

Chapter 5 Thermodynamic Properties of Real Fluids

It has already been demonstrated through the first and second laws, that the work and heat interactions between a system and its surroundings may be related to the state variables such as internal energy, enthalpy and entropy. So far we have illustrated the calculations of energy and entropy primarily for pure (component) ideal gas systems. However, in practice this is an *exception* rather than a rule as one has to deal with not only gases removed from ideal gas state, but also with liquids and solids. In addition, mixtures rather than pure components are far more common in chemical process plants. Therefore, computation of work and heat interactions for system comprised of *real* fluids requires more complex thermodynamic formulations. This chapter is devoted to development of such relations that can help calculate energy requirements for given changes of state for real systems. As in the case of ideal gases the goal is to correlate the energy and entropy changes for real fluids in terms of their volumetric and other easily measurable macroscopic properties.

5.1 Thermodynamic Property Relations for Single Phase Systems

Apart from internal energy and enthalpy, two other ones that are particularly useful in depiction of thermodynamic equilibrium are Helmholtz free energy (A) and Gibbs free energy (G). We defer expanding upon the concept of these two types of energies to chapter 6; however, we state their definition at this point as they are instrumental in the development of property correlations for real fluids.

- Specific Helmholtz free energy: $A = U - TS$..(5.1)

- Specific Gibbs free energy: $G = H - TS$..(5.2)

For a reversible process in a closed system the first law gives:

$$dU = dQ + dW$$

Or:

$$dU = TdS - PdV$$
 ..(5.3)

Using $H = U + PV$ and taking a total differential of both sides:

$$dH = dU + PdV + VdP \quad \text{..(5.4)}$$

Putting eqn. 5.3 in 5.4 we get:

$$dH = TdS + VdP \quad \text{..(5.5)}$$

In the same manner as above one may easily show that the following two relations obtain:

$$dA = -SdT - PdV \quad \text{..(5.6)}$$

$$dG = VdP - SdT \quad \text{..(5.7)}$$

Equations 5.3 to 5.7 comprise the fundamental energy relations for thermodynamic systems where there is a single phase with constant composition. In principle, they may be integrated to compute the energy changes for a system transiting from one equilibrium state to another.

5.2 Maxwell Relations

All the four types of energy relations above satisfy the mathematical condition of being continuous variables, as they are themselves functions of state variables. One can thus apply of the criterion of exact differential for these functions.

For a function of the form $P = P(X, Y)$ one can write the following total differential:

$$dP = \left(\frac{\partial P}{\partial X} \right)_Y dX + \left(\frac{\partial P}{\partial Y} \right)_X dY = MdX + NdY \quad \text{..(5.8)}$$

$$\text{Where: } M = \left(\frac{\partial P}{\partial X} \right)_Y \quad \text{and} \quad N = \left(\frac{\partial P}{\partial Y} \right)_X \quad \text{..(5.9)}$$

$$\text{Further, } \left(\frac{\partial M}{\partial Y} \right)_X = \left(\frac{\partial^2 P}{\partial Y \partial X} \right) \quad \text{and} \quad \left(\frac{\partial N}{\partial X} \right)_Y = \left(\frac{\partial^2 P}{\partial X \partial Y} \right) \quad \text{..(5.10)}$$

$$\text{It follows: } \left(\frac{\partial M}{\partial Y} \right)_X = \left(\frac{\partial N}{\partial X} \right)_Y \quad \text{..(5.11)}$$

Applying eqn. 5.11 to 5.3, 5.5, 5.6 and 5.7 one may derive the following relationships termed Maxwell relations:

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad \text{..(5.12)}$$

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P \quad \text{..(5.13)}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad \text{..(5.14)}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \quad \text{..(5.15)}$$

5.4 Relations for Enthalpy, Entropy and Internal Energy

One may conveniently employ the general energy relations and Maxwell equations to obtain expressions for change in enthalpy and entropy and internal energy for any process, which in turn may be used for computing the associated heat and work interactions.

Let $H = H(T, P)$

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

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

$$\text{Thus: } dH = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad \text{..(5.16)}$$

$$\text{Using } dH = TdS + VdP \Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V \quad \text{..(5.17)}$$

$$\text{From Maxwell relations as in eqn. 5.15: } \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \text{..(5.18)}$$

Thus using eqns. 5.17 and 5.18 in 5.16 we get:

$$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P \right] dP \quad \text{..(5.20)}$$

In the same manner starting from the general function: $U = U(T, V)$ and $\mathfrak{F} = S(T, P)$ and applying appropriate Maxwell relations one may derive the following general expressions for differential changes in internal energy and entropy.

$$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P \right] dV \quad \text{..(5.21)}$$

$$dS = C_p \frac{dT}{T} - \left(\frac{\partial V}{\partial T} \right)_P dP \quad \text{..(5.22)}$$

$$\text{Or, alternately: } dS = C_v \frac{dT}{T} + \left(\frac{\partial P}{\partial T} \right)_V dV \quad \text{..(5.23)}$$

Thus, eqns. 5.20 to 5.23 provide convenient general relations for computing enthalpy, internal energy and entropy changes as function of volumetric properties and specific heats. If a fluid is described by a suitable EOS, these equations may be conveniently integrated to obtain analytical expressions for energy and entropy changes.

