

CHAPTER TWO

Thermodynamic Properties of Fluids

Learning Objectives

- Develop from the first and second laws the **fundamental property relations** which underlie the mathematical structure of thermodynamics
- Derive equations which allow calculation of **enthalpy and entropy values from PVT and heat-capacity data.**
- Develop **generalized correlations** which provide estimates of property values in the absence of complete experimental information.

Thermodynamic Properties of Fluids

Property Relations for Homogeneous Phases

- The **1st law of thermodynamics** for a simple compressible system that undergoes an **internally reversible** process of **n moles** is:

$$d(nU)_{\text{rev}} = \delta Q_{\text{rev}} + \delta W_{\text{rev}} \quad 2.1$$

- The incremental heat interaction δQ_{rev} is related directly to the entropy change through the formal definition of entropy: (**Entropy**, the measure of a system's thermal energy per unit temperature that is unavailable for doing useful work.)

$$dS = \left(\frac{\delta Q}{T} \right)_{\text{rev}} \quad \text{or} \quad \delta Q_{\text{rev}} = Td(nS) \quad 2.2$$

- For a simple compressible system, the only **reversible work** mode is **compression and/or expansion**, that is:

$$\delta W_{\text{rev}} = -Pd(nV) \quad 2.3$$

Thermodynamic Properties of Fluids

- Substituting these expressions for δQ_{rev} and δW_{rev} into the 1st - law statement yields:

$$d(nU) = Td(nS) - Pd(nV) \quad 2.4(a)$$

- Rearranging Eq. (2.4a)

$$Td(nS) = d(nU) + Pd(nV) \quad 2.4(b)$$

- This equation contains **only properties of the system**.
- Properties depend on **state alone**, and not on the kind of **process that leads to the state**.
- Thus Eq. (2.4) applies to any process in a system of **constant mass** that results in a differential change from **one equilibrium state to another**.
- The only requirements are that the system be closed and that the change occurs between equilibrium states.

Thermodynamic Properties of Fluids

- All of the primary thermodynamic properties: **P**, **V**, **T**, **U**, and **S** are included in Eq. (2.4).

- Additionally two properties, also defined **for convenience**, are:

i. Gibbs free energy or Gibbs function, G: is a composite property involving **enthalpy** and **entropy** and is defined as:

$$\mathbf{G = H - TS} \qquad \mathbf{2.5}$$

- ✓ The **Gibbs free energy** is particularly useful in defining equilibrium conditions for reacting systems **at constant P and T**.

ii. Helmholtz Free Energy or Helmholtz Function, A: is also a property, defined similarly to the Gibbs free energy, **with the internal energy replacing the enthalpy, that is,**

$$\mathbf{A = U - TS} \qquad \mathbf{2.6}$$

- ✓ The **Helmholtz free energy** is useful in defining equilibrium conditions for reacting systems **at constant V and T**.

Thermodynamic Properties of Fluids

- The **enthalpy** was defined by the equation for **n moles** is:

$$nH = nU + P(nV) \quad 2.7$$

- **Differentiating** Eq. (2.7) gives:

$$d(nH) = d(nU) + Pd(nV) + (nV)dP$$

- When $d(nU)$ is **replaced** by Eq. (2.4(a)), this reduces to:

$$d(nH) = Td(nS) + (nV)dP \quad 2.8$$

- Similarly, **Differentiating Helmholtz Function**, Eq. (2.6):

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

- **Eliminating $d(nU)$** by Eq. (2.4(a)) gives:

$$d(nA) = -Pd(nV) - (nS)dT \quad 2.9$$

- In the same fusion, **differentiating the Gibbs function**, Eq. (2.5)

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

- **Eliminating $d(nH)$** by Eq. (2.8) gives:

$$d(nG) = (nV)dP - (nS)dT \quad 2.10$$

Thermodynamic Properties of Fluids

- All the above equations are written for the **entire mass of any closed system**.
- The immediate application of these equations is to **one mole (or to a unit mass) of a homogeneous fluid of constant composition**.
- For this case, they simplify to:

$$dU = TdS - PdV \quad 2.11$$

$$dH = TdS + VdP \quad 2.12$$

$$dA = -PdV - SdT \quad 2.13$$

$$dG = VdP - SdT \quad 2.14$$

- ✓ These *fundamental property relations*; Eqs. (2.11) through Eq. (2.14) are **general equations for a homogeneous fluid of constant composition**.

