

THERMODYNAMICS

WHAT HAPPENS WHEN SOMETHING IS HEATED ?

SPECIFIC HEAT

A cup of water in a kettle quickly boils but when the kettle is full, we know that it takes much longer to boil. In both cases the rate of energy transfer to the water was the same. So, somehow the **mass** m of an object is related to the temperature it will reach in a certain time. Put a metal saucepan with some water in it on to a cooktop. The metal quickly becomes hot but not the water. The **rise in temperature** ΔT also depends on the substance being heated. The rise in temperature of a material is characterised by its **specific heat** c . Many books use the term *specific heat capacity* (specific heat is the terminology that you should use).

Consider warming a material of mass m and specific heat c to raise its temperature by ΔT without any change in phase (state). The required energy transferred Q to the material is simply given by equation (1A)

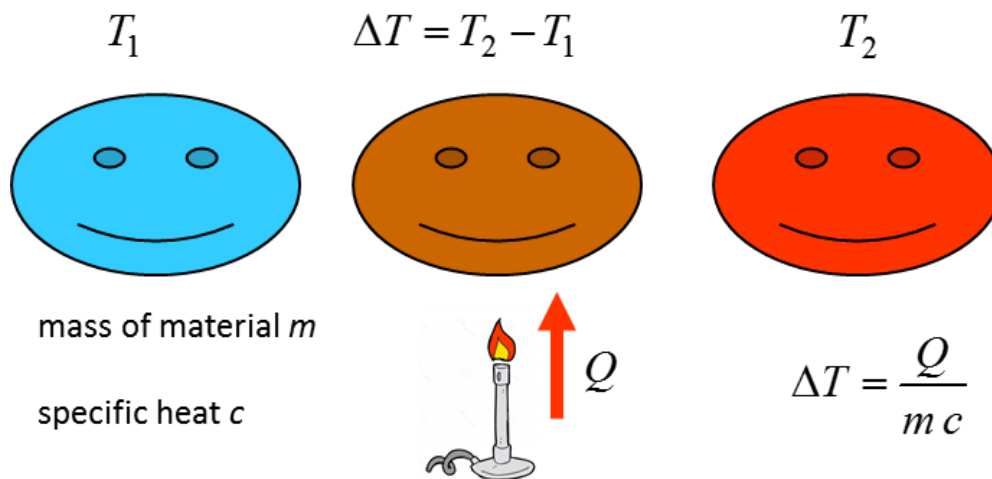
$$(1A) \quad Q = mc\Delta T \quad \text{no change in phase}$$

The rise in temperature ΔT of the material is given by equation (1B)

$$(1B) \quad \Delta T = \frac{Q}{mc} \quad \text{no change in phase}$$

The specific heat c is given by equation (1C)

$$(1C) \quad c = \frac{Q}{m \Delta T} \quad [\text{J.kg}^{-1}.\text{K}^{-1}]$$



Specific heats at constant pressure

Material	c [J.kg ⁻¹ .K ⁻¹]
water (liquid 15 °C)	4186
water (ice -5 °C)	2100
water (steam 100 °C)	2010
human body (average)	3470
alcohol (ether)	2400
wood	1700
marble CaCO ₃	860
glass	840
aluminium	900
iron	450
copper	390

Implication of Specific Heat Capacity

Water has one of the highest values for its specific heat of any common substances.

It takes a lot more energy to raise the temperature of water than most other substances, and a lot more energy is released when the temperature of water falls.

Water can store tremendous of energy because of its high specific heat. It acts as a source or sink of energy in the oceans and atmosphere. Without the presence of water, temperature variations between day and night would be much greater. This is why the daily temperature fluctuations are much smaller near the coast than inland.

Why are western European countries much warmer than the north-eastern region of Canada? Why do islands not have the extreme temperature variations as in the interior of continents?

Since water can store large amounts of energy because its high value of specific heat, it takes a long time to cool and therefore it is a good substance to use in a hot water bottle. As the temperature of the water in the bottle drops a lot of energy is given out.

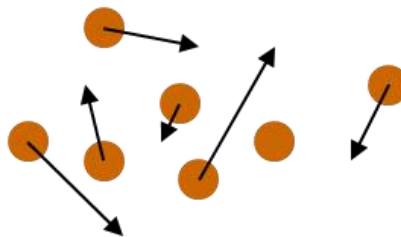
Since the human body has a large specific heat, it requires a large amount of energy given out by metabolic processes to cause a rise in body temperature.

Water because of its high value of its specific heat is a very useful cooling agent in the cooling system of a car engine. **Explain why!**

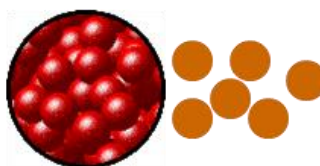
HEATS OF FUSION AND VAPORISATION

Phases of matter

Gas - very weak intermolecular forces, rapid random motion



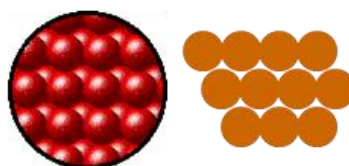
Liquid - intermolecular forces bind closest neighbours



high temp
low pressure



Solid - strong intermolecular forces



low temp
high pressure

From the equation containing the specific heat, it seems that we can keep on transferring heat to an object and raising the temperature indefinitely. In fact, the equation seems to suggest that if we put in an infinite amount of heat we will get an infinite increase in temperature. However, instinctively we know that this is not totally true since at 100 °C water starts to boil and stays at this temperature until it changes to a gas. So, the equation doesn't fully account for changes of state, which are also known as **phase changes**.

