

PREVIOUSLY ON

...*Thermodynamics*

- Joule Expansion Cooling
- Joule-Kelvin Expansion cooling
- Deriving μ_J, μ_{JK} from equation of state
- Desirable properties for coolants
- Other Thermodynamic variables
- Cooling of rubber

Additional thermodynamic coordinates for other systems

So far we assumed material properties are restricted to P , V , T and S . But there are other possibilities which can be treated similarly. The table shows different co-ordinates, distinguishing between intensive variables (like pressure P) and extensive variables (like volume V).

system	intensive variable	extensive variable	infinitesimal work ON system
gas or fluid	P	V	$-PdV$
wire or rod	\mathcal{F} (tension)	L (length)	$\mathcal{F}dL$
(electric) cell	\mathcal{E} ("emf")	Z (charge)	$\mathcal{E} dZ$
magnetic material	B_0 (induction)	\mathcal{M} (mag.moment)	$B_0 d\mathcal{M}$
dielectric material	E (electric field)	\mathcal{P} (polarisation)	$E d\mathcal{P}$

Electromagnetic Thermodynamics

- Radiation **pressure**
- **Volume** (cavity)
- **Temperature** (e.g. Black body)
- **Internal energy** in electromagnetic fields..
For notational simplicity we take $H \gg M$ (B-field = H-field)...
- Magnetic Energy = $-BM$;

Everything we need for Thermodynamics.



Defining Magnetic Central Equation

- Magnetic Energy = $-BM$;
- Magnets don't expand much, consider low pressure, so neglect PdV .

Define increasing magnetisation as "Work": $dW = \mathbf{B} \cdot d\mathbf{M}$

Magnetic Central Equation:

$$du = Tds + BdM$$

with associated Maxwell Relations such as $\left(\frac{dB}{dS}\right)_M = \left(\frac{dT}{dM}\right)_S$

We could define magnetic equivalent of *enthalpy*, Gibbs and Helmholtz free energy; four magnetic Maxwell relations, etc.

- Can use thermodynamics for magnetic **systems**.
- Definition of **systems** and **surroundings** still important.
- Definition of process determines what to treat as “work”.

Magnetic cooling: Approximations

- 1 Small induced magnetisation $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) \approx \mu_0\mathbf{H}$
- 2 *scalar* susceptibility; magnetisation parallel to field.
Generalisation to tensorial quantities is straightforward if tedious.
- 3 Negligible change in volume: no PdV work.
- 4 Use energy densities, intensive quantities (no “script” symbols).

Equipartition in Classical Mechanics

- All degrees of freedom have same energy.
- All excited of degrees of freedom contribute to entropy.



US Declaration of Independence (1776)

We hold these truths to be self-evident, that all men are created equal,
But when a long train of abuses and usurpations, pursuing invariably the same Object evinces a design to reduce them under absolute Despotism, it is their right, it is their duty, to throw off such Government,
(The King of England is an asshole because...)



Declaration of Arbroath (1320)

It is in truth not for glory, nor riches, nor honours, that we are fighting,
but for freedom.
But if he should give us or our kingdom to the English or the king of the English, we would immediately take steps to drive him out as the enemy and the subverter of his own rights and ours
(The King of the English is an auld scunner because...)

Equipartition/entropy: All Degrees of Freedom



Not just “men”.

Degrees of freedom - Many types of entropy

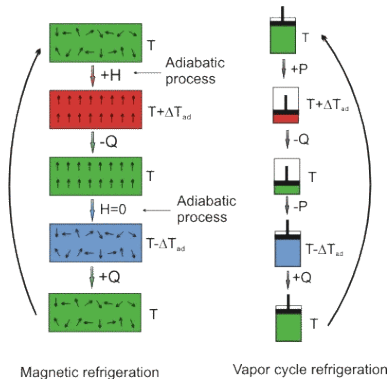
All degrees of freedom allowing disorder have entropy.

- Diatomic gases: *rotational*
- Chemical bonds: *vibrational*
- Plasmas: *electronic*
- Long molecules: *orientational*
- Magnetic materials: *spin*
- Quantised by \hbar , same as $\Delta x \Delta p$.

Only excited “Heated” degrees of freedom contribute to entropy.

Magnetic Cooling - Two types of entropy

- 1 Put paramagnet in contact with heat bath
- 2 Apply field isentropically.
Magnetic entropy \rightarrow Thermal entropy
- 3 Paramagnet loses heat to heat bath.
- 4 Remove paramagnet from heat bath
- 5 Remove field isentropically:
Thermal entropy \rightarrow magnetic entropy increases
- 6 Cold paramagnet can extract heat from fridge



Magnetic Cooling "Cycle"

a) Isothermal magnetisation loses heat:

$$\left(\frac{dQ}{dB}\right)_T = T \left(\frac{dS}{dB}\right)_T = T \left(\frac{dM}{dT}\right)_B$$

