SOME BASIC DEFINITIONS OF THERMODYNAMICS

- Heat is the name used for energy transferred by heating. [1]
- Heating is the name of the energy transfer process by which energy moves from a higher temperature body to a low-temperature body. [1] [1]
- Temperature is a measure of hotness of an object on a given scale. The hotter an object, the higher its temperature [1]. [1] In scientific terms, it is a measure of the average translational kinetic energy associated with the disordered motion of atoms and molecules within a substance. [2]
- Internal energy is the sum of all the randomly distributed kinetic and potential energies of the particles within a substance. [3]

The words 'hot' and 'heat' can cause some confusion. Hot is used to mean at a high temperature whereas heat is used to describe the amount of thermal energy or internal energy. An object does not possess 'heat' but it has internal energy that can be increased by transferring energy from a higher temperature object to the lower temperature object, i.e. heating [1]. If one object is at a higher temperature than another, there is a net flow of thermal energy from the hotter (higher temperature) object to the cooler (lower temperature) one. This heat flow will continue until thermal equilibrium is reached [2]. That is, there is no net heat flow of energy between the two bodies because they are both at the same temperature [4]. The second law of thermodynamics defines this, "energy will disperse from a concentrated form to a dilute form if it is not hindered from doing so". [2]

Particles in a substance have potential energy due to the electrostatic potential energy stored between particles or the electrostatic interatomic/intermolecular forces between the particles [3]. The lowest possible temperature is 'absolute zero' and corresponds to OK or -273.15°C. At absolute zero, a substance has minimal kinetic energy (that is the particles have no kinetic energy). However, it is not possible to reduce the potential energy of a substance to zero, even at 0 kyso an experiment can't create a substance with a zeroth energy state.

The zeroth law of thermodynamics states that if two thermodynamic systems (systems capable of transferring heat between each other) are each in thermal equilibrium with a third, then they must also be in thermal equilibrium with each other [3]. [2] The zeroth law of thermodynamics explains thermal equilibrium as an equivalence relationship. For example, "If two systems are at the same time in thermal equilibrium with a third system, they are in thermal equilibrium with each other." [2]

This equivalence relationship allows for the division of a set of systems each in its own thermodynamic equilibrium into subsets that can be uniquely 'tagged'. Temperature is an example of a labelling process, which is quantitative, using real numbers [5][4]. The zeroth law justifies the use of thermometers as suitable thermodynamic systems to provide such a labelling and thus give a measure of 'hotness'.

THE SCALE OF TEMPERATURE

The scale of temperature is a quantitative way to measure temperature, using any number of possible empirical temperature scales.

An empirical scale measures a quantity relative to a parameter. In the case of temperature, the quantity of heat in a system is measured relative to a fixed parameter, a thermometer. Empirical scales are purely based on measurements and so do not represent the absolute temperature. [6] [5]

All scales of temperature, including the modern thermodynamic temperature scale, are scales relative to the thermal properties of a particular substance or device.

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THE CELSIUS SCALE

The Celsius scale (known as the centigrade scale pre-1948) is a temperature scale used by the International System of Units (SI). The Celsius scale is based on two fixed points: the freezing point of water and the boiling point of water at 1 atm pressure. The scale is then divided into 100 increments between $0^{\circ}C$ and $100^{\circ}C$ [3]. [2]

The degree Celsius, similar to the Kelvin, is suitable for expressing both temperatures along the scale and intervals of temperature change. The Celsius scale is named after the Swedish astronomer, Anders Celsius (1701–1744), who proposed the Celsius scale [7]. [6]

In 1954, the unit degree Celsius (⁰C) and the Celsius scale were redefined by the two fixed points absolute zero and the triple point of Vienna Standard Mean Ocean Water (VSMOW), a specially purified water, with a known isotopic composition. This allows the Celsius scale to be linked to the more robust Kelvin scale (unit K), which defines the SI base unit of thermodynamic temperature [7]. [6]

