Thermodynamics of materials

04. Fundamental Equation of Thermodynamics

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Differential Form of Fundamental Equation

- From first law of thermodynamics

$$dU = TdS^{\mathrm{e}} - pdV^{\mathrm{e}} + \mu dN^{\mathrm{e}}$$

- With second law,

$$dS^{\mathrm{e}} = dS - dS^{\mathrm{ir}} \qquad dV^{\mathrm{e}} = dV \qquad dN^{\mathrm{e}} = dN$$

- In sum, we have

$$dU = T\left(dS - dS^{\mathrm{ir}}\right) - pdV + \mu dN$$

- Proceed to

$$dU = TdS - pdV + \mu dN - TdS^{\mathrm{ir}}$$

or

$$dU = TdS - pdV + \mu dN - Dd\xi \qquad D = -\left(\frac{\partial U}{\partial \xi}\right)_{S,V,N}$$

- From reversible process, i.e., the entropy change for the system is the same as the entropy exchange between the system and its surrounding,

$$TdS^{\text{ir}} = Dd\xi = 0$$

then

$$dU = TdS - pdV + \mu dN$$

This relation is valid when there are no internal irreversible processes taking place inside the system.

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Integrated Form of Fundamental Equation

- Integrated form for the fundamental equation of thermodynamics,

$$U = TS - pV + \mu N$$

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- Choose S, V, N are the natural variables of U, we can write

$$dU(S,V,N) = T(S,V,N)dS - p(S,V,N)dV + \mu(S,V,N)dN$$

- The integrated form is

$$U(S,V,N) = T(S,V,N)S - p(S,V,N)V + \mu(S,V,N)N$$

- Consequently, we have

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T(S,V,N)$$

$$\left(\frac{\partial U}{\partial V}\right)_{S,N} = -p(S,V,N)$$

$$\left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu(S,V,N)$$

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Independent Variables

- For a simple system, we have four relations, that relate the seven variables

$$U, S, V, N, T, p, \mu$$

  there are three independent variables.
- When N is fixed, two variables are enough to represent the thermodynamic property, such as

$$U(S, V) \qquad U(p, V) \qquad U(T, V)$$

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Alternative Forms of Fundamental Equations

- The integrated form of enthalpy is

$$H = U + pV = TS + \mu N$$

which is the enthalpy of a system.

- The Helmholtz equation is

$$F = U - TS = -pV + \mu N$$

- The grand potential energy is

$$\Xi = U - TS - \mu N = -pV$$

Alternative Forms of Fundamental Equations

- The integrated form of Gibbs free energy is

$$G = U - TS + pV = \mu N$$

- The chemical potential is

$$\mu = \frac{G}{N} = u - Ts + pv$$

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Differential Forms of Alternative Fundamental Equations

- The differential form of H is

$$\begin{aligned} dH &= d(U+pV) = dU + pdV + Vdp \\ &= TdS - pdV + \mu dN + pdV + Vdp = TdS + Vdp + \mu dN \end{aligned}$$

- The differential form of F is

$$\begin{aligned} dF &= d(U-TS) = dU - TdS - SdT \\ &= TdS - pdV + \mu dN - TdS - SdT = -SdT - pdV + \mu dN \end{aligned}$$

- The differential form of Ξ is

$$\begin{aligned} d\Xi &= d(U - TS - \mu N) = dU - TdS - SdT - \mu dN - Nd\mu \\ &= TdS - pdV + \mu dN - TdS - SdT - \mu dN - Nd\mu \\ &= -SdT - pdV - Nd\mu \end{aligned}$$

Differential Forms of Alternative Fundamental Equations

- The differential form of G is

$$\begin{aligned} dG &= d(U - TS + pV) = dU - SdT - TdS + pdV + Vdp \\ &= -SdT + Vdp + \mu dN \end{aligned}$$

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Gibbs-Duhem Relation

- We have

$$U - TS + pV - \mu N = 0$$

- The differential form is

$$-SdT + Vdp - Nd\mu = 0$$

which is called the Gibbs-Duhem relation.

