# Lecture 23: 3rd law and the quest for *T* = 0

- Introduction
- The Joule-Thomson effect
- The inversion diagram
- The 3rd law of thermodynamics
- Nernst's heat theorem
- Planck's statement of the 3rd law
- The unattainability statement
- Implications of the 3rd law in phase diagrams
- The quest for T → 0
- Low temperature techniques
- How to set a world record

# Notices

1. **Assignment:** I will return these tomorrow – results were mixed, some were fantastic, some where not so good…

2. **Questions:** If there are questions or topics that you'd like me to answer or address further as material for the upcoming tutorial/revision class tommorrow, please let me know. If you want to ask anonymously, feel free to just stick a note under my door.

3. **Mega-revision session:** I am currently organising my mega-revision session for the stuvac break, attendance is voluntary but very useful. I will announce the room later (probably 112), but for now I want to get an idea of the best time. There is a poll on the forum site and we can decide tomorrow – Dates include Th 6/11, F 7/11, M 10/11, Tu 11/11 and W 12/11.

4. **Final Exam:** Make sure you know when and where the exam is held. The exam is currently scheduled for Thurs 13/11 at 1:45 - 4pm in the Lower Tea room, Randwick Racecourse – This is the second last day of the exam period.

5. **CATEI:** Please go to your MyUNSW website and fill out the CATEI survey for the course. It may not seem important, but its extremely helpful for me in improving my teaching and I do care about it – I still have only 9 out of 42 responses (~21%).

# Introduction

Since the discovery of the ability to liquefy various gases with the Joule-Thompson effect, it has been possible to access temperatures well below those accessible naturally (e.g., 0°C by collecting up snow or cutting blocks of ice).

This started with solid $CO_2$ at about –50°C and liquid $N_2$ at about –196°C (or 77K), followed by liquid oxygen and hydrogen (which raised some serious flammability issues) and ultimately with liquid helium which allowed temperatures as low as –269°C (or 4K).

With some advanced techniques, you can reach temperatures as low as pK, or 1 billionth of a degree above absolute zero.

In this lecture we'll look at the Joule-Thompson effect, the third law of thermodynamics, and if time allows, a short discussion on low temperature physics to finish off the course.

# The Joule-Thomson effect

**The Joule-Thompson effect, also known as 'throttling', relies on the adiabatic free expansion of a *non-ideal* gas from very high pressure to cool it sufficiently that it condenses into a liquid or solid. This is a very important industrial process, it's how we liquefy all gases for cooling processes from making liquid nitrogen for pipe-freezing and liquid helium for MRI systems to liquefying the CFC coolant in your household refrigerator or air-conditioner.**

**The process involves taking a cylinder containing a gas under very high pressure (such a high pressure that it may be often be a liquid) and passing it through a very narrow orifice, this could be the narrow aperture of a valve, or a porous material such as a piece of sintered bronze (see the nozzle on the liquid nitrogen fill station if you do 3rd year physics lab). The expansion could be into some closed vessel, providing it's 'open' in the sense that its pressure stays low and constant, but more commonly into some open vessel.**

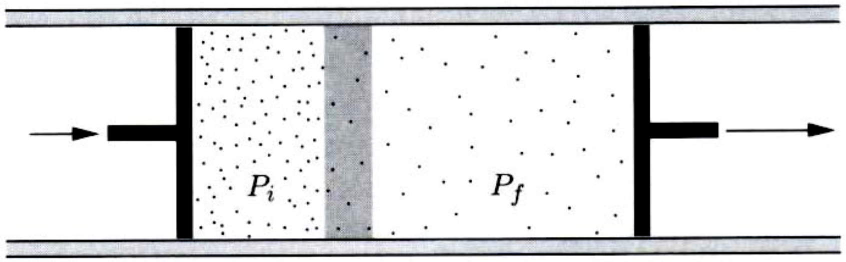
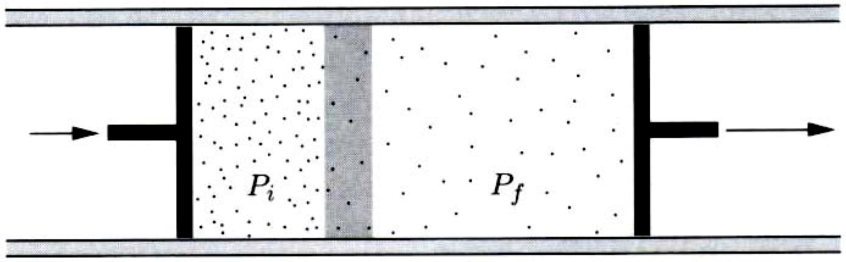


**Figure 4.10.** The throttling process, in which a fluid is pushed through a porous plug and then expands into a region of lower pressure.

