

1 Thermodynamic Relations

1.1 Relations for Energy Properties

1.1.1 Internal Energy Change dU

From first law of thermodynamics

$$dU = dQ + dW \quad (1.1)$$

For a reversible process

$$dW = -PdV$$

From second law of thermodynamics for a reversible process

$$dQ = TdS$$

Therefore Eqn.(1.1) becomes

$$dU = TdS - PdV \quad (1.2)$$

1.1.2 Enthapy Change dH

From the definition of enthalpy

$$H = U + PV \quad (1.3)$$

Differentiating

$$dH = dU + PdV + VdP$$

Substituting for dU from Eqn.(1.2)

$$dH = VdP + TdS \quad (1.4)$$

1.1.3 Gibbs Free Energy Change dG

From the definition of Gibbs free energy

$$G = H - TS$$

Differentiating

$$dG = dH - TdS - SdT$$

Substituting for dH from Eqn.(1.4)

$$dG = VdP - SdT \quad (1.5)$$

1.1.4 Helmholtz Free Energy Change dA

From the definition of Helmholtz free energy

$$A = U - TS$$

Differentiating

$$dA = dU - TdS - SdT$$

Substituting for dU from Eqn.(1.2)

$$dA = -PdV - SdT \quad (1.6)$$

1.2 Mathematical Concepts

1.2.1 Exact Differential Equations

If $F = F(x, y)$ then

$$dF = Mdx + Ndy$$

Exactness Criteria:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

If $F = F(x, y, z)$ then

$$dF = Mdx + Ndy + Pdz$$

Exactness Criteria:

$$\begin{aligned} \left(\frac{\partial M}{\partial y}\right)_{x,z} &= \left(\frac{\partial N}{\partial x}\right)_{y,z} \\ \left(\frac{\partial M}{\partial z}\right)_{x,y} &= \left(\frac{\partial P}{\partial x}\right)_{y,z} \\ \left(\frac{\partial N}{\partial z}\right)_{x,y} &= \left(\frac{\partial P}{\partial y}\right)_{x,z} \end{aligned}$$

1.2.2 Cyclic Relation Rule

For the function in the variables x, y & z

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

1.2.3 Other Relations of Importance

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial z}{\partial w}\right)_y \left(\frac{\partial w}{\partial x}\right)_y$$

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

1.3 Maxwell Relations

For the fundamental property relations:

$$dU = TdS - PdV$$

$$dA = -PdV - SdT$$

$$dG = -SdT + VdP$$

$$dH = VdP + TdS$$

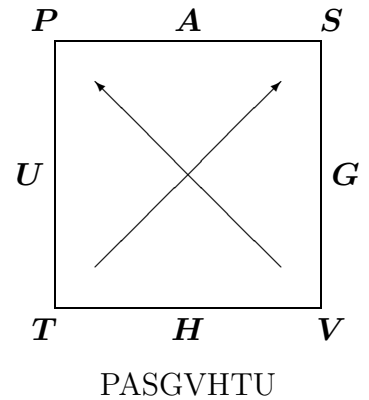
Applying exactness criteria of differential equation:

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

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

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

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$$



1.4 Relations for Thermodynamic Properties in terms of PVT and Specific heats

1.4.1 Definitions

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

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

Volume expansivity β

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

Isothermal compressibility κ

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

1.4.2 Relations for dU

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$$

Considering $U = U(T, V)$

$$dU = C_V dT + \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV$$

For van der Waals gas,

$$dU = C_V dT + \frac{a}{V^2} dV$$

1.4.3 Relations for dH

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

Considering $H = H(T, P)$

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP$$

1.4.4 Relations for dS

$$\begin{aligned} \left(\frac{\partial S}{\partial T} \right)_V &= \frac{C_V}{T} \\ \left(\frac{\partial S}{\partial T} \right)_P &= \frac{C_P}{T} \end{aligned}$$

Considering $S = S(T, V)$

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T} \right)_V dV$$

For van der Waals gas,

$$dS = \frac{C_V}{T} dT - \frac{R}{V-b} dV$$

Considering $S = S(T, P)$

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP$$

1.4.5 Relations for Specific heats

$$C_P = T \left(\frac{\partial P}{\partial T} \right)_S \left(\frac{\partial V}{\partial T} \right)_P$$
$$C_V = -T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_S$$

Specific heat differences:

$$C_P - C_V = -T \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P^2$$

For van der Waals gas,

$$C_P - C_V = T \frac{V\beta^2}{\kappa}$$

Specific heat ratio:

$$\frac{C_P}{C_V} = \frac{(\partial P / \partial V)_S}{(\partial P / \partial V)_T}$$

Specific heat variations:

$$\left(\frac{\partial C_P}{\partial P} \right)_T = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_P$$
$$\left(\frac{\partial C_V}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V$$

1.5 Two-phase Systems

Equilibrium in a closed system of constant composition:

$$d(nG) = (nV)dP - (nS)dT$$

During phase change T and P remains constant. Therefore, $d(nG) = 0$. Since $dn \neq 0$, $dG = 0$.

For two phases α and β of a pure species coexisting at equilibrium:

$$G^\alpha = G^\beta$$

where G^α and G^β are the molar Gibbs free energies of the individual phases.

$$dG^\alpha = dG^\beta$$

$$\frac{dP^{\text{sat}}}{dT} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}}$$

1.5.1 Clapeyron equation

$$\frac{dP^{\text{sat}}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}}$$

1.5.2 Clausius-Clapeyron equation

$$\ln \frac{P_2^{\text{sat}}}{P_1^{\text{sat}}} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

1.5.3 Vapor Pressure vs. Temperature

From Clausius-Clapeyron equation

$$\ln P^{\text{sat}} = A - \frac{B}{T}$$

A satisfactory relation given by *Antoine* is of the form

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

The values of the constants A , B and C are readily available for many species.

