SKF2213: CHEMICAL ENGINEERING THERMODYNAMICS

Thermodynamic Properties for Fluids

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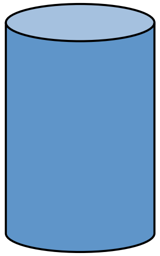
Objectives

- To develop fundamental property relations (FPR) of U,H,S,G,A,V,P,T from 1st and 2nd Law of Thermodynamic.
- Using FPR to derive equations for thermodynamic properties such as H and S.
- To use the concept of residual property in the calculation of thermodynamic property.
- To develop and utilize the generalized correlation for the calculation of residual property.
- To be able to use diagram and table of thermodynamic property.

Property Relations for Homogeneous Phases

Consider the following system,



- Closed system
- Homogeneous

  i.e. single phase and no change in composition!

  e.g. Air
- Initial conditions P_1 and T_1
- Final conditions P_2 and T_2

No phase change!!

1st Law (Energy Balance) for closed system,

$$d(nU) = \partial Q + \partial W$$

From definition of entropy *(S)*, ……..see chapter 5

$$d(nS) = \frac{\partial Q_{rev}}{T}$$

For reversible process the EB becomes,

$$d(nU) = \partial Q_{rev} + \partial W_{rev}$$

$$d(nU) = Td(nS) - Pd(nV) \qquad (6.1)$$

We know that *H=U+PV*, now let us also define,

A = U-TS	Helmholtz Energy
G = H-TS	Gibbs Energy

Differentiate these properties (*H, A and G*),

$$d\left(nH\right)=d\left(nU\right)+Pd\left(nV\right)+nVdP$$

substitute eqn 6.1 for dnU,

$$d\left(nH\right)=Td(nS)-Pd(nV)+Pd\left(nV\right)+nVdP$$

$$d\left(nH\right)=Td\left(nS\right)+nVdP$$

Continue,

$$d(nA) = d(nU) - Td(nS) - (nS)dT$$

substitute for dnU,

$$d(nA) = Td(nS) - Pd(nV) - Td(nS) - (nS)dT$$

$$d(nA) = -Pd(nV) - (nS)dT$$

$$d(nG) = d(nH) - Td(nS) - (nS)dT$$

substitute for dnH,

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

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

For $n=1$,

$$dU = TdS - PdV \qquad (6.7)$$

$$dH = TdS + VdP \qquad (6.8)$$

$$dA = -PdV - SdT \qquad (6.9)$$

$$dG = VdP - SdT \qquad (6.10)$$

These are called fundamental property relations (FPR).

Note: The unit for TS and PV is energy unit.

Notice that the FPR for Gibbs Energy is a function of commonly measured variable P and T,

$$G = G(T,P)$$

All FPRs are in the form of,

$$dF = MdX + NdY \qquad (6.11)$$

where

$$F = F(X,Y)$$

Since *F* is a state function, we can differentiate *F(X,Y)* as follows,

$$dF = \left(\frac{\partial F}{\partial X}\right)_Y dX + \left(\frac{\partial F}{\partial Y}\right)_X dY$$

So let,

$$M = \left(\frac{\partial F}{\partial X}\right)_Y \qquad N = \left(\frac{\partial F}{\partial Y}\right)_X$$

$$dF = MdX + NdY$$

Differentiate one more time,

$$\left(\frac{\partial M}{\partial Y}\right)_X = \frac{\partial^2 F}{\partial Y \partial X} \qquad \left(\frac{\partial N}{\partial X}\right)_Y = \frac{\partial^2 F}{\partial X \partial Y}$$

So,

$$\left(\frac{\partial M}{\partial Y}\right)_X = \left(\frac{\partial N}{\partial X}\right)_Y \qquad (6.12)$$

Eqn 6.12 is the criterion of exactness for an exact differential expression of Eqn 6.11.