# The Joule-Thomson effect



For doing the calculations, let's consider the system as a true free expansion. Here we have a gas at some pressure $P_i$ in the piston on the left (actually, the pressure is so high it's probably a fluid), being forced through a porous plug, which provides significant resistance to the flow, into a second piston at a pressure $P_f$ on the right, which is free to expand to accommodate the gas flowing through the plug. For a particular chunk of 'fluid', let the initial volume be $V_i$ and the final volume be $V_f$.

Since this process is an adiabatic free expansion, there is no heat flow during this process (i.e., $Q = 0$), and so:

$$\Delta U = U_f - U_i = Q + W = 0 + W_{left} + W_{right} \tag{23.1}$$

where $W_{left}$ is the (positive) work done by the piston on the left, and $W_{right}$ is the (negative) work done by the piston on the right.

# The Joule-Thomson effect

The work done on the left in pushing the entire volume through the plug is $P_iV_i$ (to first order at least) while the work done from the right is $-P_fV_f$ (to first order). Hence the change in energy is:

$$U_f - U_i = W_{left} + W_{right} = P_iV_i - P_fV_f \qquad \textbf{(23.2)}$$

pulling the *f* and *i* terms to opposite sides, we get:

$$U_f + P_fV_f = U_i + P_iV_i \qquad \text{or} \qquad H_f = H_i \qquad \textbf{(23.3)}$$

In other words, this is an example of a constant enthalpy or isenthalpic process. The purpose of this process is to cool the gas so that we can later use it to cool other things. Now if the fluid here is an ideal gas, then we have a problem, because the enthalpy is:

$$H = U + PV = \frac{1}{\gamma - 1} Nk_BT + Nk_BT = \frac{\gamma}{\gamma - 1} Nk_BT \qquad \textbf{(23.4)}$$

and since the enthalpy is constant, then the temperature will be constant and we'll get no cooling.

# The Joule-Thomson effect

This is one case where we really don't want an ideal gas. For a dense gas or a liquid, the energy *U* also contains a potential energy term due to the forces between the molecules, so:

$$H = U_{kinetic} + U_{potential} + PV \tag{23.5}$$

The force between any two molecules is weakly attractive at long distances and strongly repulsive at short distances (i.e., the Lennard-Jones potential). Under most conditions the attraction dominates, making $U_{\text{potential}}$ negative, but less negative as the pressure drops and the distance between molecules increases. To compensate for this increase in potential energy, the kinetic energy of the molecules generally drops, reducing the temperature and producing cooling.

The influence of molecular interactions is evident in how easy it is to condense various gases using the Joule-Thompson process. As the demo shows, $CO_2$, which has very strong molecular interactions, can be easily condensed into solid dry ice.

# The Joule-Thomson effect – The Demo…

If any one asks… You know nothing, ok.

# Liquefying gases

**In contrast $N_2$ and $O_2$ have weaker interactions and while they can't be liquefied by the Joule-Thompson process starting from room temperature, they can if you start from around $T$ < 160K. Starting from room temperature gas, you can achieve this by repeatedly cycling the gas around a circuit containing a Joule-Thompson condenser, as shown below. This is known as the Hampson-Linde cycle, developed in 1895.**

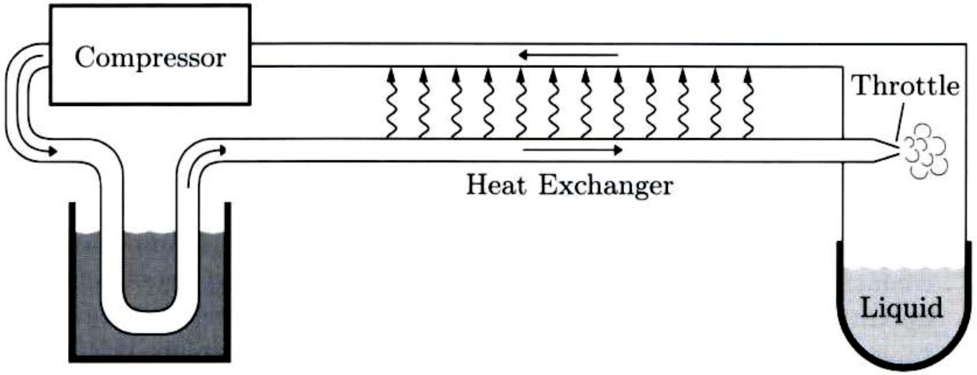


**Figure 4.11.** Schematic diagram of the Hampson-Linde cycle for gas liquefaction. Compressed gas is first cooled (to room temperature is sufficient if it is nitrogen or oxygen) and then passed through a heat exchanger on its way to a throttling valve. The gas cools upon throttling and returns through the heat exchanger to further cool the incoming gas. Eventually the incoming gas becomes cold enough to partially liquefy upon throttling. From then on, new gas must be added at the compressor to replace what is liquefied.