A temperature interval of one degree Celsius equates to a difference of one kelvin, with the null point of the Kelvin scale (0 K) at -273.15 °C and the null point of the Celsius scale (0 °C) at exactly 273.15 K. A large problem with the Celsius scale is that although the two fixed points seem easy to obtain, they vary significantly depending on the surrounding atmospheric pressure [6]. [5]

THE THERMODYNAMIC TEMPERATURE SCALE

The thermodynamic scale is different to empirical scales since it represents absolute temperatures. Lord Kelvin proposed that the scale is based on the laws of thermodynamics rather than fixed parameters relative to the properties of a material [8]. [7] This scale is defined by the third law of thermodynamics: *"The entropy of a perfect crystal at absolute zero is exactly equal to zero."* [9] [8] Where **entropy** is defined as the quantitative measure of disorder or the number of possible microstates in a system [10] [9]. Thus, a perfect crystal has only one minimum energy state, with only one microstate available. Since temperature represents the average random kinetic energies of particles within a substance, the statement of the third law holds true; absolute zero (0 K) must represent a state or the minimum possible internal energy. [8] [9]

Absolute zero is defined as being exactly 0 K and -273.15 °C. The triple point of water is the temperature at which water can exist in all three of its phases (solid, liquid and vapour forms) all in thermal equilibrium with each other. Coincidently, this is commonly termed 'the freezing point of water' at atmospheric pressure. The Kelvin scale has one hundred increments between the triple point of water and the boiling point of water. This means that the temperature of the triple point of water is defined as exactly 273.16 K (0.01 °C) [8] and the boiling point of water is exactly 373.16 K (100.01 °C).

THE ROLE OF GAS LAWS IN DEFINING THE THERMODYNAMIC TEMPERATURE SCALE

The gas laws are the conclusions of experiments investigating the relationship between the pressure, volume and temperature of an ideal gas. [2] [3]





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If the volume and mass of a gas (hence the number of moles) remains constant, the pressure of an ideal gas is directly proportional to its absolute thermodynamic temperature in Kelvin. An experiment can be conducted to measure the pressure exerted by a gas at different temperatures. The results are plotted on a graph similar to the one shown below. Extrapolating the graph beyond the axis estimates the temperature at which the pressure exerted by the gas is exactly zero. At this point, the gas particles must have minimum kinetic energy as they have no motion to cause any collisions responsible for pressure, and hence the lowest possible temperature. [11] [10]



The absolute zero of temperature has not been attained in practice; it is a theoretical prediction found by extrapolation of experimental results.

`Charles' law' is an equation that models the experimental data shown by the graph above and allows for a theoretical value of absolute zero to be found. [10] [11]

"For a fixed mass of gas at constant pressure, the volume is directly proportional to the Kelvin temperature." [11] OR $\frac{Pressure (Pa)}{Absolute Temperature (K)} = constant$

MEASURING TEMPERATURE WITH AN ANALOGUE CONTACT THERMOMETER

When a calibrated thermometer is in thermal contact with a system, it will reach thermal equilibrium once there is no longer a net heat flow between the two systems. A thermometer is then capable of indicating a quantitative measure of the temperature of the system [2]. Liquid-in-glass thermometers based on the principle that a contained material or substance expande as temperature rises. A bulb thermometer comprises of a glass bulb, containing a small quantity of liquid, attached to a narrow glass tube. As the temperature is changed, there is a small change in volume of the liquid and this drives the liquid up or down the narrow glass vessel. A scale on the glass tube correlates the expansion of the liquid to a specific temperature. Common types of bulb thermometers include alcohol-in-glass and mercury-in-glass [12]. [11]