Apply criterion of exactness to FPRs,

$$dU = TdS - PdV \qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad (6.13)$$

$$dH = TdS + VdP \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad (6.14)$$

$$dA = -PdV - SdT \qquad \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \qquad (6.15)$$

$$dG = VdP - SdT \qquad \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \qquad (6.16)$$

These (Eqn 6.13-16) are known as Maxwell's equations

Application of FPRs and Maxwell's Eqn:

Use in the derivation of the general equation for *H*

$$H = H(T, P)$$

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

Energy balance,

$$\partial Q + \partial W = dU + \cancel{dE_K} + \cancel{dE_P}$$

$$\partial Q - PdV = dU$$

$$\partial Q = dU + PdV$$

$$\partial Q = (dH)_P$$

$$C_p = \frac{\partial Q}{dT} = \left(\frac{\partial H}{dT}\right)_P$$

Note: for constant pressure process,

$$dH = dU + dPV = dU + PdV + \cancel{V\,dP}$$

So eqn (a) becomes,

$$dH = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad \text{(b)}$$

From FPR,

$$dH = TdS + VdP$$

differentiate wrt P at constant T,

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

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

From Maxwell' eqn, $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V \qquad (6.19)$$

Substitute into (b),

$$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP \qquad (6.20)$$

This general eqn for enthalpy is in term of measured variable P,V,T

Application of FPRs and Maxwell's Eqn
- to derive general equation for S

$$S = S(T,P)$$

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

From FPR,

$$dH = TdS + VdP$$

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

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

From Maxwell's equation, $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$ so, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

Substitute into (b),

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP \qquad (6.21)$$

This general eqn for entropy is in term of measured variable P,V,T

Application of General Equation of *H* (Eqn 6.20) and *S* (Eqn 6.21) for Homogenous and Constant Composition Fluid.

-For system with ideal gas, $PV = RT$, $V = \frac{RT}{P}$, so $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$

Substitute into (6.20) and (6.21),

$$dH^{ig} = C_P^{ig} dT + \left[V - T\left(\frac{R}{P}\right)\right] dP = C_P^{ig} dT + \left[\cancel{V} - V\right] dP$$

$$dH^{ig} = C_P^{ig} dT \qquad (6.23)$$

$$dS^{ig} = C_P^{ig} \frac{dT}{T} - \frac{R}{P} dP \qquad (6.24)$$

These are similar to eqn 4.2 and eqn 5.14

-Alternative forms for liquids

From Maxwell's eqn and the definition of volume expansivity,

Also from 6.19,

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P = \left(1-\beta T\right)V \qquad (6.26)$$

Substitute into 6.20,

$$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP \qquad \left(6.20\right)$$

$$dH = C_P dT + \left(1-\beta T\right)VdP \qquad (6.28)$$

This is alternative form for liquid.

For entropy,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\beta V \qquad (6.25)$$

Substitute into eqn 6.21,

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP \qquad (6.21)$$

$$dS = C_P \frac{dT}{T} - \beta V dP \qquad (6.29)$$

This is alternative form for liquid.

See example 6.2

- For incompressible liquid ($\beta = \kappa = 0$),

$$C_P = C_v$$

Let's look again at general equation for enthalpy for homogenous and constant composition system

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \qquad (6.20)$$

To use eqn 6.20, we needs

- Initial and final *T* & *P*
- *PVT* relation or *PVT* data
- C_P

For gas phase however, most C_P are tabulated for ideal gas only i.e. C_p^{ig} (Table C.1)

Unless we have actual C_P for gases, we can't use eqn 6.20 to calculate the enthalpy for real (actual) gas!!

How can we calculate the enthalpy of a real gas using an ideal gas heat capacity?

Well,

a. First we calculate H^{ig} using C_P^{ig} .

b. Then we use *PVT* relation or *PVT* data to determine the residual enthalpy (H^R) which is the DIFFERENCE between real enthalpy (H) and ideal gas enthalpy (H^{ig}).

$$\text{Residual Enthalpy} \equiv H^R = H - H^{ig}$$

c. So, the real enthalpy is found by adding H^R to the H^{ig}.

$$H = H^{ig} + H^R$$

Residual Properties

Residual Property = Real Property - Ideal Gas Property

$$H^R = H - H^{ig} \qquad S^R = S - S^{ig} \qquad G^R = G - G^{ig} \quad \text{etc.}$$

For example, to calculate ΔH or H_2-H_1 we shall use the hypothetical path.

