3.020 Lecture 6

Prof. Rafael Jaramillo

1 Thermodynamic potentials and equilibrium

1. For fixed U, the entropy S is maximized at equilibrium.
2. For fixed S and V, the internal energy U is minimized at equilibrium.
3. For fixed S and P, the enthalpy $H = U + PV$ is minimized at equilibrium.
4. For fixed T and V, the Helmholtz free energy $F = U - TS$ is minimized at equilibrium.
5. For fixed T and P, the Gibbs free energy $G = U - TS + PV$ is minimized at equilibrium

---

2 Math note (aka fun with multi)

State <u>functions</u> and independent variables

- In 3.020, state functions are functions of most 3 independent variables.

$$\underbrace{\text{e.g.}}\quad dU = TdS - PdV + \mu dN$$

implies $U = U(S, V, N)$

We may never know this state function for most materials but it's still a useful concept.

- Thermodynamic potentials have "natural" independent variables

$$\begin{gathered} S = S(U,V) \quad F = F(T,V) \\ U = U(S,V) \quad G = G(T,P) \\ H = H(S,P) \end{gathered}$$

not writing "N" dependence to be compact

- Thermodynamic potentials are related by a change of variables via Legendre transforms

$$\underbrace{U(S,V)} \Longleftrightarrow H(S,P)$$

exchanging V for P, $\quad H = U + PV$

beyond scope of 3.020

---

3 Coefficient relations and independent variables

e.g. $dU = TdS - PdV + \mu_i dN_i$

coefficients: T, P, μ_i independent variables: S, V, N_i

$$\underbrace{\frac{\partial U}{\partial S}_{V,N_i} = T, \quad \frac{\partial U}{\partial V}_{S,N_i} = -P, \quad \frac{\partial U}{\partial N_i}_{S,V,N_{j\neq i}} = \mu_i}_{\text{coefficient relations}}$$

---

4 General strategy for deriving thermodynamic relations

Problem: Given dependent state variable Z and independent state variables (X, Y), calculate ΔZ for a given process.

e.g. Find ΔV for a process involving a pressure change at fixed entropy (i.e. a reversible adiabatic process)

$$dV = \underbrace{X}\, dP + \underbrace{Y}\, dS$$

find these coefficients

1. Write exact differential

$$dV = \frac{\partial V}{\partial P}_S dP + \frac{\partial V}{\partial S}_P dS$$

Using X and Y as shorthand for unknown partial derivatives

2. Use DeHoff Table 4.5 to express dP, dS in terms of dP, dT

$$dP = \underbrace{\quad}_{0} dT + \underbrace{\quad}_{1} dP \quad \text{trivial}$$

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

$$dV = XdP + Y(\frac{C_P}{T} dT - V\alpha dP)$$

---

3. Collect terms

$$dV = Y\frac{C_P}{T} dT + (X - YV\alpha)dP$$

4. Compare to known coefficients

$$dV = V\alpha dT - V\beta dP \quad \text{‘from Table 4.5’}$$

and equate

$$\frac{\partial V}{\partial T}_P = Y\frac{C_P}{T} = V\alpha$$

$$\frac{\partial V}{\partial T}_P = X - YV\alpha = -V\beta$$

---

5. Solve for unknowns X, Y

$$Y = \frac{V\alpha T}{C_P}, \quad X = \frac{V^2\alpha^2 T}{C_P} - V\beta$$

$$\Longrightarrow \quad dV = \underbrace{(\frac{V^2\alpha^2 T}{C_P} - V\beta)dP} + \frac{V\alpha T}{C_P} dS$$

integrate this to find change ΔV for pressure change at fixed entropy for ideal gas, simplifies to

$$X = -\frac{V}{P}\frac{C_P - R}{C_P}$$

$$\text{leading to} \quad \frac{P_{final}}{P_{initial}} = (\frac{V_{initial}}{V_{final}})^{\gamma}, \quad \gamma = \frac{C_P}{C_V}$$

in PSet 2, claculate $dG = \underbrace{\quad}dP + \underbrace{\quad}dS$

---

5 Equilibrium at fixed T and P

$$\begin{aligned} G &= U + PV - TS \quad \text{is minimized} \\ dG &= dU + PdV + VdP - TdS - SdT \quad \leftarrow \text{chain rule} \\ &= TdS - PdV + \mu_i dN_i + PdV + VdP - TdS - SdT \quad \leftarrow \text{combined statement} \\ &= -SdT + VdP + \mu_i dN_i \end{aligned}$$

- independent variables: T, P, N_i
- coefficients: $-S, V, \mu_i$
- by inspection:

$$\begin{aligned} -S &= \frac{\partial G}{\partial T}_{P,N_i} \\ V &= \frac{\partial G}{\partial P}_{T,N_i} \\ \mu_i &= \frac{\partial G}{\partial N_i}_{T,P,N_{j\neq i}} \end{aligned}$$

- at fixed T and P, $dT = 0$ and $dP = 0$, and equilibrium condition reduces to

$$dG = -S\underbrace{dT}_{0} + V\underbrace{dP}_{0} + \mu_i dN_i = 0$$

because G is minimized at equilibrium

- for multicomponent, heterogeneous systems, this becomes $dG = \mu_i^k dN_i^k$ superscript k = phase label subscript i = component label
- evaluating equilibrium requires knowing how components can exchange between phases, and the effect on the μ_i^ks

---

- About independent ("natural") variables
  - If a variable is regulated, a.k.a held constant, then it should be independent
  - Identifying independent & dependent variables from problem statements is <u>KEY</u> to success at thermodynamics

    e.g. "... *at fixed pressure...*" $\longrightarrow$ choose P as one independent variable

    e.g. "...*adiabatic process...*" $\longrightarrow$ choose S as one independent variable

    e.g. "...*with temperature held constant...*" $\longrightarrow$ choose T as one independent variable

    etc.

3.020 Thermodynamics of Materials
Spring 2021

3.020 Thermodynamics of Materials
Spring 2021