



***CBEg 6162- Advanced Chemical Engineering
Thermodynamics***

Maxwell's Relation and Jacobian Methods

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CHAPTER-5-Maxwell's Relation and Jacobian Methods

- *Purpose of Maxwell's Relation*
- *Definition of Maxwell's relation*
- *How Maxwell relations are developed*
 - ✓ *Alternative Method of developing Maxwell relation*
 - ✓ *Mnemonic diagram*
 - ✓ *Jacobian Method*
- *Application of Jacobian Method*



Purpose of Maxwell Relations

- The *thermodynamics property* of interest can be classified in to *two groups* as *measurable properties -pressure, volume and temperature –* which can *be measured directly* and *non-measurable properties- entropy, Helmholtz free energy, Gibbs free energy and enthalpy- which cannot be measured directly*. All these properties are *not independent*.
 - An important task in thermodynamic is to express *the non-measurable properties in terms of the measurable property* to facilitate their estimation
 - *Maxwell relations* provide a way to exchange or expresses *differential forms of unmeasurable variables with measureable properties*.
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Maxwell Relations

- The *first derivatives (intensive parameters)* of a fundamental relation are *not all independent* and there exists *a relation among all the first derivatives*. The *differential form of that relation* was called *the Gibbs Duhem relation*.
- The relationships among the mixed second derivatives $-\frac{\partial^2 U}{\partial S \partial V}$ or $-\frac{\partial^2 U}{\partial V \partial S}$ of the fundamental relation are called *Maxwell relations*. Maxwell relations are derived as follow. The fundamental relation of a single component system in the energy representation is given by $U=U(S, V, N)$. The two mixed second derivatives of U with respect to S and V are $\frac{\partial^2 U}{\partial S \partial V}$ and $\frac{\partial^2 U}{\partial V \partial S}$. Since the order of differentiation does not affect the mixed second derivative can be written as follows



Maxwell Relations

or

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S} \quad \left[\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right)_S \right]_V = \left[\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right)_V \right]_S$$

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

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

$$\left[\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial N} \right)_S \right]_N \quad \text{and} \quad \left[\frac{\partial}{\partial N} \left(\frac{\partial U}{\partial S} \right)_N \right]_S$$

$$\mu = \left(\frac{\partial U}{\partial N} \right)_S \quad T = \left(\frac{\partial U}{\partial S} \right)_N$$

$$\left(\frac{\partial \mu}{\partial S} \right)_N = \left(\frac{\partial T}{\partial N} \right)_S$$



What are Maxwell Relations?

- ❖ if 'f' is a thermodynamic potential function expressed by x and y natural variables.

$$f = f(x, y)$$

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

which means $df = Mdx + Ndy$

- ❖ We must now take into account a rule in partial derivatives that;

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

Which implies $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \text{ if } M, N, x, y \rightarrow v, s, T, P \text{ (natural variables)}$$



What are Maxwell Relations?

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

- If M, N, y and x are expressed in terms of s, T, P and v the expression is called **Maxwell's relation** .
- the Maxwell's relation developed from four commonly used thermodynamic potentials for single component are:-

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

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

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

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



Maxwell Relations

- The *Maxwell relation* expresses *the partial derivatives of entropy with respect to pressure and volume* in terms of *the measurable quantities*.
- The *partial derivatives of entropy with respect to temperature* are related to *the (measurable quantities) heat capacity are given by*

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p \quad \text{and} \quad C_v = T \left(\frac{\partial S}{\partial T} \right)_v$$



Maxwell Relations

- The *partial derivatives of volume* with respect to *temperature and pressure* are also *measurable quantities* and are given by

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

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

- β -Coefficient of thermal expansion,
 - κ -Isothermal compressibility,
-



How Maxwell Relations are developed?