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$\Delta H = \Delta H_1 + \Delta H_2^{ig} + \Delta H_3$$

$$\Delta H = \left(H_1^{ig} - H_1\right) + \left\langle C_P^{ig} \right\rangle_H \left(T_2 - T_1\right) + \left(H_2 - H_2^{ig}\right)$$

$$\Delta H = -H_1^R + \left\langle C_P^{ig} \right\rangle_H \left(T_2 - T_1\right) + H_2^R$$

$$\Delta H = \left\langle C_P^{ig} \right\rangle_H \left(T_2 - T_1\right) + H_2^R - H_1^R \qquad (6.93)$$

Now we need to figure out how to determine H^R?

Note,

$\left\langle C_P^{ig} \right\rangle_H$ is mean heat capacity and is given by equation (4.8)

To determine H^R, let us start with the Gibbs Free Energy.

$$G = G(T,P)$$

divide by RT and differentiate,

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

Substitute FPR for dG,

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT}(VdP - SdT) - \frac{(H-TS)}{RT^2}dT = \frac{V}{RT}dP - \cancel{\frac{S}{RT}dT} - \frac{H}{RT^2}dT + \cancel{\frac{S}{RT}dT}$$

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT}dP - \frac{H}{RT^2}dT \qquad (6.37)$$

Let us do for residual Gibbs energy,

$$G^R = G - G^{ig}$$

divide by RT and differentiate,

$$d\left(\frac{G^R}{RT}\right) = d\left(\frac{G}{RT}\right) - d\left(\frac{G^{ig}}{RT}\right)$$

Apply eqn 6.37, we get

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

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}dP - \frac{H^R}{RT^2}dT \qquad (6.42)$$

Apply criterion of exactness.

$$\frac{V^R}{RT} = \left[\frac{\partial\left(G^R/RT\right)}{\partial P}\right]_T \qquad (6.43)$$

$$\frac{H^R}{RT} = -T\left[\frac{\partial\left(G^R/RT\right)}{\partial T}\right]_P \qquad (6.44)$$

Rearrange eqn 6.43 and integrate from ideal gas state (*P*=*0*) to arbitrary *P* (actual *P*),

$$\int_{ig}^{act.} d\left(G^R/RT\right) = \int_0^P \frac{V^R}{RT}\,\mathrm{dP}$$

$$\frac{G^R}{RT} - 0 = \int_0^P \frac{V^R}{RT} dP = \int \frac{V - V^{ig}}{RT} dP$$

$$\frac{G^R}{RT} = \int \left(\frac{ZRT}{P} - \frac{RT}{P} \right) \frac{1}{RT} dP$$

$$\frac{G^R}{RT} = \int \frac{(Z-1)}{P} dP \qquad (6.49)$$

Differentiate wrt. T at constant P,

$$\left(\frac{d\left(G^R/_{RT}\right)}{dT}\right)_P = \int \left[\left(\frac{\partial \left(Z/_P\right)}{\partial T}\right)_P - \cancel{\left(\frac{\partial \left(1/_P\right)}{\partial T}\right)_P} \right] dP = \int \frac{1}{P}\left(\frac{\partial Z}{\partial T}\right)_P dP = \int \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{\mathrm{P}}$$

Substitute into eqn 6.44 for H^R

- We will get,

$$\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \qquad (6.46)$$

- Similarly from,

$$\frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT}$$

We will get,

$$\frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P} \qquad (6.48)$$

- Hence, as in eqn 6.46 and 6.48, we need either *PVT* data or correlations for *Z* to solve for H^R and S^R.

