

Thermodynamic properties of fluid

- Property relations for homogenous phases
- residual properties
- Two phase systems
- Clausius-Clapeyron Equation
- Phase rule
- Duhem's theorem

Property relations for homogenous phases

- Some thermodynamic properties can be measured **directly**, but many others **cannot**. Therefore, it is **necessary** to develop some **relations between these two groups** so that the properties that **cannot be measured directly** can be **evaluated**.
- The derivations are based on the **fact** that properties are **point functions**, and the state of a simple, compressible system is completely specified by **any two independent, intensive properties**.

Fundamental property relations

First law for a closed system

$$d(nU) = dQ + dW$$

a special reversible process

$$d(nU) = dQ_{rev} + dW_{rev}$$

$$dW_{rev} = -Pd(nV)$$

$$dQ_{rev} = Td(nS)$$

$$d(nU) = Td(nS) - Pd(nV)$$

Only properties of system are involved:

It can be applied to any process in a closed system (not necessarily reversible processes).

The change occurs between equilibrium states.

For one mol of homogeneous fluid of constant composition:

$$dU = TdS - PdV$$

Enthalpy: $H = U + PV \Rightarrow dH = dU + PdV + VdP$

$$\Rightarrow dH = TdS - PdV + PdV + VdP \quad dH = TdS + VdP$$

Helmholtz energy: $F = U - TS \Rightarrow dF = dU - TdS - SdT$

$$\Rightarrow dF = TdS - PdV - TdS - SdT \quad dF = -PdV - SdT$$

Gibbs energy: $G = H - TS \Rightarrow dG = dH - TdS - SdT$

$$\Rightarrow dG = TdS + VdP - TdS - SdT \quad dG = VdP - SdT$$

- A property of a single component system may be written as general mathematical function $z = z(x,y)$.

$$dz = \left(\frac{\delta z}{\delta x}\right)_y dx + \left(\frac{\delta z}{\delta y}\right)_x dy \quad \Rightarrow \quad dz = Mdx + Ndy$$

where

$$M = \left(\frac{\delta z}{\delta x}\right)_y \quad \text{and} \quad N = \left(\frac{\delta z}{\delta y}\right)_x$$

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

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

Since properties are continuous point functions and have exact differentials, the following is true

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

Maxwell's equations

$$dz = Mdx + Ndy \quad \Rightarrow \quad \left(\frac{\delta M}{\delta y} \right)_x = \left(\frac{\delta N}{\delta x} \right)_y$$

For one mol of homogeneous fluid of constant composition:

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dF = -PdV - SdT$$

$$dG = VdP - SdT$$

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

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

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

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

Maxwell relations 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 .

These Maxwell relations are limited to simple compressible systems.

Some Common Measureable Properties

Heat Capacity at Constant Volume:

$$Q = \Delta U = C_V dT$$

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

Heat Capacity at Constant Pressure:

$$Q = \Delta H = C_P dT$$

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

Volume Expansion Coefficient:

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

Isothermal Compressibility:

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

Enthalpy change calculations $f(P,T)$

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

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

$$dH = TdS + VdP$$

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

$$\left(\frac{\partial H}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P$$

$$dH = C_P dT + \left(T \left(\frac{\partial S}{\partial P} \right)_T + V \right) dP$$

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

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

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

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

Enthalpy, entropy and internal energy change calculations $f(P,T)$

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

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

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

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

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

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

Enthalpy, entropy and internal energy change calculations $f(P,T)$

$$U = H - PV$$

For Isothermal process

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

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

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

$$\left(\frac{\partial U}{\partial P}\right)_T = (1 - \beta T)V - P\kappa V - V$$

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

$$dH = TdS + VdP$$

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

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

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

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

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

Two-phase systems

- Whenever a phase transition at constant temperature and pressure occurs, $dG = VdP - SdT$
 - The molar or specific volume, internal energy, enthalpy, and entropy changes abruptly. The exception is the molar or specific Gibbs energy, which for a pure species does not change during a phase transition.
 - For two phases α and β of a pure species coexisting at equilibrium:

