Sustainable Energy Transformation Technologies, SH2706

Lecture No 4

Title:
Thermal Energy, Heat, and Work

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Autumn 2022

Outline

- ## What is thermal energy?
  - Thermal energy versus heat
  - Thermal energy versus internal energy
- ## Work extraction
  - From pressure
  - From heat
- ## Relation between work, heat and internal energy
  - 1st of thermodynamics
- ## Thermal energy as heat storage
- ## Phase change

What is Thermal Energy?

- Thermal energy refers to collective energy contained in the **relative motion** of large number of microscopic particles in a system

- Since thermal energy results from movements of particles in a system, it is a kind of kinetic energy, however, all particles have individual velocity, random in direction and value

- Thermal energy does not include potential or kinetic energy of the system as a whole

- Qualitatively, **temperature** is a measure of the amount of the thermal energy: with increasing thermal energy the temperature increases

Thermal Energy vs Heat

- **Heat** is thermal energy that is transferred from one system to another
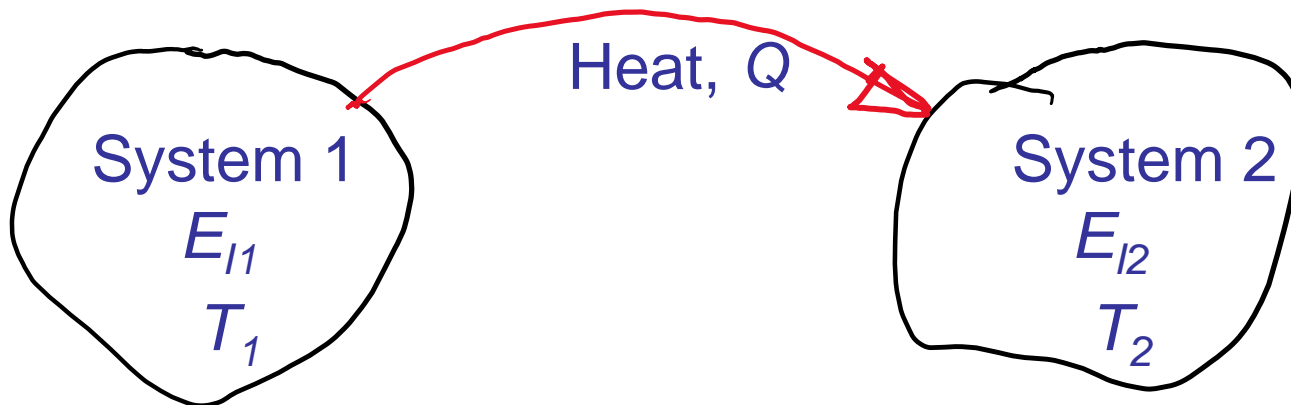
- Our common experience is that heat always "flows" from system (or region) at higher temperature to a system (or region) at lower temperature; thus $T_1 > T_2$, and $Q > 0$

Heat, *Q*

- Thus, heat is defined as **energy in transit** from a system with higher temperature to a system with lower temperature

- Due to heat transfer, the internal energy in both systems changes

- There are several known heat transfer mechanisms, such as:
  - Conduction
  - Convection
  - Radiation

Thermal Energy vs Internal Energy

- If we cool a system to a temperature of **absolute zero**, its thermal energy will be also zero.

- But the system will still have **non-zero internal energy** resulting from:
  - particle rest masses
  - nuclear binding energy
  - chemical bond energy

- Thus internal energy comprises all these energies + the thermal energy

Internal energy

thermal energy

bond energy

binding

rest mass
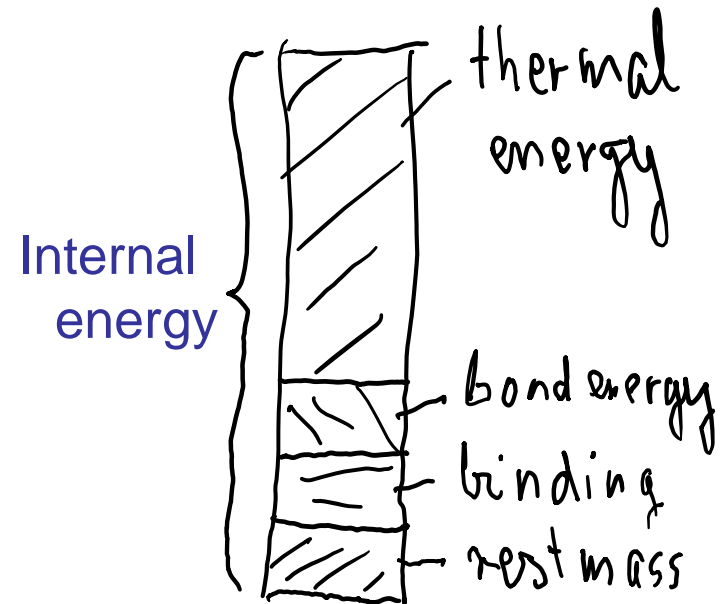
Thermal Energy vs Internal Energy

