Recap: First Law of Thermodynamics

Joule: 4.19 J of work raised 1 gram water by 1 °C. This implies 4.19 J of work is equivalent to 1 calorie of heat.

• If energy is added to a system either as work or as heat, the internal energy is equal to the net amount of heat and work transferred.
• This could be manifest as an increase in temperature or as a “change of state” of the body.
• First Law definition:

  • The increase in internal energy of a system is equal to the amount of heat added minus the work done by the system.

\[ \Delta U = Q - W \]

\[ \Delta U = \text{increase in internal energy} \]
\[ Q = \text{heat} \]
\[ W = \text{work done by system} \]

Note: Work done on a system increases \( \Delta U \).

Work done by system decreases \( \Delta U \).
Change of State & Energy Transfer

First law of thermodynamics shows how the internal energy of a system can be raised by adding heat or by doing work on the system.

\[ \Delta U = Q - W \]

Internal Energy (U) is sum of kinetic and potential energies of atoms /molecules comprising system and a change in U can result in a:
- change on temperature
- change in state (or phase).

• A change in state results in a physical change in structure.

Melting or Freezing:

• Melting occurs when a solid is transformed into a liquid by the addition of thermal energy.
• Common wisdom in 1700’s was that addition of heat would cause temperature rise accompanied by melting.
Joseph Black (18th century) established experimentally that: “When a solid is warmed to its melting point, the addition of heat results in the gradual and complete liquefaction at that fixed temperature.”

- i.e. Heat added to system while melting has no effect on its temperature.
- Called “latent” (or hidden) heat.
- Each substance has a characteristic “latent heat of fusion” \( (L_f) \) (melting).

**Example:** Ice and water are different phases of same substance.

\[
L_f(\text{ice}) = 334 \text{ kJ/kg (or 80 kcal/kg)}
\]

So, 1 kg of ice at 0 °C will be transformed into 1 kg water at 0°C with addition of 334 kJ of heat.

- This is also the amount of heat given off when 1 kg of water at 0 °C freezes.

- For a mass “m” the required heat to melt is: \( Q = \pm m \cdot L_f \)
Example: How much energy must be removed to turn 0.25 kg of water at 20 °C into ice at 0 °C?

Two step solution: Determine heat out to cool water to 0 °C, then determine heat out to transform it to ice:

\[ Q_{\text{out}} = c_w m_w (T_f - T_c) - m_w L_f \]

\[ Q_{\text{out}} = (4.2)(0.25)(-20) - (0.25)(334) \text{ kJ} \]

\[ Q_{\text{out}} = -20.9 \text{ kJ} - 83.5 \text{ kJ} \]

\[ Q_{\text{out}} \approx -100 \text{ kJ} \text{ (or } \approx -25 \text{ kcal)} \]

(Negative as heat taken out of system)

• Melting is a cooling process as it removes heat from immediate environment, e.g. ice in picnic cooler or glass melts and cools contents. In contrast:

• Freezing is a warming process as it exhausts thermal energy into immediate environment, e.g. drums of water can be used to protect fruit cellars (or sensitive scientific equipment from freezing in winter in Antarctica)!
Vaporization

- The transformation of a liquid or solid into a gas is called vaporization.
- A liquid consists of a large number of atoms or molecules that move around with a distribution of kinetic energies.
- At surface (even at room temperature) some atoms are moving fast enough to escape (i.e. evaporate).
- Some molecules will return (condense) as new ones leave.
- This creates a vapor pressure above the liquid and when the number of molecules evaporating and re-condensing is equal, the vapor pressure is said to be saturated.
- Vapor pressure is very sensitive to temperature as molecules have higher kinetic energy. Thus more can escape from the surface and this increases the rate of evaporation.
- Rate of evaporation can also be increased by increasing surface area (e.g. a wet shirt dries faster if stretched out).
- **Vaporization** is a much more **drastic physical** change than melting as the molecules are **torn** free of liquid and gain **considerable separations** (i.e. large P.E. gain).
- This requires a much **larger amount of energy**!
- **Latent heat of vaporization** \((L_v)\) is the amount of thermal energy required to evaporate 1 kg of a liquid at **constant temperature**.
- The **temperature** is usually the **boiling point**, but need not be as evaporation occurs at **any temperature**.

