

Thermodynamics for Cryogenic Applications

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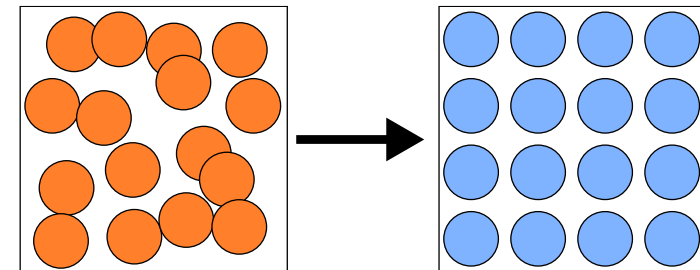
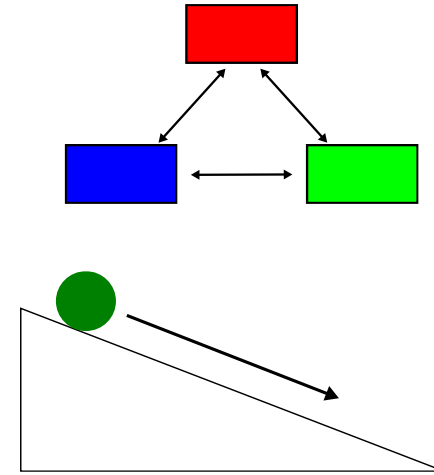


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Laws of Thermodynamics

0. Creates the concept of 'temperature'
"If two systems are both in thermal equilibrium with a third system, then they are in thermal equilibrium with each other"
1. Describes the overall conservation of energy
"Energy cannot be created or destroyed, only converted from one form to another"
Thermal energy ('heat'), work done, potential energy, electrical energy, internal energy
2. Creates the concept of 'entropy' – disorder
"Heat does not spontaneously pass from a colder to a hotter body"
Gives us a minimum amount of 'work' to do in order to perform refrigeration
Overall entropy stays constant (reversible) or increases (irreversible), never decreases.
3. Describes what happens at absolute zero temperature
"A system's entropy approaches a constant value as its temperature approaches absolute zero"
This is why we do what we do!



Temperature, Heat and Energy

- Which has more heat, a bath of cold baked beans or a piece of burning magnesium?

	Temperature (°C)	Heat (J)
Baked Beans	20	250 000 000
Magnesium	3 000	150



Temperature, Heat and Energy

- 'Heat', more strictly 'Thermal Energy'.
 - Total amount of energy held within a system in the form of vibrating molecules
 - Units as for any measurement of energy **J**, kWh (= 3 600 000 J), BTU (= 1 055 J), kcal (= 4 184 J)
- Temperature ($\neq$ Heat)
 - Measure of the average vibrational energy per atom in a substance
 - Proportion of how full a container of thermal energy is
 - Units **K**, °C (0 K = -273.15°C). °R, °F (0°R = -459.67°F)
- Power
 - Rate at which we are adding/removing heat or doing work. $P = \frac{Q}{t}$
 - Units as for any measurement of power: **W** (= J/s), kW (= 1000 W), BTU/h (= 0.29 W), hp ($\approx$ 740 W)
- Confusing stuff
 - kW/h – almost **never** need to write this – rate at which power is increasing
 - Power expressed in BTU – simply incorrect – probably means BTU/h
 - Power expressed in tons – rate of heat extraction required to freeze 1 ton of water in 24 hours



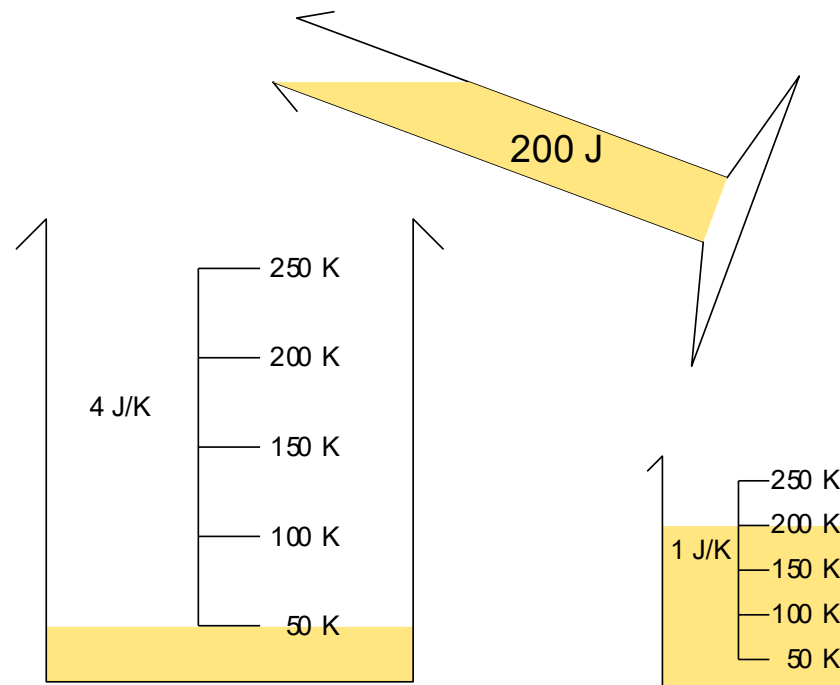
Heat Capacity

- How much energy do you need to put in to raise the temperature?
- Sometimes call this heat the 'sensible heat' – you can feel it.
- If something has a heat capacity of 1 J/K, then it takes 1 J of energy to warm it by 1 K.

$$\Delta Q = C \Delta T$$

- If you have twice as much stuff, you'll need twice as much energy. Usually use 'specific heat capacities'

$$\Delta Q = mc\Delta T$$



Substance	Specific Heat Capacity (J / K / kg)	Volumetric Heat Capacity (J / K / l)
Water	4 200	4 100
Aluminium	900	2 400
PTFE	1 500	680
Nitrogen	1 000	1.2
Helium	5 200	0.87



Example: Power, Energy, Heat Capacity, Temperature

- 3 kW electric heater, runs for 1 hour in 150 l of water (specific heat capacity 4 200 J / K / kg) which started at 10°C.
- What is the final temperature?
 1. How much heat has been put in?
3 000 J/s put in for $1 \times 60 \times 60 = 3\,600$ s
 $\Delta Q = 3\,000 \times 3\,600 = 10\,800\,000$ J (= 3 kWh)
 2. How much has the temperature risen?
150 l of water has mass 150 kg
Heat capacity of this is $150 \times 4\,200 = 630\,000$ J / K
 $\Delta T = 10\,800\,000 \div 630\,000 = 17$ K
 3. What is our final temperature?
 $10^\circ\text{C} + 17^\circ\text{C} = \underline{27^\circ\text{C}}$
 $10^\circ\text{C} = 283$ K
 283 K + 17 K = 300 K
 300 K = 27°C



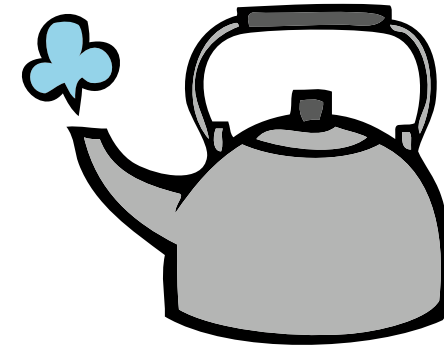
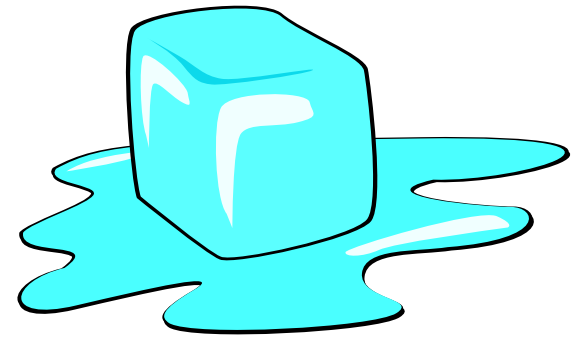
$$\Delta Q = C \Delta T$$
$$\Delta Q = mc \Delta T$$

