Thermodynamics is the physics of heat, what it is and how it is transported. Heat is the kinetic energy associated with the random motion of a large number of molecules which constitute a gas, liquid or solid. It is a statistical theory ie. properties such as pressure, temperature and density are averages.

The kelvin scale of temperature (T) is proportional to the mean kinetic energy of molecules for a gas:

$$U = \alpha \times \frac{1}{2} n RT$$

Molar gas constant 8.314 $Jmol^{-1}k^{-1}$

Internal energy

Degrees of freedom of molecular motion (x,y,z so $\alpha=3$ for most gases)

moles of gas

'Absolute' temperature /k

Ie where we can ignore the effect of intermolecular forces as molecules are moving too fast and density is low ie mean free path >> molecular dimensions

1 mole = N_A molecules
$N_A = 6.02 \times 6^{23}$
(Avogadro's number)

Celsius scale is based upon the freezing (0°C) and boiling (100°C) points of water at at 1 atmosphere (101,325 Pa)
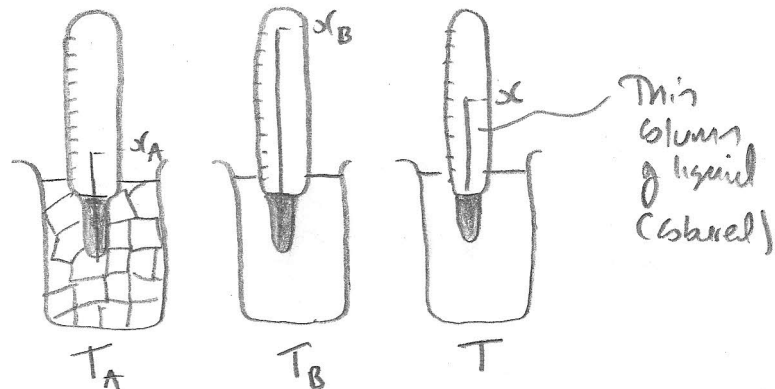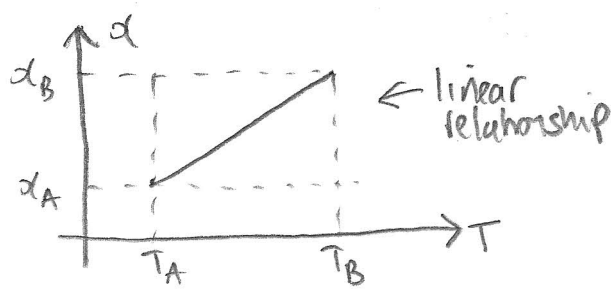
$$T_C = T - 273$$

Fahrenheit is based upon cool brine (0°F) and the human body temperature (37°C or 100°F)

$$T_F = \frac{9}{5}(T-273) + 32$$

when $T_C = -40°C$, $T_F = \frac{9}{5}(-40) + 32 = -40$ ie $T_C = T_F$

To measure temperature, we ideally require a sensor that varies (in a measurable quantity) in a linear fashion between two fixed points of known temperature (eg 0°C and 100°C).

Example: **In-glass thermometer**

α vs T graph: ← linear relationship, with α_B at T_B and α_A at T_A

Thin column of liquid (coloured)

