



Advance chemical Engineering Thermodynamics

Thermodynamic property relations

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Content



- **Property relations for homogeneous phases**
- **Residual property (or Excess Property)**
- **Finding the thermodynamic properties by using equation of state**



Property relations for homogeneous phases

- The first law for a reversible process of a closed system (constant n)

$$dU = dQ_{rev} + dW_{rev}$$

$$dU = TdS - PdV$$

for unit mole $dU = TdS - PdV$

- For a differential change from one equilibrium state to another equilibrium state
Thermodynamic laws give relations between changes in properties
 - Primary thermodynamic properties $PVTUS$
 - Derived thermodynamic properties HAG

Enthalpy	$H \equiv U + PV$	$H \equiv U + PV$
Helmholtz energy	$A \equiv U - TS$	$A \equiv U - TS$

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Property relations for homogeneous phases

Gibbs energy	$G \equiv U + PV - TS$	$G \equiv U + PV - TS$
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- Fundamental property relation for H $H = U + PV$

Differentiating $dH = dU + PdV + VdP$

Replacing dU with $TdS - PdV$ \rightarrow $dH = TdS + VdP$

- Similar expressions for A and G can be derived

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

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Property relations for homogeneous phases

Exactness of a differential of a state function

- For a state function $F(x,y)$, the total derivative is define as

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy = Mdx + Ndy$$

If
$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 F}{\partial y \partial x} = \frac{\partial^2 F}{\partial x \partial y} = \left(\frac{\partial N}{\partial x}\right)_y$$

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

- For thermodynamic property $U(S, V)$
$$dU = TdS - PdV$$

The criterion of exactness gives
$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$
 (subscript is important!)

Known as Maxwell's equation

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Property relations for homogeneous phases

Exactness of a differential of a state function

- Maxwell's equations for U, H, A, G

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

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

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

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

- The last two equations give the derivatives of entropy in terms of PVT properties that can be experimentally measured.

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Enthalpy and entropy as functions of T and P

- Chain rules for $H(T,P)$ and $S(T,P)$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

- The fundamental relationship $dH = TdS + VdP$
- $H(S,P)$ and $S(H,P)$ are less useful

- $H(T,P)$ and $S(T,P)$ are the more favored forms as functions of T and P

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P \quad \text{experimentally measurable !}$$



Enthalpy and entropy as functions of T and P

- Dividing the fundamental equation by dT at constant pressure

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

Temperature derivative of entropy

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

- Pressure derivative of entropy is given by Maxwell's equation

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



Enthalpy and entropy as functions of T and P

Pressure derivative of enthalpy

- **Dividing the fundamental equation** $dH = TdS + VdP$ **by** dP **at constant temperature**

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

by using Maxwell's equation $\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$

- Chain rules for $H(T,P)$ and $S(T,P)$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$



Enthalpy and entropy as functions of T and P

Substituting into

$$dH = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P \right] dP \quad H(T,P)$$

$$dS = C_p \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP \quad S(T,P)$$

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

$$dH^{ig} = C_p dT \quad dS^{ig} = C_p^{ig} \frac{dT}{T} - R \frac{dP}{P}$$

- Alternative forms $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

volume expansivity

isothermal compressibility



Enthalpy and entropy as functions of T and P

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

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

- For liquids away from the critical point

$$V \approx \text{const}$$

$$\beta \approx \text{const}$$

$$dH = C_p dT + (1 - \beta T) V dP \qquad dS = C_p \frac{dT}{T} - \beta V dP$$



Internal energy and entropy as functions of T and V

- Chain rules for $U(T, V)$ and $S(T, V)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

- The fundamental relationship for the internal energy

$$dU = T dS - P dV$$

- Temperature derivative of internal energy is defined as

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \qquad \text{experimentally measurable!}$$