1.6 Gibbs Free Energy as a Generating Function

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT}dG - \frac{G}{RT^2}dT$$

Substituting for dG from fundamental property relation, and from the definition of G :

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT}dP - \frac{H}{RT^2}dT$$

This is a dimensionless equation.

$$\begin{aligned}\frac{V}{RT} &= \left[\frac{\partial(G/RT)}{\partial P}\right]_T \\ \frac{H}{RT} &= -T \left[\frac{\partial(G/RT)}{\partial T}\right]_P\end{aligned}$$

When G/RT is known as a function of T and P , V/RT and H/RT follow by simple differentiation. The remaining properties are given by defining equations.

$$\begin{aligned}\frac{S}{R} &= \frac{H}{RT} - \frac{G}{RT} \\ \frac{U}{RT} &= \frac{H}{RT} - \frac{PV}{RT}\end{aligned}$$

1.7 Residual Properties

Any extensive property M is given by:

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

where M^{ig} is ideal gas value of the property, and M^R is the residual value of the property.

For example for the extensive property V :

$$V = V^{\text{ig}} + V^R = \frac{RT}{P} + V^R$$

Since $V = ZRT/P$

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

For Gibbs free enrgy

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}dP - \frac{H^R}{RT^2}dT \quad (1.7)$$

$$\frac{V^R}{RT} = \left[\frac{\partial(G^R/RT)}{\partial P}\right]_T \quad (1.8)$$

$$\frac{H^R}{RT} = -T \left[\frac{\partial(G^R/RT)}{\partial T}\right]_P \quad (1.9)$$

From the definition of G :

$$G^R = H^R - TS^R$$

$$\frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT} \quad (1.10)$$

At constant T Eqn.(1.7) becomes

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}dP$$

Integration from zero pressure to the arbitrary pressure P gives

$$\frac{G^R}{RT} = \int_0^P \frac{V^R}{RT}dP \quad (\text{const. } T) \quad (1.11)$$

where at the lower limit, we have set G^R/RT equal to zero on the basis that the zero-pressure state is an ideal-gas state. ($V^R = 0$)

Since $V^R = (RT/P)(Z - 1)$ Eqn.(1.11) becomes

$$\frac{G^R}{RT} = \int_0^P (Z - 1) \frac{dP}{P} \quad (\text{const. } T) \quad (1.12)$$

Differentiating Eqn.(1.12) at with respect to T at constant P

$$\left[\frac{\partial(G^R/RT)}{\partial T}\right]_P = \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}$$

$$\frac{H^R}{RT} = -T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \quad (\text{const. } T) \quad (1.13)$$

Combining Eqn.(1.12) and (1.13) and from Eqn.(1.10)

$$\frac{S^R}{R} = -T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z - 1) \frac{dP}{P} \quad (\text{const. } T) \quad (1.14)$$

1.8 Generalized Correlations of Thermodynamic Properties for Gases

Of the two kinds of data needed for the evaluation of thermodynamic properties, heat capacities and PVT data, the latter are most frequently missing. Fortunately, the generalized methods developed for compressibility factor Z are also applicable to residual properties.

Substituting for $P = P_c P_r$ and $T = T_c T_r$,

$$dP = P_c dP_r \quad \text{and} \quad dT = T_c dT_r$$

$$\frac{H^R}{RT_c} = -T_r^2 \int_0^{P_r} \left(\frac{\partial Z}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r} \quad (\text{const. } T_r) \quad (1.15)$$

$$\frac{S^R}{R} = -T_r \int_0^{P_r} \left(\frac{\partial Z}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r} - \int_0^{P_r} (Z - 1) \frac{dP_r}{P_r} \quad (\text{const. } T_r) \quad (1.16)$$

1.8.1 Three Parameter Models

From three-parameter corresponding states principle developed by *Pitzer*

$$Z = Z^0 + \omega Z^1$$

Similar equations for H^R and S^R are:

$$\begin{aligned} \frac{H^R}{RT_c} &= \frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c} \\ \frac{S^R}{R} &= \frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R} \end{aligned}$$

Calculated values of the quantities $\frac{(H^R)^0}{RT_c}$, $\frac{(H^R)^1}{RT_c}$, $\frac{(S^R)^0}{R}$ and $\frac{(S^R)^1}{R}$ are shown by plots of these quantities vs. P_r for various values of T_r .

$\frac{(H^R)^0}{RT_c}$ and $\frac{(S^R)^0}{R}$ used alone provide two-parameter corresponding states correlations that quickly yield coarse estimates of the residual properties.

1.8.2 Correlations from Redlich/Kwong Equation of State

$$Z = \frac{1}{1-h} - \frac{4.934}{T_r^{1.5}} \left(\frac{h}{1+h} \right)$$

where

$$h = \frac{0.08664P_r}{ZT_r}$$

and

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

1.9 Developing Tables of Thermodynamic Properties from Experimental Data

Experimental Data:

- (a) Vapor pressure data.
- (b) Pressure, specific volume, temperature (PVT) data in the vapor region.
- (c) Density of saturated liquid and the critical pressure and temperature.
- (d) Zero pressure specific heat data for the vapor.

From these data, a complete set of thermodynamic tables for the saturated liquid, saturated vapor, and super-heated vapor can be calculated as per the steps below:

1. Relation for $\ln P^{\text{sat}}$ vs. T such as

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

2. Equation of state for the vapor that accurately represents the PVT data.
3. **State: 1**
Fix values for H and S of saturated-liquid at a reference state.