- Maxwell relations are developed from *Basic thermodynamic potential relations (g, a, h and u)*
 - ✓ Internal Energy (U)
 - ✓ Gibbs Energy (G)
 - ✓ Helmholtz Free Energy (A)
 - ✓ Enthalpy (H)
-



How to derive the Maxwell relation

⊕ Internal Energy (U)

$$u = u(s, v) \equiv Z(x, y)$$

$$du = \frac{\partial u}{\partial s} ds + \frac{\partial u}{\partial v} dv$$

$$du = M ds + N dv \quad \text{where } M = \frac{\partial u}{\partial s} = T \text{ and } N = \frac{\partial u}{\partial v} = -P$$

$$\boxed{\left(\frac{\partial M}{\partial v}\right)_s = \frac{\partial^2 u}{\partial s \partial v} = \left(\frac{\partial N}{\partial s}\right)_v}$$

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



How to derive the Maxwell relation

- Then ,

$$\left(\frac{\partial M}{\partial v}\right)_s = \left(\frac{\partial T}{\partial v}\right)_s \quad \text{and} \quad \left(\frac{\partial N}{\partial s}\right)_v = - \left(\frac{\partial P}{\partial s}\right)_v \quad \text{so}$$

The first Maxwell relation which is defined by

$$\left(\frac{\partial M}{\partial v}\right)_s = \frac{\partial^2 u}{\partial s \partial v} = \left(\frac{\partial N}{\partial s}\right)_v$$

if it is M, N, x, y are expressed intermes of T, P, s, v is written as



How to derive the Maxwell relation

- From internal energy we get the first Maxwell relation expressed as follows;

$$\left(\frac{\partial T}{\partial v}\right)_s = - \left(\frac{\partial P}{\partial s}\right)_v$$

- with the same procedure the rest three Maxwell relation can be derived.

Gibbs energy

$$g = g(T, P)$$

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



How to derive the Maxwell relation

$$dg = MdT + NdP \quad \text{where } M = \left(\frac{\partial g}{\partial T}\right)_P \quad \text{and } N = \left(\frac{\partial g}{\partial P}\right)_T$$

$$\boxed{\left(\frac{\partial N}{\partial T}\right)_P = \frac{\partial^2 g}{\partial T \partial P} = \left(\frac{\partial M}{\partial P}\right)_T}$$

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

- By Definition

$$\mathbf{g = u - Ts}$$

$$dg = du - (Tds + sdT)$$

$$\text{here } du = Tds - Pdv$$

- Up on substitution on can obtain;

$$dg = vdP - sdT$$

- Finally we know that as

$$M = \left(\frac{\partial g}{\partial T} \right)_P = -s$$

$$N = \left(\frac{\partial g}{\partial P} \right)_T = v$$

Direct substitution

$$\left(\frac{\partial N}{\partial T} \right)_P = \frac{\partial^2 g}{\partial T \partial P} = \left(\frac{\partial M}{\partial P} \right)_T$$

$$\left(\frac{\partial N}{\partial T} \right)_P = \left(\frac{\partial v}{\partial T} \right)_P = \left(\frac{\partial M}{\partial P} \right)_T = - \left(\frac{\partial s}{\partial P} \right)_T$$

$$\boxed{\left(\frac{\partial v}{\partial T} \right)_P = - \left(\frac{\partial s}{\partial P} \right)_T}$$

- from the rest of chemical potentials we can obtain the following relations.

✚ From Helmholtz free energy (a)

$$a = a(T, v)$$

$$da = \left(\frac{\partial a}{\partial T}\right)_v dT + \left(\frac{\partial a}{\partial v}\right)_T dv$$

$$da = MdT + Ndv$$

$$a = u - Ts$$

$$da = -sdT - pdv$$

Up doing the same procedure we can obtain;

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

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

☼ From Enthalpy (h)

$$h = h(s, p)$$

$$dh = \left(\frac{\partial h}{\partial s}\right)_p ds + \left(\frac{\partial h}{\partial p}\right)_s dp$$

$$dh = M ds + N dp$$

$$h = u + Pv$$

$$dh = du + Pdv + vdp$$

$$\text{here } du = Tds - Pdv$$

$$dh = Tds + vdp$$

Up doing the same procedure we can obtain;

$$\left(\frac{\partial M}{\partial p}\right)_s = \frac{\partial^2 h}{\partial s \partial p} = \left(\frac{\partial N}{\partial s}\right)_p$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$$