Internal energy and entropy as functions of T and V

- Dividing the fundamental equation by dT at constant volume

$$\left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$$

- Temperature derivative of entropy

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

- By Maxwell's equation, the volume derivative of entropy is equal to

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



Volume derivative of internal energy

- Dividing the fundamental equation $dU = TdS - PdV$ by dV at constant temperature

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

Using Maxwell's equation

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

- Chain rules for $U(T, V)$ and $S(T, V)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$



Volume derivative of internal energy

$$dU = C_v dT + \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] dV \quad \rightarrow \quad U(T, V)$$

$$dS = C_v \frac{dT}{T} + \left(\frac{\partial P}{\partial T} \right)_v dV \quad \rightarrow \quad S(T, V)$$

- Volumetric property (PVT data) and heat capacity data can be used to determine all the thermodynamic properties.

- For ideal gas, $PV=RT$

$$\left(\frac{\partial P}{\partial T} \right)_v = \frac{R}{V} = \frac{P}{T}$$

$$dU^{ig} = C_v dT \qquad dS^{ig} = C_v^{ig} \frac{dT}{T} + R \frac{dV}{V}$$



Volume derivative of internal energy

- Alternative forms for liquids

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

$$dV = \beta V dT - \kappa V dP$$

- At constant volume

$$0 = \beta V dT - \kappa V dP \qquad \frac{dP}{dT} = \frac{\beta}{\kappa} \text{ (const } V)$$

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

$$dU = C_v dT + \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] dV$$

$$dU = C_v dT + \left(\frac{\beta}{\kappa} T - P \right) dV$$

$$dS = C_v \frac{dT}{T} + \left(\frac{\partial P}{\partial T} \right)_v dV$$

$$dS = C_v \frac{dT}{T} + \frac{\beta}{\kappa} dV$$



Volume derivative of internal energy

$$V = \text{const} \quad \beta = \kappa = 0$$

$$dH = C_p dT + V dP \quad (\text{with } \beta = 0)$$

Using Maxwell's relation

$$\left(\frac{\partial C_p}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P = \beta V = 0 \quad C_p \text{ is independent of } P$$

$$dS = C_p \frac{dT}{T} - \beta V dP = C_p \frac{dT}{T} \quad (\beta = 0)$$

$$dS = C_v \frac{dT}{T} + \frac{\beta}{\kappa} dV = C_v \frac{dT}{T} \quad (V = \text{const})$$

Comparing

$$C_p = C_v \text{ for incompressible fluid}$$

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The Gibbs energy as a generating function

➤ The fundamental equation is $dG = VdP - SdT$

➤ Consider dimensionless quantity G/RT

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

Replacing dG by $VdP - SdT$ and using $G = H - TS$

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

From the chain rule

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

$$\left[\frac{\partial(G/RT)}{\partial T} \right]_P = -\frac{H}{RT^2}$$

$G(P,T) \rightarrow V(P,T)$ $G(P,T) \rightarrow H(P,T)$ by differentiation

$$S = (H - G) / T \quad U = H - PV$$

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Residual Property (or Excess Property)

➤ Residual Property = Actual property – Ideal gas property, (at the same temperature and pressure)

$$M^R \equiv M - M^{ig}$$

e.g.)

$$G^R \equiv G - G^{ig} \text{ residual Gibbs energy}$$

G^R , V^R and H^R

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

subtracting

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

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Residual Property (or Excess Property)

$$\left[\frac{\partial(G^R/RT)}{\partial P}\right]_T = \frac{V^R}{RT} \quad \left[\frac{\partial(G^R/RT)}{\partial T}\right]_P = -\frac{H^R}{RT^2}$$

G^R is obtained from equation of state (or PVT data)

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}dP \quad (\text{const } T)$$

Integrating from zero pressure to the pressure of system P

$$\frac{G^R}{RT} - \left(\frac{G^R}{RT}\right)_{P=0} = \int_0^P \frac{V^R}{RT}dP$$