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

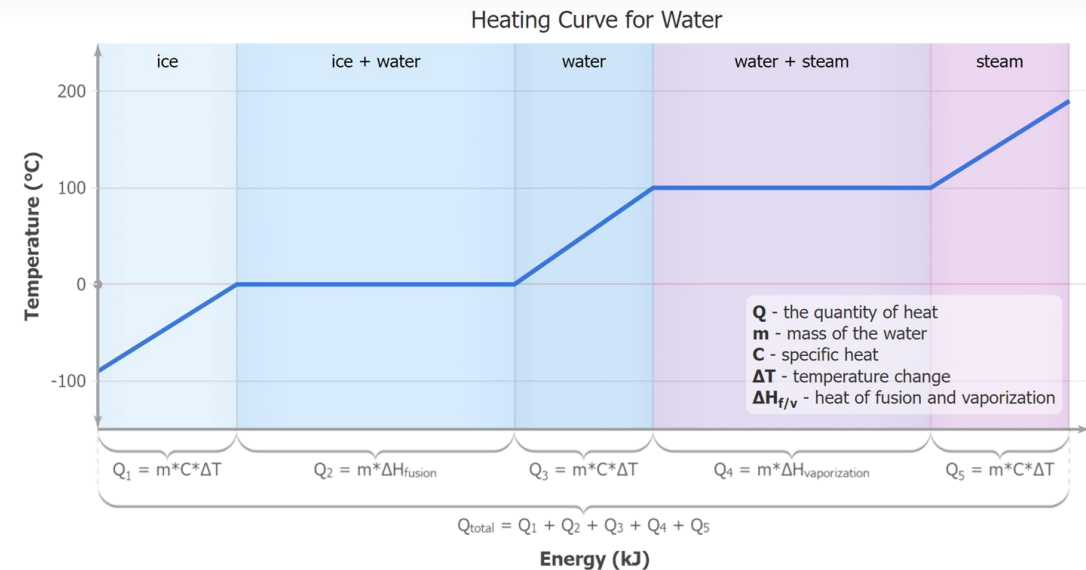


Latent Heat

- If we have some ice at 0°C and turn it into some water at 0°C, how has the amount of energy changed?
- What about changing some water at 100°C to some steam at 100°C?
- Latent heat of fusion: amount of heat released by a substance when we freeze it $\Delta Q = mL_{fusion}$
- Latent heat of vaporization: amount of heat absorbed by a substance when we boil it $\Delta Q = mL_{vaporisation}$



Substance	Specific Fusion Latent Heat (J / kg)	Specific Vaporisation Latent Heat (J / kg)
Water	330 000	2 300 000
Aluminium	400 000	10 000 000
Helium		21 000
Nitrogen	26 000	200 000



Example: Latent Heat

- How long does it take to defrost and warm to room temperature 500 g of pasta sauce using a microwave?
- Freezer at -18°C , room at 20°C , 900 W microwave. Assume sauce is all water.

1. Calculate sensible heat for warming from -18°C to 0°C

$$c_{\text{ice}} = 2\,100 \text{ J / K / kg}, m = 0.5 \text{ kg}, \Delta T = 18 \text{ K}$$

$$\Delta Q_1 = 0.5 \times 2\,100 \times 18 = 18\,900 \text{ J}$$

2. Calculate latent heat for melting

$$L_{\text{water, fusion}} = 330\,000 \text{ J / kg}, m = 0.5 \text{ kg}$$

$$\Delta Q_2 = 0.5 \times 330\,000 = 165\,000 \text{ J}$$

3. Calculate sensible heat for warming from 0°C to 20°C

$$c_{\text{water}} = 4\,200 \text{ J / K / kg}, m = 0.5 \text{ kg}, \Delta T = 20 \text{ K}$$

$$\Delta Q_3 = 0.5 \times 4\,200 \times 20 = 42\,000 \text{ J}$$

4. Calculate total heat and hence time given heating rate of 900 J / s

$$\Delta Q = 18\,900 + 165\,000 + 42\,000 = 225\,900 \text{ J}$$

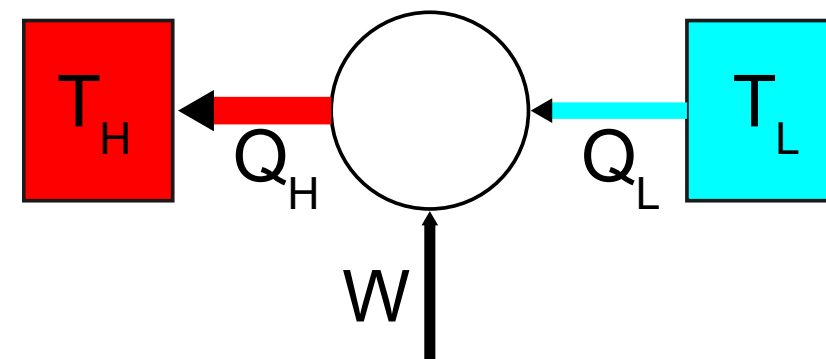
$$t = 225\,900 \div 900 = 251 \text{ s} = \underline{\underline{4 \text{ minutes, } 11 \text{ seconds}}}$$



$$\Delta Q = mc\Delta T$$
$$\Delta Q = mL_{\text{fusion}}$$

Moving Heat Around

- If we want to cool something down, we need to remove the sensible heat, and the latent heat(s) if we will be liquifying and/or freezing it.
- 1st Law: We can't destroy this thermal energy, so we move it to a reservoir at a higher temperature (usually ambient air).
- 2nd Law: We must put in some work (energy) to make the heat move from cold to hot, and the amount of heat coming out of the hot end will be more than is going in the cold end.
- The standard example is the Carnot refrigerator, which has the highest efficiency theoretically possible.



