

9. THERMODYNAMICS RELATIONS

MATHEMATICAL THEOREMS

$dz = Mdx + Ndy$ is exact differential equation, $\left[\frac{\partial M}{\partial y} \right]_x = \left[\frac{\partial N}{\partial x} \right]_y$	If $z = f(x, y)$, $\left[\frac{\partial x}{\partial y} \right]_z \cdot \left[\frac{\partial y}{\partial z} \right]_x \cdot \left[\frac{\partial z}{\partial x} \right]_y = -1$
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PROPERTIES

GIBB'S FUNCTION		HELMHOLTZ FUNCTION	
Open System Availability Function.		Closed System Availability Function.	
$G = H - TS$	$g = h - Ts$	$F = U - TS$	$f = u - Ts$
COEFFICIENT OF VOLUME EXPANSIVITY		ISOTHERMAL COMPRESSIBILITY	
$\beta = \frac{1}{v} \left[\frac{\partial v}{\partial T} \right]_p > 0$ (Due to Expansion)		$K_T = \frac{1}{v} \left[\frac{\partial v}{\partial P} \right]_T < 0$ (Due to Compression)	
$C_p = T \left[\frac{\partial s}{\partial T} \right]_p$		$C_v = T \left[\frac{\partial s}{\partial T} \right]_v$	

MAXWELL'S EQUATIONS

Derived from 1st TdS Equation, $du = Tds - Pdv$ (It's exact differential) $\therefore \left[\frac{\partial T}{\partial v} \right]_s = \left[\frac{-\partial P}{\partial s} \right]_v$	Derived from 2nd TdS Equation, $dh = Tds + vdP$ (It's exact differential) $\therefore \left[\frac{\partial T}{\partial P} \right]_s = \left[\frac{-\partial v}{\partial s} \right]_P$
Derived from $g = h - Ts$ $\Rightarrow dg = dh - d(Ts) = vdP - sdT$ $\therefore \left[\frac{\partial v}{\partial T} \right]_P = \left[\frac{-\partial s}{\partial P} \right]_T$	Derived from $f = u - Ts$ $\Rightarrow df = du - d(Ts) = -Pdv - sdT$ $\therefore \left[\frac{\partial P}{\partial T} \right]_v = \left[\frac{\partial s}{\partial v} \right]_T$

$s = f(T, v) \Rightarrow Tds = T \left[\frac{\partial s}{\partial T} \right]_v dT + T \left[\frac{\partial s}{\partial v} \right]_T dv = C_v dT + T \left[\frac{\partial P}{\partial T} \right]_v dv \dots (1)$ $s = f(T, P) \Rightarrow Tds = T \left[\frac{\partial s}{\partial T} \right]_P dT + T \left[\frac{\partial s}{\partial P} \right]_T dP = C_p dT - T \left[\frac{\partial v}{\partial T} \right]_P dP \dots (2)$	From, Above mentioned C_p, C_v Equations, 3 rd and 4 th Maxwell's equation.
$dT = \frac{T}{C_p - C_v} \left\{ \left[\frac{\partial v}{\partial T} \right]_P dP + \left[\frac{\partial P}{\partial T} \right]_v dv \right\} \dots (3)$	Equating above (1) & (2),
$s = f(P, v) \Rightarrow s = \left[\frac{\partial T}{\partial P} \right]_v dP + \left[\frac{\partial T}{\partial v} \right]_P dv \dots (4)$	From the maths theorem,
$\left[\frac{\partial T}{\partial P} \right]_v = \frac{T}{C_p - C_v} \left[\frac{\partial v}{\partial T} \right]_P \dots (5)$	Equating above (3) & (4),
$T = f(P, v) \Rightarrow \left[\frac{\partial P}{\partial v} \right]_T \cdot \left[\frac{\partial v}{\partial T} \right]_P \cdot \left[\frac{\partial T}{\partial P} \right]_v = -1 \Rightarrow \left[\frac{\partial T}{\partial P} \right]_v = -1 / \left[\frac{\partial v}{\partial T} \right]_T \cdot \left[\frac{\partial v}{\partial T} \right]_P \dots (6)$	From the maths theorem,
$C_p - C_v = -T \left[\frac{\partial v}{\partial T} \right]_P^2 \left[\frac{\partial P}{\partial v} \right]_T$	From (5) & (6)

MAYER'S EQUATION: $C_p - C_v = -T \left[\frac{\partial v}{\partial T} \right]_P^2 \left[\frac{\partial P}{\partial v} \right]_T = \frac{T v \beta^2}{K_T}$	From definition of K_T & β .
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INTERNAL ENERGY EQUATION: It's valid for Real & ideal Gas. $du = C_v dT + \left[T \left[\frac{\partial P}{\partial T} \right]_v - P \right] dv = f(dT, dv)$	From Mayer's equation, equation (1) and 1 st TdS Equation. For ideal Gas, $T \left[\frac{\partial P}{\partial T} \right]_v = P$
ENTHALPY EQUATION: It's valid for Real & ideal Gas. $dh = C_p dT + \left[T \left[\frac{\partial v}{\partial T} \right]_P - v \right] dP = f(dT, dP)$	From Mayer's equation, equation (2) and 2 nd TdS Equation. For ideal Gas, $T \left[\frac{\partial v}{\partial T} \right]_P = v$
JOULE-THOMSON COEFFICIENT EQUATION: It's valid for Real & ideal Gas. $\mu = \left[\frac{dT}{dP} \right]_h = \frac{1}{C_p} \left[T \left[\frac{\partial v}{\partial T} \right]_P - v \right]$	From Enthalpy equation, & for Throttling process $dh = 0$ For ideal Gas, $\mu = 0$