$$\therefore m = 59.02 \text{ Kg/sec}$$

## Throttling Process:

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When a fluid flows through a restriction, such as an orifice, a partly closed valve, or a porous plug, without any change in kinetic energy, the primary result of the process is a pressure drop in the fluid. Such a throttling process produces no shaft work and results in negligible change in elevation. In the absence of heat transfer, energy balance equation reduces to:

$$\Delta H = 0$$

or

$$H_2 = H_1$$

The process occurs at constant enthalpy. Since the enthalpy of an ideal gas depends on temperature only, a throttling process does not change the temperature of an ideal gas.

For example, if steam at  $P_1 = 1000 \text{ KPa}$  and  $T_1 = 300^\circ \text{C}$  is throttled to  $P_2 = 101.325 \text{ KPa}$  is throttling at constant enthalpy determine the outlet temperature.

at  $P_1$  &  $T_1 \xrightarrow{\text{real gas}} H_1 = 3052.1 \text{ KJ/Kg}$  From super steam Table

$$H_2 = H_1 = 3052.1 \text{ KJ/Kg}$$

From  $P_2$  &  $H_2 \rightarrow$  Interpolation in the steam tables at  $T_2 = 288.8^\circ \text{C}$

## Compression Processes:

Just as expansion processes result in pressure reduction in a flowing fluid, so compression processes bring about pressure increases. Compressors, pumps, fans, and vacuum pumps are all devices designed for this purpose. We are here concerned the specification of energy requirements for the steady-state compression of fluids from one pressure to a higher one.

Compressors: The compression of gases may be accomplished in equipment with rotating blades or in cylinders with reciprocating pistons. For high pressures, reciprocating compressors are required.

The energy equations are independent of the type of equipment; they are the same as for turbines or expanders, because potential and kinetic energy changes are negligible and the compression is adiabatic, represent the process by Figure (5.3).

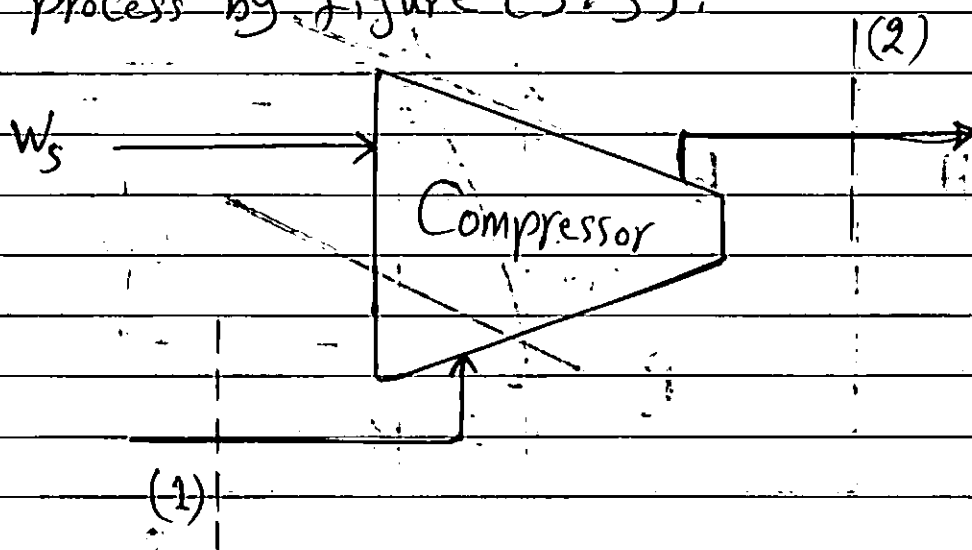


Figure (5.3): Steady State Compression Process.



In a compression process, the isentropic work,

$$W_s(\text{Isentropic}) = -(\Delta H)_s$$

is the "minimum shaft work" required for compression of a gas from a given initial state to a given discharge pressure.

Thus, define a compressor efficiency as

$$\eta = \frac{W_s(\text{Isentropic})}{W_s}$$

also given by

$$\eta = \frac{(\Delta H)_s}{\Delta H}$$

Compressor efficiency are usually in the range of 70 to 80 Percent. The compression process is shown on H-S diagram in figure (5.4):

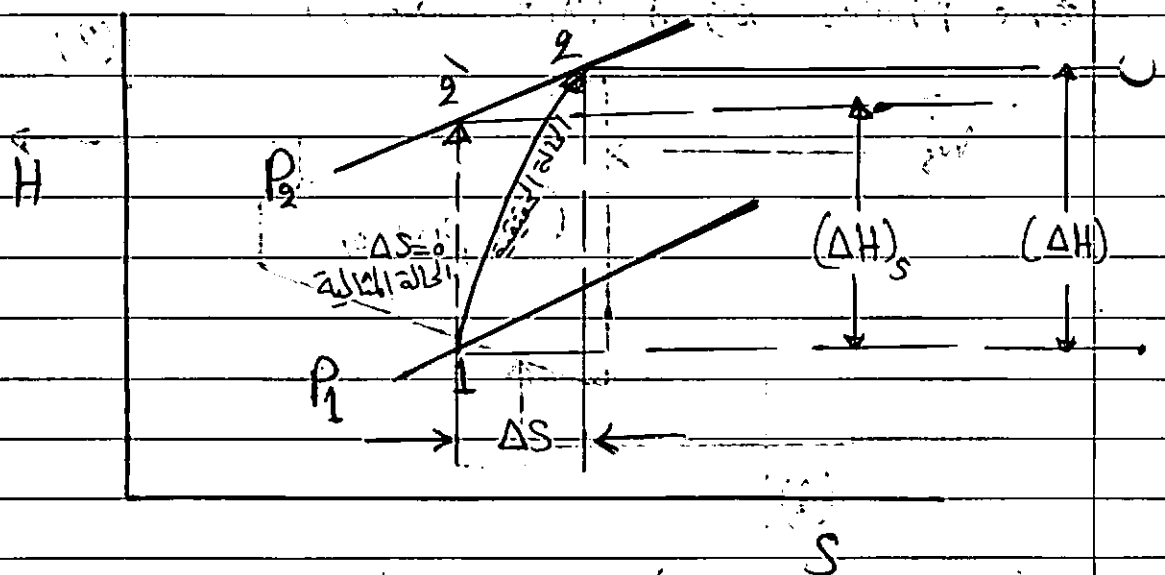


Figure (5.4): Adiabatic compression process.

The vertical path rising from point 1 to point 2 represents the isentropic compression process from  $P_1$  to  $P_2$ . The actual compression process from point 1 upward and to the right in the direction of increasing entropy at point 2 on the isobar for  $P_2$ .

Example: Saturated-vapor steam at 100 kPa ( $t_{\text{sat}} = 99.6^\circ\text{C}$ ) is compressed adiabatically to 300 kPa. If the compressor efficiency is 75 percent, what is the work required?

Solution: For saturated steam at 100 kPa,

$$S_1 = 7.3598 \text{ kJ/kg}\cdot\text{K}$$

$$H_1 = 2675.4 \text{ kJ/kg}$$

For isentropic compression to 300 kPa,

$$S_2' = S_1 = 7.3598 \text{ kJ/kg}\cdot\text{K}$$

By interpolation in the tables for "superheated steam" at 300 kPa, we find that steam with this entropy ( $S_2'$ ) has an enthalpy of

$$H_2' = 2888.8 \text{ kJ/kg}$$

Thus,

$$(\Delta H)_s = H_2' - H_1$$

$$= 2888.8 - 2675.4$$

$$= 213.4 \text{ kJ/kg}$$

$$\Delta H = \frac{(\Delta H)_s}{\eta} = \frac{213.4}{0.75} = 284.5 \text{ KJ/Kg}$$

whence,

$$H_2 = H_1 + \Delta H$$

$$= 2675.4 + 284.5$$

$$= 2959.9 \text{ KJ/Kg}$$

Again by interpolation, we find that superheated steam with this enthalpy ( $H_2$ ) has the additional properties:

$$T_2 = 246.1^\circ \text{C}$$

$$S_2 = 7.5019 \text{ KJ/Kg} \cdot \text{K}$$

the work required is,

$$-W_s = \Delta H = H_2 - H_1$$

$$= 284.5 \text{ KJ/Kg}$$

Pumps: ∴ liquids are usually moved by pumps, generally rotating equipment. The same equations apply to adiabatic pumps as to adiabatic compressors.

$$W_s = \dot{m} \Delta H$$

$$W_s = \Delta H$$

$$W_s (\text{isentropic}) = -(\Delta H)_s$$

$$\text{and } \eta = \frac{-(\Delta H)_s}{\Delta H}$$

For an isentropic process:

$$dH = T ds + V dp \quad (\text{const } s) \quad (1)$$

$$W_s (\text{isentropic}) = -(\Delta H)_s \quad (2)$$

Substitute eq. (1) into eq. (2)

$$W_s (\text{isentropic}) = - \int_{P_1}^{P_2} V \cdot dp$$

For liquids "V" is independent of "P". Integration then gives:

$$W_s (\text{isentropic}) = -(\Delta H)_s$$

$$W_s (\text{isentropic}) = -V \cdot (P_2 - P_1)$$

From Chapter Four the useful equations for liquid:

$$dH = c_p dT + V(1 - \beta T) dp$$

$$\text{and } ds = c_p \frac{dT}{T} - \beta \cdot V \cdot dp$$

Where  $\beta$  is volume expansivity.

Since temperature changes in the pumped fluid are very small and the properties of liquids are insensitive to pressure, these equations are usually integrated on the assumption that ( $c_p$ ,  $V$  and  $\beta$ ) are constant usually at initial values.

$$\Delta H \approx c_p \Delta T + V(1 - \beta T_1) \Delta P$$

$$\Delta S \approx c_p \ln \frac{T_2}{T_1} - \beta \cdot V \cdot \Delta P$$

Example: Water at ( $45^\circ\text{C}$ ) and ( $10\text{ KPa}$ ) enters an adiabatic pump and is discharged at a pressure of ( $8600\text{ KPa}$ ). Assume the pump efficiency to be 75 percent. Calculate the work of the pump, the temperature change of the water, and the entropy change of the water.

Solution: The properties for saturated liquid water at  $45^\circ\text{C}$  are:

$$V = 1010 \text{ cm}^3/\text{kg}$$

$$\beta = 425 \times 10^{-6} \text{ K}^{-1}$$

$$c_p = 4.178 \text{ KJ/kg} \cdot \text{K}$$

$$W_s (\text{isentropic}) = -(\Delta H)_s = -V \cdot (P_2 - P_1)$$

$$-(\Delta H)_s = -(1010) \cdot (8600 - 10)$$

$$= -8.676 \times 10^6 \text{ KPa} \cdot \text{cm}^3 / \text{kg}$$

$$\text{Since } 1 \text{ KJ} = 10^6 \text{ KPa} \cdot \text{cm}^3$$

$$= -8.676 \text{ KJ} / \text{kg}$$

$$\therefore \Delta H = \frac{(\Delta H)_s}{\eta} = \frac{8.676}{0.75} = 11.57 \text{ KJ/kg}$$

$$\therefore W_s = -\Delta H$$

$$= -11.57 \text{ KJ/kg}$$

The temperature change of water during pumping is:

$$\Delta H = c_p \cdot \Delta T + V(1 - \beta \cdot T) \cdot \Delta P$$

$$11.57 \frac{\text{KJ}}{\text{kg}} = 4.178 \frac{\text{KJ}}{\text{kg}} \cdot \Delta T + 1010 \frac{\text{cm}^3}{\text{kg}} \left[ 1 - (425 \times 10^{-6}) \cdot 318.15 \text{K} \right] \cdot \frac{(8600 - 10) \text{KPa}}{10^6 \text{ KPa} \cdot \text{cm}^3} \times 1 \text{KJ}$$

$$\therefore \Delta T = 0.97 \text{ K} \quad \text{or} \quad 0.97^\circ \text{C}$$

The entropy change of the water is:

$$\Delta S = c_p \cdot \ln \frac{T_2}{T_1} - \beta \cdot V \cdot \Delta P$$

$$= 4.178 \ln \frac{319.12}{318.15} - (425 \times 10^{-6}) (1010) \times \frac{8590}{10^6}$$

$$= 0.0090 \text{ KJ/kg} \cdot \text{K}$$

(23)

$$(C_1 - 0.018 \cdot (1.01)) = 0.941$$

$$0.941 \cdot 0.018 \cdot 1.01 = 0.0017$$

$$0.0017 \cdot 1.01 = 0.001717$$

$$0.941 \cdot 1.01 = 0.95041$$

$$0.941 \cdot 1.01 \cdot 1.01 = 0.9599141$$

$$0.9599141$$

$$0.941 \cdot 1.01 \cdot 1.01 = 0.9599141$$

$$0.9599141 \cdot 1.01 = 0.969413241$$

$$0.9599141 \cdot 1.01 = 0.969413241$$

$$0.969413241 \cdot 1.01 = 0.97910737341$$

$$0.97910737341 \cdot 1.01 = 0.9889084571441$$

$$0.9889084571441 \cdot 1.01 = 0.998797541715541$$

$$0.998797541715541 \cdot 1.01 = 1.00878551713269641$$

$$1.00878551713269641 \cdot 1.01 = 1.0188733723040233741$$

$$1.0188733723040233741 \cdot 1.01 = 1.029062106027063607841$$

$$1.029062106027063607841 \cdot 1.01 = 1.03935272708733424391941$$

## Chapter Six

### "Production of Power from Heat"

The kinetic energy associated with atmospheric winds is used in a few favorable locations to produce power by large windmills. The potential energy of tides is another possible source of power, but production from these sources remains insignificant in comparison with world demands for energy. Significant hydroelectric power is generated by conversion of the potential energy of water into work, a process that can in principle be accomplished with an efficiency of 100%.

A common device for the direct conversion of chemical energy into electrical energy, without the intermediate generation of heat, is the electrochemical cell, e.g. a battery. One type is the fuel cell, in which reactants are supplied continuously to the electrodes. In a conventional power plant the molecular energy of fuel is released by a combustion process. The function of the work-producing device is to convert part of the heat of combustion into mechanical energy. Thus, the thermodynamic analysis of heat engine applies equally well to conventional fuel and nuclear power plants. The internal-combustion engine is another form of heat engine, wherein high temperatures are attained by conversion of the chemical energy of a fuel directly into internal energy within the work-producing devices. Examples are Otto and diesel engines and gas turbine. This chapter is devoted to the analysis of several common heat engine cycles.



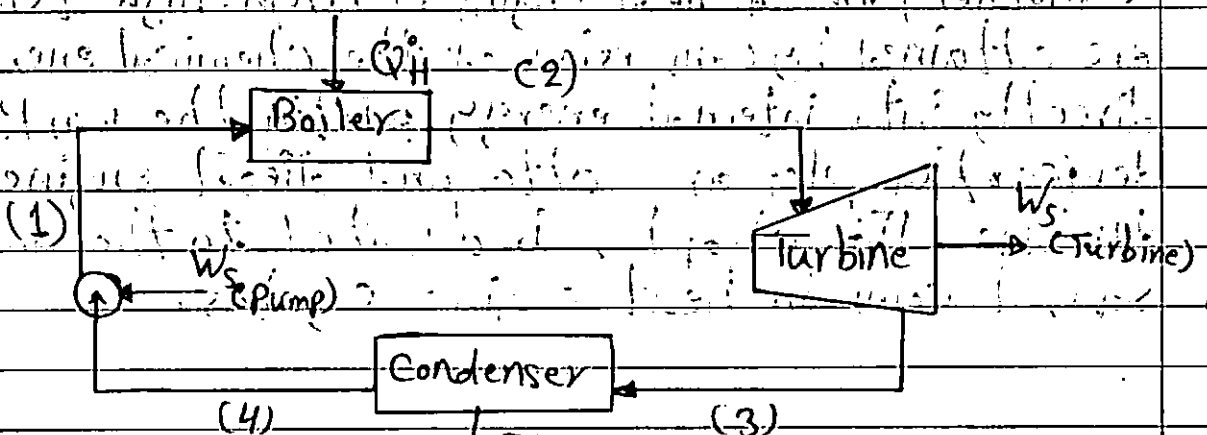
## 1) The Steam Power Plant : محطة توليد طاقة بخارية

The steam power plant is a large-scale heat engine in which the working fluid ( $H_2O$ ) is in steady-state flow successively through a pump, a boiler, a turbine, and a condenser in a cyclic process. The working fluid is separated from the heat source, and heat is transferred across boundary. In a fossil-fuel-fired plant the combustion gases are separated from the steam by boiler-tube walls.

i) The Carnot-engine cycle described in Chapter (3), operates reversibly and consist of two isothermal steps connected by two adiabatic steps. In the isothermal step at high temperature ( $T_H$ ), heat  $|Q_H|$  is absorbed by the working fluid of the engine, and in the isothermal step at lower temperature ( $T_C$ ), heat  $|Q_C|$  is discarded by the fluid.

The work produced  $W = |Q_H| - |Q_C|$  and thermal efficiency of Carnot Engine,

$$\eta = \frac{W}{|Q_H|} = 1 - \frac{T_C}{T_H}$$



Fig(1): Simple Steam Power Plant.

Figure (1) shows a simple steady-state flow process in which steam generated in a boiler is expanded in an adiabatic turbine to produce work. The discharge steam from the turbine passes to a condenser from which it is pumped adiabatically back to the boiler. The power produced by the turbine is much greater than that required by the pump, and the net power output is equal to the difference between the rate of heat input in the boiler ( $\dot{Q}_H$ ) and the rate of heat rejection in the condenser ( $\dot{Q}_C$ ).

Carnot cycle may be shown as paths on a (T-S) diagram

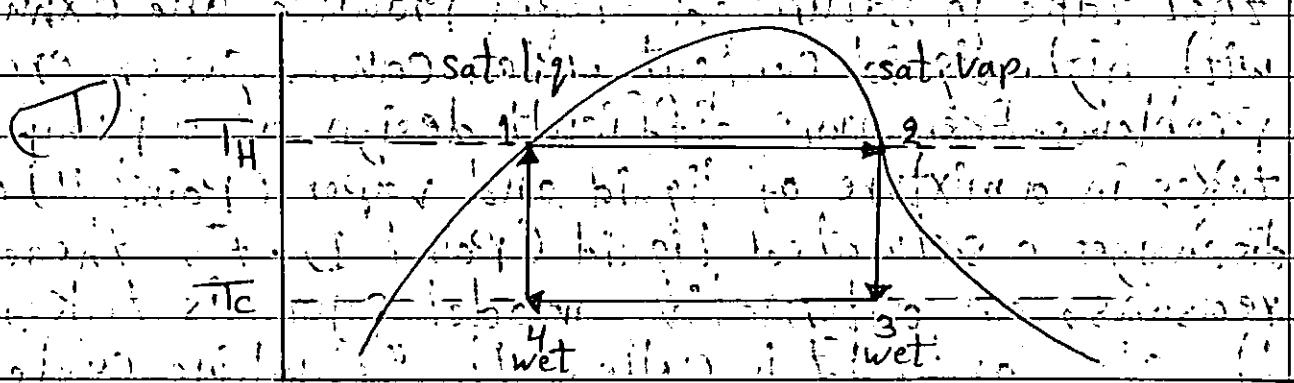


Figure (2) Carnot Cycle on T-S diagram

Step 1  $\rightarrow$  2: is the isothermal absorption of heat at ( $T_H$ ) and is represented by a horizontal line on the (T-S) diagram. This vaporization process occurs also at constant pressure and produces saturated vapor steam from saturated liquid water.

Step 2  $\rightarrow$  3: is a reversible, adiabatic expansion of saturated vapor to pressure at which [ $T_{sat} = T_C$ ]. This isentropic expansion process is represented by a vertical line on the (T-S) diagram and produces a wet vapor.

Step 3  $\rightarrow$  4: is the isothermal rejection of heat at temperature ( $T_c$ ) and is represented by a horizontal line on the ( $T-S$ ) diagram. It is condensation process but is incomplete.

Step 4  $\rightarrow$  1: Takes the cycle back to its origin producing saturated liquid water at point (1). It is an isentropic compression process for which the path is a vertical line on the ( $T-S$ ) diagram.

2) The Rankine Cycle: In Carnot cycle turbines that take in saturated steam produce an exhaust with high liquid content which causes severe erosion problems. Even more difficult design of a pump that takes in a mixture of liquid and vapor (point 4) and discharges a saturated liquid (point 1). For these reasons, an alternative model cycle is taken as the standard. It is called the "Rankine cycle", and difficulties attend the operation of equipment intended to carry out steps 2  $\rightarrow$  3 and 4  $\rightarrow$  1.

Rankine cycle differs from cycle of figure (2) in two major respects.

First, the heating step 1  $\rightarrow$  2 is carried well beyond vaporization, so as to produce a superheated vapor, and

Second, the cooling step 3  $\rightarrow$  4 brings about complete condensation, yielding saturated liquid to be pumped to the boiler.