We note that

$$\left(\frac{G^R}{RT}\right)_{P=0} = \lim_{P \rightarrow 0} \frac{G - G^{ig}}{RT} = \frac{G^{ig} - G^{ig}}{RT} = 0$$

$$V^R = V - V^{ig} = V - \frac{RT}{P} = \frac{RT}{P} \left(\frac{PV}{RT} - 1\right) = \frac{RT}{P}(Z - 1)$$

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Residual Property (or Excess Property)

Therefore

$$\frac{G^R}{RT} = \int_0^P (Z-1) \frac{dP}{P} \quad (\text{integration at const. } T)$$

In fact, the residual Gibbs energy is related to fugacity.

$$\frac{G^R}{RT} = \ln \frac{f}{P} = \ln \phi$$

where f is fugacity, and $\phi (=f/P)$ is fugacity coefficient

$$f = P \exp \left[\int_0^P (Z-1) \frac{dP}{P} \right] \quad (\text{const } T)$$

For an ideal gas

$$f = P$$

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Residual Property (or Excess Property)

H^R from the differentiation of G^R

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

Interchanging the order of differentiation and integration

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

S^R from G^R and H^R

$$G^R = H^R - TS^R$$

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

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

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Summary

$$H = H^{ig} + H^R \qquad S = S^{ig} + S^R$$

$$H^{ig} = H_0^{ig} + \int_{T_0}^T C_P^{ig} dT \qquad S^{ig} = S_0^{ig} + \int_{T_0}^T C_P^{ig} \frac{dT}{T} - R \ln \frac{P}{P_0}$$

Reference state $(T_0, P_0) \rightarrow$ The state of the system (T, P)

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

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



Residual properties are obtained from PVT properties

- Volume-explicit equation of state $V(T,P)$ or $Z(T,P)$ should be used e.g.) Volume-explicit virial equation for nonideal gas

$$Z = 1 + \frac{B}{RT} P$$

$$\frac{G^R}{RT} = \int_0^P (Z-1) \frac{dP}{P} = \int_0^P \frac{BP}{RT} \frac{dP}{P} = \frac{BP}{RT}$$

$$\frac{H^R}{RT} = -T \left[\frac{\partial (G^R / RT)}{\partial T} \right]_P = -T \left[\frac{\partial (BP / RT)}{\partial T} \right]_P = -T \frac{P}{R} \left(\frac{1}{T} \frac{dB}{dT} - \frac{B}{T^2} \right) = \frac{P}{R} \left(\frac{B}{T} - \frac{dB}{dT} \right)$$

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



Residual Properties by Equations of State $Z(T, V)$

$$\frac{G^R}{RT} = \int_0^P (Z-1) \frac{dP}{P} \quad (\text{const } T)$$

- The above equation is applicable to volume-explicit equation of state, e.g. $Z(T, P) = 1 + B'P + \dots$
- Pressure-explicit forms of equation of states $Z(T, V)$ are more common. VDW, RK, SRK, PR

Change of variables is useful

$$Z = \frac{PV}{RT} = \frac{P}{\rho RT} \quad \rho = 1/V \quad \text{molar density}$$

$$P = Z\rho RT$$

$$dP = RT(Z d\rho + \rho dZ) \quad (\text{const } T)$$

$$\frac{dP}{P} = \frac{RTZ}{P} d\rho + \frac{RT\rho}{P} dZ = \frac{d\rho}{\rho} + \frac{dZ}{Z} \quad (\text{const } T)$$



Residual Properties by Equations of State $Z(T, V)$

Substituting

$$\frac{G^R}{RT} = \int_0^P (Z-1) \frac{dP}{P} = \int_0^\rho (Z-1) \frac{d\rho}{\rho} + \int_1^Z (Z-1) \frac{dZ}{Z} \quad (\text{const } T)$$

$$\boxed{\frac{G^R}{RT} = \int_0^\rho (Z-1) \frac{d\rho}{\rho} + Z - 1 - \ln Z} \quad (\text{const } T) \quad G^R(T, V)$$

