Lecture 2: 09.12.05 Fundamental concepts continued

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Reading: Engel and Reid: 1.4, 2.1, 2.2, 2.3

ANNOUNCEMENTS:

- PS 1 POSTED: DUE NEXT TUES. 9/20

(REMINDERS)

- 3.014: ONLINE SAFETY TRAINING

Lecture 2 – introduction 1 of 13 9/11/05
Last Time

 Thermodynamics used to predict changes in state

 Material \{ State A 
 \[ V_0, N_0 \] \}

 Thermodynamic forces

 State B 
 \[ V < V_0, N_0 \]
 State C 
 \[ V > V_0, N_0 \]
 State D 
 \[ V_0, N > N_0 \]

 Pressure
 Temperature
 Magnetic fields
 Light
 (more later)
Thermodynamic variables, systems, and functions

**Thermodynamic Variables**

- Remember that classical thermodynamics is concerned with macroscopic properties

  **MACROSCOPIC THERMO VARIABLES:** \( P, V, T, N \) or \( n, \ldots \)

  **SIMPLE SYSTEM**

  **INTENSIVE**

  **MAGNITUDE DOES NOT VARY WITH SIZE (NUMBERS OF MOLES OR MATERIAL OF SYSTEM)**

  **E.G., \( P, T \)**

  **CAN VARY POINT-TO-POINT IN SPACE!**

  **ELECTRIC FIELDS:**

  \[ \vec{E} = E(x, y, z) \]

  **EXTENSIVE**

  **MAGNITUDE SCALES LINEARLY WITH SIZE OF THE SYSTEM**

  **VOLUME, INTERNAL ENERGY, ENTROPY \( (S) \)**

  **EXTENSIVE VARIABLES:**

  \[ U_{\text{TOTAL}} = U_A + U_B = 2U \]
intensive and extensive variables form coupled pairs:

\[ \text{Physics: Increment of work} = dW = [\text{Energy}] = \mathbf{F} \cdot d\mathbf{x} \]

\[ \text{FORCE} \quad \text{RESPONSE} \]

**Hydrostatic Work:** \( -PdV = [\text{Energy}] \)

- e.g. pressure and volume \( P \leftrightarrow V \)
- the product of one intensive variables multiplied by its coupled extensive variables is work

---

**The constituents of materials: components and phases**

**Components**

- The components are the irreducible molecules, compounds, or atoms that make up a system:

  \[ \text{COMPONENTS MAY OR MAY NOT = ATOMS!} \]

<table>
<thead>
<tr>
<th>Example system</th>
<th>Class of material</th>
<th>Components</th>
<th>Class of components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless Steel</td>
<td>Metal Alloy</td>
<td>Fe, Cr, C</td>
<td>Atoms</td>
</tr>
<tr>
<td>Cesium Chloride</td>
<td>Ionic Solid</td>
<td>CsCl</td>
<td>Stochiometric Compounds</td>
</tr>
<tr>
<td>Poly (Vinyl Chloride)</td>
<td>Polymer</td>
<td>Polymer Chains</td>
<td>Macromolecule</td>
</tr>
<tr>
<td>Diamond</td>
<td>Covalent Solid</td>
<td>C</td>
<td>Atom</td>
</tr>
</tbody>
</table>

**Ask: What can I remove from the system?**

- Metallic Bonding
- Ionic Bonding
phases
- Phase: A uniquely identifiable form of a material, separated from other forms of the material by an identifiable interface.

- Examples:
  - Ice
  - Liquid water

  Two different structures — same or different compositions — structure alone cannot define a phase.

Stable phases of Fe

<table>
<thead>
<tr>
<th>Stable temperature range (K)</th>
<th>Form of matter</th>
<th>Phase</th>
<th>Identification symbol of phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 3013</td>
<td>Gas</td>
<td>Gas</td>
<td>Gas</td>
</tr>
<tr>
<td>1812–3013</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
</tr>
<tr>
<td>1673–1812</td>
<td>Solid</td>
<td>Body-centered cubic</td>
<td>δ</td>
</tr>
<tr>
<td>1183–1673</td>
<td>Solid</td>
<td>Face-centered cubic</td>
<td>γ</td>
</tr>
<tr>
<td>&lt; 1183</td>
<td>Solid</td>
<td>Body-centered cubic</td>
<td>α</td>
</tr>
</tbody>
</table>
- Phases may have multiple components, and different phases may have the same components (though in different relative amounts). Phases, particularly solid phases, are often identified using Greek letters (as seen above for Fe- the solid phases are denoted $\delta$, $\gamma$, and $\alpha$).