- Thermal energy and internal energy differ by an additive constant

- Often we are interested in energy difference, so the distinction between them is not crucial

- In this course we will use different notations for the two forms of energy, since we will include chemical and nuclear energy in our considerations

- Thus, we have Internal Energy E_I = Thermal Energy ($\mathcal{U}$) + rest mass energy + chemical bond energy + nuclear binding energy

Thermal Energy vs Internal Energy

- Very often there is no distinction between these two form of energy and it is assumed that:

$$\Delta \boldsymbol{E_I} = \Delta \,\mathscr{U}$$

- This will not lead to confusion as long as no chemical bond or nuclear binding energy are changing

Energy Storage as Thermal Energy – Heat Capacity

- Thermal energy of a system can be increased by heat transfer

- This is usually accompanied with the system temperature increase

- The quantity of heat needed per unit of temperature change is a fundamental property of any material; this is known as **heat capacity** C:

$$dQ = C\,dT$$

Thermal Energy Storage

- Consider the following concept:

- A company is planning to construct a thermal solar power plant that will store some of the thermal energy in graphite blocks for nighttime usage. The claimed plant capacity will be 30 GWh/year. The company claims a storage capacity of 1 MWh/ton at 1800 °C. Is this realistic?

(D)

Solar tower

Heliostats

- Estimate the mass of graphite needed if the plant is supposed to keep up the same power during night and day. Assume the same operational parameters during whole year (365 day a' 24 h = 12 daytime + 12 nighttime)
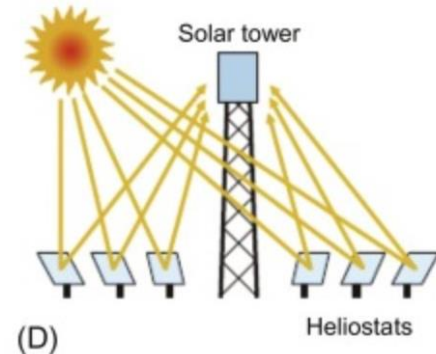
Thermal Energy Storage

- Solution: energy output during one night should be:

  30 000 MWh/365/2/night = 41.1 MWh/night =
  = 41.1 * 10^6 * 3600 J = 148 GJ = 148 000 000 kJ

- All this energy must be stored in graphite, which must be heated during the day from ambient temperature (25 °C) to temperature 1800 °C.

- We find in literature (Butland & Maddison, 1973) expressions for temperature-dependent c_p and c_v for graphite

Thermal Energy Storage

- We use $c_p(T)$, since graphite is freely expanding and changing its volume:

$$c_p(T) = 0.5412 - 2.42667 \times 10^{-6}T - 90.2725T^{-1}$$

$$-43449.3T^{-2} + 1.59309 \times 10^{7}T^{-3} - 1.43688 \times 10^{9}T^{-4}$$

- here T is temperature in kelvins and c_p is in cal/g K

- We find the average c_p in the temperature range as:

$$c_p\Big|_{298}^{2073} = \frac{4.184}{2073 - 298}\int_{298}^{2073} c_p(T)dT = 1.712 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}$$

Thermal Energy Storage

- Since $E = m \, c_p \, \Delta T$

- We can find the required mass of the graphite to store this amount of energy for temperature difference 1775 K as

  m = 148 000 000 kJ / 1775 K / 1.712 (kJ/ kg K) = 48.7 tons.

- This gives capacity 41.1/48.7 = 0.844 MWh/ton

- This is slightly lower value than the company claimed

Thermal Energy Storage

- Consider the following concept:

- A solar thermal power will concentrate solar rays to heat a molten salt (sodium nitrate + potassium nitrate). The molten salt is stored at a temperature of 300 °C and heated in a power tower to 550 °C. The salt has an average specific heat capacity 1.5 kJ/kg K in the temperature range of interest. The system can store 6000 tons of molten salt.