4. **State: 2**

Enthalpy and entropy changes during vaporization are calculated from Clapeyron equation using the $\ln P^{\text{sat}}$ vs. T data as:

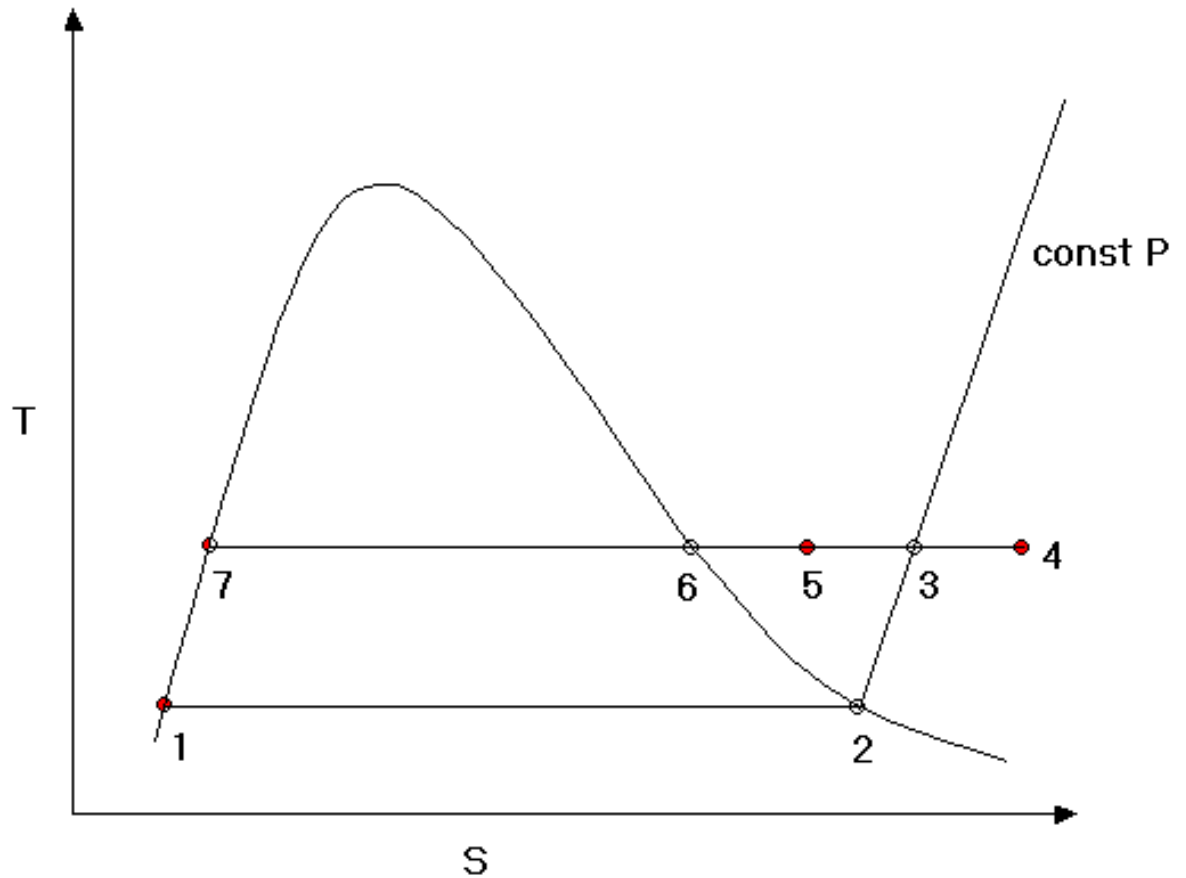
$$\frac{dP^{\text{sat}}}{dT} = \frac{\Delta H_{lv}}{T(V_v - V_l)}$$

and

$$\Delta S_{lv} = \frac{\Delta H_{lv}}{T}$$

Here V_l shall be measured, and V_v is calculated from the relation obtained in step-2.

From these values of ΔH_{vl} and ΔS_{vl} obtain the values of H and S at state: 2



5. **State: 3** Follow the constant pressure line.

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP$$
$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T} \right)_P dP$$

Here for the specific heat of vapor corresponding to the pressure at state: 2 is obtained from the relation:

$$\left(\frac{\partial C_P}{\partial P} \right)_T = -T \left(\frac{\partial^2 V}{\partial T^2} \right)$$

and from the zero pressure specific heat data.