Thermodynamic mnemonic diagram

- The *differential expression for the four commonly used thermodynamic potentials U , A , H and G* and *the four important Maxwell relations* can be conveniently recollected with the help of *a thermodynamic mnemonic diagram*
 - The *Mnemonic diagram consists of a square with two diagonal arrows pointing upwards*. The thermodynamic potentials A , G , H and U are placed on the side of the square starting with A in alphabetical order in a clockwise direction. Since the independent variable N is common to all of these potentials it need not be shown on the diagram. The other natural variables of the potentials are arranged at *the corners of the square* such that of each of the potentials is flanked by its own natural variables.
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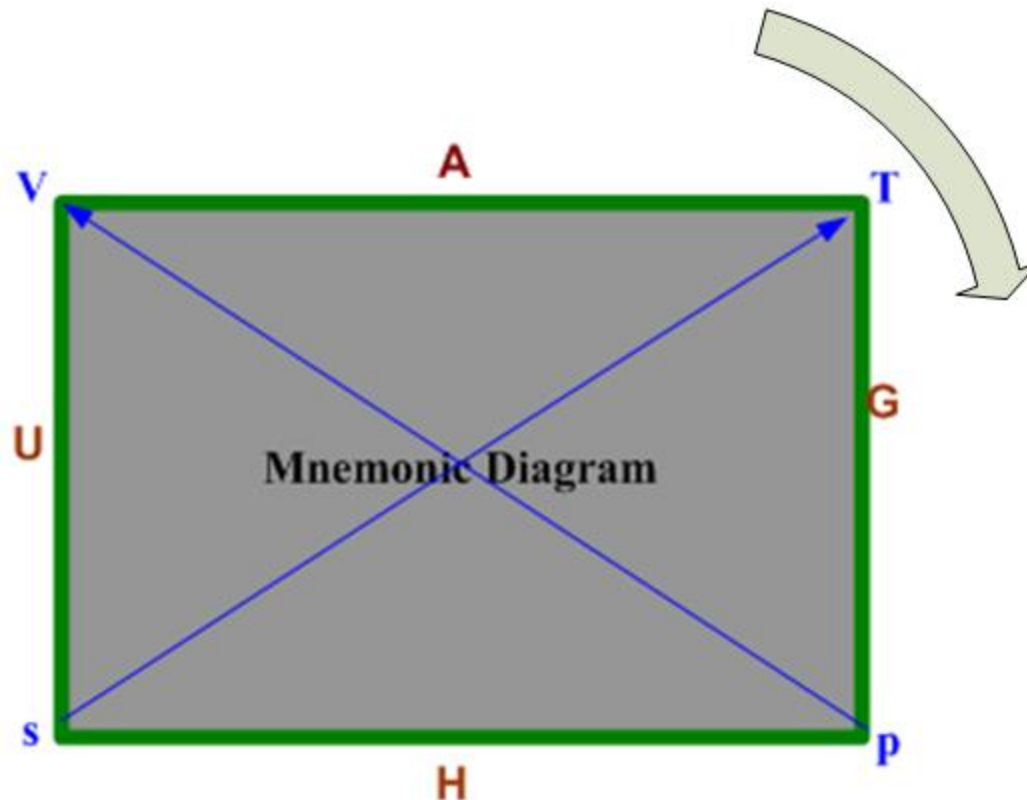
Maxwell mnemonic diagram

- The differential expression of a potential can be written in terms of the differentials of its natural variables with the help of the mnemonic diagram. The *coefficient associated differential of the natural variable* is indicated by *the diagonal arrow* and *the sign is indicated by the direction of the arrow*. An arrow *pointing away from a natural variable* indicated *a positive sign* and *an arrow pointing towards a natural variable indicated as a negative sign*; can be written as:
-



Mnemonic diagram

- Used to recollect the known four Maxwell relations derived from commonly used thermodynamic potentials. (A, U, G and H) .