In general, the temperature stays constant during any phase change.

Melting point: temperature at which a solid turns into a liquid or vice versa.

Boiling point: temperature at which a liquid turns into a gas (or vapour) or vice versa.

These points can be changed by adding impurities to the water / ice or changing the external pressure. Put a piece of string on an ice cube, which is straight out of the fridge. Sprinkle some salt on the string/ice cube. Wait a few seconds, you will then be able to lift the ice cube by the string. The string seems to have become glued to the cube. The explanation is this: The salt lowers the freezing temperature of ice. So, the melted ice soaks into the string. The salt now becomes less concentrated as it diffuses out of the region of the string so the freezing temperature is raised again. Since the rest of the ice cube is still at a temperature below freezing, the water will re-freeze including that which has soaked into the string - the string will essentially be frozen to the cube. An almost similar thing happens when you try and lick an ice tray. The tray is say at -15°C so it freezes the moisture on your tongue.

Why is energy needed to melt or vaporise a substance?

At the melting point, the latent heat of fusion does not increase the translational kinetic energy of the molecules of the solid and hence the temperature does not increase. But, instead the energy is used to overcome the potential energy associated with the forces between the molecules, that is, work is done against the attractive force to weaken the bonds between the molecules such that they can now roll over one another in the liquid phase. Similarly, energy is required for molecules held close together in the liquid phase to escape into the gas phase. Generally, much more energy is required for the transition from a liquid to a gas and then the energy required for the transition of a solid to a liquid, hence, latent heats of vaporisation are generally much higher than latent heats of fusion.

Energy is acquired or released when a material changes phase. For example, energy is required to melt ice and vaporise water. However, energy is given out if water vapour condenses or water freezes. The heat acquired or released is called the **latent heat (heat of transformation)**.

The energy transfer Q involved in a change of phase depends upon the value of the latent heat L and the total mass m of the material, that is

$$(2) \quad Q = \pm mL \quad \text{constant temperature}$$

L is a constant for a material at a given temperature and is called the latent heat of fusion (for melting) or latent heat of vaporisation (for boiling).

