

CEN 202 THERMODYNAMICS

CHAPTER 6: THERMODYNAMIC PROPERTIES OF FLUIDS

TEXT BOOK: : J. M. SMITH, H. C. VAN NESS, M. M. ABBOTT, M. T. SWIHART. "INTRODUCTION TO CHEMICAL ENGINEERING THERMODYNAMICS", EIGHTH EDITION. 2018

Thermodynamic Properties of Fluids

Fundamental property and Maxwell relations and related equations have been derived in Physical Chemistry. So the other topics will be considered in this chapter.

The Gibbs Energy as a Generating Function

The fundamental property relation for $G = G(T, P)$,

$$dG = VdP - SdT$$

(11)

has an alternative form. It follows from the mathematical identity:

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

Substitution for dG by Eq. (11) and for G by Eq. ($G = H - TS$) gives, after algebraic reduction:

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

(37)

The advantage of this equation is that all terms are dimensionless; in contrast to Eq. (11), the enthalpy rather than the entropy appears on the right side.

The Gibbs Energy as a Generating Function

Equation 37 at constant T or P can be written:

$$\frac{V}{RT} = \left[\frac{\partial(G/RT)}{\partial P} \right]_T \quad (38)$$

$$\frac{H}{RT} = -T \left[\frac{\partial((G/RT))}{\partial T} \right]_P \quad (39)$$

Given G/RT as a function of T and P, V/RT and H/RT follow by simple differentiation. The remaining properties follow from defining equations. In particular,

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

$$\frac{U}{RT} = \frac{H}{RT} - \frac{PV}{RT}$$

The Gibbs energy, G or G/RT , when given as a function of its canonical variables T and P, serves as a generating function for the other thermodynamic properties through simple mathematics, and implicitly represents complete property information.

RESIDUAL PROPERTIES

The **residual** Gibbs energy is: $G^R \equiv G - G^{ig}$, where G and G^{ig} are the actual and the ideal-gas-state values of the Gibbs energy at the same temperature and pressure. Other residual properties are defined in an analogous way.

The generic residual property is defined by:

$$M^R \equiv M - M^{ig} \rightarrow M = M^{ig} + M^R$$

where M and M^{ig} are actual and ideal-gas-state properties at the same T and P .

RESIDUAL PROPERTIES

Equation (37), written for the ideal-gas state, becomes:

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

Subtracting this equation from Eq. (37) itself gives:

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT} dP - \frac{H^R}{RT^2} dT \quad (42)$$

This fundamental residual-property relation applies to fluids of constant composition.

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

RESIDUAL PROPERTIES

it may be integrated from zero pressure to arbitrary pressure P , yielding:

$$\frac{G^R}{RT} = \left(\frac{G^R}{RT} \right)_{P=0} + \int_0^P \frac{V^R}{RT} dP \quad (\text{const } T)$$

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

(46)

The defining equation for the Gibbs energy, $G = H - TS$, may also be written for the ideal-gas state, $G^{ig} = H^{ig} - TS^{ig}$; by difference, $G^R = H^R - TS^R$, and

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

In application, entropy always appears in differences. $S = S^{ig} + S^R$ for two different states.

Then by difference:

$$\Delta S \equiv S_2 - S_1 = \left(S_2^{ig} - S_1^{ig} \right) + \left(S_2^R - S_1^R \right)$$

RESIDUAL PROPERTIES

S^R and G^R may be calculated from the equations given below:

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

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

RESIDUAL PROPERTIES

Enthalpy and Entropy from Residual Properties

General expressions for H^{ig} and S^{ig} are found by integration of related equations from an ideal-gas state at reference conditions T_0 and P_0 to an ideal-gas state at T and P and using $H = H^{ig} + H^R$ and $S = S^{ig} + S^R$:

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

The equations have alternative forms when the integrals are replaced by equivalent terms that include the mean heat capacities introduced in previous sections:

$$H = H_0^{ig} + \langle C_P^{ig} \rangle_H (T - T_0) + H^R$$
$$S = S_0^{ig} + \langle C_P^{ig} \rangle_S \ln \frac{T}{T_0} - R \ln \frac{P}{P_0} + S^R$$

TWO-PHASE SYSTEMS

If two phases α and β are in equilibrium,

$$G^\alpha = G^\beta \quad dG^\alpha = dG^\beta$$

where G^α and G^β are the molar or specific Gibbs energies of the individual phases.

For both phases;

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

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

Remember $\Delta H^{\alpha\beta} = T\Delta S^{\alpha\beta}$ from here

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

which is the **Clapeyron equation**.

Two-Phase Liquid / Vapor Systems

When a system consists of saturated-liquid and saturated-vapor phases coexisting in equilibrium, the total value of any extensive property of the two-phase system is the sum of the total properties of the phases. Written for the volume, this relation is:

$$nV = n^lV^l + n^vV^v$$

where V is the molar volume for a system containing a total number of moles $n=n^l + n^v$.

Division by n gives:

$$V = x^lV^l + x^vV^v$$

where x^l and x^v represent the mass fractions of the total system that are liquid and vapor.

With $x^l = 1 - x^v$,

$$V = (1 - x^v)V^l + x^vV^v$$

Two-Phase Liquid / Vapor Systems

The mass or molar fraction of the system that is vapor x^v is often called the quality, particularly when the fluid in question is water. Analogous equations can be written for the other extensive thermodynamic properties. All of these relations are represented by the generic equation

$$M = (1 - x^v)M^l + x^v M^v$$

where M represents V, U, H, S , etc. An alternative form is sometimes useful:

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