Mnemonic diagram

- The partial derivative of *two neighboring properties* (e.g. V and T) correspond to *the partial derivative of the two properties* on *the opposite side of the square* (e.g. S and P).
 - The arrows pointing **towards** the natural variable indicate the negative sign and **away** from the natural variable shows positive sign.
 - The differential expression of a thermodynamic potential can be written in terms of the differential of **its own natural variables** *using the mnemonic diagram.*
-



Mnemonic diagram

- using mnemonic diagram one can obtain the natural variables of the other thermodynamic potential natural variables.

$$\mathbf{u} = \mathbf{u}(\mathbf{s}, \mathbf{v})$$

$$\mathbf{g} = \mathbf{g}(\mathbf{T}, \mathbf{P})$$

$$\mathbf{a} = \mathbf{a}(\mathbf{T}, \mathbf{v})$$

$$\mathbf{h} = \mathbf{h}(\mathbf{s}, \mathbf{p})$$



Mnemonic diagram

Differential of potentials =

(sign)(coefficient)(differential of I natural variable)
+ (sign)(coefficient)(differential of II natural variable)
+ μdN

- For example, take Gibbs energy (G)

$$g = g(T, P) \quad dg = -s dT + v dP$$

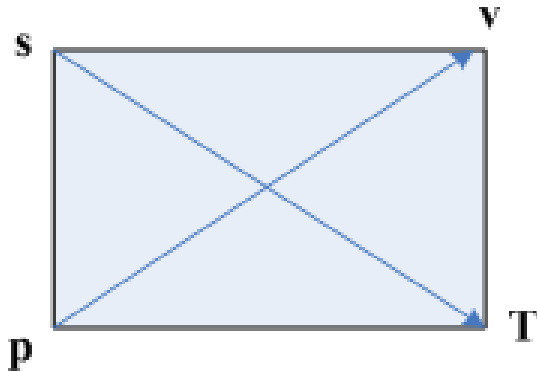
Towards the
natural
variable T

Away from
natural
variable P

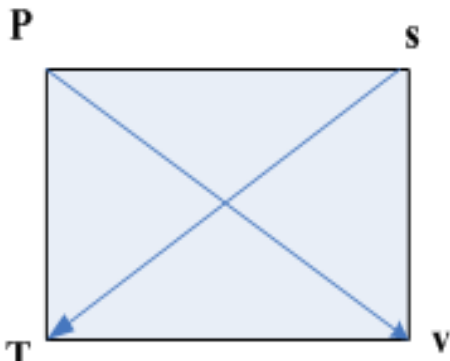
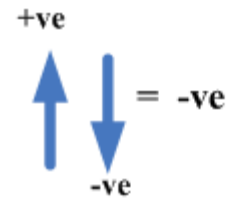


Alternative method of writing Maxwell's relation

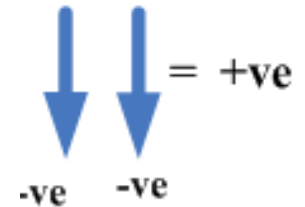
- By rotating the mnemonic diagram clock wise.



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



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





Jacobian Method of deriving Thermodynamic methods

- Definition: if $x = x(a, b)$ and $y = y(a, b)$ then the Jacobian of x and y with respect to a and b is defined as;

$$J \begin{bmatrix} x, y \\ a, b \end{bmatrix} = \begin{bmatrix} \frac{\partial x}{\partial a} & \frac{\partial x}{\partial b} \\ \frac{\partial y}{\partial a} & \frac{\partial y}{\partial b} \end{bmatrix} = \left(\frac{\partial x}{\partial a} \frac{\partial y}{\partial b} - \frac{\partial x}{\partial b} \frac{\partial y}{\partial a} \right)$$

from this definition we can write ; $\left(\frac{\partial x}{\partial y} \right)_z = \left[\frac{x, z}{y, z} \right]$



