SECOND LAW OF THERMODYNAMIC
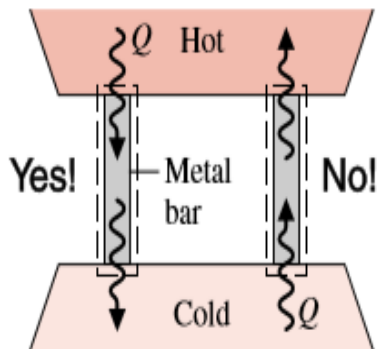
1. *Second law of Thermodynamic*

There is no mathematical proof of the second law, the basis of this law is empirical, while work. This is the basis of the second law. The heat to be converted to the work is done by a device called"Head Engine"
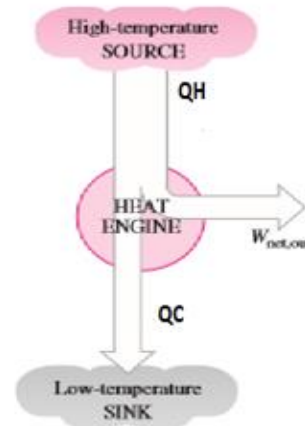

لا يوجد جهاز يحول كامل الحرارة الى شغل.

لا يمكن نقل Q من مستوى درجة الحرارة اقل الى مسنوى درجة حرارة اعلى.

2. *Heat engine:* is defined simply as a system operating in a cycle and producing useful work by .abstracting heat from a suitable heat source.
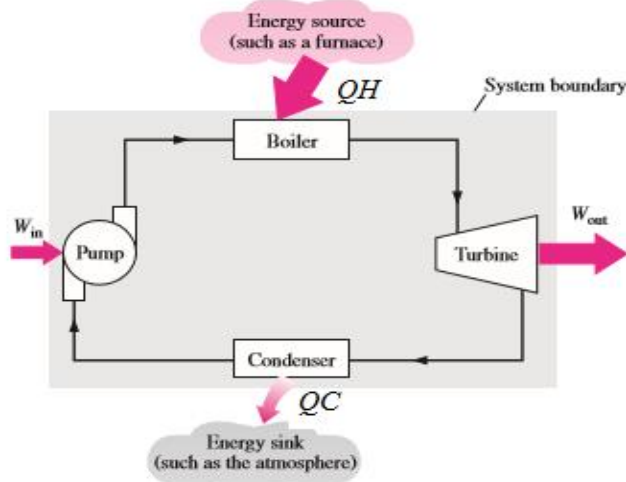
FIGURE

Schematic of a steam power plant.

FIGURE

Part of the heat received by a heat engine is converted to work, while the rest is rejected to a sink.

$$\int dQ = Q_A - Q_R$$

$$\eta = \frac{net\ work\ output}{gross\ heat\ input} = \frac{Q_A - |Q_R|}{Q_A} = \frac{W}{Q_A}$$

$$\eta = 1 - \frac{|Q_R|}{Q_A} \qquad\qquad \eta = efficiency$$

3. The Carnot cycle:

Carnot recognized that conditions for converting heat in to work with maximum efficiency were as Follows:

1- The cycle must consist of a series of processes each of which is fully reversible fully

2- All heat reception occurs at the maximum cycle temperature and all heat rejection occurs at the minimum cycle temperature. The Carnot cycle consist of four reversible processes **two isothermal** and **two adiabatic**.

Figure 6.6 Carnot vapor power cycle.
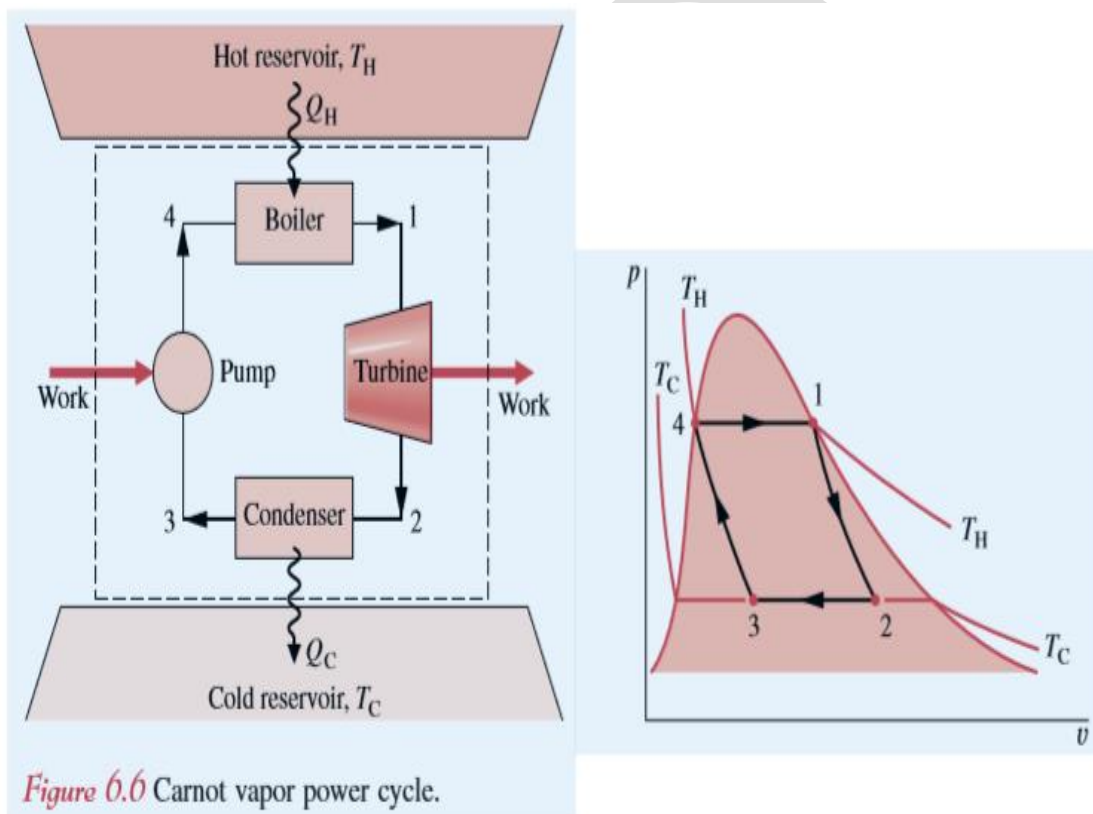
· a (3) → b(4) Adiabatic compression with temperature rising from *TC* to *TH*.(T_2-T_1)
· b (4) → c(1) Isothermal expansion to arbitrary point *c* with absorption of heat *QH*.
· c(1) → d (2)Adiabatic expansion with temperature decreasing to *TC*. (T_1-T_2)
· d (2)→ a (3)Isothermal compression to the initial state with rejection of heat *QC*.

The Four Processes applied to unit mass of working Fluid then becomes,

(4 -1) Isothermal expansion heat added $Q_A = RT_{max} \, Ln \dfrac{V1}{V4}$ (1)

(1 -2) Adiabatic expansion $\dfrac{P1}{P2} = \left(\dfrac{T1}{T2}\right)^{\frac{\gamma}{\gamma-1}} = \left(\dfrac{T_{max}}{T_{min}}\right)^{\frac{\gamma}{\gamma-1}}$ (2)

OR: $\dfrac{V1}{V2} = \left(\dfrac{T1}{T2}\right)^{\frac{-1}{\gamma-1}} = \left(\dfrac{T_{max}}{T_{min}}\right)^{\frac{-1}{\gamma-1}}$ (3)

(2-3) Isothermal compression heat rejection $Q_R = R \, T_{min} \, Ln \dfrac{V2}{V3}$ (4)

(3-4) Adiabatic compression $\dfrac{P4}{P3} = \left(\dfrac{T4}{T3}\right)^{\frac{\gamma}{\gamma-1}} = \left(\dfrac{Tmax}{Tmin}\right)^{\frac{\gamma}{\gamma-1}}$ .... (5)

OR: $\dfrac{V4}{V3} = \left(\dfrac{T4}{T3}\right)^{\frac{-1}{\gamma-1}} = \left(\dfrac{T_{max}}{T_{min}}\right)^{\frac{-1}{\gamma-1}}$ .... (6)

From eqn. (3) & (6)

$\dfrac{V4}{V3} = \dfrac{V1}{v2}$ $\therefore$ $\dfrac{V2}{V3} = \dfrac{V1}{v4}$ .... (7)

Substituting   (7)   in   (4)

$Q_R = R \, T_{min.} \, Ln \dfrac{V1}{V4}$

$\eta = 1 - \dfrac{QR}{QA} = 1 - \dfrac{R \, T_{min.} \, Ln \frac{V1}{V4}}{R \, T_{max.} \, Ln \frac{V1}{V4}}$

$\eta_{car} = 1 - \dfrac{T_{min}}{T_{max}} = 1 - \dfrac{T_2}{T_1}$

Where:- $\eta_{car} = efficiency \; of \; carnot \; cycle$

ملاحظة

1) يجب ان تكون درجات الحرارة ب (k) او (R)

2) تستخدم المعادلة $\eta = 1 - \dfrac{\text{Tmin}}{\text{Tmax}}$ فقط في ماكنة كارنوت
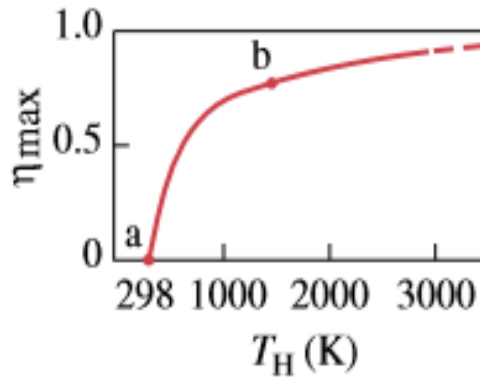
ولايجوز استخدامها للماكنة الحقيقية بل يستخدم القانون العام

يستخدم لاي ماكنة مثالية   ام غير مثالية $\eta = \dfrac{W}{Q_A}$

3-تذكر بعض المصطلحات للماكنة والمقصود منها ماكنة كارنوت هذه المصطلحات هي.

[**Ideal-- Theoretical-- Reversible –**

Max. work -- Max.Tmax. Min Tmin] ⟹   Carnot cycle.

Figure (Carnot efficiency versus T$_H$, for T$_C$ = 298 K.)

Second law of Thermodynamic can be stated:

As; It is **impossible** by a cyclic process to convert the heat absorbed by a system (heat engine) **completely in to work**

1- The heat is a bad form of energy and cannot converted completely into work.
2- Carnot cycle or Carnot engine is a reversible and ideal 50% besides. It is taken as a reference engine to **compare** with other engines.

Three further corollaries of the second law may now Presented:-

1- No engine operating between two heat reservoir each having a fixed Temperature can be more efficient then a reversible engine operating between the same temperatures
2- All reversible engine operating between two heat reservoirs each having its own fixed temperate have the same efficiency.
3- The Efficiency of any reversible engine operating between two reservoirs is independent on the nature of the working fluid but on the temperatures of the reservoir.

The Second law of "Entropy"

Second law when expanded to upon cyclic process will lead to another properly of the s system which is "**Entropy**".
From efficiency of Carnot cycle

$$\eta = 1 - \frac{Q_R}{Q_A} = 1 - \frac{T_{min}}{T_{max}}$$

$$\therefore \quad \frac{Q_R}{Q_A} = \frac{T_{min}}{T_{max}}$$

$$\frac{Q_A}{T_{max}} = \frac{Q_R}{T_{min}} \qquad\Longrightarrow\qquad \frac{Q_A}{T_{max}} - \frac{Q_R}{T_{min}} = 0$$

$$\frac{Q_A}{T_{max}} - \left(- \frac{Q_R}{T_{min}}\right) = 0 \qquad\Longrightarrow\qquad \frac{Q_A}{T_{max}} + \left(\frac{Q_R}{T_{min}}\right) = 0 \quad \text{(For entire cycle)}$$

$$\int \frac{dQ}{T} = 0 \qquad \text{OR} \qquad \frac{\Sigma Q}{T} = 0$$

Thus $\left(\frac{Q}{T}\right)$ represent a state property and is called "Entropy" $\Delta S = \frac{Q}{T}$
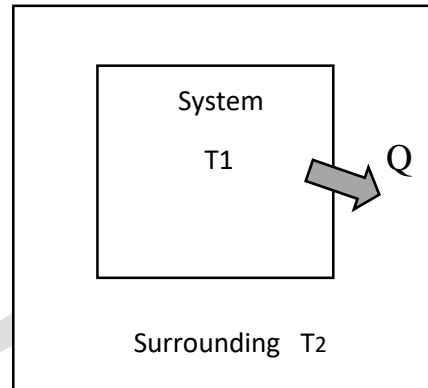
<u>When does ΔS > =   <   0 :</u>

(ΔS) system $= -\dfrac{Q}{T_1}$

(ΔS) surrounding, $= \dfrac{Q}{T_2}$

```
System

T1                    Q

Surrounding   T2
```

$(\Delta S)_{\text{sys}} + (\Delta S)_{\text{surr.}} = 0$

$-\dfrac{Q}{T_1} + \dfrac{Q}{T_2} = \dfrac{Q}{T_2} - \dfrac{Q}{T_1}$

$T_1 > T_2$

$\therefore (\Delta S)_{Tot} \geq 0 \qquad (= + ve)$

$\therefore$ The process will continue spontaneously irreversible as for as

$(\Delta S)_{Tot}$ is (+ ve) $(\Delta S)_{Tot} > 0$ (**irreversible process**)

And:

$\therefore (\Delta S)_{Tot} = 0 \qquad$ as $T_1 = T_2$ (**reversible process**)

$\therefore$ The mathematical expression of the Second law in term of entropy as property can by Stated Simply as

$(\Delta S)_{Tot} \geq 0$

i.e. $(\Delta S)_{sys} + (\Delta S)_{surr} = 0$

The entropy change of any system and It's surrounding consider together is positive and approaches zero for any process which approaches reversibility

$\partial S = \dfrac{\partial Q_{rev}}{T}$

$$\int_{1}^{2} Q_{rev} = \int_{1}^{2} TdS$$

$$Q_{rev} = \int_{1}^{2} T\,dS \qquad \ldots\ldots\ldots\ldots\ldots\ldots. \quad (1)$$

Remember

$$W_{reV} = \int_{1}^{2} PdV \qquad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

From equations (1) and (2) are can find the $Q_{rev.}$ and W_{rev},

As area under the carve on P-V and T-S diagrams
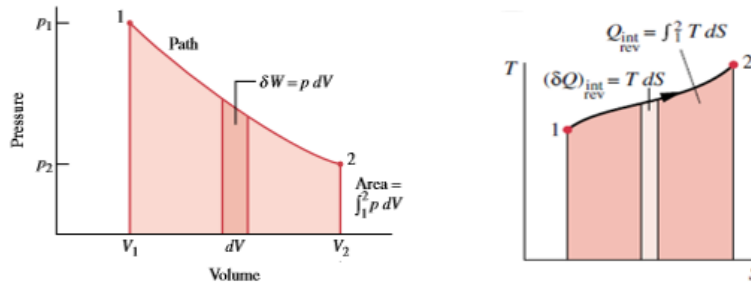
Area under the curve = W_{rev} area under the curve = Q_{rev}

$$W_{rev} = \int_{1}^{2} pdv. \qquad\qquad\qquad Q_{rev=} \int_{1}^{2} Tds$$

Example 5.1

A central power plant, rated at 800,000 kW, generates steam at 585 K and discards heat to a river at 295 K. If the thermal efficiency of the plant is 70% of the maximum possible value, how much heat is discarded to the river at rated power?

Solution 5.1

The maximum possible thermal efficiency is given by Eq. (5.7). With T_H as the steam-generation temperature and T_C as the river temperature:

$$\eta_{Carnot} = 1 - \frac{295}{585} = 0.4957 \qquad \text{and} \qquad \eta = (0.7)(0.4957) = 0.3470$$

where η is the actual thermal efficiency. Combining Eq. (5.6) with the first law, written $W = -Q_H - Q_C$, to eliminate Q_H, yields:

$$Q_C = \left(\frac{1-\eta}{\eta}\right)W = \left(\frac{1-0.347}{0.347}\right)(-800,000) = -1,505,475 \text{ kW}$$

.

This rate of heat transfer to a modest river would cause a temperature rise of several °C.

Lost Work

Work lost is the energy that becomes unavailable for work as a result of the irreversibility of the actual work process.

$$\eta = \frac{W}{Q_A} = \frac{T_{max} - T_{min}}{T_{max}}$$

$$W = Q\left(\frac{T_{max} - T_{min}}{T_{max}}\right)$$

$$(\Delta S)_{Tot} = \frac{Q}{Tmin} - \frac{Q}{Tmax} = \frac{T_{max} - T_{min}}{T_{max}}$$

$$T_{min}\,\Delta S = Q\left[\frac{T_{max} - T_{min}}{T_{max}}\right]$$

Entropy change of an ideal gas:

By the 1st Law:

$dU = dQ + dw$ (For reversible process)

$dU = dQ - pdv$

Since: $H = U + \Delta pv$

$dH = dU + pdv + vdp$

$\therefore dH = dQ_{rev.} - \cancel{P\,dV} + \cancel{PdV} + VdP$

$dQ_{rev.} = dH - vdp$

For an ideal gas: $dH = cp^{ig}\, dT$,,,, $v = \dfrac{RT}{P}$

$\therefore\ dQ_{rev.} = Cp^{ig}\, dT - \dfrac{RT}{p}\, dp$

OR

$\dfrac{dQ_{rev.}}{T} = Cp^{ig}\, \dfrac{dT}{T} - R\, \dfrac{dp}{p}$

$dS = Cp^{ig}\, \dfrac{dT}{T} - R\, \dfrac{dp}{p}$

By integration from initial state T_1 , P_1 to final of T_2, P_2 gives:

$\Delta S = \int_{T_1}^{T_2} cp^{ig}\, \dfrac{dT}{T} - R\, ln\, \dfrac{p_2}{p_1}$ (1)   حفظ المعادلة +الاشتقاق

$Cp_{ms}^{ig} = \dfrac{\int_{T_1}^{T_2} C_{p^{ig}}\ \ dT/T}{\ln(^{T_2}/_{T_1})}$

Where: (ms): is a mean value specific entropy calculations.

$\dfrac{Cp_{ms}^{ig}}{R} = A + B\, T_{lm} + T_{am}T_{lm}\left[C + \dfrac{D}{(T1T2)^2} \right]$ …………….. (2)

$T_{lm=\frac{T2-T1}{\ln(^{T2}/_{T1})}}$, $\int_{T1}^{T2} CP^{ig}\, \dfrac{dT}{T} = CP_{mS}^{ig}\, \ln\dfrac{T_2}{T_1}$

eq. (1) becomes:

$$\Delta S = CP_{ms}^{ig} \ln\frac{T_2}{T_1} - R \ln\frac{P_2}{P_1}$$ ………………   حفظ + الاشتقاق

Example:-

Methane gas at 550 k and 5 bar undergoes a reversible adiabatic expand son to 1 bar, Assuming methane an ideal gas at these condition. What is its final temperature?

 Solation:

For reversible adiabatic $\Delta S = 0$ (Isotropic)

$$\therefore \qquad \frac{Cp_{ms}^{ig}}{R} \ln\frac{T_2}{T_1} = \ln\frac{p_2}{p_1} = \ln\frac{1}{5} = -1.6094$$

Since Cp_{ms}^{ig} depends on T_2 , we rearrange this equation for iterative Solution:

$$\ln\frac{T_2}{T_1} = \frac{-1.6094}{Cp_{ms}^{ig}/R} \Rightarrow \boldsymbol{T_2 = T_1\, exp\left(\frac{-1.6094}{Cp_{ms}^{ig}/R}\right)} \qquad …… (A)$$

$\dfrac{Cp_{ms}^{ig}}{R}$ is given by (eq.2) with constants from App. C_1 :

$$\frac{Cp_{ms}^{ig}}{R} = 1.702 + 9.081*10^{-3}\, T_{lm} - 2.164*10^{-6}\, \mathrm{T}_{am}\, T_{lm} \qquad …… (B)$$

$$T_{am} = \frac{550+T_2}{2} \quad , \qquad T_{Lm} = \frac{T_2-550}{\ln(T_2/550)}$$

With initial value $T_2 < 550$, then tray & $error$ give the final value of $T_2 = 411.34\ K$

Entropy change in reversible Process:

For close system contains an ideal gas inside friction less piston-cylinder
 Entropy chauge as:

1) Isochoric process $(V = constant)$

$$\Delta S = \int_1^2 \frac{dQ}{T} = \int_1^2 \frac{Cv \ dT}{T} = Cv \ ln\frac{T2}{T1}$$
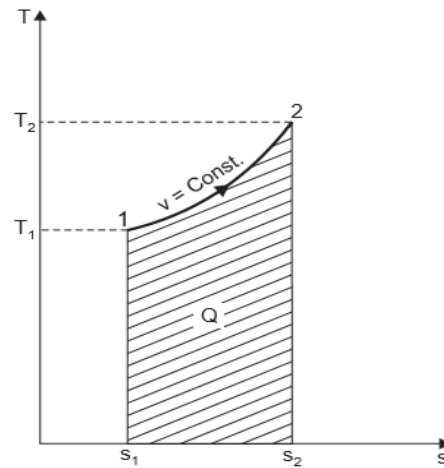
Fig. 5.25. *T-s* diagram : Constant volume process

2) Isobaric process $(P = constant)$

$$\Delta S = \int_1^2 \frac{dQ}{T} = \int_1^2 \frac{Cp \ dT}{T} = Cp \ ln\frac{T2}{T1}$$
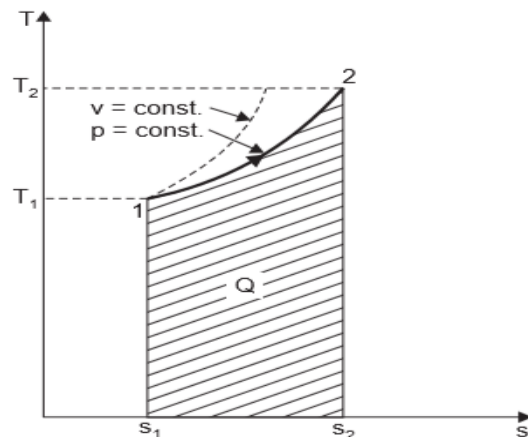
Fig. 5.26. *T-s* diagram : Constant pressure process.

3) **Isothermal process**   (T =constant):

$$\Delta S = \int_1^2 \frac{dQ}{T} = -\int_1^2 \frac{-pdv}{T} = \int_1^2 \frac{RT}{V}\frac{dv}{T} \qquad\qquad Q=W$$

$$\therefore \Delta S = R \int_1^2 \frac{dv}{v} = R\, ln\frac{V2}{V1}$$
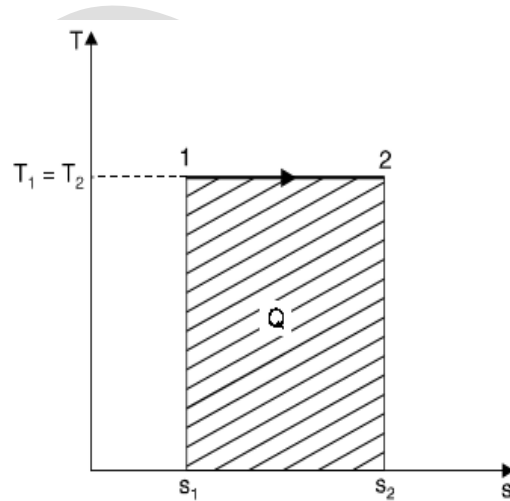
Fig. 5.27. *T-s* diagram : Isothermal process.

4) **Adiabatic process**   (isentropic   process)

dQ = 0   →   dS = 0

$\Delta S = 0$
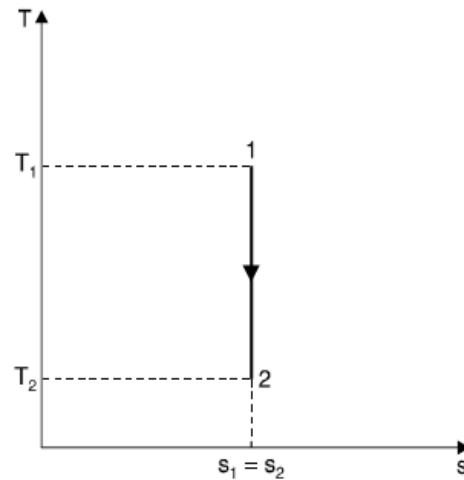
Fig. 5.28. *T-s* diagram : Adiabatic process.

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5) *Polytropic process*:

When happen any reversible process where don't stay constant any property (pressure, temperature, volume) as:

$dQ = dU - dW$

$dU = C_v \, dT$

$dQ = T \, dS$

$dw = - p \, dv$

$\int \frac{dQ}{T} = \int \frac{dU}{T} - \int \frac{-P \, dV}{T}$ $\because P = \frac{RT}{V}$

$\Delta S = \int C_v \frac{dT}{T} + \int \frac{R \, T \, dV}{V \, T}$

$\quad\quad = \int C_v \frac{dT}{T} + R \int \frac{dV}{V}$

$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$ In general.
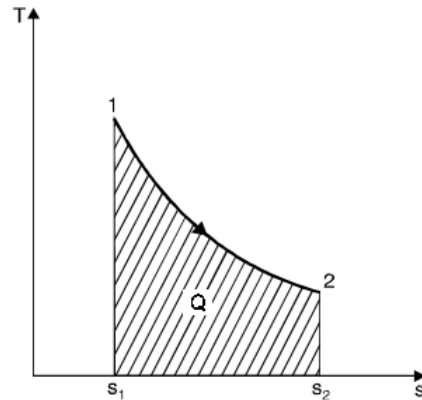
Fig. 5.29. *T-s* diagram : Polytropic process.

$pV^n = \text{cons.} = P_1 V_1{}^n = P_2 V_2^n$

$\Delta S = C_v \frac{(n-\gamma)}{(n-1)} \ln \frac{T_2}{T_1}$ (For polytrophic process)

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

Also, can we drive an equation to compute entropy Change?

$Cp = R + Cv$

$\Delta S = C_p \ln \frac{V_2}{V_1} + C_v \ln \frac{P_2}{P_1}$ H.W

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

S. No	Process	Change of entropy (per Kg)
1	General case	i. $Cv\,ln\dfrac{T2}{T1} + R\,ln\dfrac{V2}{V1}$ (In term of T and v) ii. $Cv\,ln\dfrac{P2}{P1} + Cv\,ln\dfrac{V2}{V1}$ (In term of P and v) iii. $Cp\,Ln\dfrac{T2}{T1} - R\,ln\dfrac{P2}{P1}$ (in term of T and P)
2	Constant Volume	$\Delta S = Cv\ln\dfrac{T2}{T1}$
3	Constant Pressure	$Cp\,Ln\dfrac{T2}{T1}$
4	Isothermal	$R\,ln\dfrac{V_2}{V_1}$
5	Adiabatic	Zero
6	Polytrophic	$Cv\left(\dfrac{n-\gamma}{n-1}\right)\ln\dfrac{T2}{T1}$

Example 5.2

For the ideal-gas state and constant heat capacities, Eq. (3.23b) for a reversible adiabatic (and therefore isentropic) process can be written:

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

Show that this same equation results from application of Eq. (5.10) with
$\Delta S^{ig} = 0$

Solution 5.2

Because C_P^{ig} is constant, Eq. (5.10) becomes:

$$0 = \frac{C_P^{ig}}{R}\ln\frac{T_2}{T_1} - \ln\frac{P_2}{P_1} = \ln\frac{T_2}{T_1} - \frac{R}{C_P^{ig}}\ln\frac{P_2}{P_1}$$

By Eq. (3.12) for the ideal-gas state, with $\gamma = C_P^{ig}/C_V^{ig}$:

$$C_P^{ig} = C_V^{ig} + R \qquad \text{or} \qquad \frac{R}{C_P^{ig}} = \frac{\gamma-1}{\gamma}$$

Whence,

$$\ln\frac{T_2}{T_1} = \frac{\gamma-1}{\gamma}\ln\frac{P_2}{P_1}$$

Exponentiating both sides of this equation leads to the given equation.

Example 5.4

A 40 kg steel casting (CP = 0.5 kJ·kg^{-1}·K^{-1}) at a temperature of 450°C is quenched in 150 kg of oil (CP = 2.5 kJ·kg^{-1}·K^{-1}) at 25°C. If there are no heat losses, what is the change in entropy of (a) the casting, (b) the oil, and (c) both considered together?

Solution 5.4

The final temperature t of the oil and the steel casting is found by an energy balance. Because the change in energy of the oil and steel together must be zero,

$$(40)(0.5)(t-450) + (150)(2.5)(t-25) = 0$$

Solution yields $t = 46.52$°C.

(a) Change in entropy of the casting:

$$\Delta S^t = m \int \frac{C_P dT}{T} = mC_P \ln \frac{T_2}{T_1}$$

$$= (40)(0.5) \ln \frac{273.15 + 46.52}{273.15 + 450} = -16.33 \text{ kJ·K}^{-1}$$

(b) Change in entropy of the oil:

$$\Delta S^t = (150)(2.5) \ln \frac{273.15 + 46.52}{273.15 + 25} = 26.13 \text{ kJ·K}^{-1}$$

(c) Total entropy change:

$$\Delta S_{total} = -16.33 + 26.13 = 9.80 \text{ kJ·K}^{-1}$$

Note that although the total entropy change is positive, the entropy of the casting has decreased.

The Third Law of Thermodynamic

- The Third law of Thermodynamic is state Follow:
  "The entropy of all perfect crystalline Solid is zero at absolute zero temperature"
- The Third law of Thermodynamics, often referred to as Nernst law, provides the basis for the calculation of absolute entropies of Substances.

According to this law, if the entropy is zero at   T= 0,

Measurements of heat capacities at very low temperatures provide data for the calculation from
Eq. (5.1) of entropy changes down to 0 K. When these calculations are made for different crystalline forms of the same chemical species, the entropy at 0 K appears to be the same for all forms.

When the form is non crystalline, e.g., amorphous or glassy, calculations show that the entropy of the disordered form is greater than that of the crystalline form. Such calculations, which are summarized elsewhere, 6 lead to the postulate that *the absolute entropy is zero for all perfect crystalline substances at absolute zero temperature.* While this essential idea was advanced by Nernst and

Planck at the beginning of the twentieth century, more recent studies at very low temperatures have increased confidence in this postulate, which is now accepted as the third law of thermodynamics.

If the entropy is zero at $T = 0$ K, then Eq. (5.1) lends itself to the calculation of absolute entropies. With $T = 0$ as the lower limit of integration, the absolute entropy of a gas at temperature T based on calorimetric data is:

$$S = \int_0^{T_f} \frac{(C_P)_s}{T} dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_v} \frac{(C_P)_l}{T} dT + \frac{\Delta H_v}{T_v} + \int_{T_v}^{T} \frac{(C_P)_g}{T} dT \qquad (5.35)$$

This equation7 is based on the supposition that no solid-state transitions take place and thus no heats of transition need appear. The only constant-temperature heat effects are those of melting at *Tf* and vaporization at *Tv.* When a solid-phase transition occurs, a term Δ*Ht* /*Tt* is added.

Note that although the third law implies that absolute values of entropy are obtainable, for most thermodynamic analyses, only relative values are needed. As a result, reference states other than the perfect crystal at 0 K are commonly used. For example, in the steam tables of
App. E, saturated liquid water at 273.16 K is taken as the reference state and assigned zero entropy. However, the absolute or "third law" entropy of saturated liquid water at 273.16 K is
3.515 kJ·kg−1·K−1.

Q5//

Air is contained in an insulated, rigid volume at 20 °C And 200 kpa. Paddle wheel, inserted in volume, does 720 KJ of work on the air, if the volume is 2 m³. Calculate the entropy increase? $Cv = (5/2)$ R

Solution:

Q = 0 [insulated system]

$W = \Delta U = n \, Cv \, \Delta T$

$n = \dfrac{PV}{RT} = \dfrac{200 \times 2}{0.08134 \times 293.6} = 16.412$

$720 = 16.412(0.20785)(T_2 - 293.15)$

$\mathbf{T_2 = 504.2 \ K}$

$\Delta S = n \, Cv \, ln \dfrac{T2}{T1}$ $[covs \ tant \ volune \ (rigid \ tank)]$

$\Delta s = 16,412 * 0.20785 * ln \dfrac{504.3}{293.15}$

$\Delta s = 1.8499 \ \ KJ/K$

Example 5-21

An iron cube at a temperature of 400 °C is dropped into an insulated bath containing 10 Kg Water at 25 °C. The water finally reaches a temperature of 50 °Cat steady state. Given that the Specific heat of water is equal to 4186 J/Kg.k. Find the entropy changes for the iron cube and the water. Is the process reversible? If so why?

Solution. *Given* : Temperature of iron cube   = 400°C = 673 K
Temperature of water   = 25°C = 298 K
Mass of water   = 10 kg
Temperature of water and cube after equilibrium = 50°C = 323 K
Specific heat of water, c_{pw} = 4186 J/kg K

Entropy changes for the iron cube and the water :

Is the process reversible ?

Now, Heat lost by iron cube = Heat gained by water

$$m_i\, c_{pi}\, (673 - 323) = m_w\, c_{pw}\, (323 - 298)$$
$$= 10 \times 4186\, (323 - 298)$$

∴ $$m_i\, c_{pi} = \frac{10 \times 4186\,(323 - 298)}{(623 - 323)} = 2990$$

where, m_i = Mass of iron, kg, and
c_{pi} = Specific heat of iron, J/kg K

Entropy of iron at   673 K $= m_i\, c_{pi}\, \ln\left(\dfrac{673}{273}\right)$

$$= 2990\, \ln\left(\frac{673}{273}\right)$$

$$= 2697.8 \text{ J/K} \qquad\qquad \text{[Taking 0°C as datum]}$$

Entropy of water at   298 K $= m_w\, c_{pw}\, \ln\left(\dfrac{298}{273}\right)$

$$= 10 \times 4186\, \ln\left(\frac{298}{273}\right) = 3667.8 \text{ J/K}$$

Entropy of iron at   323 K $= 2990 \times \ln\left(\dfrac{323}{273}\right) = 502.8 \text{ J/K}$

Entropy water at   323 K $= 10 \times 4186\, \ln\left(\dfrac{323}{273}\right) = 7040.04 \text{ J/K}$

Changes in entropy of iron   = 502.8 − 2697.8 = − 2195 J/K
Change in entropy of water   = 7040.04 − 3667.8 = 3372.24 J/K
Net change in entropy   = 3372.24 − 2195 = 1177.24 J/K
Since $\Delta S > 0$ hence the process is **irrevesible.**   (Ans.)