The (Rankine) cycle consists of the four steps shown by fig (3) and described as follows:

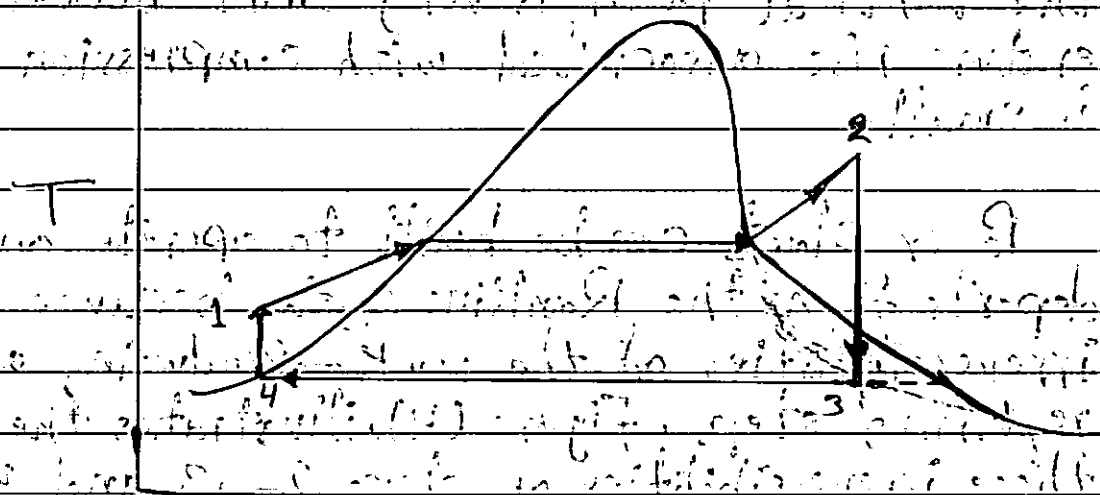


Figure (3): The Rankine Cycle

- Step 1  $\rightarrow$  2: A constant pressure heating process in a boiler. The path lies along an isobar (the pressure of the boiler) and consists of three sections:
  - heating of subcooled liquid water to its saturation temperature,
  - vaporization at constant temperature and pressure,
  - and superheating of the vapor to a temperature well above its saturation temperature.
- Step 2  $\rightarrow$  3: Reversible, adiabatic (isentropic) expansion of vapor in a turbine to the pressure of the condenser. The path normally, the superheating accomplished in step 1  $\rightarrow$  2 shifts the path far enough to the right on fig (3) that the moisture content is not too large.
- Step 3  $\rightarrow$  4: A constant pressure, constant temperature process in a condenser to produce saturated liquid at point 4.

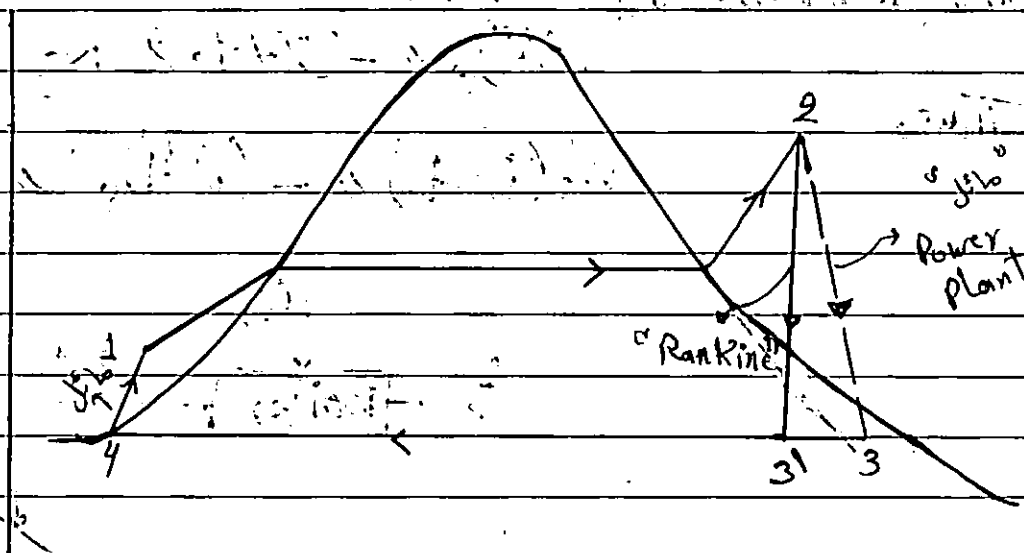
Step 4  $\rightarrow$  1: Reversible adiabatic (isentropic) Pumping of the condensed liquid to the pressure of the vertical path is very short because the temperature rise associated with compression of a liquid is small.

Power plants can be built to operate on a cycle that departs from the Rankine cycle because of the irreversibilities of the work-producing and work-requiring steps. Figure (4), illustrates the effects of these irreversibilities on steps 2  $\rightarrow$  3 and 4  $\rightarrow$  1. The lines are no longer vertical, but tend in the direction of increasing entropy. The turbine exhaust is normally still wet, but as long as the moisture content is less than about 10%, erosion problems are not serious. Slight subcooling of the condensate in the condenser may occur, but the effect is inconsequential.

The boiler serves to transfer heat from a burning fuel to the cycle, and the condenser transfers heat from the cycle to the surroundings. Neglecting kinetic and potential energy changes reduces the energy relations, and:

$$Q_{in} = m \cdot \Delta H_{2-3} \quad \text{and} \quad Q_{out} = m \cdot \Delta H_{4-1}$$

$$W_{net} = Q_{in} - Q_{out} = m \cdot (\Delta H_{2-3} - \Delta H_{4-1})$$



Figure(4): Simple Practical Power Cycle.

Example(1): Steam generated in a power plant at a pressure of (8.600 Kpa) and a temperature of (500°C) is fed to a turbine. Exhaust from the turbine enters a condenser at (10 Kpa), where it is condensed to saturated liquid which is then pumped to the boiler.

a) What is the thermal efficiency of a Rankine cycle operating at these conditions?

b) What is the thermal efficiency of a practical cycle operating at these conditions if the turbine efficiency and pump efficiency are both 0.75?

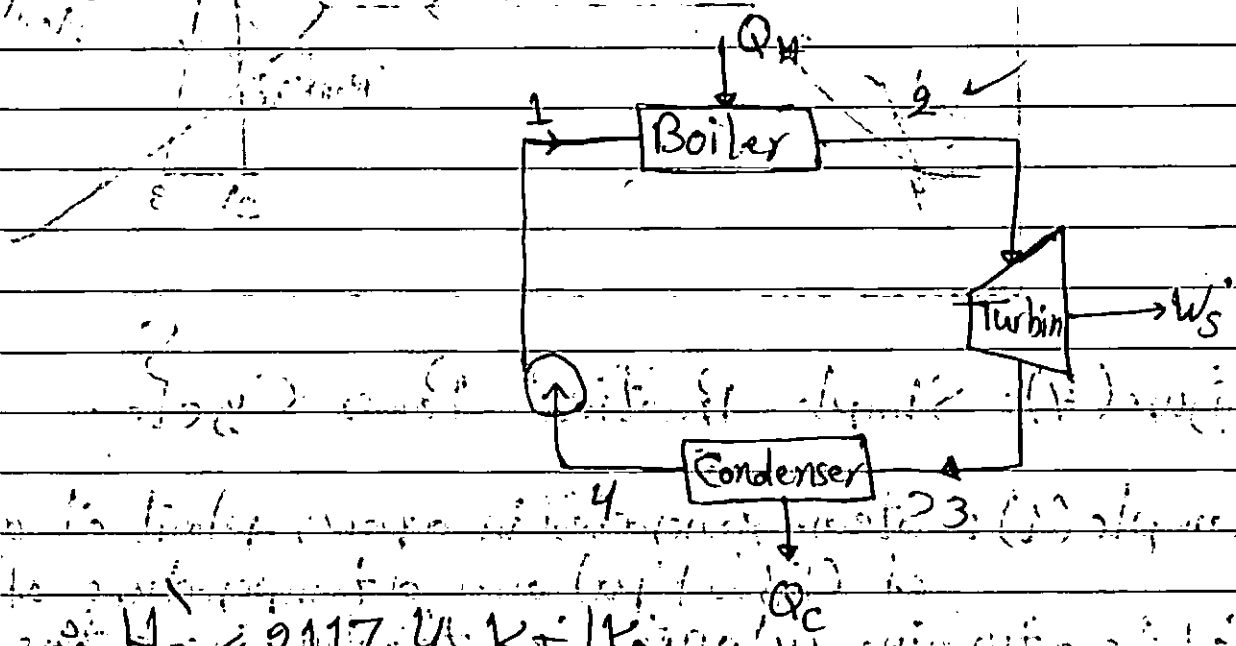
c) If the rating of the power cycle of part (b) is (80000) kW what is the steam rate and what are the heat transfer rates in the boiler and condenser?

Solution: (a) The turbine operates under the conditions of the turbine of example in chapter 5, where  $h_1 = 3391.6 \text{ kJ/kg}$  &  $s_1 = 6.6858 \text{ kJ/kgK}$  (Point 2) of  $s_2 = s_1 = 6.6858$  cycle

and  $[x' = 0.8046] \rightarrow H_2^* \text{ (Point 3) of cycle} = 2117.4$   
 $\Delta H)_s = -1274.2 \text{ KJ/Kg}$

Thus,

$$W_s(\text{isent.}) = -(\Delta H)_s = 1274.2 \text{ KJ/Kg}$$



$$H_3 = 2117.4 \text{ KJ/Kg}$$

The enthalpy of saturated liquid at (10 KPa) at  
 (Point 4) of cycle  $H_4 = 191.8 \text{ KJ/Kg}$

$$Q(\text{Condenser}) = H_4 - H_3$$

$$= 191.8 - 2117.4$$

$$= -1925.6 \text{ KJ/Kg}$$

The minus sign (-) is that the heat flows out of system.

The pump operates under essentially the same conditions as the pump of example in chapter (5).

$$W_s(\text{isentropic}) = -(\Delta H)_s = -V \cdot (P_2 - P_1)$$

$$= (1010) \cdot (8600 - 10)$$

$$= 8.676 \times 10^6 = 8676 \text{ KJ/Kg}$$

$$H_1 \approx H_4 + (\Delta H)_s$$

$$\approx 191.8 + 8.7$$

$$\approx 200.5 \text{ KJ/Kg}$$

and

$$W_s(\text{isentropic}) = -(\Delta H)_s$$

$$(\text{Pump}) \approx -8.7 \text{ KJ/Kg}$$

The enthalpy of superheated steam at 8600 Kpa and 500°C,

(Point 2) of cycle  $H_2 \approx 3391.6 \text{ KJ/Kg}$

$$Q(\text{boiler}) \approx H_2 - H_1$$

$$(\text{boiler}) + \dots \approx 3391.6 - 200.5$$

$$\approx 3191.1 \text{ KJ/Kg}$$

The net work of the Rankine cycle is the sum of the "turbine work" and the "Pump work":

$$W_s(\text{Rankine}) \approx 1274.2 + (-8.7)$$

$$\approx \underline{\underline{1265.5 \text{ KJ/Kg}}}$$

or

$$W_s(\text{Rankine}) \approx Q(\text{boiler}) + Q(\text{Condenser})$$

$$\approx 3191.1 - 1925.6$$

$$\approx \underline{\underline{1265.5 \text{ KJ/Kg}}}$$

The thermal efficiency of the cycle is:

$$\eta = \frac{W_s(\text{Rankine})}{Q(\text{boiler})}$$

$$\approx \frac{1265.5}{3191.1} \approx 0.3966$$



(b) If the turbine efficiency is 0.75, then also have from example of ch. (5)

$$\Delta H = \eta \cdot (\Delta H)_s$$

$$= 0.75 \cdot (-1974.2)$$

$$= -955.6 \text{ KJ/Kg}$$

$$W_s(\text{turbine}) = -\Delta H$$

$$\text{actual} = 955.6 \text{ KJ/Kg}$$

$$H_3 = H_2 + \Delta H$$

$$= 3391.6 + (-955.6)$$

$$= 2436.0 \text{ KJ/Kg}$$

For the condenser

$$Q(\text{condenser}) = H_4 - H_3$$

$$= 191.8 - 2436.0$$

$$= -2244.2 \text{ KJ/Kg}$$

For the pump,  $\Delta H = \frac{(\Delta H)_s}{\eta} = \frac{8.676}{0.75}$

$$= 11.57 \text{ KJ/Kg}$$

$$= 11.57 \text{ KJ/Kg}$$

$$W_s(\text{pump}) = \Delta H$$

$$\text{actual} = -11.57 \sim -11.6 \text{ KJ/Kg}$$

$$H_1 = H_4 + \Delta H$$

$$= 191.8 + 11.6$$

$$= 203.4 \text{ KJ/Kg}$$

$$Q(\text{boiler}) = H_2 - H_1$$

$$= 3391.6 - 203.4$$

$$= 3188.2 \text{ KJ/Kg}$$

The thermal efficiency of the cycle is

$$\eta = \frac{W_s(\text{net})}{Q(\text{boiler})} = \frac{\sum W_s}{Q(\text{boiler})}$$

$$= \frac{955.6 - 11.6}{3188.2} = 0.2961$$

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(C) For a power rating of  $W_s(\text{net}) = 80,000 \text{ KJ/s}$

$$W_s(\text{net}) = \dot{m} \cdot W_s(\text{net})$$

$$80,000 \text{ KJ/s} = \dot{m} \cdot (944.6)$$

$$\dot{m} = 84.75 \text{ Kg/sec}$$

$$Q(\text{boiler}) = \dot{m} \cdot Q(\text{boiler})$$

$$= 84.75 \times 3188.2$$

$$= 2.70.2 \times 10^3 \text{ KJ/sec}$$

$$Q(\text{condenser}) = \dot{m} \cdot Q(\text{cond})$$

$$= 84.75 \times 2244.2$$

$$= 190.2 \times 10^3 \text{ KJ/sec}$$

Note that

$$Q(\text{boiler}) - Q(\text{cond}) = W_s(\text{net})$$

## 2) Internal Combustion Engines: محركات الاحتراق الداخلي

In a steam power plant, the steam is an inert medium to which heat is transferred from a burning fuel or from a nuclear reactor. Therefore characterized by large heat-transfer surfaces:

- 1) for the absorption of heat by the steam at a high temperature in the boiler, and
- 2) for the rejection of heat from the steam at a relatively low temperature in the condenser.

The disadvantage is that when heat transferred through walls (the metal walls of boiler tubes) the ability of the walls withstand high temperature and pressure imposes on the temperature of heat absorption.

In an internal combustion engine, a fuel is burned within the engine itself, and the combustion product acting on a piston in a cylinder (as the working medium). High temperatures are internal, and not involve heat transfer surfaces. And there is no under goes a cyclic process, as the steam in a steam power plant. In addition, the combustion step is replaced by the addition to the air of an equivalent amount of heat. In each section, we first present a qualitative description of an internal combustion engine. Quantitative analysis is then made of an ideal cycle in which air, treated as an ideal gas with constant heat capacities, is the working medium.

## ○ (A) The Otto Engine:

The most common internal-combustion engine, because of its use in automobiles, is the Otto engine. Its cycle consists of four strokes, and starts with intake stroke at constant pressure is represented by line [0 → 1] in figure (5).

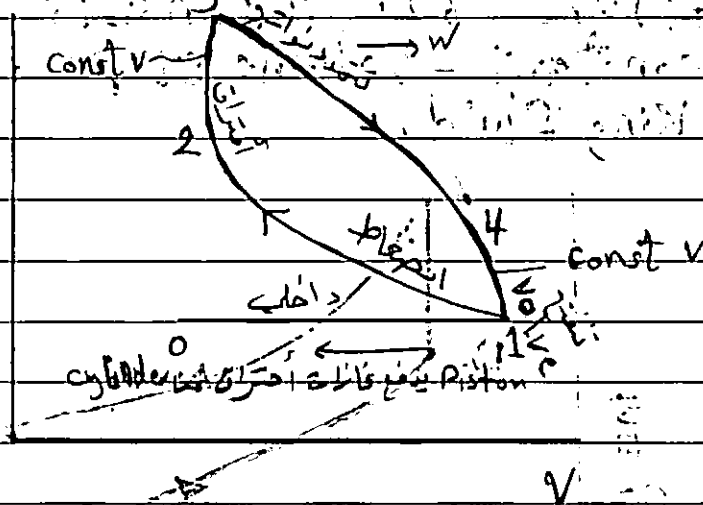


Figure (5): Otto internal-combustion engine cycle.

During the second stroke (Line 1 → 3), all valves are closed and the fuel/air mixture is compressed adiabatically, along (line 1 → 2). The mixture is then ignited and combustion occurs rapidly that the volume remains nearly constant while the pressure rises along (line 2 → 3).

During the third stroke (line 3 → 1) that work is produced. The high-temperature and high pressure products of combustion expand, approximately adiabatically, along (line 3 → 4). Then the exhaust valve opens and the pressure falls rapidly at nearly constant volume along (line 4 → 1).

○ During the fourth or exhaust stroke (line 1 → 0), the piston pushes the remaining combustion gases from the cylinder.

The effect of increasing the compression ratio, defined as the ratio of the volumes at the beginning and end of the compression stroke, is to increase the efficiency of the engine, to increase the work produced per unit quantity of fuel.

For an ideal cycle, called the "air-standard cycle", shown in figure (6): It consists of two adiabatic and two constant-volume steps, for which air is the working fluid.

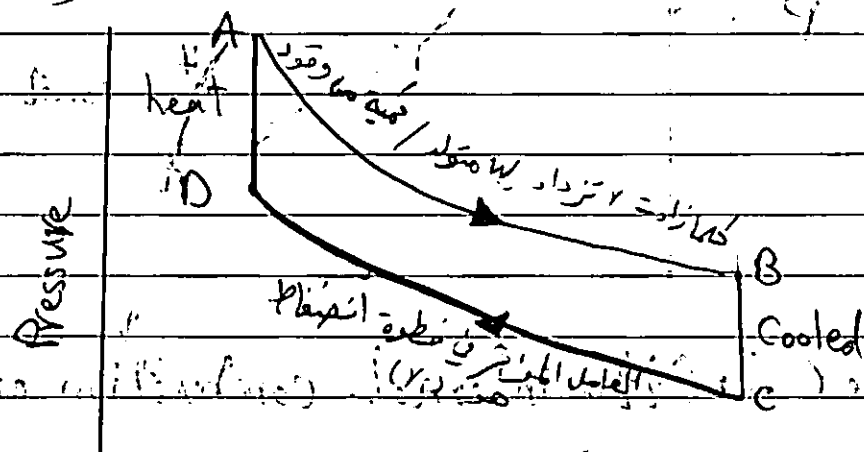


Figure (6) Air-standard Otto cycle

In step DA: sufficient heat is absorbed by the air at constant volume to raise its temperature and pressure to the values resulting from combustion in an actual Otto engine.

Step AB: The air is expanded adiabatically and reversibly.

Step BC: The air is cooled at constant volume.

Step CD: finally compressed adiabatically and reversibly to the initial state at D.

Substituting into eq. (2) leads to:

$$\gamma = 1 - \frac{V_c}{V_D} \left( \frac{P_B - P_c}{P_A - P_D} \right)$$

$$\text{with } \gamma = 1 - \frac{V_c}{V_D} \left( \frac{P_B - P_c}{P_A - P_D} \right) \text{ in (1) leads to (3)}$$

For the two adiabatic, reversible steps, we have

$$P \cdot V^\gamma = \text{const.}$$

whence:

$$P_A \cdot V_D^\gamma = P_B \cdot V_c^\gamma \quad (\text{since } V_D = V_A \text{ and } V_c = V_B)$$

$$P_c \cdot V_c^\gamma = P_D \cdot V_D^\gamma$$

These expressions are combined to eliminate the volumes:

$$\frac{P_B}{P_c} = \frac{P_A}{P_D} \quad (4)$$

Also:

$$\frac{P_c}{P_D} = \left( \frac{V_D}{V_c} \right)^\gamma = \left( \frac{V_D/V_D}{V_c/V_D} \right)^\gamma = \left( \frac{1}{r} \right)^\gamma \quad (5)$$

These equations transform eq. (3):

$$\gamma = 1 - \frac{P_B/P_c - 1}{(P_A/P_D - 1) \cdot P_D}$$

$$= 1 - \gamma \cdot \left( \frac{P_c}{P_D} \right)$$

$$= 1 - \gamma \left( \frac{1}{r} \right)^\gamma$$

$$= 1 - \left( \frac{1}{r} \right)^{\gamma-1}$$

(6)

The thermal efficiency ( $\gamma$ ) of the air-standard cycle is simply :

$$\gamma = \frac{W_s(\text{net})}{Q_{DA}} = \frac{Q_{DA} + Q_{BC}}{Q_{DA}} \quad (1)$$

for (1 mol) of air with constant heat capacities,

$$Q_{DA} = C_V \cdot (T_A - T_D)$$

$$Q_{BC} = C_V \cdot (T_C - T_B)$$

Substituting these expressions in eq (1), gives:

$$\gamma = \frac{C_V \cdot (T_A - T_D) - (T_B - T_C)}{C_V \cdot (T_A - T_D)}$$

$$\gamma = 1 - \frac{(T_B - T_C)}{(T_A - T_D)} \quad (2)$$

The thermal efficiency is also related in a simple way to the compression ratio

$$\gamma = \frac{V_C}{V_D}$$

and

$$T = \frac{P \cdot V}{R} \Rightarrow T_B = \frac{P_B \cdot V_B}{R} = \frac{P_B \cdot V_C}{R}$$

because  $V_B = V_C$  and  $V_A = V_D$

$$T_C = \frac{P_C \cdot V_C}{R}$$

$$T_A = \frac{P_A \cdot V_A}{R} = \frac{P_A \cdot V_D}{R}, \quad T_D = \frac{P_D \cdot V_D}{R}$$

## B) The Diesel Engine:

The diesel engine differs from the Otto engine primarily in that the temperature at the end of compression is sufficiently high that combustion is initiated spontaneously. This higher temperature results because of a higher compression ratio that carries the compression step to a higher pressure. The fuel is not injected until the end of the compression step, and then is added slowly enough that the combustion process occurs at approximately constant pressure. The diesel engine operates at higher compression ratios, and consequently at higher efficiency.

Example: Sketch the air-standard Diesel cycle on  $PV$  diagram, and derive an equation giving the thermal efficiency of this cycle in relation to the compression ratio  $r_c$  (ratio of volumes at the beginning and end of the compression step) and the expansion ratio  $r_e$  (ratio of volumes at the end and beginning of the expansion step).

Solution: The Diesel cycle is the same Otto cycle of the air-standard, except that the heat absorption step (corresponding to the combustion process in the actual engine) is at constant pressure, as indicated by the  $DA$  in figure (7).

