

Thermodynamics

Euler's Theorem, Maxwell Relations, Gibbs- Helmholtz equation

Semester I

MSc Chemistry

St. Mary's College, Manarcaud



Euler's Theorem

If x is a single-valued function of the variables y and z eg., a thermodynamic property of a closed system, it is possible to write for the complete differential dx ,

$$dx = M dy + N dz \dots\dots\dots 1$$

Where M and N are also functions of the variables. If z is a constant, so that dz is zero then equation 1 yields the result

$$\left(\frac{\partial x}{\partial y}\right)_z = M \dots\dots\dots 2$$

Whereas if y is maintained constant so that dy is zero

$$\left(\frac{\partial x}{\partial z}\right)_y = N \dots\dots\dots 3$$

If equation 2 is differentiated wrt z with y constant and with respect to y with z constant the results must be identical so that

$$\left(\frac{\partial M}{\partial z}\right)_y = \left(\frac{\partial N}{\partial y}\right)_z \dots\dots\dots 4$$

This result is sometimes referred to as the Euler criterion or the reciprocity relationship.

Maxwell Relations-I

- Enthalpy , $H=U+PV$
- A small change in H, $dH=dU+PdV+VdP$
- $dU+ PdV= TdS$
- $dH = TdS+ VdP$ 1
- Since $H= f(S,P)$ therefore the total differential dH is given by
- $dH =\left(\frac{\partial H}{\partial S}\right)_P dS_+ \left(\frac{\partial H}{\partial P}\right)_S dP$ 2
- On comparing the coefficients of dS and dP from equation 1 and 2 separately we get
- $\left(\frac{\partial H}{\partial S}\right)_P = T$ 3
- $\left(\frac{\partial H}{\partial P}\right)_S = V$ 4

Differentiation of equation 3 with respect to P at constant S

$$\frac{\partial}{\partial P} \left\{ \left(\frac{\partial H}{\partial S} \right)_P \right\}_S = \left(\frac{\partial T}{\partial P} \right)_S \dots\dots\dots 5$$

Differentiating equation 4 wrt S at constant P gives

$$\frac{\partial}{\partial S} \left\{ \left(\frac{\partial H}{\partial P} \right)_S \right\}_P = \left(\frac{\partial V}{\partial S} \right)_P \dots\dots\dots 6$$

H is a state function, dH is exact differential therefore,

$$\frac{\partial^2 H}{\partial P \partial S} = \frac{\partial^2 H}{\partial S \partial P} \dots\dots\dots 7$$

From equation 5 and 6 we obtain Maxwell relations

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

Maxwell relations-II

- Combined form of first and second law is
- $dU = TdS - PdV$1
- That is U is a function of entropy and volume, $U = f(S, V)$. The total differential dE is given by
- $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$2
- Comparing the coefficients of dS and dV separately in equations 1 and 2 we get
- $\left(\frac{\partial U}{\partial S}\right)_V = T$ 3
- $\left(\frac{\partial U}{\partial V}\right)_S = -P$ 4
- On differentiating wrt V at constant S, equation 3 changes to

$$\bullet \frac{\partial}{\partial V} \left[\left(\frac{\partial U}{\partial S}\right)_V \right]_S = \left(\frac{\partial T}{\partial V}\right)_S \dots\dots\dots 5$$

• On differentiating equation 4 wrt S at constant V

• $\frac{\partial}{\partial S} \left[\left(\frac{\partial U}{\partial V} \right)_S \right]_V = - \left(\frac{\partial P}{\partial S} \right)_V \dots\dots\dots 6$

• Since U is a state function and dU is exact differential, the Euler's theorem must be valid i.e,

• $\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V} \dots\dots\dots 7$

• From equations 5 and 6 we get Maxwell relations

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

Maxwell relations -III

- Helmholtz free energy (work function A) is given by
- $A = U - TS$
- Differentiation gives
- $dA = dU - TdS - SdT$
- But the combined first and second laws of thermodynamics reads
- $TdS = dU + PdV$
- $dA = -SdT - PdV \dots\dots\dots 1$
- This equation indicates that $A = f(T, V)$, hence the total differential dA may be expressed as
- $dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV \dots\dots\dots 2$

- On comparing the coefficient of dT and the coefficient of dV in equation

- $\left(\frac{\partial A}{\partial T}\right)_V = -S \dots\dots\dots 3$

- $\left(\frac{\partial A}{\partial V}\right)_T = -P \dots\dots\dots 4$

- On differentiating equation 3 wrt V at constant T

- $\frac{\partial}{\partial V} \left[\left(\frac{\partial A}{\partial T}\right)_V \right]_T = - \left(\frac{\partial S}{\partial V}\right)_T \dots\dots\dots 5$