- A multiphase system is one where the components of the system exist in multiple unique forms (structure or composition) within the system.

- Phases can have dimensions from macroscopic down to a few molecules:

Figure removed for copyright reasons.


Figure removed for copyright reasons.  

Figure removed for copyright reasons.

(Mann’s) calcium carbonate crystals stacked with interleaving protein
A few other useful definitions:

- **Mixture:** INHOMOGENEOUS MULTI-PHASE SYSTEM WHERE THE COMPONENTS ARE NOT MIXED ON A MOLECULAR LEVEL

- **Solution:** HOMOGENEOUS SYSTEM; COMPONENTS ARE MIXED ON A MOLECULAR LEVEL
Thermodynamic systems

- Thermodynamic systems can have boundary conditions that limit the exchange of energy or atoms/molecules with their surroundings. Some of the types of systems one may be interested in for materials science and engineering problems include:

<table>
<thead>
<tr>
<th>System</th>
<th>Boundary condition:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isolated</td>
<td><strong>NO ENERGY OR MOLECULES IN/OUT OF THE SYSTEM</strong></td>
</tr>
<tr>
<td>Closed</td>
<td><strong>NO MOLECULES IN/OUT</strong></td>
</tr>
<tr>
<td>Adiabatic</td>
<td><strong>NO HEAT IN/OUT</strong></td>
</tr>
<tr>
<td>Open</td>
<td><strong>MOLECULES OR ENERGY CAN PASS IN/OUT OF SYSTEM</strong></td>
</tr>
</tbody>
</table>

**ENERGY: 2 FORMS: HEAT = Q, WORK = W**

- Boundary allows no energy or matter to pass
- Boundary allows no matter to pass
- Boundary allows no heat (or matter that can carry heat) to pass
- Boundary allows matter and energy to pass
In closed multi-phase systems, molecules and energy can be exchanged among phases within the system.
Identification of processes

Types of processes

- We've stated that thermodynamics is a theory for predicting what changes will happen to a material/system. A key part of making correct predictions is identifying what processes can happen within the system.
  - Several common processes include:

<table>
<thead>
<tr>
<th>Process type</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adiabatic</td>
<td>Process where no heat passes boundaries of system</td>
</tr>
<tr>
<td>Isochoric</td>
<td>Process with no volume change</td>
</tr>
<tr>
<td>Isothermal</td>
<td>Process with no temperature change</td>
</tr>
<tr>
<td>Isobaric</td>
<td>Process at constant P</td>
</tr>
<tr>
<td>Isobarothermal</td>
<td>Process at constant T, P</td>
</tr>
</tbody>
</table>

Examples of classifying a system and process:

1. You place a thin metal film (your system) in an oven to anneal (equilibrate at elevated temperature).
   - Type of System: CLOSED
   - Process: ISOBAROTHERMAL

2. Your system is a cold glass of water, and you place it on your porch on a sunny day.
   - Type of System: OPEN
   - Process: ISOBARIC
Reversible and Irreversible Processes

Reversible Processes

- Reversible processes are idealized processes that:
  1. System is always in equilibrium
  2. Have no dissipative processes (processes where energy as heat to surroundings!)

  \[
  \text{occur "forward" or "backward" with no change in the surroundings}
  \]

- Examples:

  [Diagram showing a frictionless piston moving slowly to maintain equilibrium]
Irreversible processes

- Natural processes typically occur in only 1 direction spontaneously
  **Essentially all real processes**

  - These are irreversible processes

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Process</th>
<th>Observation of irreversibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Add a drop of food coloring to a glass of water</td>
<td>• <strong>DIFFUSION</strong></td>
<td><strong>DROPET NEVER REFORMS</strong></td>
</tr>
<tr>
<td>Expansion of a gas into a vacuum</td>
<td>•</td>
<td></td>
</tr>
<tr>
<td>Cooling of a hot object placed in a cold room</td>
<td>•</td>
<td></td>
</tr>
<tr>
<td>Melting of a solid at $T = T_m + 100^\circ$</td>
<td>•</td>
<td></td>
</tr>
</tbody>
</table>

Thus irreversible processes are driven in the one allowed direction by the second law

**2nd LAW! ENTROPY OF UNIVERSE MUST INCREASE!**

Reversal of these processes would lower entropy!
References