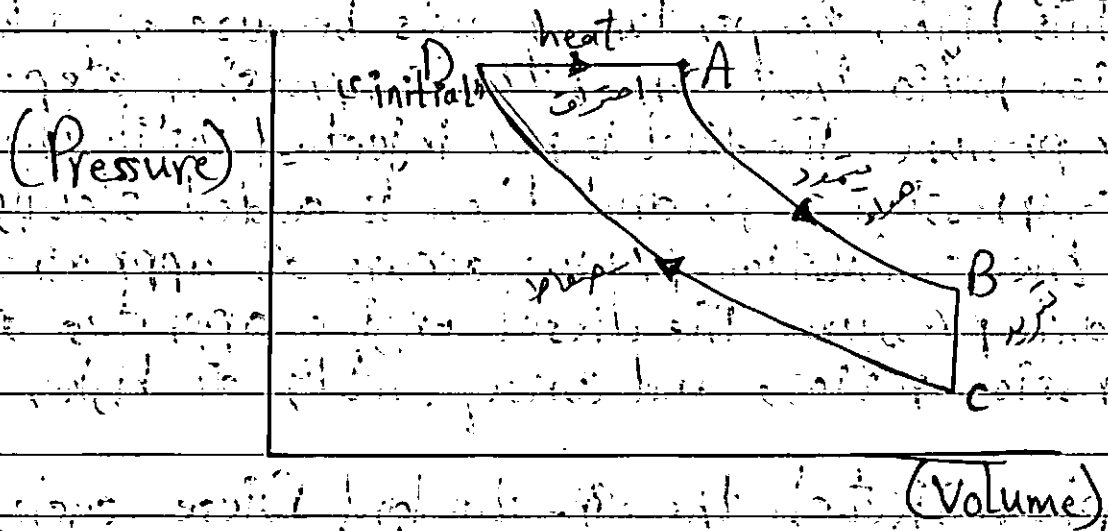
On the basis of one mole of air, considered to be an ideal gas with constant heat capacities, the heat absorbed in the cycle is:



$$Q_{DA} = C_p (T_A - T_D)$$

The heat rejected in the step BC is

$$Q_{BC} = C_v (T_C - T_B)$$



By an energy balance,

$$W_s = Q_{DA} - Q_{BC}$$

and the thermal efficiency is given by:  $\eta = \frac{Q_{DA} - Q_{BC}}{Q_{DA}}$

$$\eta = 1 - \frac{C_v (T_C - T_B)}{C_p (T_A - T_D)}$$

$$= 1 - \frac{1}{\gamma} \left( \frac{T_B - T_C}{T_A - T_D} \right) \quad (1)$$

For reversible, adiabatic expansion (step AB) and reversible, adiabatic compression (step CD),

$$\frac{T_A}{T_B} = \left( \frac{V_B}{V_A} \right)^{\gamma-1}$$

$$\frac{T_1}{T_2} = \left( \frac{V_2}{V_1} \right)^{\gamma-1}$$

and

$$\frac{T_D}{T_C} = \left( \frac{V_C}{V_D} \right)^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1}$$

By definition, the compression ratio is,

$$r_c = \frac{V_c}{V_D}$$

The expansion ratio is defined as:

$$r_e = \frac{V_B}{V_A}$$

Thus,

$$T_B = T_A \left( \frac{1}{r_e} \right)^{\gamma-1} \quad \text{--- (2)}$$

and

$$T_C = T_D \left( \frac{1}{r_c} \right)^{\gamma-1} \quad \text{--- (3)}$$

Substituting Eqs. (2) and (3) into Eq. (1) gives:

$$\gamma = 1 - \frac{1}{\gamma} \frac{[T_A (1/r_e)^{\gamma-1} - T_D (1/r_c)^{\gamma-1}]}{T_A - T_D} \quad \text{--- (4)}$$

Also,  $[P_A = P_D]$ , from ideal gas equation,

$$P_D \cdot V_D = R \cdot T_D$$

and

$$P_A \cdot V_A = R \cdot T_A$$

$$\frac{V_D}{V_A} = \frac{T_D}{T_A}$$

$$\text{also, } [V_B = V_C] \Rightarrow \frac{T_D}{T_A} = \frac{V_D/V_C}{V_A/V_B} = \left( \frac{r_e}{r_c} \right)^{\gamma-1}$$

This relation combines with eq. (4) to give:

$$T_A \propto (4) \text{ relation}$$

$$y = 1 - \frac{1}{\delta} \left[ \frac{(1/r_e)^{\delta-1} - (T_D/T_A)(1/r_c)^{\delta-1}}{1 - (T_D/T_A)} \right]$$

$$= 1 - \left(\frac{1}{\delta}\right) \left[ \frac{(1/r_e)^{\delta-1} - (r_e/r_c)(1/r_c)^{\delta-1}}{1 - (r_e/r_c)} \right]$$

or

$$y = 1 - \frac{1}{\delta} \left[ \frac{(1/r_e)^{\delta-1} - (1/r_c)^{\delta}}{(1/r_e) - (1/r_c)} \right]$$

بضرب بـ  $(1/r_e)$  مقام

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## C) The Gas-Turbine Power Plant :

Consideration of the Otto and Diesel engines has shown that direct use of the energy of high temperature and high pressure gases, without transfer of external heat, possesses some advantages in power production. The gas turbine combines in one unit the advantages of internal combustion with the advantages of the turbine.

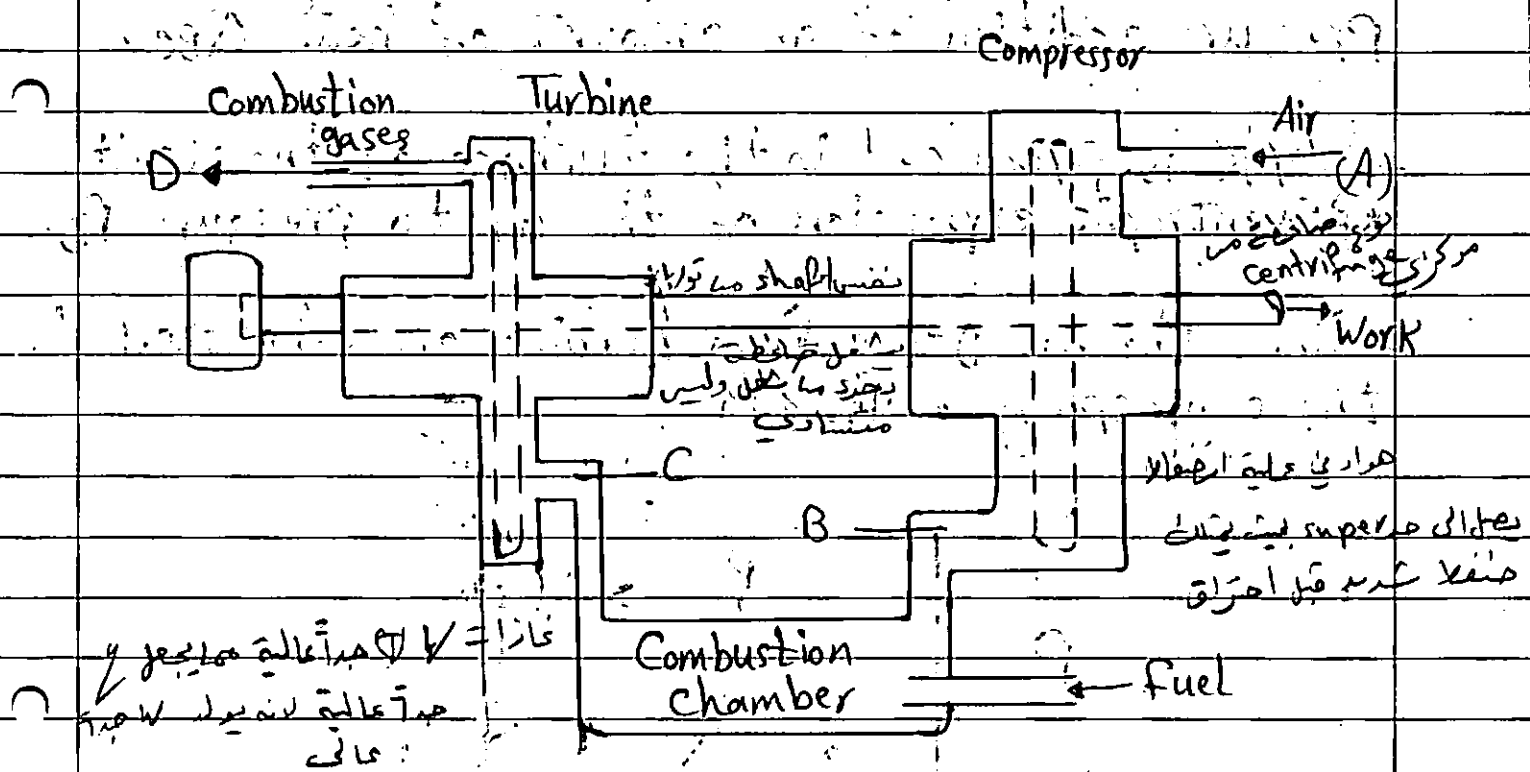


Figure (8) : Gas-turbine Power Plant.

The gas turbine is driven by high-temperature gases from a combustion space. The entering air is compressed (supercharged) to a pressure of several bars before combustion. The Centrifugal Compressor operates on the same shaft as the turbine, and part of the work of the turbine serves to drive the compressor. The higher the temperature of the combustion gases entering the turbine, the higher the efficiency of the unit, the greater work produced per unit of fuel burned.

The idealization of the gas-turbine cycle (based on air, and called "Brayton cycle") is shown on  $P-V$  diagram in figure (9).

The compression step  $AB$  is represented by an adiabatic, reversible (isentropic) path in which the pressure increases from  $P_A$  (atmospheric pressure) to  $P_B$ .

The combustion process is replaced by the constant pressure addition of an amount of heat  $Q_{BC}$ .

Work is produced in the turbine as the result of isentropic expansion of the air to pressure  $P_D$ .

Since the hot gases from turbine are exhausted to the atmosphere,  $P_D = P_A$ .

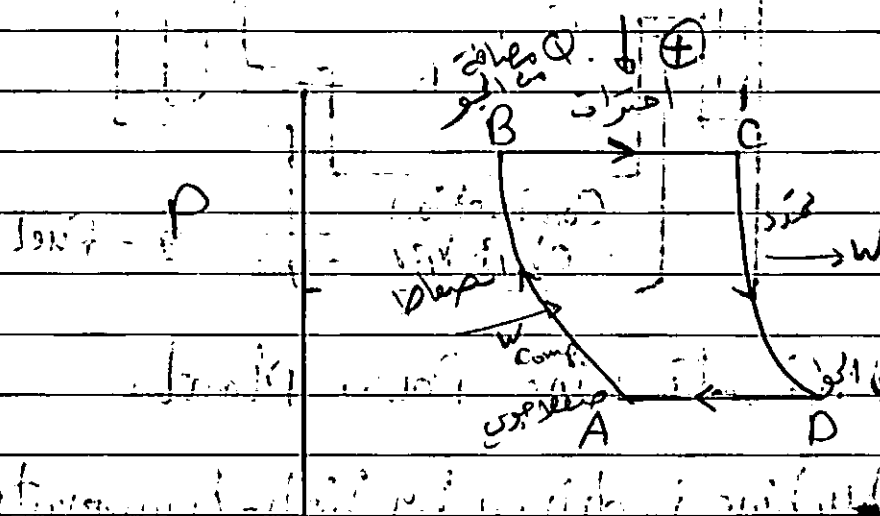


Figure (9): Ideal cycle for gas-turbine power plant with "Brayton cycle"

The thermal efficiency of the cycle is given by:

$$\eta = \frac{W_s(\text{net})}{Q_{BC}} = \frac{W_{CD} + W_{AB}}{Q_{BC}} \quad \text{--- eq. (1)}$$

where each energy quantity is based on "1 mol of air".  
 $W_s = -(\Delta H)$

The work through the compressor  $W_{AB} = H_B - H_A$

For air as ideal gas with constant heat capacities,

$$-W_{AB} = H_B - H_A = C_p (T_B - T_A)$$

Similarly, for the combustion and turbine processes,

$$Q_{BC} = C_p (T_c - T_B)$$

$$-W_{CD} = C_p (T_D - T_c)$$

Substituting these equations into eq. (1), gives:

$$\eta = \frac{-T_B + T_A - T_D + T_c}{T_c - T_B}$$

and simplifying leads to:

$$= \frac{(T_c - T_B)}{(T_c - T_B)} - \frac{(T_D - T_A)}{(T_c - T_B)}$$

$$\eta = 1 - \frac{(T_D - T_A)}{(T_c - T_B)} \quad \text{--- eq. (2)}$$

Since processes AB and CD are isentropic, the temperatures and pressures are related as:

$$\frac{T_B}{T_A} = \left( \frac{P_B}{P_A} \right)^{\frac{\gamma-1}{\gamma}}$$

and

$$\frac{T_D}{T_C} = \left( \frac{P_D}{P_C} \right)^{\frac{\gamma-1}{\gamma}}$$

"  $P_D = P_A$   
 &  $P_C = P_B$   $\Rightarrow \frac{T_D}{T_C} = \left( \frac{P_A}{P_B} \right)^{\frac{\gamma-1}{\gamma}}$

$T_A$  and  $T_D$  may be eliminated to give:

$$T_D = T_C \times \left( \frac{P_A}{P_B} \right)^{\frac{\gamma-1}{\gamma}} \quad \text{and} \quad T_A = T_B \times \left( \frac{P_A}{P_B} \right)^{\frac{\gamma-1}{\gamma}}$$

Substitute into eq. (2):

$$\gamma = 1 - \frac{T_C \times \left( \frac{P_A}{P_B} \right)^{\frac{\gamma-1}{\gamma}} - T_B \times \left( \frac{P_A}{P_B} \right)^{\frac{\gamma-1}{\gamma}}}{(T_C - T_B)}$$

$$= 1 - \left( \frac{P_A}{P_B} \right)^{\frac{\gamma-1}{\gamma}} \times \left[ \frac{T_C - T_B}{T_C - T_B} \right]$$

$$\gamma = 1 - \left( \frac{P_A}{P_B} \right)^{\frac{\gamma-1}{\gamma}} + \left( \frac{P_A}{P_B} \right)^{\frac{\gamma-1}{\gamma}} = 1$$

Problems: From 6th edition

1) 8.1

2) 8.2

3) 8.4

4) 8.12

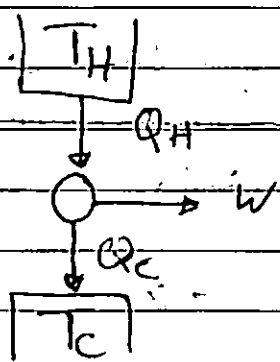
## Chapter Seven

## Refrigeration and Liquefaction

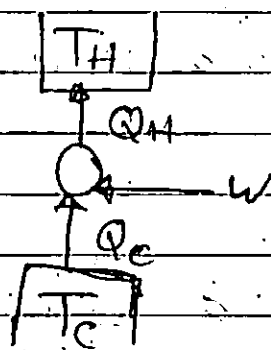
The word refrigeration implies the maintenance of a temperature below that of surroundings. Its use in the air conditioning of building and in preservation of foods, in the manufacture of ice.

Refrigeration requires continuous absorption of heat at a low temp. level, accomplished by evaporation of a liquid in a steady state flow process. The vapor formed may be returned to its original liquid state.

Refrigeration engine is exactly opposite to heat engine.



Heat Engine



Refrigeration Engine

## Importance of Refrigeration in:

Domestic Uses: Refrigerator, deep freezer, air conditioning.

Industry: Petroleum industry, liquification of gases.

Transport of gases in liquid state (LNG).



Before treating the practical refrigeration cycles, Consider the Carnot refrigerator, which a standard of comparison.

### The CARNOT Refrigerator :

Heat is transferred from a low temp. level to a higher one ; according to the second law, The cycle requires the addition of net work  $|W|$  to the system.

$$|W| = |Q_H| - |Q_C| \quad \text{--- (1)}$$

The usual measure of performance of refrigerator is called "the coefficient of performance" [COP] defined as :

$$\text{COP} = \frac{\text{heat absorbed at the lower temp.}}{\text{net work}}$$

$$\text{COP} = \frac{|Q_C|}{|W|} \quad \text{--- (2)}$$

Division of (1) by  $|Q_C|$  gives :

$$\frac{|W|}{|Q_C|} = \frac{|Q_H|}{|Q_C|} - 1$$

$$\therefore \frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C}$$

$$\therefore \frac{|W|}{|Q_C|} = \frac{T_H}{T_C} - 1 = \frac{T_H - T_C}{T_C}$$

$$W = \frac{T_c}{T_H - T_c}$$

(9.3)

or  $K = \frac{T_H}{T_H - T_c}$

This eq. applies only to a refrigerator operating on a Carnot cycle, and it gives the maximum possible value of  $(COP)$  for any refrigerator operating between given values of  $T_H$  &  $T_c$ .

Example:

For refrigeration at a temp level of  $5^\circ\text{C}$  and surroundings temp. of  $30^\circ\text{C}$ , the value of  $(COP)$  for refrigerator is:

$$W = \frac{(5 + 273.15)}{(30 + 273.15) - (5 + 273.15)} = 11.13$$

## The Vapor-Compression Cycle:

Equivalent to the Carnot cycle except that superheated vapor from the Compressor must be cooled to its saturated temp. before condensation.

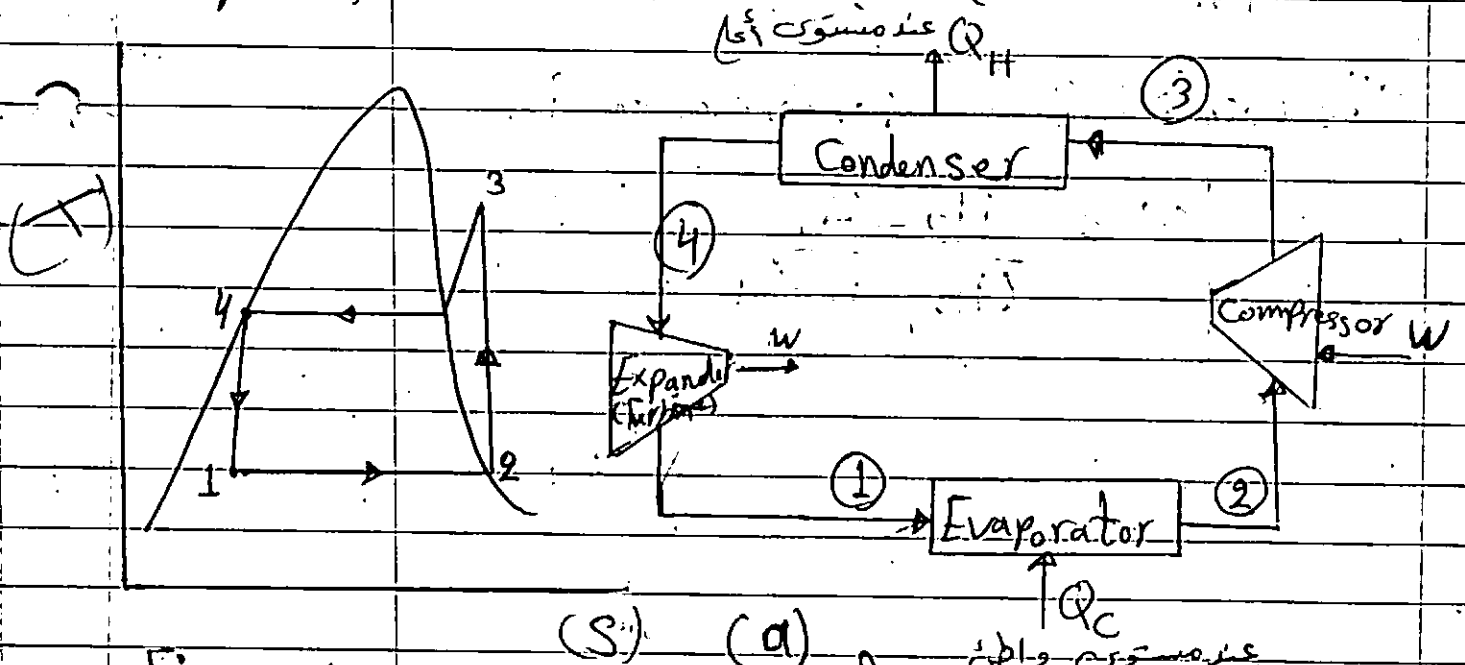


Fig: Vapor-Compression refrigeration Cycle  
Aliquid evaporating at constant pressure provides a means

for heat absorption at constant temp., after it compression to higher pressure it condensation of the vapor provides the rejection of heat at constant temp. The liquid from the condenser is returned to its original state by expansion process through a turbine from which work is obtained. ~~The compression and expansion are isentropic.~~

The heat absorbed<sup>(+)</sup> in the evaporator is:

$$|Q_c| = \Delta H = H_2 - H_1$$

The heat rejected<sup>(-)</sup> in the condenser is:

$$|Q_H| = H_3 - H_4$$

$$\therefore |W| = |Q_H| - |Q_c|$$

$$\therefore |W| = (H_3 - H_4) - (H_2 - H_1)$$

The coefficient of Performance is:

$$W = \frac{H_2 - H_1}{(H_3 - H_4) - (H_2 - H_1)}$$

The process requires a turbine or expander is used only for large installations. More commonly expansion is done by throttling the liquid from the Condenser through a partly opened valve; the throttling process occurs at [constant enthalpy]  $\Delta H = 0$ .