Q4// 2004 semester one:-

An inventor has built a heat engine for use in arctic weather station, utilizing heat from a portable nuclear reactor. The engine will be operate in cycle between a maximum temperature of 1000 k and minimum temperature of -23 °c. The inventor claims that when used in this temperature range, the cycle will produce 4630 ft.Ibf of network for each 2 kcal of heat received from the heat source. What can you say about the cycle?

Solution:-

Proplem. 5-3 page 163:-

The following heat engine produce power of 80000 kw. Determine in each case the rates at which heat is absorbed from the hot reservoir and discarded to the cold reservoir.

A// A Carnot engine operates between heat reservoirs at 600 and 300 k.

B// A practical engine operates between the same heat reservoirs but a thermal efficiency η= 0.3.

Solution:-

☞**Example 5.18.** *300 kJ/s of heat is supplied at a constant fixed temperature of 290°C to a heat engine. The heat rejection takes place at 8.5°C. The following results were obtained :*

    (i) 215 kJ/s are rejected.

    (ii) 150 kJ/s are rejected.

    (iii) 75 kJ/s are rejected.

    Classify which of the result report a reversible cycle or irreversible cycle or impossible results.

Solution. Heat supplied at 290°C = 300 kJ/s

Heat rejected at 8.5°C : (*i*) 215 kJ/s, (*ii*) 150 kJ/s, (*iii*) 75 kJ/s.

Applying *Clausius inequality* to the cycle or process, we have :

(*i*)
$$\sum_{cycle} \frac{\delta Q}{T} = \frac{300}{290 + 273} - \frac{215}{8.5 + 273}$$
$$= 0.5328 - 0.7637 = -0.2309 < 0.$$

∴   **Cycle is irreversible.** (Ans.)

(*ii*)
$$\sum_{cycle} \frac{\delta Q}{T} = \frac{300}{290 + 273} - \frac{150}{8.5 + 273}$$
$$= 0.5328 - 0.5328 = 0$$

∴   **Cycle is reversible.** (Ans.)

(*iii*)
$$\sum_{cycle} \frac{\delta Q}{T} = \frac{300}{290 + 273} - \frac{75}{8.5 + 273}$$
$$= 0.5328 - 0.2664 = 0.2664 > 0.$$

This **cycle is impossible** by second law of thermodynamics, *i.e., Clausius inequality*. **(Ans.)**

This mathematical statement of the second law affirms that every process proceeds in such a direction that the total entropy change associated with it is positive, the limiting value of zero being attained only by a reversible process. No process is possible for which the total entropy decreases.

Equation (5.19)

Thermodynamic Properties of fluids

الغرض من دراسة هذا الفصل هو ايجاد معادلات لحساب ΔH & ΔS من معلومات PVT والسعة الحرارة.وكذلك ايجاد معادلات عامة generalized correlations والتي تفيد في ايجاد ΔH , ΔS في حالة غياب معلومات عن PVT والسعة الحرارة.

*Relationship a many thermodynamic Properties for a homogeneous

  Phase of constant Composition:-

ويقصد به العلاقات الرياضة التي تربط بين الخواص الثرمو ديناميكية اللموائع هذه العلاقات هي

Maxwell s Relation

- **Internal energy**   **dU = TdS - PdV**   **…….. (1)**
- **Enthalpy**   **dH = TdS + VdP**   **…….. (2)**
- **Helmholtz energy**   **dA= - PdV - S dT**   **……. (3)**
- **Gibbs energy**   **dG = VdP – S dT**   **……. (4)**

Fundamental Property relations

***** For general eq.** $df = Mdx + Ndy$

$$\left(\frac{\partial M}{\partial y}\right)_X = \left(\frac{\partial N}{\partial X}\right)_y \quad \rightarrow exact\ eq.$$

من هذه المعادلات الاربعة اعلاه يمكن اشتقاق علاقات ماكسويل الاربعة وهي:

dU = TdS – PdV

From eq. (1) $\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial S}\right)_v$

From eq. (2) $\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial S}\right)_p$

From eq. (3) $\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$

From eq. (4) $\left(\frac{\partial V}{\partial T}\right)_p = \left(-\frac{\partial s}{\partial p}\right)_T$

المهم من دراسة هذه المعادلات هو ايجاد المعادلات الخاصة بحساب ΔH , ΔS بدلالة معلومات
PVT والسعة الحرارية

$$H = H(T, P)$$

$$S = S(T, P)$$

$$dH = (\frac{\partial H}{\partial T})_P \, dT + (\frac{\partial H}{\partial P})_T \, dp \; \ldots \ldots \ldots \ldots \ldots \ldots (1)$$

$$dS = (\frac{\partial s}{\partial T})_p \, dT + (\frac{\partial S}{\partial P})_T dP \ldots \ldots \ldots \ldots \ldots \ldots (2)$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

اذن اصبح الان من المهم ان نعرف ماذا تساوي المقادير الاربعة التالية والموجودة في المعادلة (1) ,
(2) وهي :

$$(\frac{\partial H}{\partial T})_p \quad , (\frac{\partial H}{\partial P})_T \; , \quad (\frac{\partial S}{\partial P})_T \quad , (\frac{\partial S}{\partial T})_P$$

1- $(\frac{\partial H}{\partial T})_P = c_p$ $\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$ (3)

2- $(\frac{\partial S}{\partial T})_p : -$

$\therefore$ $Note \; that$ $dH = Tds + Vdp$ $divide \; by \; \partial T$

$$\therefore (\frac{dH}{dT})_p = T(\frac{ds}{dT})_P$$

$$(\frac{\partial S}{\partial T})_p = \frac{1}{T} (\frac{dH}{dT})_p$$

$$\boxed{\therefore (\frac{\partial S}{\partial T})_p = \frac{Cp}{T} \qquad \ldots\ldots\ldots\ldots (4)}$$

3-
$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \qquad \dots\dots(5) \qquad From \text{ Maxwell s Relation}$$

(4) $\left(\frac{\partial H}{\partial P}\right)_T : -$

Note that $\qquad dH = TdS + Vdp \qquad \leftarrow divide\ by\ \partial p$

$$\left(\frac{dH}{dp}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

But $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad [From\ eq.(5)\ ]$

$$\therefore \left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \dots\dots\dots\dots(6)$$
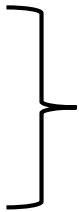
الان اصبحت المقادير الاربعة المذكورة اعلاه جميعها بدلالة معلوماتPTV والسعة الحرارية .

بعد تعريف هذه المقادير[(3)، (4) ،(5)، (6) في المعادلتن(1)، (2) يصبح لدينا

$$dH = CpdT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP \qquad \dots\dots\dots\dots(7)$$

$$ds = Cp\frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dp \qquad \dots\dots\dots\dots(8)$$

Example 1// show that for ideal gas:-

(a) $dH = cpdT$

(b) $ds = cp\frac{dT}{T} - R\frac{dp}{p}$

<u>Solution</u>

(a) $dH = cpdT + [v - T(\frac{\partial v}{\partial T})_P]\, dp$ ………….. (1)

$for\ ideal\ gas : pv = RT \implies v = \frac{RT}{P}\quad take\ the\ derivative$

$\therefore\quad (\frac{\partial v}{\partial T})_P = \frac{R}{P}$ ………….. (2)

نعوض (2) في (1) ينتج

$dH = cpdT + [v - \frac{TR}{P}]dp$

$dH = Cp\ dT + [v - v]dp$

$\boxed{dH = Cp\ dt}\qquad$ For ideal gas.

(b) $\qquad ds = cp\frac{dT}{T} - (\frac{\partial v}{\partial T})_p\ dp$ ………….. (1)

For ideal gas: $v = \frac{RT}{p} \implies (\frac{\partial v}{\partial T})_p = \frac{R}{p}$ ……… (2)

نعوض (2) في (1) ينتج

$\therefore ds = cp\frac{dT}{T} - \frac{R}{p}\ dp$

$\boxed{ds = cp\frac{dT}{T} - R\frac{dp}{p}}\qquad$ For ideal gas.

Example 2:-   show that for liquids:-

(a) $dH = cpdT + v(1 - \beta T)dp$

(b) $dS = cp \dfrac{dT}{T} - \beta vdp$

Where β is the volume expansivity? $\beta = \dfrac{1}{v}\left(\dfrac{\partial V}{\partial T}\right)p$

Solution

$dH = Cp\,dT + [\{v - T\left(\dfrac{\partial v}{\partial T}\right)_p\}\,dp\,]$ ……………..(eq. 7)

$\beta = \dfrac{1}{v}\left(\dfrac{\partial v}{\partial T}\right)_P$ ⟹ $\left(\dfrac{\partial v}{\partial T}\right)_P = V\beta$

$\therefore dH = cpdT + (v - Tv\beta)dp$

$\boxed{dH = CpdT + v(1 - T\beta)dp}$ For liquids

(b)//

$ds = Cp\dfrac{dT}{T} - \left(\dfrac{\partial V}{\partial T}\right)_p\,dp$ ……………$(eq.8)$

For liquids $\left(\dfrac{\partial v}{\partial T}\right)_P = \beta v$

$\boxed{\therefore ds = Cp\dfrac{dT}{T} - \beta v\,dp}$ For liquids

Notes:-

1- For incompressible fluid   سائل عدم الانضغاظ
   $\beta=0$ and $K=0$ where K_t = Isothermal compressibility

   Therefore $\boxed{\begin{array}{l} dH= Cp\,dT + V\,dp \\[4pt] ds = Cp\dfrac{dT}{T} \end{array}}$

2- Since β and v in   liquids are weak function of pressure , these values $(\beta \& V)$ can be taken as **constant** or taken as **average values** between p_1, and p_2

i.e. $dH = cpdT + V^{av}(1 - \beta^{av}\, T)dp$

$ds = cp\dfrac{dT}{T} - \beta^{av}V^{av}\, dp$

Example:-

Determine the enthalpy and entropy changes for liquid water for a change of state from 1bar and 25℃ to 1000 bar and 50℃ the following data for water are available:-

T ℃	P bar	Cp $j\,mol^{-1}\,k^{-1}$	V $cm^3 mol^{-1}$	β k^{-1}
25	1	75.305	18.075	256×10^{-6}
25	1000	……..	17.358	366×10^{-6}
50	1	75.314	18.24	458×10^{-6}
50	1000	,,,,,,,,,,,	17.535	568×10^{-6}

Solution:-

بما ان الخاصيتين ΔH , ΔS لاتعنمدان على الطريق مثلا باا مكان تقسيم العملية الى خطوتين : الخطواة الاولى ابثبوت الضغط والخطوة الثابته بثبوت الحرارة

Step I:-   constant pressure
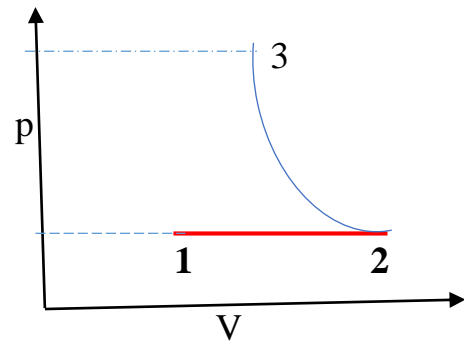
For liquids

$\mathbf{dH = cpdT + v^{av}(1\text{-}\beta^{av}T)\, dp}$

$\therefore dH = cpdT$

$Cp^{av} = \dfrac{75.305 + 75.314}{2} = 75.31\ \dfrac{J}{mol\ k}$

$\therefore \Delta H = 75.31(T_{2-}\,T_1) = 75.31(50 - 25) = 1882\ \ J/mal.$

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$$dS = Cp\frac{dT}{T} - B^{av}\ v^{av}\ dp$$

$$\Delta S = cp^{av}\ln\frac{T_2}{T_1} = 75.31\ln\frac{50+273}{25+273} = 6.06\ \ J/mol\ k$$

**Step Π**: −   Constant temperature   T= 50 °C.

$$dH = cpdT + v^{av}\ (1 - \beta^{av}T)\ dp$$

$$dH = V^{av}(1 - \beta^{av}T)dp$$

$$v^{av} = \frac{18.24+17.535}{2} = 17.887\ \ cm^3\ mol^{-1}$$

$$\beta^{av} = \frac{458\times10^{-6} + 568\times10^{-6}}{2} = 5.13 \times 10^{-4}$$

$$\Delta H_\Pi = \frac{17.887\ [\ (1- 5.13\times10^{-4}\ \ (323)]\ (1000-1)}{10\frac{bar\ cm^3}{J}} = 1490\ \ \ J/mol$$

عامل تحويل وحدات

$J = 10\ bar.cm^3$.اي يجب تحويل وحدات $bar.cm^3$ الى J .

$$ds = Cp\frac{dT}{T} - \beta\ Vdp$$

$$\Delta S_\Pi = -\beta vdp = \frac{- 5.13\times10^{-4}\ (17.887)(1000-1)}{10} = -0.916\ \ J/mol\ k.$$

$$\therefore\ \ \Delta H_T = \Delta H_i\ +\ \Delta H_{ii} = 1882 + 1490 = 3372$$

$$\Delta S_T = \Delta S_I + \Delta S_{II} = 6.06 - 0.916 = 5.143\ J/mol\ k.$$

. . . .

,,,,,,,,,,,,,,,,,,,,

Prove that: (1)

(1) $(\frac{\partial H}{\partial S})_T = T - \frac{1}{\beta}$ where: $\beta = $ Volume expansivity

(2) $(\frac{\partial v}{\partial T})_S = -\frac{CV k_2}{\beta T}$ where $K_t = $ Isothermal compressibility

(3) $(\frac{\partial p}{\partial T})_S = \frac{Cp}{T V \beta}$

(4)   Find $(\frac{\partial G}{\partial T})_T$ using the following eq. of state:

$$P (V - b) = RT$$

5   Starting from first principles and using whatever definitions you find necessary, derive an expression for Joul–Thomsn coefficient of a gas whose equation of state is $PV = n (RT - \frac{aP}{T})$

Where   a: is a positive constant. Does the temperature of this gas increase or decrease in Joul –Thomson expansion?

       (1) $dH = Tds + Vdp$

     $(\frac{dH}{ds})_T = T + V(\frac{dp}{ds})_T$

     But $\left(\frac{dp}{ds}\right)_T = -(\frac{\partial T}{\partial v})_p$

     $\therefore (\frac{dH}{ds})_T = T - V(\frac{dT}{dv})_p$

Heat effect accompanying phase of pure Substance

1- *Clapeyron equation:*

This equation involving:-

(a) The saturation pressure and temperature.

(b) The enthalpy of evaporation

(c) Specific volume of the two phases. It can be derived in a no of ways

Here, consider one of the Maxwell relations:

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

Consider saturated liquid changes to saturated vapor of pure substance.

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{dp}{dT} = \left(\frac{\partial s}{\partial v}\right)_T = \frac{S_g - S_f}{V_g - v_f} = \frac{S_{fg}}{V_{fg}}$$

$$\frac{dp}{dt} = \frac{S_{fg}}{V_{fg}}$$

$$S_{fg} = \frac{h_{fg}}{T} \qquad \longrightarrow \qquad \boxed{\frac{dp}{dt} = \frac{h_{fg}}{T\,V_{fg}}} \qquad **$$

Where $\frac{dp}{dT}$ is the slope of vapor pressure curve?

Note: At low   pressure $V_f \lll V_g$

∴ The equation becomes

$$\frac{dp}{dt} = \frac{h_{fg}}{TV_g} \qquad **$$

$$\therefore \frac{dp}{dT} = \frac{P\,h_{fg}}{T^2 R}$$

$$\int \frac{dp}{p} = \int \frac{h_{fg}\,dT}{RT^2}$$

$$ln\;p = \frac{-h_{fg}}{R\,T} + c$$

$$\boxed{ln\;p = A - \frac{B}{T}} \qquad \text{Antony equation}$$

****

Example:

Estimate ΔH of Vaporization of water at 80 ℃ ?

Given the Following date.

T (°C)	P $(K\,pa)$	V^g $(\frac{m^3}{kg})$	V^f $(\frac{m^3}{kg})$
77	41.89	3409×10^{-3}	1.029×10^{-3}
81	49.31	………	………..

Solution:-

$$\frac{dp^{sat}}{dT} = \frac{h_{fg}}{T\Delta V} \quad \rightarrow \quad h_{fg} = (\frac{dp^{sat}}{dT})\,(T)\,(\Delta V)$$

$$h_{fg} = (\frac{\Delta p}{\Delta T})(T)\,(V_g - V_l)$$

$$h_{fg} = \frac{(49.31-41.89)}{(81-77)}\,(80+273)\,(3409 \times 10^{-3} - 1.029 \times 10^{-3})$$

$$h_{fg} = 2231 \ k_J/K_g$$

عند مقارنة هذه القيمه مع القيمه الحقيقية والتي هي

$$h_{fg} = 2308$$

يتبين مقدار الخطأ هو:

$$\text{Error \%} = \frac{2308-2231}{2308} \times 100\,\% = 3.3\%$$

Clasius/Clapyron equation

يمكن استنباط معادلة اخرى من معادلة clapyron تستخدم لحساب ΔH^V (حرارة التبخر)
اذاكانت عملية التبخر تجري تحت ضغط واطي (اقل من 3bar)

$$\Delta V = V_{g-l} \qquad \text{but} \quad V_l \ll v_g$$

$$\Delta V = v_g = \frac{RT}{P^{sat}}$$

$$\therefore \frac{dp^{sat}}{dT} = \frac{\Delta H^v}{T\Delta V} = \frac{\Delta H^v}{T\left(\frac{RT}{p^{sat}}\right)} = \frac{p^{sat}\,\Delta H^v}{RT^2}$$

$$\therefore \frac{dP^{sat}/P}{dT/T^2} = \frac{\Delta H^v}{R} \qquad \text{but} \quad \frac{dT}{T^2} = -d\left(\frac{1}{T}\right)$$

$$d\,ln\,P^{sat} = \frac{-\Delta H^v}{R}\,d\left(\frac{1}{T}\right) \qquad \rightarrow \qquad ln\,P = \frac{-\Delta H^v}{R}\left(\frac{1}{T}\right) + C$$

$$\boxed{\; ln\frac{P_2^{sat}}{P_1^{sat}} = \frac{\Delta H^V}{R}\left[\frac{T_2 - T_1}{T_1\,T_2}\right] \;}$$ ** Clasius – Clapyron   equation

اذا توفرت لدينا نقاط عديدة ، يمكن رسم $ln\,P^{sat}$ مقابل $\left(\frac{1}{T}\right)$ واستخراج ميل الخط المستقيم
والذي يمثل $\dfrac{-\Delta H_v}{R}$

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Heat effect accompanying phase of pure Substance

1- *Clapeyron equation:*

This equation involving:-

(a)The saturation pressure and temperature.

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$$\frac{dp}{dt} = \frac{h_{fg}}{TV_g} \qquad **$$

$$\therefore \frac{dp}{dT} = \frac{P\, h_{fg}}{T^2 R}$$

$$\int \frac{dp}{p} = \int \frac{h_{fg}\, dT}{RT^2}$$

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81	49.31	………	………..

Solution:-

$$\frac{dp^{sat}}{dT} = \frac{h_{fg}}{T\Delta V} \quad \rightarrow \quad h_{fg} = \left(\frac{dp^{sat}}{dT}\right)(T)(\Delta V)$$

$$h_{fg} = \left(\frac{\Delta p}{\Delta T}\right)(T)(V_g - V_l)$$

$$h_{fg} = \frac{(49.31-41.89)}{(81-77)}(80+273)(3409 \times 10^{-3} - 1.029 \times 10^{-3})$$

$$h_{fg} = 2231 \ k_J/K_g$$

عند مقارنة هذه القيمه مع القيمه الحقيقية والتي هي

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$$\Delta V = V_{g-l} \qquad \text{but} \quad V_l \ll v_g$$

$$\Delta V = v_g = \frac{RT}{P^{sat}}$$

$$\therefore \frac{dp^{sat}}{dT} = \frac{\Delta H^v}{T\Delta V} = \frac{\Delta H^v}{T\left(\frac{RT}{p^{sat}}\right)} = \frac{p^{sat}\,\Delta H^v}{RT^2}$$

$$\therefore \frac{dP^{sat}/P}{dT/T^2} = \frac{\Delta H^v}{R} \qquad \text{but} \quad \frac{dT}{T^2} = -d\left(\frac{1}{T}\right)$$

$$d\ln P^{sat} = \frac{-\Delta H^v}{R}\, d\left(\frac{1}{T}\right) \quad \rightarrow \quad \ln P = \frac{-\Delta H^v}{R}\left(\frac{1}{T}\right) + C$$

$$\boxed{\ln \frac{P_2^{sat}}{P_1^{sat}} = \frac{\Delta H^V}{R}\left[\frac{T_2-T_1}{T_1\,T_2}\right]}$$ ** Clasius – Clapyron   equation

اذا توفرت لدينا نقاط عديدة ، يمكن رسم $\ln P^{sat}$ مقابل $\left(\frac{1}{T}\right)$ واستخراج ميل الخط المستقيم

والذي يمثل $\dfrac{-\Delta H_v}{R}$

Example:

For water estimate the latent heat of vaporization ΔH^v at 244 and p^{sat} at 244 ℃ using

    (a)   Clasius Clapyron equation

    (b)   Clapyron equation.

Given the following data

$T/℃$	230	240	250	260
P^s/Kpa	2797.6	3347.8	3977.6	4694.3
$V_g/(m^3/Kg) = 55.58 * 10^{-3}$		$V_L = 1.238 * 10^{-3}$ at 244 ℃		

Solution:

(a)   using clausius Clapyron equation

$$d \ln P^{sat} = - \frac{\Delta H}{R} \ d(\frac{1}{T})$$

$$\ln P^{sat.} = - \frac{\Delta H^v}{R} \ d(\frac{1}{T}) + \text{Const.}$$

من

عند   الجدول المعطى نحصل على

$\ln P^{sat.}$	**7.936**	**8.116**	**8.288**	**8.454**
$\frac{1}{T}$	$1.988 * 10^{-3}$	$1.949 * 10^{-3}$	$1.912 * 10^{-3}$	$1.876 * 10^{-3}$

رسم هذه النقاط نحصل على

Slope = - 4535

$\therefore \ \Delta H^v = -R(Slope) = -8.314(-4535) = 37703 \quad KJ/Kmol$

  OR $\Delta H^v = 2094 \quad KJ/Kg$.

$$ln\frac{P_2^{sat}}{p_1^{sat}} = \frac{-\Delta H^v}{R} \ [\frac{1}{T_2} - \frac{1}{T_1}]$$

Take $T_2 = 244℃$ (517 K)   ﴾ $T_1 = 240 ℃$ (513 K)

$P_1^{sat} = 3347.8 \ KP_a$

$$\ln\frac{P_2^{sat.}}{3347.8} = \frac{-2094}{8.314}\left[\frac{1}{517} - \frac{1}{513}\right] = 3.798 \times 10^{-3}$$

$$\frac{P_2^{sat}}{3347.8} = 1.0038 \ \rightarrow \ P_2^{sat.} = 1.0038\,(3347.8) = 3360.5 \ Kpa.$$

(b)   Clapyron equation

$\frac{dp^{sat.}}{dT} = \frac{\Delta H^v}{T\Delta v}$

$\Delta H^v = \frac{dp^s}{dT}\,(\text{T})\,(\Delta v)$

$\Delta H^v = \frac{(3977.6 - 3347.8\,)}{(250 - 240)}\,(244 + 273)(55.58 \times 10^{-3} - 1.238 \times 10^{-3})$

$\Delta H^v = 1769 \ kJ/kg$

Now to find $p^{sat.}$ at 244 °C

$\Delta p^{sat.} = \frac{\Delta H^v}{T\Delta v}\ (\Delta T) = \frac{1769 \qquad (244-240)}{(244+273)\ (55.58\times10^{-3} - 1.238\times10^{-3})} = 251.9$

$\Delta p^{sat.} = 251.9 = (p_{244}^{sat} - p_{240}^{sat}) = p_{244}^{sat} - 3347.8$

$p^{sat.} = 3599.7 kpa.$

$\dfrac{1}{T}$	$\ln P^{sat.}$
$1.998 * 10^{-3}$	7.936
$1.949 * 10^{-3}$	8.116
$1.912 * 10^{-3}$	8.288
$1.876 * 10^{-3}$	8.454

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{8.19 - 7.8}{193 \times 10^{-5} - 201.6 \times 10^{-5}} = -4535$$

$$\therefore \Delta H^v = -R \text{ (slope)} = -8.314(-4535)$$

$$= +37703 \text{ kJ/kmol}$$

$$\Delta H^V = 2094 \frac{kJ}{Kg}$$

6

2- $\underline{\Delta H^v \ and \ normal \ boiling \ point}$

Riedel equation:

$$\frac{\Delta H_n^v}{T_n} = R\left[\frac{1.092 \ (ln \ p_{c-1.013})}{0.93 - Trn}\right]$$

Where: $T_n = normal \ boiling \ point \ \ k$

ΔHn = molar latent heat of vaporization at T_n

Pc = Critical pressure (bar).

$T_{rn} = reduced \ \ temp. \ at \ T_{n.}$

Example:

Estimate the molar latent heat of vaporization of water at normal boiling point 100℃ ?

Given for water T_c=647.3 K $P_c = 220.5 \ bar$.

$\underline{Solution:}$ $\frac{\Delta H_n^v}{T_n} = R\left[\frac{1.092 \ (ln \ P_c - 1.013)}{0.93 - Trn}\right]$

$T_n = 100℃ = 373 \ k°$

R=8.314   J/mol

$P_{c=220.5}$ bar

$T_{rn} = \frac{T_n}{T_c} = \frac{373}{647.3} = 0.5762$

$\frac{\Delta Hn}{373} = 8.314 \ \left[\frac{1.092 \ (ln \ 220.5 - 1.013)}{0.93 - 0.5762}\right]$

$\frac{\Delta Hn}{373} = 112.4$ $\Delta H_n^v = 41951.25 \ J/mol$

$3 - \Delta H^v$ of pure substance at any temperature.

Can be estimated from the know value of ΔH^v of that Liquid at a certain temperature.   (Watson method)

$$\frac{\Delta H_2^v}{\Delta H_1^v} = (\frac{1-T_{r2}}{1-T_{r1}})^{0.38}$$

Example:

Given that the latent heat of vaporization of water at 100 °C is 2257 J/gm. Estimate the latent heat at 300°C ? Given T_c =647.1

Solution:

$$\frac{\Delta^\backslash H_2^v}{\Delta H_1^v} = (\frac{1-T_{r2}}{1-T_{r1}})^{0.38}$$

$\Delta H_1 = latent\ heat\ at\ 100°C = 2257$

$\Delta H_2 = latent\ heat\ at\ 300°C$

$T_{r1} = \frac{373}{647.1} = 0.577$ $T_{r2} = \frac{573}{647.1} = 0.886$

$\Delta H_2 = 2257(\frac{1-0.886}{1-0.577})^{0.38}$ =1371 J/g.

Throttling Process:-

It is a steady flow process a cross a restriction (منطقة ضيقة) with a resulting drop in pressure, a typical example is the flow through Partially open valve. This process occurs so rapidly and in such a small space that there is no time and no large area for such heat transfer.

∴ It is assumed to be adiabatic

It is flow process

$\Delta H = Q - w_s$

$\Delta H = 0$ $\longrightarrow$ $H_1 = H_2$

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Thermodynamic Properties of fluids

الغرض من دراسة هذا الفصل هو ايجاد معادلات لحساب ΔH & ΔS من معلومات PVT والسعة الحرارة.وكذلك ايجاد معادلات عامة generalized correlations والتي تفيد في ايجاد ΔH , ΔS *في حالة غياب معلومات عن PVT والسعة الحرارة.*

*Relationship a many thermodynamic Properties for a homogeneous

Phase of constant Composition:-

ويقصد به العلاقات الرياضة التي تربط بين الخواص الثرمو ديناميكية اللموائع هذه العلاقات هي

Maxwell s Relation

- **Internal energy**   **dU = TdS - PdV**   **…….. (1)**
- **Enthalpy**   **dH = TdS + VdP**   **…….. (2)**
- **Helmholtz energy**   **dA= - PdV - S dT**   **……. (3)**
- **Gibbs energy**   **dG = VdP – S dT**   **……. (4)**

Fundamental Property relations

*** For general eq. $df = Mdx + Ndy$

$$\left(\frac{\partial M}{\partial y}\right)_X = \left(\frac{\partial N}{\partial X}\right)_y \quad \rightarrow exact \ eq.$$

من هذه المعادلات الاربعة اعلاه يمكن اشتقاق علاقات ماكسويل الاربعة وهي:

dU = TdS – PdV

From eq. (1) $\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial S}\right)_v$

From eq. (2) $\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial S}\right)_p$

From eq. (3) $\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$

From eq. (4) $\left(\frac{\partial V}{\partial T}\right)_p = \left(-\frac{\partial s}{\partial p}\right)_T$

المهم من دراسة هذه المعادلات هو ايجاد المعادلات الخاصة بحساب ΔH , ΔS بدلالة معلومات PVTوالسعة الحرارية

$H = H(T,P)$

$S = S(T,P)$

$$dH = (\frac{\partial H}{\partial T})_P \, dT + (\frac{\partial H}{\partial P})_T \, dp \; \ldots\ldots\ldots\ldots\ldots\ldots. (1)$$

$$dS = (\frac{\partial S}{\partial T})_p \, dT + (\frac{\partial S}{\partial P})_T dP \ldots\ldots\ldots\ldots\ldots\ldots. (2)$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

اذن اصبح الان من المهم ان نعرف ماذا تساوي المقادير الاربعة التالية والموجودة في المعادلة (1) , (2) وهي :

$$(\frac{\partial H}{\partial T})_p \quad , (\frac{\partial H}{\partial P})_T \; , \quad (\frac{\partial S}{\partial P})_T \quad , (\frac{\partial S}{\partial T})_P$$

1- $\quad (\frac{\partial H}{\partial T})_P = \; c_p$ .... (3)

2- $\quad (\frac{\partial S}{\partial T})_p : -$

$\therefore \quad Note \; that \qquad dH = Tds + Vdp \qquad divide \; by \; \partial T$

$$\therefore (\frac{dH}{dT})_p = T(\frac{ds}{dT})_P$$

$$(\frac{\partial S}{\partial T})_p = \frac{1}{T} (\frac{dH}{dT})_p$$

$$\boxed{\therefore (\frac{\partial S}{\partial T})_p = \frac{Cp}{T} \qquad \ldots\ldots\ldots. (4)}$$

3-

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \qquad \ldots\ldots (5) \qquad \textit{From } \text{Maxwell s Relation}$$

(4) $\left(\frac{\partial H}{\partial P}\right)_T : -$

Note that $\qquad dH = TdS + Vdp \qquad \leftarrow divide\ by\ \partial p$

$$\left(\frac{dH}{dp}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

$$But\ \ \left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad [From\ eq.(5)\ ]$$

$$\therefore \left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \ldots\ldots\ldots\ldots (6)$$

الان اصبحت المقادير الاربعة المذكورة اعلاه جميعها بدلالة معلوماتPTV والسعة الحرارية .

بعد تعريف هذه المقادير] (3)، (4)، (5)، (6) في المعادلتن(1)، (2) يصبح لدينا

$$dH = CpdT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP \qquad \ldots\ldots\ldots\ldots (7)$$

$$ds = Cp\frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dp \qquad \ldots\ldots\ldots\ldots (8)$$

Example 1// show that for ideal gas:-

(a) $dH = cpdT$

(b) $ds = cp\dfrac{dT}{T} - R\dfrac{dp}{p}$

<u>Solution</u>

(a) $dH = cpdT + [v - T(\dfrac{\partial v}{\partial T})_P]\, dp$ ………….. (1)

$for\ ideal\ gas : pv = RT \Longrightarrow v = \dfrac{RT}{P}$ $take\ the\ derivative$

$\therefore\quad (\dfrac{\partial v}{\partial T})_P = \dfrac{R}{P}$ ………….. (2)

نعوض (2) في (1) ينتج

$dH = cpdT + [\mathrm{v} - \dfrac{TR}{P}]dp$

$\mathrm{dH} = \mathrm{Cp\ dT} + [v - v]dp$

$\boxed{\mathrm{dH = Cp\ dt}}$ For ideal gas.

(b) $ds = cp\dfrac{dT}{T} - (\dfrac{\partial v}{\partial T})_p\ dp$ ………….. (1)

For ideal gas: $v = \dfrac{RT}{p} \Longrightarrow (\dfrac{\partial v}{\partial T})_p = \dfrac{R}{p}$ ……… (2)

نعوض (2) في (1) ينتج

$\therefore ds = cp\dfrac{dT}{T} - \dfrac{R}{p}\ dp$

$\boxed{ds = cp\dfrac{dT}{T} - R\dfrac{dp}{p}}$ For ideal gas.