H^R from G^R and V^R

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

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

$$\frac{H^R}{RT^2} dT = (Z-1) \frac{dP}{P} - d\left(\frac{G^R}{RT}\right)$$

Dividing by dT at constant density (or volume)



Residual Properties by Equations of State $Z(T, V)$

$$\frac{H^R}{RT^2} = \frac{(Z-1)}{P} \left(\frac{\partial P}{\partial T} \right)_\rho - \left[\frac{\partial(G^R/RT)}{\partial T} \right]_\rho$$

$$P = Z\rho RT \quad \left(\frac{\partial P}{\partial T} \right)_\rho = \left(\frac{\partial}{\partial T} Z\rho RT \right)_\rho = Z\rho R + \rho RT \left(\frac{\partial Z}{\partial T} \right)_\rho$$

$$\frac{(Z-1)}{P} \left(\frac{\partial P}{\partial T} \right)_\rho = (Z-1) \left(\frac{1}{T} + \frac{1}{Z} \left(\frac{\partial Z}{\partial T} \right)_\rho \right)$$

$$\left[\frac{\partial(G^R/RT)}{\partial T} \right]_\rho = \int_0^\rho \left(\frac{\partial Z}{\partial T} \right)_\rho \frac{d\rho}{\rho} + \left(\frac{\partial Z}{\partial T} \right)_\rho - \frac{1}{Z} \left(\frac{\partial Z}{\partial T} \right)_\rho$$

Rewriting

$$\frac{H^R}{RT^2} = \frac{Z-1}{T} + \frac{Z-1}{Z} \left(\frac{\partial Z}{\partial T} \right)_\rho - \int_0^\rho \left(\frac{\partial Z}{\partial T} \right)_\rho \frac{d\rho}{\rho} - \left(\frac{\partial Z}{\partial T} \right)_\rho + \frac{1}{Z} \left(\frac{\partial Z}{\partial T} \right)_\rho$$

$$\boxed{\frac{H^R}{RT} = -T \int_0^\rho \left(\frac{\partial Z}{\partial T} \right)_\rho \frac{d\rho}{\rho} + Z - 1 \quad (\text{const } T)}$$

$H^R(T, V)$



Residual Properties by Equations of State $Z(T, V)$

S^R from G^R and H^R

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

$$\boxed{\frac{S^R}{R} = \ln Z - T \int_0^\rho \left(\frac{\partial Z}{\partial T} \right)_\rho \frac{d\rho}{\rho} - \int_0^\rho (Z-1) \frac{d\rho}{\rho} \quad (\text{const } T)}$$

$S^R(T, V)$



Residual Properties by Equations of State $Z(T, V)$

e.g.) Pressure-explicit virial equation

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} = 1 + B\rho + C\rho^2$$

$$\frac{G^R}{RT} = 2B\rho + \frac{3}{2}C\rho^2 - \ln Z$$

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

$$\frac{S^R}{R} = \ln Z - T \left[\left(\frac{B}{T} + \frac{dB}{dT} \right) \rho + \frac{1}{2} \left(\frac{C}{T} + \frac{dC}{dT} \right) \rho^2 \right]$$

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Residual Properties By Cubic Equations Of State

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\epsilon b)(V+\sigma b)}$$

$$a(T) = \Psi \frac{\alpha(T_r) R^2 T_c^2}{P_c} \quad b = \Omega \frac{RT_c}{P_c}$$

$\sigma \epsilon \Omega \Psi$ are numbers

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\epsilon b)(V+\sigma b)}$$

$$Z = \frac{PV}{RT} \rightarrow Z = \frac{V}{V-b} - \frac{a}{RT} \frac{V}{(V+\epsilon b)(V+\sigma b)} \quad a = \text{function of } T$$

Let $\rho = 1/V$

$$Z = \frac{1}{1-b\rho} - \frac{a}{RT} \frac{\rho}{(1+\epsilon b\rho)(1+\sigma b\rho)}$$