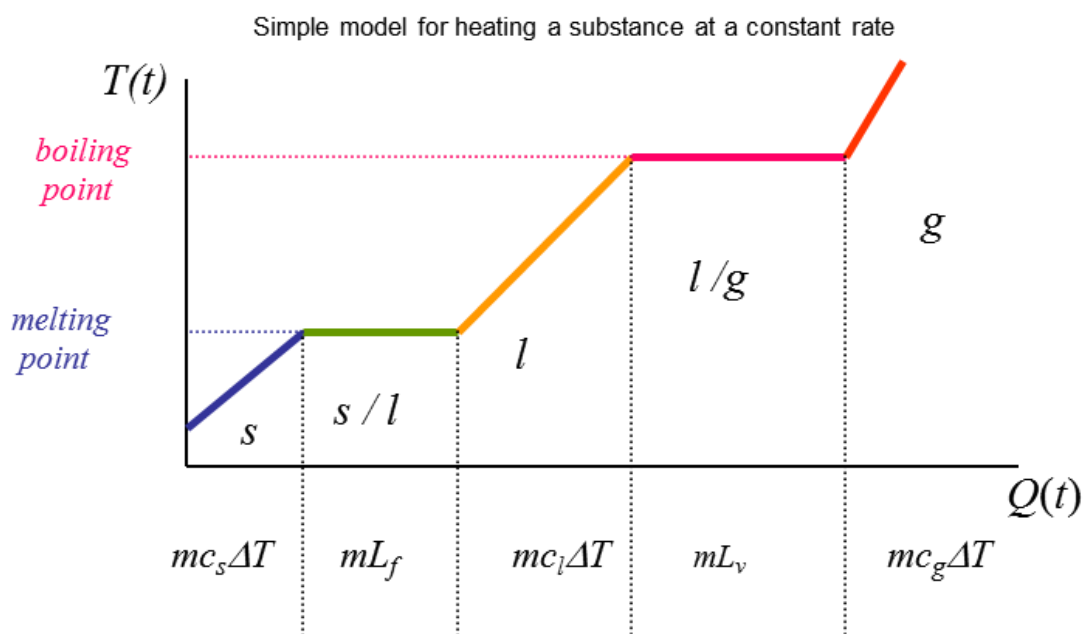
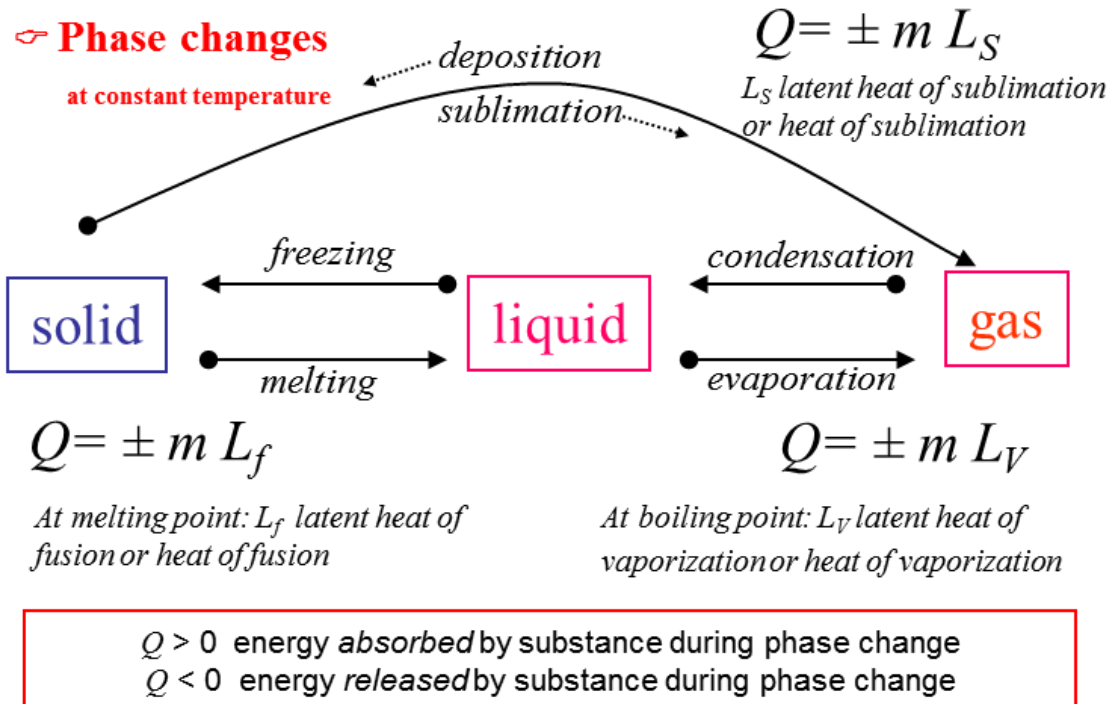
Latent heat of fusion is the energy required to melt 1 kg of a solid.

$$\text{water} \quad L_f = 3.33 \times 10^5 \text{ J.kg}^{-1} \quad \text{at } 0^\circ\text{C}$$

Latent heat of vaporisation is the energy required to evaporate 1 kg of a liquid.

$$\text{water} \quad L_v = 2.26 \times 10^6 \text{ J.kg}^{-1} \quad \text{at } 100^\circ\text{C}$$

Water has large values for its latent heats compared to other common materials.



Heating 1.0 kg ice to steam (-20 °C to 120 °C)

P = 2000 W	Time t (min)	Heat Q (kJ)	Time Ratios
Ice: -20 °C to 0 °C	0.37	44	1.0 (0.37/0.37)
Ice / Water: 0 °C	2.78	333	7.5 (2.78/0.37)
Water: 0 °C to 20 °C	0.70	84	1.9
Water: 0 °C to 100 °C	3.49	419	9.4
Water / Steam: 100 °C	18.80	2256	50.8
Steam: 100 °C to 120 °C	0.34	40	0.9

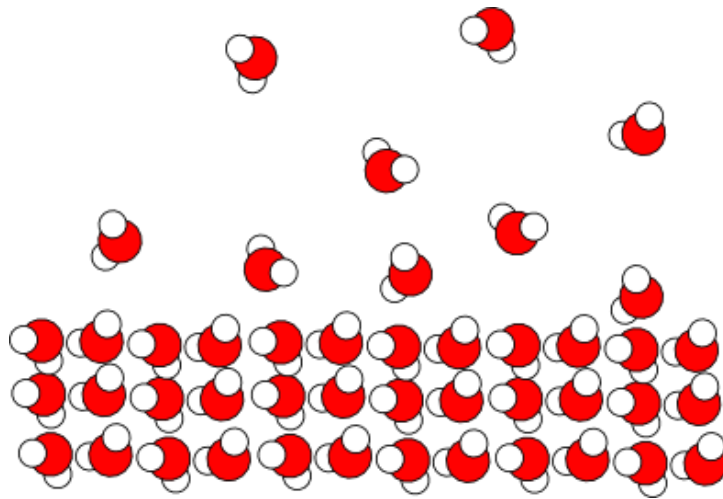
N.B. The large amount of energy required to vaporise the water.

Evaporation

The latent heat to change a liquid to a gas is not only required at the boiling point. Water can change from a liquid to a gas even at room temperature in a process called **evaporation**.

An open pan of liquid water will eventually disappear as it becomes water vapour. The change of phase from liquid to a gas that occurs at the surface is called evaporation.

