
Introductory Chemical Engineering Thermodynamics

Chapter 7 - Departure Functions

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Internal Energy Departure Function

$$U(T, V) - U^{ig}(T, V) = \int_{\infty}^V \left(\frac{\partial U}{\partial V} \right)_T - \left(\frac{\partial U}{\partial V} \right)_T^{ig} dV$$

FPR tells us $(dU)_T = T(dS)_T - P(dV)_T$

For the ideal gas $(dU^{ig})_T = T(dS^{ig})_T - P(dV^{ig})_T$

where $(dS^{ig})_T = R d \ln V$ and $P(dV^{ig})_T = RT/V dV = RT d \ln V$

Substituting we find, $(dU^{ig})_T = T^* R d \ln V - RT d \ln V = 0$

Therefore, $\left(\frac{\partial U}{\partial V} \right)_T^{ig} = 0$

Returning to the FPR, $\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - P \left(\frac{\partial V}{\partial V} \right)_T$

Maxwell's Relation $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$

Finally, $(U - U^{ig}) = \int_{\infty}^V \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV$

If we transform to density, the expressions we get are usually easier to integrate.

$$\therefore dV = \frac{-1}{\rho^2} d\rho \quad \Rightarrow \quad \frac{\partial V}{\partial \rho} = \frac{-\partial \rho}{\rho} \text{ and, at } V \rightarrow \infty, \rho \rightarrow 0$$

$$\Rightarrow \left(\frac{U - U^{ig}}{RT} \right) = \int_0^\rho \left[\frac{P}{\rho RT} - \frac{1}{\rho R} \left(\frac{\partial P}{\partial T} \right)_\rho \right] \frac{d\rho}{\rho}$$

$$\therefore \left(\frac{U(T, V) - U^{ig}(T, V)}{RT} \right) = \int_0^\rho -T \left(\frac{\partial Z}{\partial T} \right)_\rho \frac{d\rho}{\rho} = \left(\frac{U(T, P) - U^{ig}(T, P)}{RT} \right)$$

Because $U^{ig}(T, P) - U^{ig}(T, V) = \int (\partial U^{ig} / \partial V)_T dV = 0$

Example. Derive the internal energy departure function for the EOS:

$$Z = 1 + 4b\rho / (1 - b\rho) - a\rho / RT$$

$$(\partial Z / \partial T)_\rho = + a\rho / RT^2 \Rightarrow -T(\partial Z / \partial T)_\rho = -a\rho / RT$$

$$\therefore \left(\frac{U(T, V) - U^{ig}(T, V)}{RT} \right) = \int_0^\rho -T \left(\frac{\partial Z}{\partial T} \right)_\rho \frac{d\rho}{\rho} = \frac{-a}{RT} \int_0^\rho \frac{\rho}{\rho} d\rho = \frac{-a}{RT} [\rho]_0^\rho = \frac{-a\rho}{RT}$$

Helmholtz Energy: Departure Function

$$A(T, V) - A^{ig}(T, V) = \int_{\infty}^V \left[\left(\frac{\partial A}{\partial V} \right)_T - \left(\frac{\partial A}{\partial V} \right)_T^{ig} \right] dV$$

$$FPR \Rightarrow (dA)_T = -PdV \Rightarrow (dA)_T^{ig} = -\frac{RT}{V}dV = -RTd\ln V \Rightarrow \left(\frac{\partial A}{\partial V} \right)_T^{ig} = -RT \left(\frac{\partial \ln V}{\partial V} \right)_T = -\frac{RT}{V}$$

$$\text{Also } \left(\frac{\partial A}{\partial V} \right)_T = -P \Rightarrow \left(\frac{\partial A}{\partial V} \right)_T - \left(\frac{\partial A}{\partial V} \right)_T^{ig} = -P + \frac{RT}{V}$$

Transform to $\rho \Rightarrow dV = -V d\rho/\rho$

$$\Rightarrow \left(\frac{A(T, V) - A^{ig}(T, V)}{RT} \right) = \int_0^{\rho} \left(\frac{Z-1}{\rho} \right) d\rho$$

Gibbs energy departure function

As for the density dependent part, it is easy to see that,

$$G = U + PV - TS = A + PV$$

$$\Rightarrow \frac{G(T, V) - G^{id}(T, V)}{RT} = \frac{A(T, V) - A^{ig}(T, V)}{RT} + Z - 1 = \int_0^{\rho} \left(\frac{Z - 1}{\rho} \right) d\rho + Z - 1$$