$$Q_H = Q_L + W$$

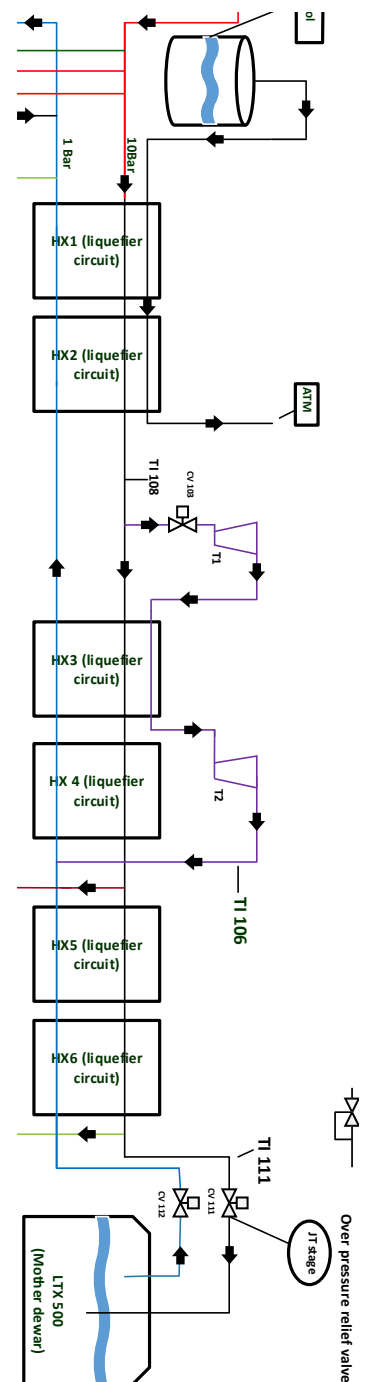
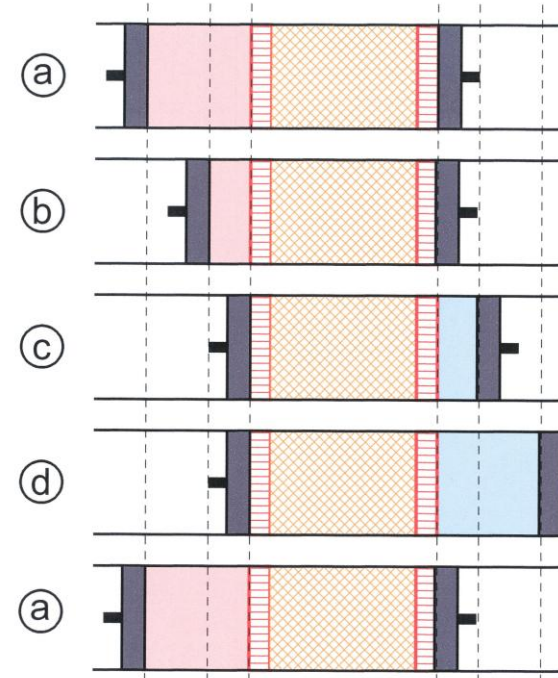
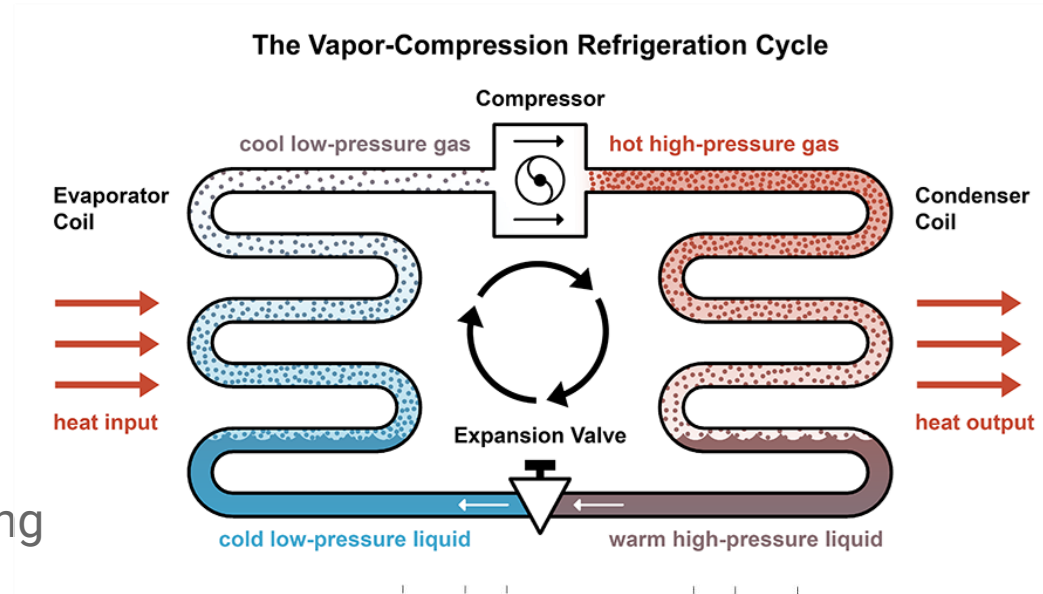
$$COP = \frac{Q_L}{W}$$

$$COP_{R,Carnot} = \frac{T_L}{T_H - T_L}$$

Device	T_H (°C / K)	T_L (°C / K)	COP
Air Conditioner	35 / 308	21 / 294	21
Freezer	21 / 294	-18 / 255	6.5
Helium Liquefier	21 / 294	-269 / 4.2	0.014

Practical Refrigeration Cycles

- Vapour-compression (reverse-Rankine) cycle
 - Very efficient, seen almost everywhere for refrigeration.
 - Uses high latent heat of vaporisation to move heat without moving much working fluid.
- For cryogenic applications, no working fluids exist that will condense at room temperature and boil at cryogenic temperatures. So use
 - Stirling cycle
 - Gas (reverse-Brayton) cycle combined with Joule-Thompson process



D. Keeping

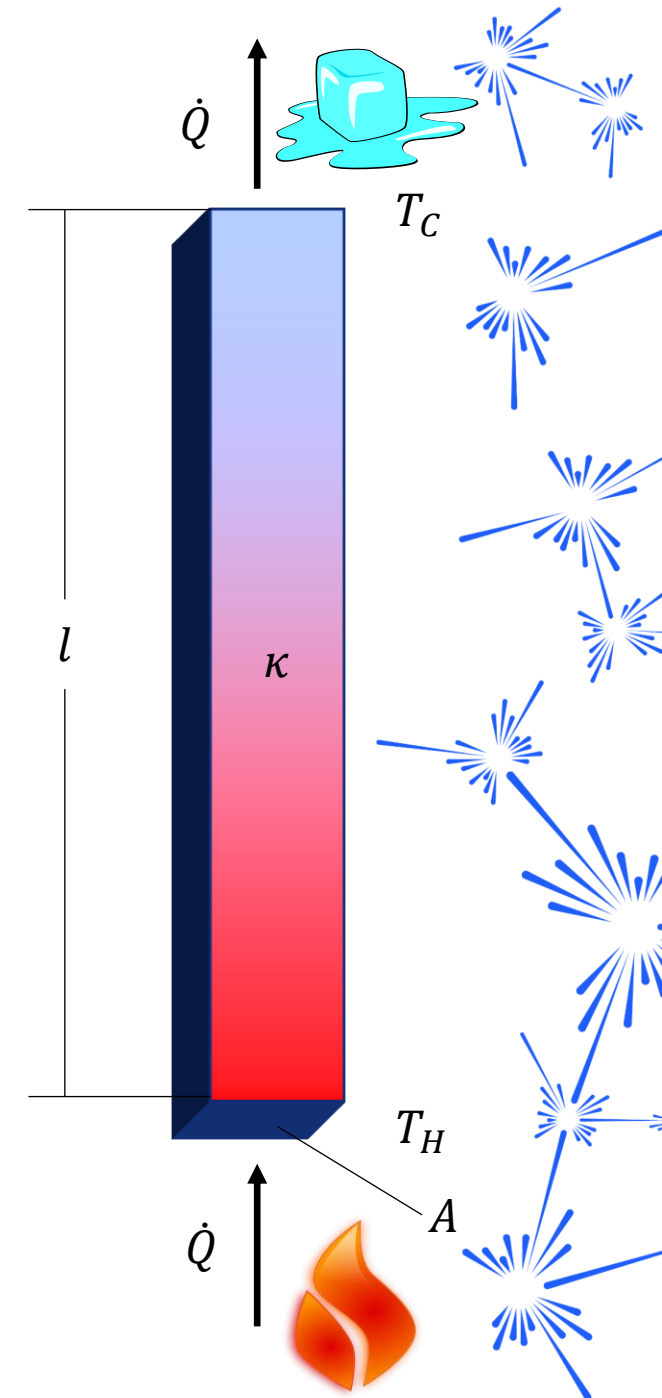
Thermal Transport – Conduction

- One can calculate the rate at which heat flows through a material (i.e. the power, $\dot{Q}$).

$$\dot{Q} = \frac{A\kappa(T_H - T_C)}{l}$$

- 1st Law tells us the heat in must be the heat out, it can't just disappear!
- κ is the thermal conductivity of the material.

Material	Thermal Conductivity (W / m / K)
Silver	406
Copper	401
Aluminium Alloy (6082)	180
Stainless Steel (304)	14.4
Alumina	36
G10 Fibreglass	0.288



Example: Helium consumption due to heat leaks from wiring

- How much does the helium boiloff in a cryostat increase after adding four 0.2 mm diameter copper wires from room temperature (293 K) into the helium bath (4.2 K)?