Thermodynamic Properties of Fluids

- Another set of equations follows from Eqs. (2.11) through Eq. (2.14) by application of the criterion of **exactness** for a differential expression.
- If $F = F(x, y)$, then the total differential of F is defined as:

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy \quad \text{or} \quad dF = Mdx + Ndy \quad 2.15$$

$$\text{Where: } M = \left(\frac{\partial F}{\partial x}\right)_y \quad \text{and} \quad N = \left(\frac{\partial F}{\partial y}\right)_x$$

- Taking the **partial derivative of M with respect to y** and of **N with respect to x** yields:

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

- The order of differentiation is immaterial for properties since they are **continuous point functions** and have **exact differentials**.
- Therefore, the two relations above are identical:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad 2.16$$

Thermodynamic Properties of Fluids

- This is an important relation for partial derivatives, and it is used in calculus to test whether a differential dF is **exact or inexact**.
- In thermodynamics, this relation forms the basis for the development of the **Maxwell relations**
- Since U , H , A , and G are properties and thus have exact differentials.
- Applying Eq. (2.16) to each of them, we obtain:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad 2.17$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad 2.18$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad 2.19$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \quad 2.20$$

Thermodynamic Properties of Fluids

- The **Eqs (2.17) through Eq. (2.20)** are called the **Maxwell relations**.
- They are **extremely valuable** in thermodynamics because they provide a means of **determining the change in entropy**, which **cannot be measured directly**, by simply measuring the changes in properties P , V , and T .
- Note that the Maxwell relations given above are limited to **simple compressible systems**.
- We develop here only a few expressions useful for evaluation of thermodynamic properties from **experimental data**.
- Their derivation requires application of Eqs. (2.11), (2.12), (2.19), and (2.20).

Thermodynamic Properties of Fluids

Enthalpy and Entropy as Functions of T and P

- The most useful property relations for the **enthalpy** and **entropy** of a homogeneous phase result when these properties are **expressed as functions of T and P**.
- What we need to know is how **H** and **S** vary with temperature and pressure; Consider first the **temperature derivatives**.

$$\left(\frac{\partial H}{\partial T}\right)_p = C_P \quad 2.21$$

- Equation (2.21) defines the **heat capacity at constant pressure**:
- Another expression for this quantity is obtained by **division of Eq. (2.12) by dT** and restriction of the result to **constant P**:

$$\left(\frac{\partial H}{\partial T}\right)_p = T \left(\frac{\partial S}{\partial T}\right)_p \quad 2.22$$

Thermodynamic Properties of Fluids

- Combination of Eq. (2.22) with Eq. (2.21) gives:

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \quad 2.23$$

- The **pressure derivative** of the **entropy** results directly from **Eq. (2.20)**:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad 2.24$$

- The corresponding **derivative for the enthalpy** is found by **division of Eq. (2.12) by dP** and restriction to **constant T**:

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

- As a result of Eq. (2.24) to the above equation becomes:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_p \quad 2.25$$

Thermodynamic Properties of Fluids

- The functional relations chosen here for H and S are:

$$\mathbf{H = H(T, P)} \qquad \mathbf{and} \qquad \mathbf{S = S(T, P)}$$

- Whence;

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

- The partial derivatives in these two equations are given by the following equations and (2.23) through (2.25):

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \qquad \mathbf{2.26}$$

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T} \right)_P dP \qquad \mathbf{2.27}$$

- These are general equations relating the properties of homogeneous fluids of **constant composition to temperature and pressure**

Thermodynamic Properties of Fluids

Internal Energy as a Function of P

- The **pressure dependence** of the internal energy is obtained by differentiation of the equation:

$$U = H - PV$$

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

- Then by Eq. (2.25):

