3.020 Lecture 8

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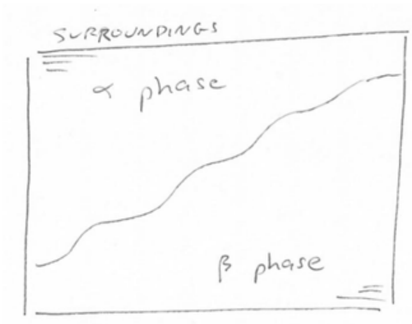
1 Equilibrium in a unary, heterogeneous system



- System with 1 component, 2 phases
- System isolated from surroundings
- Boundary is
  - rigid
  - closed
  - athermal

internal $\alpha - \beta$ boundary is the opposite

Goal : Evaluate condition for equilibrium $dS = 0$

- Work expression for dS
  - For phase α

$$dU^\alpha = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \mu^\alpha dN^\alpha$$
$$dS^\alpha = \frac{1}{T^\alpha} dU^\alpha + \frac{P^\alpha}{T^\alpha} dV^\alpha - \frac{\mu^\alpha}{T^\alpha} dN^\alpha$$

  - Likewise,

$$dS^\beta = \frac{1}{T^\beta} dU^\beta + \frac{P^\beta}{T^\beta} dV^\beta - \frac{\mu^\beta}{T^\beta} dN^\beta$$

superscript : phase labels

- Entropy is extensive, so $dS = dS^\alpha + dS^\beta$

$$dS = \frac{1}{T^\alpha} dU^\alpha + \frac{P^\alpha}{T^\alpha} dV^\alpha - \frac{\mu^\alpha}{T^\alpha} dN^\alpha + \frac{1}{T^\beta} dU^\beta + \frac{P^\beta}{T^\beta} dV^\beta - \frac{\mu^\beta}{T^\beta} dN^\beta$$

  - $\longrightarrow$ **6 variables** (U^i, V^i, N^i) where $i = \alpha, \beta$
  - $\longrightarrow$ **6 coefficients**

- Case of unconstrained optimization: $dS = 0$ requires that all 6 coefficients $= 0$ (not realistic)

- Add physical constraints to define <u>constrained</u> optimization problem

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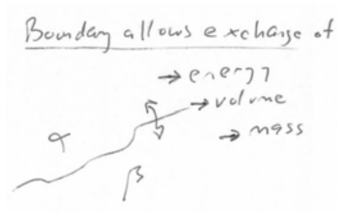
- Constraints

  (1) Conservation of energy: $dU^\alpha = -dU^\beta$

  (2) Conservation of volume: $dV^\alpha = -dV^\beta$

  (3) Conservation of mass: $dN^\alpha = -dN^\beta$



Simplifies equilibrium condition $dS = 0$ to 3 independent parameters, with 3 coefficients = 0

- Constrained optimization

$$dS = (\frac{1}{T^\alpha} - \frac{1}{T^\beta})dV^\alpha + (\frac{P^\alpha}{T^\alpha} - \frac{P^\beta}{T^\beta})dV^\alpha - (\frac{\mu^\alpha}{T^\alpha} - \frac{\mu^\beta}{T^\beta})dN^\alpha = 0$$

- Set coefficients = 0

$$\frac{1}{T^\alpha} - \frac{1}{T^\beta} = 0 \implies T^\alpha = T^\beta \longrightarrow \textbf{thermal equilibrium}$$

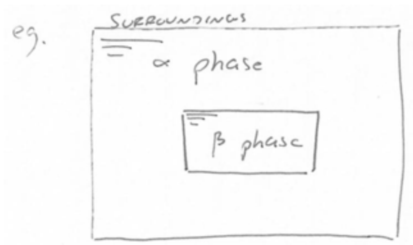
$$\frac{P^\alpha}{T^\alpha} - \frac{P^\beta}{T^\beta} = 0 \implies P^\alpha = P^\beta \longrightarrow \textbf{mechanical equilibrium}$$

$$\frac{\mu^\alpha}{T^\alpha} - \frac{\mu^\beta}{T^\beta} = 0 \implies \mu^\alpha = \mu^\beta \longrightarrow \textbf{chemical equilibrium}$$

thermodynamic equilibrium conditions for 2-phase coexistence

- Assumption to this point
  - Intensive parameters (T, P, μ) are uniform inside each phase
  - Boundary has no substance, so it doesn't contribute to total extensive quantities (U, V, S, N)
  - Spatial distribution doesn't matter

- Bounding conditions affect equilibrium



α, β phases separated by boundary that is

- rigid $\longrightarrow$ no volume exchange
- closed $\longrightarrow$ no mass exchange
- diathermal $\longrightarrow$ yes thermal exhcange

$$dS = (\frac{1}{T^\alpha} - \frac{1}{T^\beta}) = 0 \quad \longleftarrow \quad \textbf{no dV, dN terms}$$

$$T^\alpha = T^\beta \quad \textbf{at equilibrium}$$

Thermal equilibrium, but not mechanical or chemical

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2 Entropy generation during spontaneous processes

$$dS = (\frac{1}{T^\alpha} - \frac{1}{T^\beta})dU^\alpha + (\frac{P^\alpha}{T^\alpha} - \frac{P^\beta}{T^\beta})dV^\alpha - (\frac{\mu^\alpha}{T^\alpha} - \frac{\mu^\beta}{T^\beta})dN^\alpha = 0$$

- Consider $T^\alpha > T^\beta$, $\frac{1}{T^\alpha} < \frac{1}{T^\beta}$

  Hotter phase (α) will spontaneously heat the colder phase (β)

  $$dU^\alpha < 0, \quad \longrightarrow \quad dS > 0$$

  Entropy generated during heat energy transfer from hot to cold matter

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- Consider $T^\alpha = T^\beta$, $P^\alpha > P^\beta$, $\frac{P^\alpha}{T^\alpha} - \frac{P^\beta}{T^\beta} > 0$

  Higher pressure phase (α) will spontaneously expand into the lower-pressure phase (β)

  $$dV^\alpha > 0 \quad \Longrightarrow \quad dS > 0$$

- Consider $T^\alpha = T^\beta$, $\mu^\alpha > \mu^\beta$, $\frac{\mu^\alpha}{T^\alpha} - \frac{\mu^\beta}{T^\beta} > 0$

  Matter will spontaneously transform from phase with higher chemical potential (α) into phase with lower chemical potential (β)

  $$dN^\alpha < 0, \quad \Longrightarrow \quad dS > 0$$