The temperature of liquid water is related to the average translational kinetic energy of the molecules. The water molecules have a wide range of energies and move in random directions bumping into each other all the time. At one moment, a molecule could be moving very rapidly and a little later moving slowly. Some molecule at the surface gain sufficient energy to escape the surface by gaining kinetic energy from collisions with molecules below the surface and become molecules of vapour. Thus, the average kinetic energy of the liquid water molecules is decreased due to the escape of only the most energetic molecules, therefore, the temperature of the liquid water must decrease.



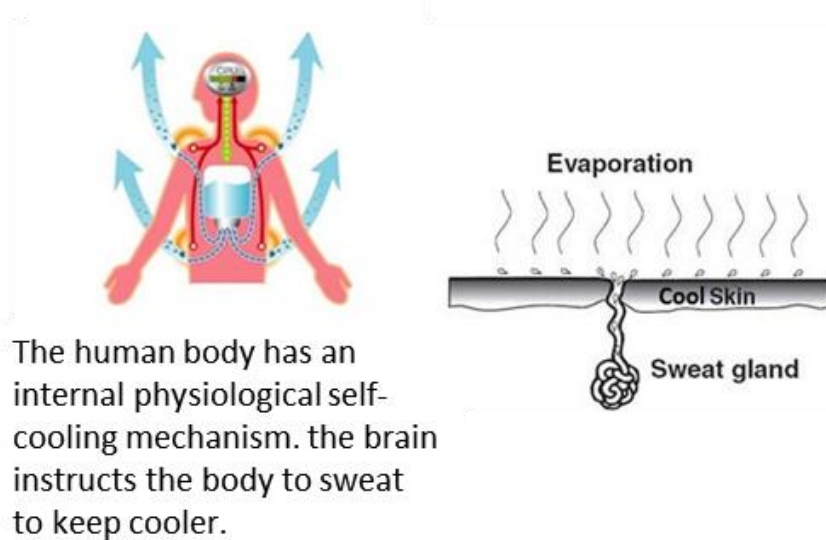
When water evaporates, it cools since energy is required (latent heat of vaporisation) comes from the water itself. So, its internal energy and therefore its temperature must drop.

water 100 °C	$L_v = 2.26 \times 10^6 \text{ J.kg}^{-1}$
--------------	--

water 20 °C	$L_v = 2.45 \times 10^6 \text{ J.kg}^{-1}$
-------------	--

Implications of latent heat

1. As a liquid evaporates it extracts energy from its surroundings and hence the surroundings are cooled. The cooling by perspiring, which removes heat from the skin surface by vaporising the perspiration. Thus, on humid days we feel less comfortable because less energy is removed from the body by the processes of perspiration and evaporation.



2. Evaporation rates increase with temperature, volatility of substance, area and lower humidity. You feel uncomfortable on hot humid days because perspiration on the skin surface does not evaporate and the body can't cool itself effectively.
3. When ether is placed on the skin it evaporates so quickly that the skin feels frozen. Ethyl chloride when sprayed on the skin evaporates so rapidly the skin is "frozen" and local surgery can be performed.
4. Evaporative air conditions cool the air by passing it over a moist surface where energy heat is absorbed from it by water evaporating from the surface.

5. The circulation of air from a fan pushes water molecules away from the skin more rapidly helping evaporation and hence cooling.



6. A canteen water bag soaked in water will keep the water cool because of evaporation.



7. When a gas condenses energy is released into the surroundings. Steam heating systems are used in buildings. A boiler produces steam and energy is given out as the steam condenses in radiators located in rooms of the building.
8. Scalding by steam produces severe burns due to the large heat of vaporisation of water released when the steam condenses on the skin. Therefore, a steam burn is much more damaging to the skin than a burn from boiling water. The steam releases considerable energy when it condenses to a liquid and wets the skin.

