In a similar way we can derive all the Maxwell's equations from the Gibbs equations.

Slide 5

Use of Maxwell Equations

Enthalpy relations

- homogeneous fluid of constant composition

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

- liquids

$$dH = C_P dT + \left[V(1 - \beta T) \right] dP$$

- ideal gases

$$dH^{ig} = C_P^{ig} dT$$

Homogeneous fluid means that there is only one phase present. Constant composition means that the concentrations of all components remain unchanged (e.g., are at steady-state).

We want an expression for enthalpy as a function of T and P (because as was stated earlier, T and P are the easiest and most accurate state properties to measure).

Mathematically we want H = H(T,P)

We can express this in a differential form as:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad \textbf{(Equation 1)}$$

We already know by the definition of enthalpy that:

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

We need an expression for $\left(\frac{\partial H}{\partial P}\right)_T$

Using Gibbs equation for dH in terms of dP and dS:

$$dH = TdS + VdP$$

Now set T constant and divide by dP:

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

Now we can substitute the Maxwell's relation:

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

To give:

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

Now substituting back into Equation 1 gives the general form for dH given in slide 5:

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

We can make this specific for liquids by recalling that the definition of the expansion coefficient for a fluid is:

$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ (e.g., the fractional increase in the molar volume of a liquid with temperature)

Re-arranging gives:

$\left(\frac{\partial V}{\partial T}\right)_P = \beta V$ which can be substituted back into the general equation and simplified to give:

$$dH = C_P dT + V\left(1-\beta T\right)dP$$

Lastly, for an ideal gas (recalling that PV=RT)

$\beta = \frac{1}{T}$ which when substituted yields:

$$dH = C_P dT + V\left(1-\frac{1}{T}T\right)dP = C_P dT + V\left(1-1\right)dP = C_P dT$$

So that for an ideal gas we can say:

$$dH^{ig} = C_P^{ig} dT$$

Slide 6

Entropy Relationships

- homogeneous fluid of constant composition

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

- liquids

$$dS = \frac{C_P}{T}dT - \beta V dP$$

- ideal gases

$$dS^{ig} = \frac{C_P^{ig}}{T}dT - \frac{R}{P}dP$$

As before we want an expression as a function of T and P (because as was stated earlier, T and P are the easiest and most accurate state properties to measure).

Mathematically we want S = S(T,P)

We can express this in a differential form as:

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \qquad \textbf{(Equation 1)}$$

We already have the Maxwell relation that states:

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

We need an expression for $\left(\frac{\partial S}{\partial T}\right)_P$

Using Gibbs equation for dH in terms of dP and dS:

dH = TdS + VdP

Now set P constant and divide by dT:

$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P + V\left(\frac{\partial P}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P + 0$$

(Note: the differential in the last term is zero since by definition dP =0.)

Note we could have just as easily said that for constant P, dP = 0 and therefore in the first step from the Gibbs equation:

$$dH = TdS + VdP = TdS + 0 \quad \text{(because } dP = 0\text{)}$$

As before $\left(\frac{\partial H}{\partial T}\right)_P = C_P = T\left(\frac{\partial S}{\partial T}\right)_P$ which upon substitution gives:

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

Now substituting back into Equation 1 gives the general form for dS given in slide 6:

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

Once again recalling that the definition of the expansion coefficient for a fluid is:

$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ (e.g., the fractional increase in the molar volume of a liquid with temperature)

As before, re-arranging gives:

$\left(\frac{\partial V}{\partial T}\right)_P = \beta V$ which can be substituted back into the general equation and simplified to give:

$$dS = C_P \frac{dT}{T} - \beta V dP$$

Lastly, for an ideal gas (recalling that PV=RT)

$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$ which when substituted yields an expression for dS for an ideal gas of:

$$dS^{ig} = C_P^{ig} \frac{dT}{T} - \frac{R}{P} dP$$

Slide 7

EXAMPLE

Compute the change in enthalpy and entropy for water being pumped from an initial pressure of 101.3 kPa and 20 °C to 3000 kPa and 60 °C. The volume expansivity of water is 6.48 $(10^{-4})K^{-1}$ at 60 °C and 3000 kPa and the heat capacity of water is 75.3 J/(mol K).

Given: T_1 = 20ºC = 293 K T_2 = 60 ºC = 333 K
P_1 = 101.3 kPa P_2 = 3000 kPa