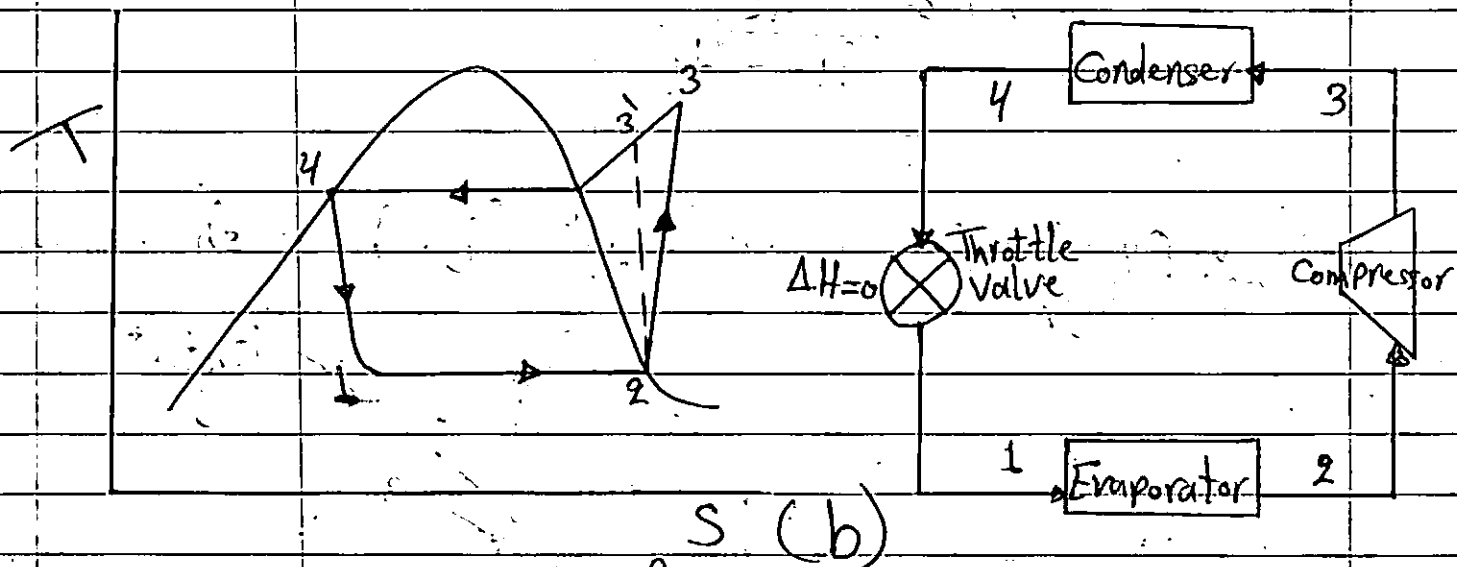


Fig: Vapor-Compression refrigeration cycle

Where the line 4  $\rightarrow$  1 represents the constant enthalpy throttling process.

Line 2  $\rightarrow$  3 representing an actual compression process, slopes in the direction of increasing entropy reflecting the irreversibility inherent in the process, the dashed line

2  $\rightarrow$  3' is the path of isentropic compression.

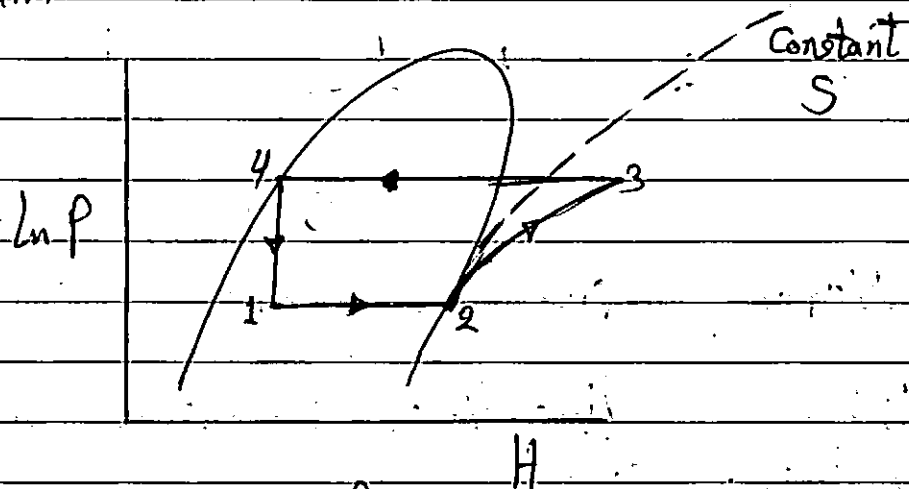
For this cycle:

$$W = \frac{H_2 - H_1}{H_3 - H_2}$$

Design of the evaporator, compressor, condenser, and auxiliary equipment requires knowledge of the rate of circulation of refrigerant ( $\dot{m}$ ). This is determined from the heat "absorbed in the evaporator" by eq:

$$\dot{m} = \frac{|Q_c|}{h_2 - h_1}$$

The vapor-compression cycle of fig. (b) is shown on a PH diagram



Vapor-Compression refrigeration cycle on PH diagram

### Comparison of Refrigeration Cycles:

The effectiveness of a refrigeration cycle is measured by "COP" its coefficient of performance.

- The highest possible value is attained by [Carnot refrigeration]
- The upper limit value is [Vapor-Compression cycle with reversible compression & expansion].
- The lower value value is [Vap. Compr. cycle with throttle]

- valve, and this is reduced further when compression is not isentropic.

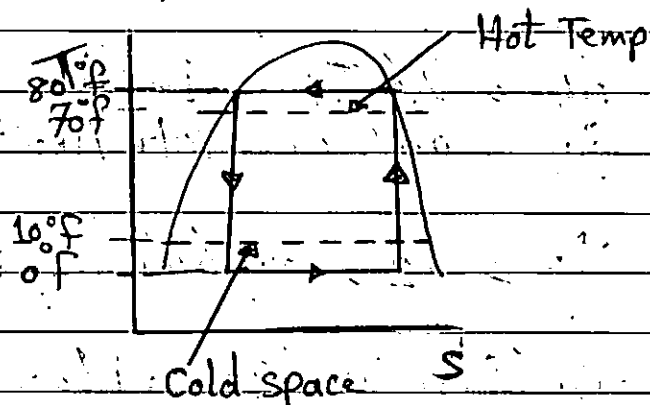
Example: A refrigerated space is maintained at  $(10^\circ\text{F})$ , and cooling water is available at  $(70^\circ\text{F})$ . The evaporator and condenser are of sufficient size that a  $(10^\circ\text{F})$  minimum temp. difference for heat transfer can be realized in each. The refrigeration capacity is  $120,000 \text{ Btu/hr}$ , and the refrigerant is Freon-12.

- a) What is the "W" for Carnot refrigerator?  
 b) Calculate "W" and "m" for vap. comp. cycle with turbine  
 c) Calculate "W" and "m" for vap. comp. cycle where throttle valve is used, if the compression efficiency is  $80\%$ .

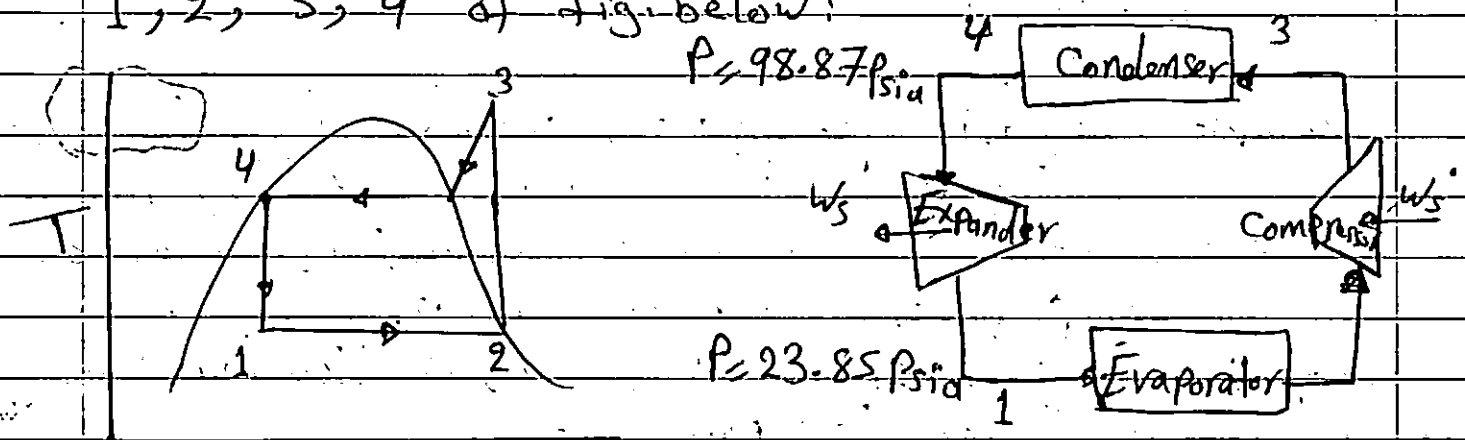
Solution: a) For a Carnot refrigerator

$$W = \frac{T_c}{T_H - T_c} = \frac{(10 + 459.67) \text{ R}}{(80 + 459.67) \text{ R} - (10 + 459.67) \text{ R}} = 5.75$$

- أقل درجة حرارة  $10^\circ\text{F}$  وذلك بدرجة كافية فالتبريد ممكن (الدرجة  
 $10^\circ\text{F}$  أقل من درجة التبريد الأكثر للثابت  $31^\circ\text{F}$  - يكون للتبريد  
 الأقصى ما بين  $0^\circ\text{F}$  و  $80^\circ\text{F}$  وليس  $10^\circ\text{F}$  و  $70^\circ\text{F}$ .



b) Freon-12 is the refrigerant; H of states 1, 2, 3, 4 of fig. below:



read from table (9.1) and fig. (9.3). From  $0^\circ\text{F}$   $\approx (10-10)^\circ\text{F}$  in table (9.1), Freon vaporizes in the evaporator at a pressure of 23.85 psia.

Its properties as "a sat. vap" at these conditions:

$$\begin{aligned} H_2^V &= 77.27 \text{ Btu/lbm} \\ S_2^V &= 0.1689 \text{ Btu/lbm} \cdot \text{R} \end{aligned}$$

From entry at  $70+10 = 80^\circ\text{F}$  in table (9.1), we find Freon-12 condenses at 98.87 psia; its properties as "sat. liq." at these conditions:

$$\begin{aligned} H_4^L &= 26.37 \text{ Btu/lbm} \\ S_4^L &= 0.0548 \text{ Btu/lbm} \cdot \text{R} \end{aligned}$$

$$\therefore S_3 = S_2 = 0.1689$$

From fig. (9.3) at  $S_3 = 0.1689$  &  $P = 98.87 \text{ psia}$

$$H_3 = 88.3 \text{ Btu/lbm}$$

State 1 is a two-phase mixture

$$\therefore S_1 = (1-x) \cdot S^L + x \cdot S^V$$

$x$ : quality (mass fraction of mixture that is vapor).

$$\therefore S_1 = S_4 = 0.0548$$

$$\therefore 0.0548 = (1-x) \cdot 0.0193 + x \cdot 0.1689$$

$$\Rightarrow x = 0.2373$$

and

$$H_1 = (1-x) \cdot H^L + x \cdot H^V$$

$$= 0.7627 \times 8.82 + 0.2373 \times 77.27$$

$$= 24.83 \text{ Btu/lbm}$$

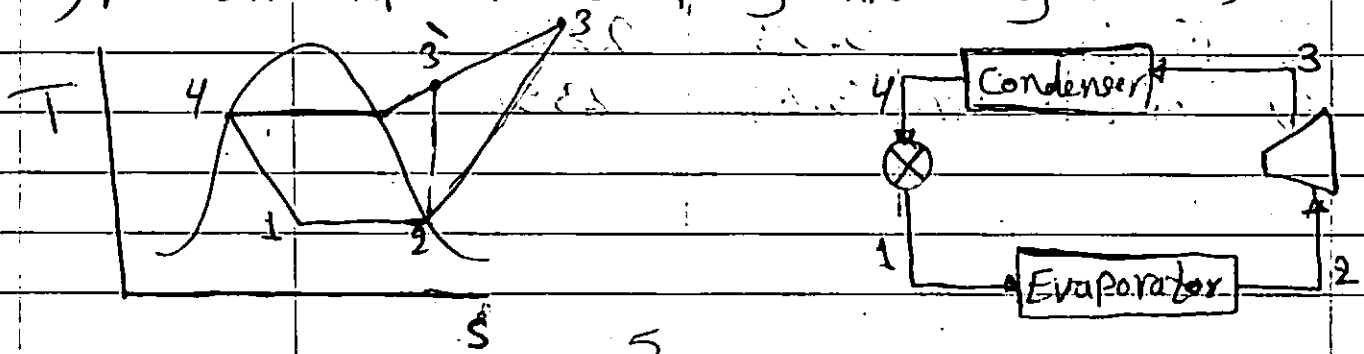
$$W = \frac{H_2 - H_1}{(H_3 - H_4) - (H_2 - H_1)}$$

$$= \frac{77.27 - 24.83}{(88.3 - 26.37) - (77.27 - 24.83)} = 5.53$$

$$(88.3 - 26.37) - (77.27 - 24.83)$$

$$m \cdot \frac{1 \text{ kcal}}{H_2 - H_1} = \frac{120,000}{77.27 - 24.83} = 2288 \text{ lbm/hr}$$

c) For the expansion step by throttling valve,





$$H_1 = H_4 = 26.37 \text{ Btu/lbm}$$

For the compression step,

$$\Delta H_s = (H_3 - H_2)_s$$

isentropic

$$= 88.3 - 77.27 = 11.03$$

For a compressor efficiency of 0.80

$$\Delta H_{\text{not isentropic}} = (H_3 - H_2) = \frac{\Delta H_s}{\eta}$$

$$= \frac{11.03}{0.8} = 13.8 \text{ Btu/lbm}$$

$$\therefore \omega = \frac{H_2 - H_1}{H_3 - H_2} = \frac{77.27 - 26.37}{13.8} = 3.69$$

The refrigerant circulation rate is:

$$\dot{m} = \frac{|Q_c|}{H_2 - H_1} = \frac{120,000}{77.27 - 26.37} = 2358 \text{ lbm/hr}$$

Cycle	$\omega$	$\dot{m}$ (lbm/hr)
a) Carnot	5.75	
b) Turbine	5.53	2288
c) Throttle Valve	3.69	2358

## ~ The Choice of Refrigerant :

The selection of a refrigerant was generally based upon its availability, its cooling range and the experience regarding the process.

Table : General Criteria for Refrigerant Acceptability

Chemical	Stable and Inert
~ - Health	Non-toxic
- Safety	Non-flammable, Non-corrosive.
- Environmental	Zero ozone depletion potential (ODP).
- Thermodynamic	Low liquid specific heat, Low viscosity, High thermal conductivity.
~ - Miscellaneous مختل	Low cost , Easy leak detection, Low freezing point.



heat from the lower cycle by operating an evaporation level at  $(T_c)$ , which is colder than level  $(T_H)$ . Finally, the heat in the upper cycle is rejected at level  $(T_H)$  to external heat sinks.

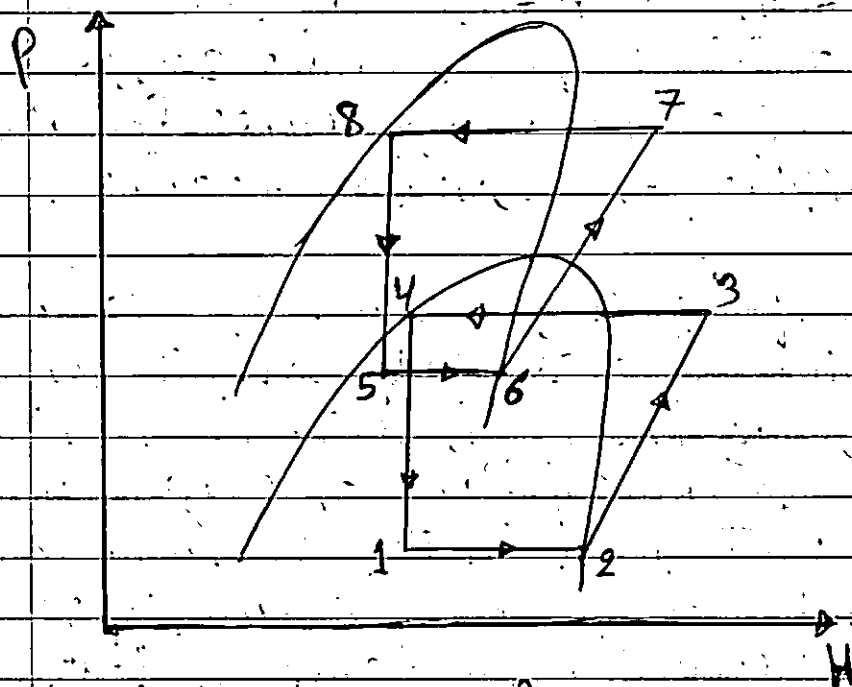


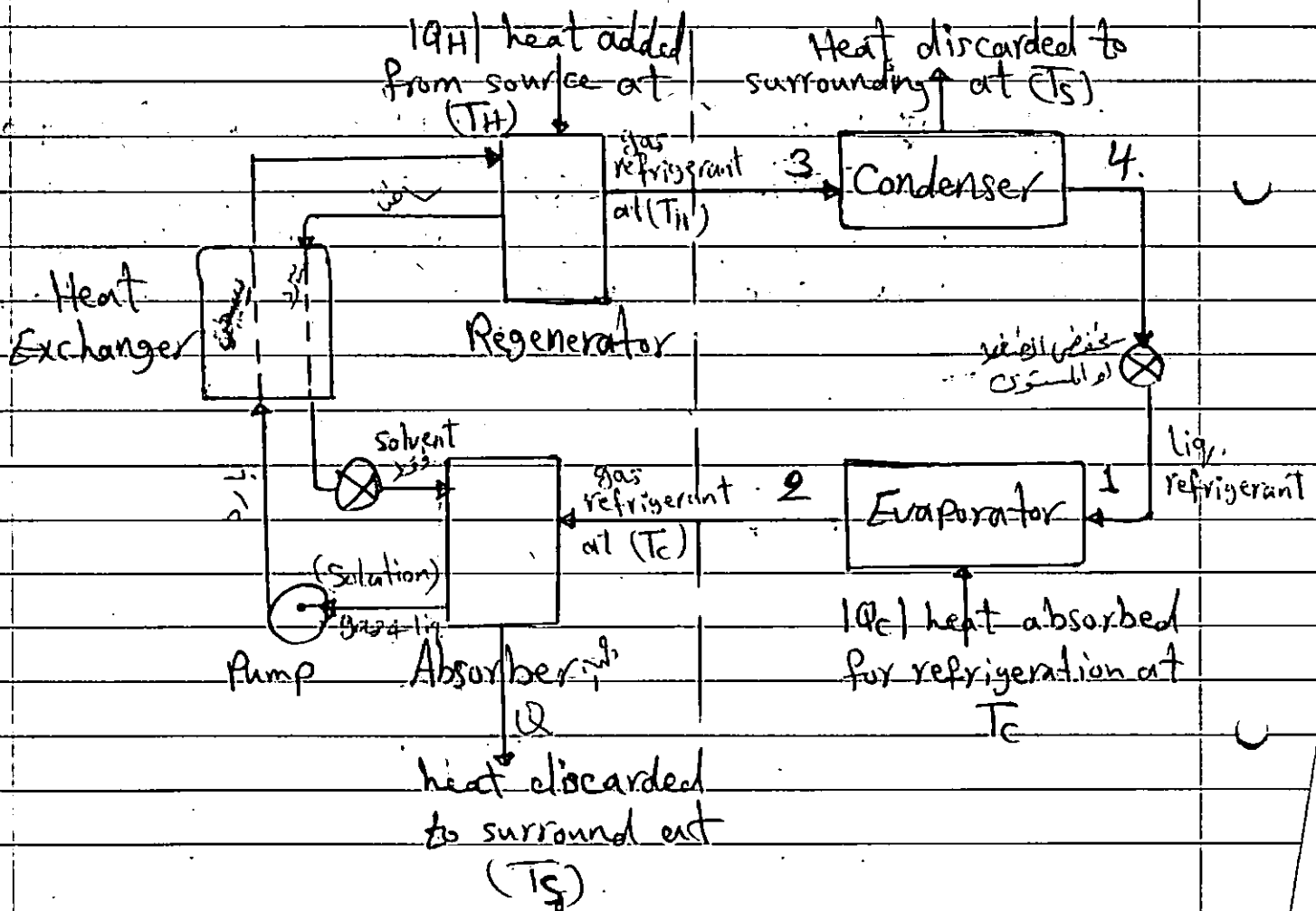
Fig. 1 A simple cascade refrigeration system on P-H diagram.

And the reasons for using cascade refrigeration system is of energy consumption, using a single refrigerant for the whole refrigeration demand may consume more shaft work than using multiple refrigerants.

# Absorption Refrigeration:

In vapor-compression refrigeration the work of compression is usually supplied by an electric motor. Thus the work for refrigeration comes ultimately from heat at a high temp. level. This suggests the direct use of heat as the energy source for refrigeration. The absorption-refrigeration machine is based on this idea.

This technique employs a solute gas as the vaporizing refrigerant and a suitable solvent for recovering and recycling the refrigerant. The refrigerant is vaporized in the chiller (or evaporator) and dissolved in the solvent liquid in the absorber. The heat of solution released in the absorber is removed by a suitable coolant. The temp limitation of this system for large scale industrial refrigeration,



water

- Refrigerant as <sup>water</sup> vapor from the evaporator is absorbed in a relatively non volatile liquid solvent as (lithium bromide solution) as the absorbent, at the pressure of the evaporator and at low temp. The heat given off in the process is discarded to the surroundings at ( $T_s$ ). The liquid solution from the absorber contains high concentration of refrigerant, passes to a pump, which raises the pressure of the liquid to that of the condenser. Heat from the higher temperature source at ( $T_H$ ) is transferred to the liquid solution, raising its temp and evaporating the refrigerant from the solvent. Vapor passes from the regenerator to the condenser, and the solvent (which now contains a relatively low concentration of refrigerant) returns to the absorber.

The work required by a Carnot refrigerator absorbing heat at temp ( $T_c$ ) and rejecting heat at temp of surrounding ( $T_s$ ), as follows:-

$$\therefore (C.O.P) = \frac{|Q_c|}{|W|} = \frac{|Q_c|}{|Q_H| - |Q_c|} \quad \text{--- (a)}$$

and

$$\therefore (C.O.P) = \frac{T_c}{T_H - T_c} \quad \text{--- (b)}$$

Equating eqs (a) & (b) :-

$$\therefore \frac{T_c}{T_s - T_c} = \frac{|Q_c|}{|W|} \quad \text{where } T_s = T_H$$

$$\therefore |W| = \frac{(T_s - T_c)}{T_c} \cdot |Q_c| \quad \text{--- (c)}$$

If a source of heat is available at  $T_H$  above that of  $T_S$  surrounding temp

$$T_S = T_C$$

$$\therefore \eta = \frac{|W|}{|Q_H|} = 1 - \frac{T_S}{T_H} = \frac{T_H - T_S}{T_H}$$

$$\therefore |Q_H| = |W| \cdot \frac{T_H}{(T_H - T_S)} \quad \text{--- (d)}$$

sub eq (c) into eq (d) :-

$$|Q_H| = |Q_C| \cdot \frac{(T_S - T_C)}{T_C} \cdot \frac{T_H}{(T_H - T_S)}$$

The Heat Pump :

Is a reversed heat engine, is a device for heating house during winter and cooling them during summer. In the winter it operates to reject heat into the building, and during the summer the flow of refrigerant is reversed and heat is absorbed from the building and rejected to the outside air.