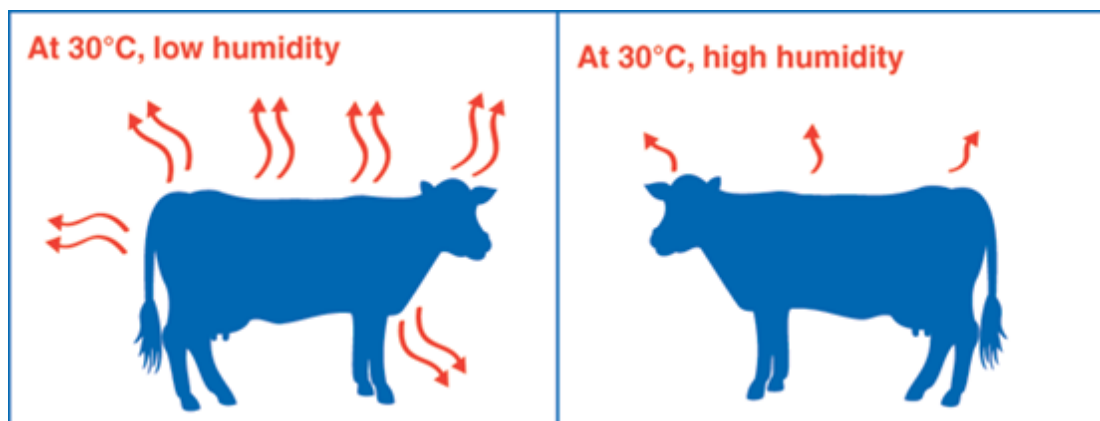


9. Why does a dog pant?



Humidity

As water evaporates it adds water to the air. The presence of water vapour in the air is referred to as *humidity*. When air contains a large amount of water vapour (moisture), the humidity is said to be high. When air contains little moisture, the humidity is said to be low or dry. The air can only hold a certain amount of moisture at a particular temperature. The air is said to be saturated when it contains a maximum amount of moisture. Hence, the more humidity the more difficult it is for water to evaporate and add more moisture to the air. The humidity is usually expressed as a percentage. For example, if the air holds half the maximum amount of water vapour that can hold, the relative humidity is said to be 50%. A room can be well heated but without good ventilation and air conditioning it can make the air dry. This causes rapid evaporation from the mucous membranes of the breathing passages, causing irritation and makes infection more likely.



The condensation of water vapour in the air (gas to a liquid) releases energy into the atmosphere. This is the source of energy in a cyclone.



What is cooking all about?



Specific heat of Aluminium is $900 \text{ J.kg}^{-1}.\text{K}^{-1}$, Copper $390 \text{ J.kg}^{-1}.\text{K}^{-1}$, Iron $450 \text{ J.kg}^{-1}.\text{K}^{-1}$. This means that less thermal energy is required to warm a copper cooking pan than a steel or aluminium or iron one of equal mass. If you recall that copper is a much better thermal conductor than either aluminium or iron. So, it is much more energy efficient to buy an all copper pan - take note of this the next time you are shopping for cookware.



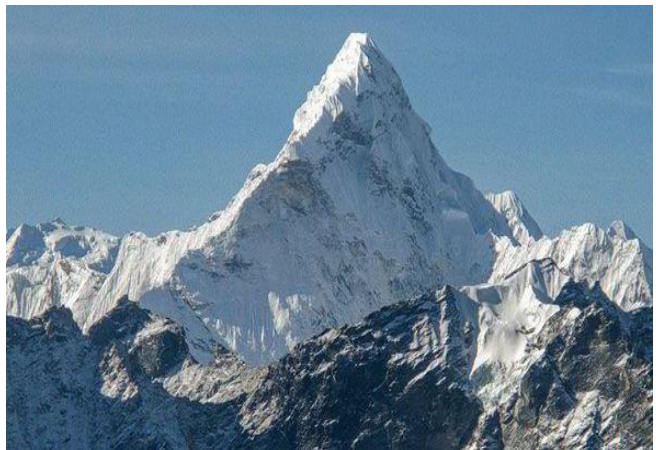
How pressure cookers work?

These are essentially cooking pots with an air tight lid. As water is heated and turns to vapour, the pressure builds up because the vapour cannot escape. Water usually boils and turns to steam (vapour) at $100\text{ }^{\circ}\text{C}$ at a pressure of 1 atmosphere (i.e 101 kPa). By increasing the pressure, the water can be warmed to higher temperatures before it changes to a vapour. This means that anything being cooked inside the pot will experience higher temperatures and therefore the cooking time will be less. But will it taste as good?



Tea on Mount Everest

The air pressure on top of Mount Everest is about half an atmosphere (i.e 50 kPa). Water will boil (and turn to vapour) at about $70\text{ }^{\circ}\text{C}$. Unfortunately, this water temperature makes a very poor cup of tea!



Example

If 2000 J are absorbed by copper plate, aluminium plate, glass plate and water, each of mass 250 g, which would be "hottest"?

$$c_{\text{Cu}} = 390 \text{ J.kg}^{-1}.\text{K}^{-1} \quad c_{\text{Al}} = 910 \text{ J.kg}^{-1}.\text{K}^{-1}$$

$$c_{\text{glass}} = 390 \text{ J.kg}^{-1}.\text{K}^{-1} \quad c_{\text{water}} = 4190 \text{ J.kg}^{-1}.\text{K}^{-1}$$

Solution

$$Q = 2000 \text{ J}$$

$$m_{\text{Cu}} = m_{\text{Al}} = m_{\text{glass}} = m_{\text{water}} = m = 250 \text{ g} = 0.250 \text{ kg}$$

$$\Delta T = \frac{Q}{mc}$$

copper

$$\Delta T = 2000 / \{(0.250)(390)\} \text{ }^{\circ}\text{C} = 21 \text{ }^{\circ}\text{C}$$

aluminium

$$\Delta T = 2000 / \{(0.250)(910)\} \text{ }^{\circ}\text{C} = 8.8 \text{ }^{\circ}\text{C}$$

glass

$$\Delta T = 2000 / \{(0.250)(840)\} \text{ }^{\circ}\text{C} = 10 \text{ }^{\circ}\text{C}$$

water

$$\Delta T = 2000 / \{(0.250)(4190)\} \text{ }^{\circ}\text{C} = 1.9 \text{ }^{\circ}\text{C}$$

Notice the small change in the temperature of the water.