**For $H_2$ and He, which have even weaker interactions, and are closer to being ideal gases, it is necessary to precool the gases even further before they will condense.**

# The inversion diagram

**Liquefaction techniques are significantly improved these days due to advancements in technology and our knowledge of the behaviour of these gases. If you plot lines of constant *H* on a plot of *T* vs *P* for a gas (such a graph is shown for Hydrogen below) you can determine two distinct regions. One where the *T* rises as you reduce *P* along an isenthalp – here a Joule-Thompson process leads to heating rather than cooling – and another where *T* decreases as you reduce *P* along an isenthalp – here a Joule-Thompson process produces cooling.**

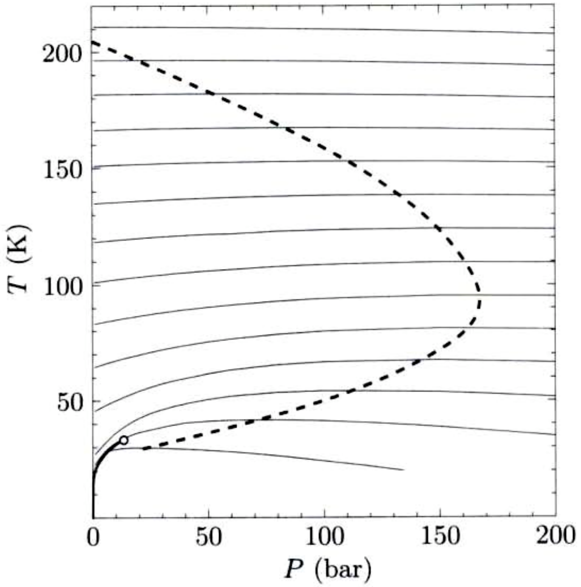


**Figure 4.12.** Lines of constant enthalpy (approximately horizontal, at intervals of 400 J/mol) and inversion curve (dashed) for hydrogen. In a throttling process the enthalpy is constant, so cooling occurs only to the left of the inversion curve, where the enthalpy lines have positive slopes. The heavy solid line at lower-left is the liquid-gas phase boundary. Data from Vargaftik (1975) and Woolley et al. (1948).

**The *T* below which cooling will occur is known as the *inversion temperature*, and the line separating the heating and cooling regions is known as the inversion curve.**

# The third law of thermodynamics

**Before we look a little more at how to make things cold, we have one last law of thermodynamics to talk about. Like the Second law, the Third law can be written in a number of 'statements', which we'll look at all at once. They are:**

**Nernst's Heat Theorem:** ***In the neighbourhood of absolute zero, all reactions in a liquid or solid in internal equilibrium take place with no change in entropy.***

**Nernst noticed in 1906 that in a number of different experiments, the change in the Gibbs free energy and Helmholtz free energy converged as *T* went towards zero, as shown below.**

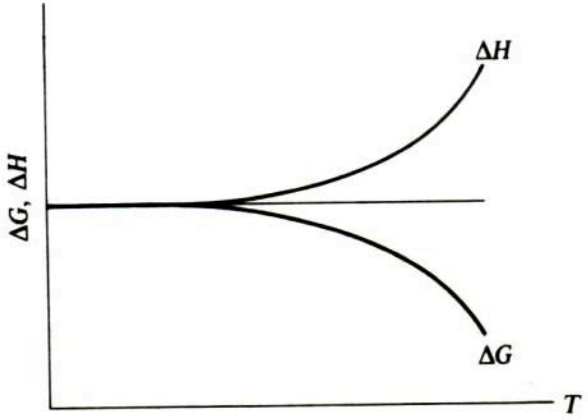


**Fig. 7–5** The temperature dependence of the change in the Gibbs function and in the enthalpy for an isobaric process.

# Nernst's heat theorem

**These can be related via:**

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P \tag{23.6}$$

**Nernst also noticed that the rates of change of *G* and *H* with temperature also approach zero in the limit of *T* → 0, in other words:**

$$\lim_{T\to 0}\left(\frac{\partial \Delta G}{\partial T}\right)_P = 0 \qquad \underline{\textit{and}} \qquad \lim_{T\to 0}\left(\frac{\partial \Delta H}{\partial T}\right)_P = 0 \tag{23.7}$$

**Eqn. 23.7(a) can be rewritten as:**

$$\lim_{T\to 0}\left(\frac{\partial (G_1 - G_2)}{\partial T}\right)_P = \lim_{T\to 0}\left[\left(\frac{\partial G_1}{\partial T}\right)_P - \left(\frac{\partial G_2}{\partial T}\right)_P\right] = 0 \tag{23.8}$$