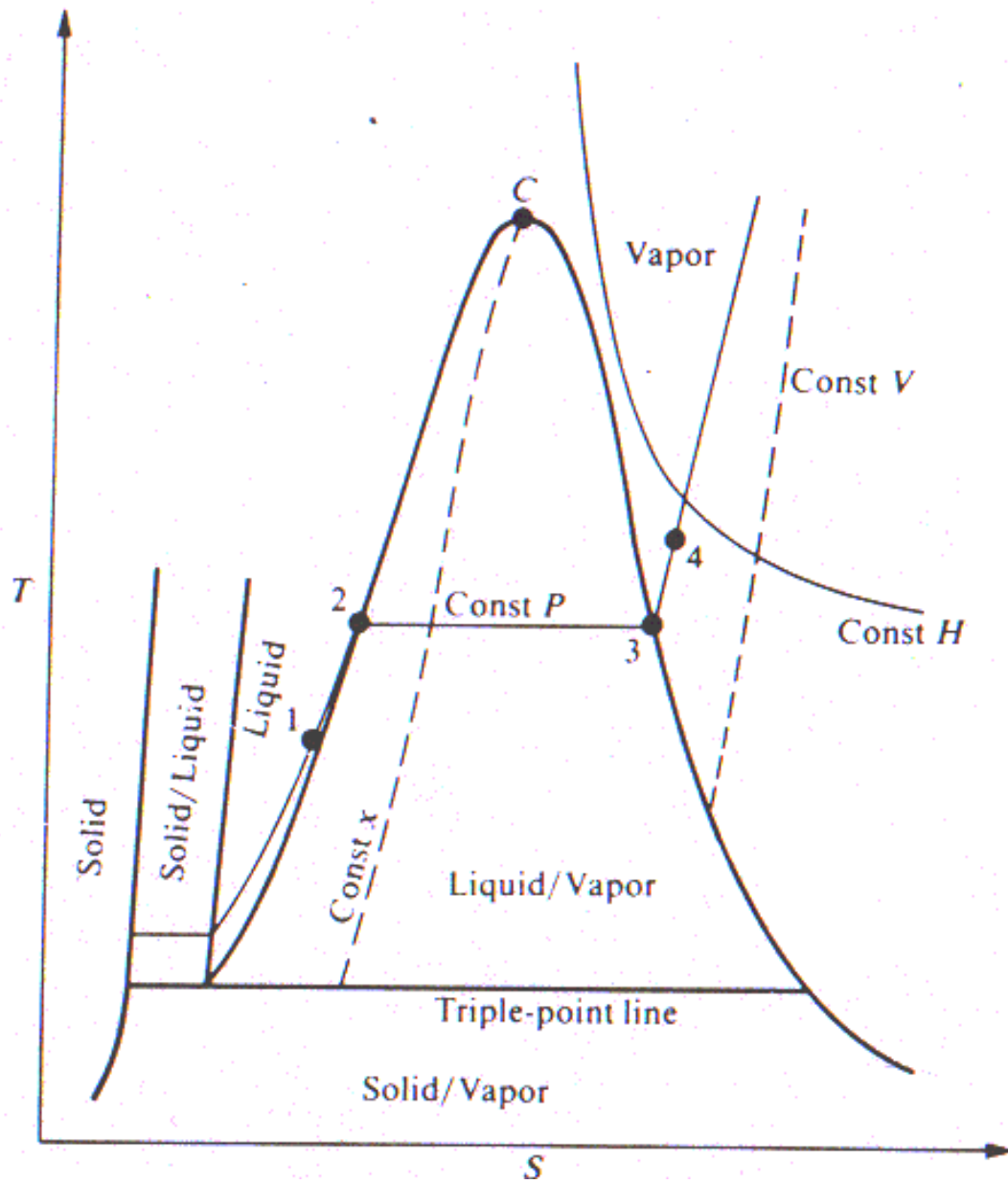
With the value of C_P for this state as calculated above, S and H values at state: 3 are calculated.

6. **State: 4, 5 & 6** The above calculation can be done along constant temperature line and the values at states 4, 5 and 6 can be obtained.

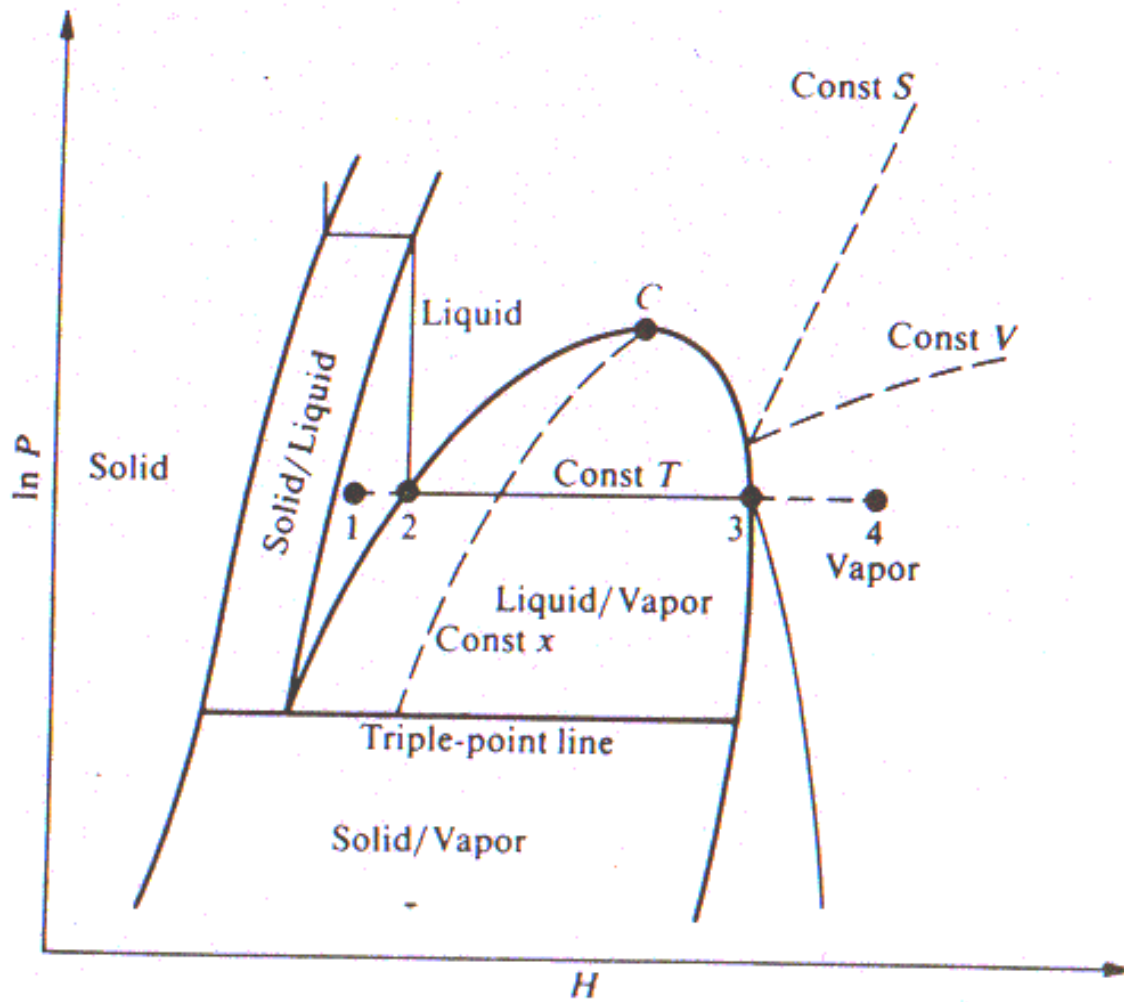
7. **State: 7** The calculations made for state: 2 can be done for the temperature at state: 6.