Why is a copper saucepan better than an aluminium one?

Example

For a 70 kg person (specific heat capacity $3500 \text{ J.kg}^{-1}.\text{K}^{-1}$), how much extra released energy would be required to raise the temperature from 37°C to 40°C ?

Solution

$$m = 70 \text{ kg} \quad c = 3500 \text{ J.kg}^{-1}.\text{K}^{-1} \quad \Delta T = (40 - 37)^\circ\text{C} = 3^\circ\text{C}$$

Specific heat $Q = m c \Delta T$

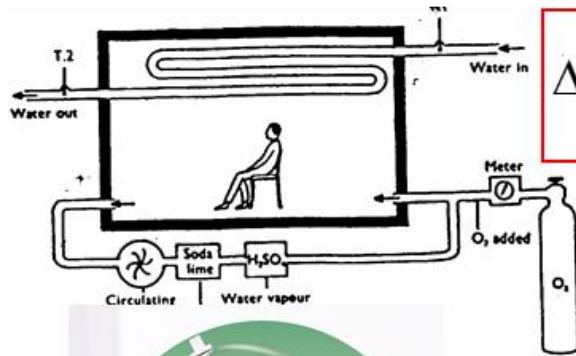
$$Q = m c \Delta T = (70)(3500)(3) = 7.45 \times 10^5 \text{ J} = 0.74 \text{ MJ}$$

A fever represents a large amount of extra energy released. The metabolic rate depends on the temperature of the body. The rate of chemical reactions is very sensitive to temperature and even a small increase in the body's core temperature can increase the metabolic rate quite significantly.

If there is an increase of about 1°C then the metabolic rate can increase by as much as 10%. Therefore, an increase in core temperature of 3°C can produce a 30% increase in metabolic rate.

If the body's temperature drops by 3°C the metabolic rate and oxygen consumption decrease by about 30%. This is why animals hibernating have a low body temperature. During heart operations, the person's temperature may be lowered.

How do we measure a person's metabolic rate?



$$\Delta T = \frac{Q}{mc}$$



Santorio Santorio weighed himself before and after a meal, conducting the first controlled test of metabolism, AD 1614.

Example

A styrofoam picnic chest has dimensions 0.5 x 0.3 x 0.35 m with walls 0.02 m thick.

1. If the temperature difference across the walls is 35 °C, at what rate will the heat conducted into the chest?
2. How many kilograms of ice do you need to put in the chest to keep the beer at 0 °C for 5 hours? Assume the beer was initially cooled to 0 °C.

The thermal conductivity of Styrofoam $k_{sty} = 0.010 \text{ W.m}^{-1}.\text{K}^{-1}$

Latent heat of fusion of ice $L_f = 333 \text{ kJ.kg}^{-1}$

Solution

(1) We are told there is a temperature difference across the walls of the chest. The rate of heat transfer only depends on this temperature difference

$$\frac{dQ}{dt} = -k A \frac{dT}{dx}$$

where A is the surface area of the box, dT is the temperature difference across the walls, dx is the wall thickness.

The box has six sides, we must now calculate the total area

$$A = (2)(0.5)(0.3) + (2)(0.3)(0.35) + (2)(0.35)(0.5) = 0.86 \text{ m}^2$$

$$dT = 35 \text{ }^{\circ}\text{C}.$$

$$\text{thickness, } dx = 0.02 \text{ m}$$

Substitute these into the rate of heat transfer equation above

$$Q = (0.01)(0.86)(35) / 0.02 = \mathbf{15.1 \text{ W}}$$

So, the rate of heat transfer across the walls of the chest is 15.1 W.

(2) In other words, the question is saying, "what is the least amount of ice that would melt after 5 hours". From part (a) we know that 15.1 J of energy can enter the chest in 1 second. So, we must work out how much energy enters in 5 hours. Then calculate how much ice this can melt.

Note that 5 hours = 5 x 3600 seconds = $1.8 \times 10^4 \text{ s}$.

So total energy in 5 hours = $(1.8 \times 10^4)(15.1) \text{ J} = 2.718 \times 10^5 \text{ J}$

The energy Q required to melt ice is given by the latent heat of fusion equation

$$Q = m L$$

where m is the mass of the ice that will melt. We can now calculate this mass by rearranging the above equation and substituting

$$m = Q / L = 2.718 \times 10^5 / 3.33 \times 10^5 = 0.82 \text{ kg}$$

Example (Calorimetry)

How many 20 g ice cubes, whose initial temperature is $-10\text{ }^{\circ}\text{C}$, must be added to 1.0 L of hot tea, whose initial temperature is $90\text{ }^{\circ}\text{C}$, in order that the final temperature of the mixture be $10\text{ }^{\circ}\text{C}$? Assume all the ice melts in the final mixture and the specific heat of tea is the same as that of water.