Example 5.1

Derive an expression for enthalpy change of a gas during an isothermal process assuming using the following EOS: $P(V - b) = RT$

[\(Click here for solution\)](#)

5.5 Residual Property Relations

An alternate method of computing energy and entropy changes for real gases involves the definition of *residual property*. The specific residual property M^R is defined as follows:

$$M^R = M(T, P) - M^{ig}(T, P) \quad \text{..(5.24)}$$

Where, $M(T, P)$ is the specific property of a real gas at a given T & P, and $M^{ig}(T, P)$ is the value of the same property if the gas were to behave ideally at the same T & P. Thus for example:

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

Using the generalized compressibility factor 'Z':

$$V^R = (ZRT / P) - (RT / P)$$

$$V^R = (Z - 1)RT / P \quad \text{..(5.25)}$$

The residual properties are usually used for gases *only*. Using such a property for a liquid (or solid) is inconvenient as then it would also include the *property change* of vapourization (and solidification) which generally are large in magnitude. This detracts from the advantage of working with the residual property as a measure of small corrections to ideal gas behaviour. Thus the use of residual functions is restricted to prediction of real gas behaviour only. To exploit the

concept of residual properties we take advantage of the Gibbs free energy as it can be used as a generating function for other thermodynamic properties.

Derivation of Residual functions:

We start from the generic equation: $G = H - TS$..(5.2)

And $dG = VdP - SdT$..(5.7)

Taking the total differential for the function G / RT :

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT}dG - \frac{G}{RT^2}dT \quad \text{..(5.26)}$$

Substituting eqn. 5.2 and 5.7 in 5.26 we get:

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT}dP - \frac{H}{RT^2}dT \quad \text{..(5.27)}$$

One may write the same equation specifically for an ideal gas, whence:

$$d\left(\frac{G^{ig}}{RT}\right) = \frac{V^{ig}}{RT}dP - \frac{H^{ig}}{RT^2}dT \quad \text{..(5.28)}$$

Subtracting eqn. 5.28 from 5.27:

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}dP - \frac{H^R}{RT^2}dT \quad \text{..(5.29)}$$

Thus we may write the following further *generative* relations:

$$\frac{V^R}{RT} = \left[\frac{\partial(G^R / RT)}{\partial P} \right]_T \quad \text{..(5.30)}$$

$$\frac{H^R}{RT} = -T \left[\frac{\partial(G^R / RT)}{\partial T} \right]_P \quad \text{..(5.31)}$$

$$\text{And further: } \frac{S^R}{RT} = \frac{H^R}{RT} - \frac{G^R}{RT} \quad \text{..(5.32)}$$

$$\text{From eqn. 5.29: } \int_0^P d\left(\frac{G^R}{RT}\right) = \frac{G^R}{RT} \Big|_P - \frac{G^R}{RT} \Big|_{P=0} ; \text{ but } \frac{G^R}{RT} \Big|_{P=0} = 0$$

$$\text{Thus: } \frac{G^R}{RT} = \int_0^P \frac{V^R}{RT} dP \quad \text{..(5.33)}$$

$$\text{Putting eqn. 5.25 in 5.33: } \frac{G^R}{RT} = \int_0^P (Z-1) \frac{dP}{P} \quad \text{..(5.34)}$$

Differentiating eqn. 5.34 w.r.t T in accordance with 5.31 gives:

$$\frac{H^R}{RT} = -T \int_0^P \left(\frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} \quad \text{..(5.35)}$$

Finally using eqns 5.32, 5.34, and 5.35:

$$\frac{S^R}{R} = -T \int_0^P \left(\frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} - \int_0^P (Z-1) \frac{dP}{P} \quad \text{..(5.36)}$$

The last two equations may be expressed in alternative forms in terms of reduced temperature and pressure:

$$\frac{H^R}{RT_C} = -T_r^2 \int_0^{P_r} \left(\frac{\partial Z}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r} \quad \text{..(5.37)}$$

$$\frac{S^R}{R} = -T_r \int_0^{P_r} \left(\frac{\partial Z}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r} - \int_0^{P_r} (Z-1) \frac{dP_r}{P_r} \quad \text{..(5.38)}$$

Example 5.2

Derive an expression for enthalpy change of a gas during an isothermal process assuming using the following EOS: $Z = 1 + AP_r / T_r$

[\(Click here for solution\)](#)

5.6 Residual Property Calculation from EOS

From Virial EOS:

Using 5.35 and 2.12 one obtains:

$$\frac{H^R}{RT} = \frac{P}{R} \left(\frac{B}{T} - \frac{dB}{dT} \right) \quad \text{..(5.39)}$$

Next, on substituting eqns. 2.13 – 2.15 in 5.37 the following relations result:

$$\frac{H^R}{RT_C} = P_r \left[\left(0.083 - \frac{1.097}{T_r^{1.6}} \right) + \omega \left(0.139 - \frac{0.894}{T_r^{4.2}} \right) \right] \quad \text{..(5.40)}$$