The advantage of a mercury thermometer over an alcohol one is that mercury, as a liquid metal, has a higher thermal conductivity than alcohol and so the thermometer responds to temperature changes more rapidly. Alcohol thermometers will also lose their calibration when they are left at a high temperature for a prolonged time. This is because alcohol has a higher vapour pressure; in fact, it is similar to atmospheric pressure. Alcohol vapour fills the empty space in the glass vessel above the maximum current temperature level. Over time, the alcohol cools back down again and condenses into this space so is 'lost' from the glass bulb, offsetting the manufacturer's calibration [13]. Mercury thermometers are much less susceptible to this effect and so hold their manufacturer's calibration more robustly. Another advantage of a standard mercury thermometer is that it can cover a wider temperature range, from -38.83 °C to 356^oC [14]. Outside of this range, the mercury freezes or evaporates respectively. However, mercury is a potent neurotoxin, and every thermometer that contains it is a potential environmental threat. Mercury is toxic to the body and so represents a high health risk if it leaks out. [12] [11] Instead, it is more common to find alcohol-in-glass thermometers, especially in school laboratories. Both alcohol and mercury are substances that were chosen for use in a bulb thermometer because their rate of expansion with temperature is relatively linear (i.e. the volume is directly proportional to the temperature).

STUDENT: Adam Ash SuttlePAG 12.2 Research Project30.03.2018However, all such analogue thermometers are not as accurate as their digital counterparts. The linear relationbetween the volume of the liquids and the temperature is only true for the relatively small temperature rangesthat the thermometers are used over. [11] [12]

The liquid in glass thermometers are calibrated by a manufacture by placing scale divisions onto the glass tube of the thermometer when the height of the liquid within the thermometer corresponds to a known temperature. The thermometer must be in thermal equilibrium with at least two objects of different known temperatures in order to calibrate it. [11] [12]

By placing a thermometer in pure ice water and allowing it to reach thermal equilibrium, the 0°C mark can be placed on the thermometer. The thermometer can then be placed in pure boiling water and allowed to reach thermal equilibrium. The 100°C mark can then be placed on the scale. The 100 scale divisions between these fixe points are then drawn onto the thermometer. Calibration must occur at atmospheric pressure [1 atm]. [12] [14] A mercury thermometer's upper-temperature limit can be extended by adding an inert gas into the space above the liquid within the thermometer. This increases the pressure on the liquid and so increases the boiling point of the liquid.

A problem with liquid-in-glass thermometers is that different substances used in them have different expansion properties. A coloured alcohol thermometer will give different intermediate readings between the 0°C to 100°C scale to a mercury thermometer. This is because their expansion rates are not entirely linear and differ. [6]

MEASURING TEMPERATURE WITH A DIGITAL CONTACT THERMOMETER

A thermocouple an electronic device used for measuring temperature. A thermocouple is comprised of at least two metal junctions. One metal junction is in contact with a body to be measured, the other is a reference junction and is connected to a body of known temperature. The thermocouple measures an unknown temperature of a body relative to the known temperature of the other body. A thermocouple device works by using three effects: [13] [15]

When two different metals are joined together at two junctions, an electromotive force (emf) is generated between the two metal junctions



Thermocouple Circuit

- 1. Seebeck effect: The magnitude of induced e.m.f. is dependent on the different metals used.
- 2. **Peltier effect:** The magnitude of the induced e.m.f. is dependent on the different temperatures of the two junctions of the circuit.
- 3. **Thomson effect**: The magnitude of induced e.m.f. is dependent on the temperature gradient along the entire length of the conductors within the circuit.

The e.m.f. suggested by the Thomson effect is negligible and it can be ignored by making a suitable selection of the metals for the two junctions. The Peltier effect is the most significant of the three for the working principle of a thermocouple as a thermometer. [15]

The two junctions of dissimilar metals are maintained at different temperatures so a 'Peltier e.m.f. ' is generated within the circuit and it is the function of the temperatures of two junctions. When the temperature of the two junctions is equal, the Peltier e.m.f. is equal but opposite in direction at each junction so they cancel. The current flowing around the Peltier circuit is zero. The total e.m.f. across the circuit is measured by a high-resistance voltmeter or the current flowing through the circuit can be measured by an ammeter. The e.m.f. or current