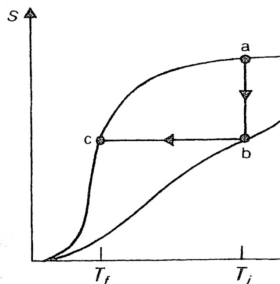
b) Adiabatic/isenthalpic demagnetisation reduces temperature

$$\left(\frac{dT}{dB}\right)_S = - \left(\frac{dT}{dS}\right)_B \left(\frac{dS}{dB}\right)_T = - \frac{T}{c_B} \left(\frac{dM}{dT}\right)_B = - \frac{TB}{c_B} \left(\frac{d\chi}{dT}\right)_B$$

Using Maxwell and product rules,

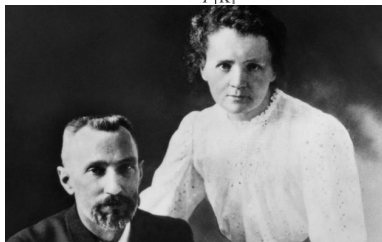
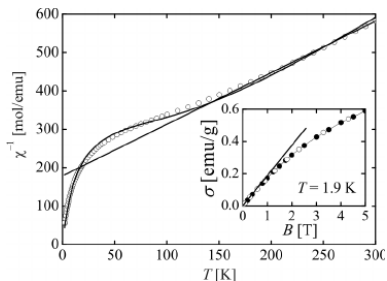
Defining susceptibility $\chi = M/B$;

and heat capacity at constant B-field. $c_B = T(\partial S/\partial T)_B$



Magnetic equation of state: Curie Law

- Curie Law of susceptibility at low T
- Defined by $M = aB/T$ or equivalently $\chi^{-1} = T/a$.
- “a” is the Curie constant (Usually C)
- Found by experiments of Pierre Curie.



Nobel prize 1903, Physics



half awarded to Antoine Henri Becquerel "in recognition of the extraordinary services he has rendered by his discovery of spontaneous radioactivity", the other half jointly to Pierre Curie and Marie Curie, nee Sklodowska "in recognition of the extraordinary services they have rendered by their joint researches on the radiation phenomena discovered by Professor Henri Becquerel."

Arrhenius 7

Marconi 6

Rayleigh 6

Becquerel 6 (+ P.

Curie 5 + M Curie 1)

...

Boltzmann 1

Arrhenius won the Chemistry prize.

What Happened next?

- *Action physiologique des rayons du radium* P. Curie & H. Becquerel (1901)
- *Sur l'étude des courbes de probabilité relatives à l'action des rayons X sur les bacilles* M. Curie (1929)
- Pierre (and Boltzmann) died in 1906
- Marie (1867-1934) won the Chemistry prize 1911,
- Daughter Irene won again in 1935 with her husband, Frederic.
- Granddaughter Helene married Michel Langevin



Curiouser and Curiouser

[International Congress of Radiology and Electricity] suggested that the name Curie, in honor of the late Prof. Curie, should if possible, be employed for a quantity of radium or the emanation. This matter was left for the consideration of the standards committee. The latter suggested that the name Curie be used as a new unit to express the quantity or mass of radium emanation [radon] in equilibrium with one gram of radium (element). (Rutherford, Nature 1910)

Radium Standards Committee decided that the curie should be based on 10^{-8} grams of radium.

the use of the name "curie" for so infinitesimally small quantity of anything is altogether inappropriate.

1 Rutherford is equivalent to 2.703×10^{-5} Curie

1 Becquerel 2.703×10^{-11} Curie

Two entropies - two-term heat capacity

Use *Schottky* non-Magnetic heat capacity $c(T, B = 0) = b/T^2$ with b a constant.

The full heat capacity is then:

$$\begin{aligned}c(T, B) &= b/T^2 + \int \left(\frac{\partial c_B}{\partial B} \right)_T dB = b/T^2 + \int T \left(\frac{\partial^2 M}{\partial T^2} \right)_B dB \\ &= b/T^2 + \int T \cdot \frac{2aB}{T^3} dB = (b + aB^2)/T^2\end{aligned}$$

Using the general result $\left(\frac{\partial c_B}{\partial B} \right)_T = T \left(\frac{\partial^2 M}{\partial T^2} \right)_B$ and the Curie Law $M = aB/T$.

Now back to the adiabatic cooling process (bc)

$$dT = -BT \cdot \frac{T^2}{(b + aB^2)} \cdot \frac{-a}{T^2} dB$$

$$\int \frac{dT}{T} = \int \frac{aB}{(b + aB^2)} dB$$

$$[\ln T]_i^f = \left[\frac{1}{2} \ln(b + aB^2) \right]_i^f$$

Plugging in the initial and final data,

$$T_f = T_i \sqrt{\frac{b + aB_f^2}{(b + aB_i^2)}}$$

Temperature is reduced by a fixed fraction each cycle.
Even with infinite cycles, it can never reach zero.

Curie-Weiss

- Curie's Law looks like another example of divergence at $T=0$.
- More careful measurement shows a form $\chi = a/(T - T_c)$
- Below T_c , paramagnet spontaneously magnetizes

redefine $T' = (T - T_c)$ to obtain

$$T_f = T_c + (T_i - T_c) \sqrt{\frac{b + aB_f^2}{(b + aB_i^2)}}$$

Now can't even cool below T_c ...