Maxwell relation

- **(Differential of potential) = (Sign) (coefficient) [Differential of I natural variable] + (sign) (coefficient) [differential of II natural variable] + μdN**
- The differential expressions for thermodynamic potentials given below

$$dU = TdS - PdV + \mu dN \text{ or } du = Tds - Pdv$$

$$dA = -SdT - PdV + \mu dN \text{ or } da = -sdT - Pdv$$

$$dH = TdS + VdP + \mu dN \text{ or } dh = Tds + vdP$$

$$dG = -SdT + VdP + \mu dN \text{ or } dg = -sdT + vdP$$



Jacobian relation

- In the thermodynamic analysis of processes we deal with a large number of relations involving the partial derivative of $p, v, T, s, u, a, h,$ and g . Jacobian notation is a convenient method of manipulating the partial derivatives.
 - The Jacobian of x, y with respect to a, b is defined as:
 - $J \left[\frac{x, y}{a, b} \right] = \left[\frac{\partial x}{\partial a} \frac{\partial y}{\partial b} - \frac{\partial x}{\partial b} \frac{\partial y}{\partial a} \right]$ usually $J \left[\frac{x, y}{a, b} \right]$ written as $\frac{[x, y]}{[a, b]}$
-



From Jacobian definition

=

A
$$\frac{[x, y]}{[p, r]} \frac{[p, r]}{[a, b]} = \frac{[x, y]}{[a, b]}$$

B
$$[x, y] = -[y, x]$$

C
$$[x, x] = 0$$

D
$$\frac{[x, z]}{[y, z]} = \left(\frac{\partial x}{\partial y} \right)_z$$

E
$$[x, y]dz + [y, z]dx + [z, x]dy = 0$$

F
$$[x, y].[z, a] + [y, z].[x, a].[z, x].[y, a] = 0$$



Jacobian rules to be Obeyed

- multiplication by unit factor

$$\begin{bmatrix} x, y \\ p, r \end{bmatrix} \begin{bmatrix} p, r \\ a, b \end{bmatrix} = \begin{bmatrix} x, y \\ a, b \end{bmatrix}$$

- Position inter changing

$$[x, y] = -[y, x]$$

- Similar domain $[x, x] = 0$
-



Jacobian Notation and Maxwell relations

$$1 \quad \left(\frac{\partial P}{\partial s} \right)_v = \frac{[P, v]}{[s, v]} = \frac{[T, s]}{[s, v]} = -\frac{[T, s]}{[v, s]} = -\left(\frac{\partial T}{\partial v} \right)_s$$

$$2 \quad \left(\frac{\partial s}{\partial v} \right)_T = \frac{[s, T]}{[v, T]} = \frac{[v, P]}{[v, T]} = -\left(\frac{\partial P}{\partial T} \right)_v$$

$$3 \quad \left(\frac{\partial v}{\partial s} \right)_P = \frac{[v, P]}{[s, P]} = \frac{[s, T]}{[s, P]} = \left(\frac{\partial T}{\partial P} \right)_s$$

$$4 \quad \left(\frac{\partial s}{\partial P} \right)_T = \frac{[s, T]}{[P, T]} = -\frac{[T, s]}{[P, T]} = -\frac{[P, v]}{[P, T]} = -\left(\frac{\partial v}{\partial T} \right)_P$$



Measurable TD Properties

1
$$C_p = T \left(\frac{\partial S}{\partial T} \right)_P = T \frac{[S, P]}{[T, P]}$$

2
$$C_v = T \left(\frac{\partial S}{\partial T} \right)_v = T \frac{[S, v]}{[T, v]}$$

3
$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P = \frac{1}{v} \frac{[v, P]}{[T, P]}$$

4
$$\kappa = \frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T = -\frac{1}{v} \frac{[v, T]}{[P, T]}$$

5
$$\frac{\beta}{\kappa} = \left(\frac{\partial P}{\partial T} \right)_v = \frac{[P, v]}{[T, v]}$$

- Function 'f' can be written in Jacobian as, if it is divided by b held 'a' constant will yield,

$$f = f(x, y)$$

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

$$\left(\frac{df}{db}\right)_a = \left(\frac{\partial f}{\partial x}\right)_y \left(\frac{dx}{db}\right)_a + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{dy}{db}\right)_a$$

$$\left[\frac{f, a}{b, a}\right] = \left[\frac{f, y}{x, y}\right] \left[\frac{x, a}{b, a}\right] + \left[\frac{f, x}{y, x}\right] \left[\frac{y, a}{b, a}\right]$$

$$\boxed{\left[\frac{f, a}{b, a}\right] = \left[\frac{f, y}{x, y}\right] \left[\frac{x, a}{b, a}\right] + \left[\frac{f, x}{y, x}\right] \left[\frac{y, a}{b, a}\right]}$$