1.10 Thermodynamic Diagrams of Importance

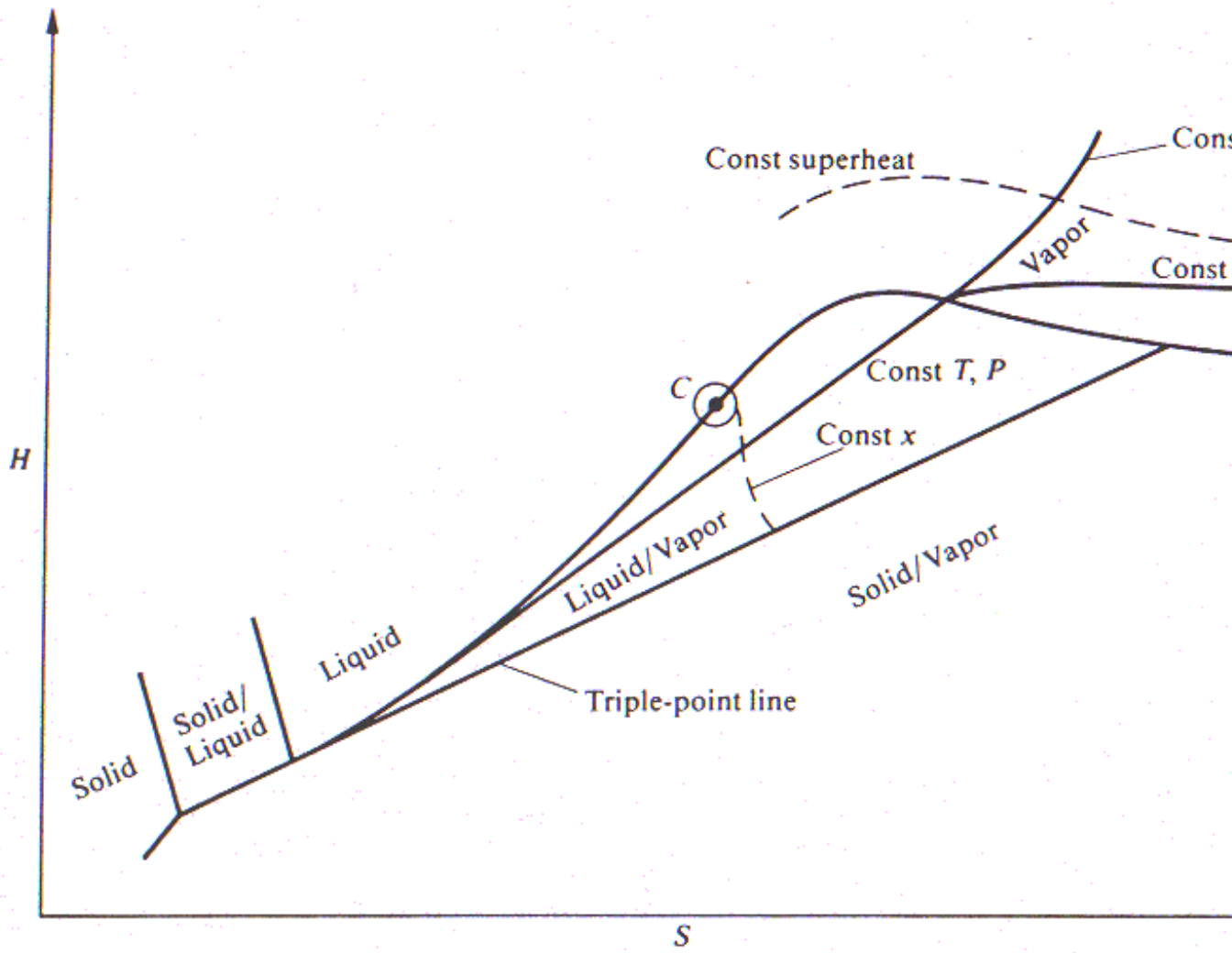
1.10.1 $T - S$ diagram



1.10.2 $P - H$ diagram

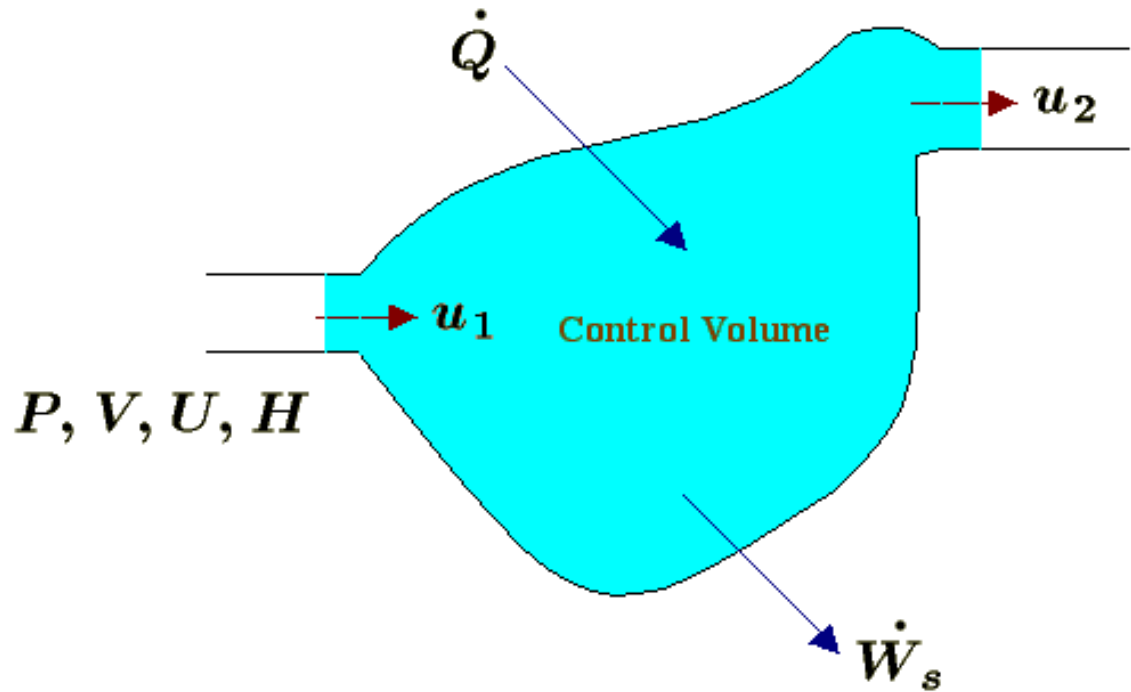


1.10.3 $H - S$ diagram



2 Thermodynamics of Flow Processes

2.1 Conservation of Mass



$$\frac{dm}{dt} + \Delta(\rho u A) = 0 \quad (2.1)$$

where the symbol Δ denotes the difference between exit and entrance streams.

For steady flow process

$$\Delta(\rho u A)_{fs} = 0 \quad (2.2)$$

Since specific volume is the reciprocal of density,

$$\dot{m} = \frac{uA}{V} = \text{constant}. \quad (2.3)$$

This is the equation of continuity.

2.2 Conservation of Energy

$$\frac{d(mU)}{dt} + \Delta[(U + \frac{1}{2}u^2 + zg)\dot{m}] = \dot{Q} - \dot{W} \quad (2.4)$$

$$W = W_s + \Delta[(PV)\dot{m}] \quad (2.5)$$

$$\frac{d(mU)}{dt} + \Delta[(H + \frac{1}{2}u^2 + zg)\dot{m}] = \dot{Q} - \dot{W}_s \quad (2.6)$$

For most applications, kinetic- and potential-energy changes are negligible. Therefore

$$\frac{d(mU)}{dt} + \Delta(H\dot{m}) = \dot{Q} - \dot{W}_s \quad (2.7)$$

Energy balances for steady state flow processes:

$$\Delta[(H + \frac{1}{2}u^2 + zg)\dot{m}] = \dot{Q} - \dot{W}_s \quad (2.8)$$