- Divide by N,

$$-sdT + vdp - d\mu = 0 \to d\mu = -sdT + vdp$$

- Using Gibbs-Duhem relation, one can obtain third potential, if we first two in a simple system.

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Entropic Representation of Fundamental Equations

- The entropic representation of fundamental equation is

$$dS = \left(\frac{1}{T}\right) dU + \left(\frac{p}{T}\right) dV - \left(\frac{\mu}{T}\right) dN$$

$$S = \left(\frac{1}{T}\right) U + \left(\frac{p}{T}\right) V - \left(\frac{\mu}{T}\right) N$$

or

$$dS = \left(\frac{1}{T}\right) dH - \left(\frac{V}{T}\right) dp - \left(\frac{\mu}{T}\right) dN$$

$$S = \left(\frac{1}{T}\right) H - \left(\frac{V}{T}\right) p - \left(\frac{\mu}{T}\right) N$$

Entropic Representation of Fundamental Equations

- From previous slide, we have

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{p}{T} \qquad \left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T}$$

$$\left(\frac{\partial S}{\partial H}\right)_{p,N} = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial p}\right)_{H,N} = -\frac{V}{T} \qquad \left(\frac{\partial S}{\partial N}\right)_{H,V} = -\frac{\mu}{T}$$

- In other forms,

$$\frac{F}{T} = \frac{U - TS}{T} = \left(\frac{1}{T}\right)U - S$$

$$\frac{G}{T} = \frac{U + pV - TS}{T} = \left(\frac{1}{T}\right)U + \left(\frac{p}{T}\right)V - S = \left(\frac{1}{T}\right)H - S$$

Entropic Representation of Fundamental Equations

- The differential forms for F/T and G/T are

$$d\left(\frac{F}{T}\right) = Ud\left(\frac{1}{T}\right) - \left(\frac{p}{T}\right)dV + \left(\frac{\mu}{T}\right)dN$$

$$d\left(\frac{G}{T}\right) = Hd\left(\frac{1}{T}\right) + \left(\frac{V}{T}\right)dp + \left(\frac{\mu}{T}\right)dN$$

- Proceed to

$$\left[\frac{\partial(F/T)}{\partial(1/T)}\right]_{V,N} = U$$

$$\left[\frac{\partial(G/T)}{\partial(1/T)}\right]_{V,N} = H$$

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Fundamental Equations With Irreversibility

- Fundamental Equations with irreversibility is

$$dU = TdS - pdV + \mu dN - Dd\xi$$

$$dH = TdS + Vdp + \mu dN - Dd\xi$$

$$dF = -SdT - pdV + \mu dN - Dd\xi$$

$$d\Xi = -SdT - pdV - Nd\mu - Dd\xi$$

$$dG = -SdT + Vdp + \mu dN - Dd\xi$$

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General Forms of Fundamental Equations of Thermodynamics

- For systems subject to other potential fields, such as electric potential and stress field, the total energy of a system should include all the interaction energies with surrounding. A more general integrated from for the fundamental equation of thermodynamics is

$$U = TS + \mu N + \gamma A + q\phi + V\sigma_{ij}\varepsilon_{ij}$$

- Under the equilibrium,

$$dU = TdS + \mu dN + \gamma dA + \phi dq + V\sigma_{ij}d\varepsilon_{ij}$$

- A set of fundamental equations on the per unit volume basis,

$$u_v = Ts_v + \mu c + \gamma A_v + \phi\rho_q + \sigma_{ij}\varepsilon_{ij}$$

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Legendre Transformation

- The fundamental equation can be described by the internal energy $U(S,V)$ by its Legendre transform,

$$F\left[\left(\frac{\partial U}{\partial S}\right)_V, V\right] = U(S,V) - \left(\frac{\partial U}{\partial S}\right)_V S$$

- With the relation,

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

we have

$$F(T,V) = U\big(S(T,V),V\big) - TS(T,V)$$

- Consistently,

$$H(S,p) = U(S,V) - \left(\frac{\partial U}{\partial V}\right)_S V = U + pV$$