Let $q = \frac{a}{bRT}$

$q = \text{function of } T$

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Residual Properties By Cubic Equations Of State

$$Z - 1 = \frac{b\rho}{1 - b\rho} - q \frac{b\rho}{(1 + \varepsilon b\rho)(1 + \sigma b\rho)}$$

$$\left(\frac{\partial Z}{\partial T}\right)_\rho = -\frac{dq}{dT} \frac{b\rho}{(1 + \varepsilon b\rho)(1 + \sigma b\rho)}$$

$$\int_0^\rho (Z - 1) \frac{d\rho}{\rho} = \int_0^\rho \frac{b}{1 - b\rho} d\rho - q \underbrace{\int_0^\rho \frac{b}{(1 + \varepsilon b\rho)(1 + \sigma b\rho)} d\rho}_I$$

$$= -[\ln(1 - b\rho)]_0^\rho - qI$$

$$= -\ln(1 - b\rho) - qI$$

$$\frac{b}{(1 + \varepsilon b\rho)(1 + \sigma b\rho)} = \frac{A}{1 + \varepsilon b\rho} + \frac{B}{1 + \sigma b\rho} = \frac{A(1 + \sigma b\rho) + B(1 + \varepsilon b\rho)}{(1 + \varepsilon b\rho)(1 + \sigma b\rho)}$$

$$\rho^0: A + B = b$$

$$\rho^1: A\sigma b + B\varepsilon b = 0$$

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Residual Properties By Cubic Equations Of State

$$A\sigma + (b - A)\varepsilon = 0 \rightarrow A = \frac{b\varepsilon}{\varepsilon - \sigma}$$

$$B = b - A = -\frac{b\sigma}{\varepsilon - \sigma}$$

When $\varepsilon = \sigma = 0$ (VDW)

$$I = \int_0^\rho b d\rho = b\rho = \frac{b}{V} = \frac{RT}{VP} = \frac{\beta}{Z} \quad \beta = bP/RT$$

When $\varepsilon \neq \sigma$

$$I = \int_0^\rho \frac{b\varepsilon}{\varepsilon - \sigma} \frac{d\rho}{1 + \varepsilon b\rho} - \int_0^\rho \frac{b\sigma}{\varepsilon - \sigma} \frac{d\rho}{1 + \sigma b\rho}$$

$$I = \frac{1}{\varepsilon - \sigma} \ln(1 + \varepsilon b\rho) - \frac{1}{\varepsilon - \sigma} \ln(1 + \sigma b\rho) = \frac{1}{\sigma - \varepsilon} \ln \frac{1 + \sigma b\rho}{1 + \varepsilon b\rho}$$

$$= \frac{1}{\sigma - \varepsilon} \ln \frac{Z + \sigma\beta}{Z + \varepsilon\beta}$$

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Residual Properties By Cubic Equations Of State

$$\frac{G^R}{RT} = \int_0^\rho (Z-1) \frac{d\rho}{\rho} + Z - 1 - \ln Z \quad (\text{const } T)$$

$$= -\ln(1-b\rho) - qI + Z - 1 - \ln Z = -\ln \frac{Z-\beta}{Z} - qI + Z - 1 - \ln Z$$

$$= -\ln(Z-\beta) - qI + Z - 1$$

$$\frac{H^R}{RT} = -T \int_0^\rho \left(\frac{\partial Z}{\partial T} \right)_\rho \frac{d\rho}{\rho} + Z - 1 \quad (\text{const } T)$$

$$-T \int_0^\rho \left(\frac{\partial Z}{\partial T} \right)_\rho \frac{d\rho}{\rho} = T \frac{dq}{dT} I \quad q = \frac{a(T)}{bRT} = \frac{\Psi \alpha(T_r)}{\Omega T_r}$$

$$T \frac{dq}{dT} = \frac{T}{T_c} \frac{dq}{d(T/T_c)} = T_r \frac{dq}{dT_r} = q \frac{\frac{1}{q} dq}{\frac{1}{T_r} dT_r} = q \frac{d \ln q}{d \ln T_r} = q \frac{d(\ln \alpha - \ln T_r)}{d \ln T_r} = q \left(\frac{d \ln \alpha}{d \ln T_r} - 1 \right) = q \left(\frac{T_r}{\alpha} \frac{d\alpha}{dT_r} - 1 \right)$$

$$\frac{H^R}{RT} = Z - 1 + \left[\frac{T_r}{\alpha} \frac{d\alpha}{dT_r} - 1 \right] qI$$