e.g.: T_A = Iced water ($0°C$)
T_B = $100°C$

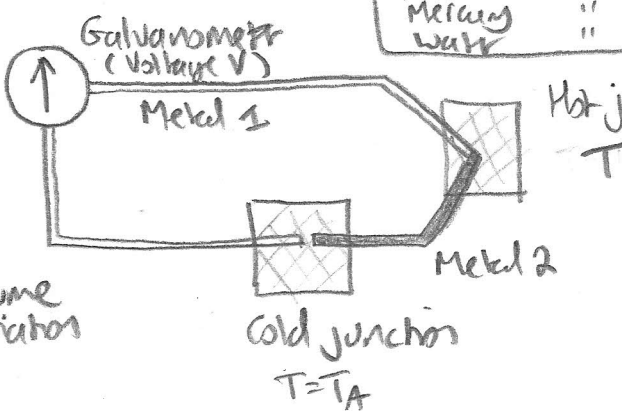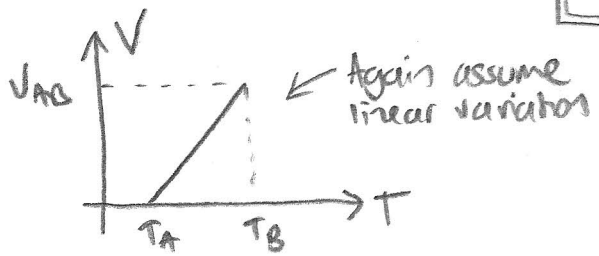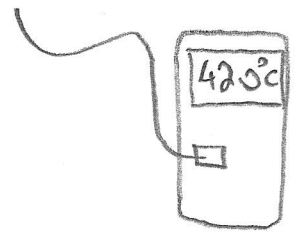$$ T = T_A + (T_B - T_A) \times \frac{\alpha - \alpha_A}{\alpha_B - \alpha_A} $$

So measure rise of liquid $\alpha - \alpha_A$ as a proportion of whole range $\alpha_B - \alpha_A$, and you have the proportional temperature rise from T_A over the range $T_B - T_A$

Enhance **sensitivity** ($\propto \frac{d\alpha}{dT}$) by

* Reduce diameter of liquid column
* increase volume of liquid
  [But this might make the thermometer too big for practical use]

* CHOOSE LIQUID SO IT IS A LIQUID!

	Melt	Boil
Alcohol	$-114.4°C$	$78.3°C$
Mercury	" $-38.9°C$	" $356.6°C$
Water	" $0°C$	" $100°C$

Example: **Thermocouple**
→ Based upon **thermoelectric effect**

Galvanometer (Voltage V)
Metal 1
Metal 2
Cold Junction $T = T_A$
Hot junction T

90% Ni
10% Cr

Chromel-Alumel (K type) are common pairs {but not Nickel is magnetic Curie temp $356°C$}

V vs T graph: ← Again assume linear variation, with V_{AB} at T_B, starting at T_A

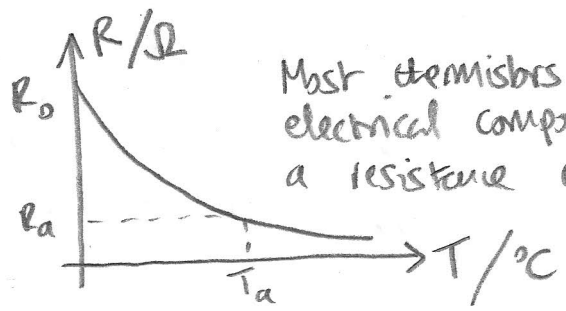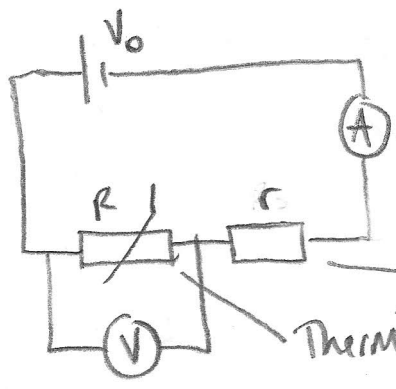So $$ T = T_A + (T_B - T_A) \times \frac{V}{V_{AB}} $$

* High melting point so much greater range of T than in-glass.
* Can be made very small
* Responds fast as small thermal mass
* Can be robust to harsh environments