Curved mirrors

Absorber tube and reconcentrator

(C)

- How much energy is stored?
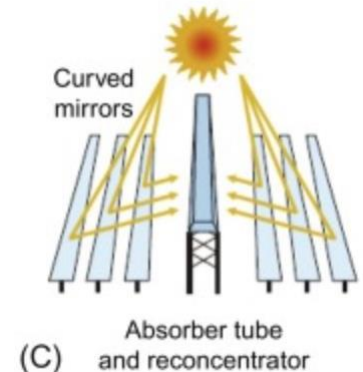
- Ans: ΔE_I = 6 000 000 kg * 1.5 kJ/kg K * (550-300) K = 2.25 x 10^{12} J = 625.05 MWh

Heat Transport with Helium

- Consider the following concept:

- High-temperature reactor uses helium to transport heat from the core out to turbines. The efficiency to convert heat to electricity is 40%. The mean core exit temperature is 1000 °C, and inlet temperature 100 °C.

- Calculate the required helium mass flow rate for 100 MWe reactor.

- How much helium is needed if a single helium cycle in the reactor circuit takes 5 minutes? Compare this to current world helium production.

Heat Transport with Helium

- The thermal power of the reactor is P_{th} = 100/0.4 MWth = 250 MWth

- We find the specific heat of helium: cp = 5.193 kJ/kg K

- From energy balance we find mass flow rate of helium, W_{He} , as:

$$P_{th} = W_{He}*c_p*\Delta T_{core}$$

$W_{He}*$ = 250 000 kWth /5.193 kJ/kg K / 900 K = 53.5 kg/s

Thus the required helium mass flow rate is 53.5 kg/s

Heat Transport with Helium

- The required helium mass during 5 min is thus m = 53.5 kg/s * 300 s = 16 050 kg

- In 2019, the estimated helium production was 160×10^6 m^3 (measured at standard metric conditions, 288.15 K and 101.325 kPa)

- We find the required helium volume from the ideal gas law as: $pV = m\, R_{He}\, T$, where R_{He} is the specific gas constant for helium $R_{He} = R/M = 2077.1$ J/kg K

- V = 16 050 kg * 2077.1 J/kg K *288.15 K/101325 Pa = 94 806 m^3

Heat Transport with Helium

- Thus one reactor requires 94 806 m^3/ 160 000 000 m^3 = 0.00059 fraction of the world helium production (less than 0.06%)

Work

- Work is another form of energy in transition

- Work from pressure:
  - when the volume of a system under pressure p expands by an amount dV, the system does work dL = p dV

- Work from heat:
  - adding heat to a gas in a fixed volume raises the temperature and the internal (thermal) energy of the gas
  - This leads to increase of pressure according to pV = nRT (R – gas constant = 8.314 J/mol K, n – number of moles of the gas)
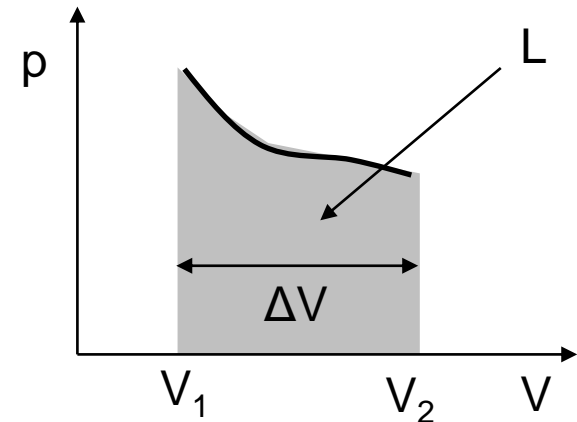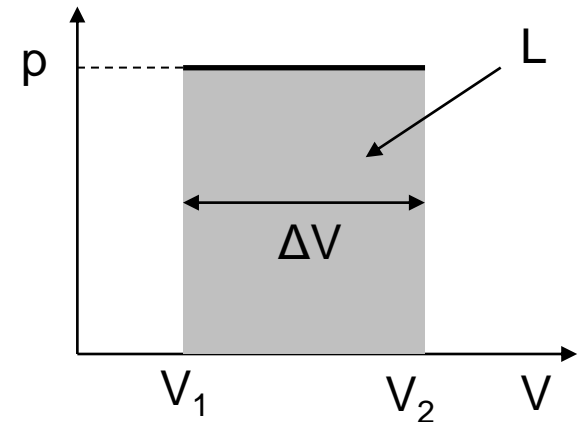 - The pressure of hot gas can be used to do mechanical work

Work from heat

- When work is done by a thermodynamic system, it is usually done by a gas (e.g. steam)