1. Calculate thermal power conducted down the wires.

$$\kappa = 4\,000^* \text{ W / m / K}, A = \pi \times 0.1^2 = 0.0314 \text{ mm}^2, l = 1 \text{ m}, T_H = 293 \text{ K}, T_L = 4.2 \text{ K}$$

$$\dot{Q} = 4 \times 3.14 \times 10^{-8} \times 4000 \times (293 - 4.2) \div 1 = 0.145 \text{ W}$$

2. Calculate boiloff rate from helium latent heat of vaporisation

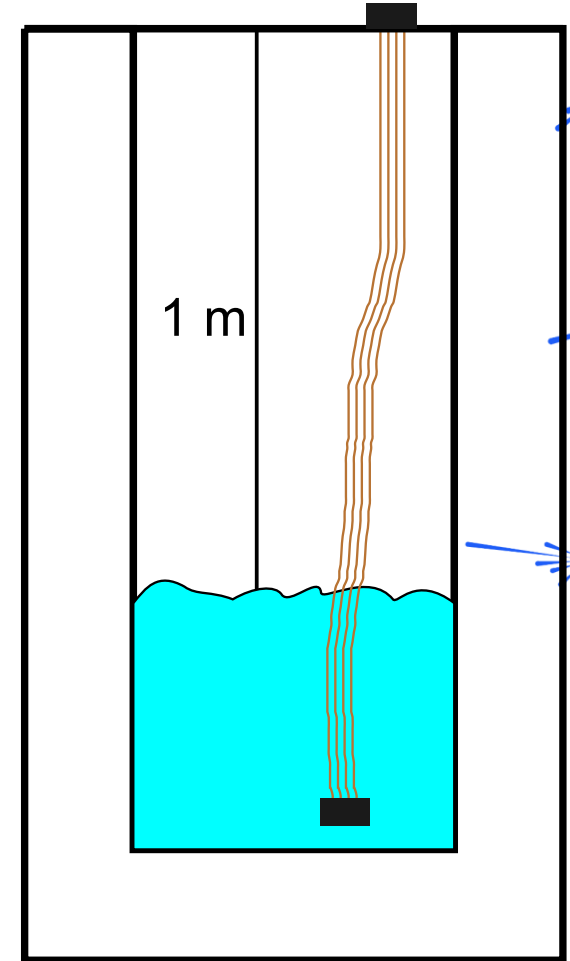
$$L_{\text{helium, vaporisation}} = 21\,000 \text{ J / kg}$$

$$\text{Rate} = 0.145 \div 21\,000 = 6.9 \times 10^{-6} \text{ kg / s}$$

3. Convert into more helpful units

$$1 \text{ day} = 24 \times 60 \times 60 = 86\,400 \text{ s}, \text{ liquid helium density } \rho = 0.125 \text{ kg / l}$$

$$\text{Rate} = 6.9 \times 10^{-6} \times 86\,400 \div 0.125 = 4.7 \text{ l / day}$$



$$\rho = \frac{m}{V} \quad \Delta Q = mL \quad \dot{Q} = \frac{A\kappa(T_H - T_C)}{l}$$

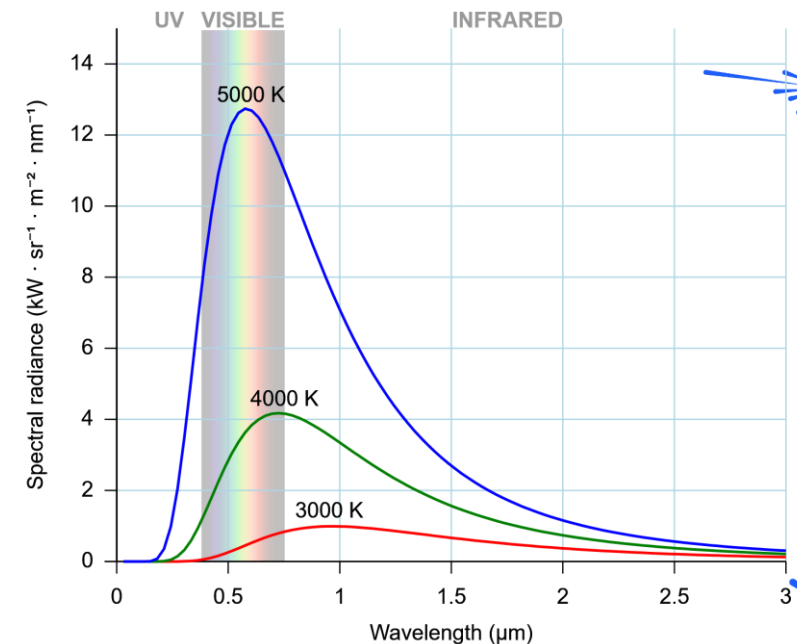
Thermal Transport – Radiation

- Everything above absolute zero radiates electromagnetic radiation.
- Called ‘black-body radiation’.
- The intensity and spectrum of this radiation depends on the temperature.
- The power radiated by a body is
$$P = A\epsilon\sigma T^4$$
- A is the surface area, $\sigma = 5.67 \times 10^{-8} \text{ W / m}^2 \text{ / K}^4$, T is the temperature (in K), ϵ is the emissivity and absorptance (0 - 1).

Material	Emissivity
Aluminium Foil	0.04
Rough Aluminium	0.2
Paper	0.93



<https://www.retrofitprojects.co.uk/thermal-imaging-survey/>



https://commons.wikimedia.org/wiki/File:Black_body.svg

Example: Helium consumption due to heat leaks from radiation

- What is the helium boiloff due to radiation in this cylindrical cryostat?

- What is the total surface area?

$$A = (\pi \times 0.3 \times 1.5) + (2 \times \pi \times 0.15^2) = 1.56 \text{ m}^2$$

- How much power from room temperature (293 K) to helium (4.2K)?

$$\sigma = 5.67 \times 10^{-8} \text{ W / m}^2 \text{ / K}^4, \epsilon_{\text{aluminium}} = 0.2$$

$$P_{in} = 1.56 \times 0.2 \times 5.67 \times 10^{-8} \times 293^4 = 130 \text{ W}$$

- How much power from helium to room temperature?

$$P_{out} = 1.56 \times 0.2 \times 5.67 \times 10^{-8} \times 4.2^4 = 5.5 \text{ } \mu\text{W}$$

- Net result

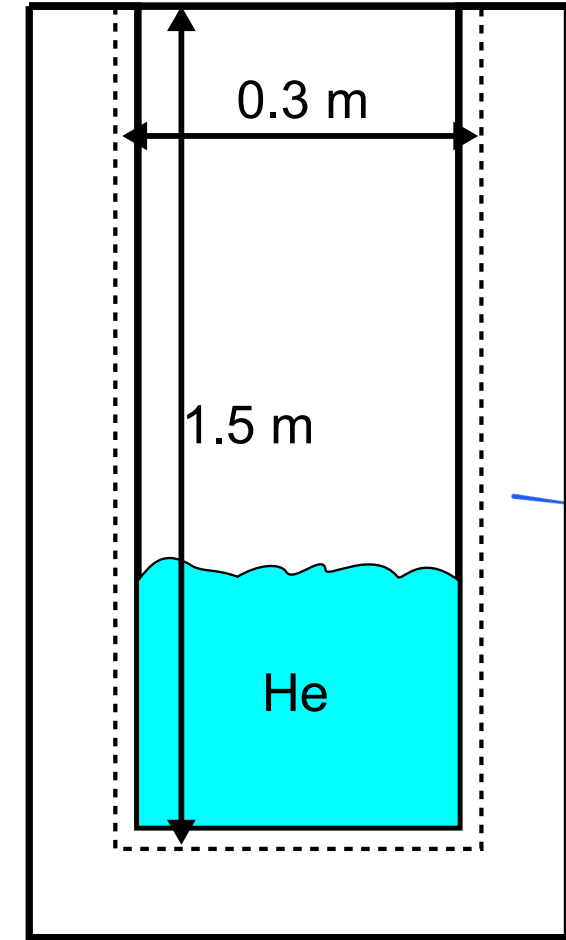
$$P_{total} = 130 - 0.0000055 = 130 \text{ W}$$

- Calculate boiloff rate

$$L_{\text{helium, vaporisation}} = 21\,000 \text{ J / kg}, 1 \text{ hour} = 60 \times 60 = 3\,600 \text{ s}, \rho_{\text{He}} = 0.125 \text{ kg / l}$$

$$\text{Rate} = 130 \div 21\,000 = 0.0062 \text{ kg / s}$$

$$0.0062 \times 3\,600 \div 0.125 = 180 \text{ l / hour!}$$



$$P = A\epsilon\sigma T^4$$

Example: Helium consumption due to heat leaks from radiation

- What is the helium boiloff due to radiation in this cylindrical cryostat with a nitrogen shield?