Similarly using 5.36 and 2.12 we get:

$$\frac{S^R}{R} = -\frac{P}{R} \left(\frac{dB}{dT} \right) \quad \text{..(5.40)}$$

Finally employing eqns. 2.13 – 2.15 in 5.38:

$$\frac{S^R}{R} = -P_r \left[\left(\frac{0.675}{T_r^{1.6}} \right) + \omega \left(\frac{0.722}{T_r^{4.2}} \right) \right] \quad \text{..(5.41)}$$

From Cubic EOS:

One may use the following form of the cubic EOS presented in chapter 2:

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + ubV + wb^2} \quad \text{..(2.21)}$$

$$\text{Or equivalently: } Z^3 + \alpha Z^2 + \beta Z + \gamma = 0 \quad \text{..(2.23)}$$

While the eqns. 5.35 and 5.36 are useful for volume explicit EOS, they are unsuitable for cubic EOS which are pressure explicit. For the latter type of EOS one may show that the appropriate equations for residual enthalpy and entropy are (see S.I. Sandler, *Chemical, Biochemical and Engineering Thermodynamics*, ch. 6, 4th Edition, Wiley India, 2006):

$$\frac{H^R}{RT} = Z - 1 + \frac{1}{RT} \int_{V=\infty}^V \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV \quad \text{..(5.42)}$$

$$\frac{S^R}{R} = \ln Z + \frac{1}{R} \int_{V=\infty}^V \left[\left(\frac{\partial P}{\partial T} \right)_V - \frac{R}{V} \right] dV \quad \text{..(5.43)}$$

The above relations may be applied to the various cubic EOSs to obtain the necessary residual property relations. The final results are shown below.

From RK-EOS:

$$\frac{H^R}{RT} = (Z-1) - \frac{3a}{2bRT} \ln\left(\frac{Z+B}{Z}\right) \quad \text{..(5.44)}$$

$$\frac{S^R}{R} = \ln(Z-B) - \frac{a}{2bRT} \ln\left(\frac{Z+B}{Z}\right) \quad \text{..(5.47)}$$

$$\text{where, } a = \frac{0.42748R^2T_C^2\alpha_{RK}(T_r)}{P_C}; b = \frac{0.08664RT_C}{P_C}$$

$$\alpha_{RK}(T_r) = T_r^{-1/2}$$

For SRK-EOS:

$$\frac{H^R}{RT} = (Z-1) + \frac{1}{RT} - \frac{T\left(\frac{\partial a}{\partial T}\right) - a}{bRT} \ln\left(\frac{Z+B}{Z}\right) \quad (5.48)$$

$$\frac{S^R}{R} = \ln(Z-B) - \frac{1}{bRT} \frac{\partial a}{\partial T} \ln\left(\frac{Z+B}{Z}\right) \quad \text{..(5.49)}$$

$$\frac{\partial a}{\partial T} = -\frac{a}{\sqrt{\alpha_{SRK}(T_r)TT_C}} \left[(0.48 + 1.574\omega - 0.176\omega^2) \right] \quad \text{..(5.51)}$$

$$\text{where, } a = \frac{0.42748R^2T_C^2\alpha_{SRK}(T_r)}{P_C}; b = \frac{0.08664RT_C}{P_C}$$

$$\text{and, } \alpha_{SRK}(T_r) = [1 + (0.48 + 1.574\omega - 0.176\omega^2)(1 - T_r^{1/2})]^2$$

For PR-EOS:

$$\frac{H^R}{RT} = (Z-1) + \frac{\left\{ T\left(\frac{\partial a}{\partial T}\right) - a \right\}}{2\sqrt{2}bRT} \ln\left[\frac{Z+B(1+\sqrt{2})}{Z+B(1-\sqrt{2})} \right] \quad \text{..(5.52)}$$

$$\frac{S^R}{R} = \ln(Z-B) - \frac{1}{2\sqrt{2}bRT} \frac{\partial a}{\partial T} \ln\left[\frac{Z+B(1+\sqrt{2})}{Z+B(1-\sqrt{2})} \right] \quad \text{..(5.53)}$$

$$\frac{\partial a}{\partial T} = -\frac{a}{\sqrt{\alpha_{PR}(T_r)TT_C}} \left[(0.37464 + 1.5422\omega - 0.62992\omega^2) \right] \quad \text{..(5.54)}$$

$$\text{where, } a = \frac{0.45724R^2T_c^2\alpha_{PR}(T_r)}{P_c}; b = \frac{0.07779RT_c}{P_c}$$

$$\text{and, } \alpha_{PR}(T_r) = [1 + (0.37464 + 1.5422\omega - 0.62992\omega^2)(1 - T_r^{1/2})]^2$$

As part of computing the residual enthalpy or entropy (and internal energy) at any set of temperature and pressure, the molar volume or correspondingly Z^{vap} needs to be *first* computed employing the usual algorithm for solving cubic EOS described in section 2.3.3.

Example 5.3

Derive expressions for H^R , S^R from RK-EOS.