Bernoulli's equation:

$$\frac{P}{\rho} + \frac{u^2}{2} + gz = 0 \quad (2.9)$$

2.3 Flow in Pipes of Constant Cross-section

$$\Delta H + \frac{\Delta u^2}{2} = 0 \quad (2.10)$$

In differential form

$$dH = -u du \quad (2.11)$$

Equation of continuity in differential form:

$$d(uA/V) = 0 \quad (2.12)$$

Since A is a constant, $d(u/V) = 0$. Therefore

$$\frac{du}{V} - \frac{u dV}{V^2} = 0$$

or

$$du = \frac{u dV}{V} \quad (\text{const. } A) \quad (2.13)$$

Substituting this in Eqn.(2.11)

$$dH = -\frac{u^2 dV}{V} \quad (2.14)$$

From the fundamental property relations

$$TdS = dH - VdP$$

Therefore

$$TdS = -\frac{u^2 dV}{V} - VdP \quad (2.15)$$

As gas flows along a pipe in the direction of decreasing pressure, its specific volume increases, and also the velocity (as $\dot{m} = uA/V$). Thus in the direction of increasing velocity, dP is negative, dV is positive, and the two terms of Eqn.(2.15) contribute in opposite directions to the entropy change. According to second law $dS \geq 0$.

$$\frac{u_{\max}^2 dV}{V} + VdP = 0 \quad (\text{const. } S)$$

Rearranging

$$u_{\max}^2 = -V^2 \left(\frac{\partial P}{\partial V} \right)_S \quad (2.16)$$

This is the speed of sound in fluid.