Since V and P correspond to the properties of the real gas, the pressure of the ideal gas at T and V is $P_1 = RT/V$. The change in Gibbs energy is

$$G^{ig}(T, p) - G^{ig}(T, V) = RT \ln(P / P_1) = RT \ln(PV / RT) = RT \ln(Z)$$

$$\Rightarrow \frac{G(T, P) - G^{ig}(T, P)}{RT} = \frac{G(T, P, V) - G^{ig}(T, V)}{RT} - \frac{G^{ig}(T, P) - G^{ig}(T, V)}{RT} = \frac{G(T, P, V) - G^{ig}(T, V)}{RT} - \ln(Z)$$

$$\Rightarrow \frac{G(T, P) - G^{ig}(T, P)}{RT} = \int_0^{\rho} \left(\frac{Z - 1}{\rho} \right) d\rho + Z - 1 - \ln(Z)$$

Summary of density dependent formulas for departure functions from equations of state.

$$\frac{(H - H^{ig})}{RT} = \int_0^{\rho} -T \left[\frac{\partial Z}{\partial T} \right] \frac{d\rho}{\rho} + Z - 1$$

$$\frac{(G(T, P) - G^{ig}(T, P))}{RT} = \int_0^{\rho} \frac{(Z - 1)}{\rho} d\rho + Z - 1 - \ln Z$$

$$\frac{(U - U^{ig})}{RT} \int_0^{\rho} -T \left[\frac{\partial Z}{\partial T} \right] \frac{d\rho}{\rho}$$

$$\frac{(A(T, V) - A^{ig}(T, V))}{RT} = \int_0^{\rho} \frac{(Z - 1)}{\rho} d\rho$$

$$\frac{(S(T, V) - S^{ig}(T, V))}{R} = \int_0^{\rho} \left[-T \left[\frac{\partial Z}{\partial T} \right]_p - (Z - 1) \right] \frac{d\rho}{\rho}$$

$$\frac{(S(T, P) - S^{ig}(T, P))}{R} = \int_0^{\rho} \left[-T \left[\frac{\partial Z}{\partial T} \right]_p - (Z - 1) \right] \frac{d\rho}{\rho} + \ln Z$$

Example 7.1. Use of PREOS to get enthalpy and entropy departures.

Propane gas undergoes a change of state from an initial condition of 5 bar and 105°C to 25 bar and 190°C. Compute the change in enthalpy and entropy.

For propane : $A=-4.224$; $B=0.3063$; $C= -1.586E-4$; $D=3.215E-8$

$T_c = 369.8$ K; $P_c = 42.49$ bar.; $\omega=0.152$

Solution:

Path, for $H(190,25) - H(105,5)$

$[H(190,25) - H^{ig}(190,25)] + [H^{ig}(190,25) - H^{ig}(105,5)] + [H^{ig}(105,5) - H(105,5)]$

Similarly for $S(190,25) - S(105,5)$

$[S(190,25) - S^{ig}(190,25)] + [S^{ig}(190,25) - S^{ig}(105,5)] + [S^{ig}(105,5) - S(105,5)]$

I. Departure Function + **II. Ideal gas** + **III. Departure function**

I. (190,25) → (190,25)^{ig}

$190 + 273.15 = 463.15\text{K}$ & 25 bar $\Rightarrow T_r = 1.25135$; $P_r = 0.58837$

PREOS $\Rightarrow Z=0.8891 \Rightarrow (H-H^{ig}) = (-0.3869) 8.314 * 463.15 = -1490$ J/mol

$(S-S^{ig}) = (-0.2757) 8.314 = -2.2918$ J/mol-K

II. (190,25)ig →(105,5)ig

$$H^{ig}(190,25) - H^{ig}(105,5) = \int C_p dT = -4.224(463-378) + 0.3063(463^2-378^2)/2 + (-1.586E-4)(463^3-378^3)/3 + (3.215E-8)(463^4-378^4)/4 = 8405 \text{ J/mole}$$

$$S^{ig}(190,25) - S^{ig}(105,5) = A \ln(T_2/T_1) + B(\Delta T) + C\Delta(T^2)/2 + D\Delta(T^3)/3 - R \ln(P_2/P_1) ;$$

$$\Delta S^{ig} = -4.224 \ln(463.15/378.15) + 0.3063(85) + (-1.586E-4)(463^2-378^2)/2 + 3.215E-8(463^3-378^3)/3 - 8.314 \ln 5 = 6.613 \text{ J/mol-K}$$

III. (105,5)→(105,5)ig

$$105 + 273 = 378.15 \text{ \& } 5 \text{ bar} \rightarrow T_r = 1.02258; P_r = 0.11767$$

$$Z = 0.9574 \Rightarrow (H-H^{ig}) = (-0.1274) 8.314 * 378.15 = -400 \text{ J/mol}$$

$$(S-S^{ig}) = (-0.0852) 8.314 = -0.7081 \text{ J/mol-K}$$

$$\Delta H^{tot} = -1490 + 8405 + 400 = 7315 \text{ J/mol}$$

(Note: Chart $\Rightarrow (1265 - 1095) * 44 = 7480 \text{ J/mol}$)

$$\Delta S^{tot} = -2.292 + 6.613 + 0.708 = 5.029 \text{ J/mol-K}$$

(Note: Chart $\Rightarrow (1.52-1.50) * 44 * 4.184 = 3.7 \text{ J/mol-K}$)

Moral: The difference between the chart and the Peng-Robinson equation is significant, but could be because of error in the Peng-Robinson equation or sensitivity to the accuracy with which the chart can be read. Entropy is especially difficult because the temperature and pressure effects tend to cancel and we end up with the small difference between large numbers. In reality, the Peng-Robinson equation is only accurate to about 10% on enthalpy if compared to a highly accurate equation.