- How much power from nitrogen temperature (77 K) to helium (4.2K)?

$$\sigma = 5.67 \times 10^{-8} \text{ W / m}^2 \text{ / K}^4, \epsilon_{\text{aluminium}} = 0.2, A = 1.56 \text{ m}^2$$

$$P_{in} = 1.56 \times 0.2 \times 5.67 \times 10^{-8} \times 77^4 = 0.62 \text{ W}$$

- How much power from helium to nitrogen temperature?

$$P_{out} = 1.56 \times 0.2 \times 5.67 \times 10^{-8} \times 4.2^4 = 5.5 \text{ } \mu\text{W}$$

- Net result

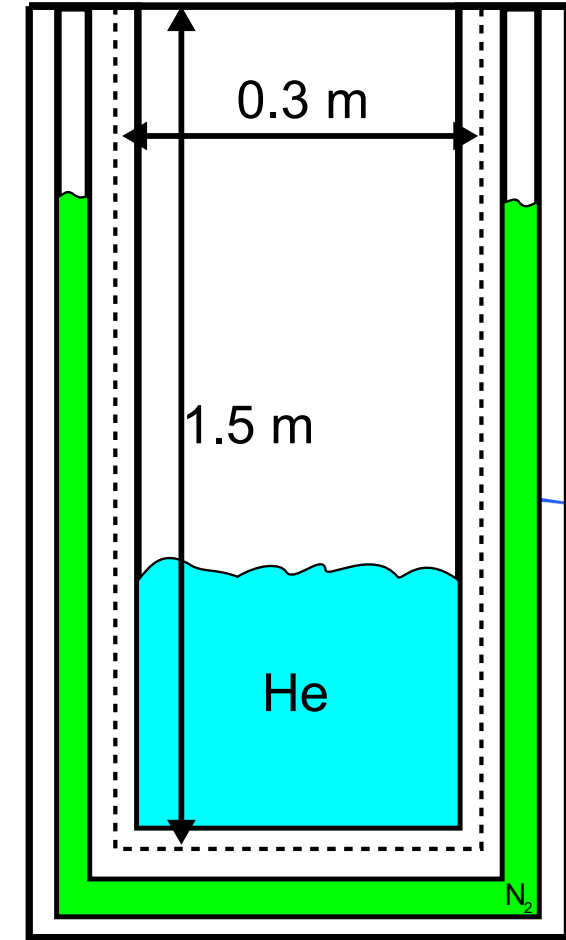
$$P_{total} = 0.62 - 0.0000055 = 0.62 \text{ W}$$

- Calculate boiloff rate

$$L_{\text{helium,vaporisation}} = 21\,000 \text{ J / kg}, 1 \text{ hour} = 60 \times 60 = 3\,600 \text{ s}, \rho_{\text{He}} = 0.125 \text{ kg / l}$$

$$\text{Rate} = 0.62 \div 21\,000 = 3.0 \times 10^{-5} \text{ kg / s}$$

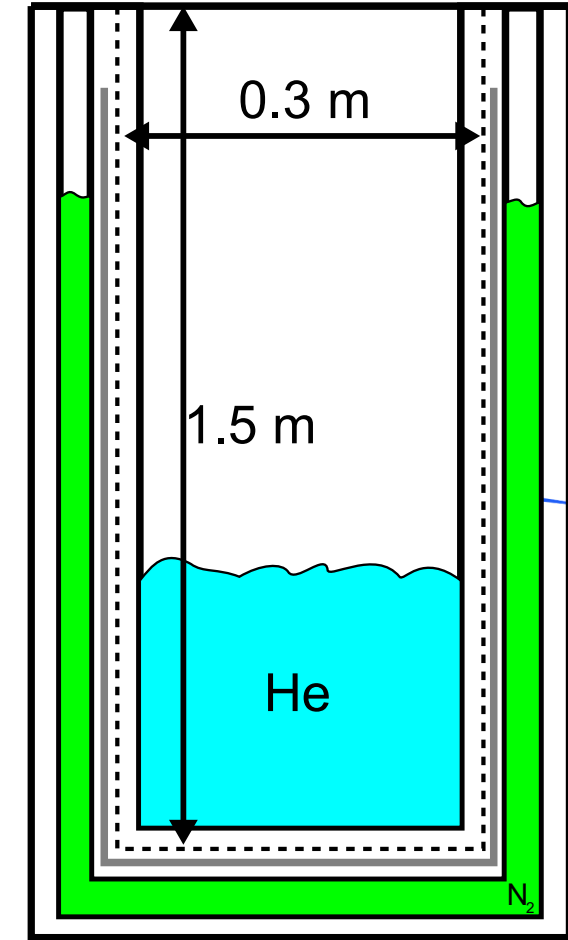
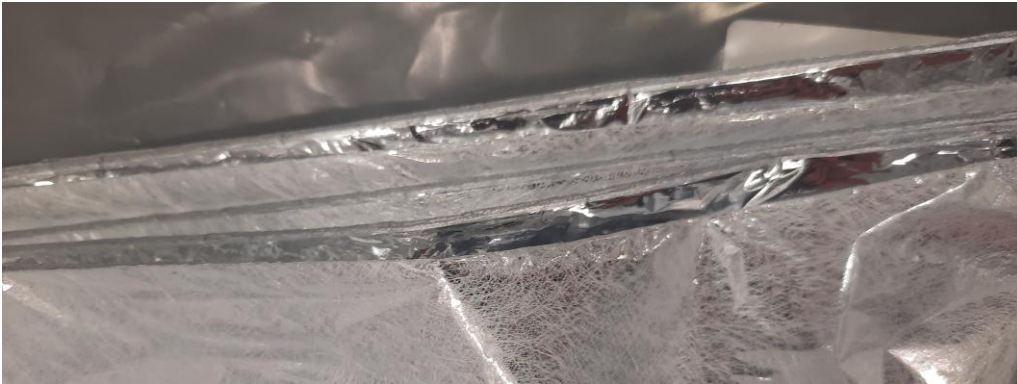
$$3.0 \times 10^{-5} \times 3\,600 \div 0.125 = 0.85 \text{ l / hour}$$



$$P = A\epsilon\sigma T^4$$

Example: Helium consumption due to heat leaks from radiation

- What if we add an additional shield not connected to anything (no cooling power) between the nitrogen bath and the helium bath?
- Previous radiation heat leak = 0.62 W
- With extra shield, heat leak = 0.31 W
- Add another shield, leak = 0.16 W
- Halves for every additional shield added