❖ Finally,

$$\boxed{[f, a] = M[x, a] + N[y, a]}$$



Jacobian Procedure of deriving a desired

- a) Express the required partial differential in Jacobian notation.

$$\left(\frac{\partial T}{\partial P}\right)_s = \left[\frac{T, S}{P, S}\right]$$

- b) if TD potentials u, g, h and a appear in the jacobian ,they can be eliminated by where f stands for TD potentials .

$$[f, a] = M[x, a] + N[y, a]$$

Like

$$dg = v dP - s dT$$

$$\boxed{[g, a] = -s[T, a] + v[P, a]}$$

C) If entropy 's' exist in jacobian, it can be eliminated by $[T, s] = [P, v]$

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

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

- d) Finally the jacobian should expressed in terms of measurable quantities $C_p, C_v, \beta, \kappa, P, T$ and v . where

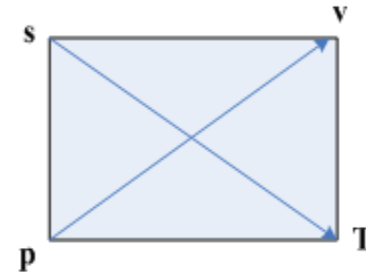
- $$\left(\frac{\partial v}{\partial T}\right)_P = \beta v$$
, β – is called thermal expansivity

- $$\left(\frac{\partial v}{\partial P}\right)_T = -\kappa v$$
, κ – isothermal compressibility

- $$\left(\frac{\partial P}{\partial T}\right)_v = \beta / \kappa$$

- the four Maxwell's relations represented in Jacobian deduce on common relation.

$$i. \left(\frac{\partial v}{\partial s} \right)_P = \left(\frac{\partial T}{\partial P} \right)_s$$



$$\left[\frac{v, P}{s, P} \right] = \left[\frac{P, v}{P, s} \right] = \left[\frac{T, s}{P, s} \right]$$

$$\boxed{[P, v] = [T, s]}$$

$$ii. \left(\frac{\partial s}{\partial P} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_P$$

$$\left[\frac{s, T}{P, T} \right] = - \left[\frac{v, p}{T, P} \right] = \left[\frac{v, p}{P, T} \right]$$

$$\boxed{[P, v] = [T, s]}$$

iii.

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

$$[P, v] = [T, s]$$

$$\left[\frac{P, v}{T, v}\right] = \left[\frac{s, T}{v, T}\right] = \left[\frac{T, s}{T, v}\right]$$

iv.

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$

$$[P, v] = [T, s]$$

$$\left[\frac{T, s}{v, s}\right] = -\left[\frac{P, v}{s, v}\right] = \left[\frac{P, v}{v, s}\right]$$



Application of Jacobian Method

- To estimate the change in one variable when some other variables is changed.
 - *estimating the change in T if P increase at constant volume .*
 - *estimating U if T and V are simultaneously changed.*
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Example

- Estimate the rise in temperature if the liquid water at 25°C is compressed isentropically from 100 kPa to 200 kPa. The following data is available for liquid water.

$$*Molar volume = 0.018 \text{ m}^3/\text{kmol}*$$

$$*C_p = 75.6 \text{ kJ/kmol K and } \beta = 2 \times 10^{-4} \text{ K}^{-1}*$$

● Adiabatic compression

- ✓ **system**: reversible and adiabatically ($s_1=s_2$) compressed ($P_1 \Rightarrow P_2$)
- ✓ estimating **the change in temperature**