Example 7.6. Use of Referenced PREOS to get enthalpy and entropy

Propane gas undergoes a change of state from an initial condition of 5 bar and 105°C to 25 bar and 190°C. Compute the change in enthalpy and entropy by using a common reference state of 230K and 0.1MPa.

For propane : $A = -4.224$; $B = 0.3063$; $C = -1.586\text{E-}4$; $D = 3.215\text{E-}8$
 $T_c = 369.8$ K; $P_c = 42.49$ bar.; $\omega=0.152$

Solution: In this example, we are directed to use a reference state such that, for enthalpy: $H_2 - H_1 = (H_2 - H_{ref}) - (H_1 - H_{ref})$, and for entropy: $S_2 - S_1 = (S_2 - S_{ref}) - (S_1 - S_{ref})$. Note the equivalence of this procedure to the way steam tables are computed. Furthermore, the computation of $H_2 - H_{ref}$ or $S_2 - S_{ref}$ is entirely equivalent to the procedure given in Example 7.1.

1. **REF**: Enter the values of T_c , P_c , ω , A , B , C , D and define the T , P , and root of interest.
2. Press **PVTF** to enter the pressure and temperature and choose the root of interest.
E.g. at 463.15 K and 2.5 MPa, $V = 1369$ cm³/mole
3. Press **UHSG** to compute internal energy, enthalpy, entropy, and Gibbs free energy.
E.g. at 463.15 K and 2.5 MPa, $H_2 - H_{ref} = 36901$ J/mole; $S_2 - S_{ref} = 109.15$ J/mole-K
4. Repeat at 378.15 K and 0.5 MPa, $H_1 - H_{ref} = 29586$ J/mole; $S_1 - S_{ref} = 104.13$ J/mole-K
5. Subtract $\Rightarrow \Delta H = 36901 - 29586 = 7315$ and $\Delta S = 109.15 - 104.13 = 5.02$ J/mole-K

Example 7.3 Enthalpy departure for PREOS

Obtain a general expression for the enthalpy departure function of the PREOS.

Solution: In the previous example we were able to obtain both pressure-explicit and density-explicit equations. Therefore, we could solve the problem two different ways. For the PREOS, we can only solve one way.

$$Z = \frac{1}{(1-b\rho) - \frac{a\rho/RT}{(1+2b\rho-b^2\rho^2)}}$$

$$-T \left(\frac{\partial Z}{\partial T} \right)_\rho = \frac{\rho T/R}{(1+2b\rho-b^2\rho^2)} \left[\frac{-a}{T^2} + \frac{1}{T} \left[\frac{da}{dT} \right] \right]$$

$$a = a_c \left[1 + \kappa \left(1 - \sqrt{T/T_c} \right) \right]^2; a_c \equiv 0.45724 \frac{R^2 T_c^2}{P_c}$$

where $\kappa = 0.37464 + 1.54226 \omega - 0.26993 \omega^2$

$$\frac{da}{dT} = a_c 2 \left[1 + \kappa \left(1 - \sqrt{\frac{T}{T_c}} \right) \right] \left[\frac{-\kappa}{\sqrt{T_c}} \frac{1}{2} T^{-1/2} \right] \Rightarrow T \frac{da}{dT} = -a_c \left[1 + \kappa \left(1 - \sqrt{T/T_c} \right) \right] \left(\kappa \sqrt{T/T_c} \right)$$

$$-T \left[\frac{\partial Z}{\partial T} \right]_\rho = \frac{b\rho}{1+2b\rho-b^2\rho^2} \left[\frac{-a}{bRT} - \frac{a_c}{bRT} - \left[1 + \kappa \left(1 - \sqrt{T/T_c} \right) \right] \left(\kappa \sqrt{T/T_c} \right) \right] \equiv \frac{b\rho}{(1+2b\rho-b^2\rho^2)} F(T_r)$$