Latent heat of fusion of ice $L_v = 3.33 \times 10^5 \text{ J. kg}^{-1}$

Specific heat of water $c_{\text{water}} = 4190 \text{ J. kg}^{-1} \text{ K}^{-1}$

Specific heat of ice $c_{\text{ice}} = 2100 \text{ J. kg}^{-1} \text{ K}^{-1}$

Assume that the tea has the same properties as water.

Note that 1 L of water has a mass of 1 kg.

Solution

Let m_{ice} be the mass of ice $m_{\text{ice}} = ?$

m_{tea} be the mass of tea = mass of water with the same volume

$m_{\text{tea}} = 1\text{kg}$.

Use conservation of energy. The energy required to melt the ice, then heat it to 10°C , must come from the tea.

The following are the three stages the ice must go through to reach the final temperature of 10°C :

(i) ice heats up from -10°C to 0°C

(ii) ice melts at 0°C

(iii) melted ice heats up from 0°C to 10°C

(iv) energy for stages (i), (ii), and (iii) must come from tea.

Energy required for (i) + (ii) + (iii) = Energy lost by tea

The expressions for the different stages are given by

(i) $m_{\text{ice}} c_{\text{ice}} \Delta T_{(i)} = m_{\text{ice}} (2100)(10) = 2.10 \times 10^4 m_{\text{ice}}$

(ii) $m_{\text{ice}} L_v = 3.33 \times 10^5 m_{\text{ice}}$

(iii) $m_{\text{ice}} c_{\text{water}} \Delta T_{(iii)} = m_{\text{ice}} (4190)(10) = 4.19 \times 10^4 m_{\text{ice}}$

(iv) $m_{\text{tea}} c_{\text{water}} \Delta T_{\text{tea}} = (1)(4190)(90) = 3.352 \times 10^5 \text{ J}$

Using the conservation of energy equation above we have

$$2.10 \times 10^4 m_{\text{ice}} + 3.33 \times 10^5 m_{\text{ice}} + 4.19 \times 10^4 m_{\text{ice}} = 3.352 \times 10^5$$

Now solving for m_{ice} we get $m_{\text{ice}} = 0.847 \text{ kg} = 847 \text{ g}$ of ice are needed. Divide this by the mass of one ice cube (20 g) to find out how many cubes are needed.

$$\text{Number of ice cubes} = (847 / 20) = 43$$

Example (Calorimetry)

How much ice at $-10.0\text{ }^{\circ}\text{C}$ must be added to 4.00 kg of water at $20.0\text{ }^{\circ}\text{C}$ to cause the resulting mixture to reach thermal equilibrium at $5.0\text{ }^{\circ}\text{C}$. Assume no energy transfer to the surrounding environment, so that energy transfer occurs only between the water and ice.

Solution

$$m_{\text{ice}} = ? \text{ kg} \quad m_{\text{water}} = 4.00 \text{ kg}$$

ICE gains energy from the water

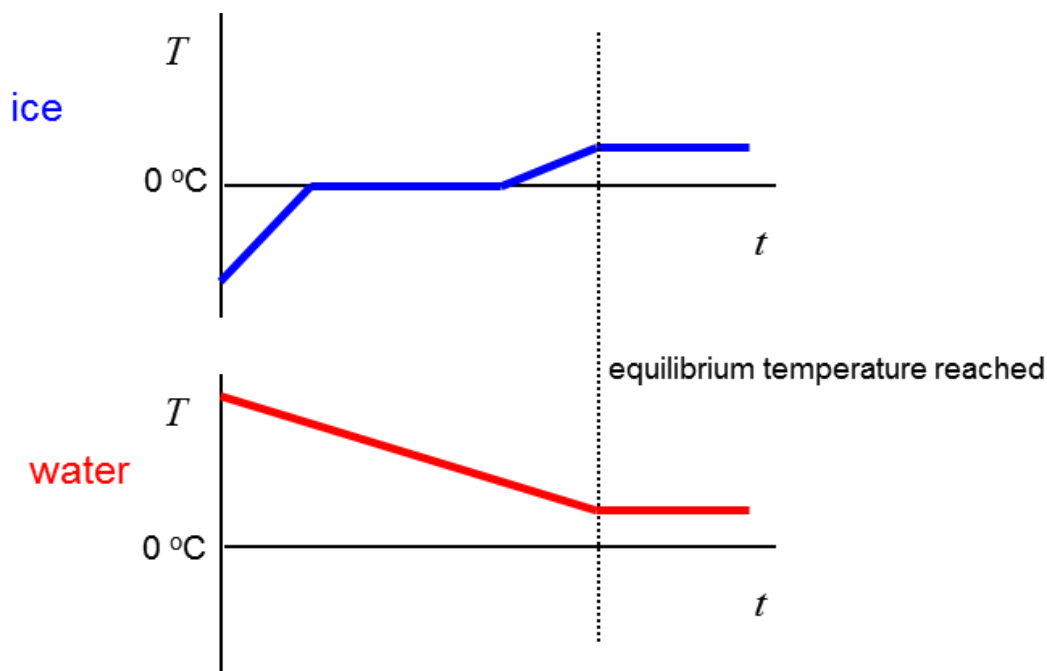


WATER losses energy to the ice



Heat gained by ice Q_{ice} = heat lost by water Q_{water}

$$Q = m c \Delta T \quad Q = m L$$



temperature rise for ice to melt $\Delta T_{\text{ice1}} = 0 - (-10) ^\circ\text{C} = 10 ^\circ\text{C}$

temperature rise of melted ice $\Delta T_{\text{ice2}} = (5 - 0) ^\circ\text{C} = 5 ^\circ\text{C}$

temperature fall for water $\Delta T = (20 - 5) ^\circ\text{C} = 15 ^\circ\text{C}$