Enthalpy for ‘real’ gas

$$H = H^{ig} + H^{R}$$

$$\text{note: } \Delta H^{ig} = H^{ig} - H_o^{ig} = \int_{T_o}^{T} C_P^{ig}\, dT$$

$$H = H_o^{ig} + \int_{T_o}^{T} C_P^{ig}\, dT + H^{R}$$

$$H^{ig} = H_o^{ig} + \int_{T_o}^{T} C_P^{ig}\, dT$$

$$H = H_o^{ig} + \left\langle C_P^{ig} \right\rangle_H \left(T - T_o\right) + H^{R} \qquad (6.52)$$

Note: Here the reference state is ideal gas at T_o , P_o.

$\Delta H = H_2 - H_1$ is calculated as follows,

$$H_1 = H_o^{ig} + \left\langle C_P^{ig} \right\rangle_H \left(T_1 - T_o\right) + H_1^{R}$$

$$H_2 = H_o^{ig} + \left\langle C_P^{ig} \right\rangle_H \left(T_2 - T_o\right) + H_2^{R}$$

$$\Delta H = H_2 - H_1 = \left\langle C_P^{ig} \right\rangle_H \left(T_2 - T_1\right) + H_2^{R} - H_1^{R} \qquad (6.93)$$

Similarly, entropy for ‘real’ gas

$$S = S^{ig} + S^{R}$$

$$S = S_o^{ig} + \int_{T_o}^{T} C_P^{ig} \frac{dT}{T} - R\ln\frac{P}{P_o} + S^{R}$$

$$S = S_o^{ig} + \left\langle C_P^{ig} \right\rangle_S \ln\frac{T}{T_o} - \mathrm{R}\ln\frac{P}{P_o} + S^{R} \qquad (6.53)$$

$$\Delta S = \left\langle C_P^{ig} \right\rangle_S \ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1} + S_2^{R} - S_1^{R} \qquad (6.94)$$

where

$$\left\langle C_P^{ig} \right\rangle_S = R\left(A + \left[BT_o + \left(CT_o^2 + \frac{D}{\tau^2 T_o^2} \right)\left(\frac{\tau+1}{2} \right) \right]\left(\frac{\tau-1}{\ln\tau} \right) \right) \qquad (5.17)$$

H^R and S^R by EOS

- Using two-term Virial Equation

Combined Eqn 3.38, 6.49 and 6.44 will give,

$$\frac{H^R}{RT} = \frac{P}{R}\left(\frac{B}{T} - \frac{dB}{dT}\right) \qquad (6.55)$$

$$\frac{S^R}{R} = -\frac{P}{R}\frac{dB}{dT} \qquad (6.56)$$

- Using three-term Virial Equation

Combined Eqn 3.40, 6.49 in term of ρ

$$\frac{H^R}{RT} = T\left[\left(\frac{B}{T} - \frac{dB}{dT}\right)\rho + \left(\frac{C}{T} - \frac{1}{2}\frac{dC}{dT}\right)\rho^2\right] \qquad (6.62)$$

Later we will show a much easier to use generalized virial-coefficient eqn…..

• Using Generic Cubic EOS

$$\frac{H^R}{RT} = Z - 1 + \left[\frac{d\ln\alpha(T_r)}{d\ln T_r} - 1 \right] qI \qquad (6.67)$$

$$\frac{S^R}{R} = \ln(Z-\beta) + \frac{d\ln\alpha(T_r)}{d\ln T_r} qI \qquad (6.68)$$

Where

$$\beta = \Omega \frac{P_r}{T_r} \qquad (3.53) \qquad\qquad q = \frac{\Psi\alpha(T)_r}{\Omega T_r} \qquad (3.54)$$

and

For $\varepsilon = \sigma$,

$$I = \frac{\beta}{Z + \varepsilon\beta}$$

For $\varepsilon \neq \sigma$,

$$I = \frac{1}{\sigma - \varepsilon} \ln\left(\frac{Z + \sigma\beta}{1 + \varepsilon\beta} \right)$$

Note: We first have to solve for *Z*, using eqn 3.52 for vapor and vapor-like root.