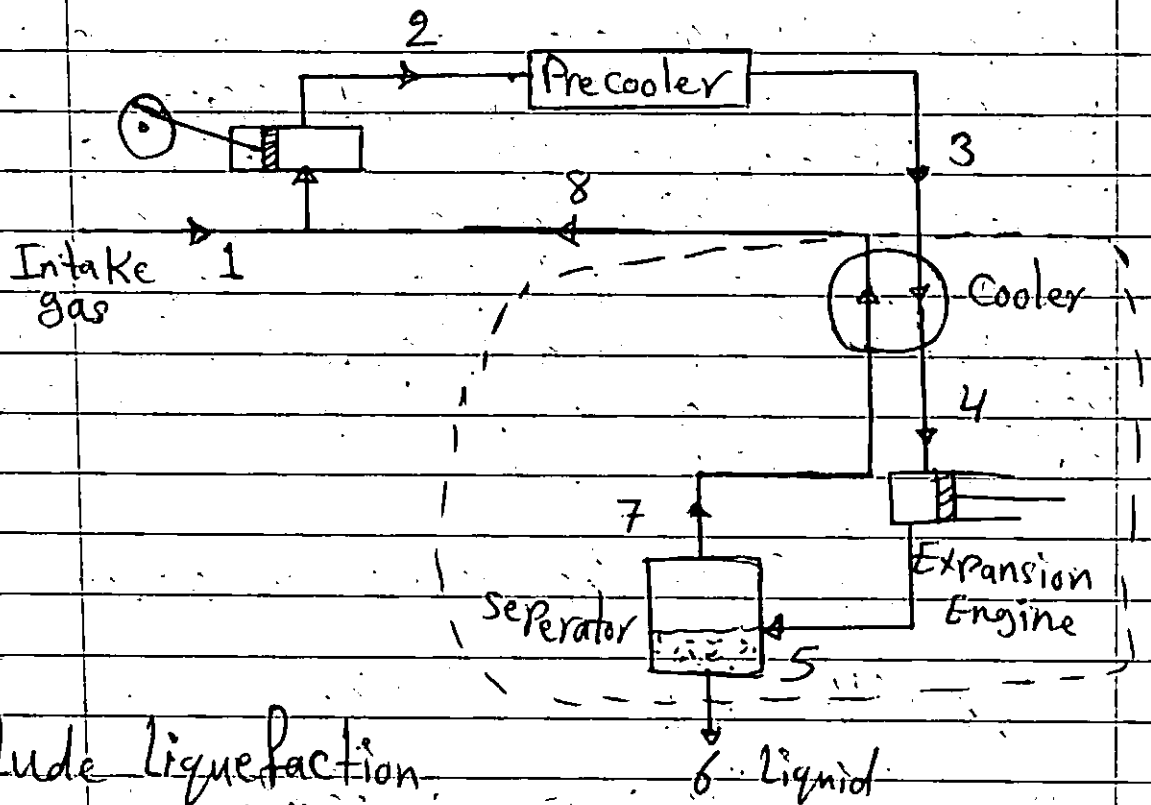
Energy balance around the separator, throttle valve, and cooler gives:

$$\Delta(m \cdot H) = 0$$

$$H_3 = H_6 \cdot Z + H_8 (1-Z)$$

where  $Z$ : the fraction of gas that is liquefied.

The flow diagram for the "Claude Process" is the same as for Linde process, except that an expansion or turbine replaces the throttle valve.



"Claude Liquefaction Process"

Energy Balance (Cooler, Expansion and separator)

$$H_3 = H_6 \cdot Z + (1-Z) \cdot H_8 + W_s$$



where  $w_s$ : work of expansion on basis of unit mass of fluid entering the cooler at point 3.

If engine operate adiabatically, the work become:  $\Delta H = Q - w_s$

$$w_s = - (H_5 - H_4)$$

Suppose that no heat leaks into the apparatus from the surrounding, that can never be exactly true.

Example: Natural gas, assumed to be pure methane, is liquefied in a simple Linde process. Compression is to be (60 bar) and precooling is to (300 K). The separator is maintained at a pressure of (1 bar), and unliquefied gas at this pressure leaves the cooler at (295 K). What fraction of the gas is liquefied in the process, and what is the temp of high-pressure gas entering throttle valve?

1)  $Z$ ? 2)  $T_4$ ?

Solution: Data for superheated methane are given:

$$H_3 = 1140 \text{ KJ/Kg at } (300 \text{ K \& } 60 \text{ bar}).$$

$$H_8 = 1188.9 \text{ KJ/Kg at } (295 \text{ K \& } 1 \text{ bar}).$$

For saturated liquid and vapor at (1 bar):

$$T^{\text{sat}} = 111.45 \text{ K} \quad H_6^L = 285.4 \text{ KJ/Kg "sat. liq."}$$

$$H_7^V = 796.9 \text{ KJ/Kg "sat. vap."}$$

Energy Balance:

$$H_6 \cdot Z + H_8 \cdot (1-Z) = H_3$$

$$\therefore Z = \frac{H_8 - H_3}{H_8 - H_6} = \frac{1188.9 - 1140.0}{1188.9 - 285.4} = 0.0541$$

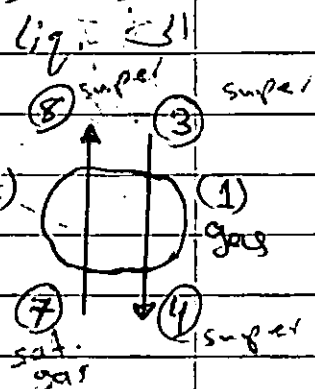
Energy Balance around the Cooler:

$$(1) (H_4 - H_3) + (1-Z) (H_8 - H_7) = 0$$

$$\therefore H_4 = H_3 - (1-Z) (H_8 - H_7)$$

$$= 1140 - (0.9459) (1188.9 - 796.9)$$

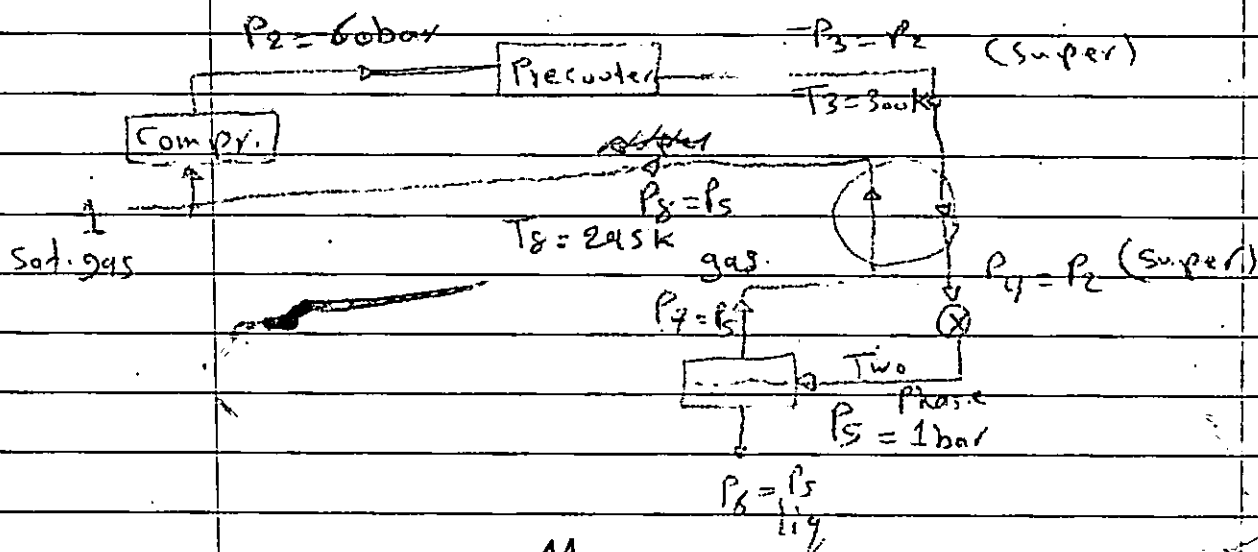
$$= 769.2 \text{ KJ/Kg}$$



Interpolation in tables for superheated methane:

at  $P = 60 \text{ bar}$  &  $H_4 = 769.2 \text{ KJ/Kg}$

$T = 206.5 \text{ K}$  (temp. of gas entering throttle valve).



Problems:

6th edition

9.2 ✓

9.3 ✓

9.4 ✓

9.5 ✓

9.7 ✓

9.8 ✓

9.10

9.13

9.14

9.15

## Chapter Eight

### Phase Equilibrium

A number of industrially important processes, such as distillation, absorption, and extraction, bring two phases into contact. When the phases are not in equilibrium, mass transfer occurs between the phases. Treatment of mass-transfer rates requires knowledge of the equilibrium states ( $T$ ,  $P$ , and compositions) of the system.

In most industrial processes coexisting phases are vapor and liquid, although liq/liq, vapor/solid, and liquid/solid systems are also encountered. In this chapter describe the calculation of temperatures, pressures, and phase compositions for systems in vapor/liquid equilibrium (VLE).

#### The Nature of Equilibrium:

Equilibrium is a static condition in which no changes occur in the macroscopic properties of a system with time. This requires a balance of all potentials that may cause change. In engineering the assumption of equilibrium is correct when it leads to an acceptable accuracy. For example, in the reboiler for a distillation column equilibrium between vapor and liquid phases is commonly assumed but it is an approximation. For vaporization rates it does not lead to an error in engineering calculations in specifying an approximate.

At equilibrium the temperature, pressure, and phase composition reach final values which remain fixed.

## Fugacity and Fugacity Coefficient:

A new property ( $f$ ) that also has a dimension of pressure is called "fugacity", it is a thermodynamic pressure. Since in a mixture of ideal gases, the fugacity of each component is equal to its partial pressure. At the region of vap-liquid equilibrium, the equation of equilibrium for each component ( $i$ ) is expressed in term of the fugacity.

$$f_i^V = f_i^L \quad \text{--- (a)}$$

The dimensionless ratio ( $f/P$ ) is a mixture property called the "activity coefficient" and given the symbol ( $\phi$ ). قابل

$$\phi = \frac{f}{P} \quad \text{--- (b)}$$

$$\phi_i^V = \frac{f_i^V}{y_i \cdot P} \quad \text{Fugacity coeff. of species (i) in the solution (gas phase).}$$

$$\phi_i^L = \frac{f_i^L}{x_i \cdot P} \quad \text{Fugacity coeff. of species (i) in the solution (liquid phase).}$$

## Rault's Law

When combined with the ideal gas and ideal solution models of phase behavior, a simple and useful equation known as Rault's Law describe the vapor-liquid equilibrium:

$$y_i \cdot P = x_i \cdot P_i^{\text{sat}}$$

where:

$P_i^{\text{sat}}$  is a vapor pressure of a liquid

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{\text{sat}}}{P}$$

$K_i$  is the equilibrium constant of vap-liq. system

Rault's Law is a model used when: <sup>First Case:</sup> vapor phase ideal gas solution and liquid phase ideal liquid solution.

A second case: when the liquid phase is non ideal

liquid solution, gas phase ideal gas solution, then:

$$y_i \cdot P = \gamma_i \cdot x_i \cdot P_i^{\text{sat}}$$

where  $\gamma_i$  is the activity coefficient which is equal to (1) in ideal solution.

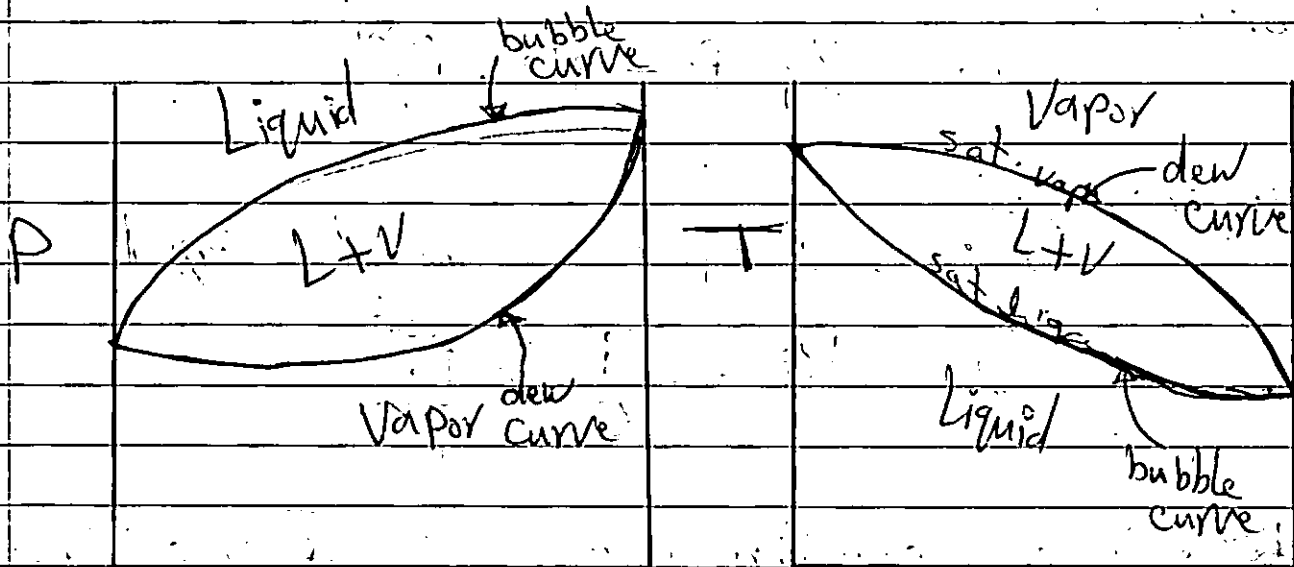
$$a_i = \gamma_i \cdot x_i$$

where  $a_i$  is the activity of species (i).

# Bubble Point and Dew Point Calculations:

Bubble Point: Just start to vaporize.

Dew Point: Just start to condense.



$X, y$

$X, y$

for dew point and bubble point calculations:

## 1) Bubble point:

Assume  $T$  or  $P$ .

Component	$x$	$K$	$y = K \cdot x$
A	—	—	—
B	—	—	—
C	—	—	—

$$\sum y = 1$$

2) Dew Point: Assume  $T$  or  $P$ .

<u>Component</u>	<u><math>y</math></u>	<u><math>K</math></u>	<u><math>x = \frac{y}{K}</math></u>
A	—	—	—
B	—	—	—
C	—	—	—

$$\sum x = 1$$

Example: Pg. 305, ch. 10

The binary system acetonitrile (1)/nitromethane (2) conforms closely to Raoult's law. Vapor pressure for the pure species are given by the following Antoine equations:

$$\ln P_1^{\text{sat}} / \text{KPa} = 14.2724 - \frac{2945.47}{T/^\circ\text{C} + 224.0}$$

$$\ln P_2^{\text{sat}} / \text{KPa} = 14.2043 - \frac{2972.64}{T/^\circ\text{C} + 209.00}$$

a) Prepare a graph showing  $P$  vs.  $x_1$  and  $P$  vs.  $y_1$  for a temp. at  $75^\circ\text{C}$ .

b) Prepare a graph showing  $T$  vs.  $x_1$  and  $T$  vs.  $y_1$  for a pressure of 70 KPa.

Solution:

a) At  $(75^\circ\text{C})$ , vap. pressure, from equations of Antoine eqs gives are:



$$P_1^{\text{sat}} = 83.21 \text{ KPa}$$

$$P_2^{\text{sat}} = 41.98 \text{ KPa}$$

From Raoult's Law:

$$y_1 \cdot P = x_1 \cdot P_1^{\text{sat}} \quad (1)$$

$$y_2 \cdot P = x_2 \cdot P_2^{\text{sat}} \quad (2)$$

$$y_1 + y_2 = 1 \quad (3)$$

Sub. eq (1) + (2) into (3)

$$P = x_1 \cdot P_1^{\text{sat}} + x_2 \cdot P_2^{\text{sat}}$$

$$x_2 = 1 - x_1$$

$$P = x_1 \cdot P_1^{\text{sat}} + (1 - x_1) \cdot P_2^{\text{sat}}$$

$$P = x_1 (P_1^{\text{sat}} - P_2^{\text{sat}}) + P_2^{\text{sat}}$$

Thus (a) plot of  $[P]$  vs.  $[x_1]$  is a straight line connecting  $P = P_2^{\text{sat}}$  at  $x_1 = 0$  with  $P = P_1^{\text{sat}}$  at  $x_1 = 1$ .

For example: when  $x_1 = 0.2$

$$P = 0.2 (83.21 - 41.98) + 41.98 = 50.23 \text{ KPa}$$

Corresponding value of  $y_1$ :

$$y_1 = \frac{x_1 \cdot P_1^{\text{sat}}}{P} = \frac{0.2 \cdot 83.21}{50.23} = 0.3313$$

- b) When Pressure is fixed, the temperature varies along with  $x_1$  and  $y_1$ .

the temperature range is bounded by the saturation temperatures  $t_1^{\text{sat}}$  and  $t_2^{\text{sat}}$ , the temperatures at which the "pure species" exert vapor pressure equal to  $P$ . For the present system,  $T$  are calculated from {Antoine equation} with :-

$$P_i^{\text{sat}} = P = 70 \text{ KPa}$$

$$t_1^{\text{sat}} = \frac{2945.47}{14.2724 - \ln P_1^{\text{sat}}} - 224.0$$

$$= 69.84^\circ \text{C}$$

$$t_2^{\text{sat}} = \frac{2972.64}{14.2043 - \ln P_2^{\text{sat}}} - 209.0$$

$$= 89.58^\circ \text{C}$$

Select values of  $(t)$  between  $t_1^{\text{sat}}$  and  $t_2^{\text{sat}}$ , calculate  $P_1^{\text{sat}}$  and  $P_2^{\text{sat}}$  for these temperatures, and evaluate  $x_1$  by :-

$$x_1 = \frac{P - P_2^{\text{sat}}}{P_1^{\text{sat}} - P_2^{\text{sat}}}$$

For example,  $t = 78^\circ \text{C}$

From Antoine eq:  $P_1^{\text{sat}} = 91.76 \text{ KPa}$

(1)  $P_2^{\text{sat}} = 46.84 \text{ KPa}$

$$X_1 = \frac{70 - 46.84}{91.76 - 46.84}$$

$$= 0.5156$$

and

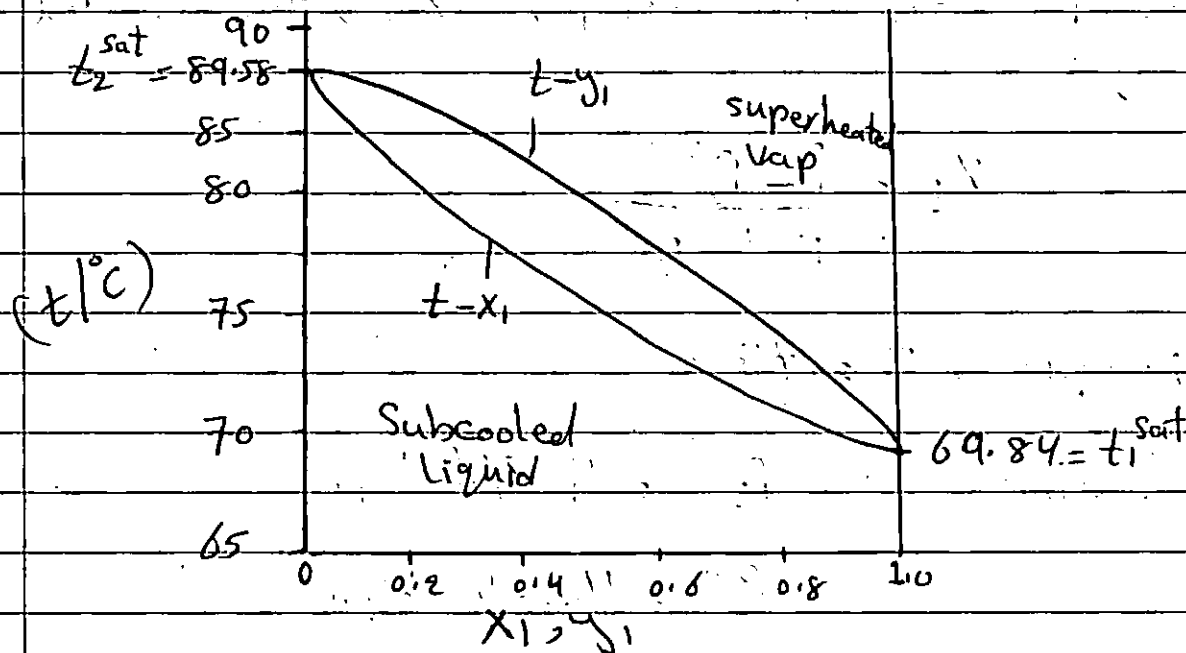
$$Y_1 = \frac{X_1 \cdot P^{\text{sat}}}{P}$$

$$= \frac{0.5156 \times 91.76}{70}$$

$$= 0.6759$$

The results are given in the following table:

$t / ^\circ\text{C}$	$X_1$	$Y_1$
$t_2^{\text{sat}}$ (89.58)	0.00	0.00
تقریب 86	0.1424	0.2401
82	0.3184	0.4742
78	0.5156	0.6759
74	0.7378	0.8484
$t_1^{\text{sat}}$ (69.84)	1.00	1.00



## Binary Systems:

Calculate  $T$  Bubble, Known  $[X_k]$  and  $P$ :

From Raoult's Law  $y \cdot P = x \cdot p^{sat}$

$$\begin{aligned} \therefore P &= x_1 \cdot p_1^{sat} + x_2 \cdot p_2^{sat} \\ &= p_2^{sat} \cdot \left[ x_1 \cdot \frac{p_1^{sat}}{p_2^{sat}} + x_2 \right] \end{aligned}$$

$$\therefore p_2^{sat} = \frac{P}{x_1 \cdot \alpha_{12} + x_2}$$

where  $\alpha_{12} = \frac{p_1^{sat}}{p_2^{sat}}$

$$\ln \alpha_{12} = \ln p_1^{sat} - \ln p_2^{sat}$$

- assume  $p_i^{sat} = P$

- From Antoni eq, calculate  $t_1^{sat}$  &  $t_2^{sat}$ :

$$t^{sat} = \frac{B_i}{A_i - \ln p_i^{sat}} - C_i$$

Iteration:-

i) Choose value of  $(t)$  as intermediate and find  $\alpha_{12}$  value.

ii) Calculate  $p_2^{sat}$ .

iii) Calculate  $(t)$  from Antoni eq at  $p_2^{sat}$  value.

iiii) Find new  $\alpha_{12}$ , then find  $p_2^{sat}$  and new  $(t)$  until iteration to convergence.