- The work done by a gas under constant pressure is $\Delta L = p\Delta V$

- For variable pressure:

$$L = \int_{V_1}^{V_2} p\, dV$$

- Work done by a system decreases the **internal energy** of the system, as given by the **1st Law**: important for **heat engines**

Relation between Work, Heat and Internal Energy

- The **first law of thermodynamics** states that the internal (thermal) energy of a system increases when heat is added (transferred) to it and it decreases if the system does work

$$\Delta E_I = \Delta Q - \Delta L$$

- The equation represents the energy conservation principle

Compressed Air Energy Storage

- Consider the following concept:

- Wind/solar energy can be stored in tanks, where air is compressed. When energy is needed, the expanding air will be used in turbines. This is so-called Compressed Air Energy Storage (CAES)

  Both isothermal and adiabatic compression can be considered

Compressed air locomotive

  Use 1st Law to compare the two methods

CAES

- According to 1st Law applied to CAES:

$$-pdV = dE_I - dQ$$

- When gas is compressed, work pdV < 0 is done on it

- When the process is **isothermal**, gas must exchange heat dQ with the environment, and $dE_I = 0$

- The work done to compress air from V_1, p_1 to V_2, p_2 is

$$L = \int_{V_1}^{V_2} pdV = p_2 V_2 \ln \frac{p_1}{p_2}$$

- When the process is adiabatic, dQ = 0, the internal energy of the gas increases, and it heats up

CAES

- From 1st Law, and ideal gas law, the work *L* is equal to the internal energy increase and can be found as

$$L = \int_{V_1}^{V_2} p\,dV = \frac{p_1 V_1}{\kappa - 1}\left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{\kappa-1}{\kappa}}\right]$$

- here

$$\kappa = \frac{c_p}{c_v}$$

CAES

- Let us compare work needed to compress 1 m^3 of air from ambient pressure p_1 = 0.1 MPa to pressure p_2 = 7 MPa (κ=1.4)

- (a) isothermal:

$$L_{iso} = p_2 V_2 \ln \frac{p_1}{p_2} = 7 \cdot 10^6 \text{ Pa} \times 1 \text{ m}^3 \ln \frac{0.1}{7} = -29.7 \text{ MJ} = -8.26 \text{ kWh}$$

- (b) adiabatic

$$L_{adiab} = \frac{p_1 V_1}{\kappa - 1} \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{\kappa-1}{\kappa}} \right] = \frac{p_2 V_1}{\kappa - 1} \left[\frac{p_1}{p_2} - \left(\frac{p_1}{p_2} \right)^{\frac{1}{\kappa}} \right] =$$

$$\frac{p_2 V_2}{1 - \kappa} \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{1-\kappa}{\kappa}} \right] = \frac{7 \times 10^6 \text{Pa} \times 1 \, m^3}{1 - 1.4} \left[1 - \left(\frac{7 \times 10^6 \text{Pa}}{0.1 \times 10^6 \text{Pa}} \right)^{\frac{1-1.4}{1.4}} \right] = -12.2 \text{MJ} = -3.42 \text{ kWh}$$

CAES

- The calculated work is negative, since it must be done on air. As can be seen, the absolute magnitude of the required work is greater for the isothermal process.

- The calculated work is valid for a closed system. Since CAES operates as open system, the work done by ambient pressure must be taken into account:

$$L_{amb} = V_2 * (p_2 - p_1) = 1m^3 * (7-0.1) * 10^6 = 6.9 \text{ MJ}$$

- Thus for the isothermal process, the net energy stored in 1 m^3 of air is 29.7 MJ – 6.9 MJ = 22.8 MJ (=6.33 kWh)

CAES

- In conclusion: adiabatic CAES can store less energy. Also temperature rise $T_2/T_1 = (p_2/p_1)^{[(\kappa-1)/\kappa]}$ can be very high

- However, isothermal CAES require large and expensive intercoolers to keep air isothermal during compression

- In practice, neither adiabatic nor isothermal compression/expansion can be achieved with high efficiency

