

Thermodynamics

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Thermodynamic Properties of Fluids

- ☐ Property Relations for Homogeneous Phases
- ☐ Residual Properties
- ☐ Residual Properties by Equation of State
- ☐ Two-Phase Systems
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Thermodynamic Properties of Fluids

Property relations for Homogeneous Phases

Applications of first and second law of thermodynamics in developing mathematical structure of thermodynamics → property relations

Include [P, V, T] and U, H, S, C_p ...

Phase rule specifies the number of intensive properties, but it does not provide any information on how the values of these intensive properties can be calculated.

In the first law, for a **closed reversible system**, with n moles of a gas,

$$d(nU) = dQ_{rev} + dW_{rev} \dots (1) \quad dW_{rev} = -Pd(nV) \dots (2)$$

$$dQ_{rev} = Td(nS) \dots (3)$$

Combine Eq. (2) and (3) with (1): **$d(nU) = Td(nS) - Pd(nV) \dots (4)$**

**Fundamental property relation,
connecting U, S and PVT**

Primary thermodynamic properties: P, V, T, U and S

Other properties can be estimated from these primary parameters

Thermodynamic Properties of Fluids

Property relations for Homogeneous Phases

Enthalpy: $H = U + PV \dots (5)$

Helmholtz **free** energy $A = U - TS \dots (6)$

Gibbs **free** energy $G = H - TS \dots (7)$

The word **free** originally had the connotation of energy available to perform useful work, under appropriate conditions. The word, *free* is usually omitted.

For n moles from eq. (5):

$$d(nH) = d(nU) + Pd(nV) + (nV)dP \dots (8)$$

Replacing $d(nU)$ from Eq. (4) into Eq. (8):

$$d(nH) = [Td(nS) - Pd(nV)] + Pd(nV) + (nV)dP$$

$$\rightarrow d(nH) = Td(nS) + (nV)dP \dots \dots \dots (9)$$

From Eq. (6):

$$d(nA) = d(nU) - Td(nS) - nSd(T) \rightarrow d(nA) = -Pd(nV) - (nS)dT \dots (10)$$

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Property relations for Homogeneous Phases

From

$$G = H - TS \dots (7)$$

Replace $d(nH)$ from Eq. (9)

$$d(nG) = d(nH) - Td(nS) - nSd(T)$$

$$\rightarrow d(nG) = \cancel{Td(nS)} + (nV)dP - \cancel{Td(nS)} - nSd(T)$$

$$\rightarrow \mathbf{d(nG) = (nV)dP - nSd(T) \dots \dots (11)}$$

For ONE mole of gas, the important equations are:

$$\mathbf{dU = TdS - PdV \dots \dots (12)}$$

$$\mathbf{dH = TdS + VdP \dots \dots (13)}$$

$$\mathbf{dA = -PdV - SdT \dots \dots (14)}$$

$$\mathbf{dG = VdP - SdT \dots \dots (15)}$$

These fundamental property relations are general equations for a homogeneous fluid of constant composition

Thermodynamic Properties of Fluids

Property relations for Homogeneous Phases

Maxwell's Equations

From Eqs. (12) to (15)

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy \dots (16)$$

$$\text{Or, } dF = Mdx + Ndy \dots \dots \dots (17)$$

$$M = \left(\frac{\partial F}{\partial x}\right)_y ; \quad N = \left(\frac{\partial F}{\partial y}\right)_x \dots (18)$$

The criterion of exactness for a differential expression,
If $F = F(x, y)$, then the total differential of F is: \rightarrow

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 F}{\partial y \partial x} \quad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 F}{\partial x \partial y} \dots \dots \dots (19)$$

$$\therefore \frac{\partial^2 F}{\partial y \partial x} = \frac{\partial^2 F}{\partial x \partial y} \quad \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \dots \dots \dots (20)$$