[\(Click here for solution\)](#)

5.7 Generalized Correlations for computing dH and dS for a real gas:

The approach based on the use of the compressibility factors can be applied to the present instance to evolve generalized correlations for computing enthalpy and entropy changes for gases. We start with the Pitzer-type expression for the compressibility factor:

$$Z = Z^0 + \omega Z^1 \quad \text{..(2.25)}$$

Differentiating with respect to the reduced temperature we get:

$$\left(\frac{\partial Z}{\partial T_r}\right)_{P_r} = \left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} + \omega \left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r} \quad \text{..(5.55)}$$

Thus using eqn. 5.54 we may recast eqns. 5.37 and 5.38 as follows:

$$\frac{H^R}{RT_c} = -T_r^2 \int_0^{P_r} \left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} - \omega T_r^2 \int_0^{P_r} \left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} \quad \text{..(5.56)}$$

$$\text{And: } \frac{S^R}{R} = - \int_0^{P_r} \left[T_r \left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} + Z^0 - 1 \right] \frac{dP_r}{P_r} - \omega \int_0^{P_r} \left[\left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r} + Z^1 \right] \frac{dP_r}{P_r} \quad \text{..(5.57)}$$

Both the above equations may be rewritten individually as follows:

$$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c} \quad \text{..(5.58)}$$

$$\text{Where, } \frac{(H^R)^0}{RT_c} = -T_r^2 \int_0^{P_r} \left(\frac{\partial Z^0}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r} \quad \text{..(5.59a)}$$

And:

$$\frac{(H^R)^1}{RT_c} = -T_r^2 \int_0^{P_r} \left(\frac{\partial Z^1}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r} \quad \text{..(5.59b)}$$

Similarly:

$$\frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R} \quad \text{..(5.60)}$$

$$\frac{(S^R)^0}{R} = - \int_0^{P_r} \left[T_r \left(\frac{\partial Z^0}{\partial T_r} \right)_{P_r} + Z^0 - 1 \right] \frac{dP_r}{P_r} \quad \text{..(5.61a)}$$

$$\frac{(S^R)^1}{R} = - \int_0^{P_r} \left[\left(\frac{\partial Z^1}{\partial T_r} \right)_{P_r} + Z^1 \right] \frac{dP_r}{P_r} \quad \text{..(5.61b)}$$

The term $\frac{(H^R)^0}{RT_c}$ in eqn. 5.59a constitutes the *first order* enthalpy departure, and $\frac{(H^R)^1}{RT_c}$ (in eqn.

5.59b) the *second order* (with respect to simple fluids) enthalpy departure at specified T_r and P_r .

The same is true for the corresponding entropic terms provided by eqns. 5.61a and 5.61b.

The evaluation of the integrals in eqns. 5.59 to 5.62 may be carried out assuming an EOS. The most widely used approach is that of Lee and Kesler who employed a modified form of the BWR EOS (eqn. 2.17) to extend their generalized correlation to residual property estimation. Figs. 5.1 and 5.2 respectively provide values of $(H^R)^0 / RT_c$, and $(H^R)^1 / RT_c$ respectively. Similar plots for the entropy terms $(S^R)^0 / R$, and $(S^R)^1 / R$ are also available; however, here the plot of the entire entropy term $(-S^R)$ as function of T_r and P_r is shown in fig. 5.3. Table of

values of all the above (eqns. 5.59 to 5.62) are also available as functions of T_r and P_r at discrete intervals (see for example: J.M. Smith, H.C. Van Ness and M.M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 6th ed., McGraw-Hill, 2001).

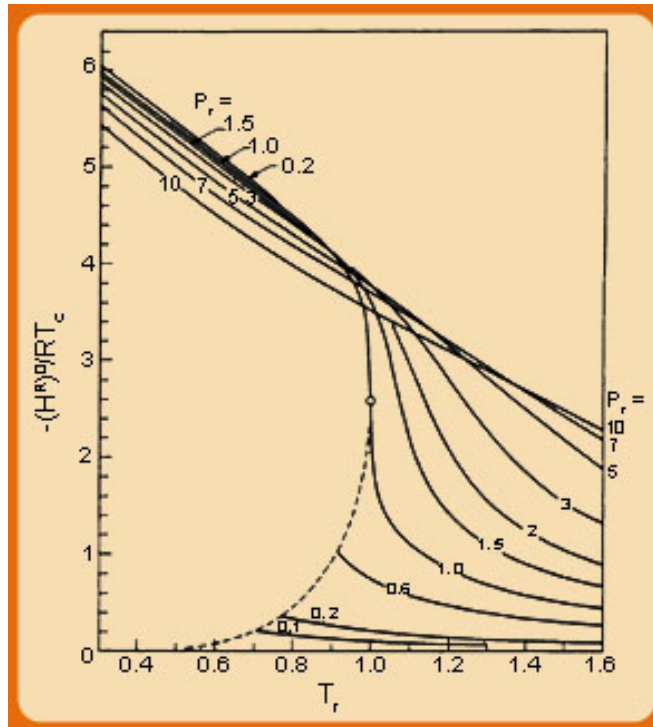


Fig. 5.1 Correlation of $-H_R^0/RT_c$ drawn from tables of Lee-Kesler (Source: *AIChE J.*, pp. 510-527, 1975)

