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
  \textbf{internal }\alpha-\beta\textbf{ boundary is the opposite}

Goal: Evaluate condition for equilibrium \( dS = 0 \)

- Work expression for \( dS \)
  - For phase \( \alpha \)
    \[ dU^\alpha = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \mu^\alpha dN^\alpha \]
    \[ dS^\alpha = \frac{1}{T^\alpha} dU^\alpha + \frac{P^\alpha}{T^\alpha} dV^\alpha - \frac{\mu^\alpha}{T^\alpha} dN^\alpha \]
  - Likewise,
    \[ dS^\beta = \frac{1}{T^\beta} dU^\beta + \frac{P^\beta}{T^\beta} dV^\beta - \frac{\mu^\beta}{T^\beta} dN^\beta \]

- Entropy is extensive, so \( dS = dS^\alpha + dS^\beta \)
  \[ dS = \frac{1}{T^\alpha} dU^\alpha + \frac{P^\alpha}{T^\alpha} dV^\alpha - \frac{\mu^\alpha}{T^\alpha} dN^\alpha + \frac{1}{T^\beta} dU^\beta + \frac{P^\beta}{T^\beta} dV^\beta - \frac{\mu^\beta}{T^\beta} dN^\beta \]
  - \( \rightarrow 6 \text{ variables } (U^i, V^i, N^i) \) where \( i = \alpha, \beta \)
  - \( \rightarrow 6 \text{ coefficients} \)

- Case of unconstrained optimization: \( dS = 0 \) requires that all 6 coefficients = 0 (not realistic)
• Add physical constraints to define constrained optimization problem

• 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

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

• Set coefficients = 0

\[\frac{1}{T^\alpha} - \frac{1}{T^\beta} = 0 \quad \Rightarrow \quad T^\alpha = T^\beta \quad \rightarrow \quad \text{thermal equilibrium}\]

\[\frac{P^\alpha}{T^\alpha} - \frac{P^\beta}{T^\beta} = 0 \quad \Rightarrow \quad P^\alpha = P^\beta \quad \rightarrow \quad \text{mechanical equilibrium}\]

\[\frac{\mu^\alpha}{T^\alpha} - \frac{\mu^\beta}{T^\beta} = 0 \quad \Rightarrow \quad \mu^\alpha = \mu^\beta \quad \rightarrow \quad \text{chemical equilibrium}\]

thermodynamic equilibrium conditions for 2-phase coexistence

• Assumption to this point

  – Intensive parameters \((T, P, \mu)\) 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
\( \alpha, \beta \) phases separated by boundary that is

- rigid \( \rightarrow \) no volume exchange
- closed \( \rightarrow \) no mass exchange
- diathermal \( \rightarrow \) yes thermal exchange

\[
dS = \left( \frac{1}{T_\alpha} - \frac{1}{T_\beta} \right) = 0 \quad \leftarrow \quad \text{no } dV, \text{ dN terms}
\]

\( T_\alpha = T_\beta \) at equilibrium

Thermal equilibrium, but not mechanical or chemical

## 2 Entropy generation during spontaneous processes

\[
dS = \left( \frac{1}{T_\alpha} - \frac{1}{T_\beta} \right)dU^\alpha + \left( \frac{P_\alpha}{T_\alpha} - \frac{P_\beta}{T_\beta} \right)dV^\alpha - \left( \frac{\mu_\alpha}{T_\alpha} - \frac{\mu_\beta}{T_\beta} \right)dN^\alpha = 0
\]

- Consider \( T_\alpha > T_\beta, \quad \frac{1}{T_\alpha} < \frac{1}{T_\beta} \)
  
  Hotter phase (\( \alpha \)) will spontaneously heat the colder phase (\( \beta \))

  \( dU^\alpha < 0, \quad \rightarrow \quad dS > 0 \)

Entropy generated during heat energy transfer from hot to cold matter

- Consider \( T_\alpha = T_\beta, \quad P_\alpha > P_\beta, \quad \frac{P_\alpha}{T_\alpha} - \frac{P_\beta}{T_\beta} > 0 \)

  Higher pressure phase (\( \alpha \)) will spontaneously expand into the lower-pressure phase (\( \beta \))

  \( dV^\alpha > 0 \quad \implies \quad dS > 0 \)

- Consider \( T_\alpha = T_\beta, \quad \mu_\alpha > \mu_\beta, \quad \frac{\mu_\alpha}{T_\alpha} - \frac{\mu_\beta}{T_\beta} > 0 \)

  Matter will spontaneously transform from phase with higher chemical potential (\( \alpha \)) into phase with lower chemical potential (\( \beta \))

  \( dN^\alpha < 0, \quad \implies \quad dS > 0 \)
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