2.4 General Relationship between Velocity and Cross-sectional Area

$$d(uA/V) = 0$$

$$\frac{1}{V}(u dA + A du) - uA \frac{dV}{V^2} = 0$$

or

$$\frac{u dA + A du}{uA} = \frac{V dV}{V^2}$$

From the fundamental property relation for dH and from steady flow energy equation

$$-V dP = u du \quad (\text{const. } S)$$

i.e., $V = -u du/dP$ at constant S . Therefore

$$\frac{dA}{A} + \frac{du}{u} = \frac{u du}{-V^2 (\partial P / \partial V)_S}$$

From the relation for velocity of sound, the above equation becomes

$$\frac{dA}{A} + \frac{du}{u} = \frac{u du}{u_{\text{sonic}}^2}$$

Therefore

$$\frac{dA}{A} = \frac{u du}{u_{\text{sonic}}^2} - \frac{du}{u} = \left(\frac{u^2}{u_{\text{sonic}}^2} - 1 \right) \frac{du}{u}$$

The ratio of actual velocity to the velocity of sound is called the *Mach Number* M .

$$\frac{dA}{A} = (M^2 - 1) \frac{du}{u} \quad (2.17)$$

Depending on whether M is greater than unity (supersonic) or less than unity (subsonic), the cross sectional area increases or decreases with velocity increase.

includegraphics{supersonic.eps}

includegraphics{subsonic.eps}

includegraphics{convergddiverg.eps}

2.5 Nozzles

$$u_2^2 - u_1^2 = -2 \int_{P_1}^{P_2} V dP = \frac{2\gamma P_1 V_1}{\gamma - 1} \left[1 - \left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} \right] \quad (2.18)$$

From the definition of sound velocity

$$u_{\max}^2 = -V^2 \left(\frac{\partial P}{\partial V} \right)_s$$

and from the evaluation of the derivative $(\partial P/\partial V)_s$ for the isentropic expansion of ideal gas with constant heat capacities from the relation $PV^\gamma = \text{const}$,

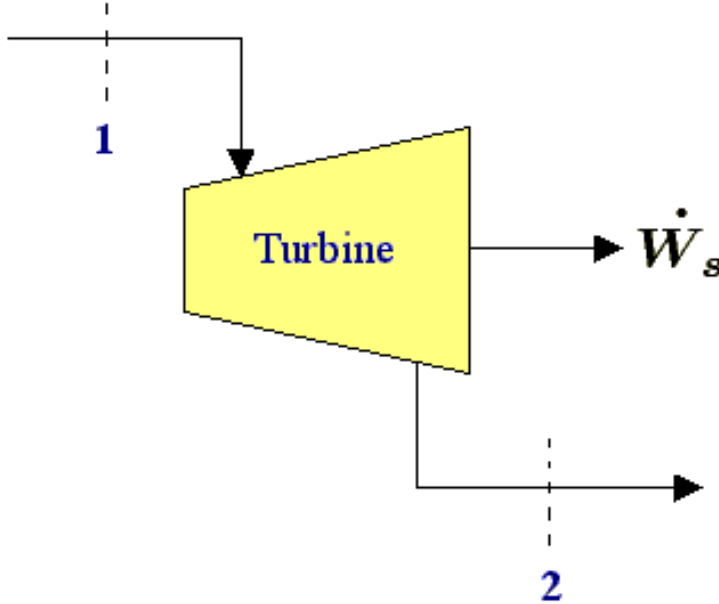
$$u_{\text{throat}}^2 = \gamma P_2 V_2 \quad (2.19)$$

Substituting this value of the throat velocity for u_2 in Eqn.(2.18) and solving for the pressure ratio with $u_1 = 0$ gives

$$\frac{P_2}{P_1} = \left(\frac{2}{\gamma + 1} \right)^{\gamma/(\gamma-1)} \quad (2.20)$$

The speed of sound is attained at the throat of a conerging/diverging nozzle only when the pressure at the throat is low enough that the critical value of P_2/P_1 is reached. If insufficient pressure drop is available in the nozzle for the velocity to become sonic, the diverging section of the nozzle acts as a diffuser.

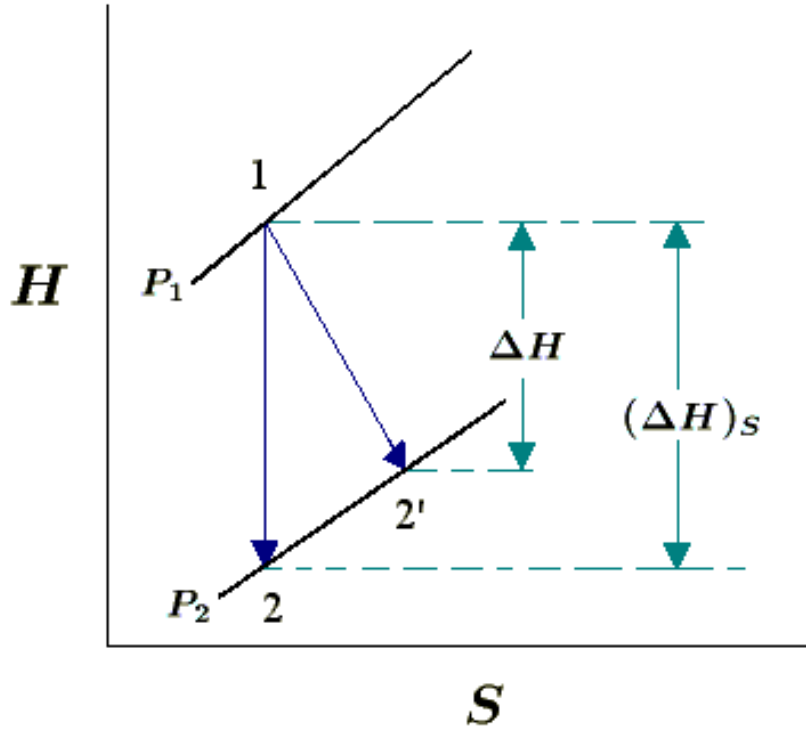
2.6 Turbines



$$\dot{W}_s = -\dot{m}\Delta H \quad (2.21)$$

and

$$W_s = -\Delta H \quad (2.22)$$



$$W_s(\text{isentropic}) = -(\Delta H)_s \quad (2.23)$$

$$\eta = \frac{W_s}{W_s(\text{isentropic})} = \frac{\Delta H}{(\Delta H)_s} \quad (2.24)$$