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Summary

$$\frac{G^R}{RT} = Z - 1 - \ln(Z - \beta) - qI$$

$$\frac{H^R}{RT} = Z - 1 + \left[\frac{T_r}{\alpha} \frac{d\alpha}{dT_r} - 1 \right] qI$$

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

where $\beta = \frac{bP}{RT}$ $q = \frac{a(T)}{bRT}$

$$I = \frac{\beta}{Z} \quad \text{for VDW} \quad I = \frac{1}{\sigma - \varepsilon} \ln \left(\frac{Z + \sigma\beta}{Z + \varepsilon\beta} \right) \quad \text{for RK, SRK, PR}$$

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Two-phase Systems

- Abrupt changes in volume, internal energy, enthalpy and entropy across the phase boundary. However, Gibbs energy does not change at phase transition

Consider a closed system containing two coexisting phases α and β

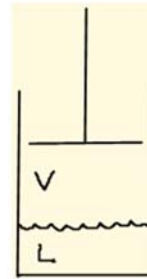
$$dG = V dP - S dT \quad (n = \text{const.})$$

where G is the total Gibbs energy of the two-phase system

$$G = G^\alpha + G^\beta = n^\alpha G^\alpha + n^\beta G^\beta$$

$$V = V^\alpha + V^\beta = n^\alpha V^\alpha + n^\beta V^\beta$$

$$S = S^\alpha + S^\beta = n^\alpha S^\alpha + n^\beta S^\beta$$



In fact, each individual phase is an open system

For an open system $G(T, P, n) = nG(T, P)$

$$dG = V dP - S dT + \mu dn$$



Two-phase Systems

$$\mu \equiv \left(\frac{\partial G}{\partial n} \right)_{P,T} \quad \text{chemical potential for pure species}$$

$$\mu = \left[\frac{\partial nG(T, P)}{\partial n} \right]_{P,T} = G \quad \text{equal to the molar Gibbs energy}$$

For coexisting phases at the same T and P ($P = P^{sat}$)

$$dG^\alpha = V^\alpha dP - S^\alpha dT + \mu^\alpha dn^\alpha$$

$$dG^\beta = V^\beta dP - S^\beta dT + \mu^\beta dn^\beta$$

Adding the two expressions

$$dG = V dP - S dT + \mu^\alpha dn^\alpha + \mu^\beta dn^\beta$$

Compare with $dG = V dP - S dT$ (of the overall closed system)

$$\mu^\alpha dn^\alpha + \mu^\beta dn^\beta = 0$$



Two-phase Systems

Mass conservation requires $n^\alpha + n^\beta = \text{const.}$

$$dn^\alpha + dn^\beta = 0$$

$$(\mu^\alpha - \mu^\beta) dn^\alpha = 0$$

Since dn^α is arbitrary

$$\boxed{\mu^\alpha = \mu^\beta}$$

Equality of chemical potential for phase equilibrium

$$G^\alpha = G^\beta \quad \text{for pure species}$$

Clapeyron equation (for coexisting phases)

$$G^\alpha = G^\beta$$

For a very small (differential) change in temperature or in saturation pressure

$$dG^\alpha = dG^\beta$$

Substituting the fundamental equation of dG

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Two-phase Systems

$$V^\alpha dP^{sat} - S^\alpha dT = V^\beta dP^{sat} - S^\beta dT$$

$$\frac{dP^{sat}}{dT} = \frac{S^\beta - S^\alpha}{V^\beta - V^\alpha} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}}$$