- On differentiating equation 4 wrt T and V

- $\frac{\partial}{\partial T} \left[\left(\frac{\partial A}{\partial V}\right)_T \right]_V = - \left(\frac{\partial P}{\partial T}\right)_V \dots\dots\dots 6$

- Since A is a state function and dA is exact differential hence

- $\frac{\partial^2 A}{\partial V \partial T} = \frac{\partial^2 A}{\partial T \partial V} \dots\dots\dots 7$

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

Maxwell relations-IV

Consider Gibbs free energy $G = H - TS$

A small change in G can be written as

$$\begin{aligned}dG &= dH - SdT - TdS \\ &= TdS + VdP - SdT - TdS\end{aligned}$$

$$dG = -SdT + VdP \dots\dots\dots 1$$

Let us write G as function of T and P as $G = f(T, P)$, hence the total differential dG may be expressed as

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \dots\dots\dots 2$$

On comparing the coefficient of dT and the coefficient of dP in equation 1 and 2

$$S = - \left(\frac{\partial G}{\partial T}\right)_P \dots\dots\dots 3$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T \dots\dots\dots 4$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \dots\dots\dots 3$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \dots\dots\dots 4$$

• On differentiating 3 wrt P at constant T

$$\frac{\partial}{\partial P} \left[\left(\frac{\partial G}{\partial P}\right)_T \right]_P = - \left(\frac{\partial S}{\partial P}\right)_T \dots\dots\dots 5$$

• On differentiating 4 wrt T at constant P

$$\frac{\partial}{\partial T} \left[\left(\frac{\partial G}{\partial P}\right)_T \right]_P = \left(\frac{\partial V}{\partial T}\right)_P \dots\dots\dots 6$$

• Since G is a state function and hence $\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial^2 G}{\partial P \partial T}$

• Equation 5 and 6 gives

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

• Where $\alpha = V^{-1} \left(\frac{\partial V}{\partial T}\right)_P$

Significance of Maxwell Relations

- The use of these relations can reduce the tedious experimental work into simple paper and pen exercise.
- For example, the variation of entropy with volume at a constant temperature cannot be studied directly by experimental method as we do not have any apparatus such as entropymeter.
- The same can be evaluated by using the values of α the coefficient of thermal expansion and β the compressibility coefficient for any substance by using Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\beta}$
- Similarly the knowledge of the value of α of a substance assists us to study the isothermal change in entropy with the change in pressure
- Maxwell relations are also very useful to deduce many other thermodynamic relations viz., the Clapeyron equation, thermodynamic equation of state etc. which are very important to deduce some more information about the system.

Gibbs- Helmholtz equation

- Consider a process taking place at constant pressure
- Free energy of the process is given as
- $G = H - TS$ 1
- $= (U + PV) - TS$

Differentiating the above equation

$$dG = (dU + PdV) + VdP - TdS - SdT$$

$$dG = dq + vdP - TdS - SdT \quad (\text{From First law})$$

$$dG = TdS + VdP - TdS - SdT \quad (\text{From Second law})$$

$$dG = VdP - SdT \quad \text{.....2}$$

- The process is at constant pressure
- $dG = -SdT$ 3
- At initial state $dG_1 = -S_1dT$ 4
- For final state $dG_2 = -S_2 dT$ 5
- Comparing equation 4 and 5
- $dG_2 - dG_1 = -(S_2 - S_1) dT$
- $d\Delta G = -\Delta SdT$
- $\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = -\Delta S$ 6
- We know $\Delta G = \Delta H - T\Delta S$
- $-\Delta S = \frac{\Delta G - \Delta H}{T}$ 7 equating 6 and 7 we get
- $\frac{\Delta G - \Delta H}{T} = \left[\frac{\partial(\Delta G)}{\partial T}\right]_P$
- $\Delta G = \Delta H + T \left[\frac{\partial(\Delta G)}{\partial T}\right]_P \longrightarrow$ This is the Gibbs Helmholtz equation

- Gibbs Helmholtz equation is applicable to all processes occurring at constant pressure.
- Calculate ΔG for a reaction at a temperature other than 298K
- Calculate the effect of a temperature change on the equilibrium constant K_p
- It has been used for calculating the enthalpy change ΔH for a process or a reaction provided the values of free energy changes at two different temperatures are known
- For a reaction at constant volume, the corresponding equation will be
- $$\Delta A = \Delta U + T \left[\frac{\partial(\Delta A)}{\partial T} \right]_v$$