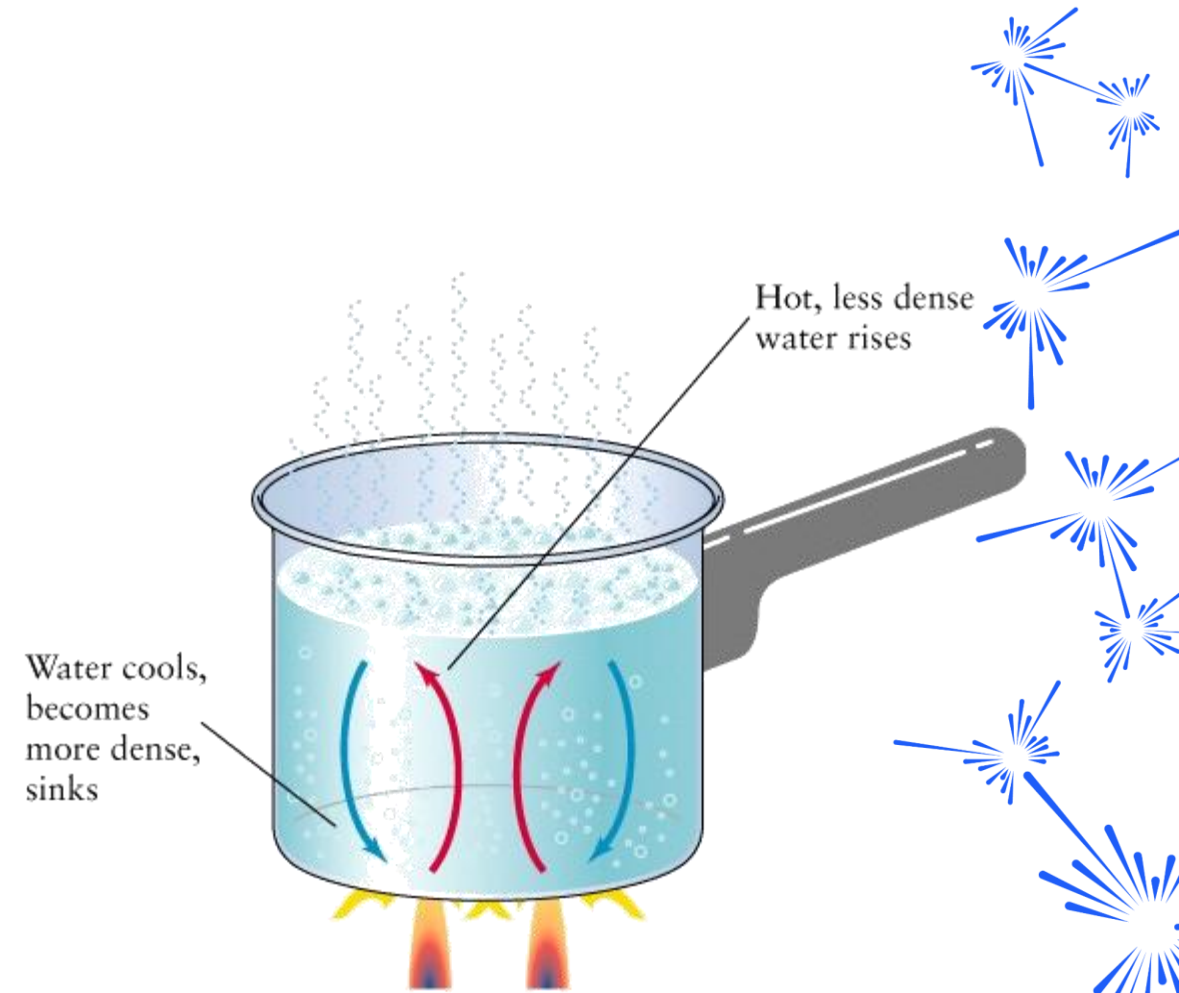


$$P = A\epsilon\sigma T^4$$

Thermal Transport – Convection

- Movement of heat by moving to some fluid (liquid or gas) which then itself moves somewhere cooler, taking the heat with it.
- Natural convection occurs due to gravity acting on a fluid which becomes less dense at higher temperatures...‘Heat Rises’.
- Natural convection complicated to calculate.
- Forced convection involves the fluid being moved by some other means (e.g. a fan in air, a pump in water).
- Power transferred by forced convection is given from the equation for sensible heat using the mass flow rate of the substance and change in temperature across the system.

$$\dot{Q} = \dot{m}c\Delta T$$



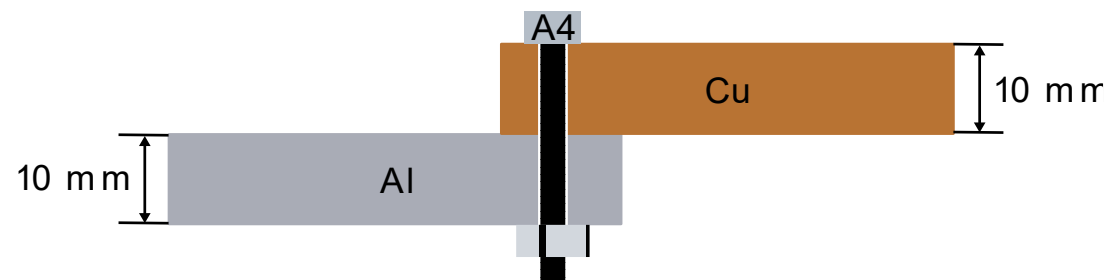
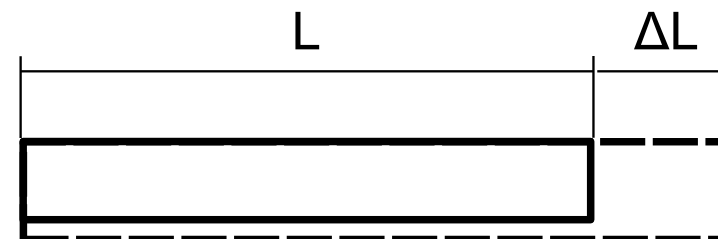
Thermal Expansion

- Materials expand when heated, shrink when cooled.

$$\Delta L = L\alpha\Delta T$$

- ΔL change in length, L original length, ΔT change in temperature and α linear expansion coefficient.

Material	Expansion Coefficient
Nylon	70×10^{-6}
Aluminium	23×10^{-6}
Brass	18.5×10^{-6}
Copper	16.4×10^{-6}
Stainless 316	16.0×10^{-6}
Molybdenum	5.0×10^{-6}



Example – Molybdenum Washer Selection to Counter Thermal Contraction

- What thickness of molybdenum washer is required to stop this assembly coming loose when cooled from room to helium temperature?

1. Calculate how much each component will shrink.

$$\Delta L_{Al} = 10 \times 23.0 \times 10^{-6} \times (293 - 4.2) = 0.066 \text{ mm}$$

$$\Delta L_{Cu} = 10 \times 16.4 \times 10^{-6} \times (293 - 4.2) = 0.047 \text{ mm}$$

$$\Delta L_{SS} = 20 \times 16.0 \times 10^{-6} \times (293 - 4.2) = 0.092 \text{ mm}$$

2. Calculate how much of a gap will open up.

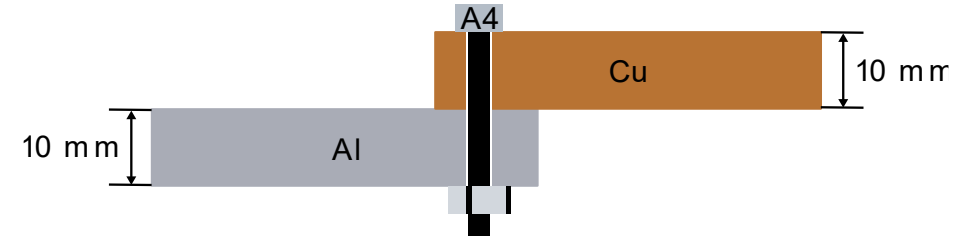
$$Gap = \Delta L_{Al} + \Delta L_{Cu} - \Delta L_{SS}$$

$$Gap = 0.066 + 0.047 - 0.092 = 0.021 \text{ mm}$$

3. Calculate required molybdenum thickness.

$$L_{Mo} = \frac{0.021}{(16.0 - 5.0) \times 10^{-6} \times (293 - 4.2)} = 6.73 \text{ mm}$$