(2)

[illegible]

## Multi component Systems :

- 1) For a BUBL - P calculation, given  $\{X_K\}$  and  $T$ , Calculate  $\{Y_K\}$  and  $P$ .

Raoult's Law gives  $Y_K \cdot P = X_K \cdot P_K^{\text{sat}}$  ( $K=1, 2, \dots, N$ )

then  
bubl Press.

$$P = \sum_K X_K \cdot P_K^{\text{sat}}$$

$$Y_K = \frac{X_K \cdot P_K^{\text{sat}}}{P}$$

- 2) For a DEW - P calculation, know  $\{Y_K\}$  and  $T$ , Calculate  $\{X_K\}$  and  $P$ .

Raoult's Law gives  $Y_K \cdot P = X_K \cdot P_K^{\text{sat}}$  ( $K=1, 2, \dots, N$ )

then  
dew Press

$$P = \frac{1}{\sum_K (Y_K / P_K^{\text{sat}})}$$

$$X_K = \frac{Y_K \cdot P}{P_K^{\text{sat}}}$$

- 3) A BUBL - T calculation of  $\{Y_K\}$ , given  $\{X_K\}$  and  $P$ ,

$$\text{or } P = \sum_K X_K \cdot P_K^{\text{sat}}$$

$$\text{or } P = P_i^{\text{sat}} \sum_K X_K \cdot \frac{P_K^{\text{sat}}}{P_i^{\text{sat}}}$$

(3)

where  $(i)$ : is an arbitrarily selected member of set  $\{K\}$ .

$$P_i^{\text{sat}} = \frac{P}{\sum_K x_K \cdot \alpha_{Ki}}$$

where  $\alpha_{Ki} = \frac{P_K^{\text{sat}}}{P_i^{\text{sat}}}$

by Antoine eq.:

$$\ln \alpha_{Ki} = A_K - A_i - \frac{B_K}{(t + C_K)} + \frac{B_i}{(t + C_i)}$$

An iterative Procedure starts with an initial value of  $t$  provided by eq.:-

"initial temp":  $t_0 = \sum_K x_K \cdot t_K^{\text{sat}}$

where  $t_K^{\text{sat}} = \frac{B_K}{A_K - \ln P_K^{\text{sat}}} - C_K$

at  $P_K^{\text{sat}} = P$ , given value

then yields  $P_i^{\text{sat}}$ , and we get an improved value of  $(t)$  from the Antoine equation

$$t = \frac{B_i}{A_i - \ln P_i^{\text{sat}}} - C_i$$

This calculational sequence is repeated until there is no significant change in  $(t)$  from one iteration to the next.

Final values of  $P_K^{\text{sat}}$  are found from Antoine Eq. at calculate temperature, then the final

Y<sub>K</sub> values come from Raoult's Law

$$Y_K = \frac{X_K \cdot P_K^{\text{sat}}}{P}$$

4) A DEW T calculation of {X<sub>K</sub>}, given {Y<sub>K</sub>} and P;

$$P = \frac{1}{\sum_K (Y_K / P_K^{\text{sat}})}$$

$$P = \frac{P_i^{\text{sat}}}{\sum_K Y_K (P_i^{\text{sat}} / P_K^{\text{sat}})}$$

تجزیه

$$P_i^{\text{sat}} = P \sum_K (Y_K / \alpha_{Ki})$$

An iterative process starts with an initial value of  $t$  provided by eq:

$$t_0 = \sum_K Y_K \cdot t_K^{\text{sat}}$$

then yields  $P_i^{\text{sat}}$ , and get a value of  $(t)$  from Antoine eq

$$t = \frac{B_i}{A_i - \ln P_i^{\text{sat}}} - C_i$$

then  $P_K^{\text{sat}}$  from Antoine eq, and  $X_K$  by

$$X_K = \frac{Y_K \cdot P}{P_K^{\text{sat}}}$$



Example: For the acetone (1) / acetonitrile (2) / nitromethane (3) system, we have the following Antoine equations:

$$\ln P_1^{\text{sat}} = 14.5463 - \frac{2940.46}{t + 237.22}$$

$$\ln P_2^{\text{sat}} = 14.2724 - \frac{2945.47}{t + 224.00}$$

$$\ln P_3^{\text{sat}} = 14.2043 - \frac{2972.64}{t + 209.00}$$

where  $t$  is in ( $^{\circ}\text{C}$ ) and the vapor pressures are in (KPa). Assuming that Raoult's Law is appropriate to this system, Calculate:

a)  $P$  and  $\{y_k\}$ , given that  $t = 80^{\circ}\text{C}$ ,  $x_1 = 0.25$ ,  $x_2 = 0.35$  and  $x_3 = 0.40$ .

b)  $P$  and  $\{x_k\}$ , given that  $t = 70^{\circ}\text{C}$ ,  $y_1 = 0.50$ ,  $y_2 = 0.30$  and  $y_3 = 0.20$ .

c)  $t$  and  $\{y_k\}$ , given that  $P = 80 \text{ KPa}$ ,  $x_1 = 0.30$ ,  $x_2 = 0.45$  and  $x_3 = 0.25$ .

d)  $t$  and  $\{x_k\}$ , given that  $P = 90 \text{ KPa}$ ,  $y_1 = 0.60$ ,  $y_2 = 0.20$  and  $y_3 = 0.20$ .

Solution: a) BUBL  $P$  calculation for  $t = 80^{\circ}\text{C}$  and given  $\{x_k\}$ .

Calculate  $P_1^{\text{sat}} = 195.75$  KPa,  $P_2^{\text{sat}} = 97.84$  KPa,  $P_3^{\text{sat}} = 50.32$  KPa  
from Antoine eq.

$$P = \sum_K X_K \cdot P_K^{\text{sat}}$$

$$= (0.25)(195.75) + (0.35)(97.84) + (0.40)(50.32)$$

$$= 103.31 \text{ Kpa.}$$

$$Y_K = \frac{X_K \cdot P_K^{\text{sat}}}{P}$$

$$\therefore Y_1 = 0.4737, Y_2 = 0.3315, Y_3 = 0.1948$$

$$\therefore \sum Y_K = 1$$

b) DEW P calculation, for  $t = 70^\circ\text{C}$  and given  $\{Y_K\}$ :

From Antoine:  $P_1^{\text{sat}} = 144.77$ ,  $P_2^{\text{sat}} = 70.37$ ,  $P_3^{\text{sat}} = 43.80 \text{ Kpa.}$   
eq.:-

$$P = \frac{1}{\sum_K (Y_K / P_K^{\text{sat}})}$$

$$= \frac{1}{\left( \frac{0.50}{144.77} + \frac{0.30}{70.37} + \frac{0.20}{43.80} \right)}$$

$$= 74.27 \text{ Kpa}$$

and

$$X_K = \frac{Y_K \cdot P}{P_K^{\text{sat}}}$$

$$\therefore X_1 = 0.2565, X_2 = 0.3166, X_3 = 0.4269$$

$$\therefore \sum X_K = 1$$

(5)

c) BUBL T calculation, For ternary system with  $i=3$ , final  $P_i^{sat}$  are found from:

$$P_3^{sat} = \frac{P}{X_1 \cdot \alpha_{13} + X_2 \cdot \alpha_{23} + X_3 \cdot \alpha_{33}}$$

$$= \frac{80}{(0.30 \alpha_{13} + 0.45 \alpha_{23} + 0.25 \cdot 1)}$$

Setting  $P_1^{sat}$ ,  $P_2^{sat}$  and  $P_3^{sat}$  in Antoine eq. equal to (80 Kpa), we find:

$$t_1^{sat}, 52.07, t_2^{sat}, 73.81, t_3^{sat}, 93.64^\circ\text{C}$$

then gives  $t_0 = \sum_K X_K \cdot t_K^{sat}$

$$= (0.3)(52.07) + (0.45)(73.81) + (0.25)(93.64)$$

$$= 72.25^\circ\text{C}$$

$P_1^{sat}, 155.15 \text{ Kpa}$ ,  $P_2^{sat}, 75.91 \text{ Kpa}$  &  $P_3^{sat}, 37.88 \text{ Kpa}$   
for this initial temp., we find that

$$\alpha_{13} = 4.0951 \quad \text{and} \quad \alpha_{23} = 2.0037$$

$$\therefore P_3^{sat} = 33.61 \text{ Kpa}$$

$$\text{and } t = \frac{B_3}{A_3 - \ln P_3^{sat}} - C_3$$

$$= \frac{2972.64}{14.2043 - \ln 33.61} - 209.00$$

$$= 69.09^\circ\text{C}$$

~ This new value of  $(t)$  allows the calculations to be repeated. Further iteration leads to a final value of

$$t = 68.60^\circ\text{C}$$

At this temp.,  $P_1^{\text{sat}} = 138.56 \text{ Kpa}$

$$P_2^{\text{sat}} = 67.08 \text{ Kpa} \text{ and } P_3^{\text{sat}} = 32.98 \text{ Kpa.}$$

and by 
$$Y_K = \frac{X_K \cdot P_K^{\text{sat}}}{P}$$

$$\therefore Y_1 = 0.5196, Y_2 = 0.3773, Y_3 = 0.1031$$

d) DEW T calculation, take  $i=3$

$$P_3^{\text{sat}} = P \left( \frac{Y_1}{\alpha_{13}} + \frac{Y_2}{\alpha_{23}} + \frac{Y_3}{\alpha_{33}} \right)$$

$$= 90 \left( \frac{0.6}{\alpha_{13}} + \frac{0.2}{\alpha_{23}} + 0.2 \right)$$

~ at  $P = 90 \text{ Kpa}$ , the saturation temperatures are:

$$t_1^{\text{sat}} = 55.47, t_2^{\text{sat}} = 77.40, t_3^{\text{sat}} = 97.32^\circ\text{C}$$

$$t_o = \sum_K Y_K \cdot t_K^{\text{sat}}$$

$$= 68.23^\circ\text{C}$$

at this temp., find  $\alpha_{13} = 4.2123$ ,  $\alpha_{23} = 2.0370$

$$\text{eg } \frac{P_1^{\text{sat}}}{P_3^{\text{sat}}} = \text{---} \quad \text{eg } \frac{P_2^{\text{sat}}}{P_3^{\text{sat}}} = \text{---}$$

$$\therefore P_3^{\text{sat}} = 39.66 \text{ Kpa.}$$

(6)

$$\text{By eq. } t = \frac{B_i}{A_i - \ln p_i^{\text{sat}}} - C_i$$

$$t = 73.95^\circ\text{C}$$

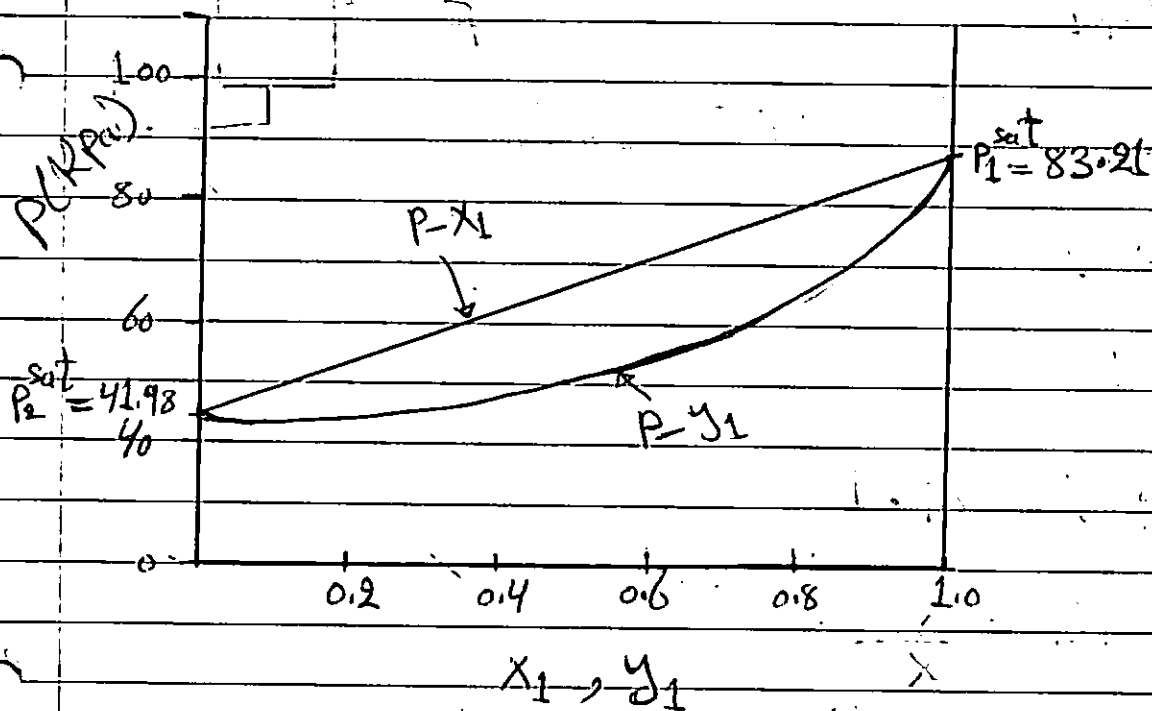
At this temp,  $p_1^{\text{sat}} = 163.47$ ,  $p_2^{\text{sat}} = 80.37$ ,  
 $p_3^{\text{sat}} = 40.39 \text{ KPa}$

$$X_k = \frac{y_k \cdot p}{p_k^{\text{sat}}}$$

$$X_1 = 0.3303, X_2 = 0.2240, X_3 = 0.4457$$

$X_1$	$y_1$	$P$
0	0	41.98
0.2	0.3313	50.23
0.4	0.5692	58.47
0.6	0.7483	66.72
0.8	0.8880	74.96
1.0	1.0	83.21

then the graph is as follow:

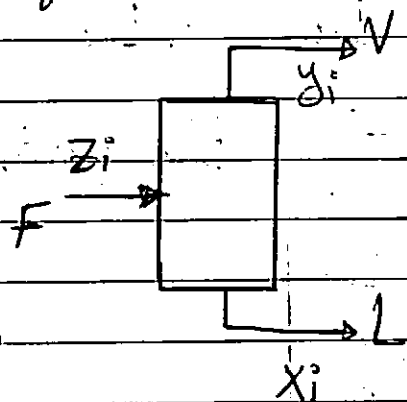


## Flash Calculation:

When the liquid under pressure passes through a valve to a pressure low enough that some of the liquid vaporizes or flashes producing a two phase stream of vapor and liquid in equilibrium.

Total  
T, M, B:

$$F = V + L$$



For 1 mole feed  $F = 1 \text{ mole}$

$$1 = L + V$$

Component  
C, M, B

$$Z_i = y_i \cdot V + x_i \cdot L$$

$$\text{but } K_i = \frac{y_i}{x_i}$$

$$Z_i = y_i \cdot V + \frac{y_i}{K_i} (1 - V)$$

$$Z_i \cdot K_i = y_i \cdot V \cdot K_i + y_i (1 - V)$$

$$Z_i \cdot K_i = y_i [K_i \cdot V + (1 - V)]$$

$$y_i = \frac{Z_i \cdot K_i}{K_i \cdot V + (1 - V)}$$

$$\Rightarrow y_i = \frac{Z_i \cdot K_i}{1 + V(K_i - 1)}$$

$$\sum y_i = 1 = \sum \frac{z_i \cdot K_i}{1 + V(K_i - 1)}$$

and from:

$$z_i = y_i \cdot V + x_i \cdot L \quad \text{and} \quad K_i = \frac{y_i}{x_i}$$

$$z_i = K_i \cdot x_i \cdot (1 - L) + x_i \cdot L$$

$$= x_i [K_i(1 - L) + L]$$

$$x_i = \frac{z_i}{K_i(1 - L) + L} \Rightarrow x_i = \frac{z_i}{K_i + L(1 - K_i)}$$

$$\sum x_i = 1 = \sum \frac{z_i}{K_i + L(1 - K_i)}$$

Example: (10.3); Pg. (315).

The system acetone (1) / acetonitrile (2) / nitromethane (3) at 80°C and 110 kPa has the overall composition,  $z_1 = 0.45$ ,  $z_2 = 0.35$ ,  $z_3 = 0.2$ . Determine  $L$ ,  $V$ ,  $x_i$  and  $y_i$ .

Solution: We must test the system is actually in the two phase region this should be determined before a flash calculation; a flash occurs when the pressure of the system lies between the bubble point pressure  $P_b$  and the dew point pressure  $P_d$ .

The vapor pressure of the pure species at 80°C are:

$$P_1^{\text{sat}} = 195.75, \quad P_2^{\text{sat}} = 97.84 \quad \text{and} \quad P_3^{\text{sat}} = 50.32 \text{ kPa}$$



First, we do a Bubble P calculation with  $z_i = x_i$  to determine  $P_b$ :

$$P_b = x_1 \cdot P_1^{\text{sat}} + x_2 \cdot P_2^{\text{sat}} + x_3 \cdot P_3^{\text{sat}}$$

$$\therefore P_b = (0.45 \times 195.75) + (0.35 \times 97.84) + (0.2 \times 50.32) \\ = 132.40 \text{ KPa}$$

Second, we do a Dew P calculation with  $z_i = y_i$  to determine  $P_d$ :

$$P_d = \frac{1}{y_1/P_1^{\text{sat}} + y_2/P_2^{\text{sat}} + y_3/P_3^{\text{sat}}}$$

$$= \frac{1}{(0.45/195.75) + (0.35/97.84) + (0.2/50.32)} \\ = 101.52 \text{ KPa}$$

The given pressure lies between  $P_b$  and  $P_d$  so flash calculation

$$K_1 = \frac{P_1^{\text{sat}}}{P} = \frac{195.75}{110} = 1.7795$$

$$K_2 = 0.8895, \quad K_3 = 0.4575$$

$$\sum y_i = 1 = \sum \frac{z_i \cdot K_i}{1 + V(K_i - 1)}$$

$$\frac{(0.45 \times 1.7795)}{1 + 0.7795 \cdot V} + \frac{(0.35 \times 0.8895)}{1 - 0.1105 \cdot V} + \frac{(0.2 \times 0.4575)}{1 - 0.5425 \cdot V} = 1$$

~ Solution for V by trial yields:

$$V = 0.7364 \text{ mole}$$

$$L = 1 - V$$

$$= 1 - 0.7364$$

$$= 0.2636 \text{ mole}$$

$$\therefore y_1 = \frac{(0.45) \times (1.7795)^{K_1}}{1 + (0.7795) \times (0.7364)} = 0.5087$$

$$y_2 = 0.3389$$

$$y_3 = 0.1524$$

$$\therefore x_1 = \frac{y_1}{K_1} = \frac{0.5087}{1.7795} = 0.2859$$

$$x_2 = 0.3810$$

$$x_3 = 0.3331$$

$$\sum x_i = \sum y_i = 1$$

Problems:-

10.10

10.6

10.7

10.12

10.8

10.9

10.14

10.16

## Chapter Nine

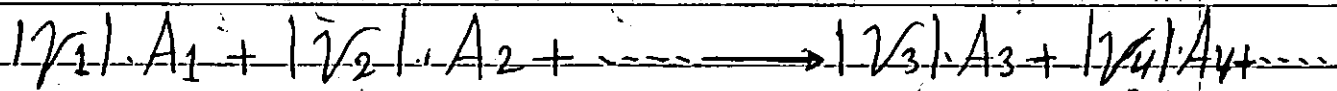
### Chemical Reaction Equilibrium

The transformation of raw materials into products of greater value by means of chemical reaction is a major industry, and a number of commercial products is obtained by chemical synthesis. Sulfuric acid, ammonia, ethylene, propylene, etc., are examples of chemicals product. These in turn are used in the large-scale manufacture of fibers, paints, detergents, etc. Clearly the chemical engineer must be familiar with chemical reactor design and operation.

The choice of operation conditions still be determined by equilibrium considerations. Calculation of equilibrium conversions is based on the fundamental equations of chemical reaction equilibrium.

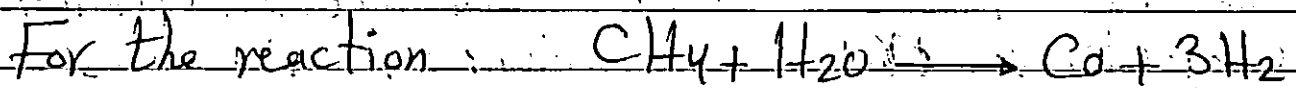
#### The Reaction Coordinates:

The general chemical reaction is written as:



where the  $|v_i|$  are stoichiometric coefficients and  $A_i$  stand for chemical formulas.

The sign "Positive" for products and "negative" for reactants.



the stoichiometric numbers, are:

$$\nu_{\text{CH}_4} = -1, \quad \nu_{\text{H}_2\text{O}} = -1, \quad \nu_{\text{CO}} = 1, \quad \nu_{\text{H}_2} = 3$$

The stoichiometric number for any inert species present is "Zero".