H^R and S^R from Generalized Correlations

from

$$P = P_c P_r \qquad dP = P_c dP_r$$
$$T = T_c T_r \qquad dT = T_c dT_r$$

Substitute into eqn 6.46 and 6.48,

$$\frac{H^R}{R} = -T_c^2 T_r^2 \int_o^{P_r} \left(\frac{\partial Z}{T_c \partial T_r}\right)_{P_r} \frac{P_c dP_r}{P_c P_r} = -T_r^2 \int_o^{P_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} \qquad (6.83)$$

$$\frac{S^R}{R} = -T_c T_r \int_o^{P_r} \left(\frac{\partial Z}{T_c \partial T_r}\right)_{P_r} \frac{P_c dP_r}{P_c P_r} - \int_o^{P_r} (Z-1) \frac{P_c dP_r}{P_c P_r} = -T_r \int_o^{P_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} - \int_o^{P_r} (Z-1) \frac{dP_r}{P_r} \qquad (6.84)$$

The Lee/Kesler Correlation

From

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

$$\left(\frac{\partial Z}{\partial T_r}\right)_{P_r} = \left(\frac{\partial Z^o}{\partial T_r}\right)_{P_r} + \omega\left(\frac{\partial Z'}{\partial T_r}\right)_{P_r}$$

Substitute into eqn 6.83 and 6.84,

$$\frac{H^R}{RT_c} = -T_r^2\int_o^{P_r}\left(\frac{\partial Z^o}{\partial T_r}\right)_{P_r}\frac{dP_r}{P_r} - \omega T_r^2\int_o^{P_r}\left(\frac{\partial Z'}{\partial T_r}\right)_{P_r}\frac{dP_r}{P_r}$$

$$\frac{S^R}{R} = -T_r\int_o^{P_r}\left[\left(\frac{\partial Z^o}{\partial T_r}\right)_{P_r} + \omega\left(\frac{\partial Z'}{\partial T_r}\right)_{P_r}\right]\frac{dP_r}{P_r} - \int_o^{P_r}\left(Z^o + \omega Z' - 1\right)\frac{dP_r}{P_r}$$

$$\frac{S^R}{R} = -\int_o^{P_r}\left[T_r\left(\frac{\partial Z^o}{\partial T_r}\right)_{P_r} + Z^o - 1\right]\frac{dP_r}{P_r} - \omega\int_o^{P_r}\left[T_r\left(\frac{\partial Z'}{\partial T_r}\right)_{P_r} + Z'\right]\frac{dP_r}{P_r}$$

$$\frac{H^R}{RT_c} = \frac{\left(H^R\right)^0}{RT_c} + \omega\frac{\left(H^R\right)^1}{RT_c} \qquad (6.85)$$

$$\frac{S^R}{R} = \frac{\left(S^R\right)^0}{R} + \omega\frac{\left(S^R\right)^1}{R_c} \qquad (6.86)$$

Tables E5-E12 developed by Lee/Kesler give the values for the followings,

$$\frac{\left(H^R\right)^0}{RT_c}, \quad \frac{\left(H^R\right)^1}{R_cT_c}, \quad \frac{\left(S^R\right)^0}{R}, \quad \frac{\left(S^R\right)^1}{R_c}$$

Substitute these values into equation 6.85, we get

$$H^R = \left[\frac{\left(H^R\right)^0}{RT_c} + \omega\frac{\left(H^R\right)^1}{RT_c}\right]\mathrm{RT_c}$$

- Generalized second-virial-coefficient

$$Z = 1 + B^{o}\frac{P_r}{T_r} + \omega B^{'}\frac{P_r}{T_r}$$

Differentiate,

$$\left(\frac{\partial Z}{\partial T_r}\right)_{P_r} = P_r\left(\left(\frac{dB^{o}}{dT_r}\right)\left(\frac{1}{T_r}\right) + B^{o}\frac{d\left(\frac{1}{T_r}\right)}{dT_r}\right) + \omega P_r\left(\left(\frac{dB^{'}}{dT_r}\right)\left(\frac{1}{T_r}\right) + B^{'}\frac{d\left(\frac{1}{T_r}\right)}{dT_r}\right)$$

$$\left(\frac{\partial Z}{\partial T_r}\right)_{P_r} = P_r\left(\left(\frac{dB^{o}}{dT_r}\right)\left(\frac{1}{T_r}\right) - \frac{B^{o}}{T_r^{2}}\right) + \omega P_r\left(\left(\frac{dB^{'}}{dT_r}\right)\left(\frac{1}{T_r}\right) - \frac{B^{'}}{T_r^{2}}\right)$$