4. Be careful with rounding. Select 6.8 mm (or 7.0 mm) washer.



Material	$\alpha / 10^{-6}$
Aluminium	23
Copper	16.4
Stainless 316	16.0
Molybdenum	5.0

$$\Delta L = L \alpha \Delta T$$

$$L = \frac{\Delta L}{\alpha \Delta T}$$

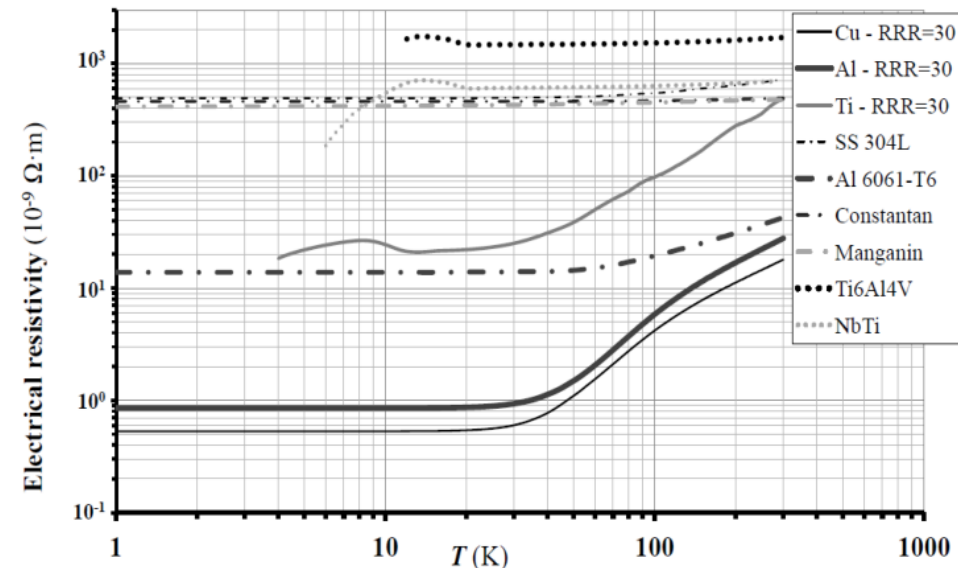
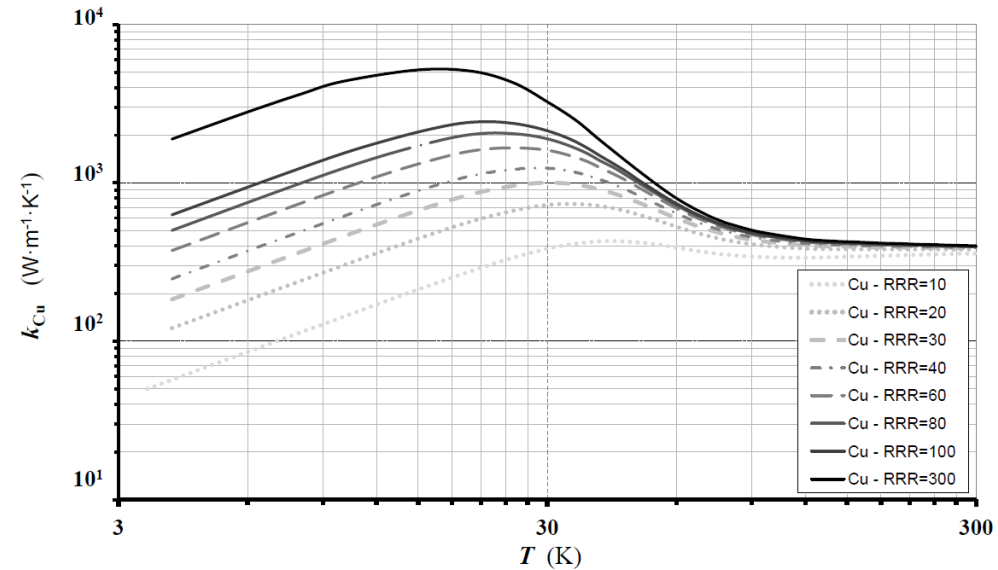
Cryogenic Complications

- Various material “constants” we have seen are not constant as we cool to very low temperatures.
 - Heat capacities
 - Thermal conductivities
 - Thermal expansion coefficients
- Presents two problems
 - What are these values at the temperatures of interest?
 - How do we account for them changing over a region of interest (e.g. heat down a wire when the bottom has a different thermal conductivity to the bottom)?



Cryogenic Complications – Thermal Conductivity

- Can try and look up thermal conductivities. Can be very different for different material grades and treatments.
- Calculate an average conductivity over the temperature range of interest (as used in a previous example) good enough for rough estimates.
- For metals, can measure or look up the electrical resistivity (ρ) and calculate the thermal conductivity (κ) at the current temperature (T) using the Wiedemann–Franz law:
$$\kappa = \frac{LT}{\rho}, L = 2.44 \times 10^{-8} \text{ V}^2/\text{K}^2$$
- Works well for materials with constant electrical resistivity.



Cryogenic Complications – Thermal Conductivity

$$dq = \frac{A\kappa(T)}{l} dT$$

- Have tabulated ‘integrated’ thermal conductivities for some materials

$$\int_{T_i=1K}^{T_j} \kappa(T) dT$$

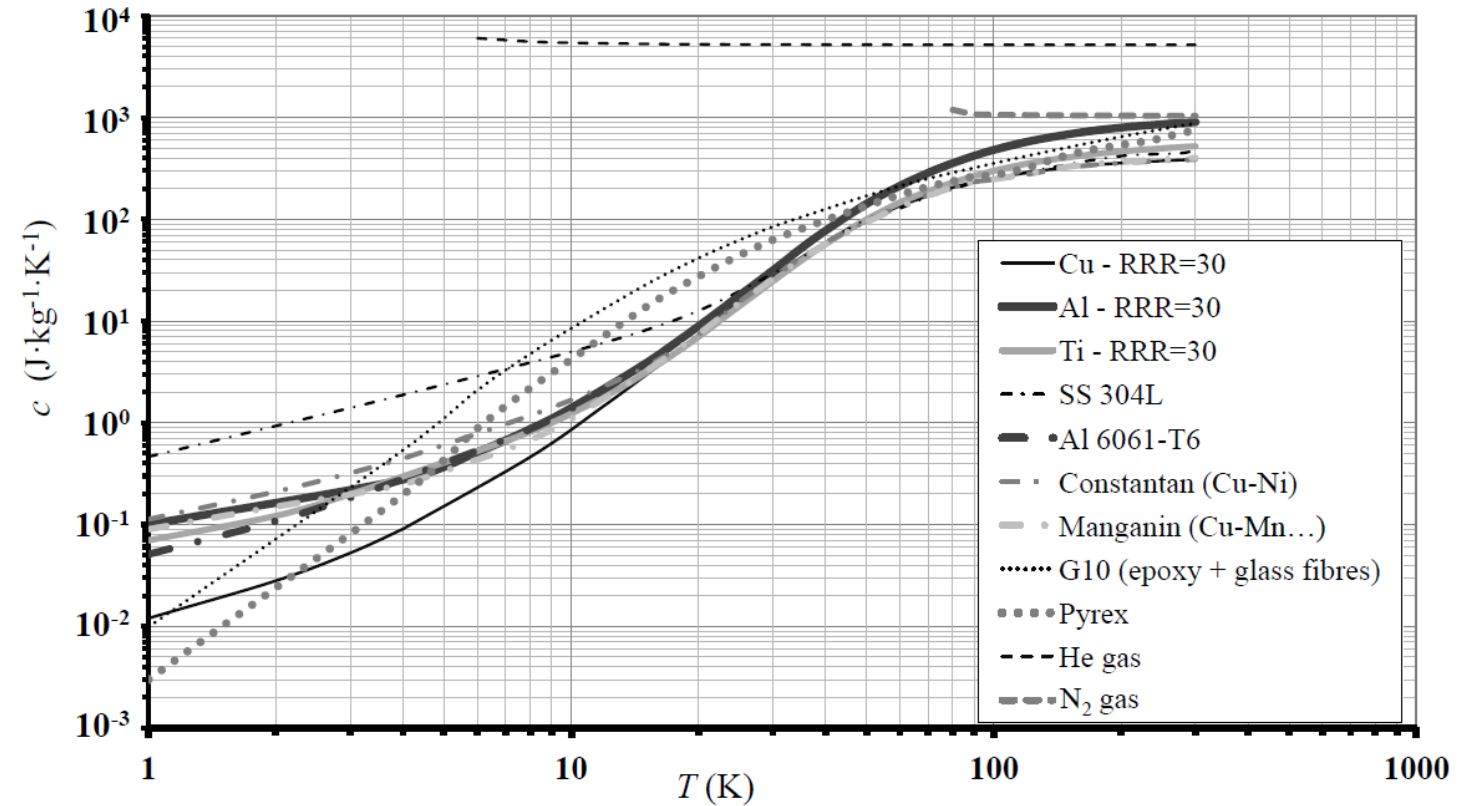
- Accurate and convenient *if you can find the data for your material*. Subtract high temperature value from low temperature value, multiply by A/l.
- Otherwise, need to write a computer program to work out the thermal conductivity in small sections.