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Example 2:-   show that for liquids:-

$$(a) \quad dH = cpdT + v(1 - \beta T)dp$$

$$(b) \quad dS = cp\,\frac{dT}{T} - \beta vdp$$

Where β is the volume expansivity? $\beta = \frac{1}{v}\left(\frac{\partial V}{\partial T}\right)p$

Solution

dH= Cp dT + [{v − T $\left(\frac{\partial v}{\partial T}\right)_p$} dp] ………………..(eq. 7)

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

$\therefore dH = cpdT + (v - Tv\beta)dp$

$$\boxed{dH = CpdT + v(1 - T\beta)dp}$$ For liquids

(b)//

$$ds = Cp\,\frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_p dp \quad …………(eq.\,8)$$

For liquids $\left(\frac{\partial v}{\partial T}\right)_P = \beta v$

$$\boxed{\therefore ds = Cp\,\frac{dT}{T} - \beta v\,dp}$$ For liquids

Notes:-

1- For incompressible fluid   سائل عدم الانضغاظ
   $\beta = 0$ and $K = 0$ where K_t = Isothermal compressibility

Therefore
$$\boxed{\begin{array}{l} dH = Cp\ dT + V\ dp \\ ds = Cp\,\frac{dT}{T} \end{array}}$$

2- Since β and v in   liquids are weak function of pressure , these values $(\beta \& V)$ can be taken as **constant** or taken as **average values** between p_1, and p_2

i.e. $dH = cpdT + V^{av}(1 - \beta^{av}\,T)dp$

$ds = cp\dfrac{dT}{T} - \beta^{av}V^{av}\,dp$

Example:-

Determine the enthalpy and entropy changes for liquid water for a change of state from 1bar and 25℃ to 1000 bar and 50℃ the following data for water are available:-

T °C	P bar	Cp $j\,mol^{-1}\,k^{-1}$	V cm^3mol^{-1}	β k^{-1}
25	1	75.305	18.075	256×10^{-6}
25	1000	……..	17.358	366×10^{-6}
50	1	75.314	18.24	458×10^{-6}
50	1000	,,,,,,,,,,,	17.535	568×10^{-6}

Solution:-

بما ان الخاصيتين ΔH , ΔS لاتعنمدان على الطريق مثلا باا مكان تقسيم العملية الى خطوتين : الخطواة الاولى ابثبوت الضغط والخطوة الثابته بثبوت الحرارة

Step I:-   constant pressure
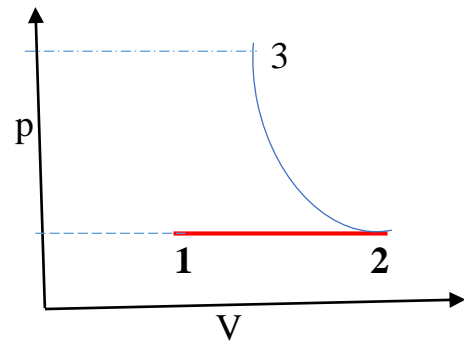
For liquids

$\mathbf{dH = cpdT + v^{av}(1\text{-}\beta^{av}T)\,dp}$

$\therefore dH = cpdT$

$Cp^{av} = \dfrac{75.305+75.314}{2} = 75.31\,\dfrac{J}{mol\,k}$

$\therefore \Delta H = 75.31(T_{2-}\,T_1) = 75.31(50 - 25) = 1882\quad J/mal.$

6

$$\mathrm{dS} = \mathrm{Cp}\frac{dT}{T} - B^{av}\ v^{av}\ dp$$

$$\Delta S = cp^{av}\ln\frac{T_2}{T_1}\ = 75.31\ln\frac{50+273}{25+273}\ = 6.06\ \ J/mol\ k$$

Step Π:−   Constant temperature   T= 50 °C.

$$dH = cpdT + v^{av}\ (1 - \beta^{av}\mathrm{T})\ \mathrm{dp}$$

$$\mathrm{dH} = V^{av}(1 - \beta^{av}\mathrm{T})\mathrm{dp}$$

$$v^{av} = \frac{18.24 + 17.535}{2} = \ 17.887\ \ cm^3\ mol^{-1}$$

$$\beta^{av} = \ \frac{458\times10^{-6}\ + 568\times10^{-6}}{2} = 5.13\times10^{-4}$$

$$\Delta H_{\Pi} = \frac{17.887\ [\ (1-\ 5.13\times10^{-4}\ \ \ (323)]\ (\ 1000-1)}{10\frac{bar\ cm^3}{J}} = 1490\ \ \ J/mol$$

عامل تحويل وحدات

$J = 10$ bar. cm^3 .اي يجب تحويل وحدات bar. cm^3 الى J .

$$\mathrm{ds} = \mathrm{Cp}\frac{dT}{T} - \ \beta\ \mathrm{Vdp}$$

$$\Delta S_{\Pi} = -\beta vdp = \frac{-\ 5.13\times10^{-4}\ (17.887)(1000-1)}{10} = -\ 0.916\ \ J/mol\ k.$$

$$\therefore\ \ \Delta H_T = \Delta H_i\ +\ \Delta H_{ii} = 1882 + 1490 = 3372$$

$$\Delta S_T = \Delta S_I + \Delta S_{II} = 6.06 - 0.916 = 5.143\ J/mol\ k.$$

. . . .

,,,,,,,,,,,,,,,,,,,,,

Prove that: (1)

(1) $(\frac{\partial H}{\partial S})_T = T - \frac{1}{\beta}$ where: $\beta =$ Volume expansivity

(2) $(\frac{\partial v}{\partial T})_S = -\frac{CV k_2}{\beta T}$ where $K_t =$ Isothermal compressibility

(3) $(\frac{\partial p}{\partial T})_S = \frac{Cp}{T V \beta}$

(4) Find $(\frac{\partial G}{\partial T})_T$ using the following eq. of state:

$$P (V - b) = RT$$

5   Starting from first principles and using whatever definitions you find necessary, derive an expression for Joul–Thomsn coefficient of a gas whose equation of state is $PV = n (RT - \frac{aP}{T})$

Where   a: is a positive constant. Does the temperature of this gas increase or decrease in Joul –Thomson expansion?

(1) $dH = Tds + Vdp$

$(\frac{dH}{ds})_T = T + V (\frac{dp}{ds})_T$

But $(\frac{dp}{ds})_T = -(\frac{\partial T}{\partial v})_p$

$\therefore (\frac{dH}{ds})_T = T - V (\frac{dT}{dv})_p$

Heat effect accompanying phase of pure Substance

1- *Clapeyron equation:*

This equation involving:-

(a)The saturation pressure and temperature.

(b)The enthalpy of evaporation

(c) Specific volume of the two phases. It can be derived in a no of ways

Here, consider one of the Maxwell relations:

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

Consider saturated liquid changes to saturated vapor of pure substance.

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{dp}{dT} = \left(\frac{\partial s}{\partial v}\right)_T = \frac{S_g - S_f}{V_g - v_f} = \frac{S_{fg}}{V_{fg}}$$

$$\frac{dp}{dt} = \frac{S_{fg}}{V_{fg}}$$

$$S_{fg} = \frac{h_{fg}}{T} \qquad \longrightarrow \qquad \boxed{\frac{dp}{dt} = \frac{h_{fg}}{T\,V_{fg}}} \qquad **$$

Where $\dfrac{dp}{dT}$ is the slope of vapor pressure curve?

Note: At low   pressure $V_f \lll V_g$

∴ The equation becomes

$$\frac{dp}{dt} = \frac{h_{fg}}{TV_g} \qquad **$$

$$\therefore \frac{dp}{dT} = \frac{P\,h_{fg}}{T^2 R}$$

$$\int \frac{dp}{p} = \int \frac{h_{fg}\,dT}{RT^2}$$

$$ln\,p = \frac{-h_{fg}}{R\,T} + c$$

$$\boxed{ln\,p = A - \frac{B}{T}} \qquad \text{Antony equation}$$

****

Example:

Estimate ΔH of Vaporization of water at 80 °C ?

Given the Following date.

T (°C)	P (K pa)	V^g ($\frac{m^3}{kg}$)	V^f ($\frac{m^3}{kg}$)
77	41.89	3409×10^{-3}	1.029×10^{-3}
81	49.31	………	………..

Solution:-

$$\frac{dp^{sat}}{dT} = \frac{h_{fg}}{T\Delta V} \quad \rightarrow \quad h_{fg} = (\frac{dp^{sat}}{dT})\,(T)\,(\Delta V)$$

$$h_{fg} = (\frac{\Delta p}{\Delta T})(T)\,(V_g - V_l)$$

$$h_{fg} = \frac{(49.31-41.89)}{(81-77)}\,(80+273)\,(3409 \times 10^{-3} - 1.029 \times 10^{-3})$$

$$h_{fg} = 2231 \ k_J/K_g$$

عند مقارنة هذه القيمه مع القيمه الحقيقية والتي هي

$$h_{fg} = 2308$$

يتبين مقدار الخطأ هو:

$$\text{Error \%} = \frac{2308-2231}{2308} \times 100 \% = 3.3\%$$

Clasius/Clapyron equation

يمكن استنباط معادلة اخرى من معادلة clapyron تستخدم لحساب ΔH^V (حرارة التبخر)

اذاكانت عملية التبخر تجري تحت ضغط واطي (اقل من 3bar)

$$\Delta V = V_{g-l} \qquad \text{but} \quad V_l \ll v_g$$

$$\Delta V = v_g = \frac{RT}{P^{sat}}$$

$$\therefore \frac{dp^{sat}}{dT} = \frac{\Delta H^v}{T\Delta V} = \frac{\Delta H^v}{T\left(\frac{RT}{p^{sat}}\right)} = \frac{p^{sat}\,\Delta H^v}{RT^2}$$

$$\therefore \frac{dP^{sat}/P}{dT/T^2} = \frac{\Delta H^v}{R} \qquad \text{but} \quad \frac{dT}{T^2} = -d\left(\frac{1}{T}\right)$$

$$d\,ln\,P^{sat} = \frac{-\Delta H^v}{R}\,d\left(\frac{1}{T}\right) \quad \rightarrow \quad ln\,P = \frac{-\Delta H^v}{R}\left(\frac{1}{T}\right) + C$$

$$\boxed{ln\,\frac{P_2^{sat}}{P_1^{sat}} = \frac{\Delta H^V}{R}\left[\frac{T_2-T_1}{T_1\,T_2}\right]}$$

** Clasius – Clapyron   equation

اذا توفرت لدينا نقاط عديدة ، يمكن رسم $ln\,P^{sat}$ مقابل $\left(\frac{1}{T}\right)$ واستخراج ميل الخط المستقيم

$$\frac{-\Delta H_v}{R}$$

والذي يمثل

Example:

For water estimate the latent heat of vaporization ΔH^v at 244 and p^{sat} at 244 ℃ using

(a)   Clasius Clapyron equation
(b)   Clapyron equation.

Given the following data

$T/℃$	230	240	250	260
P^s/Kpa	2797.6	3347.8	3977.6	4694.3
$V_g/(m^3/Kg) = 55.58 * 10^{-3}$		$V_L = 1.238 * 10^{-3} \ at \ 244\ ℃$		

Solution:

(a)   using clausius Clapyron equation

$$d \ln P^{sat} = - \frac{\Delta H}{R} \ d(\frac{1}{T})$$

$$\ln P^{sat.} = -\frac{\Delta H^v}{R} \ d(\frac{1}{T}) + \text{Const.}$$

من

عند   الجدول المعطى نحصل على

ln $P^{sat.}$	7.936	8.116	8.288	8.454
$\dfrac{1}{T}$	$1.988* 10^{-3}$	$1.949* 10^{-3}$	$1.912* 10^{-3}$	$1.876* 10^{-3}$

رسم هذه النقاط نحصل على

Slope = - 4535

∴ $\Delta H^v = -R(Slope) = -8.314(-4535) = 37703$ $KJ/Kmol$

 OR $\Delta H^v = 2094$ KJ/Kg .

$ln\dfrac{P_2^{sat}}{p_1^{sat}} = \dfrac{-\Delta H^v}{R} \ [\dfrac{1}{T_2} - \dfrac{1}{T_1}]$

Take $T_2 = 244℃$ (517 K)   ، $T_1 = 240\ ℃$ (513 K)

$P_1^{sat} = 3347.8 \; KP_a$

$$\ln \frac{P_2^{sat.}}{3347.8} = \frac{-2094}{8.314} \left[\frac{1}{517} - \frac{1}{513} \right] = 3.798 \times 10^{-3}$$

$$\frac{P_2^{sat}}{3347.8} = 1.0038 \; \rightarrow \; P_2^{sat.} = 1.0038 \,(3347.8) = 3360.5 \; Kpa.$$

(b)   Clapyron equation

$\dfrac{dp^{sat.}}{dT} = \dfrac{\Delta H^v}{T\Delta v}$

$\Delta H^v = \dfrac{dp^s}{dT}\,(\mathrm{T})\,(\Delta v)$

$\Delta H^v = \dfrac{(3977.6 - 3347.8\,)}{(250 - 240)}\,(244 + 273)(55.58 \times 10^{-3} - 1.238 \times 10^{-3})$

$\Delta H^v = 1769 \; kJ/kg$

Now to find $p^{sat.}$ at 244 °C

$\Delta p^{sat.} = \dfrac{\Delta H^v}{T\Delta v}\;(\Delta T) = \dfrac{1769 \qquad (244-240)}{(244+273)\;(55.58\times10^{-3} - 1.238\times10^{-3})} = 251.9$

$\Delta p^{sat.} = 251.9 = (p_{244}^{sat} - p_{240}^{sat}) = p_{244}^{sat} - 3347.8$

$\;\;\color{red}{p^{sat.} = 3599.7 kpa.}$

$\dfrac{1}{T}$	$\ln P^{sat.}$
$1.998 * 10^{-3}$	7.936
$1.949 * 10^{-3}$	8.116
$1.912 * 10^{-3}$	8.288
$1.876 * 10^{-3}$	8.454

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{8.19 - 7.8}{193 \times 10^{-5} - 201.6 \times 10^{-5}} = -4535$$

$$\therefore \Delta H^v = \text{-R (slope)} = -8.314(-4535)$$

$$= +37703 \text{ kJ/kmol}$$

$$\Delta H^V = 2094 \, \frac{kJ}{Kg}$$

2- $\underline{\Delta H^v\ and\ normal\ boiling\ point}$

Riedel equation:

$$\frac{\Delta H_n^v}{T_n} = R\left[\frac{1.092\ (ln\ p_{c-1.013})}{0.93 - Trn}\right]$$

Where: $T_n = normal\ boiling\ point$ k

ΔHn = molar latent heat of vaporization at T_n

Pc = Critical pressure (bar).

$T_{rn} = reduced\ temp.\ at\ T_n.$

Example:

Estimate the molar latent heat of vaporization of water at normal boiling point 100℃ ?

Given for water T_c=647.3 K $P_c = 220.5\ bar$.

Solution: $\frac{\Delta H_n^v}{T_n} = R\left[\frac{1.092\ (\ln P_c - 1.013)}{0.93 - Trn}\right]$

$T_n = 100℃ = 373\ k°$

R=8.314   J/mol

$P_{c=220.5}$ bar

$T_{rn} = \frac{T_n}{T_c} = \frac{373}{647.3} = 0.5762$

$\frac{\Delta Hn}{373} = 8.314\ \left[\frac{1.092\ (\ln 220.5 - 1.013)}{0.93 - 0.5762}\right]$

$\frac{\Delta Hn}{373} = 112.4$ $\implies$ $\Delta H_n^v = 41951.25\ J/mol$

$3 - \Delta H^v$ of pure substance at any temperature.

Can be estimated from the know value of ΔH^v of that Liquid at a certain temperature.   (Watson method)

$$\frac{\Delta H_2^v}{\Delta H_1^v} = (\frac{1-T_{r2}}{1-T_{r1}})^{0.38}$$

Example:

Given that the latent heat of vaporization of water at 100 °C is 2257 J/gm. Estimate the latent heat at 300°C ? Given T_c =647.1

Solution:

$$\frac{\Delta^1 H_2^v}{\Delta H_1^v} = (\frac{1-T_{r2}}{1-T_{r1}})^{0.38}$$

$\Delta H_1 = latent\ heat\ at\ 100°C = 2257$

$\Delta H_2 = latent\ heat\ at\ 300°C$

$T_{r1} = \frac{373}{647.1} = 0.577$ $\qquad\qquad$ $T_{r2} = \frac{573}{647.1} = 0.886$

$\Delta H_2 = 2257(\frac{1-0.886}{1-0.577})^{0.38}$ =1371 J/g.

Throttling Process:-

It is a steady flow process a cross a restriction (منطقة ضيقة) with a resulting drop in pressure, a typical example is the flow through Partially open valve. This process occurs so rapidly and in such a small space that there is no time and no large area for such heat transfer.

∴ It is assumed to be adiabatic

It is flow process

$$m_i \quad\quad m_o$$
$$h_i \quad\quad h_o$$

$\Delta H = \cancel{Q} - \cancel{w_s}$

$\Delta H = 0$ $\quad\Longrightarrow\quad$ $H_1 = H_2$

*** **Residual Property**:-   الخاصية المتبقية

$$M^R = M^{act} - M^{ideal}$$

It is the difference between actual and ideal gas property at same temperature and pressure.

M^R = Residual property.

$M^{act} = Actual\ property$.

$M^{ideal} = Ideal\ property$.

For example: $H^R = H^{act.} - H^{ideal}$

$$V^R = V^{act.} - V^{ideal}\ \to \frac{ZRT}{P} - \frac{RT}{P} = \frac{RT}{P}(z-1)$$

$$s^R = s^{act} - s^{ideal}$$

Let as find the change in enthalpy and entropy for a component where there is a change in state from conditions T_1 , p_1 $\to T_2$,p_2

Real T_1 , p_1 T_2 ,P_2 *Real*

$-H_1^R$ H_2^R

$-S_1^R$ S_2^R

ideal $T_{1,}$ p_1 $\Delta H^{ideal}, \Delta S^{ideal}$ $T_{2,}$ p_2 *ideal*
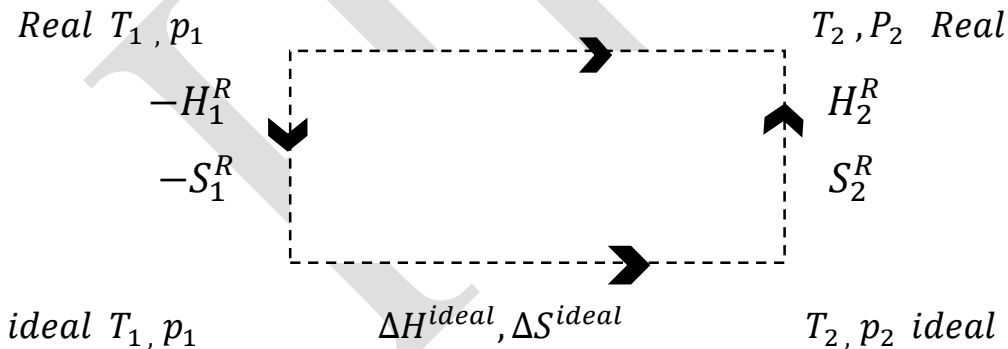
$$\Delta H^{act} = \int_{T_1}^{T_2} Cp\ dT + H_2^R - H_1^R \qquad ....\ (1)$$

$$\Delta S^{act} = \int_{T_1}^{T_2} Cp\ \frac{dT}{T} - R\ln\frac{P_2}{P_1} + S_2^R - S_1^R \qquad ....\ (2)$$

س:كيف يتم حساب H^R ، S^R ؟توجد طريقتان:-

GENERALIZED PROPERTY CORRELATIONS FOR GASES

First method: **Lee – kesler generalized equation**

$$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c} \quad (6.66) \quad \Bigg| \quad \frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R} \quad (6.67)$$

Using Figs; 6.2, 6.11, 6.12, 6.13 to evaluate the above quantities?

Calculated values of the quantities $(H^R)^0/RT_c$, $(H^R)^1/RT_c$, $(S^R)^0/R$, and $(S^R)^1/R$ as determined by Lee and Kesler are given as functions of Tr and Pr in Tables D.5 through D.12. These values, together with Eqs. (6.66) and (6.67), allow estimation of residual enthalpies and entropies on the basis of the three-parameter corresponding-states principle as developed by Lee and Kesler (Sec. 3.7).
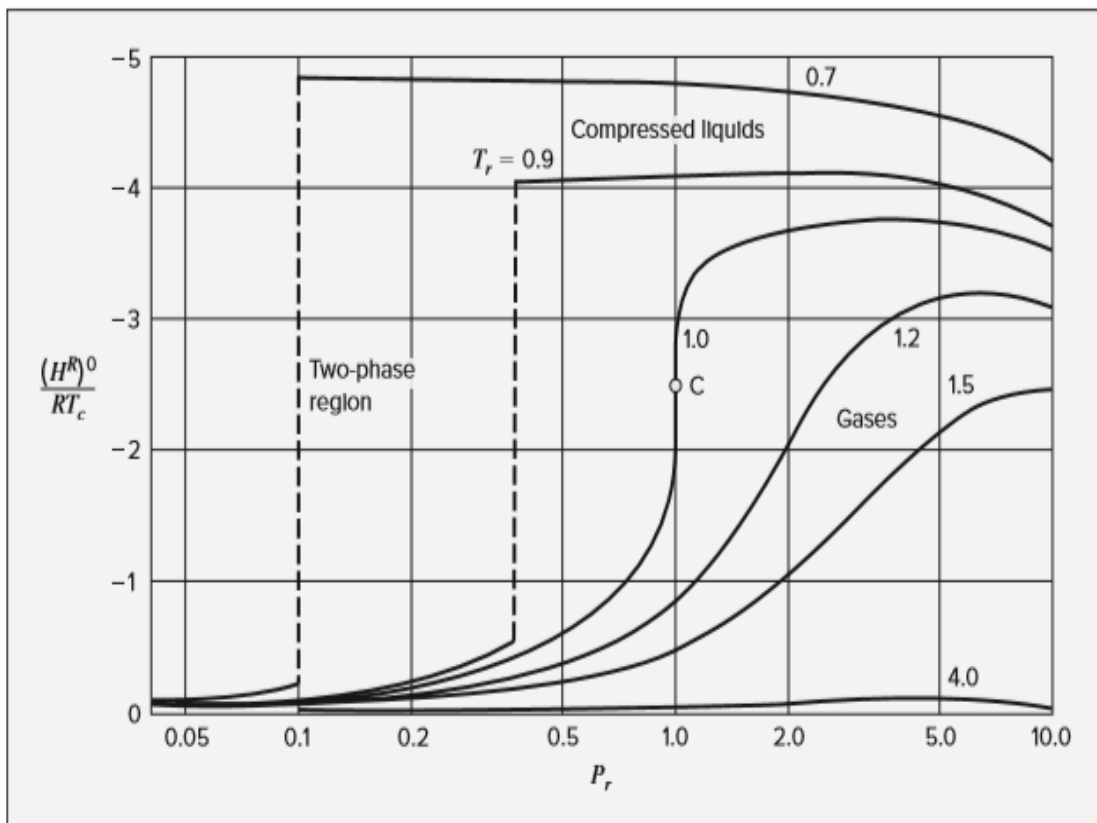
Figure 6.2: The Lee/Kesler correlation for $(H^R)^0/RT_c$ as a function of T_r and P_r.

Second method: **(Virial equation)**   طريقة المعادلات

$$\frac{H^R}{RT_C} = P_r\left[B^\circ - T_r\frac{dB^\circ}{dT_r} + \omega\left(B' - T_r\frac{dB'}{dT_r}\right)\right] \qquad \ldots\ldots\ldots(1)$$

$$\frac{S^R}{R} = -P_r\left(\frac{dB^\circ}{dT_r} + \omega\,\frac{dB'}{dT_r}\right) \qquad \ldots\ldots\ldots\ldots(2)$$

$$\frac{H^R}{RT_c} = P_r\left[B^0 - T_r\frac{dB^0}{dT_r} + \omega\left(B^1 - T_r\frac{dB^1}{dT_r}\right)\right] \qquad (6.68)$$

$$\frac{S^R}{R} = -P_r\left(\frac{dB^0}{dT_r} + \omega\frac{dB^1}{dT_r}\right) \qquad (6.69)$$

Where:-

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

$$\frac{dB^\circ}{dT_r} = \frac{0.675}{T_r^{\,2.6}}$$

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

$$\frac{dB'}{dT_r} = \frac{0.722}{T_r^{\,5.2}}$$

$B^0 = 0.083 - \dfrac{0.422}{T_r^{1.6}}$ (3.61)	$B^1 = 0.139 - \dfrac{0.172}{T_r^{4.2}}$ (3.62)
$\dfrac{dB^0}{dT_r} = \dfrac{0.675}{T_r^{2.6}}$ (6.70)	$\dfrac{dB^1}{dT_r} = \dfrac{0.722}{T_r^{5.2}}$ (6.71)

ملاحظة: اذا كانت الظروف الاولى للغاز قريبة من ظروف الغاز المثالي اي بحدود
ضغط اقل من 3 bar $H_1^R \simeq 0$ فيمكن اعتبار   كذلك الحال للظروف الثانية اذا
كانت قريبة من الغاز المثالي فيمكن اعتبار $H_2^R \simeq 0$. ولاداعي لحسابها .

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Exampel:

Propane gas at 1 bar and 50 °C is compressed to a final state of 125 bar and 245 °C . Estimate the molar volume of the propane in the final state and the enthalpy and entropy changes for the process. In itś initial state, Propane may be assumed an ideal gas.

Given $T_c = 369.8\ k$, $P_c = 42.5\ bar$ $\omega = 0.152$

$C_p = 10.08 + 0.239\ T - 0.733 \times 10^{-4} T^2$ *J/mol.K.*

Solution:

$323\ k/1\ bar$ (1) ⋯⋯⋯⋯⋯→⋯⋯⋯⋯⋯ (2) $125\ bar/518\ k$

$-H_1^R$ H_2^R

$-S_1^R$ S_2^R

$\Delta H^{ideal}, \Delta S^{ideal}$
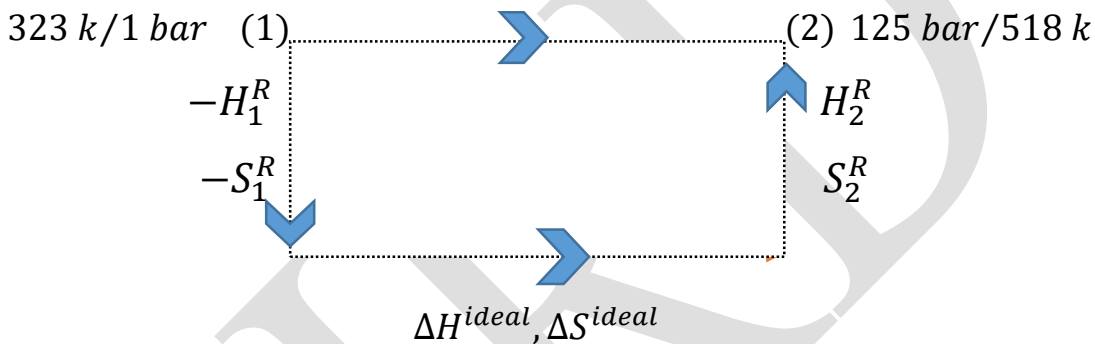
$$\Delta H = \int_{T_1}^{T_2} Cp\ dT + H_2^R - \cancel{H_1^R} \qquad H_1^R \simeq 0$$

$$\Delta S = \int Cp\frac{dT}{T} - R\ ln\frac{P_2}{P_1} + S_2^R - \cancel{S_1^R} \qquad S_1^R \simeq 0$$

لان الظروف الاولى
تقريبا مثالية

Calculation of ΔH:-

$$\frac{H_2^R}{RT_c} = P_r\left[B^\circ - T_r\frac{dB^\circ}{dT_r} + \omega(B' - T_r\frac{dB'}{dT_r})\right]$$

$$T_{r2} = \frac{T_2}{T_c} = \frac{518}{369.8} = 1.4 \qquad P_{r2} = \frac{p_2}{p_c} = \frac{125}{42.5} = 2.94$$

$$B^\circ = 0.083 - \frac{0.422}{T_r^{1,6}} = 0.083 - \frac{0.422}{(1.4)^{1.6}} = -0.163$$

$$B' = 0.139 - \frac{0.172}{T_r^{4.2}} = 0.139 - \frac{0.172}{(1.4)^{4.2}} = 0.0971$$

$$\frac{dB^\circ}{dT_r} = \frac{0.675}{T_r^{2.6}} = \frac{0.675}{1.4^{2.6}} = 0.281$$

$$\frac{dB'}{dT_r} = \frac{0.722}{T_r^{5.2}} = \frac{0.72\ 2}{1,4^{5.2}} = 0.1255$$

$$\frac{H_2^R}{RT_c} = 2.94\,[-0.163 - 1.4(0.281) + 0.152\,(0.0971 - 1.4(0.1255) = -1.67$$

$$H_2^R = -1.67(8.314)(369.8) = -5137 \; J/\,\textbf{mol}.$$

$$\int_{T_1}^{T_2} Cp\, dT = \int_{323}^{518} (10.08 + 0.239\,T - 0.733 \times 10^{-4}\,T^2)dT$$

$$\int_{T_1}^{T_2} Cp\, dT = 19012\, J/mol.$$

$$\Delta H = 19012 - 5137 = 13875 \quad J/mol$$

Calculation of ΔS:

$$\frac{S_2^R}{R} = -P_r\left(\frac{dB^\circ}{dT_r} + \omega\frac{dB'}{dt}\right) = -2.94(0.281 + 0.152(0.1255)\, -0.88$$

$$S_2^R = (-0.88)(8.314) = -7.316 \quad J/mol.k$$

$$\Delta S = \int_{323}^{518} Cp\,\frac{dT}{T} - R\,ln\frac{P_2}{P_1} + S_2^R$$

$$\Delta S = \int_{313}^{518} \left(\frac{10.08 + 0.239T - 0.733 \times 10^{-4}T^2}{T}\right) dT - 8.314\,ln\frac{125}{1} - 7.316$$

$$\Delta S = 45.3 - 40.14 - 7.316 = -2.14 \; J/mol.K$$

Calculation of V_2

$$V_2 = \frac{ZRT_2}{P_2}$$

$$Z = z^\circ + \omega \, z'$$

$$z^\circ = 1 + B^\circ \, \frac{P_r}{T_r} = 1 + (-0.163)\left(\frac{2.94}{1.4}\right) = 0.6577$$

$$Z' = B' \frac{P_r}{T_r} = (0.0971)\left(\frac{2.94}{1.4}\right) = 0.2039$$

$$Z = Z^\circ + \omega \, z' = 0.6577 + 0.2039(0.152) = 0.688$$

$$\therefore V_2 = \frac{0.688(82.07)(518)}{125} = 233 \ cm^3/mol$$

Example: Prove the following relations

(1) $\left(\frac{\partial u}{\partial T}\right)_s = Cv \left(\frac{\partial \ln T}{\partial \ln p}\right)_v$

(2) $\left(\frac{\partial H}{\partial T}\right)_s = Cp \left(\frac{\partial \ln T}{\partial \ln V}\right)_p$

(3) $H = -T^2 \left[\frac{\partial (G/T)}{\partial T}\right]_P$

(4) $U = -T^2 \left[\frac{\partial (A/T)}{\partial T}\right]_v$

(5) $\left(\frac{\partial u}{\partial v}\right)_T = T^2 \left[\frac{\partial (P/T)}{\partial T}\right]_v$

(6) $\left(\frac{\partial u}{\partial S}\right)_T = -P^2 \left[\frac{\partial (T/p)}{\partial p}\right]_v$

(7) $dS = \frac{Cv}{T} \left(\frac{\partial T}{\partial P}\right)_V \, dP + \frac{CP}{T} \left(\frac{\partial T}{\partial v}\right)_p \, dV$

- **Step** $1 \rightarrow 1^{ig}$: A hypothetical process that transforms a real gas into an ideal gas at T_1 and P_1. The enthalpy and entropy changes for this process are:

$$H_1^{ig} - H_1 = -H_1^R \qquad\qquad S_1^{ig} - S_1 = -S_1^R$$

- **Step** $1^{ig} \rightarrow 2^{ig}$: Changes in the ideal-gas state from (T_1, P_1) to (T_2, P_2). For this process,

$$\Delta H^{ig} = H_2^{ig} - H_1^{ig} = \int_{T_1}^{T_2} C_P^{ig}\, dT \tag{6.76}$$
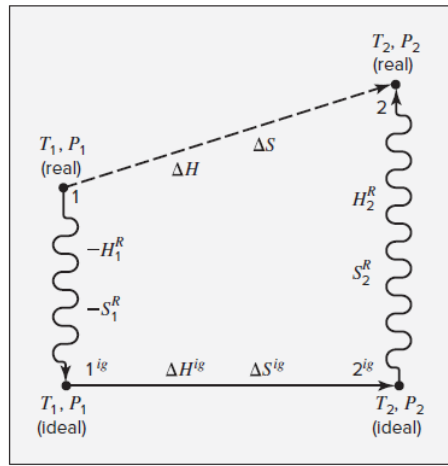
Figure 6.3: Computational path for property changes ΔH and ΔS.

$$\Delta S^{ig} = S_2^{ig} - S_1^{ig} = \int_{T_1}^{T_2} C_P^{ig} \frac{dT}{T} - R \ln\frac{P_2}{P_1} \tag{6.77}$$

- **Step** $2^{ig} \rightarrow 2$: Another hypothetical process that transforms the ideal gas back into a real gas at T_2 and P_2. Here,

$$H_2 - H_2^{ig} = H_2^R \qquad\qquad S_2 - S_2^{ig} = S_2^R$$

Equations (6.72) and (6.73) result from addition of the enthalpy and entropy changes for the three steps.

Example 6.4

Supercritical CO_2 is increasingly used as an environmentally friendly solvent for cleaning applications, ranging from dry cleaning clothing to degreasing machine parts to photoresist stripping. A key advantage of CO_2 is the ease with which it is separated from "dirt" and detergents. When its temperature and pressure are reduced below the critical temperature and vapor pressure respectively, it vaporizes, leaving dissolved substances behind. For a change in state of CO_2 from 70°C and 150 bar to 20°C and 15 bar, estimate the changes in its molar enthalpy and entropy.

Solution 6.4

We follow the three-step computational path of Fig. 6.3. Step 1 transforms the real fluid at 70°C and 150 bar into its ideal-gas state at the same conditions. Step 2 changes conditions in the ideal-gas state from the initial to the final conditions of T and P. Step 3 transforms the fluid from its ideal-gas state to the real-gas final state at 20°C and 15 bar.

The residual-property values required for calculating the changes of Steps 1 and 3 depend on the reduced conditions of the initial and final states. With critical properties from Table B.1 of App. B:

$$T_{r_1} = 1.128 \qquad P_{r_1} = 2.032 \quad T_{r_2} = 0.964 \quad P_{r_2} = 0.203$$

A check of Fig. 3.10 indicates that the Lee/Kesler tables are required for the initial state, whereas the second-virial-coefficient correlation should be suitable for the final state.