- Additional losses are due to friction and irreversibility of processes
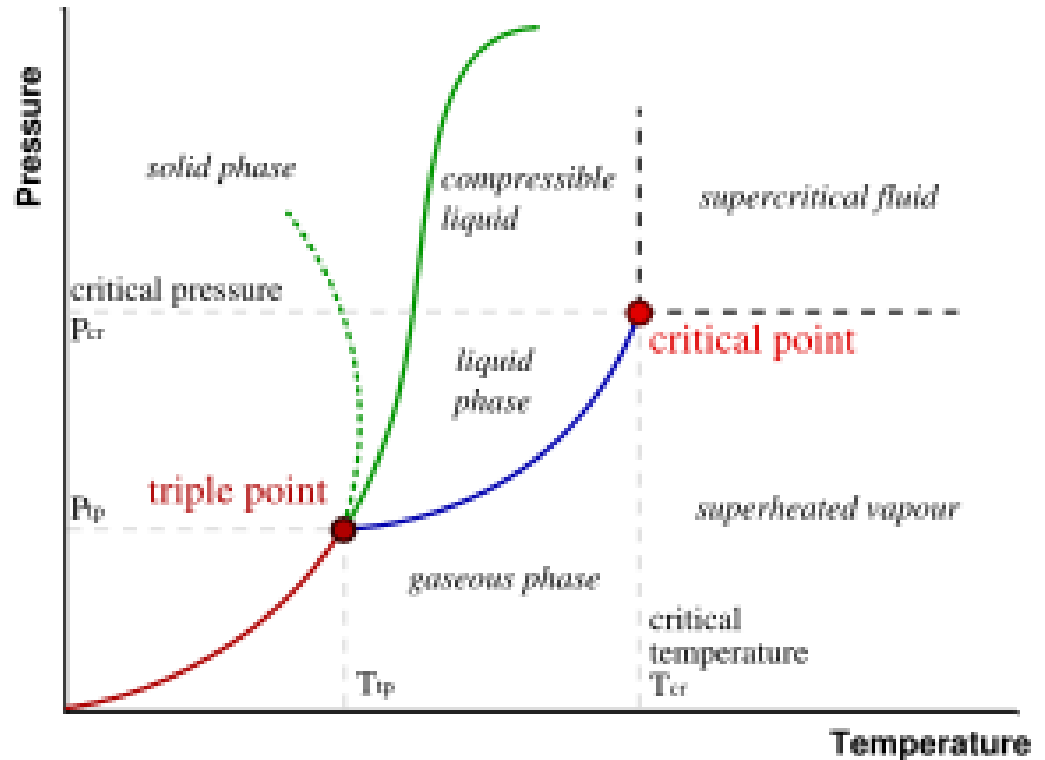
Phase change

- Phase change is a process when a certain substance undergoes transition from one phase to another