$$G^{\alpha} = G^{\beta}$$

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

$$G^{\alpha} = G^{\beta} \rightarrow dG^{\alpha} = dG^{\beta}$$

$$dG = VdP - SdT$$

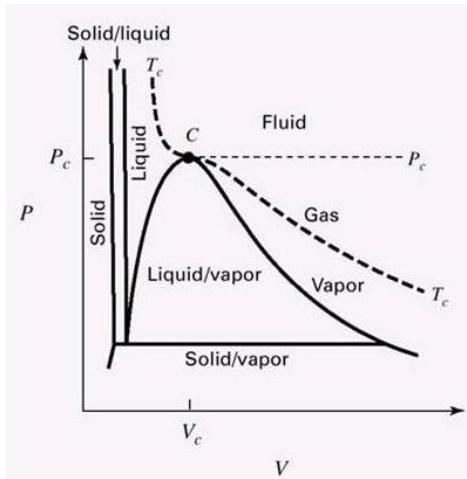
$$V^{\alpha} dP^{sat} - S^{\alpha} dT = V^{\beta} dP^{sat} - S^{\beta} dT$$

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

$$dH = TdS + VdP$$

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

The latent heat of phase transition



The Clapeyron equation

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

$$\Delta V^{\alpha\beta} = V^v = \frac{RT}{P^{sat}}$$

Ideal gas, and $V^l \ll V^v$

$$\ln \frac{P_2^{sat}}{P_1^{sat}} = \frac{\Delta H^{lv}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Integrating
between two
saturation
states

$$\Delta H^{lv} = -R \frac{d \ln P^{sat}}{d(1/T)}$$

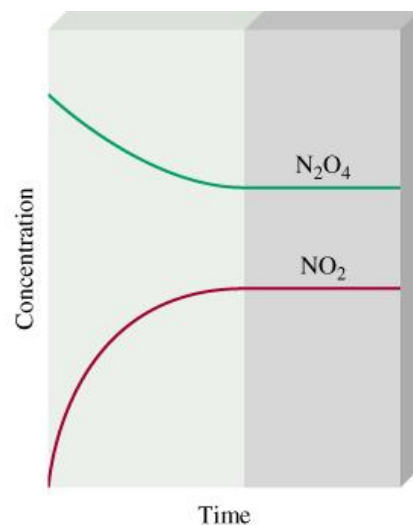
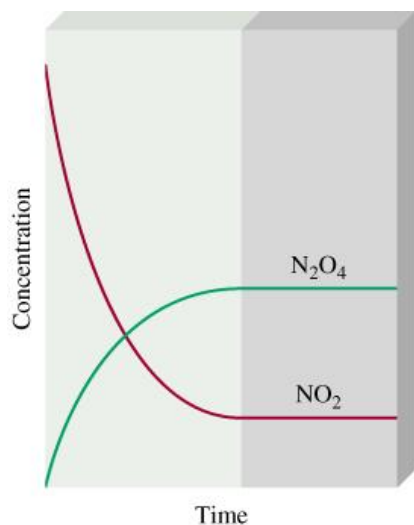
The Clausius/Clapeyron equation

Phase equilibrium

- So far we have only dealt with pure substances and constant composition mixtures.
- We will move a step further where the desired outcome is the composition change.
- Application
 - Distillation, absorption, and extraction bring phases of different composition into contact.
- Both the extent of change and the rate of transfer depend on the departure of the system from equilibrium.

The nature of equilibrium

- A static condition in which no changes occur in the **macroscopic** properties of a system with time.
- At the **microscopic** level, conditions are not static.
 - The average rate of passage of molecules is the same in both directions, and no net interphase transfer of material occurs.



The T, P, composition reaches final value which will remain fixed: equilibrium

Measures of composition

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graph TD; A[Measures of composition] --> B[Mass or mole fraction]; A --> C[Molar concentration]; A --> D[Molar mass for a mixture or solution];
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Mass or
mole fraction

$$x_i \equiv \frac{m_i}{m} = \frac{\dot{m}_i}{\dot{m}}$$

Molar
concentration

$$C_i \equiv \frac{x_i}{V}$$

Molar mass for
a mixture or
solution

$$M = \sum_i x_i M_i$$

PHASE RULE & DUHEM'S THEOREM

Equilibrium states are determined by;

- Phase Rule
- Duhem's Theory

The Phase Rule

The number of intensive variables that is independently fixed in a system at equilibrium

$$F = 2 - \pi + N$$

Where : F – degrees of freedom

π – No of phase

N – No of species

Duhem's Theorem

For any closed system formed initially from given masses of prescribed chemical species, the equilibrium state is completely determined when any **two (2)** independent variables are fixed. The two independent variable may be intensive or extensive

- The number of independent intensive variables is given by the phase rule
- $F = 1$, at least one of the two variables must be extensive
- $F = 0$, both must be extensive