Thus, for Step 1, interpolation in Lee/Kesler tables D.7, D.8, D.11, and D.12 provides the values:

$$\frac{(H^R)^0}{RT_c} = -2.709, \quad \frac{(H^R)^1}{RT_c} = -0.921, \quad \frac{(S^R)^0}{R} = -1.846, \quad \frac{(S^R)^1}{R} = -0.938$$

Then:

$$\Delta H_1 = -H^R(343.15 \text{ K}, 150 \text{ bar})$$
$$= -(8.314)(304.2)[-2.709 + (0.224)(-0.921)] = 7372 \text{ J·mol}^{-1}$$
$$\Delta S_1 = -S^R(343.15 \text{ K}, 150 \text{ bar})$$
$$= -(8.314)[-1.846 + (0.224)(-0.938)] = 17.09 \text{ J·mol}^{-1}\text{·K}^{-1}$$

For Step 2, the enthalpy and entropy changes are calculated by the usual heat-capacity integrals, with polynomial coefficients from Table C.1. The ideal-gas-state entropy change caused by the pressure change must also be included.

$$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c} \quad (6.66) \qquad \frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R} \quad (6.67)$$

$$\Delta H_2 = 8.314 \times \text{ICPH}(343.15, 293.15; 5.547, 1.045 \times 10^{-3}, 0.0, -1.157 \times 10^5)$$
$$= -1978 \text{ J·mol}^{-1}$$
$$\Delta S_2 = 8.314 \times \text{ICPS}(343.15, 293.15; 5.547, 1.045 \times 10^{-3}, 0.0, -1.157 \times 10^5)$$
$$-(8.314) \ln (15/150)$$
$$= -6.067 + 19.144 = 13.08 \text{ J·mol}^{-1}\cdot\text{K}^{-1}$$

Finally, for Step 3,

$$\Delta H_3 = H^R(293.15 \text{ K, 15 bar})$$
$$= 8.314 \times 304.2 \times \text{HRB}(0.964, 0.203, 0.224) = -660 \text{ J·mol}^{-1}$$
$$\Delta S_3 = S^R(293.15 \text{ K, 15 bar})$$
$$= 8.314 \times \text{SRB}(0.964, 0.203, 0.224) = -1.59 \text{ J·mol}^{-1}\cdot\text{K}^{-1}$$

Sums over the three steps yield overall changes, $\Delta H = 4734$ J·mol^{-1} and $\Delta S = 28.6$ J·mol^{-1}·K^{-1}. The largest contribution here comes from the residual properties of the initial state, because the reduced pressure is high, and the super-critical fluid is far from its ideal-gas state. Despite the substantial reduction in temperature, the enthalpy actually increases in the overall process.

For comparison, the properties given in the NIST fluid-properties database, accessed through the NIST Chemistry Webbook, are:

$$H_1 = 16{,}776 \text{ J·mol}^{-1} \qquad S_1 = 67.66 \text{ J·mol}^{-1}\cdot\text{K}^{-1}$$
$$H_2 = 21{,}437 \text{ J·mol}^{-1} \qquad S_1 = 95.86 \text{ J·mol}^{-1}\cdot\text{K}^{-1}$$

From these values, considered accurate, overall changes are $\Delta H = 4661$ J·mol^{-1} and $\Delta S = 28.2$ J·mol 1·K^{-1}. Even though the changes in residual properties make up a substantial part of the total, the prediction from generalized correlations agrees with the NIST data to within 2 percent.

Extension to Gas Mixtures

Although no fundamental basis exists for extension of generalized correlations to mixtures, reasonable and useful approximate results for mixtures can often be obtained with *pseudocritical parameters* resulting from simple linear mixing rules according to the definitions:

$$\omega \equiv \sum_i y_i \omega_i \quad (6.78) \qquad T_{pc} \equiv \sum_i y_i T_{c_i} \quad (6.79) \qquad P_{pc} \equiv \sum_i y_i P_{c_i} \quad (6.80)$$

The values so obtained are the mixture ω and pseudocritical temperature and pressure, T_{pc} and P_{pc}, which replace T_c and P_c to define *pseudoreduced parameters*:

$$T_{pr} = \frac{T}{T_{pc}} \quad (6.81) \qquad P_{pr} = \frac{P}{P_{pc}} \quad (6.82)$$

These replace T_r and P_r for reading entries from the tables of App. D, and lead to values of Z by Eq. (3.57), H^R/RT_{pc} by Eq. (6.66), and S^R/R by Eq. (6.67).

Example 6.5

Estimate V, H^R, and S^R for an equimolar mixture of carbon dioxide (1) and propane (2) at 450 K and 140 bar by the Lee/Kesler correlations.

Tables D.1 – D.4 Correlation for the compressibility factor (664-668) edition eight

Example 6.5

Estimate V, H^R, and S^R for an equimolar mixture of carbon dioxide(1) and propane(2) at 450 K and 140 bar by the Lee/Kesler correlations.

Solution 6.5

The pseudocritical parameters are found by Eqs. (6.78) through (6.80) with critical constants from Table B.1 of App. B:

$$\omega = y_1 \omega_1 + y_2 \omega_2 = (0.5)(0.224) + (0.5)(0.152) = 0.188$$
$$T_{pc} = y_1 T_{c_1} + y_2 T_{c_2} = (0.5)(304.2) + (0.5)(369.8) = 337.0 \text{ K}$$
$$P_{pc} = y_1 P_{c_1} + y_2 P_{c_2} = (0.5)(73.83) + (0.5)(42.48) = 58.15 \text{ bar}$$

Then,

$$T_{pr} = \frac{450}{337.0} = 1.335 \quad P_{pr} = \frac{140}{58.15} = 2.41$$

Values of Z^0 and Z^1 from Tables D.3 and D.4 at these reduced conditions are:

$$Z^0 = 0.697 \quad \text{and} \quad Z^1 = 0.205$$

First method: *Lee – kesler generalized equation*

$$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c} \quad (6.66) \quad \left| \quad \frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R} \quad (6.67) \right.$$

By Eq. (3.57),

$$Z = Z^0 + \omega Z^1 = 0.697 + (0.188)(0.205) = 0.736$$

Whence,

$$V = \frac{ZRT}{P} = \frac{(0.736)(83.14)(450)}{140} = 196.7 \text{ cm}^3 \cdot \text{mol}^{-1}$$

Similarly, from Tables D.7 and D.8, with substitution into Eq. (6.66):

$$\left(\frac{H^R}{RT_{pc}}\right)^0 = -1.730 \quad \left(\frac{H^R}{RT_{pc}}\right)^1 = -0.169$$

$$\frac{H^R}{RT_{pc}} = -1.730 + (0.188)(-0.169) = -1.762$$

and

$$H^R = (8.314)(337.0)(-1.762) = -4937 \text{ J} \cdot \text{mol}^{-1}$$

From Tables D.11 and D.12 and substitution into Eq. (6.67),

$$\frac{S^R}{R} = -0.967 + (0.188)(-0.330) = -1.029$$

and

$$S^R = (8.314)(-1.029) = -8.56 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Two-Phase Liquid / Vapor Systems

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

$$nV = n^l V^l + n^v V^v$$

Where V is the molar volume for a system containing a total number of moles $n = n^1 + n^v$.

Division by n gives:

$$V = x^l V^l + x^v V^v$$

Where x^1 and x^v represent the mass fractions of the total system that are liquid and vapor.

With $x^1 = 1 - x^v$,

$$\boxed{V = (1 - x^v)V^l + x^v V^v}$$

In this equation the properties V, V^1, and V^v may be either molar or unit-mass values.

The **mass or molar fraction** of the system that is vapor **x^v** is **often called the quality,** particularly when the fluid in question is water. Analogous equations can be written for the other extensive thermodynamic properties. All of these relations are represented by the **generic equation**

$$\boxed{M = (1 - x^v)M^l + x^v M^v} \qquad (6.96\text{a})$$

Where **M** represents **V, U, H, S,** etc. An alternative form is sometimes useful:

$$M = M^l + x^v \Delta M^{lv} \qquad (6.96\text{b})$$

X^v= Quality

1-X= Part of liquid

$$X = \frac{m^V}{m^L + m^V} \qquad \text{.................} \qquad 1 - X = \frac{m^L}{m^L + m^V}$$

$$m^V = \frac{V^V}{v^V} \qquad\qquad m^L = \frac{V^L}{v^L} = \frac{Volume\ of\ liquid}{specific\ volume\ from\ table}$$

$$\textbf{\textit{NOTE}}: \quad m^t = m^L + m^V \qquad\qquad V^t = V^L + V^V$$

$$specific\ volume \qquad v^t = \frac{V^t}{m^t}$$

1

6.7 TABLES OF THERMODYNAMIC PROPERTIES

In many instances thermodynamic properties are tabulated. This has the advantage that data can be presented more precisely than in diagrams, but the need for interpolation is introduced.

Thermodynamic tables for saturated steam from its **normal freezing** point to the **critical point** and for **superheated steam** over a substantial pressure range appear in App. E. Values are given at intervals close enough that **linear interpolation is satisfactory.**

 The **first table** shows the equilibrium properties of **saturated liquid and saturated vapor** at even increments of temperature. The enthalpy and entropy are arbitrarily assigned values of zero for the saturated-liquid state at the triple point.

 The second table is for the gas region and gives properties of superheated steam at temperatures higher than the saturation temperature for a given pressure. Volume (V), internal energy (U), enthalpy (H), and entropy (S) are tabulated as functions of pressure at various temperatures. The steam tables are the most thorough compilation of properties for any single material. However, tables are available for a number of other substances.12 Electronic versions of such tables generally eliminate the need for manual interpolation.

Steam tables	
1-satureated steam	**2- Superheat steam**
At boiling point temperature	**More than boiling point temperature**
A// Dry **X=1** $M = M^V$ **B// Wet** (two phase) **0 < X< 1** $M = (1 - x^v)M^l + x^v M^v$	**X=1** $M = M^V$ **ONLY** vapour

TABLE E.1 Properties of Saturated Steam

V = SPECIFIC VOLUME cm^3·g^{-1} H = SPECIFIC ENTHALPY kJ·kg^{-1}

U = SPECIFIC INTERNAL ENERGY kJ·kg^{-1} S = SPECIFIC ENTROPY kJ·kg^{-1}·K^{-1}

t (°C)	T (K)	P (kPa)	SPECIFIC VOLUME V			INTERNAL ENERGY U			ENTHALPY H			ENTROPY S		
			sat. liq.	evap.	sat. vap.	sat. liq.	evap.	sat. vap.	sat. liq.	evap.	sat. vap.	sat. liq.	evap.	sat. vap.
0	273.15	0.611	1.000	206300.	206300.	−0.04	2375.7	2375.6	−0.04	2501.7	2501.6	0.0000	9.1578	9.1578
0.01	273.16	0.611	1.000	206200.	206200.	0.00	2375.6	2375.6	0.00	2501.6	2501.6	0.0000	9.1575	9.1575
1	274.15	0.657	1.000	192600.	192600.	4.17	2372.7	2376.9	4.17	2499.2	2503.4	0.0153	9.1158	9.1311
2	275.15	0.705	1.000	179900.	179900.	8.39	2369.9	2378.3	8.39	2496.8	2505.2	0.0306	9.0741	9.1047
3	276.15	0.757	1.000	168200.	168200.	12.60	2367.1	2379.7	12.60	2494.5	2507.1	0.0459	9.0326	9.0785
4	277.15	0.813	1.000	157300.	157300.	16.80	2364.3	2381.1	16.80	2492.1	2508.9	0.0611	8.9915	9.0526
5	278.15	0.872	1.000	147200.	147200.	21.01	2361.4	2382.4	21.01	2489.7	2510.7	0.0762	8.9507	9.0269
6	279.15	0.935	1.000	137800.	137800.	25.21	2358.6	2383.8	25.21	2487.4	2512.6	0.0913	8.9102	9.0014
7	280.15	1.001	1.000	129100.	129100.	29.41	2355.8	2385.2	29.41	2485.0	2514.4	0.1063	8.8699	8.9762
8	281.15	1.072	1.000	121000.	121000.	33.60	2353.0	2386.6	33.60	2482.6	2516.2	0.1213	8.8300	8.9513
9	282.15	1.147	1.000	113400.	113400.	37.80	2350.1	2387.9	37.80	2480.3	2518.1	0.1362	8.7903	8.9265
10	283.15	1.227	1.000	106400.	106400.	41.99	2347.3	2389.3	41.99	2477.9	2519.9	0.1510	8.7510	8.9020
11	284.15	1.312	1.000	99910.	99910.	46.18	2344.5	2390.7	46.19	2475.5	2521.7	0.1658	8.7119	8.8776
12	285.15	1.401	1.000	93830.	93840.	50.38	2341.7	2392.1	50.38	2473.2	2523.6	0.1805	8.6731	8.8536
13	286.15	1.497	1.001	88180.	88180.	54.56	2338.9	2393.4	54.57	2470.8	2525.4	0.1952	8.6345	8.8297
14	287.15	1.597	1.001	82900.	82900.	58.75	2336.1	2394.8	58.75	2468.5	2527.2	0.2098	8.5963	8.8060
15	288.15	1.704	1.001	77980.	77980.	62.94	2333.2	2396.2	62.94	2466.1	2529.1	0.2243	8.5582	8.7826
16	289.15	1.817	1.001	73380.	73380.	67.12	2330.4	2397.6	67.13	2463.8	2530.9	0.2388	8.5205	8.7593
17	290.15	1.936	1.001	69090.	69090.	71.31	2327.6	2398.9	71.31	2461.4	2532.7	0.2533	8.4830	8.7363
18	291.15	2.062	1.001	65090.	65090.	75.49	2324.8	2400.3	75.50	2459.0	2534.5	0.2677	8.4458	8.7135
19	292.15	2.196	1.002	61340.	61340.	79.68	2322.0	2401.7	79.68	2456.7	2536.4	0.2820	8.4088	8.6908
20	293.15	2.337	1.002	57840.	57840.	83.86	2319.2	2403.0	83.86	2454.3	2538.2	0.2963	8.3721	8.6684
21	294.15	2.485	1.002	54560.	54560.	88.04	2316.4	2404.4	88.04	2452.0	2540.0	0.3105	8.3356	8.6462
22	295.15	2.642	1.002	51490.	51490.	92.22	2313.6	2405.8	92.23	2449.6	2541.8	0.3247	8.2994	8.6241
23	296.15	2.808	1.002	48620.	48620.	96.40	2310.7	2407.1	96.41	2447.2	2543.6	0.3389	8.2634	8.6023
24	297.15	2.982	1.003	45920.	45930.	100.6	2307.9	2408.5	100.6	2444.9	2545.5	0.3530	8.2277	8.5806
25	298.15	3.166	1.003	43400.	43400.	104.8	2305.1	2409.9	104.8	2442.5	2547.3	0.3670	8.1922	8.5592
26	299.15	3.360	1.003	41030.	41030.	108.9	2302.3	2411.2	108.9	2440.2	2549.1	0.3810	8.1569	8.5379
27	300.15	3.564	1.003	38810.	38810.	113.1	2299.5	2412.6	113.1	2437.8	2550.9	0.3949	8.1218	8.5168
28	301.15	3.778	1.004	36730.	36730.	117.3	2296.7	2414.0	117.3	2435.4	2552.7	0.4088	8.0870	8.4959
29	302.15	4.004	1.004	34770.	34770.	121.5	2293.8	2415.3	121.5	2433.1	2554.5	0.4227	8.0524	8.4751

1- Table E.1 Properties of Saturated Steam page 684

Need to   P   <u>or</u>   T

2- Table E.2 Properties of Superheated Steam page 692

Need to   P   and   T

TABLE E.2 Properties of Superheated Steam

TEMPERATURE: /°C
(TEMPERATURE: T kelvins)

P/kPa (θ^{sat}/°C)		sat. liq.	sat. vap.	75 (348.15)	100 (373.15)	125 (398.15)	150 (423.15)	175 (448.15)	200 (473.15)	225 (498.15)	250 (523.15)
1 (6.98)	V	1.000	129200.	160640.	172180.	183720.	195270.	206810.	218350.	229890.	241430.
	U	29.334	2385.2	2480.8	2516.4	2552.3	2588.5	2624.9	2661.7	2698.8	2736.3
	H	29.335	2514.4	2641.5	2688.6	2736.0	2783.7	2831.7	2880.1	2928.7	2977.7
	S	0.1060	8.9767	9.3828	9.5136	9.6365	9.7527	9.8629	9.9679	10.0681	10.1641
10 (45.83)	V	1.010	14670.	16030.	17190.	18350.	19510.	20660.	21820.	22980.	24130.
	U	191.822	2438.0	2479.7	2515.6	2551.6	2588.0	2624.5	2661.4	2698.6	2736.1
	H	191.832	2584.8	2640.0	2687.5	2735.2	2783.1	2831.2	2879.6	2928.4	2977.4
	S	0.6493	8.1511	8.3168	8.4486	8.5722	8.6888	8.7994	8.9045	9.0049	9.1010
20 (60.09)	V	1.017	7649.8	8000.0	8584.7	9167.1	9748.0	10320.	10900.	11480.	12060.
	U	251.432	2456.9	2478.4	2514.6	2550.9	2587.4	2624.1	2661.0	2698.3	2735.8
	H	251.453	2609.9	2638.4	2686.3	2734.2	2782.3	2830.6	2879.2	2928.0	2977.1
	S	0.8321	7.9094	7.9933	8.1261	8.2504	8.3676	8.4785	8.5839	8.6844	8.7806
30 (69.12)	V	1.022	5229.3	5322.0	5714.4	6104.6	6493.2	6880.8	7267.5	7653.8	8039.7
	U	289.271	2468.6	2477.1	2513.6	2550.2	2586.8	2623.6	2660.7	2698.0	2735.6
	H	289.302	2625.4	2636.8	2685.1	2733.3	2781.6	2830.0	2878.7	2927.6	2976.8
	S	0.9441	7.7695	7.8024	7.9363	8.0614	8.1791	8.2903	8.3960	8.4967	8.5930
40 (75.89)	V	1.027	3993.4	......	4279.2	4573.3	4865.8	5157.2	5447.8	5738.0	6027.7
	U	317.609	2477.1	......	2512.6	2549.4	2586.2	2623.2	2660.3	2697.7	2735.4
	H	317.650	2636.9	......	2683.8	2732.3	2780.9	2829.5	2878.2	2927.2	2976.5
	S	1.0261	7.6709	......	7.8009	7.9268	8.0450	8.1566	8.2624	8.3633	8.4598
50 (81.35)	V	1.030	3240.2	......	3418.1	3654.5	3889.3	4123.0	4356.0	4588.5	4820.5
	U	340.513	2484.0	......	2511.7	2548.6	2585.6	2622.7	2659.9	2697.4	2735.1
	H	340.564	2646.0	......	2682.6	2731.4	2780.1	2828.9	2877.7	2926.8	2976.1
	S	1.0912	7.5947	......	7.6953	7.8219	7.9406	8.0526	8.1587	8.2598	8.3564
75 (91.79)	V	1.037	2216.9	......	2269.8	2429.4	2587.3	2744.2	2900.2	3055.8	3210.9
	U	384.374	2496.7	......	2509.2	2546.7	2584.2	2621.6	2659.0	2696.7	2734.5
	H	384.451	2663.0	......	2679.4	2728.9	2778.2	2827.4	2876.6	2925.8	2975.3
	S	1.2131	7.4570	......	7.5014	7.6300	7.7500	7.8629	7.9697	8.0712	8.1681
100 (99.63)	V	1.043	1693.7	......	1695.5	1816.7	1936.3	2054.7	2172.3	2289.4	2406.1
	U	417.406	2506.1	......	2506.6	2544.8	2582.7	2620.4	2658.1	2695.9	2733.9
	H	417.511	2675.4	......	2676.2	2726.5	2776.3	2825.9	2875.4	2924.9	2974.5
	S	1.3027	7.3598	......	7.3618	7.4923	7.6137	7.7275	7.8349	7.9369	8.0342

Example 1:   P= 40 Kpa,   T= 200 °C, H

Solution: Superheated steam

H= H ^{v} = 2878.2 KJ/ Kg.

Example 2: P=40 Kpa,   T=130 ºC, H?

Solution: Superheated

H	T
2732.3	125
X	130
2780.9	150

The solution will be done by linear interpolation method

$$y_m = y_1 + \left(\frac{y_2 - y_1}{X_2 - X_1}\right)(X_m - X_1) \qquad \text{..........General equation}$$

$$H_m = H_1 + \left(\frac{H_2 - H_1}{T_2 - T_1}\right)(T_m - T_1)$$

$$H_m = 2732.3 + \left(\frac{2780.9 - 2732.3}{150 - 125}\right)(130 - 125)$$

$$H_m = 2742.02 \ \ KJ/Kg$$

$$\frac{y_m - y_1}{X_m - X_1} = \left(\frac{y_2 - y_1}{X_2 - X_1}\right)$$

Example3:   T= 20 ºC,   X= 0.9, find H, P ^{sat}?

Solution: from temperature go to steam table.

$$P^{Sat} = 2.337 \ Kpa \qquad Saturated \ ((wet)$$

$$H = (1 - X) \ H^L + X \ H^V$$

$$H = (1 - 0.9) \ 83.86 + (0.9) \ 2538.2$$

$$H = 2292.766 \ KJ/Kg$$

Example 4: T=20 ºC, Dry steam   H?

Solution: H= H^V= 2538.2 KJ/Kg

Example 5: P =40 Kpa, T= 75 °C,   X= 0.8, find H?

Solution: *Saturated* steam(*wet*)

$$H = (1 - X) H^L + X H^V$$

$$H = (1 - 0.8) 317 + (0.8) 2636$$

$$H = 2172.2 \; KJ/Kg$$

Example 6: P =40 Kpa, T= 75 °C,   Dry steam find H?

Solution: H= H^V= 2636   KJ/Kg

Example 6.9

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, determine the downstream state of the steam and ΔH for P_1 = 1000 kPa, t_1 = 250°C, and P_2 = 200 kPa.

Solution 6.9

Because the process is both reversible and adiabatic, there is no change in the entropy of the steam. For the initial temperature of 250°C at 1000 kPa, no entries appear in the tables for superheated steam. **Interpolation between values for 240°C and 260°C yields**, at 1000 kPa,

$$H_1 = 2942.9 \; kJ \cdot kg^{-1} \qquad S_1 = 6.9252 \; kJ \cdot kg^{-1} \cdot K^{-1}$$

For the final state at **200 kPa,**

$$S_2 = S_1 = 6.9252 \; kJ \cdot kg^{-1} \cdot K^{-1}$$

Because the entropy of saturated vapor at 200 Pa is greater than S_2, the final state must lie in the two-phase liquid/vapor region. **Thus t_2 is the saturation temperature at 200 kPa, given in the superheat tables as t_2 = 120.23°C.** Equation (6.96a) applied to the entropy becomes:

$$S_2 = (1 - x_2^v)S_2^l + x_2^v S_2^v$$

Numerically,

$$6.9252 = 1.5301(1 - x_2^v) + 7.1268 x_2^v$$

Where the values 1.5301 and 7.1268 are entropies of saturated liquid and saturated vapor at 200 kPa. Solving,

$$x_2^v = 0.9640$$

The mixture is 96.40% vapor and 3.60% liquid. Its enthalpy is obtained by further application of Eq. (6.96a):

$$H_2 = (0.0360)\ (504.7) + (0.9640)\ (2706.3) = 2627.0\ kJ \cdot kg^{-1}$$

Finally,

$$\Delta H = H_2 - H_1 = 2627.0 - 2942.9 = -315.9\ kJ \cdot kg^{-1}$$

For a nozzle, under the stated assumptions the steady-flow energy balance, Eq. (2.31), becomes

$$\Delta H + \frac{1}{2}\Delta u^2 = 0$$

Thus the decrease in enthalpy is exactly compensated by an increase in kinetic energy of the fluid. In other words, the velocity of a fluid increases as it flows through a nozzle, which is its usual purpose.

3.6. PROPERTY DIAGRAMS IN COMMON USE

Besides P-V diagram which is useful because pressure and volume are easily visualized and the T-S chart which is used in general thermodynamic work, there are other charts which are of practical **use for particular applications.**

The specific enthalpy-specific entropy chart is used for steam plant work and the pressure-specific enthalpy chart is **used in refrigeration work.**

Sketches of these charts are shown in Fig. 3.1. These charts are drawn for H_2O (water and steam) and represent the correct shape of the curves for this substance.
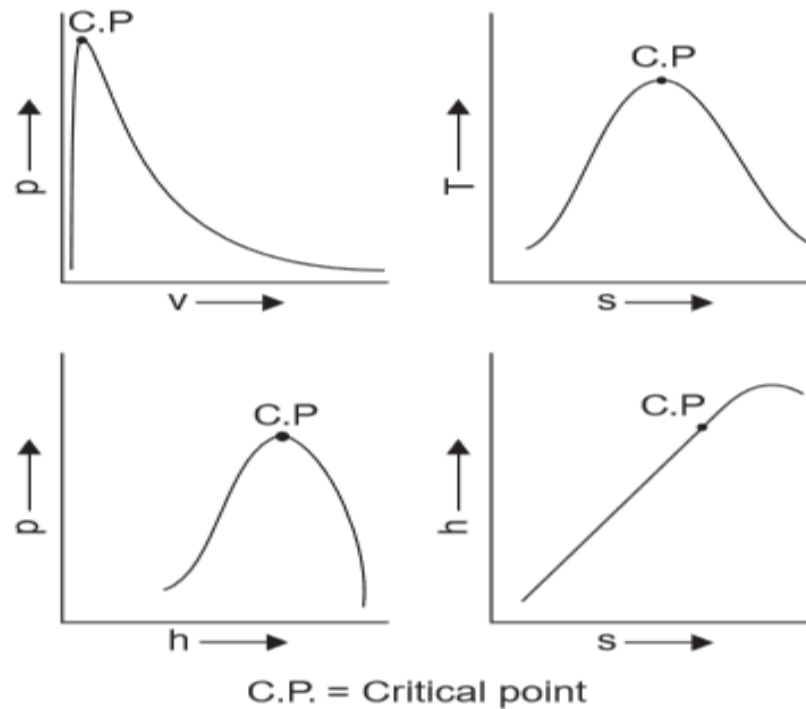
C.P. = Critical point

Fig. 3.1

3.7. FORMATION OF STEAM

The process of formation of steam is discussed in detail in the following few pages:

Consider a cylinder fitted with a piston which can move freely upwards and downwards in it. Let, for the sake of simplicity, there be 1 kg of water at 0°C with volume vf m3 under the piston [Fig 3.2 (i)]. Further let the piston is loaded with load W to ensure heating at constant pressure. Now if the heat is imparted to water, a rise in temperature will be noticed and this rise will continue till boiling point is reached. The temperature at which water starts boiling depends upon the pressure and as such for each pressure (under which water is heated) there is a different boiling point. This boiling temperature is known as the temperature of formation of steam or saturation temperature.

t_s = Saturation temp.

t_{sup} = Temperature of superheated steam

v_f = Volume of water

v_g = Volume of dry and saturated steam
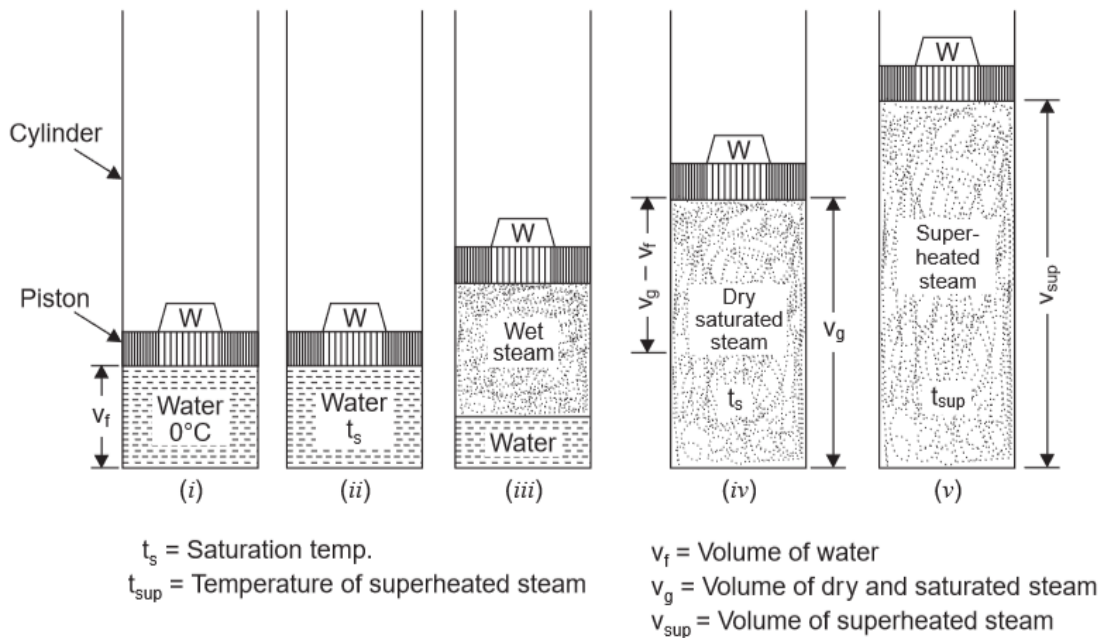
v_{sup} = Volume of superheated steam

Fig. 3.2: Formation of Steam

It may be noted during heating up to boiling point that there will be slight increase in volume of water due to which piston moves up and hence work is obtained as shown in Fig. 3.2 (ii). This work, however, is so small that is can be neglected. Now, if supply of heat to water is continued it will be noticed that rise of temperature after the boiling point is reached nil but piston starts moving upwards which indicates that there is increase is volume which is only possible if steam formation occurs. The heat being supplied does not show any rise of temperature but changes water into vapour 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 [Fig. 3.2 (iii)] and if heating of steam is further progressed [as shown in Fig. 3.2 (iv)] such that all the water particles associated with steam are evaporated, the steam so obtained is called dry and saturated steam. If vg m^3 is the volume of 1 kg of dry and saturated steam then work done on the piston will be

$$P (V_g - V_f) \qquad\qquad ... (3.1)$$

Where p is the constant pressure (due to weight 'W' on the piston).

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.

This phase of steam formation is illustrated in Fig. 3.2 (v). Fig. 3.3 shows the graphical representation of formation of steam.
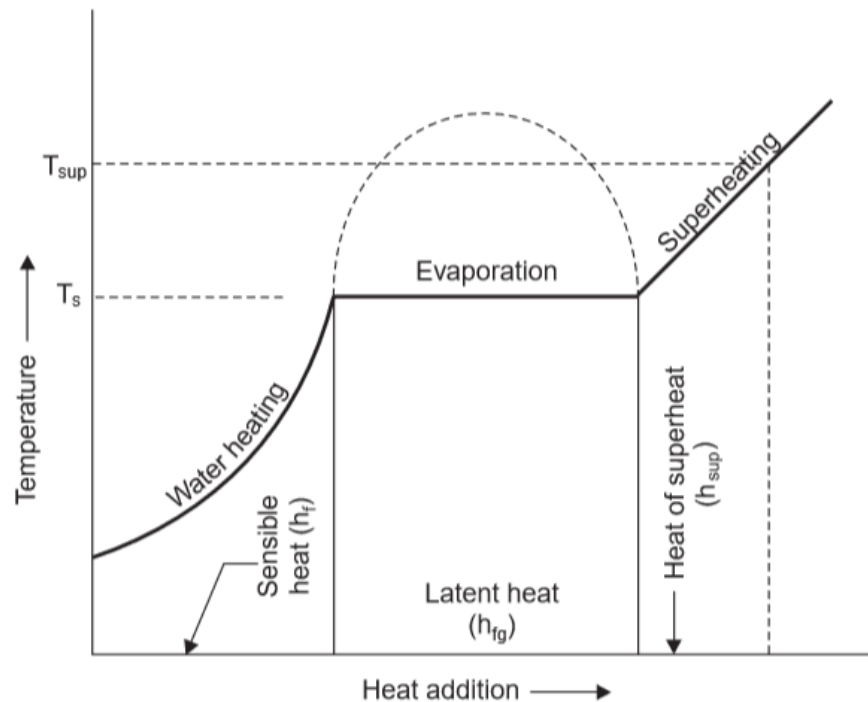
Fig. 3.3. Graphical representation of formation of steam.

3.8. IMPORTANT TERMS RELATING STEAM FORMATION

1. Sensible heat of water (h_f). *It is defined as the quantity of heat absorbed by 1 kg of water when it is heated from 0 °C (freezing point) to boiling point.* It is also called total heat (or enthalpy) of water or liquid heat invariably. It is reckoned from 0°C where sensible heat is taken as zero. If 1 kg of water is heated from 0°C to 100°C the sensible heat added to it will be $4.18 \times 100 = 418$ kJ but if water is at say 20°C initially then sensible heat added will be $4.18 \times (100 - 20) = 334.4$ kJ. This type of heat is denoted by letter h_f 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 kJ/kg K at low pressures but at high pressures it is different from this value.

2. 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.*

3. 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' or 'q'.

If　　　　　　　　m_s = Mass of dry steam contained in steam considered, and

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m_w = Weight of water particles in suspension in the steam considered,

Then, $$x = \frac{m_s}{m_s + m_w}$$ ... (3.2)

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.

   Note. No steam can be completely dry and saturated, so long as it is in contact with the water from which it is being formed.

4. 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.**

In other words,

$$h = h_f + x\ h_{fg}$$ ... (3.3)

If steam is dry and saturated,   then x = 1 and hg = h_f + h_{fg}.

5. 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. Superheating is always carried out at constant pressure. The additional amount of heat supplied to the steam during superheating is called as 'Heat of superheat' and can be calculated by using the specific heat of superheated steam at constant pressure (C_{ps}), the value of which varies from 2.0 to 2.1 kJ/ kg K depending upon pressure and temperature.

If T_{sup}. - T_s are the temperatures of superheated steam in K and wet or dry steam,

Then (T_{sup} - T_s) is called 'degree of superheat'.

The total heat of superheated steam is given by

$$h_{sup} = h_f + h_{fg} + C_{ps}\ (T_{sup} - T_s)$$ ...(3.4)

Superheated steam behaves like a gas and therefore it follows the gas laws. The value of n for this type of steam is 1.3 and the law for the adiabatic expansion is $pv^{1.3}$ = constant.

The advantages obtained by using 'superheated' steam are as follows:

i.   By superheating steam, its heat content and hence its capacity to do work is increased without having to increase its pressure.
ii.   Superheating is done in a superheated which obtains its heat from waste furnace gases which would have otherwise passed uselessly up the chimney.
iii.   High temperature of superheated steam results in an increase in thermal efficiency.
iv.   The superheated steam is at a temperature above that corresponding to its pressure, it can be considerably cooled during expansion in an engine before its temperature falls below that at which it will condense and thereby become wet. Hence, heat

losses due to condensation of steam on cylinder walls etc. are avoided to a great extent.