Latent heat of vaporization of water at 100 °C:

\[
L_v = 2259 \text{ kJ/kg} \quad \text{(or } \approx 540 \text{ kcal/kg)}
\]

- **Steam** therefore contains **far more energy** than an equal amount of boiling water! – very dangerous!
- **Vaporization** is a **cooling process** as escaping molecules are **very energetic** and leave behind slower (i.e. lower average K.E. ones). This **reduces temperature** of liquid.
- **Amount of heat to vaporize** or **condense** mass \((m)\) is \(Q = \pm m \cdot L_v\)
**Practical Uses:**

- **Perspiration** – water on skin evaporates and cools body. (Don’t towel off!) we lose about $\frac{1}{2}$ liter/day = 1.2 MJ.
- **Blowing hot liquid** to remove vapor above it and allow more to escape thereby cooling liquid.
- **Outdoor air currents** cause food to **cool** more quickly…

*Example latent heats of fusion and vaporization:*

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting/Freezing pt (°C)</th>
<th>Heat of fusion (kJ/kg)</th>
<th>Boiling point (°C)</th>
<th>Heat of vaporization (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>high</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>0</td>
<td>334</td>
<td>100</td>
<td>2259</td>
</tr>
<tr>
<td><strong>low</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alcohol</td>
<td>-114</td>
<td>104</td>
<td>78</td>
<td>854</td>
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<td>Copper</td>
<td>1083</td>
<td>205</td>
<td>2336</td>
<td>5069</td>
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<tr>
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<td></td>
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<tr>
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<td>1063</td>
<td>67</td>
<td>2600</td>
<td>1578</td>
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<tr>
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<td>Mercury</td>
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<td>296</td>
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<tr>
<td>Oxygen</td>
<td>-218</td>
<td>14</td>
<td>-183</td>
<td>213</td>
</tr>
</tbody>
</table>

*Water* is therefore an excellent **moderator** as it has high **specific heat** and **high latent heats**.
**Boiling**

- We have discussed how evaporation takes place at a liquid’s “free” surface at any temperature.
- Under special circumstances it can also occur throughout the body of liquid… called **boiling**.
- **At boiling:** Tiny pockets of vapor generated at any point within liquid have a lower density and (higher velocity atoms) than surrounding medium creating small spheres of vapor.

- Any liquid will boil at a **specific temperature** when its saturated vapor pressure **equals** surrounding (atmosphere) pressure.

**Example water vapor pressures:**

- At 0 ºC water vapor pressure = 0.006 Atm
- 60 ºC = 0.2 Atm
- 100 ºC = 1.0 Atm
Boiling Process

- Bubbles begin to form at **walls** and **bottom** of vessel (which are hotter).
- **Nucleation sites** for bubble formation are **tiny pockets of air** or **particles of dust**.
- It’s therefore very **hard** to boil extremely **pure water**.
- **Initially** the bubbles of vapor form rapidly, rise a little and then **disappear** when they enter **colder region** of liquid above (they are cooled and vapor pressure decreases) collapse!
- Only when **upper regions** of water reach **100 °C** will true boiling take place throughout liquid.
- Bubbles can then reach and **burst at surface** liberating a **large amount of vapor** with a great deal of energy! (2259 kJ /kg; 540 kcal /kg).
**Boiling (cont’d)**

• Feeding further heat will **cause boiling to continue** without changing liquid’s **temperature**.

• **Steam** therefore has a **lot of energy** (~2.2 MJ /kg) and can be used to **transfer heat** from boiler to radiators where it’s given up by **condensing** back (as latent heat) to liquid.

• **Boiling point** depends on **external pressure**. At lower pressure vapor bubbles can form **more easily** etc.

• Mount Everest (9 km) **pressure = 0.4 Atm** and $T_{\text{boiling}} = 74 ^\circ C$.

• Water is boiled off milk at low pressure without cooking it.

• **Pressure cooker** raises $T_{\text{boiling}}$ to typically **121 ^\circ C** (+1 Atmos). Cooking reactions **double** for every ~10 ^\circC (beyond 100 ^\circC )!
Phase diagram of water. If we take a block of ice at atmospheric pressure and slowly raise its temperature, it melts completely at 273 K (0 °C) and remains liquid until 373 K (100 °C), whereupon it completely vaporizes.

**Melting point curve**

**Sublimation curve**

**Critical point**

**Boiling point curve**

"O" is triple point water - solid, liquid and gas /vapor co-exist. Temp = 0.01 °C.

"C" is a critical point – above this gas does not liquefy or solidify – it only gets denser as pressure increases. Example: Jupiter’s atmosphere (H, He).
The Phase Diagrams of H₂O and CO₂

H₂O

Pressure (atm) vs. Temperature (°C)

CO₂

Pressure (atm) vs. Temperature (°C)