Since $G^\beta - G^\alpha = 0 = (H^\beta - H^\alpha) - T(S^\beta - S^\alpha) = \Delta H^{\alpha\beta} - T\Delta S^{\alpha\beta}$

$$\Delta S^{\alpha\beta} = \frac{\Delta H^{\alpha\beta}}{T}$$

Substituting, we obtain the Clapeyron equation

$$\boxed{\frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}}}$$

(exact)

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Two-phase Systems

Clausius-Clapeyron equation

Approximation for vapor-liquid equilibrium

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

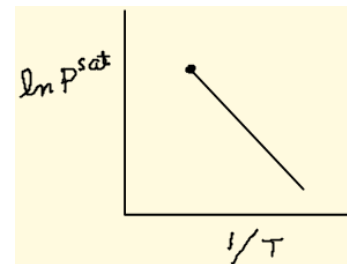
When $T_r < 0.7$ (far away from the critical temperature), it is reasonable to assume that the molar volume of liquid is negligible compared to that of the vapor and that the vapor phase is ideal

$$\Delta V^{lv} = V^v - V^l \cong V^v = \frac{RT}{P^{sat}}$$

$$\frac{RT^2}{P^{sat}} \frac{dP^{sat}}{dT} = \Delta H^{lv}$$

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

ΔH^{lv} is proportional to the slope of $\ln P^{sat}$ vs. $1/T$



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Temperature dependence of the vapor pressure P^{sat}

Assuming a simple linear dependence

$$\ln P^{sat} = A - \frac{B}{T} \quad A, B \text{ are constants for a substance}$$

Antoine equation (empirical, practical use)

$$\ln P^{sat} = A - \frac{B}{T+C} \quad A, B, C \text{ are constants for a substance}$$

(Table B.2)

Wagner equation

$$\ln P_r^{sat} = \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1-\tau} \quad \tau = 1 - T_r$$

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Finding the saturated pressure by using equation of state

Maxwell's equal area rule for coexisting phases

Define Gibbs' free energy $G = U + PV - TS$

Fundamental relation $dG = SdT + VdP$

For coexisting vapor and liquid

$T_{vap} = T_{liq}$ ($= T_{sat}$) thermal equilibrium the same temperature

$P_{vap} = P_{liq}$ ($= P_{sat}$) mechanical equilibrium the same pressure

$G_{vap} = G_{liq}$ ($= G_{sat}$) chemical equilibrium the same chemical

potential

Following isotherm of equation state (at constant T)

$$dG = VdP = d(PV) - PdV$$

Integrating $d(PV) - PdV$ from (V_{liq}, P_{sat}) to (V_{vap}, P_{sat}) along the isotherm

$$\int d(PV) - \int PdV = \int dG$$

$$\int dG = \Delta G = G_{vap} - G_{liq} = 0$$

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Finding the saturated pressure by using equation of state

Thus $\int d(PV) - \int PdV = 0$

$$\int d(PV) = \Delta(PV) = P_{sat}V_{vap} - P_{sat}V_{liq} = P_{sat}(V_{vap} - V_{liq})$$

$$\int PdV = \int (P - P_{sat} + P_{sat})dV = \int (P - P_{sat})dV + P_{sat} \int dV = \int (P - P_{sat})dV + P_{sat}(V_{vap} - V_{liq})$$

$$\int d(PV) - \int PdV = \int (P - P_{sat})dV = 0$$

Maxwell's equal area rule

$$\int (P - P_{sat})dV = 0$$

Saturation pressure that makes the above integral zero is determined by trial and error.