6. Volume of wet and dry steam. If the steam has dryness fraction of x, then 1 kg of this steam will contain x kg of dry steam and (1 – x) kg of water. If v_f is the volume of 1 kg of water and v_g is the volume of 1 kg of perfect dry steam (also known as specific volume), then volume of 1 kg of wet steam = volume of dry steam + volume of water.

$$= x\,v_g + (1 - x)\,v_f \qquad\qquad \text{... (3.5)}$$

Note. The volume of v_f at low pressures is very small and is generally neglected. Thus is general, the volume of 1 kg of wet steam is given by, $x\,v_g$ and density $\frac{1}{xv_g}$ kg/m³.

$$
\begin{aligned}
&= xv_g + v_f - xv_f \\
&= v_f + x(v_g - v_f) \\
&= v_f + xv_{fg} &&\text{...[3.5 }(a)] \\
&= v_f + xv_{fg} + v_{fg} - v_{fg} \\
&= (v_f + v_{fg}) - (1 - x)\,v_{fg} \\
&= v_g - (1 - x)v_{fg} &&\text{...[3.5 }(b)]
\end{aligned}
$$

7. Volume of superheated steam.

As superheated steam behaves like a perfect gas its volume can be found out in the same way as the gases.

If, v_g = Specific volume of dry steam at pressure p,

            T_s = Saturation temperature in K,

            T_{sup} = Temperature of superheated steam in K, and

            v_{sup} = Volume of 1 kg of superheated steam at pressure p,

Then,

$$\frac{p.v_g}{T_s} = \frac{p.v_{sup}}{T_{sup}}$$

OR $$v_{Sup} = \frac{v_g\,T_{Sup}}{T_S} \qquad\qquad \text{... (3.6)}$$

3.9. 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. Tabulated values are also 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 kPa);

t_s = Saturation temperature (°C);

h_f = Enthalpy of saturated liquid (kJ/kg);

h_{fg} = Enthalpy or latent heat of vapourisation (kJ/kg);

h_g = Enthalpy of saturated vapour (steam) (kJ/kg);

S_f = Entropy of saturated liquid (kJ/kg K);

S_{fg} = Entropy of vapourisation (kJ/kg K);

S_g = Entropy of saturated vapour (steam) (kJ/kg K);

V_f = Specific volume of saturated liquid (m^3/kg);

V_g = Specific volume of saturated vapour (steam) (m^3/kg).

Also, $h_{fg} = h_g - h_f$ ...... Change of enthalpy during evaporation

$S_{fg} = S_g - S_f$ ...... Change of entropy during evaporation

$V_{fg} = V_g - V_f$ ...... Change of volume during evaporation.

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

The internal energy of steam ($u = h - pv$) is also tabulated in some steam tables.

Two-Phase Liquid / Vapor Systems

6.7 TABLES OF THERMODYNAMIC PROPERTIES

In many instances thermodynamic properties are tabulated. This has the advantage that data can be presented more precisely than in diagrams, but the need for interpolation is introduced.

Thermodynamic tables for saturated steam from its **normal freezing** point to the **critical point** and for **superheated steam** over a substantial pressure range appear in App. E. Values are given at intervals close enough that **linear interpolation is satisfactory.**

 The **first table** shows the equilibrium properties of **saturated liquid and saturated vapor** at even increments of temperature. The enthalpy and entropy are arbitrarily assigned values of zero for the saturated-liquid state at the triple point.

 The second table is for the gas region and gives properties of **superheated steam** at temperatures higher than the saturation temperature for a given pressure. Volume (V), internal energy (U), enthalpy (H), and entropy (S) are tabulated as functions of pressure at various temperatures. The steam tables are the most thorough compilation of properties for any single material. However, tables are available for a number of other substances.12 Electronic versions of such tables generally eliminate the need for manual interpolation.

Steam tables	
1-satureated steam	**2- Superheat steam**
At boiling point temperature	**More than boiling point temperature**
A// Dry **X=1** $M = M^V$ **B// Wet (two phase)** **0 < X < 1** $M = (1 - x^v)M^l + x^v M^v$	**X=1** $M = M^V$ **ONLY** vapour

TABLE E.1 Properties of Saturated Steam

V = SPECIFIC VOLUME $cm^3 \cdot g^{-1}$ H = SPECIFIC ENTHALPY $kJ \cdot kg^{-1}$

U = SPECIFIC INTERNAL ENERGY $kJ \cdot kg^{-1}$ S = SPECIFIC ENTROPY $kJ \cdot kg^{-1} \cdot K^{-1}$

				SPECIFIC VOLUME V		INTERNAL ENERGY U			ENTHALPY H			ENTROPY S		
t (°C)	T (K)	P (kPa)	sat. liq.	evap.	sat. vap.	sat. liq.	evap.	sat. vap.	sat. liq.	evap.	sat. vap.	sat. liq.	evap.	sat. vap.
0	273.15	0.611	1.000	206300.	206300.	−0.04	2375.7	2375.6	−0.04	2501.7	2501.6	0.0000	9.1578	9.1578
0.01	273.16	0.611	1.000	206200.	206200.	0.00	2375.6	2375.6	0.00	2501.6	2501.6	0.0000	9.1575	9.1575
1	274.15	0.657	1.000	192600.	192600.	4.17	2372.7	2376.9	4.17	2499.2	2503.4	0.0153	9.1158	9.1311
2	275.15	0.705	1.000	179900.	179900.	8.39	2369.9	2378.3	8.39	2496.8	2505.2	0.0306	9.0741	9.1047
3	276.15	0.757	1.000	168200.	168200.	12.60	2367.1	2379.7	12.60	2494.5	2507.1	0.0459	9.0326	9.0785
4	277.15	0.813	1.000	157300.	157300.	16.80	2364.3	2381.1	16.80	2492.1	2508.9	0.0611	8.9915	9.0526
5	278.15	0.872	1.000	147200.	147200.	21.01	2361.4	2382.4	21.01	2489.7	2510.7	0.0762	8.9507	9.0269
6	279.15	0.935	1.000	137800.	137800.	25.21	2358.6	2383.8	25.21	2487.4	2512.6	0.0913	8.9102	9.0014
7	280.15	1.001	1.000	129100.	129100.	29.41	2355.8	2385.2	29.41	2485.0	2514.4	0.1063	8.8699	8.9762
8	281.15	1.072	1.000	121000.	121000.	33.60	2353.0	2386.6	33.60	2482.6	2516.2	0.1213	8.8300	8.9513
9	282.15	1.147	1.000	113400.	113400.	37.80	2350.1	2387.9	37.80	2480.3	2518.1	0.1362	8.7903	8.9265
10	283.15	1.227	1.000	106400.	106400.	41.99	2347.3	2389.3	41.99	2477.9	2519.9	0.1510	8.7510	8.9020
11	284.15	1.312	1.000	99910.	99910.	46.18	2344.5	2390.7	46.19	2475.5	2521.7	0.1658	8.7119	8.8776
12	285.15	1.401	1.000	93830.	93840.	50.38	2341.7	2392.1	50.38	2473.2	2523.6	0.1805	8.6731	8.8536
13	286.15	1.497	1.001	88180.	88180.	54.56	2338.9	2393.4	54.57	2470.8	2525.4	0.1952	8.6345	8.8297
14	287.15	1.597	1.001	82900.	82900.	58.75	2336.1	2394.8	58.75	2468.5	2527.2	0.2098	8.5963	8.8060
15	288.15	1.704	1.001	77980.	77980.	62.94	2333.2	2396.2	62.94	2466.1	2529.1	0.2243	8.5582	8.7826
16	289.15	1.817	1.001	73380.	73380.	67.12	2330.4	2397.6	67.13	2463.8	2530.9	0.2388	8.5205	8.7593
17	290.15	1.936	1.001	69090.	69090.	71.31	2327.6	2398.9	71.31	2461.4	2532.7	0.2533	8.4830	8.7363
18	291.15	2.062	1.001	65090.	65090.	75.49	2324.8	2400.3	75.50	2459.0	2534.5	0.2677	8.4458	8.7135
19	292.15	2.196	1.002	61340.	61340.	79.68	2322.0	2401.7	79.68	2456.7	2536.4	0.2820	8.4088	8.6908
20	293.15	2.337	1.002	57840.	57840.	83.86	2319.2	2403.0	83.86	2454.3	2538.2	0.2963	8.3721	8.6684
21	294.15	2.485	1.002	54560.	54560.	88.04	2316.4	2404.4	88.04	2452.0	2540.0	0.3105	8.3356	8.6462
22	295.15	2.642	1.002	51490.	51490.	92.22	2313.6	2405.8	92.23	2449.6	2541.8	0.3247	8.2994	8.6241
23	296.15	2.808	1.002	48620.	48620.	96.40	2310.7	2407.1	96.41	2447.2	2543.6	0.3389	8.2634	8.6023
24	297.15	2.982	1.003	45920.	45930.	100.6	2307.9	2408.5	100.6	2444.9	2545.5	0.3530	8.2277	8.5806
25	298.15	3.166	1.003	43400.	43400.	104.8	2305.1	2409.9	104.8	2442.5	2547.3	0.3670	8.1922	8.5592
26	299.15	3.360	1.003	41030.	41030.	108.9	2302.3	2411.2	108.9	2440.2	2549.1	0.3810	8.1569	8.5379
27	300.15	3.564	1.003	38810.	38810.	113.1	2299.5	2412.6	113.1	2437.8	2550.9	0.3949	8.1218	8.5168
28	301.15	3.778	1.004	36730.	36730.	117.3	2296.7	2414.0	117.3	2435.4	2552.7	0.4088	8.0870	8.4959
29	302.15	4.004	1.004	34770.	34770.	121.5	2293.8	2415.3	121.5	2433.1	2554.5	0.4227	8.0524	8.4751

1- Table E.1 Properties of Saturated Steam page 684

Need to   P   or   T

2- Table E.2 Properties of Superheated Steam page 692

Need to   P   and   T

TABLE E.2 Properties of Superheated Steam

TEMPERATURE: t°C
(TEMPERATURE: T kelvins)

P/kPa (θ^sat/°C)		sat. liq.	sat. vap.	75 (348.15)	100 (373.15)	125 (398.15)	150 (423.15)	175 (448.15)	200 (473.15)	225 (498.15)	250 (523.15)
1 (6.98)	V	1.000	129200.	160640.	172180.	183720.	195270.	206810.	218350.	229890.	241430.
	U	29.334	2385.2	2480.8	2516.4	2552.3	2588.5	2624.9	2661.7	2698.8	2736.3
	H	29.335	2514.4	2641.5	2688.6	2736.0	2783.7	2831.7	2880.1	2928.7	2977.7
	S	0.1060	8.9767	9.3828	9.5136	9.6365	9.7527	9.8629	9.9679	10.0681	10.1641
10 (45.83)	V	1.010	14670.	16030.	17190.	18350.	19510.	20660.	21820.	22980.	24130.
	U	191.822	2438.0	2479.7	2515.6	2551.6	2588.0	2624.5	2661.4	2698.6	2736.1
	H	191.832	2584.8	2640.0	2687.5	2735.2	2783.1	2831.2	2879.6	2928.4	2977.4
	S	0.6493	8.1511	8.3168	8.4486	8.5722	8.6888	8.7994	8.9045	9.0049	9.1010
20 (60.09)	V	1.017	7649.8	8000.0	8584.7	9167.1	9748.0	10320.	10900.	11480.	12060.
	U	251.432	2456.9	2478.4	2514.6	2550.9	2587.4	2624.1	2661.0	2698.3	2735.8
	H	251.453	2609.9	2638.4	2686.3	2734.2	2782.3	2830.6	2879.2	2928.0	2977.1
	S	0.8321	7.9094	7.9933	8.1261	8.2504	8.3676	8.4785	8.5839	8.6844	8.7806
30 (69.12)	V	1.022	5229.3	5322.0	5714.4	6104.6	6493.2	6880.8	7267.5	7653.8	8039.7
	U	289.271	2468.6	2477.1	2513.6	2550.2	2586.8	2623.6	2660.7	2698.0	2735.6
	H	289.302	2625.4	2636.8	2685.1	2733.3	2781.6	2830.0	2878.7	2927.6	2976.8
	S	0.9441	7.7695	7.8024	7.9363	8.0614	8.1791	8.2903	8.3960	8.4967	8.5930
40 (75.89)	V	1.027	3993.4	......	4279.2	4573.3	4865.8	5157.2	5447.8	5738.0	6027.7
	U	317.609	2477.1	......	2512.6	2549.4	2586.2	2623.2	2660.3	2697.7	2735.4
	H	317.650	2636.9	......	2683.8	2732.3	2780.9	2829.5	2878.2	2927.2	2976.5
	S	1.0261	7.6709	......	7.8009	7.9268	8.0450	8.1566	8.2624	8.3633	8.4598
50 (81.35)	V	1.030	3240.2	......	3418.1	3654.5	3889.3	4123.0	4356.0	4588.5	4820.5
	U	340.513	2484.0	......	2511.7	2548.6	2585.6	2622.7	2659.9	2697.4	2735.1
	H	340.564	2646.0	......	2682.6	2731.4	2780.1	2828.9	2877.7	2926.8	2976.1
	S	1.0912	7.5947	......	7.6953	7.8219	7.9406	8.0526	8.1587	8.2598	8.3564
75 (91.79)	V	1.037	2216.9	......	2269.8	2429.4	2587.3	2744.2	2900.2	3055.8	3210.9
	U	384.374	2496.7	......	2509.2	2546.7	2584.2	2621.6	2659.0	2696.7	2734.5
	H	384.451	2663.0	......	2679.4	2728.9	2778.2	2827.4	2876.6	2925.8	2975.3
	S	1.2131	7.4570	......	7.5014	7.6300	7.7500	7.8629	7.9697	8.0712	8.1681
100 (99.63)	V	1.043	1693.7	......	1695.5	1816.7	1936.3	2054.7	2172.3	2289.4	2406.1
	U	417.406	2506.1	......	2506.6	2544.8	2582.7	2620.4	2658.1	2695.9	2733.9
	H	417.511	2675.4	......	2676.2	2726.5	2776.3	2825.9	2875.4	2924.9	2974.5
	S	1.3027	7.3598	......	7.3618	7.4923	7.6137	7.7275	7.8349	7.9369	8.0342

Example 1:   P= 40 Kpa,   T= 200 °C,H ?

Solution: **Superheated steam**

H= H ^{v} = 2878.2 KJ/ Kg.

Example 2: P=40 Kpa,   T=130 ºC, H?

Solution: Superheated

H	T
2732.3	125
X	130
2780.9	150

The solution will be done by linear interpolation method

$$y_m = y_1 + \left(\frac{y_2 - y_1}{X_2 - X_1}\right)(X_m - X_1) \qquad \ldots\ldots\ldots\text{General equation}$$

$$H_m = H_1 + \left(\frac{H_2 - H_1}{T_2 - T_1}\right)(T_m - T_1)$$

$$H_m = 2732.3 + \left(\frac{2780.9 - 2732.3}{150 - 125}\right)(130 - 125)$$

$$H_m = 2742.02 \quad KJ/Kg$$

$$\frac{y_m - y_1}{X_m - X_1} = \left(\frac{y_2 - y_1}{X_2 - X_1}\right)$$

Example3: T= 20 ºC,   X= 0.9, find H, P sat?

Solution: from temperature go to steam table.

$$P^{Sat} = 2.337 \, Kpa \qquad Saturated \, ((wet)$$

$$H = (1 - X) \, H^L + X \, H^V$$

$$H = (1 - 0.9) \, 83.86 + (0.9) \, 2538.2$$

$$H = 2292.766 \, KJ/Kg$$

Example 4: T=20 ºC, Dry steam   H?

Solution: H= H^V= 2538.2 KJ/Kg

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Example 5: P =40 Kpa, T= 75 °C,   X= 0.8, find H?

Solution: *Saturated* **steam**(*wet*)

$$H = (1 - X) H^L + X H^V$$

$$H = (1 - 0.8) 317 + (0.8) 2636$$

$$H = 2172.2 \ KJ/Kg$$

Example 6: P =40 Kpa, T= 75 °C,   Dry steam find H?

Solution: H= H^V= 2636   KJ/Kg

Example 6.9

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, determine the downstream state of the steam and ΔH for P_1 = 1000 kPa, t_1 = 250°C, and P_2 = 200 kPa.

Solution 6.9

Because the process is both reversible and adiabatic, there is no change in the entropy of the steam. For the initial temperature of 250°C at 1000 kPa, no entries appear in the tables for superheated steam. **Interpolation between values for 240°C and 260°C yields**, at 1000 kPa,

H$_1$ = 2942.9 kJ·kg^{-1} S$_1$ = 6.9252 kJ·kg^{-1}·K^{-1}

For the final state at **200 kPa,**

S$_2$ = S$_1$ = 6.9252 kJ·kg^{-1}·K^{-1}

Because the entropy of saturated vapor at 200 Pa is greater than S$_2$, the final state must lie in the two-phase liquid/vapor region. **Thus t$_2$ is the saturation temperature at 200 kPa, given in the superheat tables as t$_2$ = 120.23°C.** Equation (6.96a) applied to the entropy becomes:

$$S_2 = (1 - x_2^v)S_2^l + x_2^v S_2^v$$

Numerically,

$$6.9252 = 1.5301(1 - x_2^v) + 7.1268 x_2^v$$

Where the values 1.5301 and 7.1268 are entropies of saturated liquid and saturated vapor at 200 kPa. Solving,

$$x_2^v = 0.9640$$

The mixture is 96.40% vapor and 3.60% liquid. Its enthalpy is obtained by further application of Eq. (6.96a):

$$H_2 = (0.0360)\,(504.7) + (0.9640)\,(2706.3) = 2627.0 \text{ kJ·kg}^{-1}$$

Finally,

$$\Delta H = H_2 - H_1 = 2627.0 - 2942.9 = -315.9 \text{ kJ·kg}^{-1}$$

For a nozzle, under the stated assumptions the steady-flow energy balance, Eq. (2.31), becomes

$$\Delta H + \frac{1}{2}\Delta u^2 = 0$$

Thus the decrease in enthalpy is exactly compensated by an increase in kinetic energy of the fluid. In other words, the velocity of a fluid increases as it flows through a nozzle, which is its usual purpose.

3.7. FORMATION OF STEAM

The process of formation of steam is discussed in detail in the following few pages:

Consider a cylinder fitted with a piston which can move freely upwards and downwards in it. Let, for the sake of simplicity, there be 1 kg of water at 0°C with volume vf m3 under the piston [Fig 3.2 (i)]. Further let the piston is loaded with load W to ensure heating at constant pressure. Now if the heat is imparted to water, a rise in temperature will be noticed and this rise will continue till boiling point is reached. The temperature at which water starts boiling depends upon the pressure and as such for each pressure (under which water is heated) there is a different boiling point. This boiling temperature is known as the temperature of formation of steam or saturation temperature.

t_s = Saturation temp.
t_{sup} = Temperature of superheated steam

v_f = Volume of water
v_g = Volume of dry and saturated steam
v_{sup} = Volume of superheated steam

Fig. 3.2: Formation of Steam

It may be noted during heating up to boiling point that there will be slight increase in volume of water due to which piston moves up and hence work is obtained as shown in Fig. 3.2 (ii). This work, however, is so small that is can be neglected. Now, if supply of heat to water is continued it will be noticed that rise of temperature after the boiling point is reached nil but piston starts moving upwards which indicates that there is increase is volume which is only possible if steam formation occurs. The heat being supplied does not show any rise of temperature but changes water into vapour 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 [Fig. 3.2 (iii)] and if heating of steam is further progressed [as shown in Fig. 3.2 (iv)] such that all the water particles associated with steam are evaporated, the steam so obtained is called dry and saturated steam. If vg m^3 is the volume of 1 kg of dry and saturated steam then work done on the piston will be

$$P (V_g - V_f) \qquad\qquad\qquad ... (3.1)$$

Where p is the constant pressure (due to weight 'W' on the piston).

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.

This phase of steam formation is illustrated in Fig. 3.2 (v). Fig. 3.3 shows the graphical representation of formation of steam.

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Fig. 3.3. Graphical representation of formation of steam.

6.19.

A two-phase system of liquid water and water vapor in equilibrium at 8000 kPa consists of equal volumes of liquid and vapor. If the total volume V^t = 0.15 m3, what is the total enthalpy H^t and what is the total entropy S^t?

Solution:

Two – phase (Wet), P= 12000 KPa

Equal volume of liquid and vapour

$$V^L = V^V = 0.05 \text{ m}^3$$

$$H = (1 - X) H^L + X H^V \quad \dots\dots\dots\dots. (1)$$

$$S = (1 - X) S^L + X S^V \quad \dots\dots\dots\dots.. (2)$$

$$v = (1 - X) v^L + X v^V \quad \dots\dots\dots\dots\dots.. (3)$$

$$v = \frac{v^t}{m^t} \quad \dots\dots\dots\dots (4)$$

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$$m^t = m^L + m^V$$

$$m^t = \frac{V^L}{v^L} + \frac{V^V}{v^V} \ldots \ldots \ldots (5)$$

From table (Page) P=12000 KPa	
$v^L = 1.527 * 10^{-3}$	$v^V = 14.286 * 10^{-3} \, cm^3/gm$
$H^L = 1491.8$	$H^V = 2089.2 \, KJ/Kg$
$S^L = 3.49$	$S^V = 5.5002 \, KJ/Kg.K$

Sub. In equation (5)

$$m^t = \frac{0.05}{1.527 * 10^{-3}} + \frac{0.05}{14.286 * 10^{-3}}$$

$$m^t = 36.2438 \quad Kg$$

$$v^t = \frac{V^t}{m^t} = \frac{0.1}{36.2438} = 2.759 * 10^{-3} \, m^3/kg \ldots \ldots \ldots \ldots \ldots .. (3)$$

$$v^t = (1 - X)\, v^L + X\, v^V$$

$$2.759 * 10^{-3} = (1 - X)1.527 * 10^{-3} + X\,(4.286 * 10^{-3})$$

$$X = 0.0966 \cong 0.1$$

Sub. In equation (1)

$$H = (1 - X)\, H^L + X\, H^V$$

$$H = (1 - 0.1)1491.8 + 0.1\,(2089.2)$$

$$H = 1342.62 + 2089.2$$

$$H = 1551.54 \, KJ/Kg$$

Sub. In equation (2)

$$S = (1 - X)\, S^L + X\, S^V$$

$$S = (1 - 0.1)3.49 + 0.1\,(5.5002)$$

$$S = 3.141 + 0.55002$$

S = 3.691 KJ/Kg.K

6.22.

Wet steam at 230°C has a density of 0.025 g·cm^{-3}. Determine x, H, and S.

Solution:

$$H = (1 - X)\, H^L + X\, H^V \qquad \text{... ... ...} (1)$$

$$S = (1 - X)\, S^L + X\, S^V \qquad \text{... ... ...} (2)$$

$$v = (1 - X)\, v^L + X\, v^V \qquad \text{... ... ...} (3)$$

From table (Page 684) T=230 °C	
V^L= 1.209	V^v= 71.45 Cm^3/gm
H^L= 990.3	H^v= 2802 KJ/Kg
S^L= 2.6102	S^v= 6.2107 KJ/Kg.K

$$v = (1 - X)\, v^L + X\, v^V \qquad \text{... ... ...} (3)$$

$$25.79 = (1 - X)1.209 + X\,(71.45)$$

$$\textbf{X= 0.35}$$

$$S = (1 - X)\, S^L + X\, S^V \qquad \text{... ... ...} (2)$$

$$S = (1 - 0.35)2.6102 + 0.35\,(6.2107) \qquad \text{... ... ...} (2)$$

$$S = 3.87 \text{ KJ/Kg.K}$$

$$H = (1 - X)\, H^L + X\, H^V \qquad \text{... ... ...} (1)$$

$$H = (1 - 0.35)990.3 + 0.35\,(2802) \qquad \text{... ... ...} (1)$$

$$H = 1624.395 \; KJ/Kg$$

6.23.

A vessel of 0.15 m^3 volume containing saturated-vapor steam at 150 °C is cooled to 30 °C. Determine the final volume and mass of liquid water in the vessel.

Solution:

From table (Page 684) T=230 °C	
Temp. = 150 °C sat. steam	V^t= 0.15 m^3
Temp. = 30 °C cooled	V^L=? and m^L=?

From the temperature 150 °C   go to the saturated steam table gat the:-

$$v^{Vap.} = 392.4 \ ^{cm^3}/_{gm} = 0.3928 \ ^{m^3}/_{kg}$$

Take only vapour because the temperature is higher than 100 °C .

$$m^t = \frac{0.15 \ m^3}{0.3928 \ ^{m^3}/_{kg}} = 0.3818 \ kg$$

At the temperature 30 °C go to the saturated steam table and obtained the (vapour+ liquid) two phase

At 30°C	
$v^{Vap.} = 32.89 \ ^{m^3}/_{kg}$	$v^{L.} = 0.001004 \quad ^{m^3}/_{kg}$

$$v^t = (1 - X) \ v^L + X \ v^V$$

$$0.3928 = (1 - X)0.001004 + X \ (32.89)$$

$$X = 0.01191$$

$$(1 - X) = 0.9888$$

$$mass \ of \ liquid = m^t * (1 - X) = \ 0.3818 * 0.9888 = 0.3775 \ kg$$

$$mass \ of \ vapour = m^t * (X) = \ 0.3818 * 0.01191 = 0.0045 \ kg$$

$$volume \ of \ liquid = \ v^L * m = 0.001004 * 0.3775 = 0.000379 \ m^3$$

$$volume \ of \ vapour = \ v^v * m = 32.89 * 0.0045 = 0.148005 \ m^3$$

Chapter 7:   *Thermodynamic Properties of Fluid*

Isenthalpic and Isentropic Process

Isenthalpic process: is irreversible process, adiabatic process at constant enthalpy [$\Delta H = 0$] i.e. Joule Thomson expansion or free expansion or throwing process or Free Expansion $(\frac{\partial T}{\partial p})_H$

Isentropic process: is reversible process and adiabatic at constant entropy [$\Delta s = 0$]

Note: Isenthalpic is cheaper to use then isentropic.

Isenthalpic process	*Isentropic process*
1. Irreversible process	1. reversible process
2. Adiabatic process $dQ = 0$	2. Adiabatic process $dQ = 0$
3. Constant enthalpy $\Delta H = 0$	3. Constant entropy $\Delta S = 0$
i. e. Joule Thomson expansion Free expansion Throttling process Free Expansion $(\frac{\partial T}{\partial p})_H$	

*** *Maximum Velocity in pipe*

Flow of gases

As gas flows along a pipe in the direction of decreasing pressure. Its specific volume increasing and Velocity increases.

$$\Delta H + \frac{\Delta u^2}{2} + g\Delta Z = Q - W$$

1. $Q = 0$
2. $\Delta Z = 0$
3. $constant(A)$
4. $W_s = 0$

$$\Delta H + \frac{\Delta u^2}{2} = 0 \qquad \dots\dots (1)$$ In differential from

$$dH = -udu \qquad \dots\dots (2)$$ *Energy equation*

1

$$\rho u A = \frac{1}{v} u A = m^{\circ} = constant \; ; \quad (m^{\bullet} = mass\; flow\; rate)\left(\rho = \frac{1}{v}\right)$$

$$d\left(\frac{uA}{v}\right) = 0 \qquad v\;(specific\; volume)$$

$$du = \frac{vudv}{v^2} \implies du = \frac{udv}{v} \qquad \dots\dots (3)$$

Sub. Equation (3) in equation (2) obtain

$$dH = -u\frac{udv}{v} \qquad \implies$$

$$dH = -\frac{u^2 dv}{v} \qquad \dots\dots (4)$$

$$d\left(\frac{u}{v}\right) = 0 \quad \text{When } A = constant$$

$$d(uv^{-1}) = 0$$

$$\frac{du}{v} - \frac{udv}{v^2} = 0$$

$$v^{-1}du + u(-v^{-2}dv) = 0$$

$$\frac{du}{v} + \left(-\frac{udv}{v^2}\right) = 0$$

$$\frac{du}{v} - \frac{udv}{v^2} = 0$$

$$du = \frac{vudv}{v^2}$$

$$du = \frac{u\, dv}{v} \qquad \dots\dots\dots\dots (3)$$

For case of maximum velocity $dS = 0$

$$TdS = dH - vdp \qquad \dots\dots (5)$$

Sub. Equation (4) in equation (5) obtain

$$0 = -\frac{u^2 dv}{v} - vdP$$

$$vdP = -\frac{u^2 dv}{v}$$

$$\boxed{u_{max}^2 = -v^2\left(\frac{dp}{dv}\right)_s} \qquad \textit{Speed of sound in fluid}$$

Isentropic flow the max. Velocity

Expansion process:

Flow process accompanied by sharp reduction in pressure are called expansion process. They include flow Through Nozzles Through turbines or expanders and Through Throttling Devices such as orifice's and valves.

Expansion process:

1. Sharp reduction in pressure
2. Through nozzles
3. Through turbines or expander
4. Through throttling (orifices and valve)

Nozzle:
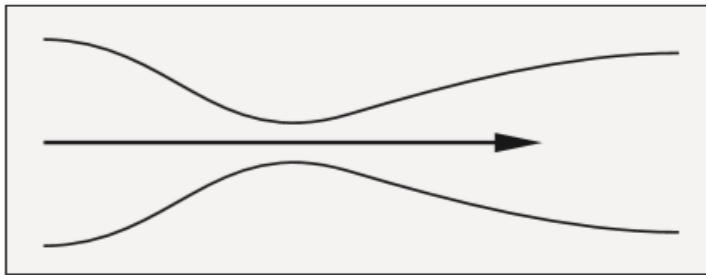
Figure 7.1:
Converging/diverging
nozzle.

A Nozzle is device That causes The inter change of internal and kinetic energy of a fluids result of changing cross - sectional area available for flow nozzle have converging and diverging section are used separately or combined, nozzle closed in turbine, jet engine, ejectors and diffusers.

$$w_s = 0$$

Energy equation $dH = -udu$

Mechanical energy $-vdp = udu + dF$

The flow in nozzle is *nearly adiabatic* because the *velocity is high* (*short residence time of fluid*) and *the area for heat transfer is small.*

The relation of velocity to pressure in an isentropic nozzle can be expressed analytically for the ideal-gas state and constant heat capacities. Combination of Eqs. (6.9) and (7.3) for isentropic flow gives:

The fundamental property relation appropriate to this application is:

$$dH = T\, dS + V\, dP \qquad (6.9)$$

The appropriate energy balance is Eq. (2.31). With Q, W_s and Δz all set equal to zero,

$$\Delta H + \frac{\Delta u^2}{2} = 0$$

In differential form, $$dH = -u\, du \qquad (7.3)$$

The continuity equation, Eq. (2.26), is also applicable. Because $\dot{m}$ is constant, its differential form is:

$$d(uA/V) = 0$$

or $$\frac{dV}{V} - \frac{du}{u} - \frac{dA}{A} = 0 \qquad (7.4)$$

If the flow is isentropic

$$-vdp = udu \qquad \ldots\ldots\ldots\ldots..(1)$$

For constant flow d (uA/v) = 0 for constant A

$$\mathbf{du = u\frac{dv}{v}} \qquad \ldots\ldots\ldots\ldots\ldots.(2)$$

Eq. (2) substitute in eq. (1) for isentropic flow give The Throat Velocity

$$U^2_{Throat} = -v^2 (\frac{dp}{dv})_s$$

This equation shows that in the converging section of converging / diverging nozzle the maximum obtainable fluid Velocity is the speed sound reached at the throat.

With $pv^\gamma = constant$ AND integration of eq. (1) gives:-

For mechanical energy

$$\boldsymbol{u_2^2 - u_1^2 = -2 \int_{p_1}^{p_2} vdp = \frac{2\gamma\, p_1 v_1}{\gamma-1} \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}\right]}$$

And $$u^2_{Throat} = \gamma\, p_2 v_2$$

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Solving for the pressure ratio with $U_1 = 0$ gives

$$\frac{p_2}{p_1} = \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma}{\gamma-1}}$$

Another equation that is applicable to any type of nozzle as long as the flow is Isentropic

$$\frac{dA}{A} = (M^2 - 1)\ \frac{du}{u}$$

$$M = Mach\ No. = \frac{Actual\ velocity}{Speed\ of\ sound}$$

Depending on weather M is **greater** than unity (supersonic) or

Less than unity (subsonic).

The cross-sectional are an increases or decreases with Velocity increase.

The relation of velocity to pressure in an isentropic nozzle can be expressed analytically for the ideal-gas state and constant heat capacities. Combination of Eqs. (6.9) and (7.3) for isentropic flow gives:

$$u\ du = -V\ dP$$

Integration, with nozzle entrance and exit conditions denoted by 1 and 2, yields:

$$u_2^2 - u_1^2 = -2\int_{P_1}^{P_2} V\ dP = \frac{2\gamma P_1 V_1}{\gamma - 1}\left[1 - \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}\right] \tag{7.11}$$

where the final term is obtained upon elimination of V by Eq. (3.23c), $PV^\gamma = $ const.

Equation (7.11) may be solved for the pressure ratio P_2/P_1 for which u_2 reaches the speed of sound, i.e., where

$$u_2^2 = c^2 = -V^2\left(\frac{\partial P}{\partial V}\right)_S$$

The derivative is found by differentiation with respect to V of $PV^\gamma = $ const.:

$$\left(\frac{\partial P}{\partial V}\right)_S = -\frac{\gamma P}{V}$$

Substitution then yields:

$$u_2^2 = \gamma P_2 V_2$$

With this value for u_2^2 in Eq. (7.11) and with $u_1 = 0$, solution for the pressure ratio at the throat gives:

$$\frac{P_2}{P_1} = \left(\frac{2}{\gamma+1}\right)^{\gamma/(\gamma-1)} \tag{7.12}$$

Throttling Process:

When fluid flows through a restriction, such as an orifice, partially closed valve or a porous plug, without any appreciable change in kinetic energy the primary result of the Process is a pressure drop in the fluid, such a throttling Process produce no shaft work and result in negligible change in elevation.

In absence of heat transfer the Process occurs at constant enthalpy.

This process occurs so rapidly and in such a small space that there is no time and no large area for such heat transfer.

∴ It is assumed to be adiabatic

$$\Delta H = \cancel{Q} - \cancel{w_s}$$

$$\Delta H = 0 \qquad or \qquad H_2 = H_1$$

A Throttling process does not change in the Temperature of an ideal gas but for real gases caused "decreased in temperature"

It is flow process
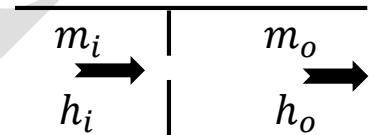
Joule-Thomson Coefficient (μ_J) :-

$$\mu_J = \left(\frac{\partial T}{\partial P}\right)_H$$

1. If μ_J is $+Ve$ this means temperature drop during throttling

If μ_J is $-Ve$ this means temperature rises during throttling

Turbines or Expanders:

The expansion of a gas in a nozzle to produce a high – Velocity stream is process converts internal energy in to kinetic energy. This Kinetic energy can in turn be converted in to shaft work when the stream impinges a blades attached to rotating shaft.