- Best known examples:
  - melting ice: phase change of water from solid (ice) to liquid
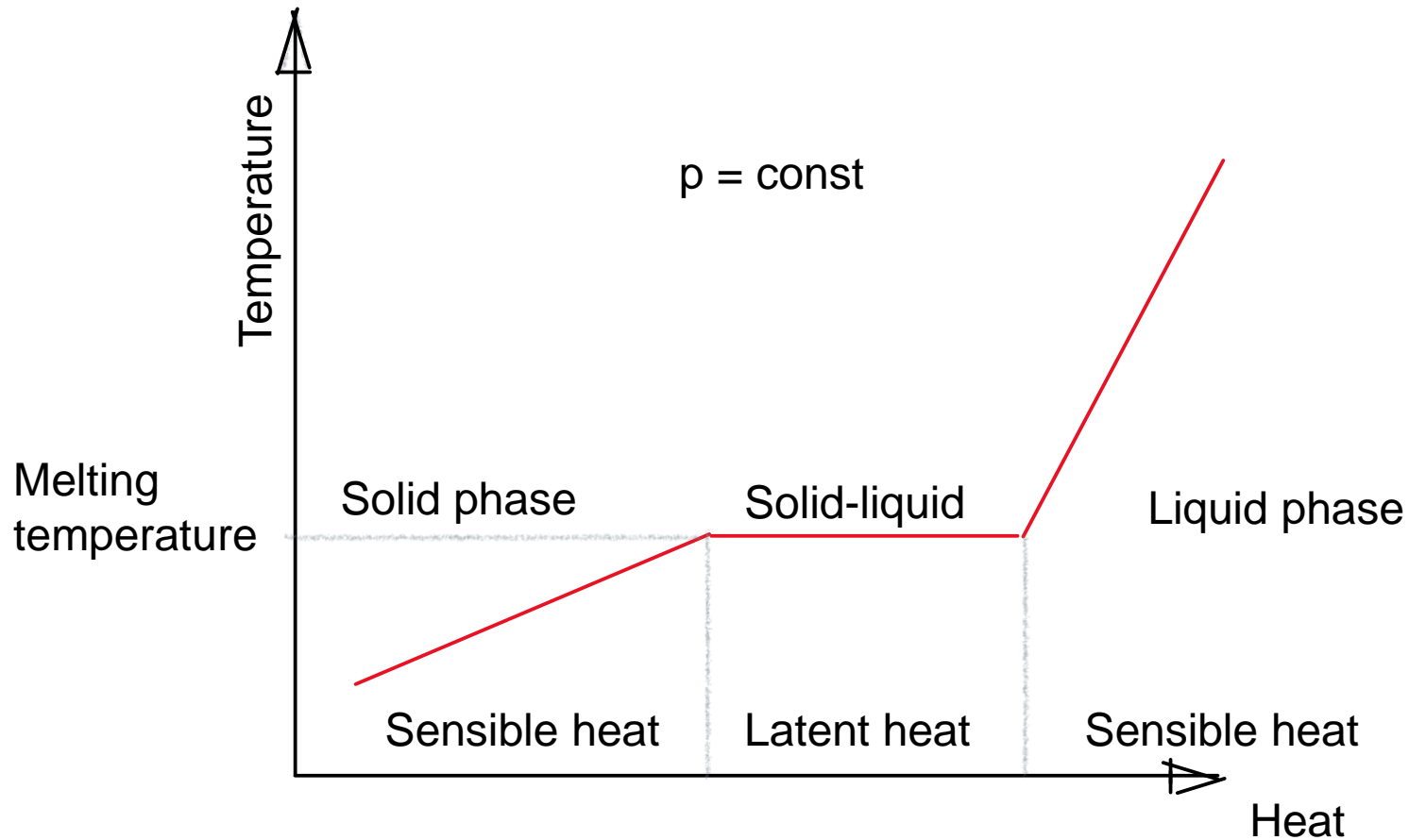 - boiling: phase change from liquid (water) to gas (steam)
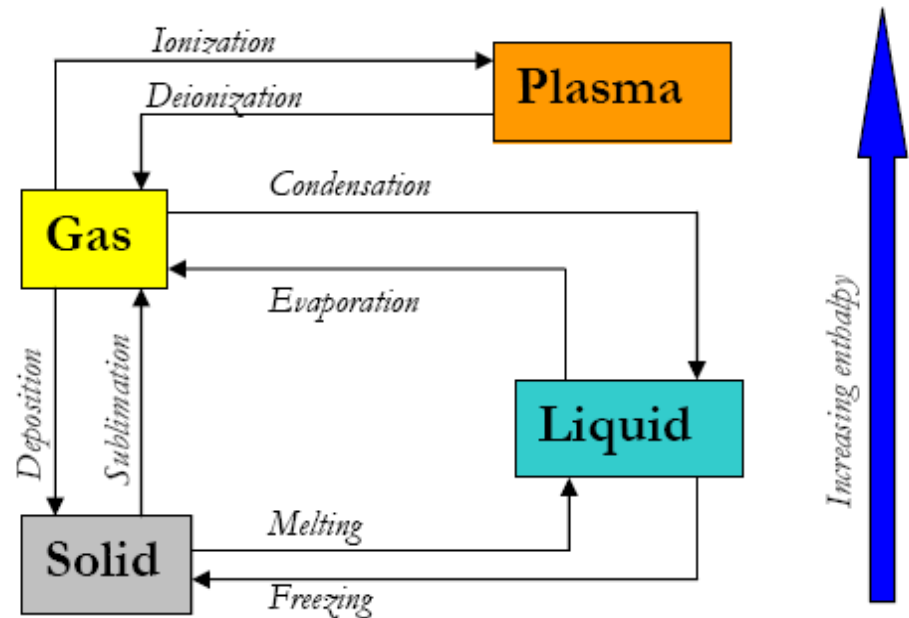
Phase diagram

- A typical phase diagram: note the anomalous behavior of water (green dotted line)
  - solid state (ice) is less dense than water! (ice floats on water)
- Triple point: pure water, ice and water vapor coexist in a stable equilibrium at exactly 273.16 K and 611.73 Pa

Temperature vs heat

p = const

Temperature

Melting temperature

Solid phase

Solid-liquid

Liquid phase

Sensible heat

Latent heat

Sensible heat

Heat

Phase Change Material - PCM

- Phase change materials (PCM) are used for thermal energy storage

- They offer significant energy storage over a moderate (or even zero) temperature increase