Substitute into eqn 6.83 and 6.84,

$$\frac{H^{R}}{RT_c} = -T_r\left[\int_{o}^{P_r}\left(\frac{\partial B^{o}}{\partial T_r} - \frac{B^{o}}{T_r}\right) + \omega\left(\frac{\partial B^{'}}{\partial T_r} - \frac{B^{'}}{T_r}\right)\right]dP_r$$

$$\frac{S^{R}}{R} = -\int_{o}^{P_r}\left(\frac{\partial B^{o}}{\partial T_r} - \omega\frac{\partial B^{'}}{\partial T_r}\right)dP_r$$

As B^0 and B^1 are function of T only, the terms in parenthesis are constants, so integrate at constant T gives:

$$\frac{H^R}{RT_c} = P_r\left[B^0 - T_r\frac{\partial B^0}{\partial T_r} + \omega\left(B^1 - T_r\frac{\partial B^1}{\partial T_r}\right)\right] \qquad (6.87)$$

$$\frac{S^R}{R} = -P_r\left(\frac{\partial B^0}{\partial T_r} - \omega\frac{\partial B^1}{\partial T_r}\right) \qquad (6.88)$$

Where

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \qquad (3.65)$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \qquad (3.66)$$

$$\frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}} \qquad (6.89)$$

$$\frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}} \qquad (6.90)$$

Z, H^R and S^R for Mixtures

$$Z = Z^0 + \omega Z^1 \qquad (3.57)$$

$$\frac{H^R}{RT_c} = \frac{\left(H^R\right)^0}{RT_c} + \omega \frac{\left(H^R\right)^1}{RT_c} \qquad (6.85)$$

$$\frac{S^R}{R} = \frac{\left(S^R\right)^0}{R} + \omega \frac{\left(S^R\right)^1}{R_c} \qquad (6.86)$$

Where,

$$\omega_P = \sum_i y_i \omega_i \qquad \mathrm{T_{pc}} = \sum_{\mathrm{i}} \mathrm{y_i} T_{ci} \qquad \mathrm{P_{pc}} = \sum_{\mathrm{i}} \mathrm{y_i} P_{ci}$$

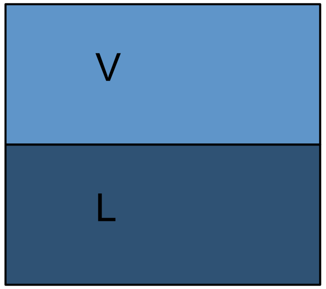
$$\mathrm{T_{pr}} = \frac{T}{T_{pc}} \qquad P_{\mathrm{pr}} = \frac{P}{P_{pc}} \leftarrow$$ Pseudo-reduced parameters

Refer to Table E5-E12 for values of,

$$\frac{\left(H^R\right)^0}{RT_c}, \quad \frac{\left(H^R\right)^1}{R_c T_c}, \quad \frac{\left(S^R\right)^0}{R}, \quad \frac{\left(S^R\right)^1}{R_c}$$

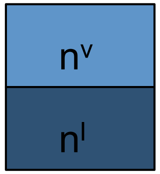
Refer to Table E1-E4 for values Z^0 and Z^1

Phase Equilibrium for System with Pure Substance



T, P

Two-Phase Systems



- Closed system
- Two phase in equilibrium (vapor-liquid equilibrium, VLE) at T, P, n^l, n^v