$F(T_r)$ is shorthand. Also $B \equiv bP/RT \Rightarrow b\rho = B/Z$ and $A \equiv aP/R^2T^2 \Rightarrow a/bRT = A/B$

$$\int_0^{b\rho} -T \left(\frac{\partial Z}{\partial T} \right)_T \frac{d(b\rho)}{b\rho} = \int_0^{b\rho} \frac{b\rho}{(1+2b\rho-b^2\rho^2)} F(T_r) \frac{d(b\rho)}{b\rho} =$$

$$\frac{F(Tr)}{\sqrt{8}} \left[\ln \left(\frac{1-\sqrt{2}}{1+\sqrt{2}} \right) \left(\frac{b\rho(1+\sqrt{2})+1}{b\rho(1-\sqrt{2})+1} \right) \right]_0^{b\rho} = \frac{F(Tr)}{\sqrt{8}} \ln \left[\frac{1+(1+\sqrt{2})b\rho}{1+(1-\sqrt{2})b\rho} \right]$$

Note $\frac{B}{Z} = \frac{\frac{bp}{RT}}{p} = b\rho \Rightarrow \int_0^{b\rho} -T \left(\frac{\partial Z}{\partial T} \right)_T \frac{d(b\rho)}{b\rho} = \frac{F(Tr)}{\sqrt{8}} \ln \left[\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B} \right]$

$$\frac{(H - H^{ig})}{nRT} = Z - 1 + \frac{1}{\sqrt{8}} \ln \left[\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B} \right] \left[\frac{-a}{bRT} - \frac{a_c}{bRT} \left[1 + \kappa(1 - \sqrt{T_r}) \right] \kappa \sqrt{T_r} \right]$$

$$= Z - 1 - \ln \left[\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B} \right] \frac{A}{B\sqrt{8}} \left[1 + \frac{\kappa\sqrt{Tr}}{\sqrt{\alpha}} \right]$$

Example 7.4 Gibbs Departure for PREOS.

Obtain a general expression for the Gibbs energy departure function of the PR-EOS.

$$Z = \frac{1}{(1-b\rho)} - \frac{a\rho/RT}{(1+2b\rho-b^2\rho^2)}$$

$$Z-1 = \frac{1}{1-b\rho} - \frac{1-b\rho}{1-b\rho} - \frac{a\rho/RT}{(1+2b\rho-b^2\rho^2)} = \frac{b\rho}{(1-b\rho)} - \frac{a\rho/RT}{(1+2b\rho-b^2\rho^2)}$$

$$\frac{(G(T, p) - G^{id}(T, p))}{nRT} = \int_0^p \frac{(Z-1)}{\rho} d\rho + Z-1 - \ln Z$$

$$= \ln(1-b\rho) - \ln Z + Z - 1 + \frac{a}{bRT\sqrt{8}} \ln \left[\frac{1 + (1 + \sqrt{2})b\rho}{1 + (1 - \sqrt{2})b\rho} \right]$$

$$= \ln(Z-B) - \ln \left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right] \frac{A}{B\sqrt{8}}$$

Example 7.7 Liquefaction revisited

Reevaluate the liquefaction of methane considered previously using the methane chart by performing the analogous calculations with the PR EOS.

Natural gas, assumed here to be pure methane, is liquefied in a simple Linde process. Compression is to 60 bar and precooling is to 300K. The separator is maintained at a pressure of 1 bar and unliquefied gas at this pressure leaves the cooler at 295 K. What fraction of the gas is liquefied in the process?

$T_c = 190.6$; $P_c = 4.60\text{MPa}$; $\omega = 0.008$; $C_p \approx C_p(200\text{K}) \approx 28.45\text{ J/mol-K}$

Solution: To facilitate comparison to chart, set the reference enthalpies equal.

Let: $H_{ref} = H^{satL}(1\text{bar}) = 4538\text{J/mol}$ (283.6 J/g as given on chart, $T^{sat}(1\text{bar}) = 111.0\text{K}$).

$$H_{60}^{300} = \left(H_{60}^{300} - {}^{id}H_{60}^{300} \right) + \left({}^{id}H_{60}^{300} - {}^{id}H_1^{111} \right) + \left({}^{id}H_1^{111} - H_1^{satL} \right) + H_{ref}$$

$$= -0.4334(8.314)300 + 28.45(300-111) + 8.9453(8.314)111 + 4538 = 17089\text{ J/mole}$$

$$H_8 = H_1^{295} = \left(H_1^{295} - {}^{id}H_1^{295} \right) + \left({}^{id}H_1^{295} - {}^{id}H_1^{111} \right) + \left({}^{id}H_1^{111} - H_1^{satL} \right) + H_{ref}$$

$$= 0 + 28.45(295-111) + 8255 + 4538 = 18028\text{J/mole}$$

$$H_6 \equiv 4538 \text{ E-Bal} \Rightarrow H_3 = qH_8 + (1-q)H_6 \Rightarrow q = 0.9304 \Rightarrow 6.96\% \text{ liquefied}$$

This compares to 7.13% when we read the chart to the best of our ability.