- Potential energy and heat transfer are negligible
- The inlet and exit pipes are sized to make fluid Velocities relatively low.
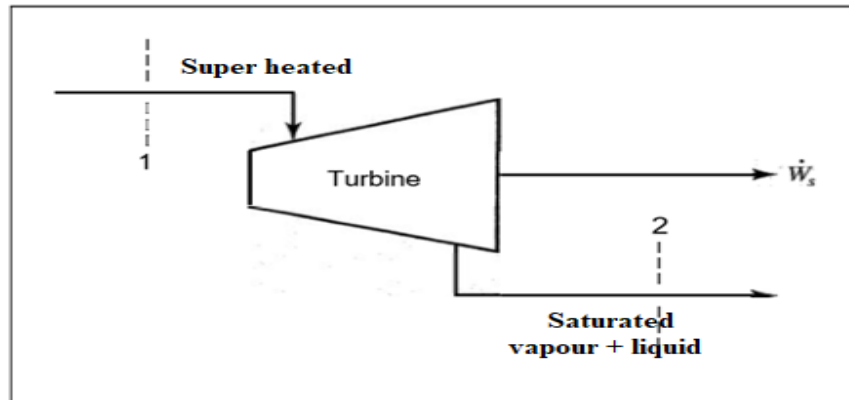
Figure 7.3   Steady-state flow through a turbine or expander

$$\dot{W}_s = \dot{m}\, \Delta H = \dot{m}(H_2 - H_1) \quad (7.13)$$

$$W_s = \Delta H = H_2 - H_1 \qquad (7.14)$$

$$\dot{w}_S = -\dot{m}\, \Delta H$$

$$w_s = -\Delta H$$

When the operation is isentropic (reversible and adiabatic)

For expansion process, the isentropic work is the maximum shaft work obtained from an adiabatic turbine with given inlet conditions and given discharge pressure. Actual turbines produce less work, because the actual expansion process is irreversible.

$$w_s\ (isentropic) = -(\Delta H)_s$$

The Turbine efficiency

$$[\eta = \frac{W_S}{W_{S(isentropic)}} \quad \text{OR} \quad \eta = \frac{\Delta H}{\Delta H_s}\ ] \qquad حفظ$$
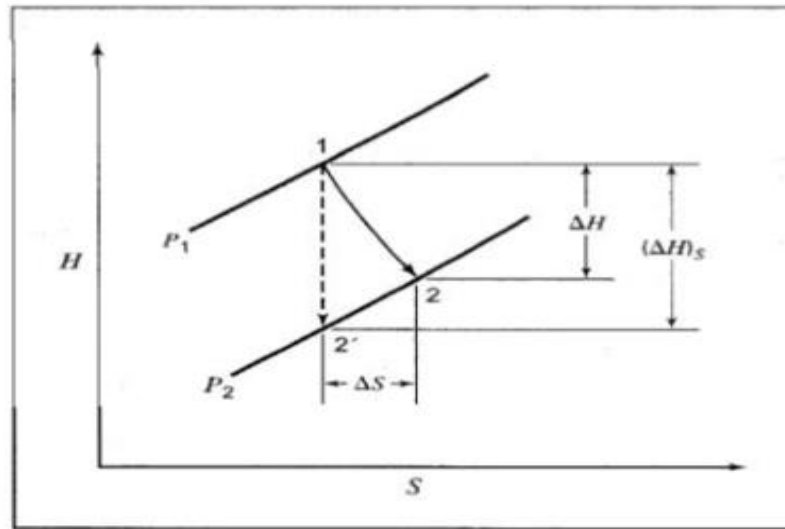
Figure 7.4 Adiabatic expansion process in a turbine or expander

Example 7.6

A steam turbine with rated capacity of 56,400 kW (56,400 kJ·s^{-1}) 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 0.75. Determine the state of the steam at discharge and the mass rate of flow of the steam.

Solution 7.6

At the inlet conditions of 8600 kPa and 500°C, the steam tables provide:

$$H_1 = 3391.6 \text{ kJ} \cdot \text{kg}^{-1} \qquad\qquad S_1 = 6.6858 \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$$

If the expansion to 10 kPa is isentropic, then, $S_2' = S_1 = 6.6858$ kJ· kg^{-1}·K^{-1}.

Steam with this entropy at 10 kPa is wet. Applying the "lever rule" [Eq. (6.96 b),

With M = S and $x^v = x_2'$], the quality is obtained as follows:

$$S_2'' = S_2^l + x_2''(S_2^v - S_2^l)$$

Then, $6.6858 = 0.6493 + x_2'(8.1511 - 0.6493)$ $x_2' = 0.8047$

This is the quality (fraction vapor) of the discharge stream at point 2′. The enthalpy H_2' is also given by Eq. (6.96b), written:

$$H_2' = H_2^l + x_2'(H_2^v - H_2^l)$$

Thus, $H_2' = 191.8 + (0.8047)(2584.8 - 191.8) = 2117.4 \text{ kJ·kg}^{-1}$
$(\Delta H)_S = H_2' - H_1 = 2117.4 - 3391.6 = -1274.2 \text{ kJ·kg}^{-1}$

and by Eq. (7.16),

$$\Delta H = \eta(\Delta H)_S = (0.75)(-1274.2) = -955.6 \text{ kJ·kg}^{-1}$$

Whence, $H_2 = H_1 + \Delta H = 3391.6 - 955.6 = 2436.0 \text{ kJ·kg}^{-1}$

Thus the steam in its actual final state is also wet, with its quality given by:

$$2436.0 = 191.8 + x_2(2584.8 - 191.8) \qquad x_2 = 0.9378$$

Then $S_2 = 0.6493 + (0.9378)(8.1511 - 0.6493) = 7.6846 \text{ kJ·kg}^{-1}\cdot\text{K}^{-1}$

This value may be compared with the initial value of $S_1 = 6.6858$.
The steam rate $\dot{m}$ is given by Eq. (7.13). For a work rate of 56,400 kJ·s^{-1},

$$\dot{W}_s = -56,400 = \dot{m}(2436.0 - 3391.6) \qquad \dot{m} = 59.02 \text{ kg·s}^{-1}$$

Compression process:

Compression process result in pressure increases, compressors, pumps, fans, blower and vacuum pump are all devices designed for this purpose.

Compressors:

The Compression of gases may be accomplished in equipment with rotating blades (like a turbine operating in reverse) or in cylinder with reciprocating pistons for adiabatic compression.
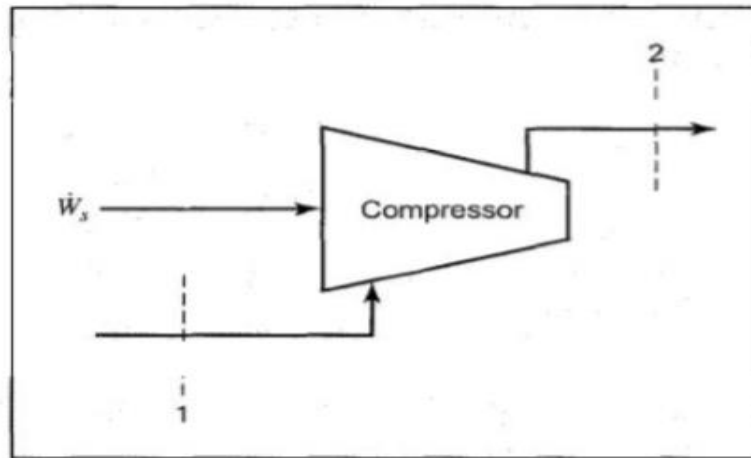
Figure 7.5 Steady-state compression process

$$\dot{w}_S = -\dot{m}\,\Delta H$$
$$w_S = -\Delta H$$

In a compression process the isentropic work which is the minimum shaft work required for compression of gas from a given initial stat to given discharge pressure is given by equation:

$$W_S(isentropic) = -(\Delta H)_S$$

The compression efficiency

$$\eta = \frac{W_S\ (isentropic)}{W_S} \qquad \text{And}$$

$$\eta = \frac{(\Delta H)_S}{\Delta H}$$
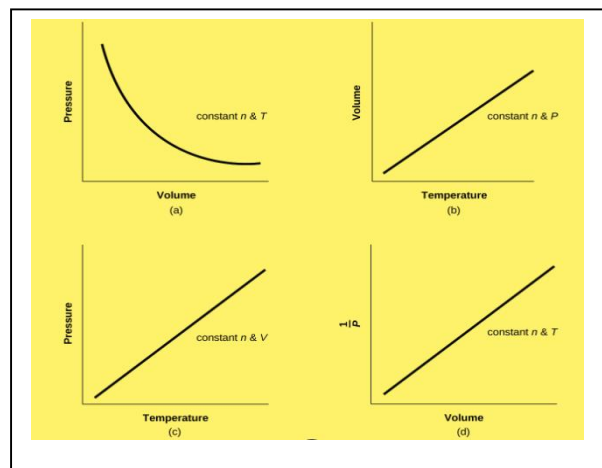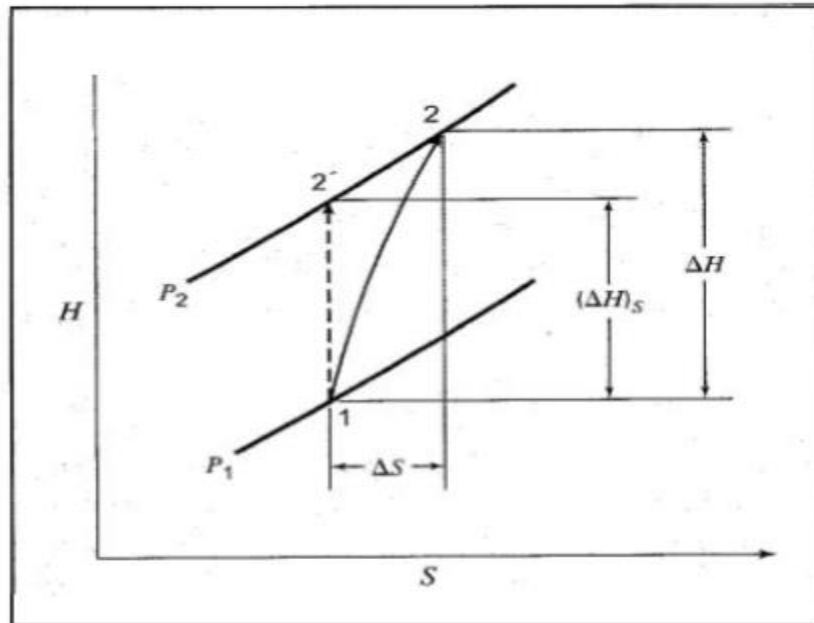
Figure 7.6 Adiabatic compression process

PUMPS:

Liquid are usually moved by pumps, generally rotating equipment. The same equation apply to adiabatic pumps as to adiabatic compressors.

$$\dot{w}_S = -\dot{m}\,\Delta H \qquad\qquad OR \qquad\qquad w_S = -\Delta H$$

The compression efficiency

$$\eta = \frac{W_S\ (isentropic)}{W_S}$$

And

$$\eta = \frac{(\Delta H)_S}{\Delta H}$$

For an isentropic process
$$dH = Vdp \qquad (constant)\ S$$
$$W_S(isentropic) = -(\Delta H)_S = -\int_{P_1}^{P_2} Vdp$$

The usual assumption for liquid is that V is dependent of P.

$$W_S(isentropic) = -(\Delta H)_S = -V(P_2 - P_1)$$
$$dH = Cp \, dT + V(1 - \beta T) \, dP$$

And

$$dS = Cp \, \frac{dT}{T} - \beta V dP$$

Because of temperature change in pumped fluid are very small and since the properties of liquid are insensitive to pressure. We assume that Cp, V and β are constant

$$\Delta H = Cp \, \Delta T + V(1 - \beta T) \, \Delta P$$

And

$$\Delta S = Cp \, ln \frac{T_2}{T_1} - \beta V \, \Delta P$$

Example 7.2

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·s^{-1}. 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 7.2

The required area ratios are determined by conservation of mass [Eq. (2.26)], and the velocity u is found from the integrated form of Eq. (7.3), a steady-state energy balance that includes enthalpy and kinetic energy terms:

$$\frac{A}{A_1} = \frac{u_1 V}{V_1 u} \qquad \text{and} \qquad u^2 = u_1^2 - 2(H - H_1)$$

For velocity units of m·s^{-1}, u^2 has the units, m^2·s^{-2}. Units of J·kg^{-1} for H are consistent with these, because 1 J = 1 kg·m^2·s^{-2}, and 1 J·kg^{-1} = 1 m^2·s^{-2}.
   Initial values for entropy, enthalpy, and specific volume are obtained from the steam tables:

$$S_1 = 7.2997 \text{ kJ·kg}^{-1}\text{·K}^{-1} \qquad H_1 = 3059.8 \text{ kJ·kg}^{-1} \qquad V_1 = 371.39 \text{ cm}^3\text{·g}^{-1}$$

Thus,

$$\frac{A}{A_1} = \left(\frac{30}{371.39}\right)\frac{V}{u} \tag{A}$$

and

$$u^2 = 900 - 2(H - 3059.8 \times 10^3) \tag{B}$$

Because the expansion is isentropic, $S = S_1$; steam-table values at 600 kPa are:

$$S = 7.2997 \text{ kJ·kg}^{-1}\text{·K}^{-1} \qquad H = 3020.4 \text{ kJ·kg}^{-1} \qquad V = 418.25 \text{ cm}^3\text{·g}^{-1}$$

From Eq. (B), $u = 282.3$ m·s^{-1}

By Eq. (A), $\dfrac{A}{A_1} = \left(\dfrac{30}{371.39}\right)\left(\dfrac{418.25}{282.3}\right) = 0.120$

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Area ratios for other pressures are evaluated the same way, and the results are summarized in the following table.

P/kPa	$V/cm^3 \cdot g^{-1}$	$u/m \cdot s^{-1}$	A/A_1	P/kPa	$V/cm^3 \cdot g^{-1}$	$u/m \cdot s^{-1}$	A/A_1
700	371.39	30	1.0	400	571.23	523.0	0.088
600	418.25	282.3	0.120	300	711.93	633.0	0.091
500	481.26	411.2	0.095	200	970.04	752.2	0.104

The pressure at the throat of the nozzle is about 380 kPa. At lower pressures, the nozzle clearly diverges.

Example 7.3

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·s⁻¹. Assuming that steam exists in its ideal-gas state and constant heat capacity. Calculate: (a) The critical pressure ratio and the velocity at the throat. (b) The discharge pressure for a Mach number of 2.0 at the nozzle exhaust.

The ratio of specific heats for steam $(\gamma) = 1.3$

$$\frac{P_2}{P_1} = \left(\frac{2}{\gamma + 1}\right)^{\gamma/(\gamma-1)} \tag{7.12}$$

$$u_2^2 - u_1^2 = -2\int_{P_1}^{P_2} V\, dP = \frac{2\gamma P_1 V_1}{\gamma - 1}\left[1 - \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}\right] \tag{7.11}$$

Solution 7.3

(a) The ratio of specific heats for steam is about 1.3. Substituting in Eq. (7.12),

$$\frac{P_2}{P_1} = \left(\frac{2}{1.3 + 1}\right)^{1.3/(1.3-1)} = 0.55$$

The velocity at the throat, equal to the speed of sound, is found from Eq. (7.11), which contains the product $P_1 V_1$. For steam in its ideal-gas state:

$$P_1 V_1 = \frac{RT_1}{\mathcal{M}} = \frac{(8.314)(573.15)}{0.01802} = 264{,}511 \text{ m}^2\text{·s}^{-2}$$

In this equation $R/\mathcal{M}$ has the units:

$$\frac{\text{J}}{\text{kg·K}} = \frac{\text{N·m}}{\text{kg·K}} = \frac{\text{kg·m·s}^{-2}\text{m}}{\text{kg·K}} = \frac{\text{m}^2\text{·s}^{-2}}{\text{K}}$$

Thus $RT/\mathcal{M}$, and hence $P_1 V_1$, is in m²·s⁻², the units of velocity squared. Substitution in Eq. (7.11) gives:

$$u_{\text{throat}}^2 = (30)^2 + \frac{(2)(1.3)(264{,}511)}{1.3 - 1}\left[1 - (0.55)^{(1.3-1)/1.3}\right] = 296{,}322$$

$$u_{\text{throat}} = 544.35 \text{ m·s}^{-1}$$

This result is in good agreement with the value obtained in Ex. 7.2, because the behavior of steam at these conditions closely approximates the ideal-gas state.

(b) For a Mach number of 2.0 (based on the velocity of sound at the nozzle throat) the discharge velocity is:

$$2u_{\text{throat}} = (2)(544.35) = 1088.7 \text{ m·s}^{-1}$$

Substitution of this value in Eq. (7.11) allows calculation of the pressure ratio:

$$(1088.7)^2 - (30)^2 = \frac{(2)(1.3)(264{,}511)}{1.3-1}\left[1 - \left(\frac{P_2}{P_1}\right)^{(1.3-1)/1.3}\right]$$

$$\left(\frac{P_2}{P_1}\right)^{(1.3-1)/1.3} = 0.4834 \qquad \text{and} \qquad P_2 = (0.0428)(700) = 30.0 \text{ kPa}$$

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Example 7.8

Saturated-vapor steam at 100 kPa (t^{sat} = 99.63°C) is compressed adiabatically to 300 kPa. If the compressor efficiency is 0.75, what is the work required and what are the properties of the discharge stream?

Solution 7.6

For saturated steam at 100KPa,

$$S_1 = 7.3598 \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1} \qquad\qquad H_1 = 2675.4 \text{ kJ} \cdot \text{kg}^{-1}$$

For isentropic compression to 300 KPa, $S_2' = S_1 = 7.3598 \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$.

Interpolation in the tables for superheated steam at 300 KPa shows that steam with this entropy has the enthalpy:

$$H_2^{''} = 2888.8 \; KJ.Kg^{-1}$$

Thus, $(\Delta H)_S = 2888.8 - 2675.4 = 213.4 \; KJ.Kg^{-1}$

$$by \; Eq. (7.17),, \qquad (\Delta H) = \frac{(\Delta H)_S}{\eta} = \frac{213.4 \; KJ.Kg^{-1}}{0.75} = 284.5 \; KJ.Kg^{-1}$$

$$and \quad H_2 - H_1 + \Delta H = 2675.4 + 284.5 = 2959.9 \; KJ.Kg^{-1}$$

For superheated steam with this enthalpy, interpolation yields:

$$T_2 = 246.1 \, °C \qquad\qquad S_2 = 7.5019 \; KJ.Kg^{-1} \, K^{-1}$$

Moreover, by eq. (7.14), the work required is:

$$W_S = \Delta H = H_2 - H_1 \qquad \rightarrow\rightarrow\rightarrow \quad W_S = \Delta H = 284.5 \; KJ.Kg^{-1}$$

Example 7.9

If methane (assumed to be in its ideal-gas state) is compressed adiabatically from 20°C and 140 kPa to 560 kPa, estimate the work requirement and the discharge temperature of the methane. The compressor efficiency is 0.75.

Solution 7.9

where for simplicity the superscript ig has been omitted from the mean heat capacity. If the compression is isentropic, $\Delta S = 0$, and this equation becomes:

$$T_2' = T_1 \left(\frac{P_2}{P_1} \right)^{R/\langle C_P' \rangle_S} \tag{7.18}$$

with T_2' the temperature that results when compression from T_1 and P_1 to P_2 is *isentropic* and where $\langle C_P' \rangle_S$ is the mean heat capacity for the temperature range from T_1 to T_2'.

Applied to isentropic compression, Eq. (4.10) here becomes:

$$(\Delta H)_S = \langle C_P' \rangle_H (T_2' - T_1)$$

In accord with Eq. (7.15), $W_s \text{(isentropic)} = \langle C_P' \rangle_H (T_2' - T_1)$ (7.19)

Solution 7.9

Application of Eq. (7.18) requires evaluation of the exponent R / $\langle$ CP′ $\rangle$ S. This is provided by Eq. (5.13), which for the present computation is represented by:
$\langle$ CP′ $\rangle$ S/R = MCP(293.15, T 2 ; 1.702, 9.081 × 10 −3 , −2.164 ×10 −6 , 0.0)

$$\frac{\langle C_P' \rangle_S}{R} = \text{MCPS}(293.15, T_2; 1.702, 9.081 \times 10^{-3}, -2.164 \times 10^{-6}, 0.0)$$

Where the constants for methane are from Table C.1 of App. C. Choose a value for T2 ′ somewhat higher than the initial temperature T1 = 293.15 K.

The exponent in Eq. (7.18) is the reciprocal of $\langle$ CP′ $\rangle$ S /R. With P2 /P1 = 560/140 = 4.0 and T1 = 293.15 K, find a new value of T2 ′.

The procedure is repeated until no further significant change occurs in the value of T2 ′. This process produces the values:

$$\frac{\langle C_P' \rangle_S}{R} = 4.5574 \qquad \text{and} \qquad T_2' = 397.37 \text{ K}$$

For the same T1 and T2 ′, evaluate $\langle$ CP′ $\rangle$ H /R by Eq. (4.9):
$$\frac{\langle C_P' \rangle_H}{R} = \text{MCPH}(293.15, 397.37; 1.702, 9.081 \times 10^{-3}, -2.164 \times 10^{-6}, 0.0) = 4.5774$$

Whence, $\langle$ CP′ $\rangle$ H = (4.5774) (8.314) = 38.506 J·mol $^{-1}$ ·K $^{-1}$
Then by Eq. (7.19),
$\qquad\qquad$ Ws (isentropic) = (38.056) (397.37 − 293.15) = 3966.2 J·mol $^{-1}$

The actual work is found from Eq. (7.20):

$$\text{Ws} = 3966.2 / 0.75 = 5288.3 \text{ J·mol}^{-1}$$

Application of Eq. (7.21) for the calculation of T2 gives:

$$T_2 = 293.15 + \frac{5288.3}{\langle C_P \rangle_H}$$

Because $\langle C_P \rangle$ H depends on T2, we again iterate. With T $2'$ as a starting value, this leads to the results:

T$_2$ = 428.65 K   or   t $_2$ = 155.5 °C

And $\langle C_P \rangle_H = 39.027$ J·mol $^{-1}$ ·K $^{-1}$

Example 7.10:

Water at 45°C and 10 kpa enters an adiabatic pump and discharged at pressure of 8600 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 7.10

The following are properties for saturated liquid water at 45 °C (318.15K):

$$\beta = 425 \times 10^{-6}\ k^{-1} \qquad c_p = 4.178\ \frac{k_J}{k_g\ k} \qquad v = 1010\ cm^3/k_g$$

$$\eta \equiv \frac{(\Delta H)_S}{\Delta H} \qquad\qquad (7.17)$$

$$W_S(isentropic) = (\Delta H)_S = V(P_2 - P_1) \qquad\qquad eq.\,(7.24)$$

$\Delta H = C_P \Delta T + V(1 - \beta T)\,\Delta P$ (7.25)	$\Delta S = C_P \ln\dfrac{T_2}{T_1} - \beta V\,\Delta P$ (7.26)

By Eq. (7.24),

$$W_s(\text{isentropic}) = (\Delta H)_S = (1010)(8600 - 10) = 8.676 \times 10^6\ \text{kPa·cm}^3\text{·kg}^{-1}$$

Because $1\ \text{kJ} = 10^6\ \text{kPa·cm}^3$,

$$W_s(\text{isentropic}) = (\Delta H)_S = 8.676\ \text{kJ·kg}^{-1}$$

By Eq. (7.17), $\qquad \Delta H = \dfrac{(\Delta H)_S}{\eta} = \dfrac{8.676}{0.75} = 11.57\ \text{kJ·kg}^{-1}$

and $\qquad\qquad\qquad W_s = \Delta H = 11.57\ \text{kJ·kg}^{-1}$

The temperature change of the water during pumping, from Eq. (7.25):

$$11.57 = 4.178\ \Delta T + 1010\left[1 - (425 \times 10^{-6})(318.15)\right]\frac{8590}{10^6}$$

Solution for ΔT gives:

$$\Delta T = 0.97\ \text{K} \qquad \text{or} \qquad 0.97°\text{C}$$

The entropy change of the water is given by Eq. (7.26):

$$\Delta S = 4.178\ \ln\frac{319.12}{318.15} - (425 \times 10^{-6})(1010)\frac{8590}{10^6} = 0.0090\ \text{kJ·kg}^{-1}\text{·K}^{-1}$$

Chapter 7

Maximum velocity in pipe

يحدث لها نقصان في الضغط و يزداد لها الحجم النوعي و تزداد pipeجريان الغازات داخل
السرعة .

Expansion process:

1. Sharp reduction in pressure
2. Through nozzles
3. Through turbines or expander
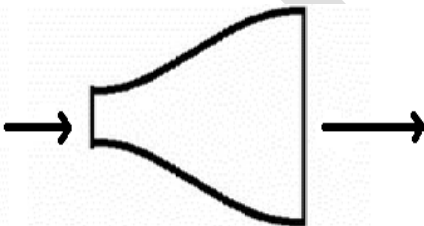4. Through throttling (orifices and valve)
1. Nozzles :
   a// converging
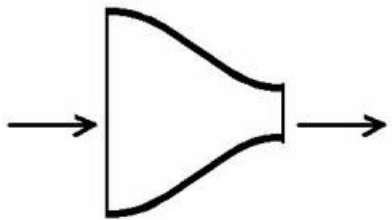
يحدث تغيرات في طاقة الجهد والطاقة (nozzleاختراع ال)
الحركية نتيجة لتغيرات في المساحة المقطعية المتاحة لجريان
المائع و هو يمتلك منطقتين احداهما توسع و الاخرى تضيق .
يستخدم مع nozzle)يستخدم للفصل او المزج . و ال)
(turbines)او ، (jet)او ، (ejectors)او ، (diffuser)

b//diverging

$$W_S = 0 \quad and \quad gsZ = 0$$

بسبب السرعة العالية اي adiabatic و هو يقترب من عمل)
ان زمن البقاء سوف يقل و مساحة انتقال الحرارة صغيرة . (

$dH = -udu$ (*energy equation*)

$-\text{v}dP = udu$
$\qquad\qquad + dF$ (*mechanical energy*)

If the flow is isentropic

dF ( )بما ان $dS = 0$ اذن العملية مثالية ؛ اذن الحد ( )
يختفي

$\qquad -\text{v}dP = udu$ »»»»»»»»» 1

For   constant   flow $d\left(\dfrac{uA}{\text{v}}\right) =$
0 *for constant A*

من المشتقة و الترتيب نحصل على

$$\frac{du}{\text{v}} - \frac{udv}{\text{v}^2} = 0$$

$$du = \frac{udv}{\text{v}} \text{ »»»»»»»»» } 2$$

نعوض المعادلة (2) في (1)نحصل على

Sub. Equation (2) in equation (1)

$-\text{v}dP = u\dfrac{udu}{\text{v}}$ (بالترتيب)

$-\text{v}^2 \dfrac{\partial P}{\partial \text{v}} = u_{throat}^2$ (حفظ)

$dH = -udu$ (*energy equation*)

$-\text{v}dP = udu + dF$ (*mechanical energy*)

IF the flow is isentropic

بما ان $dS = 0$ اذن العملية مثالية ؛ اذن الحد
(dF) يختفي

$-\text{v}dP = udu$ (1)

For constant flow

$d\left(\dfrac{uA}{\text{v}}\right) = 0$ *for constant A*

من المشتقة و الترتيب نحصل على

$$\frac{du}{\text{v}} - \frac{udv}{\text{v}^2} = 0$$

$du = \dfrac{udv}{\text{v}}$ (2)

Sub. Equation (2) in equation (1)

$-\text{v}dP = u\dfrac{udu}{\text{v}}$ (بالترتيب)

$-\text{v}^2 \dfrac{\partial P}{\partial \text{v}} = u_{throat}^2$ (حفظ)

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

<u>From mechanical energy:</u>

$-vdP = udu$ mechanical energy isentropic

Integration the above equation:

$$-\int vdP = \frac{\Delta u^2}{2}$$

$$u_2^2 - u_1^2 = -2 \int vdp$$

$$Pv^\gamma = C$$

$$v^\gamma = \frac{C}{P} \implies v = \left(\frac{C}{P}\right)^{\frac{1}{\gamma}}$$

$$u_2^2 - u_1^2 = -2 \int \left(\frac{C}{P}\right)^{\frac{1}{\gamma}} dp$$

$$u_2^2 - u_1^2 = -2 \, (C)^{\frac{1}{\gamma}} \int \frac{dp}{(P)^{\frac{1}{\gamma}}}$$

$$u_2^2 - u_1^2 = -2 \, (C)^{\frac{1}{\gamma}} \left[\frac{P^{1-\frac{1}{\gamma}}}{1-\frac{1}{\gamma}} \right]_{P_1}^{P_2}$$

$$u_2^2 - u_1^2 = \frac{-2 \, (C)^{\frac{1}{\gamma}}}{1-\frac{1}{\gamma}} \left[P_2^{1-\frac{1}{\gamma}} - P_1^{1-\frac{1}{\gamma}} \right]$$

$$u_2^2 - u_1^2 = \frac{-2 \, (C)^{\frac{1}{\gamma}} P_1^{1-\frac{1}{\gamma}}}{1-\frac{1}{\gamma}} \left[\frac{P_2^{1-\frac{1}{\gamma}}}{P_1^{1-\frac{1}{\gamma}}} - \frac{P_1^{1-\frac{1}{\gamma}}}{P_1^{1-\frac{1}{\gamma}}} \right]$$

$$u_2^2 - u_1^2 = \frac{-2\,\gamma\,(C)^{\frac{1}{\gamma}} P_1\, P_1^{-\frac{1}{\gamma}}}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right]$$

$$u_2^2 - u_1^2 = \frac{2\,\gamma\,P_1 \left(\frac{C}{P_1}\right)^{\frac{1}{\gamma}}}{\gamma - 1}\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right]$$

$$u_2^2 - u_1^2 = \frac{2\,\gamma\,P_1 v_1^{\frac{1}{\gamma}}}{\gamma - 1}\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right]$$

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

The speed of sound is obtained in the throat and converging nozzle. For the isentropic expansion of an ideal gas:

$$P_1 v_1^{\gamma} = Constant$$

$$P_1\,\gamma\,v_1^{\gamma-1} dv + v_1^{\gamma}\,dP = 0$$

$$\gamma\,P_1\,v_1^{\gamma-1} dv + v_1^{\gamma}\,dP = 0$$

$$\gamma\,P_1\,v_1^{\gamma-1} dv = -v_1^{\gamma}\,dP$$

$$\gamma\,P_1\,v_1^{\gamma-1} = -v_1^{\gamma}\,\frac{dP}{dv}$$

$$\gamma\,P_1\,\frac{v_1^{\gamma}}{v_1} = -v_1^{\gamma}\,\frac{dP}{dv}$$

$$\gamma\,P_1\,\frac{1}{v_1} = -\frac{dP}{dv}$$

$$\gamma\,P_1\,v_1 = -v_1^{2}\,\frac{dP}{dv}$$

$$\gamma P_1 \frac{P_2 \ v_2}{P_1} = -v_1{}^2 \frac{dP}{dv}$$

$$\gamma P_2 \ v_2 = -v_1{}^2 \left(\frac{\partial P}{\partial v}\right)_S$$

$$\gamma P_2 \ v_2 = u_{throat}^2$$

//

***The relation between the cross-sectional area velocity, and the local Mach number at any axial position in the nozzle.

Prove: $\frac{dA}{A} = (M^2 - 1)\frac{du}{u}$

* From continuity equation

$$d\frac{uA}{v} = 0 \ ; \ let \ uA = x$$

$$d\frac{x}{v} = 0$$

Differential :

$$\frac{v dx - x dv}{v^2} = 0$$

$$\frac{1}{v}dx - x\frac{dv}{v^2} = 0$$

$$\frac{1}{v}dx = x\frac{dv}{v^2}$$

$$\frac{1}{v}(udA + Adu) = uA\frac{dv}{v^2}$$

$$\frac{dA}{A} + \frac{du}{u} = \frac{\text{v}}{\text{v}^2} d\text{v} \qquad (1)$$

From mechanical energy:

$$-\text{v}dP = udu$$

$$\text{v} = -u \frac{du}{dP} \qquad (2)$$

بتعويض المعادلة (2) في (1) نحصل على

$$\frac{dA}{A} + \frac{du}{u} = \frac{-u\frac{du}{dP}d\text{v}}{\text{v}^2}$$

$$\frac{dA}{A} + \frac{du}{u} = \frac{udu}{-\text{v}^2 \left(\frac{\partial P}{\partial \text{v}}\right)_s}$$

$$\frac{dA}{A} = \frac{udu}{u_{max}^2} - \frac{du}{u}$$

$$\Delta H + \frac{\Delta u^2}{2} + g\Delta Z = Q - W$$

$$\Delta H + \Delta u^2 = Q$$

$$dH + udu = Q$$

$$dH = TdS + \text{v}dP$$

$$dQ = 0$$

$$dS = 0$$

$$dH = \text{v}dP$$

بالتعويض في المعادلة (1)

$$\text{v}dP + udu = 0$$

$$-\text{v}dP = udu$$

Chapter 8   *Production of Power from Heat*

8.1 THE STEAM POWER PLANT
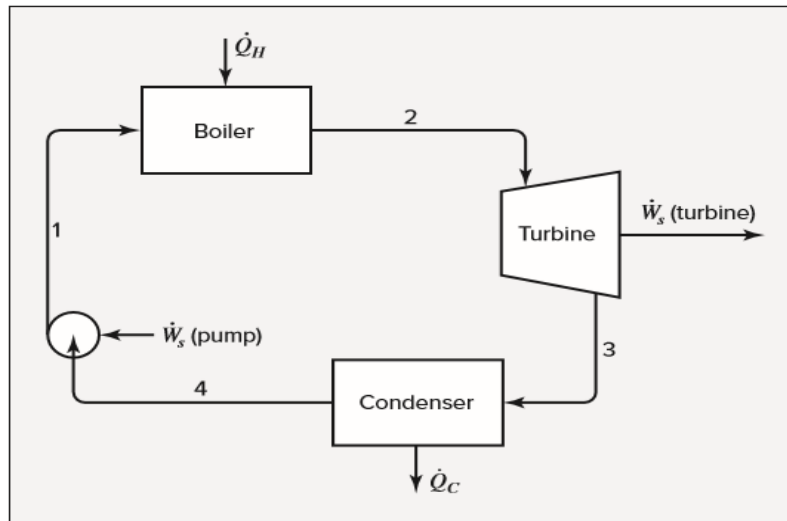
Figure 8.1: Simple steam power plant.

In this chapter we can study three types of cycles Steam power plants in relation to the Carnot, Rankine and Practical regenerative cycles.