If guessed value of P_{sat} is too high, $\int (P - P_{sat})dV < 0$

If guessed value of P_{sat} is too low, $\int (P - P_{sat})dV > 0$

One possible way of improving next guess of P_{sat} is

$$P_{sat}^{new} = P_{sat} + \int (P - P_{sat})dV / (V_{vap} - V_{liq})$$

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Corresponding states correlations for vapor pressure P^{sat}

Reliable for non-polar and non-associating liquids

Lee and Kesler correlations

$$\ln P_r^{sat}(T_r) = \ln P_r^0(T_r) + \omega \ln P_r^1(T_r)$$

where

$$\ln P_r^0(T_r) = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln T_r + 0.169347 T_r^6$$

$$\ln P_r^1(T_r) = 15.2518 - \frac{15.6875}{T_r} - 13.4712 \ln T_r + 0.43577 T_r^6$$

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Generalized Property Correlations for Residual Properties

The correlation for the compressibility factor

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

Integration of the compressibility factor gives

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

$$\frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R}$$

Each term depends on T_r and P_r and obtained by looking up Tables

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Generalized Property Correlations for Residual Properties

For gases at low pressures, the second-virial coefficient can be obtained

$$Z = 1 + \frac{B}{RT}P \qquad Z - 1 \propto P$$

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

Corresponding generalized correlations are

$$Z = 1 + \frac{B}{RT}P = 1 + \frac{\hat{B}}{T_r}P_r$$

$$\hat{B} = B^0 + \omega B^1 \qquad B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \qquad B^1 = 0.139 - \frac{0.0172}{T_r^{4.2}}$$

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

$$\frac{S^R}{R} = -P_r \left(\frac{dB^0}{dT_r} + \omega \frac{dB^1}{dT_r} \right) \qquad S^R \propto P$$

$$\frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}} \qquad \frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}}$$



Enthalpy and Entropy Difference

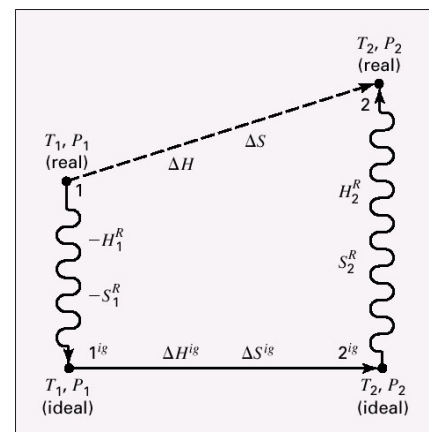
$$H_1 = H_0^{ig} + \int_{T_0}^{T_1} C_P^{ig} dT + H_1^R \qquad H_2 = H_0^{ig} + \int_{T_0}^{T_2} C_P^{ig} dT + H_2^R$$

Taking the difference for $\Delta H = H_2 - H_1$

$$\Delta H = \int_{T_1}^{T_2} C_P^{ig} dT + H_2^R - H_1^R$$

no effect of the reference state 0

Figure 6.6: Calculational path for property changes ΔH and ΔS .



$$S_1 = S_0^{ig} + \int_{T_0}^{T_1} C_P^{ig} \frac{dT}{T} - R \ln \frac{P_1}{P_0} + S_1^R \quad S_2 = S_0^{ig} + \int_{T_0}^{T_2} C_P^{ig} \frac{dT}{T} - R \ln \frac{P_2}{P_0} + S_2^R$$

Taking the difference for $\Delta S = S_2 - S_1$

$$\Delta S = \int_{T_1}^{T_2} C_P^{ig} \frac{dT}{T} - R \ln \frac{P_2}{P_1} + S_2^R - S_1^R$$

no effect of the reference state 0



Gas Mixtures

Although there is no theoretical basis for extensions of generalized correlations to mixtures

If simple mixing rules to obtain pseudo-critical parameters are used

$$\omega = \sum_i y_i \omega_i$$

$$T_{pc} = \sum_i y_i T_{ci}$$

$$P_{pc} = \sum_i y_i P_{ci}$$

Pseudo-reduced parameters are defined by

$$T_{pr} = \frac{T}{T_{pc}} \quad P_{pr} = \frac{P}{P_{pc}}$$

Generalized correlations can be used in the same manner

