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.

$$\boxed{\Delta U = Q - W}$$

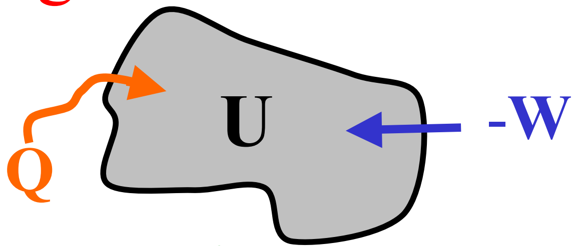
ΔU = increase in internal energy
Q = heat
W = work done by system

Note: Work done **on** a system **increases** ΔU.
Work done **by** system **decreases** ΔU.

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).

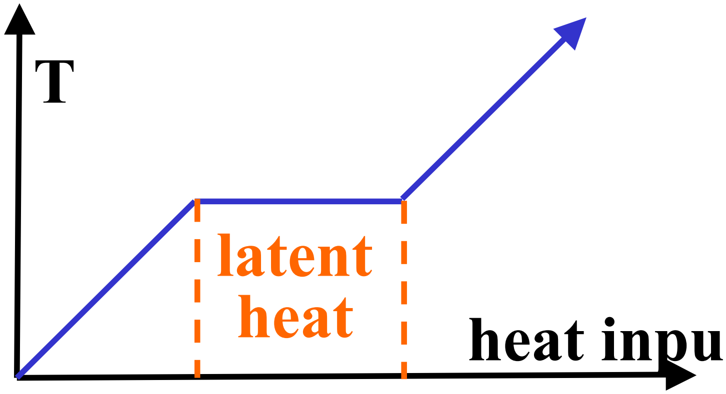
- A **change in state** results in a **physical change** in structure.

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.

$$L_{f\ (ice)} = 334\ kJ\ /kg\ (or\ 80\ kcal\ /kg)$$

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

- This is also the amount of heat **given off** when 1 kg of water at 0 ºC **freezes.**
- For a **mass "m"** the required heat to $\genfrac{}{}{0pt}{}{\text{melt}}{\text{freeze}}$ is: $\mathbf{Q = \pm m.L_f}$

Example: How much energy must be removed to turn 0.25 kg of water at 20 ºC into ice at 0 ºC?

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

$$Q_{out} = c_w.m_w.(T_f - T_c) - m_w.L_f$$

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

$$Q_{out} = -20.9\ \text{kJ} - 83.5\ \text{kJ} \quad \text{larger}$$

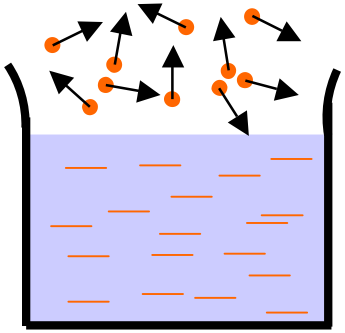
$$Q_{out} \approx -100\ \text{kJ}\ (\text{or} \approx -25\ \text{kcal})$$

(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 ºC:

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

- **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 $\begin{matrix}\text{vaporize}\\\text{condense}\end{matrix}$ mass (m) is $\mathbf{Q = \pm\, m.\, L_v}$

Practical Uses:

- **Perspiration** – water on skin **evaporates** and cools body. (Don't towel off!) ; we loose about ½ 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:

	Material	Melting/Freezing pt (ºC)	Heat of fusion (kJ /kg)	Boiling point (ºC)	Heat of vaporization (kJ /kg)
high	Water	0	334	100	2259
low	Alcohol	-114	104	78	854
	Copper	1083	205	2336	5069
	Gold	1063	67	2600	1578
low	Mercury	-39	12	357	296
low	Oxygen	-218	14	-183	213

* **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

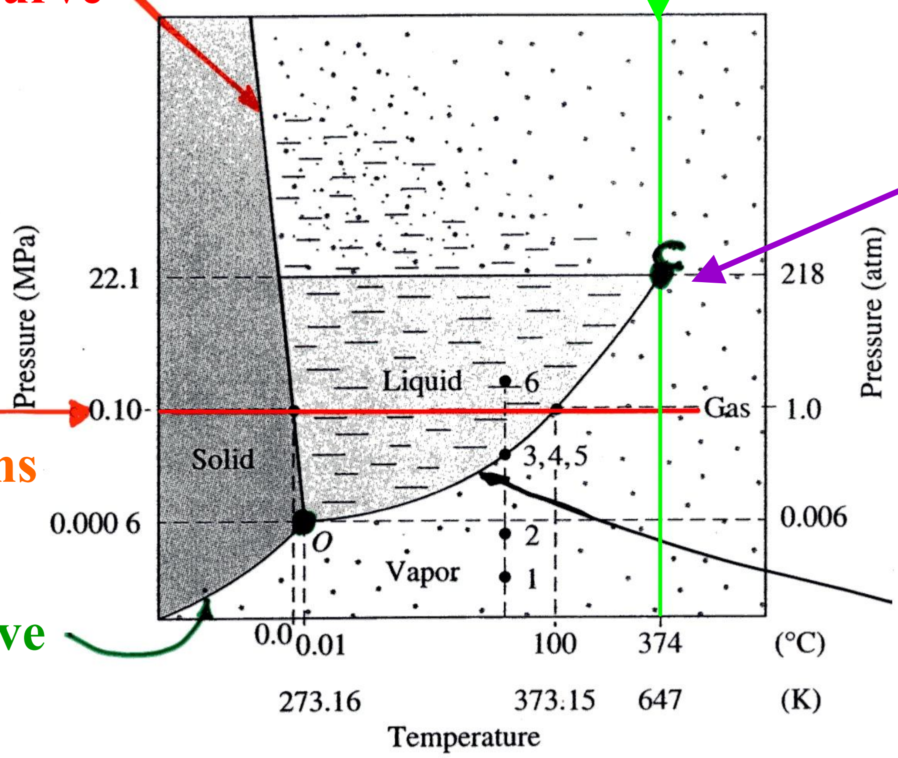
Boiling Process

- 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 ºC** 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 $T_{boiling}$ = 74 ºC.
- Water is boiled off milk at low pressure without cooking it.
- **Pressure cooker** raises $T_{boiling}$ to typically 121 ºC (+1 Atmos). Cooking reactions **double** for every **~10 ºC** (beyond 100 ºC)!

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 ºC) and remains liquid until 373 K (100 ºC), whereupon it completely vaporizes.



Melting point curve

Gas does not solidify

Critical point

Normal conditions

Sublimation curve

Boiling point curve

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

"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 H_2O and CO_2