**but $(\partial G/\partial T)_P = -S$, so:**

$$\boxed{\lim_{T\to 0}(S_1 - S_2) = \lim_{T\to 0}\Delta S = 0} \tag{23.9}$$

**which is exactly Nernst's heat theorem as we stated earlier.**

# Planck's statement of the 3rd law

In 1911, Planck one step further and made the hypothesis that not only does the entropy *difference* vanish as $T \to 0$, but that:

**Planck's statement of the Third Law:** ***The entropy of every solid or liquid substance in internal equilibrium at absolute zero is itself zero.***

Planck is just saying:

$$\boxed{\lim_{T\to 0} S = 0} \qquad (23.10)$$

The full argument for this is much longer, but basically, at absolute zero there can only be one possible microstate for the system (otherwise Nernst's theorem wouldn't hold), hence $\Omega = 1$ and $S = k_B \ln\Omega = 0$. In effect though, Planck is simply setting the reference entropy in our earlier equations:

$$S = C_P \ln T - nR\ln P + S_0 \qquad\qquad S = C_V \ln T - nR\ln V + S_0 \qquad (19.29/30)$$

to be $S_0 = 0$ at $T_r = 0$ – It's a very convenient and sensible thing to do!

# The unattainability statement

**Note also that since:**

$$S(V,T)=\int_0^T C_V\,\frac{dT}{T} \qquad \textbf{and} \qquad S(P,T)=\int_0^T C_P\,\frac{dT}{T} \qquad \textbf{(23.11)}$$

**this means that**

$$\boxed{\lim_{T\to 0} C_P = \lim_{T\to 0} C_V = 0} \qquad \textbf{(23.12)}$$

**The Unattainability statement of the Third Law:** ***It is impossible to reduce the temperature of a system to absolute zero in any finite number of operations.***

**The most efficient method for reaching absolute zero is to isolate the system from its surroundings and reduce its temperature belo that of the surroundings in an adiabatic process in which the work is done by the system solely at the expense of its internal energy. Consider a reversible adiabatic process, which takes a system from state 1 to state 2 by a path that changes some property *X* (it could be *P* or *V* or whatever) and the temperature *T* of the system. It follows from Eqn. 23-11 that:**

$$S(X_a,T_a)=\int_0^{T_a} C_{X_a}\,\frac{dT}{T} \qquad \textbf{and} \qquad S(X_b,T_b)=\int_0^{T_b} C_{X_b}\,\frac{dT}{T} \qquad \textbf{(23.13)}$$

# The unattainability statement

**In a reversible adiabatic process,**

$$S_1(X_a, T_a) = S_2(X_b, T_b) \qquad \textbf{(23.14)}$$

**and therefore**

$$\int_0^{T_a} C_{X_a} \frac{dT}{T} = \int_0^{T_b} C_{X_b} \frac{dT}{T} \qquad \textbf{(23.15)}$$

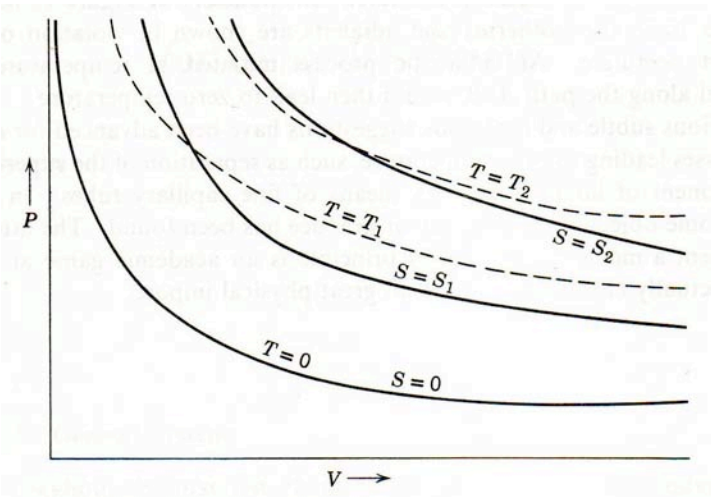
**If the process continues until $T_b = 0$, since each of the integrals converges,**

$$\int_0^{T_a} C_{X_a} \frac{dT}{T} = 0 \qquad \textbf{(23.16)}$$

**However, $C_{Xa}$ is greater than zero for $T_a$ not equal to zero (see Eqn. 23-12) and so Eqn. 23-16 cannot be true and therefore absolute zero of temperature cannot be obtained.**

# The unattainability statement

**The Unattainability statement of the Third Law:** ***It is impossible to reduce the temperature of a system to absolute zero in any finite number of operations.***