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P \quad 2.25$$

- Substitute Eq. (2.25) to the above equations:

$$\left(\frac{\partial U}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial P}\right)_T \quad 2.28$$

Thermodynamic Properties of Fluids

The Ideal-Gas State

- The coefficients of dT and dP in **Eqs. (2.26) and (2.27)** are evaluated from heat-capacity and PVT data.
- The ideal-gas state provides an example of PVT behavior:

$$PV^{\text{ig}} = RT \qquad \left(\frac{\partial V^{\text{ig}}}{\partial T} \right)_P = \frac{R}{P}$$

- Where: superscript "ig" denotes an ideal-gas value.

$$dH^{\text{ig}} = C_p^{\text{ig}} dT \qquad 2.29$$

$$dS^{\text{ig}} = C_p^{\text{ig}} \frac{dT}{T} - R \frac{dP}{P} \qquad 2.30$$

Thermodynamic Properties of Fluids

Alternative Forms for Liquids

- Eq (2.23) through (2.26) are expressed in an alternative form by elimination of $\left(\frac{\partial V}{\partial T}\right)_P$ in favor of the volume expansivity β by Eq. (1.3) and of $\left(\frac{\partial V}{\partial P}\right)_T$ in favor of the isothermal compressibility κ by Eq. (1.4):

$$\left(\frac{\partial S}{\partial P}\right)_T = -\beta V \quad 2.31$$

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

$$\left(\frac{\partial H}{\partial P}\right)_T = (1 - \beta T)V \quad 2.32$$

$$\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial U}{\partial P}\right)_T = (\kappa P - \beta T)V \quad 2.33$$

- The above general equations, incorporating β and κ are usually applied only **to liquids**.
- However, for liquids not near the critical point, the volume itself is small, as are β and κ .

Thermodynamic Properties of Fluids

Alternative Forms for Liquids

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad 2.24$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \quad 2.25$$

$$\left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T \quad 2.28$$

Thermodynamic Properties of Fluids

- Thus at most conditions pressure has little effect on the properties of liquids;

✓ Which is the special case of **an incompressible fluid**.

- When $\left(\frac{\partial V}{\partial T}\right)_P$ is replaced in Eqs. (2.26) and (2.27) in favor of the volume expansivity, they become:

$$dH = C_P dT + (1 - \beta T) V dP \quad 2.34$$

$$dS = C_P \frac{dT}{T} - \beta V dP \quad 2.35$$

- Since **β and κ are weak functions of pressure for liquids**, they are usually **assumed constant** at appropriate average values for integration of the final terms of Eqs. (2.34) and (2.35).

Thermodynamic Properties of Fluids

Internal Energy and Entropy as Functions of T and V

- **Temperature** and **volume** often serve as **more convenient** independent variables than do **temperature** and **pressure**.
- The most useful property relations are then for **internal energy** and **entropy**.
- Required here are the derivatives $(\partial U/\partial T)_V$, $(\partial U/\partial V)_T$, $(\partial S/\partial T)_V$ and $(\partial S/\partial V)_T$.

- The first two of these is directly from Eq. (2.11): $(dU = TdS - PdV)$

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

- Eq. (2.36) defines the heat capacity at constant volume:

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \quad 2.36$$

Thermodynamic Properties of Fluids

- With Eq. (2.36); the left side of the above equation becomes:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad 2.37$$

- With Eq. (2.19); the right side of the above eq becomes: $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad 2.38$$

- The chosen functional relations here are:

$$U = U(T, V)$$

$$S = S(T, V)$$

- Whence;

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

- The partial derivatives in these two equations are given by Eqs. (2.36), (2.37), (2.38), and (2.19):

Thermodynamic Properties of Fluids

- The following equations are therefore, the general equations relating the **internal energy** and **entropy** of homogeneous fluids of **constant composition to temperature and volume**.

$$dU = C_V dT + \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV \quad 2.39$$

$$dS = C_V \frac{dT}{T} + \left(\frac{\partial P}{\partial T} \right)_V dV \quad 2.40$$