The changes in the numbers of moles of the species present are in direct proportion to the stoichiometric numbers. If 0.5 mol of  $\text{CH}_4$  disappears by reaction, 0.5 mol of  $\text{H}_2\text{O}$  must also disappear, simultaneously 0.5 mol of  $\text{CO}$  and 1.5 mol of  $\text{H}_2$  are formed by reaction. Applying this principle to a differential amount of reaction, we can write:

$$\boxed{\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \frac{dn_3}{\nu_3} = \frac{dn_4}{\nu_4} = \dots = d\epsilon} \quad (1)$$

Each term is related to an amount of reaction as represented by a change in the number of moles of a chemical species. Since all terms are equal, they can be identified collectively with a single quantity  $d\epsilon$ .

The general relation between a differential change  $dn_i$  in the number of moles of a reacting species and  $d\epsilon$  is therefore:

$$\boxed{dn_i = \nu_i \cdot d\epsilon} \quad (i=1, 2, \dots, N)$$

The new variable  $\epsilon$ : called the reaction coordinate, characterizes or degree to which a reaction has taken place.

Equation (1) define changes in  $\epsilon$  with respect to changes in the numbers of moles of the reacting species.

$$\sum_{i=1}^N dn_i = \sum_{i=1}^N \nu_i d\epsilon$$

or

$$n_i = n_{i0} + \nu_i \epsilon \quad (i=1, 2, \dots, N)$$

$$\sum_{i=1}^N n_i = \sum_{i=1}^N n_{i0} + \epsilon \cdot \sum_{i=1}^N \nu_i$$

or

$$n = n_0 + \nu \epsilon$$

where:

$$n \equiv \sum n_i$$

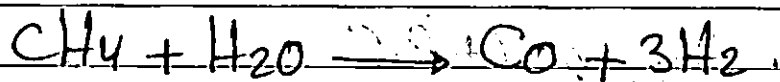
$$n_0 \equiv \sum n_{i0}$$

$$\nu \equiv \sum \nu_i$$

The mole fractions ( $y_i$ ) of the species present are related to ( $\epsilon$ ) by:

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \nu_i \epsilon}{n_0 + \nu \epsilon}$$

Example (1):- For a system in which the following reaction occurs,



assume there are present initially (2 mol  $\text{CH}_4$ ), (1 mol  $\text{H}_2\text{O}$ ), (1 mol  $\text{CO}$ ), and (4 mol  $\text{H}_2$ ). Determine expressions for the mole fractions  $y_i$  as functions of  $\epsilon$ .

Solution: For the given reaction:

$$\nu = -1 - 1 + 1 + 3 = (2)$$

$$n_i^0 = n_i^0 + \nu_i \epsilon$$

$$n_{CH_4} = 2 - \epsilon$$

$$n_{H_2O} = 1 - \epsilon$$

$$n_{CO} = 1 + \epsilon$$

$$n_{H_2} = 4 + 3\epsilon$$

$$n_T = 8 + 2\epsilon$$

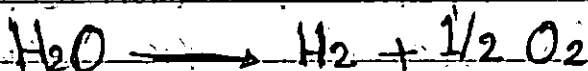
$$y_{CH_4} = \frac{n_{CH_4}}{n_T} = \frac{2 - \epsilon}{8 + 2\epsilon}$$

$$y_{H_2O} = \frac{1 - \epsilon}{8 + 2\epsilon}$$

$$y_{CO} = \frac{1 + \epsilon}{8 + 2\epsilon}$$

$$y_{H_2} = \frac{4 + 3\epsilon}{8 + 2\epsilon}$$

Example (2): Consider a vessel which initially contains only  $(n_0)$  moles of water vapor. If decomposition occurs according to the reaction



final expressions which relate the number of moles and the mole fraction of each chemical species to the reaction coordinate  $\epsilon$ .

Solution: For the given reaction,

$$\nu = -1 + 1 + \frac{1}{2} = -\frac{1}{2}$$

$$n_{\text{H}_2\text{O}} = n_0 - \epsilon$$

$$n_{\text{H}_2} = +\epsilon$$

$$n_{\text{O}_2} = +\frac{1}{2}\epsilon$$

$$n_t = n_0 + \frac{1}{2}\epsilon$$

$$y_{\text{H}_2\text{O}} = \frac{n_0 - \epsilon}{n_0 + \frac{1}{2}\epsilon}$$

$$y_{\text{H}_2} = \frac{\epsilon}{n_0 + \frac{1}{2}\epsilon}$$

$$y_{\text{O}_2} = \frac{\frac{1}{2}\epsilon}{n_0 + \frac{1}{2}\epsilon}$$

The fractional decomposition of water vapor is

$$\frac{n_0 - n_{\text{H}_2\text{O}}}{n_0} = \frac{n_0 - (n_0 - \epsilon)}{n_0} = \frac{\epsilon}{n_0}$$



## More Independent Reaction:

When two or more independent reactions proceed simultaneously, let subscript  $(j)$  the reaction index, and associate a separate reaction coordinate  $\xi_j$  with each reaction. The stoichiometric numbers associated with both a species and a reaction. Thus  $\nu_{ij}$  designates the stoichiometric number of species  $(i)$  in reaction  $(j)$ . Since the number of moles of a species  $(n_i)$  may change because of several reactions, the general eq:

$$dn_i = \sum_j \nu_{ij} d\xi_j \quad (i=1, 2, \dots, N)$$

Integration from  $n_i = n_{i0}$  and  $\xi_j = 0$

$$n_i = n_{i0} + \sum_j \nu_{ij} \cdot \xi_j \quad \text{--- (A)}$$

Summing over all species yields

$$n = \sum_i n_{i0} + \sum_i \sum_j \nu_{ij} \xi_j$$

or

$$n = n_0 + \sum_j \left( \sum_i \nu_{ij} \right) \xi_j$$

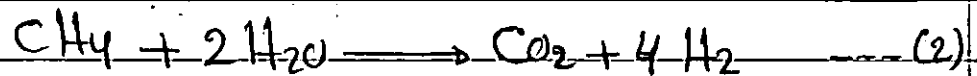
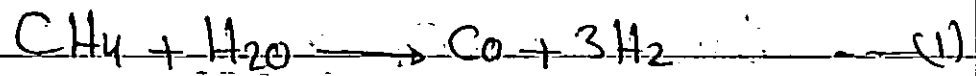
$$\text{so } \nu_j \equiv \sum_i \nu_{ij}$$

Then:  $n = n_0 + \sum_j \nu_j \xi_j \quad \text{--- (B)}$

Combination of eq (B) with eq (A) gives mole fraction:

$y_i = \frac{n_{i0} + \sum_j \nu_{ij} \xi_j}{n_0 + \sum_j \nu_j \xi_j}$
---

Example (3): Consider a system in which the following reactions occur:



Where the numbers (1) and (2) indicate the value of  $j$ , the reaction index. If there are present initially 2 mol  $\text{CH}_4$  and 3 mol  $\text{H}_2\text{O}$ , determine expressions for the  $y_i$  as functions of  $\epsilon_1$  and  $\epsilon_2$ .

Solution: The stoichiometric numbers  $\nu_{i,j}$  can be arrayed as follows:

$j$	$\text{CH}_4$	$\text{H}_2\text{O}$	$\text{CO}$	$\text{CO}_2$	$\text{H}_2$	$\nu_{i,j}$
1	-1	-1	1	0	3	$2 = (3 + 1 - 1 - 1)$
2	-1	-2	0	1	4	$2 = (4 + 1 - 2 - 1)$

$$n_i = n_{0i} + \nu_i \cdot \epsilon_1 + \nu_j \cdot \epsilon_2$$

$$n_{\text{CH}_4} = 2 - \epsilon_1 - \epsilon_2$$

$$n_{\text{H}_2\text{O}} = 3 - \epsilon_1 - 2\epsilon_2$$

$$n_{\text{CO}} = \epsilon_1$$

$$n_{\text{CO}_2} = \epsilon_2$$

$$n_{\text{H}_2} = 3\epsilon_1 + 4\epsilon_2$$

$$n_T = 5 + 2\epsilon_1 + 2\epsilon_2$$

$$y_{CH_4} = \frac{2 - \epsilon_1 - \epsilon_2}{5 + 2\epsilon_1 + 2\epsilon_2}$$

$$y_{H_2O} = \frac{3 - \epsilon_1 - 2\epsilon_2}{5 + 2\epsilon_1 + 2\epsilon_2}$$

$$y_{CO} = \frac{\epsilon_1}{5 + 2\epsilon_1 + 2\epsilon_2}$$

$$y_{CO_2} = \frac{\epsilon_2}{5 + 2\epsilon_1 + 2\epsilon_2}$$

$$y_{H_2} = \frac{3\epsilon_1 + 4\epsilon_2}{5 + 2\epsilon_1 + 2\epsilon_2}$$

The composition of the system is a function of two variables  $\epsilon_1$  &  $\epsilon_2$ .

The Standard Gibbs Energy Change and the Equilibrium Constant:

The standard Gibbs energy change of reaction ( $\Delta G^\circ$ ) depends on temperature and ( $K$ ) is also a function of temperature at fixed pressure in its standard state.

$$\Delta G^\circ = -R \cdot T \cdot \ln K$$

where

$K$ : equilibrium constant.

$$\frac{\Delta G^\circ}{RT} = -\ln K \quad \text{ie. (1)}$$

$$\Delta H^\circ = -R \cdot T^2 \cdot \frac{d(\Delta G^\circ / RT)}{dT}$$

Since the standard-state temperature is that of the equilibrium mixture, the standard property changes of reaction, such as  $\Delta G^\circ$ ,  $\Delta H^\circ$  vary with the equilibrium temperature.

$$\therefore \frac{d(\Delta G^\circ/RT)}{dT} = -\frac{\Delta H^\circ}{RT^2}$$

There fore  $\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$  (\*)

Integration

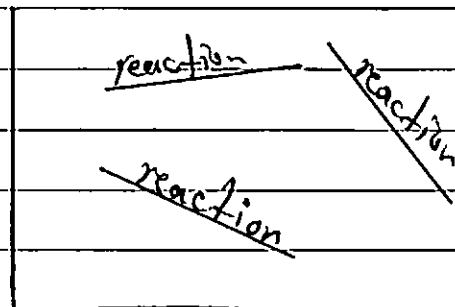
$$\ln \frac{K_2}{K_1} = \frac{(-\Delta H^\circ)}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (A)$$

This approximate equation implies that a plot of  $(\ln K)$  vs. the reciprocal of absolute temperature is a straight line.

Figure (13.8), a plot of  $\ln K$  vs.  $1/T$  for a number of reactions, Pg. (509).

eq. (\*) rearrangement :-

$$\ln K = \int \frac{\Delta H^\circ}{RT^2} dT + I \quad (A) \quad \ln K$$



eq. (A):

$$\frac{1}{T} \times 10^4 / K^{-1}$$

1) If  $\Delta H$  is constant

$$\ln K = -\frac{\Delta H}{R} \cdot \frac{1}{T} + C$$

2) If  $\Delta H$  is not constant

(2) via

$$\Delta H^\circ = J + R \left[ \frac{\Delta A}{2} T + \frac{\Delta B}{2} T^2 + \frac{\Delta C}{3} T^3 - \frac{\Delta D}{T} \right]$$

Then:

$$\ln K = -\frac{J}{R \cdot T} + \Delta A \cdot \ln T + \frac{\Delta B}{2} \cdot T + \frac{\Delta C}{6} \cdot T^2 + \frac{\Delta D}{2 \cdot T^2} + I$$

$$\therefore \Delta G^\circ = -R \cdot T \cdot \ln K$$

$$\Delta G^\circ = -R \cdot T \left[ \Delta A \cdot \ln T + \frac{\Delta B}{2} \cdot T + \frac{\Delta C}{6} \cdot T^2 + \frac{\Delta D}{2 \cdot T^2} + I \right]$$

$$\ln K = \frac{1}{R} \int \left( J + R \left[ \Delta A \cdot T + \frac{\Delta B}{2} \cdot T^2 + \frac{\Delta C}{3} \cdot T^3 - \frac{\Delta D}{T} \right] \right) dT$$

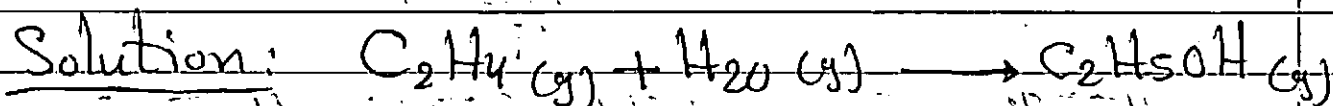
$$= \frac{J}{R} \int \frac{dT}{T^2} + \frac{R \cdot \Delta A}{R} \int \frac{dT}{T} + \frac{\Delta B \cdot R}{2 \cdot R} \int T dT + \frac{R}{R} \cdot \frac{\Delta C}{3} \cdot \int \left( \frac{T^3}{T^2} \right) dT - \frac{R}{R} \cdot \Delta D \int \frac{dT}{(T \cdot T^2)} \rightarrow T^3$$

$$= -\frac{J}{R \cdot T} + \Delta A \cdot \ln T + \frac{\Delta B}{2} \cdot T + \frac{\Delta C}{3 \times 2} \cdot \frac{T^2}{2} + \frac{\Delta D}{2 \cdot T^2} + I$$

$$\ln K = -\frac{J}{R \cdot T} + \Delta A \cdot \ln T + \frac{\Delta B}{2} \cdot T + \frac{\Delta C}{6} \cdot T^2 + \frac{\Delta D}{2 \cdot T^2} + I$$

Example (4): Pg. 510 / ch. 15

Calculate the equilibrium constant for the vapor phase hydration of ethylene at  $[145 \text{ and } 320]^\circ\text{C}$  from the data given in tables 4.1, 4.4, and 15.1 (Gibbs energy).



$$\Delta = \text{Product} - (\text{Reactant})$$
$$\text{C}_2\text{H}_5\text{OH} - \text{C}_2\text{H}_4 - \text{H}_2\text{O}$$

From tables of heat capacities

$$\Delta A = 3.518 - 1.424 - 3.470$$
$$= -1.376$$

$$\Delta B = (20.001 - 14.394 - 1.450) \times 10^{-3}$$
$$= 4.157 \times 10^{-3}$$

$$\Delta C = (-6.002 + 4.392 - 0.00) \times 10^{-6}$$
$$= -1.610 \times 10^{-6}$$

$$\Delta D = (-0.000 - 0.000 - 0.121) \times 10^{-5}$$
$$= -0.121 \times 10^{-5}$$

evaluation of constants (J) and (I) requires two temperature applied:

$$\Delta H_{298}^\circ = -235100 - 52510 - (-241818)$$
$$= -45792 \text{ J/mol.}$$

$$\Delta G_{298}^\circ = -168490 - 68430 - (-228572)$$
$$= -8348 \text{ J/mol.}$$

$$\ln K = \frac{-\Delta G^\circ}{R \cdot T} = \frac{-(-8348)}{8.314 \times 298.15} = 3.3677$$

$$\frac{\Delta H_{298}}{R} = \frac{J}{R} + \Delta A \cdot T + \frac{\Delta B}{2} \cdot T^2 + \frac{\Delta C}{3} \cdot T^3 - \frac{\Delta D}{T}$$

$$\frac{-45792}{8.314} = \frac{J}{R} - 1.376 \times 298.15 + \frac{4.157 \times 10^{-3}}{2} \cdot (298.15)^2 - 1.610 \times 10^{-6} \cdot (298.15)^3 - \frac{(0.121 \times 10^5)}{298.15}$$

$$\therefore \frac{J}{R} = -5308.7$$

Sub.  $\left(\frac{J}{R} = -5308.7\right)$  for known value at  $T = 298.15 \text{ K}$  to find  $(I)$ .

$$\frac{\Delta G^\circ}{R \cdot T} = \frac{J}{R \cdot T} - \left[ \Delta A \cdot \ln T + \frac{\Delta B}{2} \cdot T + \frac{\Delta C}{6} \cdot T^2 + \frac{\Delta D}{2T^2} + I \right]$$

$$\frac{-8348}{8.314 \times 298.15} = \frac{-5308.7}{298.15} + 1.376 \ln 298.15$$

$$- \frac{4.157 \times 10^{-3}}{2} \cdot 298.15 + \frac{1.610 \times 10^{-6}}{6} \cdot (298.15)^2 + \frac{0.121 \times 10^5}{2 \cdot (298.15)^2} - I$$

$$\therefore I = -7.125$$

$$\therefore \ln K = -\frac{J}{R \cdot T} + 4A \cdot \ln T + \frac{4B}{2} \cdot T + \frac{4C}{6} \cdot T^2 + \frac{4D}{2 \cdot T^2} + I$$

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$$\therefore \ln K = \frac{5308.7}{T} - 1.376 \cdot \ln T + 2.0785 \times 10^{-3} \cdot T$$

$$- 0.2683 \times 10^{-6} \cdot T^2 - \frac{12100}{2 \cdot T^2} - 7.125$$

$$\text{For } T_1 = 145 + 273.15 = 418.15 \text{ K}$$

$$T = 320 + 273.15 = 593.15 \text{ K}$$

$$\text{at } T_1 = 418.15 \text{ K} : \ln K_1 = -1.948 \Rightarrow K = 14.26 \times 10^{-2}$$

$$T_2 = 593.15 \text{ K} : \ln K_2 = -5.840 \Rightarrow K = 2.91 \times 10^{-3}$$



15.1) 9)

15.2)

# Chapter Ten

## Thermodynamic Analysis of Processes

The purpose of this chapter is to present a procedure for the analysis of practical processes from the thermodynamic point of view. It is an extension of the ideal work and lost work in the first law.

Although applications of thermodynamics to processes are often based on the assumption of reversibility, real irreversible processes are nevertheless amenable to thermodynamic analysis. The goal of such an analysis is to determine how efficiencies in each step of a process. The cost of energy is of concern in any manufacturing operation, and the first step in any attempt to reduce energy requirements is to determine where and to what extent energy is wasted through process irreversibilities. The treatment here is limited to steady-state flow processes, because of their predominance in industrial practice.

### Second-Law Relation for Steady-State Flow Processes

The general energy balance for steady-state flow processes is given by equation:

$$\Delta \left( H + \frac{1}{2} u^2 + g \cdot Z \right)_{in} = Q - W_s$$

Also, write a general second law relation for such process

The basic requirement is given by :-

$$\Delta S_{\text{tot}} \geq 0$$

with respect to the control volume for a steady flow process in surroundings at temperature  $T_0$  :

$$\left\{ \begin{array}{l} \text{Net rate of entropy} \\ \text{transport out by flowing} \\ \text{streams} \end{array} \right\} + \left\{ \begin{array}{l} \text{rate of entropy change} \\ \text{of surroundings from} \\ \text{heat transfer} \end{array} \right\} \geq 0$$

$$\text{Whence } \Delta(m \dot{S})_{fs} + \frac{\dot{Q}_{\text{surr}}}{T_0} \geq 0 \quad (*)$$

Since heat transfer with respect to the surroundings is negative of heat transfer with respect to the system,

$$\dot{Q}_{\text{surr}} = -\dot{Q}$$

Therefore, rate of entropy generation ( $\dot{S}_{\text{tot}}$ ) is defined as:

$$\dot{S}_{\text{tot}} \equiv \Delta(m \dot{S})_{fs} - \frac{\dot{Q}}{T_0} \geq 0$$

For the special case of a single stream flowing through the control volume, this becomes :-

$$\dot{S}_{\text{tot}} \equiv m \dot{S} - \frac{\dot{Q}}{T_0} \geq 0$$

Division by  $(m)$  provides an equation based on a unit amount of fluid flowing through the control volume :-

$$\Delta S_{\text{tot}} \equiv \Delta S - \frac{Q}{T_0} \geq 0$$

The equality in the preceding equations applies to reversible processes.

### Calculation of Ideal Work:

In any steady-state flow process requiring work, there is an absolute minimum amount which must be extended to accomplish the desired change of state of the fluid flowing through the control volume. In a process producing work, there is an absolute maximum amount which may be accomplished as the result of a given change of state of the fluid flowing through the control volume. In either case, this limiting value is called the "ideal work",  $W_{ideal}$ . It is the work resulting when the change of state of the fluid is accomplished completely reversibly. The requirement of complete reversibility for a process implies the following:

1. All changes within the control volume are reversible.
2. Heat transfer to or from the surroundings is also reversible.

Our objective is to compare the "actual work" of a process with the "work of the reversible process".

For any completely reversible process, the entropy generation is "zero", and equation (6) becomes:

$$Q = T_o \Delta(m \cdot S)_{fs}$$

$T_o$ : Surroundings Temperature.

Substitution of this expression for  $Q$  in energy balance gives:

$$\Delta \left[ \left( H + \frac{1}{2} u^2 + g \cdot z \right) m \right]_{fs} = T_o \Delta (m \cdot s)_{fs} - W_s^{rev}$$

$W_s^{rev}$ : work for a reversible process.

We call this work the "ideal work",  $W_{ideal}$ .

Thus  $W_{ideal} = T_o \Delta (m \cdot s)_{fs} - \Delta \left[ \left( H + \frac{1}{2} u^2 + g \cdot z \right) m \right]_{fs}$

In most applications to chemical processes, the kinetic and potential energy terms are negligible compared with the others.

$$W_{ideal} = T_o \Delta (m \cdot s)_{fs} - \Delta (m \cdot H)_{fs}$$

For the special case of a single stream flowing through the control volume,

$$W_{ideal} = m \cdot (T_o \Delta S - \Delta H)$$

Division by  $(m)$  puts this equation on a unit mass basis:

$$w_{ideal} = T_o \Delta S - \Delta H$$

These equations give the work of completely reversible processes associated with given property changes in the following streams.

When the same property change occurs in an "actual process", the actual work  $W_s$  or  $(W_s)$  is given by an energy balance, and compare the actual work with ideal work.