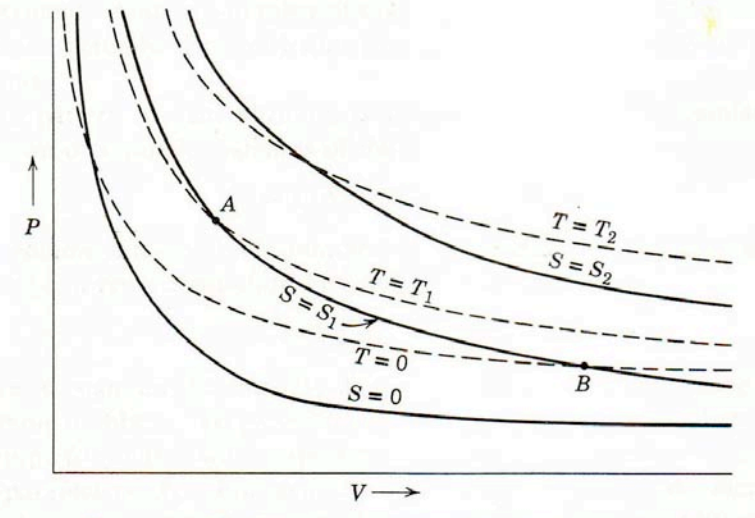
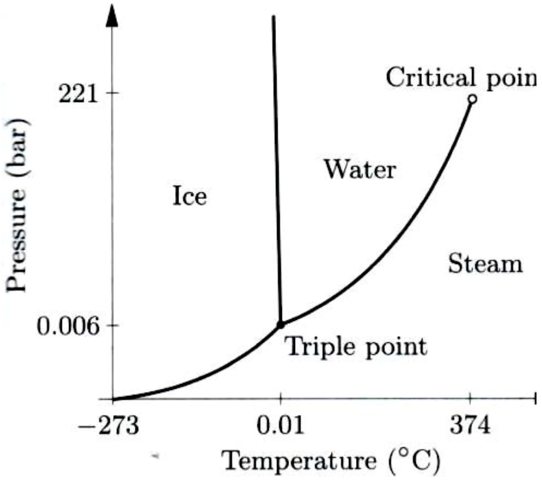


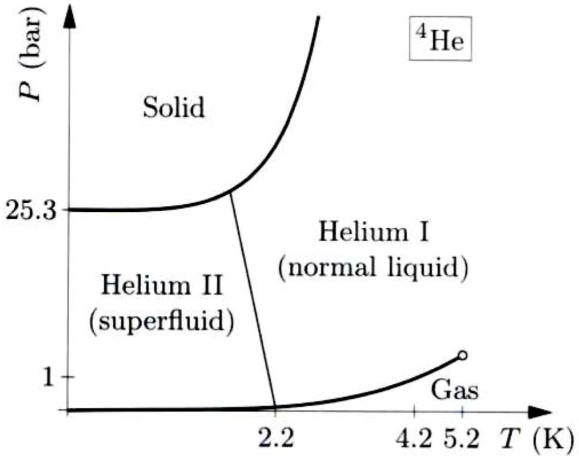
**Figure 10.3** Isotherms and adiabats near zero temperature.

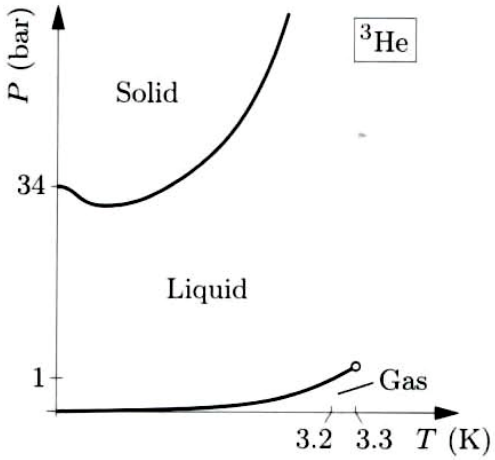
**There is a simpler argument, which relies on the properties of a PV-diagram, namely that adiabats can't cross one another. This ultimately leads to a more accepted version of the unattainability statement, which is that T = 0 cannot be obtained by a series of adiabatic processes instead. You can hatch other plots, but usually they are undermined by various practical issues…**

# Implications of the 3rd law in phase diagrams

**You can see the Third law in just about every phase diagram where temperature appears on one of the axes, providing it goes to low enough temperature of course.**



