# Thermodynamics 3

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# This lecture

- Heat capacity and specific heat
- Carnot cycle
- Partial pressures
- Entropy change of an ideal gas
- Thermal expansion
- Phase changes
- T-S diagrams
- Clausius-Clapeyron relation
- Conduction
- Convection
- Radiation
- Black bodies

# Heat capacity and specific heat

- In lecture 2, saw heat capacity of a system for constant volume and constant pressure
- This is an extensive quantity, depends on size of system
- **Specific heat capacity**, or just specific heat, is the intensive quantity. Units J $K^{-1}$ $kg^{-1}$ or J $K^{-1}$ $mol^{-1}$
- In physics, we use heat capacity more than specific heat as we are interested in the behaviour of systems rather than materials

# Carnot cycle

- In lecture 2, discussed efficiency $\eta$. What is the most efficient cycle?
- The **Carnot cycle** is the most efficient possible as it is reversible: want no nett entropy change during any process
- Adiabatic: $Q = 0$ so no entropy change
- Isothermal processes (if working substance is at same temperature as reservoir):
  $\Delta S = Q_{\mathrm{res}}/T + Q_{\mathrm{ws}}/T = Q_{\mathrm{res}}/T - Q_{\mathrm{res}}/T = 0$
- A cycle constructed from these two processes is the Carnot cycle

# Carnot cycle

- For a Carnot cycle between $T_H$ and $T_C$: $Q$=0 during adiabats.
- Work in an isothermal process $W = -\int PdV = -\int_{V_i}^{V_f} \frac{NkT}{V} dV = -NkT \ln\left(V_f/V_i\right)$, and since $\Delta U = 0 = Q + W$
- Heat goes in during isothermal expansion at $T_H$, heat goes out isothermal expansion $T_C$

$$Q_{\text{in}} = -\left(-NkT_H \ln\left(V_1/V_2\right)\right)$$

$$Q_{\text{out}} = -\left(-NkT_C \ln\left(V_4/V_3\right)\right)$$

$$\eta = W/Q_{\text{in}} = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}}$$

$$\eta_{\text{Carnot}} = 1 - \frac{NkT_C \ln\left(V_4/V_3\right)}{NkT_H \ln\left(V_1/V_2\right)} = 1 - \frac{T_C \ln\left(V_4/V_3\right)}{T_H \ln\left(V_1/V_2\right)}$$

# Carnot cycle

- For adiabats: $VT^{f/2} = \text{constant!}$
- $V_1 T_H^{f/2} = V_4 T_C^{f/2} \rightarrow V_4 = V_1 (T_H/T_C)^{f/2}$
- $V_2 T_H^{f/2} = V_3 T_C^{f/2} \rightarrow V_3 = V_2 (T_H/T_C)^{f/2}$

$$\ln\left(\frac{V_4}{V_3}\right) = \ln\left(\frac{V_1 (T_H/T_C)^{f/2}}{V_2 (T_H/T_C)^{f/2}}\right) = \ln\left(\frac{V_1}{V_2}\right)$$

So from previous slide

$$\eta_{\text{Carnot}} = 1 - \frac{T_C \ln(V_4/V_3)}{T_H \ln(V_1/V_2)} = 1 - \frac{T_C}{T_H}$$

**Best efficiency, but really really slow**

# Partial pressures

- Have mixtures of different molecules in a gas
- The **partial pressure** of each constituent type of particle is the pressure that it would have if it were alone in the vessel, and the total pressure is the sum of these partial pressures.

# Entropy change of ideal gas

- Construct convenient path: adiabats and isotherms
- Entropy change? Measuring the **absolute entropy** is a pretty tough ask

# Entropy change of ideal gas

- Can get **absolute entropy** for ideal gas using the **Sackur-Tetrode equation**
- Absolute? Entropy at 0 K is zero for perfectly ordered thing
- Briefly, find the multiplicity of an ideal gas
- Need quantum mechanics ideas and calculate the area of the momentum hypersphere!

# Thermal expansion

Constituent particles occupy finite volumes; more energy available increase volume per particle.