- Equation (1.5) applied to a change of state at constant volume becomes: and the **alternative forms of eq (2.39 & 2.40) are:**

$$\frac{dV}{V} = \beta dT - \kappa dP \leftrightarrow \left(\frac{\partial P}{\partial T} \right)_V = \frac{\beta}{\kappa}$$

$$dU = C_V dT + \left(\frac{\beta}{\kappa} T - P \right) dV \quad 2.41$$

$$dS = C_V \frac{dT}{T} + \frac{\beta}{\kappa} dV \quad 2.42$$

Thermodynamic Properties of Fluids

The Gibbs Energy as a Generating Function

- The fundamental property relations for homogenous fluids of constant composition given by Eqs. (2.11) through (2.14) show that each of the thermodynamic properties U , H , A , and G is functionally related to a special pair of variables.

- In particular:

$$dG = VdP - SdT \quad 2.14$$

- Expresses the functional relation: $G = G(P, T)$
- Thus the special or **canonical** (variables conform to a general rule that is both **simple and clear**) variables for the Gibbs energy are **temperature and pressure**.
- Since these **variables can be directly measured and controlled**, the **Gibbs energy is a thermodynamic property of great potential utility**.

Thermodynamic Properties of Fluids

The Gibbs Energy as a Generating Function

- An alternative form of Eq. (2.14), a fundamental property relation, follows from the **mathematical identity**:

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

- Substitution for **dG** by Eq. (2.14) and for **G=H-TS** gives, after algebraic reduction:

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT} dP - \frac{H}{RT^2} dT \quad 2.43$$

- The advantage of this equation is that:
 - ✓ **All terms are dimensionless;**
 - ✓ Moreover, in contrast to Eq. (2.14), the **enthalpy** rather than the **entropy** appears on the right side.

Thermodynamic Properties of Fluids

- Eqs such as Eqs. (2.14) and (2.43) are too general for direct practical application, but they are readily applied in **restricted form**.

- Thus, from Eq. (2.43),

$$\frac{V}{RT} = \left[\frac{\partial(G/RT)}{\partial P} \right]_T \quad 2.44$$

$$\frac{H}{RT} = -T \left[\frac{\partial(G/RT)}{\partial T} \right]_P \quad 2.45$$

- When G/RT is known as a **function of T and P**, V/RT and H/RT follow by simple differentiation.

Thermodynamic Properties of Fluids

- The remaining properties are given by defining equations.

- In particular,

$$\frac{S}{R} = \frac{H}{RT} - \frac{G}{RT} \quad \text{and} \quad \frac{U}{RT} = \frac{H}{RT} - \frac{PV}{RT}$$

- Thus, when we know how G/RT (or G) is related to its canonical variables, T and P , i.e., when we are given $G/RT = g(T, P)$, we can evaluate all other thermodynamic properties by simple mathematical operations.

✓ *The Gibbs energy when given as a function of T and P therefore serves as a **generating function** for the other thermodynamic properties, and implicitly represents complete property information.*

Thermodynamic Properties of Fluids

- The partial derivatives in these two equations are given by Eqs. (2.36), (2.37), (2.38), and (2.19):

$$dU = C_V dT + \left(\frac{\beta}{\kappa} T - P \right) dV \quad 2.41$$

$$dS = \frac{C_V}{T} dT + \frac{\beta}{\kappa} dV \quad 2.42$$

Example

- Determine the enthalpy and entropy changes of liquid water for a change of state from 1bar and 298.15K to 1000bar and 323.15K. The following data for water are available.

T/K ($t/^\circ\text{C}$)	P/bar	$C_P/\text{kJ kmol}^{-1} \text{K}^{-1}$	$V/10^{-3} \text{m}^3 \text{kmol}^{-1}$	β/K^{-1}
298.15(25)	1	75.305	18.071	256×10^{-6}
298.15(25)	1000	18.012	366×10^{-6}
323.15(50)	1	75.314	18.234	458×10^{-6}
323.15(50)	1000	18.174	568×10^{-6}