- Main phase change materials
  - Hydrate salts (e.g. $Na_2HPO_4 \cdot 12H_2O$, T_m=40 °C, i_{sf}=279 kJ/kg)
  - Paraffin waxes (20-carbon, T_m=36.7 °C, i_{sf}=246 kJ/kg)
  - Fatty acids (e.g. stearic acid, T_m=69.4 °C, i_{sf}=199 kJ/kg)
  - Eutectics of organic and non-organic compounds (e.g. Quinone, T_m=115 °C, i_{sf}=171 kJ/kg)

  - here T_m – melting temperature, i_{sf} – latent heat of melting

Stored Heat

- When PCM is heated from temperature T_1 to temperature T_2, and $T_1 < T_m < T_2$, then the stored heat in mass m is as follows

$$Q = m \left[\int_{T_1}^{T_m} c_s(T)dT + i_{sf} + \int_{T_m}^{T_2} c_f(T)dT \right]$$

- where:
  - $c_s(T)$ – temperature-dependent specific heat of solid
  - $c_f(T)$ – temperature-dependent specific heat of fluid

Stored Heat

- Consider the following concept:

- A layer of 20-carbon paraffin is proposed to cover a wall in order to store solar energy. The temperature of the paraffin should never exceed the melting temperature. What should be the minimum thickness of the paraffin layer, when the mean insolation during the daytime (12 h) is 200 W/m^2, and the initial ("cold") paraffin temperature is 15 °C? The density of the paraffine is 755 kg/m^3.

Paraffin layer
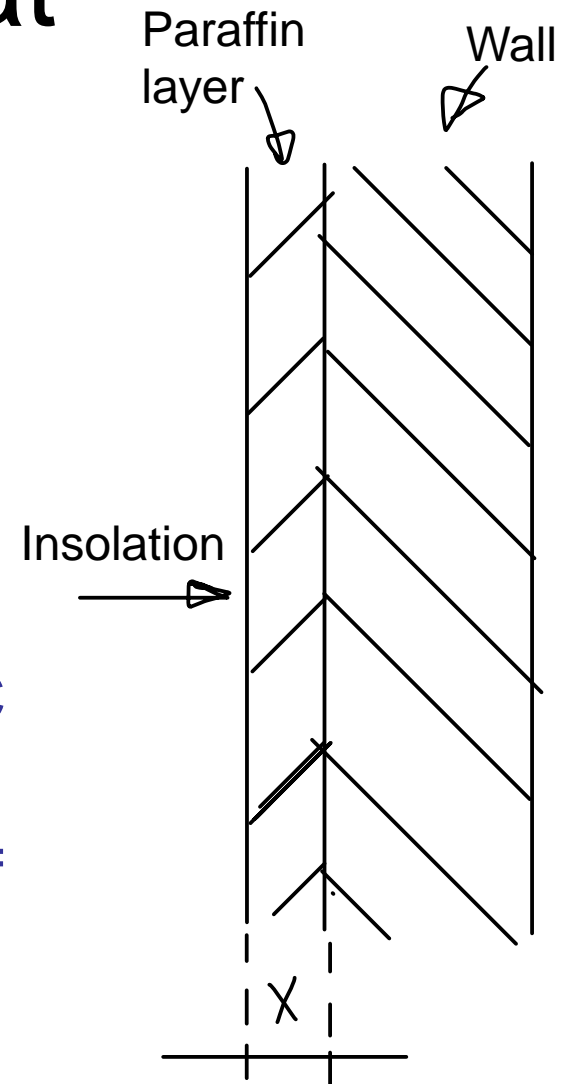
Wall

Insolation

Stored Heat

Paraffin layer   Wall
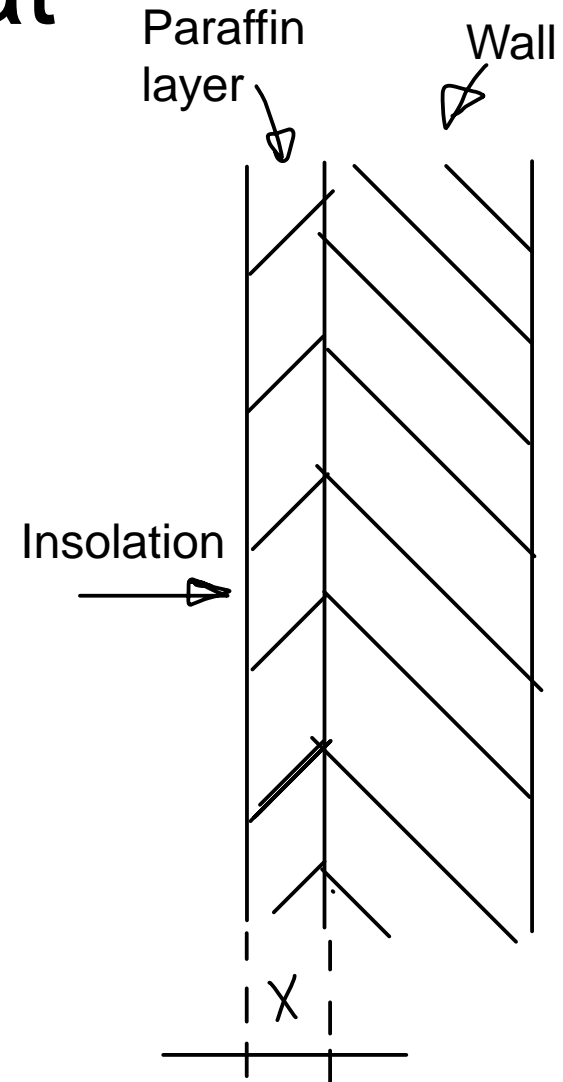
- We consider 1 m² of the wall and write the energy balance