N.B. all temperature changes are positive

$$c_{\text{ice}} = 2000 \text{ J.kg}^{-1}.\text{K}^{-1} \quad c_{\text{water}} = 4190 \text{ J.kg}^{-1}.\text{K}^{-1}$$

$$L_f = 3.33 \times 10^5 \text{ J.kg}^{-1}$$

Conservation of energy Energy lost by water = Energy gained by ice

Specific heat capacity $Q = m c \Delta T$

Phase change $Q = m L$

energy lost water (fall in temperature) = energy gained by ice (rise in temp ice + melting + rise in temp water)

$$m_{\text{water}} c_{\text{water}} \Delta T_{\text{water}} = m_{\text{ice}} c_{\text{ice}} \Delta T_{\text{ice1}} + m_{\text{ice}} L_f + m_{\text{ice}} c_{\text{water}} \Delta T_{\text{ice2}}$$

$$m_{\text{ice}} = \frac{m_{\text{water}} c_{\text{water}} \Delta T_{\text{water}}}{c_{\text{ice}} \Delta T_{\text{ice1}} + L_f + c_{\text{water}} \Delta T_{\text{ice2}}}$$

$$m_{\text{ice}} = \frac{(4)(4190)(15)}{(2000)(10) + (3.33 \times 10^5) + (4190)(5)} = 0.67 \text{ kg}$$

In such problems, you need to be careful to include all changes in temperature and changes in phase.

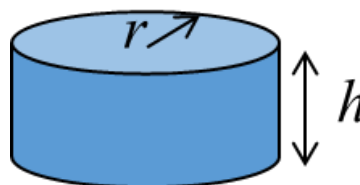
Example

The energy released when water condenses during a thunderstorm can be very large. Calculate the energy released into the atmosphere for a typical small storm.



Solution

Assume 10 mm of rain falls over a circular area of radius 1 km



$$h = 10 \text{ mm} = 10^{-2} \text{ m} \quad r = 1 \text{ km} = 10^3 \text{ m}$$

$$\text{volume of water } V = \pi r^2 h = \pi (10^6)(10^{-2}) = 3 \times 10^4 \text{ m}^3$$

$$\text{mass of water } m = ? \text{ kg} \quad \text{density of water } \rho = 10^3 \text{ kg.m}^{-3}$$

$$m = \rho V = (10^3)(3 \times 10^4) = 3 \times 10^7 \text{ kg}$$

latents heats – change of phase

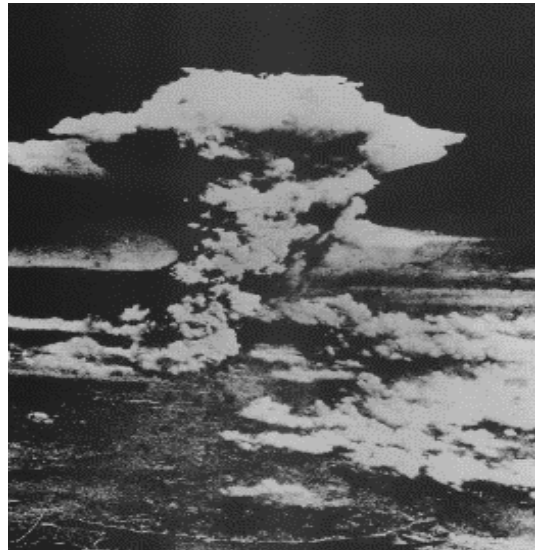
$$Q = mL \quad L_v = 2.26 \times 10^6 \text{ J.kg}^{-1}$$

$$Q = m L_v = (3 \times 10^7)(2.26 \times 10^6) = 7 \times 10^{13} \text{ J}$$

The energy released into the atmosphere by condensation for a small thunder storm is more than 10 times greater than the energy released by one of the atomic bombs dropped on Japan in WW2.



This calculation gives an indication of the enormous energy transformations that occur in atmospheric processes.



Activity

Manufacturers claim that microwaves give out a certain amount of power, usually around 700 or 800 W. By placing a litre of water in the microwave and heating it for a certain time, by measuring the temperature of the water before and after heating we can work out whether the manufacturer's claim is true.

$$\text{Power} = (\text{Energy Transferred})/(\text{time interval})$$

1 litre of water has a mass of 1 kilogram

specific heat of water is $c = 4190 \text{ J.kg}^{-1}.\text{K}^{-1}$.