1- *Carnot cycle*
2- *Rankine cycle*
3- *Practical cycle*

1- *Carnot cycle*

(Step 1-2) in a boiler at constant temp. and pressure.

(Step 2-3) in a turbine at constant entropy.

(Step 3-4) in condenser at constant temp. and pressure.

(Step 4-1) in pump at constant entropy.

$$\eta_{\text{Carnot}} = 1 - \frac{T_C}{T_H}$$
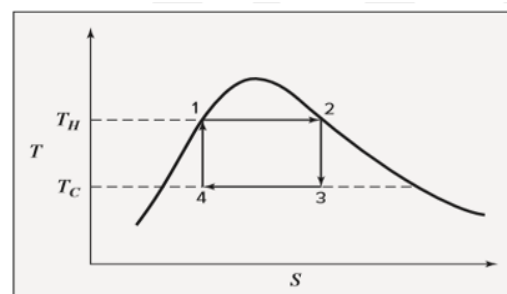
Figure 8.2: Carnot cycle on a TS diagram

Figure 8.1 shows a simple steady-state steady-flow cyclic process in which steam generated in a boiler is expanded in an adiabatic turbine to produce work.

The discharge stream from the turbine passes to a condenser from which it is pumped adiabatically back to the boiler.

The processes that occur as the working fluid flows around the cycle are represented by lines on the TS diagram of Fig. 8.2. The sequence of these lines conforms to a Carnot cycle, as described in Chapter 5. The operation as represented is reversible, consisting of two isothermal steps connected by two adiabatic steps.

➢ Step 1 → 2 is isothermal vaporization taking place in a boiler at temperature T_H, wherein heat is transferred to saturated-liquid water at rate Q_H, producing saturated vapor.

➢ Step 2 → 3 is reversible adiabatic expansion of saturated vapor in a turbine producing a two-phase mixture of saturated liquid and vapor at T_C. This isentropic expansion is represented by a vertical line.

➢ Step 3 → 4 is an isothermal partial-condensation process at lower temperature TC, wherein heat is transferred to the surroundings at rate Q_C.

➢ Step 4 → 1 is an isentropic compression in a pump. Represented by a vertical line, it takes the cycle back to its origin, producing saturated liquid water at point 1.

The power produced by the turbine W turbine is much greater than the power requirement of the pump W pump,

The net power output is equal to the difference between the rate of heat input in the boiler and the rate of heat rejection in the condenser.

The thermal efficiency of this cycle is:

$$\eta_{Carnot} = 1 - \frac{T_C}{T_H} \qquad (5.7)$$

Clearly, η increases as T_H increases and as T_C decreases. Although the efficiencies of practical heat engines are lowered by irreversibilities, it is still true that their efficiencies are increased when the average temperature at which heat is absorbed in the boiler is increased and when the average temperature at which heat is rejected in the condenser is decreased.

2- *The Rankine Cycle*

The thermal efficiency of the Carnot cycle just described and given by Eq. (5.7) could serve as a standard of comparison for actual steam power plants. However, severe practical difficulties attend the operation of equipment intended to carry out steps 2 → 3 and 4 → 1.

Turbines that take in saturated steam produce an exhaust with high liquid content, which causes severe erosion problems. Even more difficult is the 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 cycle is taken as the standard, at least for fossil-fuel-burning power plants. It is called the Rankine cycle, and it differs from the cycle of Fig. 8.2 in two major respects. First, the heating step 1 → 2 is carried well beyond vaporization so as to produce a superheated vapor, and second, the cooling step 3 → 4 brings about complete condensation, yielding saturated liquid to be pumped to the boiler. The Rankine cycle therefore consists of the four steps shown in   Fig. 8.3 and described as follows:

- ➢ 1 → 2 A **constant-pressure** heating process in a boiler. The step 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.
- ➢ 2 → 3 **Reversible, adiabatic (isentropic)** expansion of vapor in a turbine to the pressure of the condenser. The step normally crosses the saturation curve, producing a wet exhaust. However, the superheating accomplished in step 1 → 2 shifts the vertical line far enough to the right on Fig. 8.3 that the moisture content is not too large.
- ➢ 3 → 4 A **constant-pressure, constant-temperature process** in a condenser to produce saturated liquid at point 4.
- ➢ 4 → 1 **Reversible, adiabatic (isentropic) pumping** of the saturated liquid to the pressure of the boiler, producing compressed (subcooled) liquid. The vertical line (whose length is exaggerated in Fig 8.3) is very short because the temperature rise associated with compression of a liquid is small.
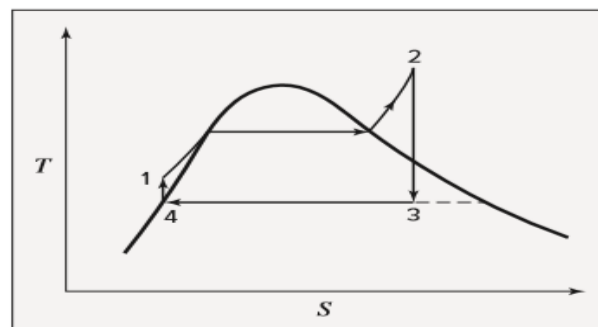
Figure 8.3: Rankine cycle on a TS diagram.

3- *Practical power cycle.*

Power plants actually operate on a cycle that departs from the Rankine cycle **due to irreversibilities of the expansion and compression steps.**
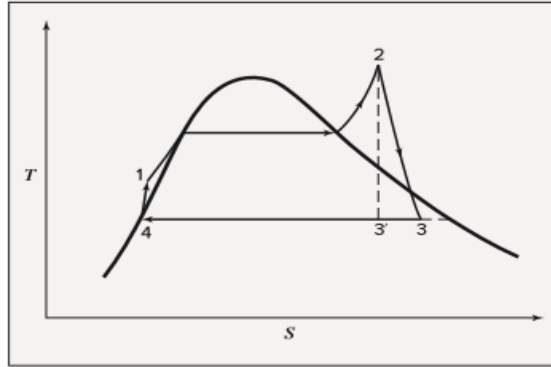

Figure 8.4: Simple practical power cycle.

Figure 8.4 illustrates the effects of these irreversibilities on steps $2 \to 3$ and $4 \to 1$. The lines are no longer vertical but **tend in the direction of increasing entropy.**

The **turbine exhaust** is normally still wet, but with sufficiently low moisture content, 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 (or from a nuclear reactor or even a solar-thermal heat source) to the cycle, and the condenser transfers heat from the cycle to the surroundings.

Neglecting kinetic- and potential-energy changes reduces the energy relations, Eqs. (2.30) and (2.31), to:

$$Q^{°} = m^{°} \Delta H \qquad (8.1) \qquad \&\&\& \qquad Q = \Delta H \qquad (8.2)$$

Turbine and pump calculations were treated in detail in Secs. 7.2 and 7.3.

Example 8.1:

Steam generated in a power plant at a pressure of 8600 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 carnot engine operating at the same temperature levels?
b) What is the thermal efficiency of a Rankine cycle operating at these conditions?
c) What is the thermal efficiency of a practical cycle operating at these conditions if the turbine efficiency and pump efficiency are both 0.75?
d) If the rating of the power cycle of part (c) is 80,000 kW, what is the steam rate and what are the heat-transfer rates in the boiler and condenser?

(a) *Carnot efficiency:*

$T_H = 500+ 273 = 773$ K
T_C = sat. Temp. at 10 kPa $t^{sat} = 45.83 \, °C$

$$\eta_{carnot} = \frac{T_H - T_C}{T_H} = \frac{773 - 318}{773} = 0.587$$

(b) **Rankine cycle:**

Point 2:

The enthalpy and entropy of superheated steam at 8,600 kPa and 500°C is:

H 2 = 3391.6 KJ.kg $^{-1}$

S2 = 6.6858 KJ.kg $^{-1}$.K^{-1}
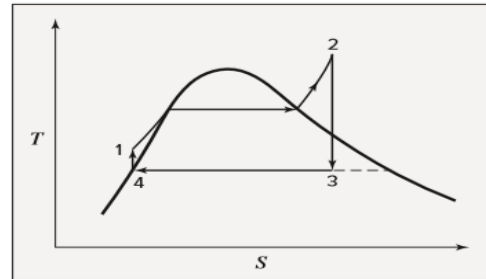
Point 3:
S3"= S2= 6.6858

If the expansion to 10 kPa is isentropic, then, S3 ′ = S₂ = 6.6858 kJ ·kg $^{-1}$ ·K $^{-1}$.
Steam with this entropy at 10 kPa is wet.

$$S^{sat} = 8.1511$$

$$S_3" < S^{sat} \rightarrow TWO\ PHAS$$
$$S_3" = X\ S^V + (1 - X)S^L$$
$$6.6858 = X(S^V - S^L) + S^L \rightarrow$$
$$6.6858 = X(8.1511 - 0.6493) + 0.6493 \rightarrow$$
$$X = 0.804$$

$$H_3 = X\ H^V + (1 - X)H^L$$

$$H_3 = X(H^V - H^L) + H^L \rightarrow$$
$$H_3 = 0.804(2584 - 191.8) + 191.8 = 2117.4 \ KJ.Kg^{-1}$$

$$\mathbf{H_3} = 2117.4 \text{ kJ·kg} -1$$

Point 4:

The enthalpy of **saturated liquid** condensate at 10 kPa (and t ^{sat} = 45.83° C) is:

H 4 = 191.8 KJ.kg $^{-1}$

$$V_4 = 1.01 \times 10^{-3} \ m^3.Kg^{-1}$$
$$W_P = V_4(P_4 - P_1) = (1.01 \times 10^{-3})[10 - 8600] = -8.67 \ KJKg^{-1}$$

$$W_P = (H_4 - H_1) \rightarrow \ H_1 = H_4 - W_P = 191.8 + 8.67 = 200.47 \ KJKg^{-1}$$

$$H_1 = 200.47 \ KJKg^{-1}$$

$$W_T = (H_2 - H_3) = 3391.6 - 2117.4 = 1274.2 \ KJKg^{-1}$$

Q$_H$ (boiler) = H 2 − H 1 = 3391.6 − 200.5 = 3191.1 KJ.kg $^{-1}$

$$\eta_{Cycle} = \frac{W_{net}}{Q_H} = \frac{W_P + W_T}{Q_H} = \frac{-8.67 + (3391.6 - 2117.4)}{(3391.6 - 200.47)} = \frac{W_P + (H_2 - H_3)}{(H_2 - H_1)} = 0.396$$

(C)

a turbine efficiency $\eta_T = 0.75$ & Pump efficiency $\eta_p = 0.75$

H 2 = 3391.6 KJ.kg $^{-1}$

$$\mathbf{H3"} = 2117.4 \text{ kJ} \cdot \text{kg} - 1$$

$$(W_T)_S = -\Delta H_S = (H_2 - H_3")$$
$$= 3391.6 - 2117.4$$
$$= 1274.2 \ KJKg^{-1}$$

$$\eta_T = \frac{(W_T)_{act.}}{(W_T)_S}$$
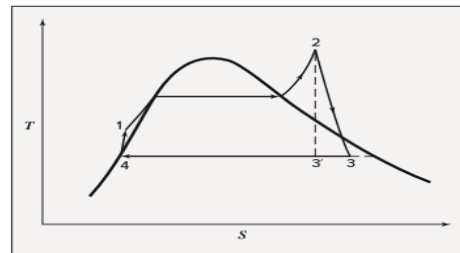
$$(W_T)_{act.} = \eta_T(W_T)_S = 0.75(1274.2) = 955.65 \ KJKg^{-1}$$

$$(W_T)_{act.} = (H_2 - H_3) \rightarrow$$

$$H_3 = H_2 - (W_T)_{act.} = 3391.6 - 955.65 = 2435.95 \ KJKg^{-1}$$

$$H_4 = 191.8 \ KJKg^{-1} \qquad from \ the \ previous \ branch$$

$$\eta_{P \ act} = \frac{(W_P)_S}{(W_P)_{act}}$$

$$(W_P)_{act} = \frac{(W_P)_S}{\eta_P} = \frac{V_4(P_4 - P_1)}{\eta_P} = \frac{-1.01 \times 10^{-3}(10 - 8600)}{(0.75)} = -11.56 \ KJKg^{-1}$$

but $(W_P)_{act.} = (H_4 - H_1) \rightarrow$

$$H_1 = H_4 - (W_p)_{act.} = 191.8 + 11.56 = 203.3 \ KJKg^{-1}$$

$$\eta_{Cycl} = \frac{W_{net}}{Q_H} = \frac{W_T + W_P}{Q_H} = \frac{955.65 - 11.56)}{(3391.6 - 203.3)} = \frac{W_T + W_P}{(H_2 - H_1)} = 0.296$$

$$Q_C = \Delta H = H_4 - H_3 = 191.8 - 2435.95 = -2244.15 \ KJKg^{-1}$$

Which may be compared with the result of part (b).

(D) For a power rating of 80,000 kW:

$$W_S^\circ(net) = m^\circ W_S(net)$$

$$or \qquad m^\circ = \frac{Ws^\circ}{Ws \ (net)} = \frac{Ws^\circ}{W_T - W_P} = \frac{80,000 \ KJ.S^{-1}}{944.0 \ KJ.Kg^{-1}} = 84.75 \ \ kgS^{-1}$$

$$Q_H^\circ(Boiler)$$

$$Q_H^\circ = Q_H \times m^\circ = (H_2 - H_1)m^\circ = (3391.6 - 203.3)84.75 = 270 \times 10^3 KJs^{-1}$$

$$Q_C^\circ(Condenser)$$

$$Q_C^\circ = Q_C \times m^\circ = (H_4 - H_3)m^\circ = (-2244.15) \ 84.75 = -190.07 \times 10^3 KJs^{-1}$$

Note that

Q ˙ (boiler) + Q ˙ (condenser) = − W˙s (net)

Example 8.2:

Steam enters the turbine of a power plant operating on Rankine cycle at 3500 kPa, and exhaust at 20 kPa. Determine the cycle efficiency and the quality of the steam exit from the turbine. If the turbine inlet temp. is 400 °C.

Solution

POINT 2:
T= 400 °C.
P=3500 KPa
From S.T.:
H2=3222.5
S2= 6.8294
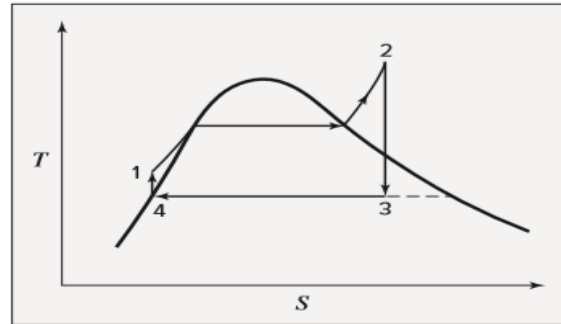
Point 3:
S3'= S2= 6.8294

$$S_3 < S^V \quad \rightarrow TWO\ PHAS$$
$$S_3'' = X\ S^V + (1 - X)S^L$$
$$6.8 = X(S^V - S^L) + S^L \rightarrow$$
$$6.8 = X(7.9 - 0.832) + 0.832 \rightarrow$$
$$X = 0.849$$

$$H_3 = X\ H^V + (1 - X)H^L$$
$$H_3 = X(H^V - H^L) + H^L \rightarrow$$
$$H_3 = 0.849(2609 - 251) + 251 = 2253\ \ KJ.Kg^{-1}$$

POINT4:
$$H_4 = 251.4\ \ KJ.Kg^{-1}$$
$$V_4 = 1.017 \times 10^{-3}\ \ m^3.Kg^{-1}$$
$$W_P = V_4(P_4 - P_1) = (1.017 \times 10^{-3})[20 - 3500] = -3.53\ KJKg^{-1}$$

$$W_P = (H_4 - H_1) \rightarrow H_1 = H_4 - W_P = 251.14 + 3.53 = 247.6$$

$$H_1 = 247.6\ \ KJKg^{-1}$$

$$\eta_C = \frac{W_{net}}{Q_H} = \frac{W_P + W_T}{Q_H} = \frac{-3.53 + (3222.5 - 2253)}{(3222.5 - 247.6)} = \frac{W_P + (H_2 - H_3)}{(H_2 - H_1)} = 0.32$$

$$\eta_{Carnot} = \frac{T_H - T_C}{T_H} = \frac{(400 + 273) - (60.09 + 273)}{(400 + 273)} = 0.5$$

Chapter *9*   **Refrigeration and Liquefaction**

<u>Refrigeration:</u> means the maintenance of a temperature below that of the surrounding. Refrigeration system absorber heat at a given temp and discharges it at higher temp.

Carnot heat pump or refrigerator.
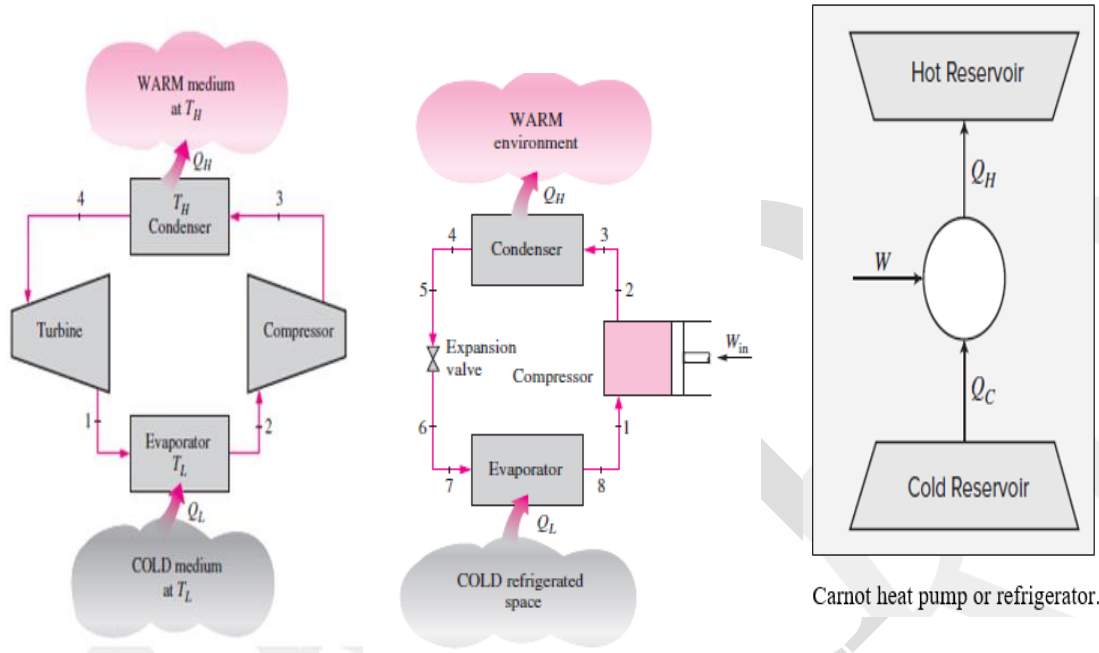
<u>Coefficient of performance C.O.P:</u>

It is defined as the efficiency of the refrigeration cycle i.e. the rate of the heat absorbed in the low level reservoir (freezer) to the network input to the cycle refrigeration cycle.

$$C.O.P = \frac{Q_A}{wnet} = \frac{Q_A}{Q_R - Q_A}$$

<u>*Refrigeration Capacity*</u>$(Q_A^°)$: It is defined as the rate of heat $(\frac{KJ}{S}, \text{kw}, \frac{Btu}{hr}, ton .....)$ **absorbed from the cold source** some time defined as the **refrigeration rate**

Mass rate of refrigeration ($m^°$): the Mass rate flow of refrigeration needed to accomplish a given Refrigeration capacity.

$$Refrigeration\ capacity = \ Q_A\ m^° \rightarrow Capacity_{ton} = \frac{Q_A . m}{12000} \qquad = \frac{Btu/Ibm\ \ Ibm/hr}{12000}$$

$$Q_A^° = Q_A * m^°$$

ملاحظه : في بعض الاحيان قد تعطى المعلومات بالوحدات البريطانية وال capacity بالوحدة ال ton

في هذه الحالة يجب تحويل ال ton الى Btu/hr

$$ton * 12000 = \frac{Btu}{hr} \qquad\qquad \boldsymbol{ton = \ 3.5 \ kw}$$

Capacity of refrigeration: is usually given in tons of refrigeration, this term had it's original in the ice making industry where cooling capacity was given in term of tons of ice melting per day.

Ton of refrigeration: is defined as a rate of heat absorbed to change ton of water at 32°F to ice at 32°F in one day.

The Choice of Refrigerant:
The factors that should be considered in the working fluid circulated during the cycle.
Such characteristics as **toxicity**, **flammability**, **cost**, **corrosion properties**, and vapor pressure are of greater importance in the choice of refrigerant.
Moreover, So that air cannot leak into the refrigeration system, the vapor pressure of the refrigerant at the evaporator temperature should be greater than atmospheric pressure.

علاوة على ذلك ، حتى لا يتسرب الهواء إلى نظام التبريد ، يجب أن يكون ضغط بخار مادة التبريد عند درجة حرارة المبخر أكبر من الضغط الجوي.

These many requirements limit the choice of refrigerants to relatively few fluids.
Example 1:
A refrigeration machine required 57 Btu/min of power per ton of refrigeration, assuming the heat load is always 200 Btu/Ibm what is:-

1- Refrigerant circulation rat (m°).
2- C.O.P.

Solution:

Q_A =200 Btu/lbm   , W= 57 Btu/min

$$Capacity \qquad Q_A^{\circ} = 1 \ ton \ = \ 12000 \ Btu/hr$$

$$Q_A^{\circ} = m^{\circ} Q_A$$

$(a) \quad m^{\circ} = \frac{Q_A^{\circ}}{Q_A} = \frac{12000}{200} = 60 \ lbm/hr.$

$(b) \qquad C.O.P = \frac{Q_A^{\circ}}{W^{\circ}} = \frac{12000 \frac{Btu}{hr} * \frac{1}{60}}{57 \ Btu/min} = 3.5 \ .$

2

Types of refrigeration cycle
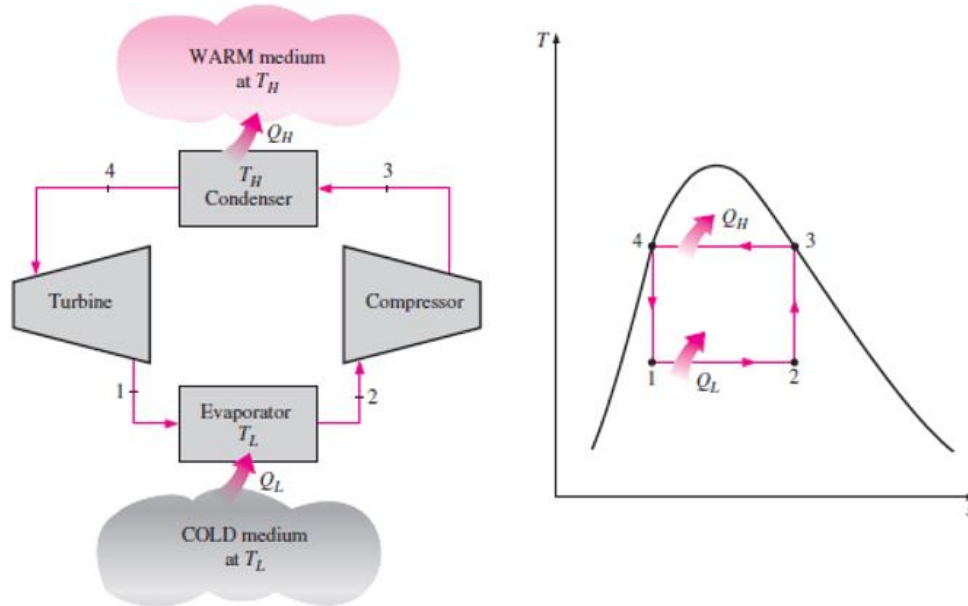
1- Carnot cycle (reverse Carnot cycle).

Figure 1. The Carnot Refrigerator and the Reversed Carnot Cycle

Step 2-3: **Isentropic** *compression of wet vapour*
Step 3-4: **Isothermal** *heat rejection at constant T.*
Step 4-1: **Isentropic** *expansion of sat. liquid.*
Step 1-2 **Isothermal** *heat addition (absorbed) at const. T&P.*

$$C.O.P = \frac{T_c}{T_H - T_c} \qquad unit\ of\ T\ in\ k°\ OR\ R°\ only$$

2- *Vapour – compression cycle*

A- *With Turbine as unit of expansion*
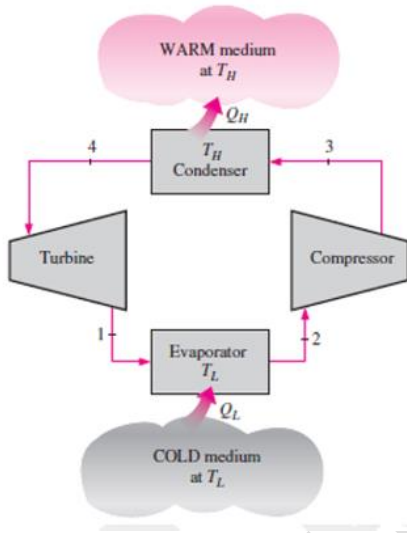
Block diagram.

Step 1-2   *Evaporator, Constant temp, and pressure*

$Q_A = H_2 - H_1$

Step 2-3   *Compressor*

$W_{act} = H_2 - H_3$ *if the compressor has efficiency*

$(w)_s = H_2 - H_3^-$ *ideal work*

Compressor efficiency $= \dfrac{ideal\ work}{actual\ work}$

<div dir="rtl">ملاحظه: اذا لم يذكر شي عن كفاءة الضاغطة فتؤخذ الكفاءة على انها 100%</div>

step 3−4   *Condenser, constant pressure.*
$Q_R = H_4 - H_3$

Step 4-1   *Turbine, isentropic ($\eta_T = 100\%$)*

$$C.O.P = \frac{Q_A}{W_{net}} = \frac{Q_A}{|Q_R| - Q_A}$$

$$\therefore cop = \frac{H_2 - H_1}{(H_3 - H_4) - (H_2 - H_1)}$$

4

B- With expansion valve: (ideal cycle vapor compression).
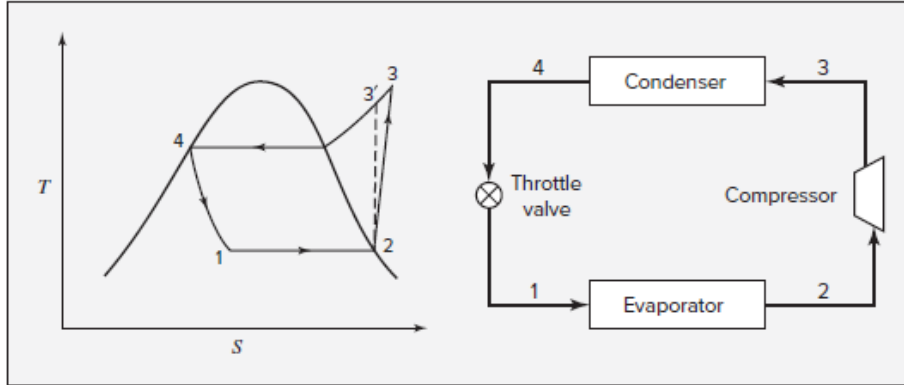
Figure 9.1: Vapor-compression refrigeration cycle.

$$C.O.P = \frac{H_2 - H_1}{H_3 - H_2}$$

ملاحظه : اذا لم يذكر شيئ عن نوع الدورة فتؤخذ على انها نوع B

ملاحظات : تختلف هذه الدورة عن دورة كارنوت كون ظروف النقطة (3) اي ظروف الدخول الى condenser هو بخار محمص super heated وليس بخار مشبع كما في كارنوت

- في الدورة A يكون التمدد بواسطة Turbine اي $\Delta s = 0$
- في الدورة B يكون التمدد بواسطة Throttling valve اي $\Delta H = 0$

Example 2:

Consider an ideal refrigeration cycle that utilize fereon-12. As the working fluid the temperature of the refrigeration in the evaporator is 0°F and in the condenser is 100 °F, the refrigeration is circulated at a rate of 200 lbm/hr, Determine:

1- C.O.P
2- Capacity of the plant in tons of refrigeration.
3- C.O.P of Carnot.

Solution:

ملاحظة : هنا لم يذكر شيئ عن كفاءة المكيس فيؤخذ على انها 100% اي ان المكيس يحدث isentropic

$$\Delta s = 0$$

$$cop = \frac{H_2 - H_1}{H_3 - H_2}$$

Point 2: sat. vapor

$$H_2 = 77.27 \; {}^{Btu}/_{lbm}$$

(see text book, page 280)

$$S_2 = 0.1689 \; {}^{Btu}/_{lbm.R}$$

Point 4: Sat. liquid at 100°F , P^{sat} =131.86 ps

$$H_4 = 31.1 \; Btu/hr \qquad under \; sat. liquid$$

H$_4$ =H$_1$ (throttling valve $\Delta H = 0$

Point 3 : super-heated vapor (isentropic compression) $s_2 = s_3 = 0.1689 \; {}^{Btu}/_{lbm} .R$

$$from \; S_2 \& P_3 \rightarrow H_3 = 90.3 \; {}^{Btu}/_{lbm} \; \text{(Fig 9.3) page 282}$$

1- $cop = \frac{H_2 - H_1}{H_3 - H_2} = \frac{77.27 - 31.1}{90.3 - 77.27} = 3.55$

2- Capacity $Q_A^{°} = Q_A * m^{°}$

$Q_A = H_2 - H_1 = 77.27 - 31.1 = 46.17 \; {}^{Btu}/_{lbm}$

$capacity = 46.17 * 200 = 9234 \; {}^{Btu}/_{hr}$

$= \dfrac{9234}{12000} = 0.769 \; ton$

$C.O.P = \dfrac{T_c}{T_H - T_C} = \dfrac{0 + 46}{100 - 0} = 4.6$

Example 3:
A refrigeration system requires 1 KW of power for a refrigeration rate of 3 KJ/S.

- a- What is the coefficient of performance?
- b- How much heat is rejection from the system?
- c- If the heat rejection is at 35℃, what is the lowest temperature.

The system can possibly maintain?

$$cop_{cor} = \frac{T_C}{T_H - T_C}$$

Solution:

a- $cop = \dfrac{Q_A}{W_{net}} = \dfrac{3}{1} = 3$

b- Q$_R$ = W+Q$_A$ = 3+1 = 4 KJ/s

c- $(cop)_{carn} = \dfrac{T_C}{T_H - T_C} = \dfrac{T_C}{308 - T_C}$

$\rightarrow T_C = 231 \; K^{°}$

$\dfrac{T_H - T_C}{T_C} = \dfrac{1}{cop}$

$\dfrac{T_H}{T_C} - 1 = \dfrac{1}{3}$

$\dfrac{T_H}{T_C} = \dfrac{1}{3} + 1$

$\dfrac{3}{4} T_H = T_C$

Plotting of ideal compression cycle on
T- S,   P- H,   P-V diagrams:

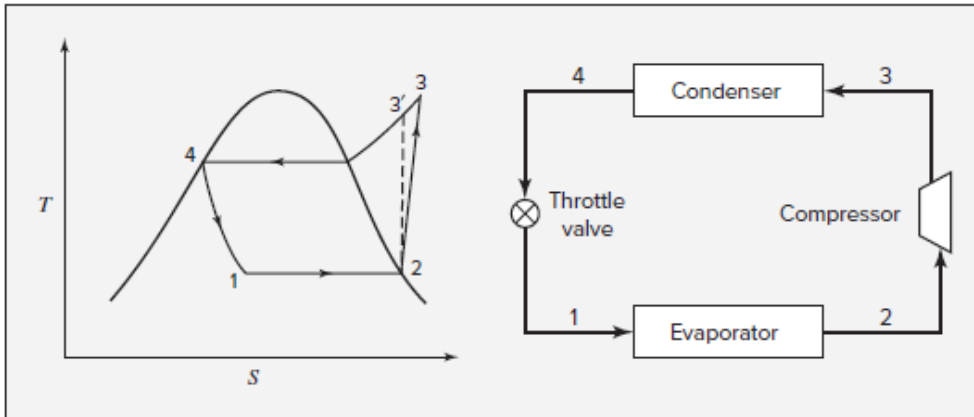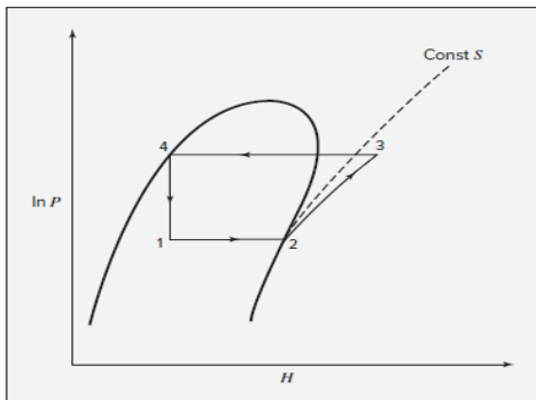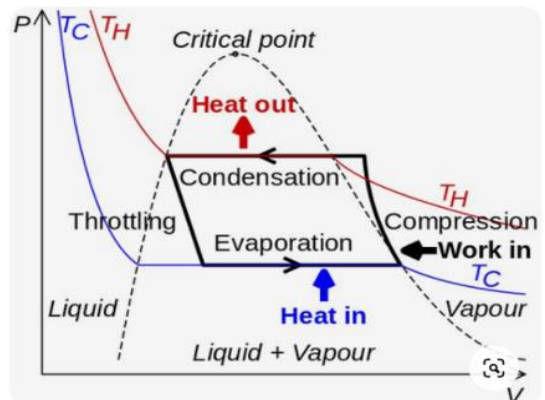**Figure 9.1**: Vapor-compression refrigeration cycle.

Step 1-2 constant p
Step 4-1 const. H
Step 4-3 const. P
Step 2-3 nearly const. S

P-H diagram

P-V   diagram.