Table A.3: $\int_0^T \kappa(T) dT$ of different materials; data compiled from [5] and considering $T_{\text{REF}} = 1 \text{ K}$

T (K)	SS304	Cu- RRR=300	Cu- RRR=30	Brass	Constantan	Manganin	Invar	Ti- 6Al- 4V	Al- RRR=30	6061- T6	5083- T0	Nb- Ti
2	0.073		69	1.0	0.18	0.124	0.0388	0.17	42.8	3.5	1.06	0.04
4	0.40	3560	345	6.0	1.31	0.773	0.276	0.80	214	17.7	5.61	0.27
6	1.02	8360	807	16.0	3.87	2.12	0.819	1.78	501	41.4	13.7	0.76
8	1.96	14 900	1450	31.0	8.03	4.22	1.7	3.07	900	74.6	25.3	1.5
10	3.3	22 800	2270	51	13.9	7.1	2.95	4.67	1410	118	40.5	2.5
15	8.5	46 600	5130	128	38.2	18.6	7.93	9.91	3190	272	95.2	6.0
20	16.7	72 900	8910	235	74.8	35.9	15.6	16.7	5590	487	173	11.1
25	28.1	95 800	13 500	370	124	59.7	26	24.7	8560	765	273	17.4
30	42.8	115 000	18 400	525	184	89.6	39.1	33.8	11 900	1100	395	25.2
35	61.2	130 000	23 300	697	252	125	54.7	43.8	15 400	1480	538	34.4
40	82.9	140 000	28 000	883	328	166	72.9	54.8	18 900	1900	701	45.0
50	136	155 000	36 200	1280	497	260	117	79.4	25 300	2840	1080	70.4
60	199	164 000	42 900	1730	679	367	170	107	30 500	3900	1540	101
70	271	171 000	48 400	2210	865	483	232	137	34 800	5020	2050	138
77	326	176 000	51 800	2580	997	569	281	160	37 300	5830	2440	167
80	350	177 000	53 300	2740	1050	607	302	171	38 300	6180	2610	180
90	436	182 000	57 800	3320	1250	739	379	207	41 400	7370	3220	228
100	527	187 000	62 000	3950	1440	877	462	245	44 200	8580	3870	280
120	725	196 200	70 270	5330	1847	1165	640	329	49 240	11 040	5280	398
140	940	204 900	78 200	6860	2269	1467	834	422	53 830	13 560	6820	530
160	1170	213 300	86 100	8500	2700	1781	1040	522	58 300	16 130	8490	673
180	1414	221 700	94 000	10 240	3140	2107	1258	630	62 800	18 780	10 270	824
200	1667	229 900	101 800	12 080	3600	2447	1482	744	67 300	21 480	12 170	983
220	1937	238 200	109 600	13 950	4060	2797	1732	865	71 800	24 180	14 170	1150
240	2207	246 300	117 400	16 050	4530	3167	1982	993	76 400	27 080	16 370	1323
260	2487	254 400	125 100	18 150	5000	3557	2242	1127	80 900	30 080	18 570	1503
280	2777	262 500	132 900	20 350	5480	3967	2502	1265	85 400	33 180	20 970	1687
300	3077	270 500	140 600	22 650	5970	4397	2772	1415	90 000	36 380	23 470	1875

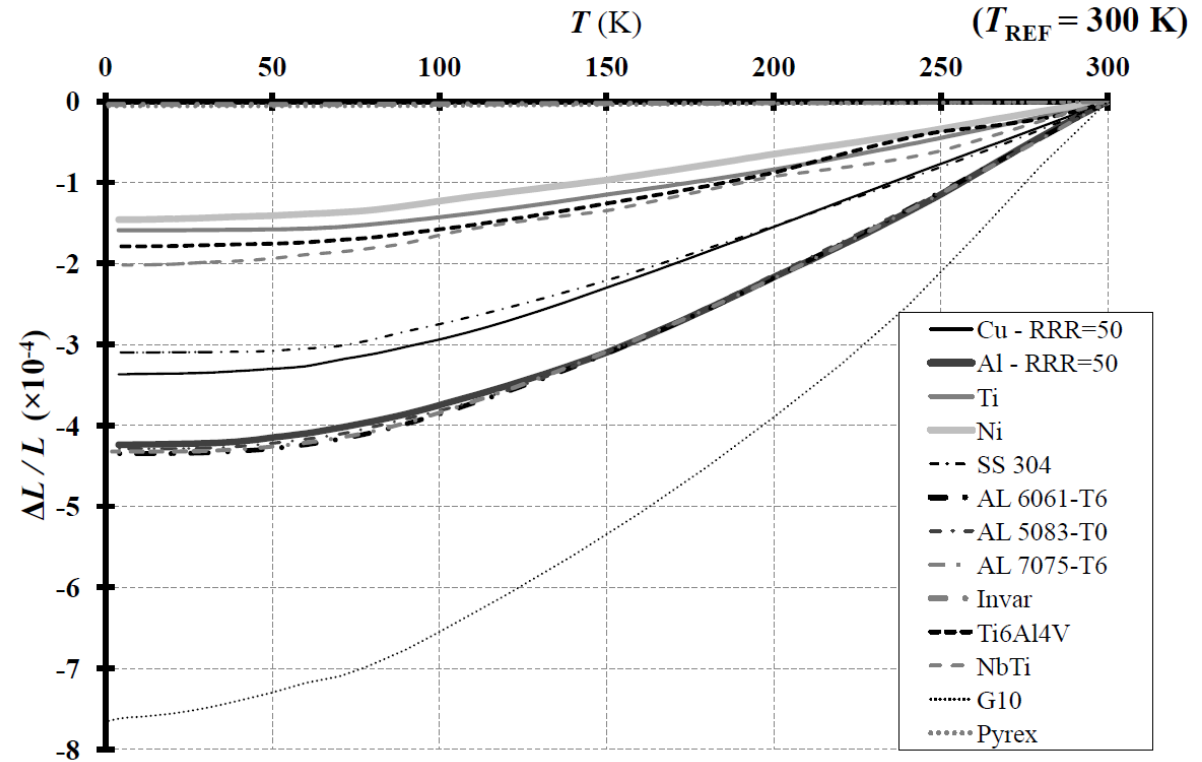
Cryogenic Complications – Heat Capacity

- Similar story.
- More limited options in terms of calculation from other known values or tabulated results.



Cryogenic Complications – Thermal Expansion

- Similar story.
- Graph shows integrated thermal expansion coefficients so account for changes in the coefficient with temperature.
- Crucially, order doesn't swap round so room temperature values still good for determining if fasteners will come loose.



Questions?

Thank you



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