(2) * 95% Ni, 2% Al, 2% Mn, 1% Si

Example: **Thermistor**
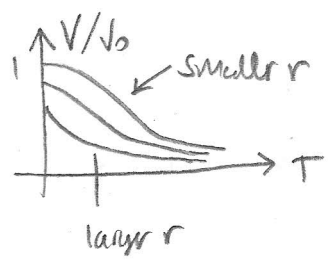

Most thermistors (a semiconductor electrical component) will have a resistance that exponentially decays with temperature

$$\frac{1}{2} \quad \boxed{R = R_0 e^{-kT}} \quad *$$

[Find k from $\quad R_a = R_0 e^{-kT_a} \quad$ so $\quad \ln\left(\frac{R_a}{R_0}\right) = -kT_a$

$\therefore \quad \boxed{k = \dfrac{\ln R_0/R_a}{T_a}} \quad \uparrow$ ie find (R, T) at a fixed point via measurement.
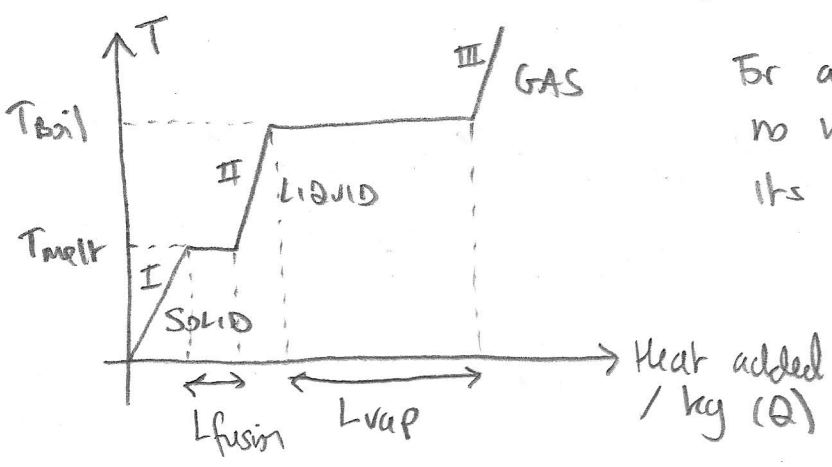
Note $\quad \boxed{V = \dfrac{V_0 R}{R+r}}$

Compared to thermocouple and in-glass thermometer a thermistor is highly non-linear

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LATENT HEAT ← the amount of energy required to overcome intermolecular forces and ∴ change the state of a substance from solid to liquid to gas.

For an insulated substance (ie no heat loss) which is heated from its solid phase

$\swarrow \frac{1}{2} \, 1/\text{gradient}$

I : $\dfrac{dQ}{dT} = C_{solid}$

$\uparrow$ $\boxed{\text{specific heat capacity}}$

II : $\dfrac{dQ}{dT} = C_{liquid}$

III : $\dfrac{dQ}{dT} = C_{gas}$

Specific means 'per unit mass'

L_{fusion} is the specific **latent heat of fusion** (solid ⟷ liquid)

L_{vap} " " " " " **Vaporization** (liquid ⟷ gas)

Which occurs at constant T

So when gas → liquid ENERGY IS RELEASED. This drives many weather systems such as Hurricanes. (ie when water vapor condenses as it rises to form clouds).

* or at least decays strongly with temperature T

③

	T_{melt}/°C	T_{boil}/°C	L_{fus}/Jkg⁻¹	L_{vap}/Jkg⁻¹	c_{solid}	c_{liq}	c_{gas}
Water	0	100	33.5×10^4	22.6×10^5	2090	4186	1930
Alcohol (ethyl)	−114	78.3	10.8×10^4	8.55×10^5	970	2440	1000
Copper	1083	2566	20.7×10^4	47.3×10^5	385	386	380