Example 5:

A refrigeration uses **refrigeration -12** as the working fluid and operate an ideal vapour-compressor refrigeration cycle between $0.12 \ and \ 0.7 \ Mpa$. The mass flow rate of the refrigeration is $0.1 \ ^{kg}/_{s}$. Show the cycle on a T-S diagram with respect to **saturation lines**. Determine:

7

a- The rate of heat removal from the refrigeration space and the power input to the compressor.
b- The rate of heat rejected to the environment.
c- The coefficient of performance

Solution:

M=0.1 kg/s=0.22 lbm/s
0.7 MPa=102.9 psi
0.12 Mpa=17.64 psi

Point 2
Saturated vap.
$H_2 = 75.76 \ ^{Btu}/_{lbm}$
$S_2 = 0.1703 \ ^{Btu}/_{lbmR°}$

Point 4
Saturated liquid
P4=102.9 psi, H4=26.83 = H1 (since expansion value)

Point 3
$P_3 = 102.9 \ psi$ from fig 9-3
$S_2 = S_3 = 0.1703$ H3=89 Btu/lbm

$Q_A = \Delta H = H_2 - H_1 = 75.76 - 26.83 = 48.93 \ ^{Btu}/_{lbm \ R}$
$Q_A^° = 48.98 * 0.22 = 10.76 \ ^{Btu}/_{sec.}$

$w = -\Delta H$
$w = -(H_3 - H_2) = H_2 - H_3 = 75.76 - 89 = -13.24 \ ^{Btu}/_{lbm}$
$w^° = -13.24 * 0.22 = -2.91 \ ^{Btu}/_{sec.}$

$Q_R = \Delta H = H_4 - H_3 = 26.83 - 89 = -62.17 \ ^{Btu}/_{lbm}$

$Q_R^° = -62.17 * 0.22 = -13.6 \ ^{Btu}/_{sec.}$

$$cop = \frac{H_2 - H_1}{H_3 - H_2} = \frac{75.76 - 26.83}{89 - 75.76} = \frac{48.93}{13.24} = 3.69.$$

*** **Modification of vapor compression Refigration**

1- Adding Heat Exchanger

Addition of heat exchanger to exchange heat between liquid comings from condenser with vapor coming from evaporator.

اضافة مبادل حراري لاستخدامه في عملية التبادل الحرارة بين السائل القادم من المكثف مع البخار القادم من المبخر

The vapor from evaporator will be heated to higher temperature before reaching the compressor and this will be effect on (work and COP), the work of the compressor will be less and COP will be higher.

البخار القادم من المبخر سوف يسخن الى اعلى درجة حرارية ممكنة قبل وصوله الى الضاغطة وهذا بدوره سوف يؤثر على الشغل ومعامل الاداء .. حيث يقلل من الشغل المبذول على الضاغطة وزيادة معامل الاداء.......
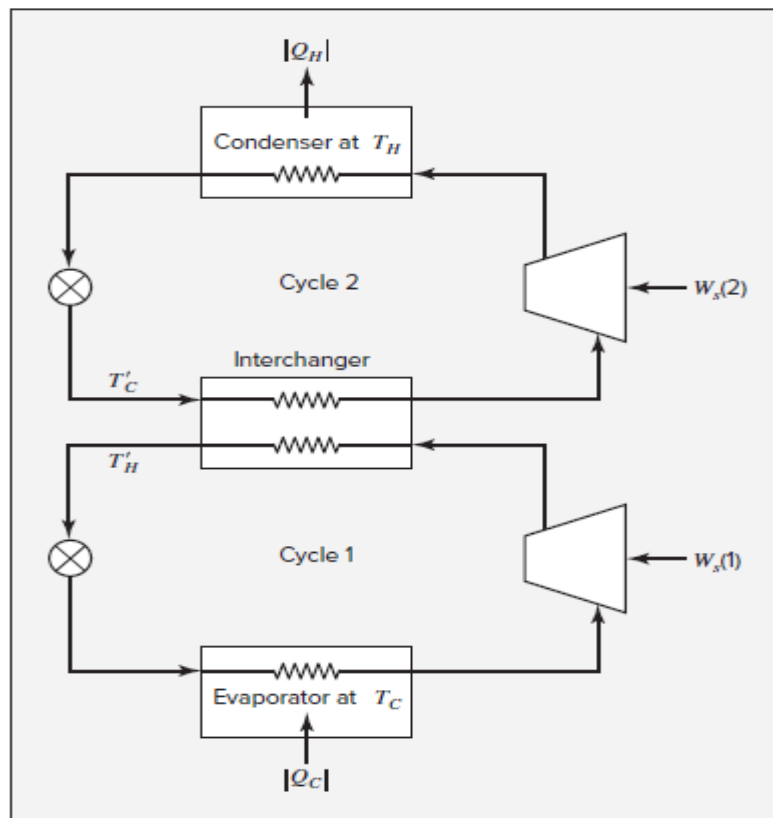
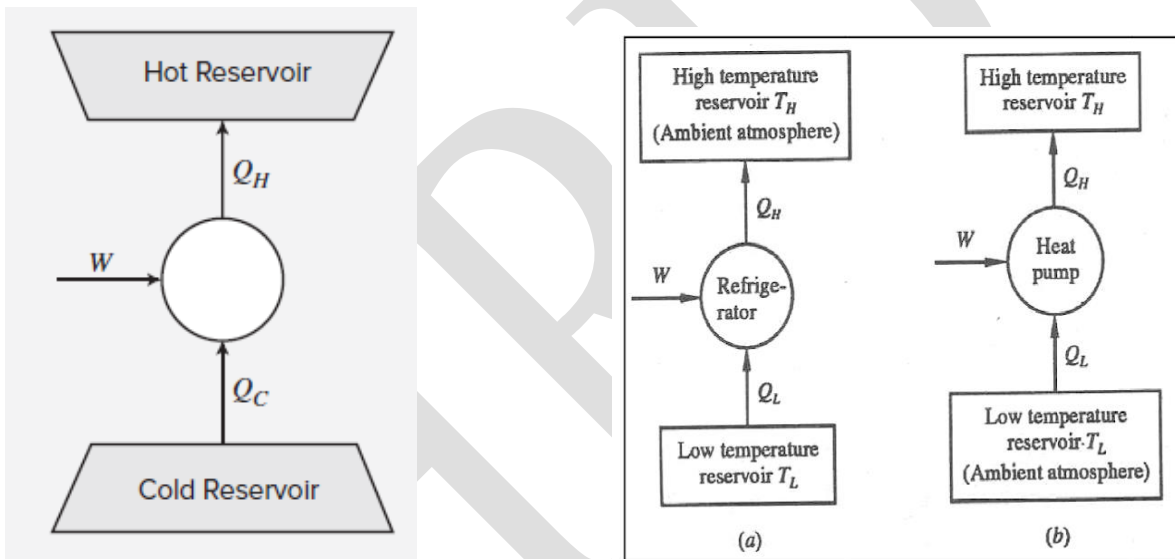

Figure 9.3: A two-stage cascade refrigeration system.

2- **Heat pump:** is a reverse heat engine and defined as a device for heating houses and commercial building during the winter and cooling during the summer.

For heat pump.

$$cop = \frac{Q_R}{w} = \frac{Q_R}{Q_A - Q_R}$$

For heat pump (max. efficiency)

$$cop = \frac{T_H}{T_H - T_C}$$

Schematic Diagram of Refrigerator(a) and Heat Pump (b)

$$\mathbf{Q_H = Q_R} ;\quad \boldsymbol{Q_A = Q_C = Q_L}\quad \textit{Note}$$

Example 4:

Determine the **maximum possible C.O.P** for a cycle heat pump that is to **pump heat** from an ambient temp. of *Zero* 0 °C to the interior of a house at 20 °C ?

Repeat for an ambient temp. of −20 °C.

Solution:

Heat pump $T_H = 20°C$ $T_c = 0$

a- $cop = \dfrac{Q_R}{w} = \dfrac{Q_R}{Q_R - Q_A} = \dfrac{T_H}{T_H - T_C}$

$$cop = \frac{20 + 273}{(20 + 273) - (0 + 273)} = 14.65$$

b- $T_H = 20°C$ $T_c = -20$

$$cop = \frac{293}{293 - (-20 + 273)} = 7.32$$

Example 9.2

A house has a winter heating requirement of 30 kJ·s−1 and a summer cooling requirement of 60 kJ·s−1. Consider a heat-pump installation to maintain the house temperature at 20°C in winter and 25°C in summer. This requires circulation of the refrigerant through interior exchanger coils at 30°C in winter and 5°C in summer. Underground coils provide the heat source in winter and the heat sink in summer. For a year-round ground temperature of 15°C, the heat-transfer characteristics of the coils necessitate refrigerant temperatures of 10°C in winter and 25°C in summer. What are the minimum power requirements for winter heating and summer cooling?

Solution 9.2

The minimum power requirements are provided by a Carnot heat pump. For winter heating, the house coils are at the higher-temperature level *TH*, and the heat requirement is *QH* = 30 kJ·s−1. Application of Eq. (5.4) gives:

$$Q_C = -Q_H \frac{T_C}{T_H} = 30\left(\frac{10 + 273.15}{30 + 273.15}\right) = 28.02 \text{ kJ·s}^{-1}$$

This is the heat absorbed in the ground coils. By Eq. (9.1),

$$W = -Q_H - Q_C = 30 - 28.02 = 1.98 \text{ kJ·s}^{-1}$$

Thus the power requirement is 1.98 kW.

For summer cooling, *QC* = 60 kJ·s−1, and the house coils are at the lower temperature level *TC*. Combining Eqs. (9.2) and (9.3) and solving for *W*:

$$W = Q_C \frac{T_H - T_C}{T_C} = 60\left(\frac{25 - 5}{5 + 273.15}\right) = 4.31 \text{ kJ·s}^{-1}$$

The power requirement here is therefore 4.31 kW. Actual power requirements for practical heat pumps are likely to be more than twice this lower limit.

3- ABSORPTION REFRIGERATION

The Absorption refrigeration machine which used to absorption the high temperature from heat engine that used to generators power for compresser and this may be based on the following.

$$C.O.P = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C} \qquad OR \qquad \frac{W}{Q_C} = \frac{T_S - T_C}{T_C}$$

The work of a compressor (W) may be obtaind from heat engine operating between T_S & T_H

    $When \qquad T_S = The\ temp.\ of\ the\ surrounding$

$$\frac{Q_H}{W} = \frac{T_H}{T_H - T_S} \qquad OR \qquad \frac{W}{Q_H} = \frac{T_H - T_S}{T_H}$$

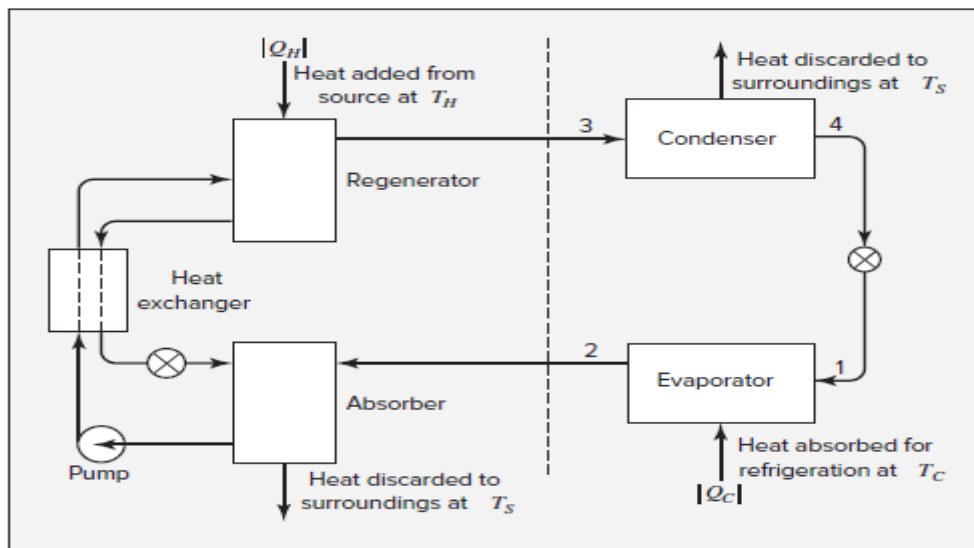$$and \qquad Q_H = W \frac{T_H}{T_H - T_S} = Q_C \frac{T_S - T_C}{T_C} \frac{T_H}{T_H - T_S}$$

Figure 9.4: Schematic diagram of an absorption-refrigeration unit.

EXAMPLE:

Calculate the minimum possible value of $\frac{Q_H}{Q_C}$ for the following system refrigeration at temperature level (-10 ℃) (TC = 263.15 K) and a heat source of condensing steam at atmospheric pressure (TH = 373.15 K). For a surroundings temperature of 30℃ (TS = 303.15 K).

Solution:

$$and \qquad Q_H = Q_C \left(\frac{T_S - T_C}{T_C}\right) \left(\frac{T_H}{T_H - T_S}\right)$$

$$\frac{Q_H}{Q_C} = \left(\frac{T_S - T_C}{T_C}\right) \left(\frac{T_H}{T_H - T_S}\right)$$

$$\frac{Q_H}{Q_C} = \left(\frac{303.15 - 263.15}{263.15}\right) \left(\frac{373.15}{373.15 - 303.15}\right) = 0.81$$

For an actual absorption refrigerator, the value would be on the order of three times this result.

Example :
Avapor – compression refrigeration system. The minimum temperature difference for heat transfer is (10 ℉). Ammonia is the refrigerat evaporating at (22 ℉) and condensing at 80 ℉, the heat load on the evaporater is 2000 Btu/sec. If the compressor efficiency is 75 percent.
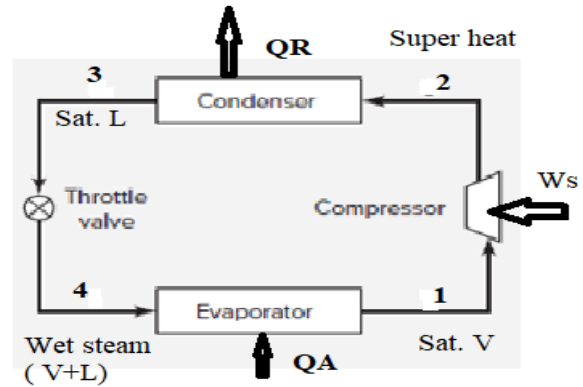Calculate:
1. coff.of performance (COP)
2. rate of circulation (m⁰)
3. Power (Ws)

For A// system without H.E.

B// system with H.E.

Solution:

At Point 1

$$S_1 = S_V = 1.2933 \ \text{Btu/lbm R}$$
$$H_2 = H_V = 618.33 \ \text{Btu/lbm}$$

$Obtian$ from fig $9-2$ $at\ temp.\ T1 = 22\ ^oF$

At   Point 2

Assume isentropic compressor $S_2^- = S_1 = 1.2933$

$$We\ find\ H_2^-\ from\ S_2^- \& p_2$$

$P^{sat.}at\ 80\ ^\circ F = 153$ $\&$ $P^{sat.}at\ 22\ ^\circ F = 50.36$ $from\ table\ 9.2\ page\ 285$

$\because\ P^{sat.}at\ 80\ ^\circ F\ is\ a\ known\ and\ intropy\ S_2^-\ also\ a\ known\ now\ we\ can\ get\ H_2^-\ from\ the\ figure$

$$H_2^- = 685 \ ^{Btu}/_{lbm}$$
$$W_s(isentropic) = -(H_2^- - H_1) = -(685 - 618.33) = -66.7 \ ^{Btu}/_{lbm}$$

$$W_s = \frac{W_s(isentropic)}{\eta} = \frac{-66.7}{0.75} = -88.89 \ ^{Btu}/_{lbm}$$

At Point 3

$T_3 = 80 ^\circ F$ $from\ table\ 9.2\ page\ 286$ $H_3 = H^L = 132 \ ^{Btu}/_{lbm}$

$\because Throttling\ valve\ (\ \Delta H = 0)\ \rightarrow\ H_4 = H_3 = 132 \ ^{Btu}/_{lbm}$

$$Q_A = H_1 - H_4 = 618.3 - 132 = 486 \ ^{Btu}/_{lbm}$$

$$(1) \qquad COP = \frac{Q_A}{-W_S} = \frac{486}{88.89} = 5.47$$

$(2)\ The\ rate\ of\ circulation\ (m^\circ)$ $m^\circ = \dfrac{Q_A^\circ}{H_1 - H_4} = \dfrac{2000 \ ^{Btu}/_{lbm}}{486 \ ^{Btu}/_{lbm}} = 4.19 \ ^{Ibm}/_{sec}$

$(3)\ Power\ (W_s)$ $W_s = -88.89 \ ^{Btu}/_{lbm} \times 4.19 \ ^{Ibm}/_{sec} = 372.94 \ ^{Btu}/_{sec}$

9.6 LIQUEFACTION PROCESSES:-

Liquefied gases are **used for a variety of purposes**. For example, liquid propane in cylinders serves as a domestic fuel, **liquid oxygen is carried in rockets**, natural gas is liquefied for ocean transport, and **liquid nitrogen provides low-temperature refrigeration**. Gas mixtures (e.g., air) are liquefied for separation into their component species by distillation.

Liquefaction results when a gas is cooled to a temperature in the two-phase region. This may be accomplished in several ways:-

1. By heat exchange at constant pressure.
2. By an expansion process from which work is obtained.
3. By a throttling process.

The first method requires a heat sink at a temperature lower than that to which the gas is cooled, and is most commonly used to precool a gas prior to its liquefaction by the other two methods. An external refrigerator is required for a gas temperature below that of the surroundings.

The **three methods** are illustrated in Fig. 9.5. The constant-pressure process (1) approaches the **two-phase region (and liquefaction)** most closely for a given drop in temperature.

*The throttling process (3) does not result in liquefaction unle*ss the initial state is at a low enough temperature and high enough pressure for the **constant-enthalpy process** to cut into the two-phase region. This is **indeed the situation for an initial state at** A′, but not at A, where the temperature is the same but the pressure is lower than at A.

The change of state from A to A′ may be accomplished by compression of the gas to the pressure **at B** and constant-pressure cooling to A′. Reference to **a PH diagram** for air6 shows that at a **temperature of 160 K**, the pressure must be **greater than about 80 bar for any liquefaction** to occur along a path of constant enthalpy.

***Thus, if air is compressed to at least 80 bar and cooled below 160 K, it can be partially liquefied by throttling. An efficient process for cooling the gas is by countercurrent heat exchange with that portion of the gas which does not liquefy in the throttling process.
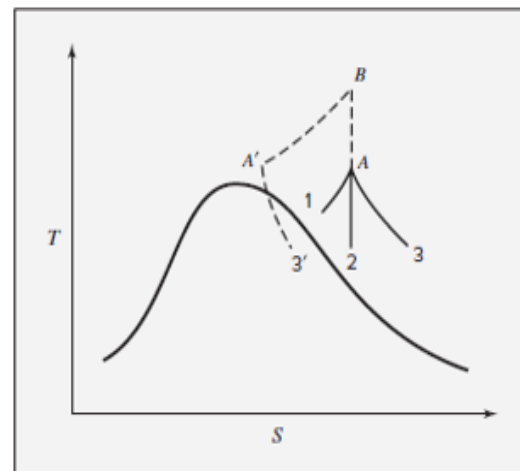

Figure 9.5: Cooling processes on a *TS* diagram.

وبالتالي ، إذا تم ضغط الهواء إلى 80 بار على الأقل وتبريده إلى أقل من 160 كلفن ، فيمكن تسييله جزئيًا عن طريق الاختناق. تتم عملية تبريد الغاز بكفاءة من خلال التبادل الحراري للتيار المعاكس مع ذلك الجزء من الغاز الذي لا يتحول إلى سائل في عملية الاختناق.

Liquefaction by isentropic expansion along process (2) occurs from lower pressures (for given temperature) than by throttling. For example, continuation of process (2) from initial state A ultimately results in liquefaction.

The throttling process (3) is commonly employed in small-scale commercial liquefaction plants. The temperature of the gas **must decrease during expansion**, and this indeed occurs with **most gases at usual conditions of temperature and pressure**. The exceptions are hydrogen and helium, which increase in temperature upon throttling unless the initial temperature is below about 100 K for hydrogen and 20 K for helium.

Liquefaction of these gases by throttling requires initial cooling to temperatures lower than obtained by method 1 or 2.

Liquefaction system:-

There are two main liquefaction system

1- Linde liquefaction process.
2- Claude liquefaction process

The Linde liquefaction process,

The simplest kind of liquefaction system, known as the Linde process.

Which depends solely on throttling expansion, is shown in Fig. 9.6. **After compression**, the gas is **precooled to ambient temperature**. It may be even **further cooled by refrigeration.** The lower the temperature of the gas entering the throttle valve, the greater the fraction of gas that is liquefied.

For example, a refrigerant evaporating in the cooler at −40°C provides a lower temperature at the valve than if water at 20°C is the cooling medium.
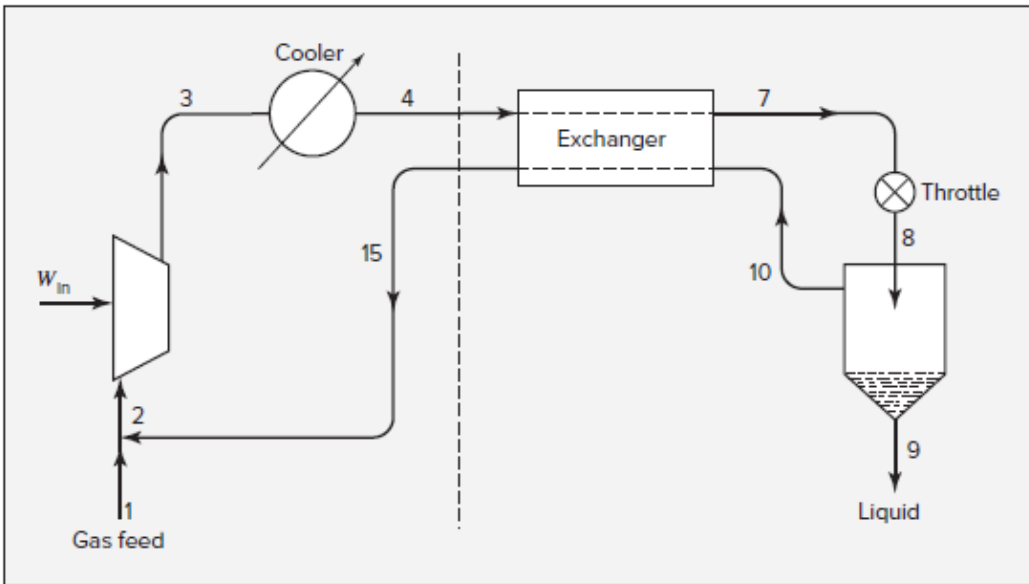
Figure 9.6: Linde liquefaction process.

Energy balance around the separator, throttling valve, and cooler gives:-

$$H_6 z + H_8 (1 - z) = H_3$$

$$H_9 z + H_{15} (1 - z) = H_4$$

Where z: the fraction of the gas that is liquefied

A more efficient liquefaction process would replace the throttle valve with an expander, but operating such a device into the two-phase region is impractical. **The Claude process**, shown in Fig. 9.7, is based in part on this idea. Gas at an intermediate temperature is extracted from the heat-exchange system and passed through an expander from which it exhausts as a saturated or slightly superheated vapor. The remaining gas is further cooled and throttled through a valve to produce liquefaction as in the Linde process.

The unliquefied portion, which is saturated vapor, mixes with the expander exhaust and returns for recycle through the heat-exchanger system.

An energy balance, Eq. (2.30), applied to that part of the process lying to the right of the dashed vertical line yields:

$$\dot{m}_9 H_9 + \dot{m}_{15} H_{15} - \dot{m}_4 H_4 = \dot{W}_{out}$$

If the expander operates adiabatically, $\dot{W}_{out}$ as given by Eq. (7.13) is:

$$\dot{W}_{out} = \dot{m}_{12}(H_{12} - H_5)$$

Moreover, by a mass balance, $\dot{m}_{15} = \dot{m}_4 - \dot{m}_9$. The energy balance, after division by $\dot{m}_4$, therefore becomes:

$$\frac{\dot{m}_9}{\dot{m}_4} H_9 + \frac{\dot{m}_4 - \dot{m}_9}{\dot{m}_4} H_{15} - H_4 = \frac{\dot{m}_{12}}{\dot{m}_4}(H_{12} - H_5)$$

With the definitions, $z \equiv \dot{m}_9/\dot{m}_4$ and $x \equiv \dot{m}_{12}/\dot{m}_4$, solution of this equation for z yields:

$$z = \frac{x(H_{12} - H_5) + H_4 - H_{15}}{H_9 - H_{15}} \qquad (9.7)$$

In this equation z is the fraction of the stream entering the heat-exchanger system that is liquefied, and x is the fraction of this stream that is drawn off between the heat exchangers and

Figure 9.7: Claude liquefaction process.

Example 9.2

Natural gas, assumed here to be pure methane, is liquefied in a simple linde process (Fig.9-6). Compression is to 60 bar and precooling is to 300 K. The separator is maintained at pressure of 1 bar, and un-liquefied gas at this pressure leaves the cooler at 295k. What fraction of the gas is liquefied in the process, and what is the temp. of high-pressure gas interring the throttling valve?

Solution:

Data for methane are given in perrye chemical engineering hand book from table of properties for superheated methane

$$H_3 4 = 1140 \ ^{kJ}/_{kg} \qquad (at \ 300 \ k \ \& \ 60 \ bar)$$

$$H_8 15 = 1188.9 \ ^{KJ}/_{Kg} \qquad (at \ 295 \ k \ \& \ 1 \ bar)$$

By interpolation in table of properties from sat. liq. & vap. We find for pressure of 1 bar that

$$T^{sat.} = 111.45 \ k \qquad at \ 1 \ bar$$

$$H_6 9 = 285.4 \ ^{kJ}/_{kg} \qquad (sat.liq.)$$

$$H_7 10 = 769.9 \ ^{KJ}/_{Kg} \qquad (sat.vap.)$$

From E.B.

Figure 9.6: Linde liquefaction process.

$$H_6 \ 9z + \ H_8 \ 15 \ (1 - z) = H_3 \ 4$$
$$H_6 z + \ H_8 - \ H_8 z = H_3$$
$$(H_6 - H_8) \ z = H_3 - \ H_8$$

$$\mathbf{z} = \frac{H_3 - H_8}{H_6 - H_8} = \frac{H_8 - H_3}{H_8 - H_6} = \frac{1188.9 - 1140}{1188.9 - 285.4} = \mathbf{0.0541}$$

$\therefore$ 5.41 $percent \ of \ gas \ entering \ the \ throttling \ valve \ and \ converted \ to \ liquid$

E.B. around the cooler:

$$(H_4 - H_3) + (1 - z)(H_8 - H_7) = 0$$
$$H_4 = H_3 - (1 - z)(H_8 - H_7)$$
$$H_4 = 1140 - (0.9459) \ (1188.9 - 796.9)$$

$$H_4 = 769.2 \quad \frac{KJ}{kg}$$

By interpolation in table for superheated methane at 60 bar gives the temp. of gas entering the throttling valve **as 206.5 k**
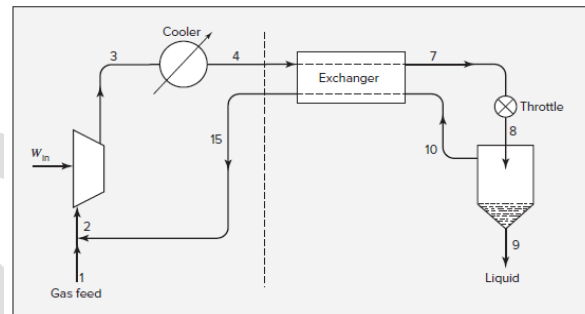
Example 9.3

Natural gas, assumed here to be pure methane, is liquefied in a Claude process. Compression is to 60 bar and precooling is to 300 K. The expander and throttle exhaust to a pressure of 1 bar. Recycle methane at this pressure leaves the exchanger system (point 15, Fig. 9.7) at 295 K. Assume no heat leaks into the system from the surroundings, an expander efficiency of 75%, and an expander exhaust of saturated vapor. For a draw-off to the expander of 25% of the methane entering the exchanger system (x = 0.25), what fraction z of the methane is liquefied, and what is the temperature of the high-pressure stream entering the throttle valve?
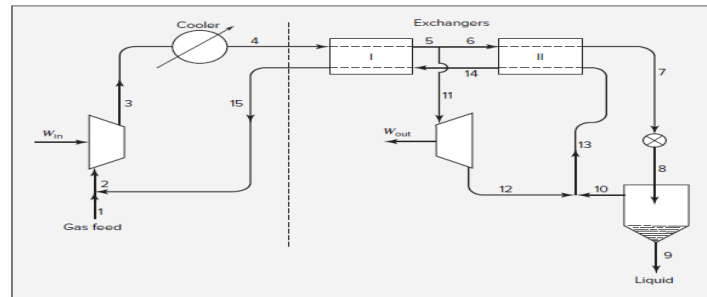
Solution:-

Figure 9.7: Claude liquefaction process.

Solution 9.3

Data for methane are available in the NIST WebBook,[7] from which the following values were obtained:

$$H_4 = 855.3 \text{ kJ·kg}^{-1} \qquad \text{(at 300 K and 60 bar)}$$
$$H_{15} = 903.0 \text{ kJ·kg}^{-1} \qquad \text{(at 295 K and 1 bar)}$$

For saturated liquid and vapor, at a pressure of 1 bar:

$$T^{\text{sat}} = 111.5 \text{ K}$$
$$H_9 = -0.6 \text{ kJ·kg}^{-1} \qquad \text{(saturated liquid)}$$
$$H_{12} = 510.6 \text{ kJ·kg}^{-1} \qquad \text{(saturated vapor)}$$
$$S_{12} = 4.579 \text{ kJ·kg}^{-1}\text{·K}^{-1} \quad \text{(saturated vapor)}$$

The enthalpy at the draw-off point between exchangers I and II, H_5, is required for solution of Eq. (9.7). The expander efficiency η is known, as is H_{12}, the enthalpy of the expander exhaust. The calculation of H_5 ($=H_{11}$), the expander inlet enthalpy, is less straightforward than the usual calculation of the exhaust enthalpy from the entrance enthalpy. The equation defining expander efficiency can be written:

$$\Delta H = H_{12} - H_5 = \eta(\Delta H)_S = \eta(H'_{12} - H_5)$$

Solution for H_{12} yields:

$$H_{12} = H_5 + \eta(H'_{12} - H_5) \tag{A}$$

where H'_{12} is the enthalpy at 1 bar as the result of *isentropic* expansion from point 5. This enthalpy is readily found once the conditions at point 5 are known. Thus a trial calculation is indicated, wherein the first step is to assume temperature T_5. This leads to values for H_5 and S_5, from which H'_{12} can be found. All quantities in Eq. (A) are then known, and their substitution into this equation shows whether or not it is satisfied. If not, a new value is chosen for T_5, and the process continues until Eq. (A) is satisfied. For example, at 60 bar and 260 K, the enthalpy and entropy are 745.27 kJ·kg^{-1} and 4.033 kJ·kg^{-1}·K^{-1}, respectively. The saturated liquid and vapor at 1 bar have $S^l = -0.005$ and $S^v = 4.579$, respectively. Using these values, isentropic expansion from 260 K and 60 bar to 1 bar would give a vapor fraction of 0.8808. This would give:

$$H'_{12} = H_9 + 0.8808(H_{12} - H_9) = 449.6 \ \text{kJ·kg}^{-1}$$

Using this value in Eq. (A) yields $H_{12} = 508.8$ kJ·kg^{-1}, which is below the known value of $H_{12} = 510.6$ kJ·kg^{-1}. Thus, T_5 must be higher than the assumed value of 260 K. Repeating this process (in an automated fashion using a spreadsheet) for other values of T_5 shows that Eq. (A) is satisfied for:

$$T_5 = 261.2 \ \text{K} \quad H_5 = 748.8 \ \text{kJ·kg}^{-1} \quad \text{(at 60 bar)}$$

Substitution of values into Eq. (9.7) now yields:

$$z = \frac{0.25(510.6 - 748.8) + 855.3 - 903.0}{-0.6 - 903.0} = 0.1187$$

Thus 11.9% of the methane entering the exchanger system is liquefied.

The temperature at point 7 depends on its enthalpy, which is found from energy balances on the exchanger system. Thus, for exchanger I,

$$\dot{m}_4(H_5 - H_4) + \dot{m}_{15}(H_{15} - H_{14}) = 0$$

With $\dot{m}_{15} = \dot{m}_4 - \dot{m}_9$ and $\dot{m}_9/\dot{m}_4 = z$, this equation may be rearranged to give:

$$H_{14} = \frac{H_5 - H_4}{1 - z} + H_{15} = \frac{748.8 - 855.3}{1 - 0.1187} + 903.0$$

Then,

$$H_{14} = 782.2 \ \text{kJ·kg}^{-1} \quad T_{14} = 239.4 \ \text{K (at 1 bar)}$$

where T_{14} is found by evaluating H for methane at 1 bar and varying the temperature to match the known H_{14}.

For exchanger II,

$$\dot{m}_7(H_7 - H_5) + \dot{m}_{14}(H_{14} - H_{12}) = 0$$

With $\dot{m}_7 = \dot{m}_4 - \dot{m}_{12}$ and $\dot{m}_{14} = \dot{m}_4 - \dot{m}_9$ and with the definitions of z and x, this equation upon rearrangement becomes:

$$H_7 = H_5 - \frac{1-z}{1-x}(H_{14} - H_{12}) = 748.8 - \frac{1 - 0.1187}{1 - 0.25}(782.2 - 510.6)$$

Then

$$H_7 = 429.7 \text{ kJ·kg}^{-1} \quad T_7 = 199.1 \text{ K(at 60 bar)}$$

As the value of x increases, T_7 decreases, eventually approaching the saturation temperature in the separator, and requiring an exchanger II of infinite area. Thus x is limited on the high side by the cost of the exchanger system.

The other limit is for $x = 0$, the Linde system, for which by Eq. (9.8),

$$z = \frac{855.3 - 903.0}{-0.6 - 903.0} = 0.0528$$

In this case only 5.3% of the gas entering the throttle valve emerges as liquid. The temperature of the gas at point 7 is again found from its enthalpy, calculated by the energy balance:

$$H_7 = H_4 - (1 - z)(H_{15} - H_{10})$$

Substitution of known values yields:

$$H_7 = 855.3 - (1 - 0.0528)(903.0 - 510.6) = 483.6 \text{ kJ·kg}^{-1}$$

The corresponding temperature of the methane entering the throttle valve is $T_7 = 202.1 \text{ K}$.