$dT = \left(\frac{\partial T}{\partial P}\right)_s dP = \left[\frac{T, S}{P, S}\right] dP = \frac{[P, v]}{[P, s]} dp$, multiply by unit factor

$$\left[\frac{P, v}{P, s}\right] \left[\frac{P, T}{P, T}\right] = \left[\frac{P, T}{P, s}\right] \left[\frac{P, v}{P, T}\right] = \frac{T}{C_p} \beta v = \frac{\beta v T}{C_p}$$

$$dT = \frac{\beta v T}{C_p} dp$$

● isothermal compression

- ✓ **System**: compressed isothermally from P_1 to P
- ✓ estimate the **change in internal energy**

$$du = \left(\frac{\partial u}{\partial P} \right)_T dP = \frac{[u, T]}{[P, T]} dp = \frac{T[v, P] - P[v, T]}{[P, T]} dp$$

$$du = \left\{ -T \left(\frac{\partial v}{\partial T} \right)_P - P \left(\frac{\partial v}{\partial P} \right)_T \right\} dp$$

$[u, x] = T[s, x] - P[v, x]$

$[P, v] = [T, s]$

$$= \{-T\beta v + Pkv\} dp = \{v(Pk - \beta T)\} dp$$

$du = \{v(Pk - \beta T)\} dp$

● Internal energy as a function of T and V

- ✓ **system** : Temperature and volume changed **simultaneously**
- ✓ Estimate change in **internal energy** of

the system

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

$$du = \left[\frac{u, v}{T, v} \right] dT + \left[\frac{u, T}{v, T} \right] dv$$

$$du = \frac{T[s, v] - p[v, v]}{[T, v]} dT + \frac{T[s, T] - P[v, T]}{[v, T]} dv$$

$$\boxed{P[v, v] = 0}$$

$$du = \left\{ \frac{T[s, v]}{[T, v]} \right\} dT + \left\{ \frac{T[s, T]}{[v, T]} - P \right\} dv$$

$$du = \{C_v\} dT + \left\{ \frac{T[v, p]}{[v, T]} - P \right\} dv$$

$$du = \{C_v\} dT + \left\{ T \beta / \kappa - P \right\} dv$$

● Enthalpy as a function of T and P

- ✓ **system:** Temperature and pressure changed **simultaneously**
- ✓ estimate change in **enthalpy**

- $dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP$

$$dh = \left[\frac{h, P}{T, P}\right] dT + \left[\frac{h, T}{P, T}\right] dP$$

$$\boxed{[h, x] = T[s, x] + v[P, x]}$$

$$dh = \frac{T[s, P] + v[P, P]}{[T, P]} dT + \frac{T[s, T] + v[P, T]}{[P, T]} dP$$

$$dh = \left\{ \frac{T[s, P]}{[T, P]} \right\} dT + \left\{ \frac{T[s, T]}{[P, T]} + v \right\} dP$$

$$\boxed{dh = \{C_P\}dT + \{-\beta vT + v\}dP}$$

● Joule -Thomson coefficient

- estimated from a knowledge of fundamental relation and equation of state of a fluid
 - ❖ Design of refrigeration equipment
 - ❖ Joule-thomson coefficient is defined as

$$\mu_{\pi} = \left(\frac{\partial T}{\partial P} \right)_h$$

$$\mu_{\pi} = \frac{[T, h]}{[P, h]} = \frac{[h, T]}{[h, P]} = \frac{T[s, T] + v[P, T]}{T[s, P] + v[P, P]} \quad \boxed{v[P, P] = 0}$$

$$\mu_{\pi} = \frac{T[v, P] + v[P, T]}{T[s, P]} \quad \boxed{[h, x] = T[s, x] + v[P, x]}$$

- Remember

$$C_P = T \left[\frac{s, P}{T, P} \right] \rightarrow [T, P] \frac{C_P}{T} = [s, P]$$

$$\mu_\pi = \frac{T[v, P] + v[P, T]}{C_P [T, P]}$$

$$\mu_\pi = \frac{T}{C_P} \beta v - \frac{v}{C_P} = \frac{v}{C_P} (T\beta - 1)$$

Summary

basic equations	Maxwell relations	working equations
$dU = TdS - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$	$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$
$dH = TdS + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$	$dH = C_P dT - \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] dP$
$dA = -PdV - SdT$	$\left(\frac{\partial S}{\partial V}\right)_T = +\left(\frac{\partial P}{\partial T}\right)_V$	$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$
$dG = VdP - SdT$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$	$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$