* Note $L_{vap} \gg L_{fus}$

* Note $c_{liq} > c_{solid}$ for water & alcohol c in $Jkg^{-1}k^{-1}$

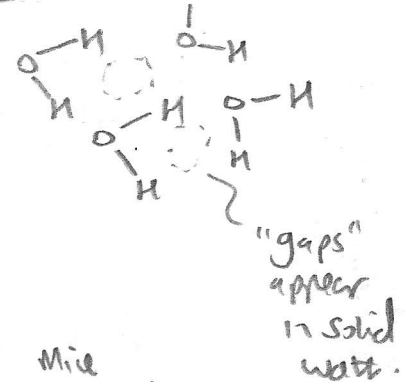This can be explained by the nature and structure of the water and alcohol molecules e.g hydrogen bonding, More modes of motion than translation $H \overset{O}{\longleftrightarrow} H$ etc   ↖ which explains why liquid water is more dense than solid water

In each particular state

$$\boxed{\Delta Q = cM\Delta T} \longleftarrow \text{Temperature change}$$

↑ Total heat added (to M kg now!)
↑ specific heat capacity
↖ mass

"gaps" appear in solid water.

Calculating L_{fus} for water

* Determine mass of beaker
* Add warm water, record temperature, record new mass
* Add an ice cube of known temperature (assume 0°C)
* Wait till melted, record T and total mass.

Heat balance (assume no loss)

ICE $M_{ice} L + c M_{ice}(T - T_{ice})$
(energy added)

WATER $c M_W (T_W - T)$
(energy lost to ice cube)

↑ if ice cube melted AND raised to temp T.

Insulated beaker
① m_B ← mass balance.
② T_w Ice T_{ice} T_w $M_B + M_W$
③ T T $M_B + M_W + M_{ice}$

← You can do this more dynamically using a thermocouple inside the beaker

[DATALOGGER]

A add warm water
B add ice cube
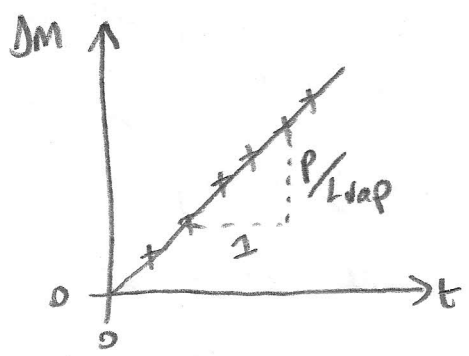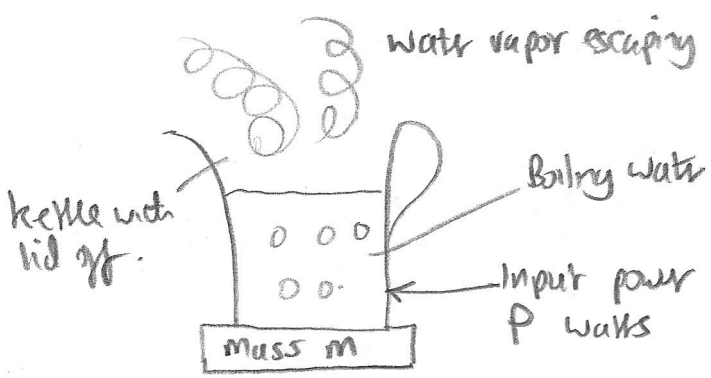C ice cube melted
D heat loss, system temp → room temperature

④

So

$$L = \frac{C M_W (T_W - T) - C M_{ice}(T - T_{ice})}{M_{ice}}$$

For water $L \simeq 335 \text{ kJ/kg}$

Calculating Lvap for water

kettle with lid off.
water vapor escaping
Boiling water
Input power P watts
mass m

ΔM vs t graph with gradient P/L_{vap}

Wincell 2018
P = 1.04 kw
$\Rightarrow L_{vap} = 2480 \text{ kJ/kg}$

* Heat water in kettle
* once boiling has started, zero mass balance and log mass lost (the balance will read -ve) vs time.

* If no heat loss (there will be some!)

$$Pt = \Delta M \times L_{vap}$$

heat input from electrical supply

Energy required to vaporize ΔM kg g water.