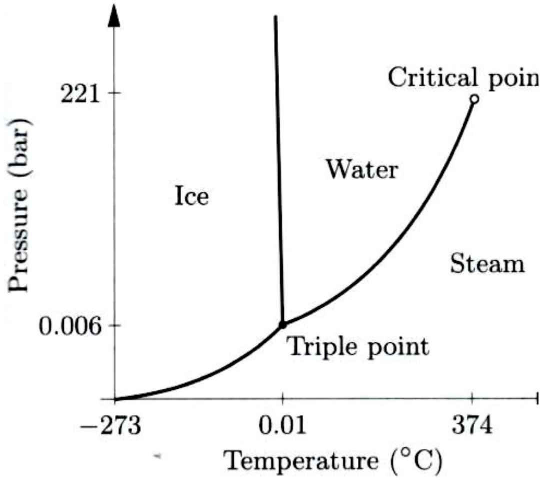


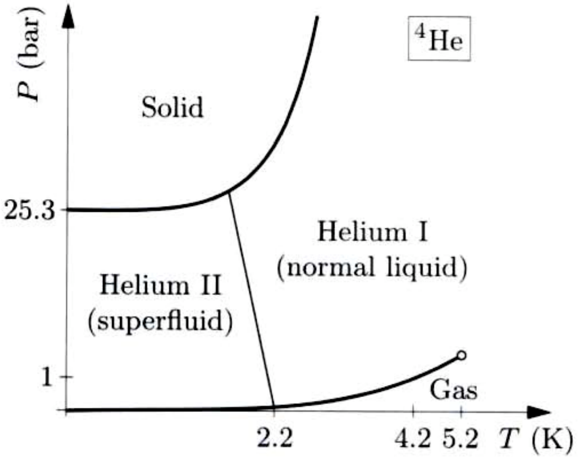


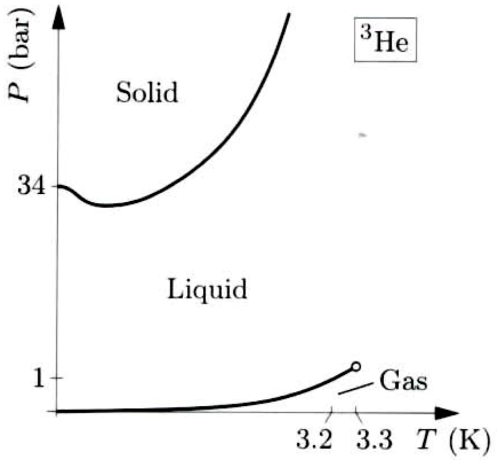
**In each case you'll notice that the phase boundaries become horizontal as you approach *T* = 0. Why is this?**

# Implications of the 3rd law in phase diagrams

**You can see the Third law in just about every phase diagram where temperature appears on one of the axes, providing it goes to low enough temperature of course.**







**In each case you'll notice that the phase boundaries become horizontal as you approach *T* = 0. Why is this? Well the third law says that both the change in entropy Δ *S* and the entropy *S* itself head towards zero in the limit of *T* = 0. Now if we remember back to the Clausius-Clapeyron equation last lecture:**

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \tag{21.5}$$

**But as $T \rightarrow 0$ then $\Delta S \rightarrow 0$, and so *dP*/*dT* must also head towards zero, which implies horizontal phase boundaries in the low *T* limit, as we observe in our phase diagrams.**

# The quest for $T \rightarrow 0$

This last version of the Third law is probably my favourite version, as its what makes low temperature physics challenging. But I think the real significance is in Eqn. 23-12 though:

$$\lim_{T \to 0} C_P = \lim_{T \to 0} C_V = 0 \tag{23.12}$$

What does this say? It says that the heat capacity of the system heads towards zero as you approach $T = 0$. Remembering that $C = dQ/dT$, this means that the amount of heat you need to add/remove from the system to change $T$ by some amount decreases as you approach $T = 0$.

While at first this seems great in terms of how little heat it takes to increase $T$, in going the other direction towards lower $T$, it means that any amount of heat leaking into the system will work against you, and the colder it is, the worse this problem is, making it exponentially harder to get to lower and lower temperatures.

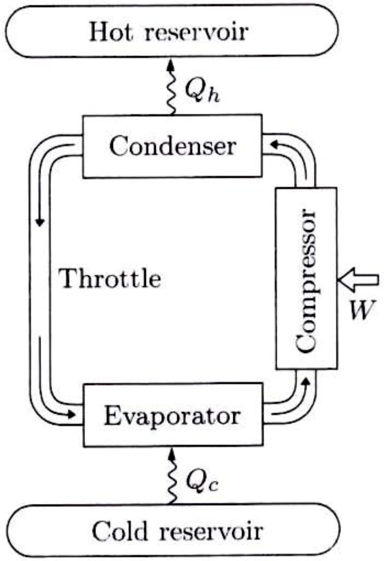
Temperatures as low as 10mK (a hundredth of a degree above absolute zero) are routine today, but are still difficult to achieve.