For this system,

$$G(T,P,n^l,n^V)$$

$$\cancel{d(nG)} = \left(\frac{\partial nG}{\partial T}\right)_{P,n^l,n^v} \cancel{dT} + \left(\frac{\partial nG}{\partial P}\right)_{T,n^l,n^v} \cancel{dP} + \left(\frac{\partial nG}{\partial n^l}\right)_{T,P,n^v} dn^l + \left(\frac{\partial nG}{\partial n^v}\right)_{T,P,n^l} dn^v$$

For constant T, P and overall composition,

$$0 = \bar{G}^l dn^l + \bar{G}^v dn^v$$

Where we define partial molar property as,

$$\bar{G}^{l} = \left(\frac{\partial nG}{\partial n^{l}}\right)_{T,P,n^{v}} \qquad \bar{G}^{v} = \left(\frac{\partial nG}{\partial n^{v}}\right)_{T,P,n^{l}}$$

Since this is pure substance, the partial molar property of liquid is actually the property of liquid!! i.e.

$$\bar{G}^{l} = G^{l} \qquad \text{and} \qquad \bar{G}^{v} = G^{v}$$

Note: Definition of Partial Molar Properties in Chapter 11

$$\bar{M}_i = \left[\frac{\partial (nM)}{\partial n_i} \right]_{P,T,n_j} \qquad (11.7)$$

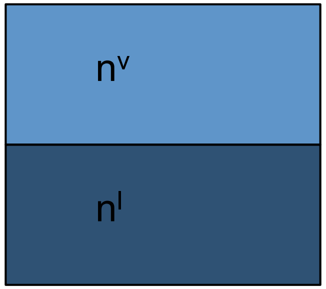
Where $M \equiv V, U, H, S, G$ etc.

M_i is a property of pure species i

$\bar{M}_i$ is property of species i inside the mixture or solution

Continue,

Also from mole balance,



$$n^l + n^v = n^t$$

Note: Closed system

$$dn^l + dn^v = \cancel{dn^t}$$

$$dn^l = -dn^v$$

Substitute,

$$0 = \bar{G}^l dn^l - \bar{G}^v dn^l$$

$$\left(G^l - G^v\right) dn^l = 0$$

$$G^l = G^v$$

This is the phase equilibrium criteria (or vapor liquid equilibrium criteria) for pure substance.

Let us check our steam table at $T^{sat} = 100^oC$,

$$G^v = H^V - TS^V = 2676 - 373.15(7.3554) = -68.6 \quad kJ / kg$$

$$G^l = H^l - TS^l = 419.1 - 373.15(1.3069) = -68.6 \quad kJ / kg$$

Consider system A at 2 different equilibrium conditions,

in equilibrium at saturation conditions 1:

T_1, P_1, G^{l1}, G^{v1}

and

in equilibrium at saturation conditions 2:

T_2, P_2, G^{l2}, G^{v2}

From equilibrium criteria,

$$G^{l1} = G^{V1} \qquad \text{Eqn 1}$$

$$G^{l2} = G^{V2} \qquad \text{Eqn 2}$$

Let *Eqn 2* – *Eqn 1*,

$$G^{l2} - G^{l1} = G^{V2} - G^{V1}$$

$$dG^{l} = dG^{v}$$

From FPR,

$$V^{l} dP^{sat} - S^{l} dT = V^{v} dP^{sat} - S^{v} dT$$

$$\frac{dP^{sat}}{dT} = \frac{\Delta S^{lv}}{\Delta V^{lv}}$$

$$dH = TdS + V\cancel{dP}$$

But for vaporization of pure substance at constant P,

$$\Delta H^{lv} = T\Delta S^{lv} + 0$$

Substitute,

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{lv}}{T\Delta V^{lv}}$$ Persamaan Clapeyron (6.72) or (4.11)

The equation could also be written as follows,

$$\frac{d\ln P^{sat}}{d(1/T)} = -\frac{\Delta H^{lv}}{R\Delta Z^{lv}}$$ Clapeyron Equation (6.74)