So $$\frac{d\Delta M}{dt} = \frac{P}{L_{vap}}$$

∴ Find gradient g ΔM vs t line g best fit and

$$L_{vap} = \frac{P}{gradient}$$

Since non-negligible heat loss, expect measurement Lvap to be an over-estimate. For water $L_{vap} \simeq 2260 \text{ kJ/kg}$
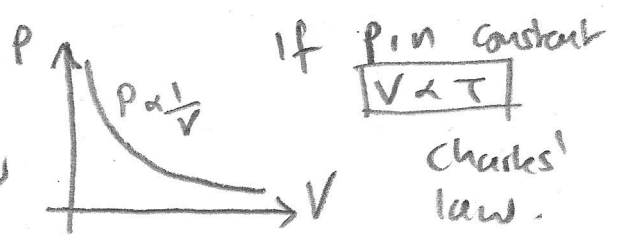
IDEAL GASES $pV = nRT$

* Neglect intermolecular forces
* Assumes far many 'point particles' colliding elastically
* Mean free path g molecules prior to collision >> molecular size

T in constant: $pV = const$ — Boyle's law

P pressure
V volume
n # moles g gas
R molar gas constant $8.314 \text{ J mol}^{-1}\text{K}^{-1}$
T Temperature /K

$P \propto \frac{1}{V}$

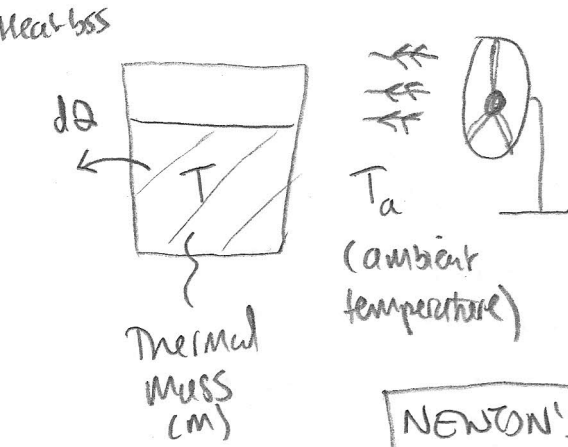If P in constant
$V \propto T$
Charles' law.

Cooling Curves

If one can prevent localized heating of the surrounding air (eg by use of a fan) and T is low enough for ∎radiative∎ heat transfer to be ≈ negligible

∎CONDUCTION∎ is the main mechanism for heat transfer to ambient.

Heat loss

dQ

T

Thermal mass (m)

T_a (ambient temperature)

∎NEWTON'S LAW OF COOLING∎ (based upon Fourier's law of conduction - ie ∎heat flux ∝ temperature gradient∎)

{ Heat flow ∝ temp. difference }

$$\frac{dQ}{dt} = -\alpha(T - T_a)$$

$$dQ = mc\,dT$$

↑ mass ↑ specific heat capacity

(α will be ∝ to surface area of thermal mass and ∝ $\frac{1}{\text{thickness}}$ ↖Δx of any walls)

Note ∎$\frac{kA}{\Delta x} = \alpha$∎

k is the THERMAL CONDUCTIVITY

So

$$mc\frac{dT}{dt} = -\alpha(T - T_a)$$

$$\int_{T_0}^{T} \frac{dT}{T - T_a} = -\frac{\alpha}{mc}\int_0^t dt \quad \therefore \quad \left[\ln(T - T_a)\right]_{T_0}^{T} = -\frac{\alpha t}{mc}$$

$\int \frac{f'(x)}{f(x)}dx = \ln|f(x)| + c$

$$\therefore \quad \ln\left(\frac{T - T_a}{T_0 - T_a}\right) = -\frac{\alpha t}{mc}$$

$$\therefore \quad \boxed{T = T_a + (T_0 - T_a)e^{-\alpha t/mc}}$$

$\boxed{\frac{mc}{\alpha} = \tau}$ is the 'characteristic time'

⑥