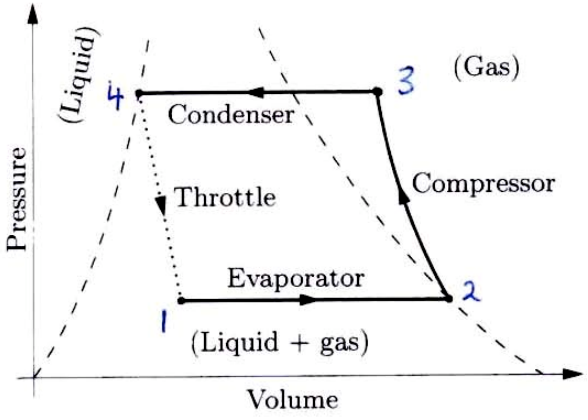
# Low temperature techniques

**The current world record low temperature is 100 picokelvin (i.e., $1 \times 10^{-10}$ K) achieved in the 1998/1999 by researchers at Helsinki University in Finland using nuclear magnetic cooling of Rhodium.**

**Before I talk very briefly about how you achieve temperatures this low, I want to quickly look at four key techniques commonly used for lowering temperature.**

1. **Refrigeration:** **We've already dealt with this in an earlier lecture so I'll say little about it, except that you can use the same cyclical process used in your household fridge (with some changes in the gas, etc) to get as low as 10-20K.**





**See lecture 11 for details.**

# Low temperature techniques

2. **Direct contact with liquid cryogens:** A very common way to cool materials to low temperatures is to immerse them in a liquid cryogen (most commonly nitrogen to reach 77K/–196°C or helium 4K/–269°C) or bring them into thermal contact with a liquid cryogen (either by pipework or by having some space in between filled with an ‘exchange’ gas).

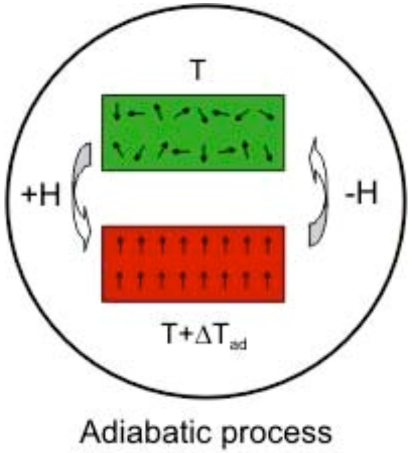
   Immersion is easy with nitrogen but can be more dangerous with helium because it has a low latent heat of vaporization (i.e., it doesn’t take much heat to turn it from liquid to gas and 1L liquid makes about 700L of gas). Liquid helium is commonly used to cool the superconducting magnets used in MRI imaging systems.

3. **Evaporative cooling:** If you take a liquid and pump away the vapour with a vacuum pump, then the liquid will start to cool. Why? Because the removal of the vapour increases the evaporation rate, which means more heat is pulled from the liquid to make up the latent heat required to achieve the liquid-vapour transition.

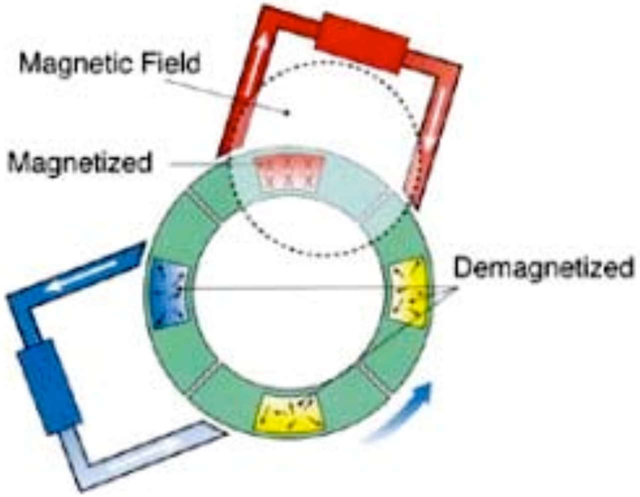
   This process has its limits with most substances because eventually they become solid (it works terribly with liquid nitrogen for example) but it works really well with liquid helium because it has no solid transition (at low $P$). With $^4$He you can reach 1.2K this way, with $^3$He you can reach 0.3K and if you have a mixture of the two in the right ratio, you can reach 0.01K.

# Low temperature techniques

4. **Adiabatic Demagnetization:** **If you take a magnetic system and isolate it from outside heat sources/sinks (i.e., make any process adiabatic so that *Q* = 0), then you can use a magnetic field to change add/remove magnetic ordering to the system and thereby change its temperature.**