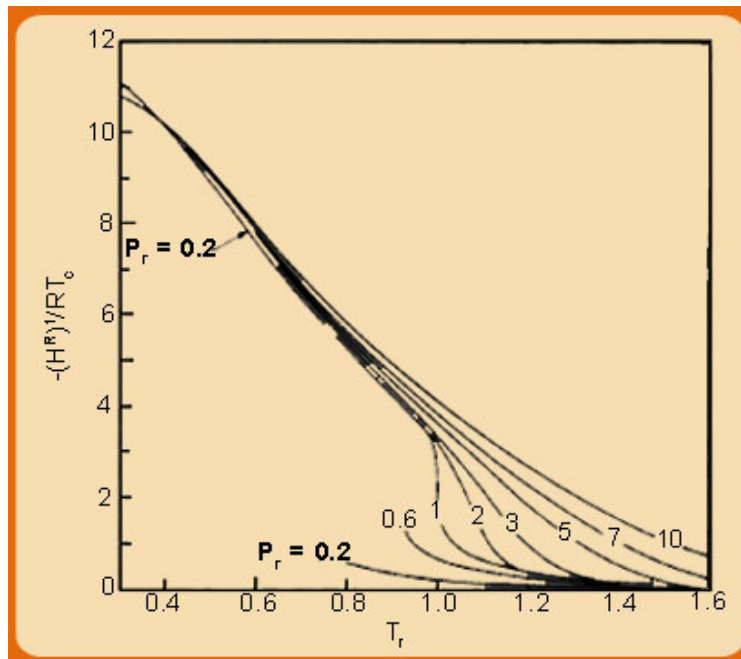


Fig. 5.2 Correlation of $-H_R^1/RT_C$ drawn from tables of Lee-Kesler (Source: *AIChE J.*, pp. 510-527, 1975)

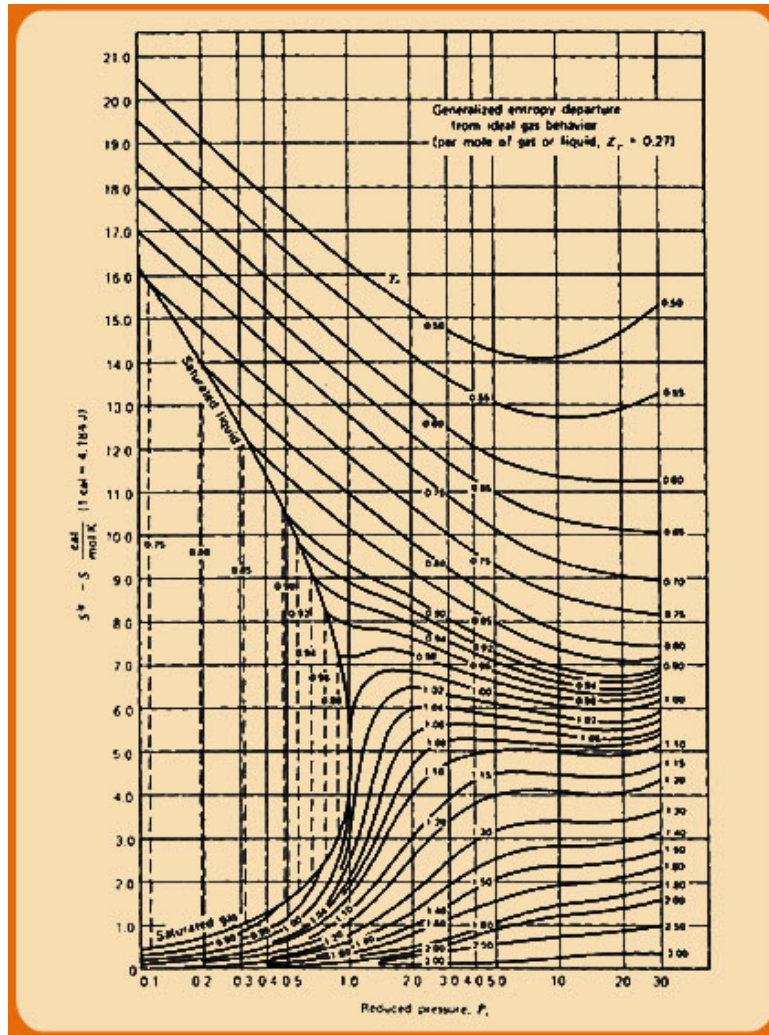


Figure 5.3 Generalized entropy departure functions using corresponding states.
 [Source: O.A. Hougen, K.M. Watson, and R.A. Ragatz, *Chemical Process Principles Charts*, 2nd ed., John Wiley & Sons, New York, 1960]

5.8 Computation of ΔH and ΔS for a Gas using Generalized Departure Functions

The residual function equations presented in the last section are particularly useful for estimating finite changes in enthalpy and entropy for real gases undergoing change in either closed or open system processes. We consider that a pure fluid changes state from (T_1, P_1) to (T_2, P_2) ; shown schematically in fig. 5.4.