Applying the above concept, one can derive **Maxwell's equations** from Eq. (12) to (15)

$$dU = TdS - PdV \dots \dots (12)$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \dots \dots (21)$$

$$\begin{aligned} \left(\frac{\partial U}{\partial S}\right)_V &= T ; \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \\ \left(\frac{\partial T}{\partial V}\right)_S &= \frac{\partial^2 U}{\partial V \partial S} ; \quad -\left(\frac{\partial P}{\partial S}\right)_V = \frac{\partial^2 U}{\partial S \partial V} \end{aligned}$$

Thermodynamic Properties of Fluids

Property relations for Homogeneous Phases

Maxwell's Equations

$$dH = TdS + VdP \dots\dots (13)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \dots\dots (22)$$

$$dA = -PdV - SdT \dots\dots (14)$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \dots\dots (23)$$

$$dG = VdP - SdT \dots\dots (15)$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \dots\dots (24)$$

$$\begin{aligned} \left(\frac{\partial H}{\partial S}\right)_P &= T ; \left(\frac{\partial H}{\partial P}\right)_S = V \\ \left(\frac{\partial T}{\partial P}\right)_S &= \frac{\partial^2 H}{\partial P \partial S} ; \quad \left(\frac{\partial V}{\partial S}\right)_P = \frac{\partial^2 H}{\partial S \partial P} \end{aligned}$$

$$\begin{aligned} \left(\frac{\partial A}{\partial V}\right)_T &= -P ; \left(\frac{\partial A}{\partial T}\right)_V = -S \\ -\left(\frac{\partial P}{\partial T}\right)_V &= \frac{\partial^2 A}{\partial V \partial T} ; \quad -\left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial^2 A}{\partial T \partial V} \end{aligned}$$

$$\begin{aligned} \left(\frac{\partial G}{\partial P}\right)_T &= V ; \left(\frac{\partial G}{\partial T}\right)_P = -S \\ \left(\frac{\partial V}{\partial T}\right)_P &= \frac{\partial^2 G}{\partial P \partial T} ; \quad -\left(\frac{\partial S}{\partial P}\right)_T = \frac{\partial^2 G}{\partial T \partial P} \end{aligned}$$

Thermodynamic Properties of Fluids

Property relations for Homogeneous Phases

Enthalpy and Entropy as Functions of T and P

Heat capacity at constant P: $\left(\frac{\partial H}{\partial T}\right)_P = C_P \dots\dots (25)$

Comparing eq. (25) and (26):

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \dots (27)$$

From Eq. (13): $dH = TdS + VdP \dots\dots (13)$

Differentiate w.r.t T at constant P: $\left(\frac{\partial H}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P \dots\dots (26)$

From Eq. (24): pressure derivative of Entropy $\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P \dots\dots (24)$

From Eq. (13): $dH = TdS + VdP \dots\dots (13) \rightarrow \left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V \dots\dots (28)$

Combining eq. (24) and (28): $\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P \dots\dots (29)$

Thermodynamic Properties of Fluids

Property relations for Homogeneous Phases

Enthalpy and Entropy as Functions of T and P

The functional relations chosen here for H and S are: $H = H(T, P)$ and $S = S(T, P)$.

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \dots (30)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \dots (32)$$

Applying the definition of C_P and Eq. (29):

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T}\right)_P \right] dP \dots (31)$$

From Eq. (27) and (24):

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP \dots (33)$$

General equations relating H and S to T and P , of homogeneous fluid of constant composition

Internal Energy as a Function of P Internal energy is given by: $U = H - PV$

Differentiation with respect to P yields: $\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - P \left(\frac{\partial V}{\partial P}\right)_T - V$

Using Eq. (29):

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

$$\left(\frac{\partial U}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial P}\right)_T \dots (34)$$

Thermodynamic Properties of Fluids

Property relations for Homogeneous Phases

The Ideal Gas State

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

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \dots (31)$$

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T} \right)_P dP \dots (33)$$

$$dH = C_P dT + \left[V - \frac{RT}{P} \right] dP$$

$$dS = C_P^{ig} \frac{dT}{T} - R \frac{dP}{P} \dots (36)$$

$$dH = C_P^{ig} dT \dots (35)$$

Alternative Forms for Liquids

Volume expansivity, β : $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$

Replace $\left(\frac{\partial V}{\partial T} \right)_P$ by βV

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \dots (24)$$

$$\rightarrow \left(\frac{\partial S}{\partial P} \right)_T = \beta V \dots (37)$$

$$\left(\frac{\partial H}{\partial P} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_P \dots (29)$$

$$\rightarrow \left(\frac{\partial H}{\partial P} \right)_T = V(1 - \beta T) \dots (38)$$