$$Q = m\left[\int_{T_1}^{T_m} c_s(T)dT + i_{sf}\right]$$

Insolation

- In this energy balance we assume that paraffin is first heated from 15 C to T_m, and next melted. Here Q = 200 W/ m² * 1 m² * 12 h * 3600 s/h = 8.64 MJ. This is insolation energy per m²
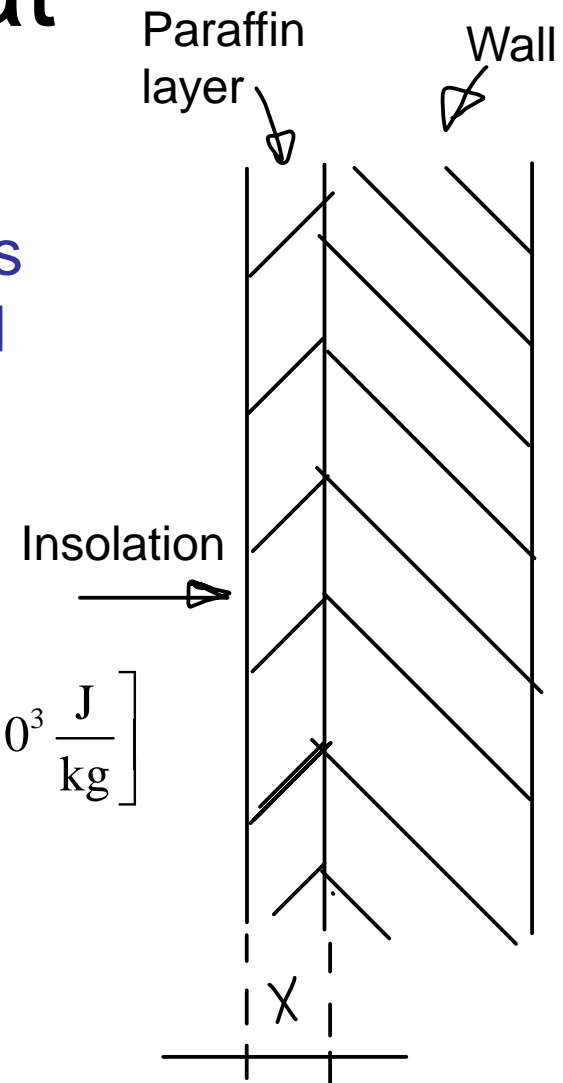
Stored Heat

Paraffin layer

Wall

- The energy stored in paraffin after melting of 1m^2 of layer with thickness x is (specific heat is 1970 J/kg K and latent heat 246 kJ/kg)

Insolation

$$Q = m \left[\int_{T_1}^{T_m} c_s(T) dT + i_{sf} \right] =$$

$$1m^2 \cdot x \cdot 755 \frac{\text{kg}}{\text{m}^3} \left[1970 \frac{\text{J}}{\text{kg} \cdot \text{K}} \left(36.7°\text{C} - 15°\text{C} \right) + 246 \cdot 10^3 \frac{\text{J}}{\text{kg}} \right]$$

- Equating the two expressions for Q we find x = 0.0395 m

X

What have we learned

- Thermal energy is a part of the internal energy
  - they are different by an additive constant
- Heat and work is energy in transition
- Energy (e.g. solar energy) can be stored as thermal energy
  - heat capacity
- Compressed Air Energy Storage (CAES)
  - isothermal versus adiabatic
- Phase-change energy storage
  - PCM – phase change materials