**(n.b. *H* is magnetic field not enthalpy here)**

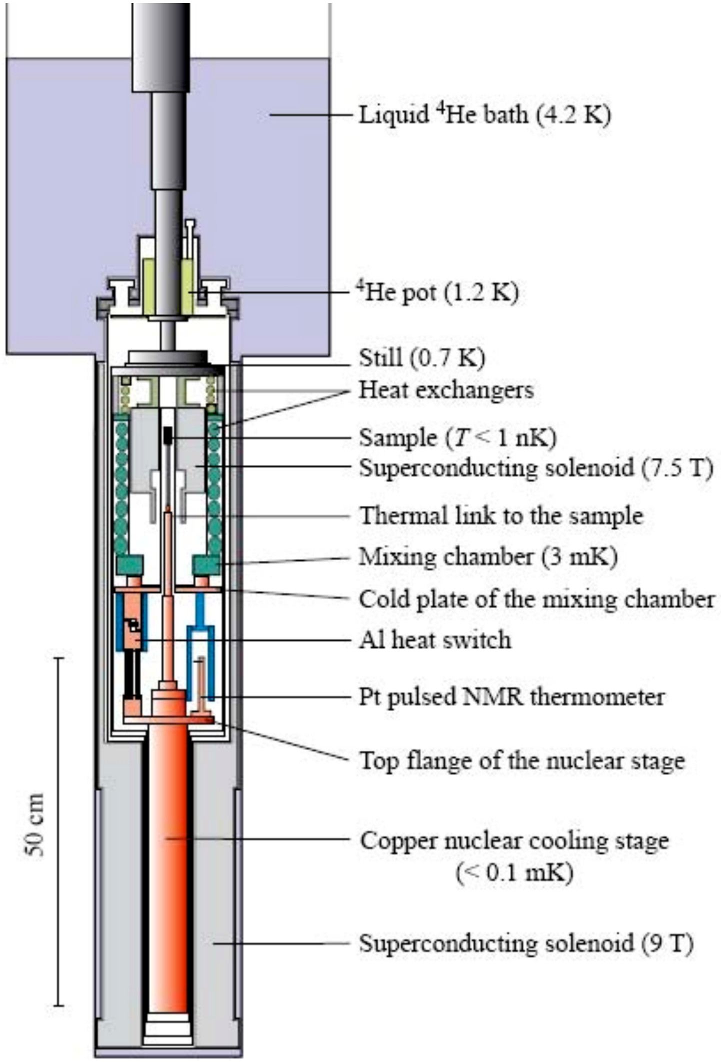


**How does this work? Because *Q* = *TdS* = 0 for this process. If you decrease the entropy by ordering the spins with a field *dS* < 0 and so *T* must increase to keep *Q* = 0. Likewise, if you switch off the field, the spins will spontaneously disorder themselves increasing the entropy, *dS* > 0 and the temperature *T* must fall.**

**This technique is currently being explored as a way to replace vapour-cycle fridges (like the ones you have at home – see above right) because they are far more energy efficient. That said, there are some serious technical challenges involved as well.**

# How to set a world record

**The current world record low temperature is 100 picokelvin (i.e., $1 \times 10^{-10}$ K) achieved in 1998/9 by researchers at Helsinki University in Finland using nuclear magnetic cooling of Rhodium. How do they do this (in brief)?**



# How to set a world record

1. The Rh is cooled to 4K by contact with liquid He using an exchange gas. When the Rh reaches 4K, it is isolated from the liquid He by pumping out the exchange gas and replacing it with a high vacuum.
2. The Rh is connected thermally to a ‘$^4$He pot’ and a ‘mixing chamber’, which are connected to a vacuum pump. The $^4$He pot and mixing chamber are cooled to ~1.2K and 3mK respectively by evaporative cooling, hence cooling the Rh to ~5mK.
3. The Rh is located in a superconducting solenoid, and while it is thermally connected to the mixing chamber, it is taken to a magnetic field sufficient to align all of its spins (i.e., a comparatively low entropy state) at a constant temperature $T$ = 5mK.
4. The thermal connection between the Rh and the mixing chamber is broken (via some kind of heat switch), thermally isolating the Rh and making it an adiabatic system. The magnetic field is then switched off. Because $Q = TdS$, as the spins lose their order (i.e., $dS$ increases) then $T$ needs to decrease to compensate and keep $Q = 0$, hence reducing the temperature of the Rh to $\mu$K and below.

If you are interested in learning more about this, please see the website for the article “Towards the absolute zero” by Olli Lounasmaa in Physics Today, or feel free to come ask me ☺.

# Summary

- **The Joule-Thompson effect involves the adiabatic free expansion of a gas through a porous plug. This is an isenthalpic process.**

- **For an ideal gas, where $H = (\gamma/\gamma - 1)Nk_BT$, for non-ideal gases the intermolecular interactions can produce warming or cooling for $T$ below the inversion temperature. The Joule-Thomson process is used heavily in industry for liquefying gases.**

- **Nernst's heat theorem states that *In the neighbourhood of absolute zero, all reactions in a liquid or solid in internal equilibrium take place with no change in entropy*. Planck added to this soon after by stating that *The entropy of every solid or liquid substance in internal equilibrium at absolute zero is itself zero.***

- **These versions of the third law imply that $\Delta S$, $S$, $C_P$ and $C_V$ all go to zero as $T \rightarrow 0$.**

- **A key implication of the third law is that it is impossible to reach $T = 0$ and the closer you go, the harder it becomes to reduce the temperature because the reducing $C$ means that any small amount of heat leaking into the system will push the temperature up.**