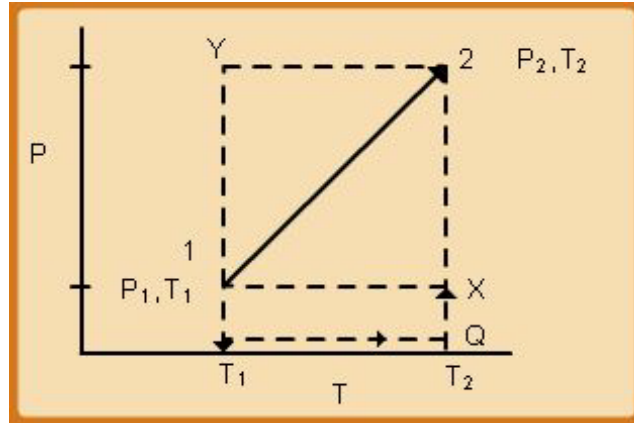
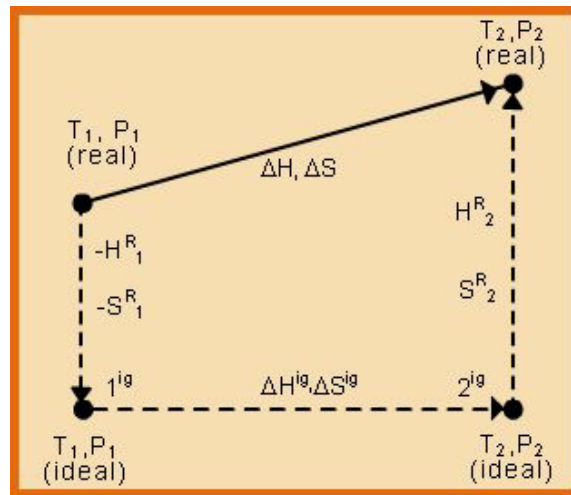


Fig. 5.4 Schematic of a General Thermodynamic Process on P – T co-ordinates

Since the departure functions H^R and S^R capture deviations from ideal gas behaviour at the same temperature as the real gas, one can conceive of the pathway between states ‘1’ and ‘2’ to be decomposed into following steps (see fig 5.5):

- Real gas state at (T_1, P_1) to ideal gas state (*ig*) at (T_1, P_1)
- Ideal gas state at (T_1, P_1) to ideal gas state at (T_2, P_2)
- Ideal gas state at (T_2, P_2) to real gas state at (T_2, P_2)



5.5 Pathway for calculating ΔH and ΔS for Real Gases

- For step ‘a’ the change of enthalpy is given by: $H_1^{ig} - H_1 = -H_1^R$
- For step ‘b’ the change of enthalpy is given by: $H_2^{ig} - H_1^{ig} = \Delta H^{ig}$
- For step ‘c’ the change of enthalpy is given by: $H_2 - H_2^{ig} = H_2^R$

Therefore, the overall change of enthalpy is given by:

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

Using eqn. 3.8: $H_2 - H_1 = H_2^R - H_1^R + \int_{T_1}^{T_2} C_p^{ig} dT$..(5.63)

The same considerations apply for computing the change of entropy between the two states:

$$\Delta S = S_2 - S_1 = S_2^R - S_1^R + \Delta S^{ig}$$

Using eqn. 4.21: $S_2 - S_1 = S_2^R - S_1^R + \int_{T_1}^{T_2} C_p^{ig} dT / T - R \ln(P_2 / P_1)$..(5.64)

Generalized residual property relations may be used for calculation of change in internal energy i.e. $U_2 - U_1$ for a process in the following manner:

$$U_2 - U_1 = (H_2 - P_2 V_2) - (H_1 - P_1 V_1)$$

Or: $U_2 - U_1 = (H_2 - H_1) - (P_2 V_2 - P_1 V_1)$..(5.65)

The term $(H_2 - H_1)$ can be calculated using eqn. 5.63, while the term $(P_2 V_2 - P_1 V_1)$ may be computed after obtaining V_1 and V_2 applying the generalized compressibility factor approach.

One may, however, also use the generalized residual property charts for internal energy for the same purpose (fig. 5.6).

Example 5.5

Estimate the final temperature and the work required when 1 mol of n-butane is compressed isentropically in a steady-flow process from 1 bar and 50°C to 7.8 bar.