Thermodynamic Properties of Fluids

Property relations for Homogeneous Phases

Alternative Forms for Liquids

Isothermal compressibility, κ : $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$

Replace $\left(\frac{\partial V}{\partial T} \right)_P$ by βV

Replace $\left(\frac{\partial V}{\partial P} \right)_T$ by $-\kappa V$

$$\left(\frac{\partial U}{\partial P} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_P - P \left(\frac{\partial V}{\partial P} \right)_T \dots\dots (34)$$

$$\left(\frac{\partial U}{\partial P} \right)_T = -\beta VT + P\kappa V$$

$$\left(\frac{\partial U}{\partial P} \right)_T = V(\kappa P - \beta T) \dots\dots (39)$$

For an incompressible fluid:

From Eq. (31): $dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP$

$$dH = C_P dT + [V - \beta VT] dP \rightarrow dH = C_P dT + V[1 - \beta T] dP \dots\dots (40)$$

From Eq. (33): $dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T} \right)_P dP$

$$dS = C_P \frac{dT}{T} - \beta V dP \dots\dots (41)$$

Thermodynamic Properties of Fluids

Property relations for Homogeneous Phases

Internal Energy as Functions of T and V

Remember Eq. (12)

$$dU = TdS - PdV$$

From Eq. (12)

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

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

Definition of C_V : $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \dots (42)$$

From Eq. (23) – one of the Maxwell's equation

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

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \dots (43)$$

Let us use the functional relations of U and S : $U = U(T, V)$, and $S = S(T, V)$

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

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

$$dU = C_V dT + \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right] dV \dots (44)$$

$$dS = C_V \frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V dV \dots (45)$$

General equations relating U and S to T and V , of homogeneous fluid of constant composition

Thermodynamic Properties of Fluids

Property relations for Homogeneous Phases

Internal Energy as Functions of T and V

From the definition of β and κ ,

$$\frac{dV}{V} = \beta dT - \kappa dP$$

Alternative form of Eq. (44) and (45)

$$dU = C_V dT + \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV \dots (44)$$

$$dU = C_V dT + \left[T \frac{\beta}{\kappa} - P \right] dV \dots (47)$$

For a constant volume process:

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{\beta}{\kappa} \dots (46)$$

$$dS = C_V \frac{dT}{T} + \left(\frac{\partial P}{\partial T} \right)_V dV \dots (45)$$

$$dS = C_V \frac{dT}{T} + \frac{\beta}{\kappa} dV \dots (48)$$

Gibbs Energy as a Generating Function

The definition of G : $dG = VdP - SdT \dots (15)$

Functional relation: $G = G(P, T)$

Replace dG from (15), and $G = H - TS$ into (49)

Alternative to the above equation (15)

From the mathematical identity:

$$d \left(\frac{G}{RT} \right) = \frac{1}{RT} dG - \frac{G}{RT^2} dT \dots (49)$$

$$d \left(\frac{G}{RT} \right) = \frac{V}{RT} dP - \frac{H}{RT^2} dT \dots (50)$$

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Gibbs Energy as a Generating Function

From Eq. (50):
$$d\left(\frac{G}{RT}\right) = \frac{V}{RT} dP - \frac{H}{RT^2} dT \dots (50)$$

Differentiate wrt P at constant $T \rightarrow$

$$\frac{V}{RT} = \left[\frac{\partial(G/RT)}{\partial P} \right]_T \dots \dots (51)$$

Differentiate wrt T at constant $P \rightarrow$

$$\frac{H}{RT} = -T \left[\frac{\partial(G/RT)}{\partial T} \right]_P \dots \dots (52)$$

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