2.7 Throttling Processes

$$\Delta H = 0$$

Joule-Thomson Coefficient:

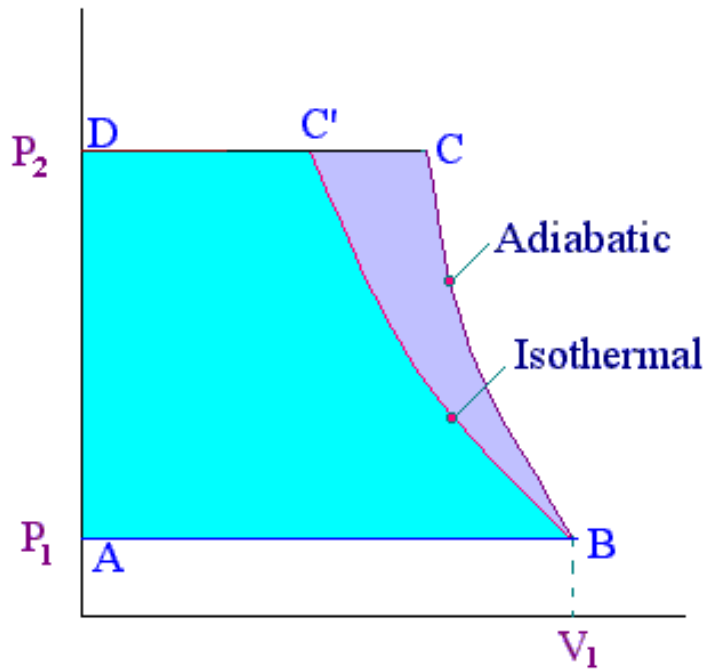
$$\mu_J = \left(\frac{\partial T}{\partial P} \right)_H = \frac{T(\partial V / \partial T)_P - V}{C_P}$$

For ideal gases $\mu_J = 0$. For a real gas u_J can be positive, zero or negative.

Any gas for which volume is linear with temperature along an isobar will have a zero Joule-Thomson coefficient. i.e., if $V/T = \text{constant} = \phi(P)$, $\mu_J = 0$.

Inversion curve: $T - P$ diagram. The points in the curve correspond to $\mu_J = 0$. In the region inside the curve μ_J is positive.

2.8 Compression



$$W = - \int_{P_1}^{P_2} V dP$$

For reversible-adiabatic compression

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

Effect of clearance on work of compression:

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

Multistage compression:

$$\text{Optimum compression ratio per stage} = \left(\frac{P_2}{P_1}\right)^{1/n}$$

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

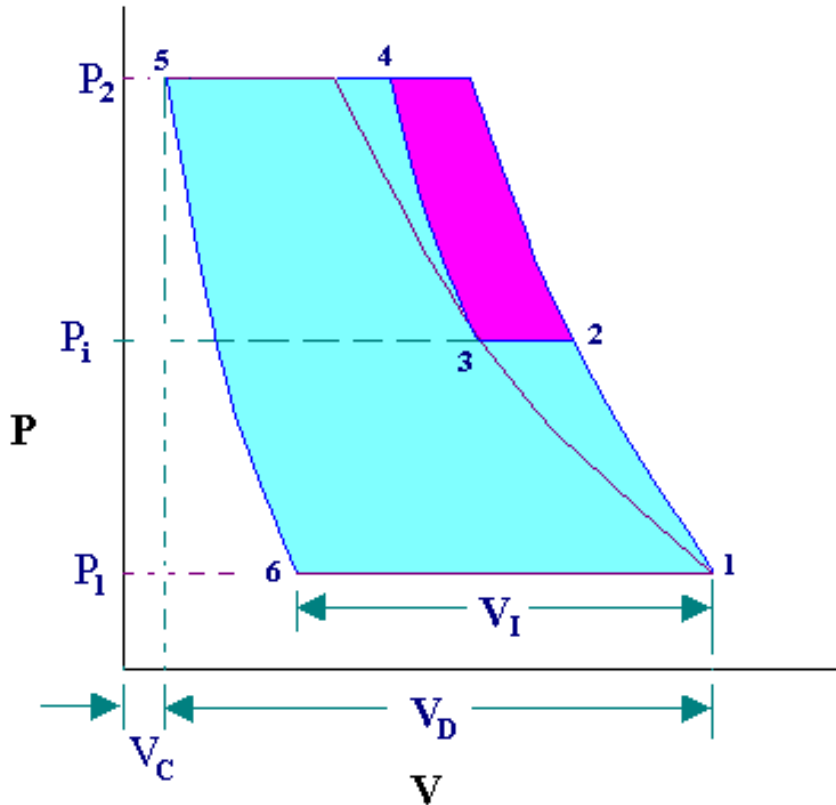
Relation between V_D and V_I :

$$V_I = V_D \left[1 + C - C \left(\frac{P_2}{P_1}\right)^{1/\gamma} \right]$$

where $C = V_C/V_D$ For compression in multistages,

$$V_I = V_D \left[1 + C_1 - C_1 \left(\frac{P_2}{P_1}\right)^{\frac{1}{n\gamma}} \right]$$

where C_1 is the clearance in the first stage.



2.9 Ejectors