[\(Click here for solution\)](#)

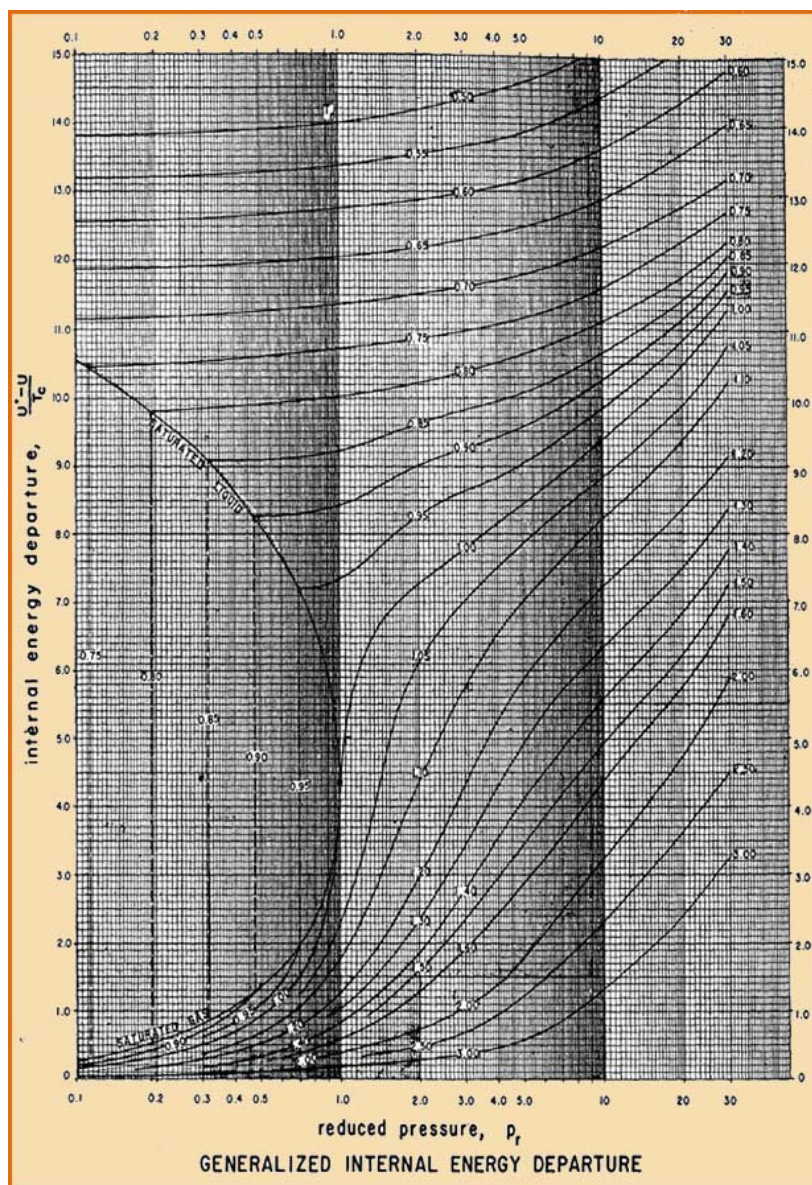


Figure 5.6 Generalized internal energy departure functions using corresponding states
 [Source: O.A. Hougen, K.M. Watson, and R.A. Ragatz (1960), *Chemical Process Principles Charts*, 2nd ed., John Wiley & Sons, New York]

5.9 Extension to Gas Mixtures

The generalized equations developed for ΔH and ΔS in the last section may be extended to compute corresponding changes for a real gaseous mixture. The method used is the same as that

developed in section 2.4 through the definition of pseudo-critical mixture properties using linear mixing rules:

$$T_{C,m} = \sum_i y_i T_{C,i} \quad P_{C,m} = \sum_i y_i P_{C,i} \quad \omega_m = \sum_i y_i \omega_i \quad \text{..(2.32)}$$

Using the above equations pseudo-reduced properties are computed:

$$T_{r,m} = T / T_{C,m} \quad \text{and} \quad P_{r,m} = P / P_{C,m}$$

Further calculations of changes in internal energy, enthalpy, and entropy follow the same principles developed in the last section.

Example 5.6

Calculate the changes in enthalpy and entropy per mole when a mixture of 70 mole % ethylene (1) and 30 mole% propylene (2) at 323K and 10 bar is taken to 60 bar and 600 K using the generalized compressibility factor approach.

$$C_{p1}^{ig} = 4.196 + 154.565 \times 10^{-3} T - 81.076 \times 10^{-6} T^2 + 16.813 \times 10^{-9} T^3;$$

$$C_{p2}^{ig} = 3.305 + 235.821 \times 10^{-3} T - 117.58 \times 10^{-6} T^2 + 22.673 \times 10^{-9} T^3$$

[\(Click here for solution\)](#)

5.10 Relations for ΔH and ΔS for Liquids

One starts with the generic equations for dH and dS developed in section 5.4.

$$dH = C_p dT + \left[V - T \left(\frac{\partial V}{\partial P} \right)_T \right] dP \quad \text{..(5.20)}$$

$$dS = C_p \frac{dT}{T} - \left(\frac{\partial V}{\partial T} \right)_P dP \quad \text{..(5.22)}$$

As discussed in section 2.3, for liquids it is often simpler to use *volume expansivity* and *isothermal compressibility* parameters for computing thermodynamic properties of interest. Thus from eqn. 2.3:

$$\text{Volume Expansivity, } \beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

