3.020 Lecture 6

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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.

e.g.
$$dU = TdS - PdV + \mu dN$$

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

$$S = S(U, V) \quad F = F(T, V)$$
$$U = U(S, V) \quad G = G(T, P)$$
$$H = H(S, P)$$

not writing "N" dependence to be compact

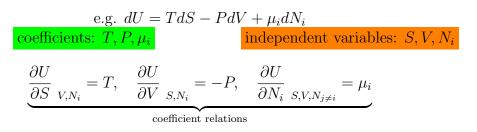
• Thermodynamic potentials are related by a change of variables via Legendre transforms

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

exchanging V for P, H = U + PV

beyond scope of 3.020

3 Coefficient relations and independent variables



4 <u>General strategy</u> 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

$$dP = \underbrace{}_{0} dT + \underbrace{}_{1} dP \quad \text{trivial}$$
$$dS = \frac{C_P}{T} dT - V \alpha dP$$
$$dV = X dP + Y (\frac{C_P}{T} dT - V \alpha dP)$$

3. Collect terms

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

4. Compare to known coefficients

$$dV = V\alpha dT - V\beta dP$$
 '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

$$Y = \frac{V\alpha T}{C_P}, \quad X = \frac{V^2 \alpha^2 T}{C_P} - V\beta$$
$$\implies \quad dV = \underbrace{(\frac{V^2 \alpha^2 T}{C_P} - V\beta)dP}_{P} + \frac{V\alpha T}{C_P}dS$$

integrate this to find change ΔV for pressure change at fixed entropy

for ideal gas, simplifies to

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

leading to $\frac{P_{final}}{P_{initial}} = (\frac{V_{initial}}{V_{final}})^{\gamma}, \quad \gamma = \frac{C_P}{C_V}$
in PSet 2, claculate $dG = \underbrace{dP + \underbrace{dS}}$

5 Equilibrium at fixed T and P

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

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

$$-S = \frac{\partial G}{\partial T} _{P,N_i}$$
$$V = \frac{\partial G}{\partial P} _{T,N_i}$$
$$\mu_i = \frac{\partial G}{\partial N_i} _{T,P,N_j \neq i}$$

• 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^k s
- 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.

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