STUDENT: Adam Ash SuttlePAG 12.2 Research Project30.03.2018measured can be calibrated directly against the unknown temperature. This means that the voltage or currentoutput obtained from the thermocouple circuit can give a value of an unknown temperature directly. [13] [15]

MEASURING TEMPERATURE BY EMITTED RADIATION

Stefan-Boltzmann's law relates the temperature of a body to the emitted electromagnetic radiation from its surface. [14] [2] The law refers to the concept of a blackbody: an idealised object that emits an equal amount of infrared radiation as that given to it. Increasing the temperature of an object will result in a larger propertion of energy being emitted as infrared radiation. The total emissive power (E) of a black body is proportional to the fourth power of the body's absolute temperature (T): $E = \varepsilon \sigma A T^4$ Where: where E is the total radiant energy flux emitted per unit area, σ is Stefan's constant, 5.67 × 10–8 W m⁻²K⁻⁴, A the area, and ε the emissive efficiency and T is the surface temperature. [14] [2]

Common terrestrial bodies do not have significant amounts of heat energy (like stars) and so almost all the surface radiation emitted falls within the wavelength range of $3-100 \ \mu\text{m}$. This long wavelength radiation is infrared is often referred to as the thermal infrared (TIR). [16]

The limitation of using such a relationship between surface temperature and emitted infrared is the Stefan-Boltzmann law is devised for black-bodies that are perfect emitters, whose emissivity \in =1. However, most natural surfaces are not perfect emitters as their emissivity varies with wavelength. Most infrared sensors/thermocouples approximate their objects to be approximated 'grey bodies' which have a constant and diffuse emissivity with no wavelength dependence. This does, however, make them less accurate than an absolute temperature of the surface, measured by an electronic contact thermometer. Moreover, not all the radiation emitted by a surface reaches the sensor; some wavelengths may be absorbed by atmospheric gases and suspended particles. The sensitivity of the sensor is not equal to all thermal wavelengths. [16]

Infrared thermometers (IRTs) are non-imaging and utilise non-contact thermocouples and the Stefan-Boltzmann law. They are commonly portable, hand-held temperature guns' and some models have the option of continuous measurements - which have to be connected to a data logger. They measure the average temperature a surface based on the infrared radiation emitted from the surface within the field of view of the sensor. The advantages of an IRT are: they are relatively cheap, data can be recorded rapidly and they do not require an external power source. They can be portable in-the-field or installed as a permanent device. [17]

Thermal imaging cameras predominantly use microbolometer sensors. They are more expensive than IRTs to manufacture as they have more parts and sophisticated electronics. However, a major advantage is that provide images with thermal temperatures and a colour key showing relative temperatures across the image. Thermal imaging cameras are very precise and often give. Thermal imaging cameras have the capability to record thousands of individual temperature measurements of a surface temperature at different points across the surface area whereas an ART will only record a singular surface temperature at one point. This makes thermal imaging cameras very convenient and quick to use as they are a high-throughput measurement device. [17]

CONCLUSION

The concept of temperature is as fundamental to physical properties as other common base quantities agreed by Systeme International (SI) measurements —time, length, mass, electrical current, amount of substance, luminous intensity [1]. Temperature is an important property of a system that determines the direction of energy transfer based on the second law of thermodynamics. In a qualitative manner, the temperature can be used to describe the sensation of warmth or coldness. When a calibrated thermometer is put in thermal contact with a system it reaches thermal equilibrium and has a scale that allows for a quantitative measure of the temperature. Heat energy refers to the state of energy an object (the sum of randomly distributed kinetic energies). [2]

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An iceberg has a low temperature (low average kinetic energy) but it has a very large heat due to the vast number of particles/molecules. A lit match, however, has a high temperature but lower heat than an iceberg as there are significantly fewer particles. [18]

Together, heat and temperature make up major components of the three principal laws of thermodynamics.

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