Using eqn. 2.3 in 5.20 and 5.22 the following relations obtain:

$$dH = C_p dT + [1 - \beta T] dP \quad \text{..(5.66)}$$

$$dS = C_p \frac{dT}{T} - \beta V dP \quad \text{..(5.67)}$$

The above equations may also be used to compute the properties of a compressed liquid state. Since the volumetric properties of liquids are very weakly dependent of pressure one can often use the saturated liquid phase properties as reference points and integrate the eqns. 5.66 to 5.67 (at constant temperature) to obtain enthalpy and entropy respectively. The relevant equations are:

$$H_i = H_i^{sat} + \int_{P_i^{sat}}^P V_i (1 - \beta_i T) dP \quad \text{..(5.68)}$$

$$S_i = S_i^{sat} - \int_{P_i^{sat}}^P \beta_i V_i dP \quad \text{..(5.69)}$$

In the last two equations, the molar volume V_i may be set equal to $V_i^{sat} (liq.)$, and the volume expansivity approximated to that at the saturated liquid point at the given temperature.

5.11 Applications to real fluid processes in process plant equipments

In a typical process plant one encounters a variety of flow devices such pumps, compressors, turbines, nozzles, diffusers, etc. Such devices are not subject to heat transfer *by design* as are heat exchangers, condensers, evaporators, reactors, etc. However, the flow devices typically are subject to mechanical irreversibility owing to existence of dissipative forces such as fluid viscosity and mechanical friction, which results in reduction of their efficiency. In addition such devices may be subject to thermal irreversibility as their operation may not be truly adiabatic. Therefore, it is necessary to compute the efficiency of such devices in relation to a perfectly reversible (isentropic) process between their inlet and outlet.

The performance of a flow device is expressed in terms of *isentropic efficiency* in which the actual performance of the device is compared with that of an isentropic device for the same inlet conditions and exit pressure. For example, the isentropic efficiency η_T of a **turbine** (which essentially converts fluid enthalpy to shaft work, fig. 5.7) is defined as:

$$\eta_T = \frac{\text{Power output of the actual turbine}}{\text{Power out put of the turbine, if it were isentropic}} = \frac{H_i - H_e}{H_i - H_e^s} \quad \text{..(5.69)}$$

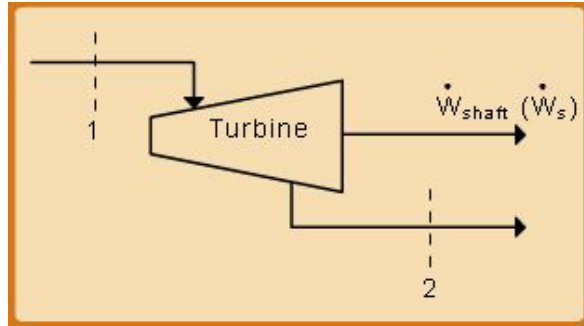


Fig.5.7 Schematic of a Turbine

Where, H_i = enthalpy of the fluid at the inlet of the turbine, H_e = enthalpy of the fluid at the exit of the actual turbine, H_e^s = enthalpy of the fluid at the exit of the turbine, if it were isentropic.

Similarly, the isentropic efficiency η_c of a **compressor** (fig. 5.8) or a pump η_p (which convert applied shaft work to fluid enthalpy) is given by:

$$\eta_c \text{ (or } \eta_p) = \frac{(W_s)^s}{(W_s)} = \frac{H_e^s - H_i}{H_e - H_i} \quad \text{..(5.70)}$$

Where, H_i = enthalpy of the fluid at the inlet to the compressor (or pump), H_e = enthalpy of the fluid at the exit of the *actual* compressor (pump), and H_e^s = enthalpy of the fluid at the exit of an isentropic compressor (or pump), and W_s represents the shaft work per mole (or mass) of fluid in the two situations.

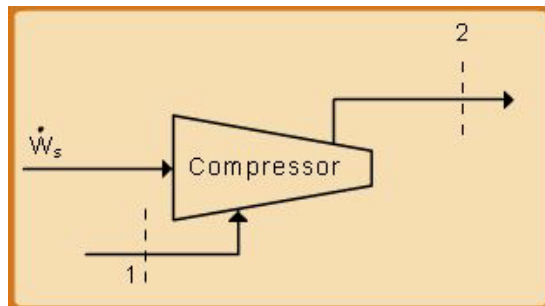


Fig.5.8 Schematic of a Turbine

The isentropic efficiency η_N of a **nozzle**, which is used to achieve high fluid velocity at exit (by conversion of enthalpy to kinetic energy) is given by:

$$\eta_N = \frac{(V_2^2)/2}{(V_2^s)^2/2} = \frac{\text{Kinetic energy of gas leaving the actual nozzle}}{\text{Kinetic energy of gas leaving the nozzle, if it were isentropic}} \quad \text{..(5.71)}$$

Example 5.7

A certain gas is compressed adiabatically from 293 K and 135 KPa to 550 KPa. What is the work needed? What is the final T_2 ? Assume ideal gas behavior. Compressor $\eta = 0.8$.

For the gas: $C_p^{ig} = 1.65 + 8.9 \times 10^{-3}T - 2.2 \times 10^{-6}T^2$

Assignment - Chapter 5