At low pressure (ideal gas), $V^v = \dfrac{RT}{P^{sat}}$, and also $V^l << V^v$

Clapeyron eqn 6.72 becomes,

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{vap}}{\dfrac{RT^2}{P^{sat}}}$$ Clausius/Clapeyron equation

or,

$$\frac{\dfrac{dP^{sat}}{P^{sat}}}{\dfrac{dT}{T^2}} = \frac{\Delta H^{vap}}{R}$$ and $$\Delta H^{vap} = -R\frac{d\ln P^{sat}}{d\left(\dfrac{1}{T}\right)}$$

To solve this equation, we only need either vapor pressure data or equation relating vapor pressure to boiling point.,

Vapor Pressure (P^sat) vs Boiling Point Temp (T^sat)

1. Antoine equation,

$$\ln P^{sat} = A - \frac{B}{T^{sat} + C} \qquad (6.76)$$

See Table B2 for the constants

2. Wagner equation,

$$lnP_r^{sat} = \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1-\tau} \qquad (6.77)$$

$$\tau = 1 - T_r$$

3. AIChE (1984) equation,

$$lnP^{sat} = A + \frac{B}{T^{sat}} + ClnT^{sat} + D(T^{sat})^E$$

4. Also, we could use Lee and Kesler Correlations

$$lnP_r^{sat}\left(T_{r)}\right) = lnP_r^0\left(T_{r)}\right) + \omega lnP_r^1\left(T_{r)}\right) \qquad (6.78)$$

Where,

$$lnP_r^0\left(T_{r)}\right) = 5.92714 - \frac{6.09648}{\mathrm{T_r}} - 1.28862\ln T_r + 0.169347T_r^6$$

$$lnP_r^1\left(T_{r)}\right) = 15.2518 - \frac{15.6875}{\mathrm{T_r}} - 13.4721\ln T_r + 0.43577T_r^6$$

$$\omega = \frac{lnP_{rn}^{sat}\left(T_{r)}\right) - lnP_r^0\left(T_{rn}\right)}{lnP_r^1\left(T_{rn}\right)}$$

Note: This correlation was developed for non-polar liquids.

Thermodynamic Properties for Two-Phase Liquid/Vapor System

$$M = M^{l} + x^{v}\Delta M^{lv}$$

$$M \equiv V, U, H, S \text{ etc.}$$

x^{v} is also known as **quality**, that is the mass fraction of vapor in the system,

$$x^{v} = m^{v}/m^{T} = n^{v}/n^{T}$$

Thermodynamic Diagrams

Show the relationship of thermodynamic variables (T, P,V, H, S) on a graph for a particular substance.

For example:

- TS Diagram, PH Diagram, PV Diagram, HT Diagram
- HS Diagram (known as Mollier Diagram)

Useful for analysis of thermodynamic processes as the paths of processes are easily traced and visualized.

Thermodynamic Tables

- Thermodynamic table enable us to read values of thermodynamic properties accurately.

- Usually requires interpolation (as well as extrapolation).

  For example:

  - Ammonia Table, Freon Table, Methane Table, Propane Table
    - Saturated Table

      $(T\ vs\ P, V^{sat\ liq}, \Delta V^{lv}, V^{sat\ vap}, U^{sat\ liq}, \Delta U^{lv}, U^{sat\ vap},$

      $H^{sat\ liq}, \Delta H^{lv}, H^{sat\ vap}, S^{sat\ liq}, \Delta S^{lv}, S^{sat\ vap})$
    - Superheated Table (P *and* T *vs* V, U, H, S)
    - Compressed Liquid Table

- After completion of chapter 3 and 6, you should be well equipped to develop thermodynamic table of a pure substance.

IAPWS

For further reading,

- **The International Association for the Properties of Water and Steam**
- http://www.iapws.org/
- Provide internationally accepted formulations for the properties of steam, water and selected aqueous solutions for scientific and industrial applications.
- You can get software written based on IAPWS formulations

Reference

Smith J.M., Van Ness H.C. , and Abbott M. M. , Introduction to Chemical Engineering Thermodynamics, 7th Edition, McGraw Hill, New York, 2001.