When  $W_{ideal}$  is "Positive", it is the maximum work obtainable from a given change in the properties of the flowing streams and is larger than  $W_s$ . In this case, the thermodynamic efficiency " $\eta$ " as the ratio of the actual work to the ideal work:-

$$\eta_{\text{Max}} = \frac{\eta_{\text{work}}}{\eta_{\text{Produced}}} = \frac{W_s}{W_{ideal}}$$

When  $W_{ideal}$  is "negative",  $|W_{ideal}|$  is the minimum work required to bring about a given change in the properties of the flowing streams, and is smaller than  $|W_s|$ . In this case, the thermodynamic efficiency " $\eta$ " as the ratio of the ideal work to the actual work:-

$$\eta_{\text{Minimum}} = \frac{\eta_{\text{work}}}{\eta_{\text{required}}} = \frac{W_{ideal}}{W_s}$$

Example: What is the maximum work that can be obtained in a steady-state flow process from (1 mol) of nitrogen "assumed an ideal gas" at 800K and 50 bar? Take the temperature and pressure of the surroundings as 300K and 1.0133 bar.

Solution: The maximum possible work is obtained from any completely reversible process that reduces the nitrogen to  $T_4$  P of surroundings.

$$W_{\text{ideal}} = T_0 \cdot \Delta S - \Delta H$$

$$\Delta H = C_{Pm} \cdot (T_2 - T_1)$$

$$C_{Pm} = A + B \cdot T_{\text{am}} + \frac{C}{3} (4 \cdot T_{\text{am}}^2 - T_1 \cdot T_2) + \frac{D}{T_1 \cdot T_2}$$

The constants in Table (4.) require use of Kelvin temperature

$$T_{\text{am}} = \frac{T_1 + T_2}{2} = 550 \text{ K}$$

$$C_{Pm} = 3.280 + (0.000593)(550) + \frac{4000}{800 \cdot 300}$$

$$= 3.623$$

$$\Rightarrow \Delta H = 3.623 \times 8.314 \times (300 - 800)$$

$$= -15060 \text{ J/mol}$$

$$\Delta S = C_{Pm} \cdot \ln \frac{T_2}{T_1} - R \cdot \ln \frac{P_2}{P_1}$$

$$C_{Pm} = A + B \cdot T_{\text{lm}} + T_{\text{am}} \cdot T_{\text{lm}} \left[ C + \frac{D}{(T_1 \cdot T_2)^2} \right]$$

$$T_{\text{lm}} = \frac{(T_2 - T_1)}{\ln(T_2/T_1)} = 509.77 \text{ K}$$

$$\frac{C_{Pm}}{R} = \frac{3.280 + (0.000593)(509.77) + 550 \cdot 509.77 \cdot \frac{4000}{(800)^2(300)^2}}{8.314}$$

$$= 3.602$$

$$\Delta S = 3.602 \times 8.314 \times \ln \frac{300}{800} = 8.314 \times \ln \frac{1.0133}{50}$$

$$= 3.042 \text{ J/mol.K}$$

$$\therefore W_{\text{ideal}} = 300 \times 3.042 - (-15060)$$

$$= 15973 \text{ J/mol}$$

### Lost Work:

The energy that becomes unavailable for work as the result of "irreversibilities" in a process is called the lost work, and is defined as the difference between the ideal work for a process and the actual work of the process. Thus by definition,

$$W_{\text{lost}} = W_{\text{ideal}} - W_s$$

In terms of rates this is written:

$$\dot{W}_{\text{lost}} = \dot{W}_{\text{ideal}} - \dot{W}_s$$

The ideal work rate is given by:

$$\dot{W}_{\text{ideal}} = T_0 \Delta(\dot{m} s)_{fs} = \Delta \left[ (H + \frac{1}{2} u^2 + gz) \dot{m} \right]_{fs}$$

The actual work rate comes from eqn-

$$\dot{W}_s = \dot{Q} - \Delta \left[ (H + \frac{1}{2} u^2 + gz) \dot{m} \right]_{fs}$$

The difference between these two equations gives:-



$$W_{lost} = T_o \cdot \Delta(\dot{m} \cdot S)_{fs} - \dot{Q}$$

For the special case of a single stream flowing through the control volume,

$$W_{lost} = m \cdot T_o \cdot \Delta S - \dot{Q}$$

Division of this equation by  $(\dot{m})$  gives

$$W_{lost} = T_o \cdot \Delta S - \dot{Q}$$

As a result of eq.  $S_{total} = \Delta(\dot{m} \cdot S)_{fs} - \frac{\dot{Q}}{T_o} \geq 0$

We can write by

$$T_o \cdot S_{total} = T_o \cdot \Delta(\dot{m} \cdot S)_{fs} - \dot{Q}$$

Since the "right-hand sides" of this equation and of equation of  $W_{lost}$  are identical, it follows that:

$$W_{lost} = T_o \cdot S_{total}$$

for flow on the basis of a unit amount of fluid

$$W_{lost} = T_o \cdot \Delta S_{total}$$

The second law of thermodynamics,

$$\Delta S_{total} \geq 0$$

or,

$$S_{total} \geq 0$$

Whence  $W_{lost} \geq 0$  ;  $W_{lost} \geq 0$

- When a process is completely "reversible", the lost work is "Zero".
- For "irreversible" processes, the lost work; the energy that becomes unavailable for work, is Positive.

The greater the irreversibility of a process, the greater the rate of entropy production and the greater the amount of energy that becomes unavailable for work. Thus even irreversibility carries with it a price.

Example: Saturated vapor steam at 100 KPa ( $t = 99.63^\circ\text{C}$ ) is compressed adiabatically to 300 KPa. If the compression efficiency is 75 percent. Determine:

- a) the work required
- b) the thermodynamic efficiency of the compression process if  $T_0 = 300\text{K}$
- c) the lost work associated with the compression process

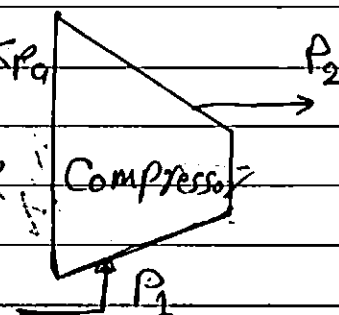
Solution: From saturated steam table at  $P = 100\text{KPa}$

$$S_1 = 7.3598 \text{ KJ/Kg.K}$$

$$H_1 = 2675.4 \text{ KJ/Kg}$$

for isentropic compression to  $P_2 = 300\text{KPa}$

$$S_2 = S_1 = 7.3598 \text{ KJ/Kg.K}$$



From superheated steam table at  $P_2$  and  $S_2$  by interpolation:-

$$H_2 = 2888.8 \text{ KJ/Kg}$$

$$\Delta H)_s = H_2 - H_1$$

$$= 2888.8 - 2675.4$$

$$= 213.4 \text{ KJ/Kg}$$

$$\Delta H)_{act} = \frac{\Delta H)_s}{\gamma} = 284.5 \text{ KJ/Kg}$$

$$H_2 = H_1 + \Delta H$$

$$= 2675.4 + 284.5$$

$$= 2959.9 \text{ KJ/Kg}$$

Again by interpolation, we find that superheated steam with  $P_2$  and  $H_2$

$$S_2 = 7.5019 \text{ KJ/KgK}$$

$$\therefore W_s = -\Delta H$$

$$= -284.5 \text{ KJ/Kg} \quad \text{①}$$

and

$$W_{ideal} = T_0 \Delta S - \Delta H$$

$$= 300 (7.5019 - 7.3598) - 284.5$$

$$= -241.9 \text{ KJ/Kg}$$

$$\Rightarrow \frac{\eta}{\gamma} = \frac{W_{ideal}}{W_s}$$

$$= \frac{-241.9}{-284.5} = 0.850 \quad \text{②}$$

The compressor efficiency (0.75) is based on reversible compression to a final state where  $S_2 = S_1$ , is

different from the thermodynamic efficiency (0.85) which is based on reversible compression to the final state where  $S_2 > S_1$ .

$$W_{\text{lost}} = T_0 \Delta S - Q$$

Since the compression process is adiabatic ( $Q = 0$ )

$$W_{\text{lost}} = 300 \times (0.1421) = 42.6 \text{ KJ/Kg} \quad \text{③ p.p.}$$

This result is also given by:

$$W_{\text{lost}} = W_{\text{ideal}} - W_s$$

$$= -241.9 - (-284.5) = 42.6 \text{ KJ/Kg}$$

## Thermodynamic Analysis of Steady-State Flow Processes:

Many Processes consist of a number of steps, and lost work calculations are then made for each step separately.

$$\therefore W_{\text{lost}} \propto T_o \cdot S_{\text{total}}$$

Summing over the steps of a process gives:

$$\sum W_{\text{lost}} \propto T_o \cdot \sum S_{\text{total}}$$

Dividing the two eqs:

$$\frac{W_{\text{lost}}}{\sum W_{\text{lost}}} = \frac{S_{\text{tot}}}{\sum S_{\text{tot}}}$$

Thus an analysis of lost work, made by calculation of the fraction, is the same as an analysis of the rate of entropy generation:

$$\therefore \sum W_{\text{lost}} \propto W_{\text{ideal}} - W_s$$

1) For a work-producing process, all of these work quantities are "positive" and

$$W_{\text{ideal}} > W_s$$

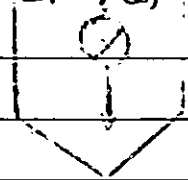
Therefore write the preceding equation as

$$W_{\text{ideal}} \propto W_s + \sum W_{\text{lost}}$$

2) For a work-requiring process,  $W_s$  and  $W_{ideal}$  are negative, and

$$|W_s| > |W_{ideal}|$$

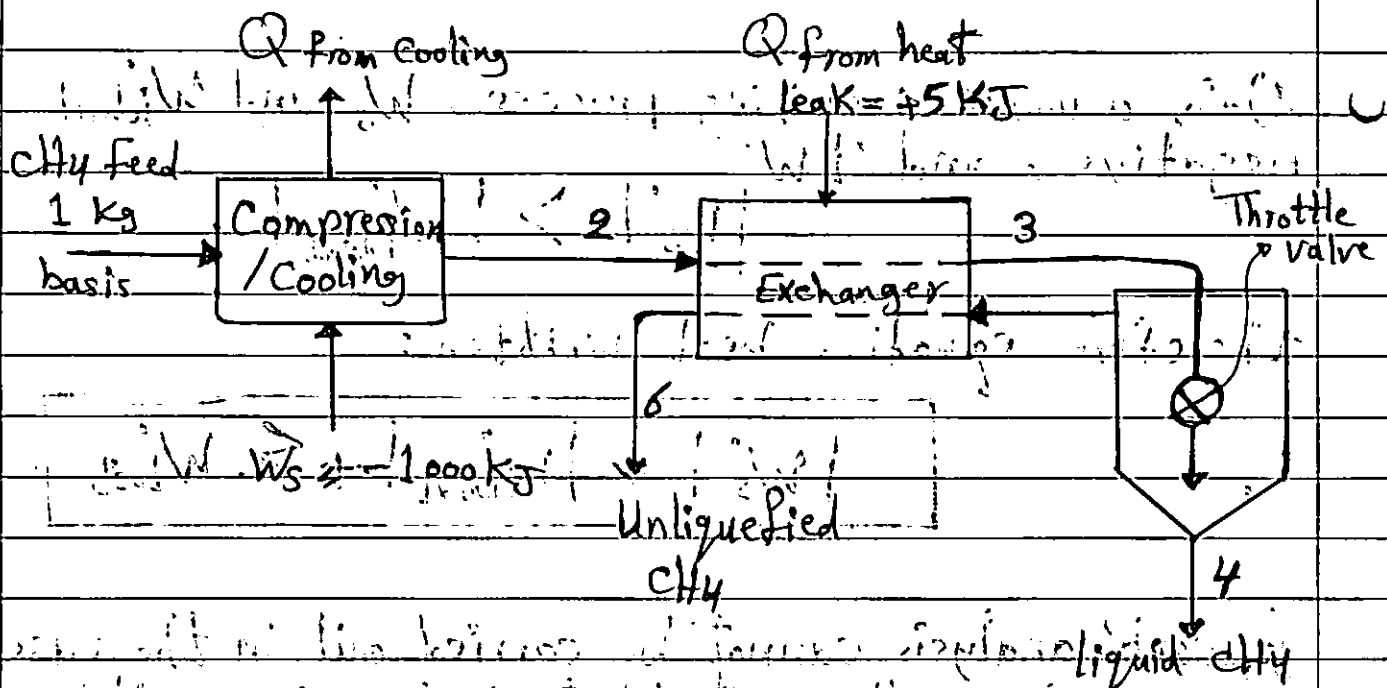
therefore equation best written:



$$|W_s| = |W_{ideal}| + \sum W_{lost}$$

A work analysis cannot be carried out in the case where a process is inefficient that  $W_{ideal}$  is positive, indicating that the process should produce work, but  $W_s$  is negative, indicating that the process in fact requires work. A lost work or entropy-generation analysis is always possible.

Example 80: Methane is liquefied in a simple Linde system, as shown in Figure below. The methane enters the compressor at [1 bar and 300 K] and after compression to [60 bar] is cooled back to [300 K]. The product is saturated liquid methane at [1 bar]. The unliquefied methane, also at [1 bar], is returned through a heat exchanger where it is heated to [295 K] by the high pressure methane. A heat leak into the heat exchanger of [5 KJ] is assumed for each kilogram of methane entering the compressor. Heat leaks to other parts of the liquefier are assumed negligible. Make a thermodynamic analysis of the process for a surrounding temperature of  $T_0 = 300$  K. Compressor efficiency is 75 percent.

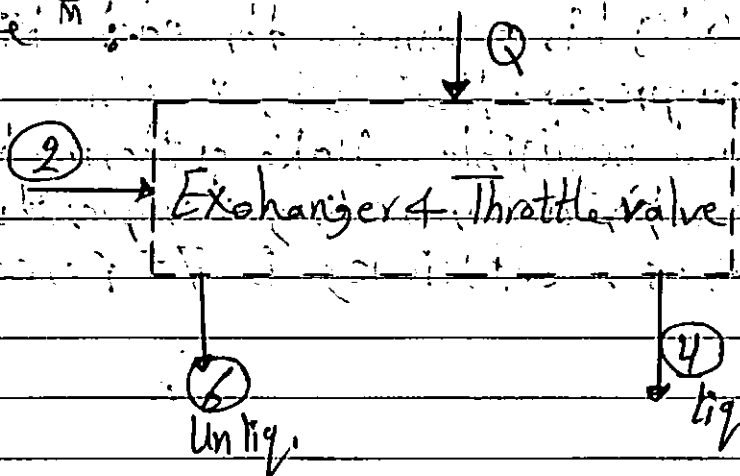


Data are from Perry and Green:

Point	State of CH <sub>4</sub>	T/K	P/bar	H/KJ/kg	S/KJ/kg.K
1	Superheated vapor	300	1	1199.8	11.629
2	Superheated vapor	300	60	1140.0	9.359
3	Superheated vapor	207.1	60	772.0	7.798
4	Saturated liquid	111.5	1	285.4	4.962
5	Saturated vapor	111.5	1	796.9	9.523
6	Superheated vapor	295.0	1	1188.9	11.589

Solution: The fraction of methane that is liquefied ( $Z$ ) is calculated by energy balance on "exchanger and throttle valve".

We take basis  
(1 kg) of CH<sub>4</sub>  
entering.



$$[H_4 \cdot Z + H_6(1-Z)] - H_2 = Q$$

$$Z = \frac{H_6 - H_2 - Q}{H_6 - H_4}$$

$$= \frac{1188.9 - 1140 - 5}{1188.9 - 285.4} = 0.0486 \quad \text{because heat leak}$$

$$W_{\text{ideal}} = T_0 \Delta S - \Delta H$$

The ideal work depends on the overall changes in the methane passing through the liquefier.

$$= T_0 [S_4 \cdot Z + (1-Z) \cdot S_6 - S_1] - [Z \cdot H_4 + (1-Z) \cdot H_6 - H_1]$$

$$= 300 [0.0486 \times 4.962 + 0.9514 \times 11.589 - 11.629] - [0.0486 \times 285.4 + 0.9514 \times 1188.9 - 1199.8]$$

$$W_{\text{ideal}} = -53.8 \text{ KJ}$$

"negative" is required

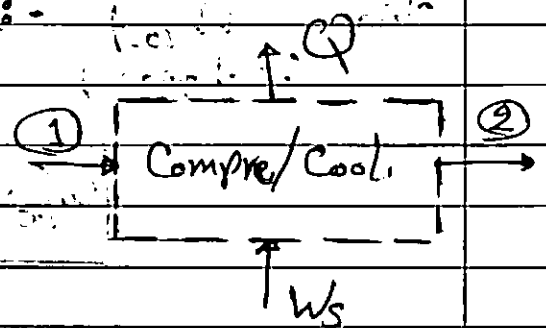
Energy balance for (Compressor/Cooling) step to calculate the heat transfer :-

$$Q = \Delta H + W_s$$

$$= (H_2 - H_1) + W_s$$

$$= 1140 - 1199.8 - 1000$$

$$= -1059.8 \text{ KJ}$$



Then calculate "entropy generation" :-

$$S_{\text{total}} = S_2 - S_1 = \frac{Q}{T_0}$$

(Compressor/cooling)



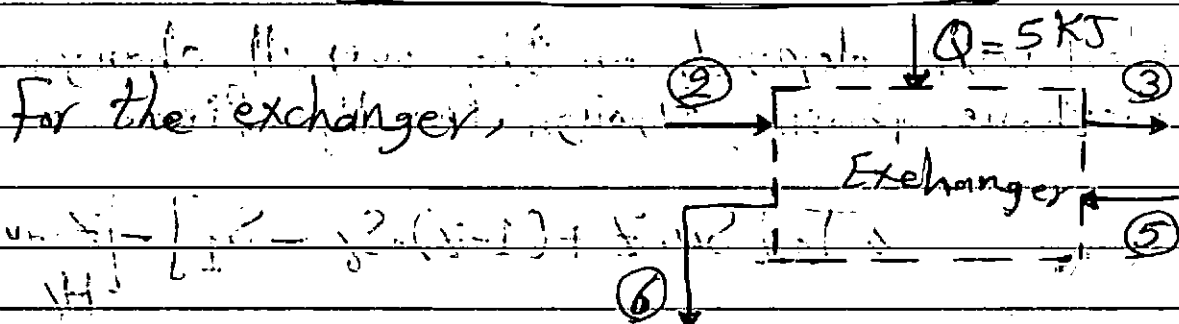
$$= 9.359 - 11.629 + \frac{1059.8}{300} = 5.111$$

$$= 1.2627 \text{ KJ/Kg.K}$$

and  $W_{\text{lost}} = T_0 \cdot S_{\text{total}}$   
(compression/cooling)

$$= 300 \times 1.2627$$

$$W_{\text{lost}} = 378.81 \text{ KJ/Kg}$$



$$S_{\text{tot}}^{\text{(exchanger)}} = (S_6 - S_5)(1-z) + (S_3 - S_2)(1) - \frac{Q}{T_0}$$

$$= (11.589 - 9.523)(0.9514) + (7.798 - 9.359) - \frac{5}{300}$$

$$= 0.3879 \text{ KJ/Kg.K}$$

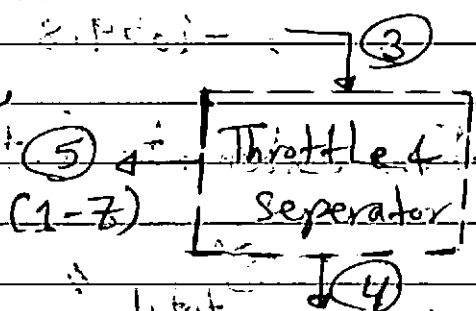
and  $W_{\text{lost}} = T_0 \cdot S_{\text{total}}$   
(exchanger)

$$= 300 \times 0.3879$$

$$W_{\text{lost}} = 116.41 \text{ KJ/Kg}$$

for the throttle and separator,

assume "adiabatic operation"



$$S_{\text{total}}^{\text{throttle}} = [z \cdot S_4 + (1-z) \cdot S_5] - S_3 - \frac{Q}{T_0}$$

$$= (0.0486)(4.962) + (0.9514)(9.523) - 7.798$$

$$= 1.5033 \text{ KJ/Kg.K}$$

and

$$W_{\text{lost}}^{\text{throttle}} = T_0 \cdot S_{\text{total}}^{\text{throttle}}$$

$$= 300 \times 1.5033$$

$$W_{\text{lost}} = 451.0 \text{ KJ/Kg}$$

∞ The work analysis, based on equation:-

$$|W_s| = |W_{\text{ideal}}| + \sum W_{\text{lost}}$$

$$= |53.8| + (378.8 + 116.4 + 451.0)$$

$$= 1000 \text{ KJ/Kg}$$

Equipment	$S^{\circ} / \text{KJ/Kg.K}$	Percent ( $S_{\text{tot}}^{\circ} / \sum S_{\text{tot}}^{\circ}$ )
(Compression/Cooling)	1.2627	40.0
Exchanger	0.3879	12.3
Throttle	1.5033	47.7
	$\sum = 3.1539$	$\sum = 100.0$

Note the largest loss in work and entropy generation occurs in the "throttling step". Elimination of this irreversible process in favor of a turbine results increase in efficiency.

From the standpoint of energy conservation, the thermodynamic efficiency of a process should be as high as possible, and the entropy generation or lost work as low as possible. The final design of a process depends largely on economic considerations, and the cost of energy is an important factor. The thermodynamic analysis of a specific process shows the locations of the major inefficiencies, and hence the pieces of equipment or steps in the process that could be altered or replaced to advantage. One function of the chemical engineer is to try to devise a better process and to use to keep the capital expenditure low.

Example: A process based on the following data:

$$S_{in} - S_{out} = \frac{Q}{T} + S_{gen}$$

$$(0.0125 + 0.0012) - 0.0025 = \frac{Q}{T} + S_{gen}$$

$$0.0112 = \frac{Q}{T} + S_{gen}$$

Unit	Value	Unit
S <sub>in</sub>	0.0125	Entropy
S <sub>out</sub>	0.0025	Entropy
F.F.H	0.0012	Entropy
0.0012	0.0012	Entropy

The above equation has shown that the total entropy change is 0.0112. This is the same as the entropy change of the system. The entropy change of the surroundings is 0.0012. The entropy change of the universe is 0.0112. The entropy change of the system is 0.0012. The entropy change of the surroundings is 0.0012. The entropy change of the universe is 0.0112.