- 1D:
$$\frac{dL}{L} = \alpha dT$$
- 2D:
$$\frac{dA}{A} = \frac{d(L^2)}{L^2} = \frac{2LdL}{L^2} = 2\alpha dT$$
- 3D
$$\frac{dV}{V} = \dots$$
- Fluid:
$$dV = V\beta dT$$

# Phase changes

- Adding heat can change the **phase** of a substance
- Common phases: solid, liquid, gas, plasma
- And much much more! Active areas of research (materials, cold atoms), ideas and concepts (magnets, poppy seeds)
- Phase changes occur at constant temperature
- Heating curve for water?

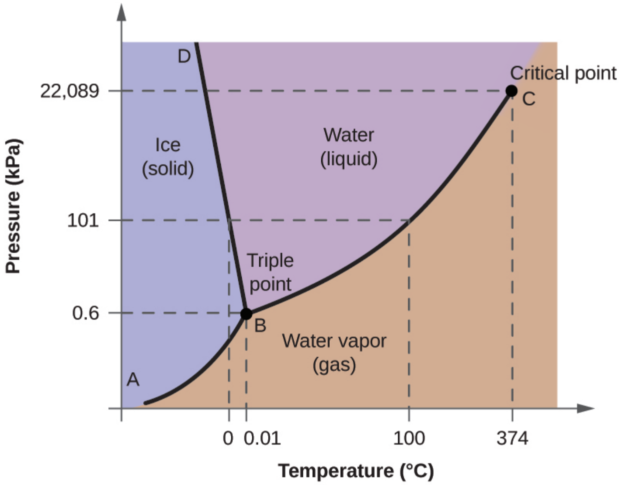
# Phase changes

- Are associated with a **latent heat**
- To change phase of a mass $m$ of a substance, must provide energy
$$Q = Lm$$
- $L$ is latent heat (of fusion, vaporisation, sublimation)

# Phase diagrams

- Usually one phase is thermodynamically stable at a given temperature and pressure
- As we change between two phases, for some $T$ and $p$, two phases can coexist
- A phase diagram shows these relationships

# Phase diagrams




https://opentextbc.ca/chemistry

# T-S diagrams

- Temperature vs. entropy
- $dS = \frac{đQ}{T}$
- Area under the curve: heat transferred to system during ideal process
- Closed cycle enclosed area: total work done by (clockwise) or total work done on (anticlockwise) for a *reversible* process

# Clausius-Clapeyron relation

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

# Heat again

- Heat is the spontaneous energy flow caused by a difference in temperature (doesn't matter how this happens)
- Conduction
- Convection
- Radiation

# Conduction

- **Conduction** occurs between two systems in thermal contact
- Diffusion of heat by particles colliding
- Rate of heat flow depends on: area $A$, temperature difference $dT$, distance over which heat flows $dx$
- Put it together!

# Note on the general idea of diffusion of stuff

**Diffusion** (of particles, of momentum in a fluid, of anything $n$) always looks like

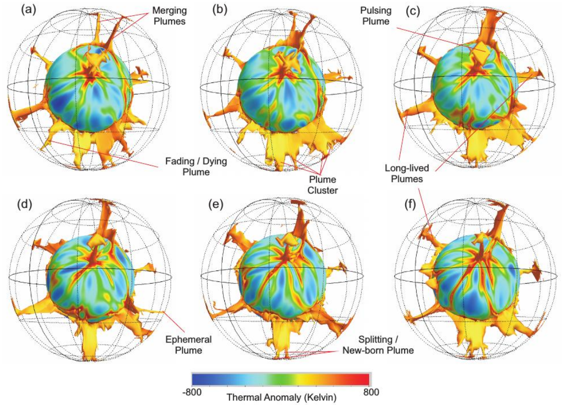
$$J_x = -D\frac{dn}{dx}$$

where $J_x$ is magnitude of the flux of $n$ across a surface with thickness $dx$, and $D$ is **diffusion coefficient** in $\mathrm{m^2\ s^{-1}}$.
Flux = amount of $n$ per unit area per unit time

http://images.dpchallenge.com/

# Convection

- **Convection** is a beautiful thing: chunks of fluid carry energy from one part to another
- Marvellous mantle plumes `http://rses.anu.edu.au/`




- Hot stuff rises $\rightarrow$ draws in cooler fluid at base $\rightarrow$ sets up **convection cell** which mixes fluid and conveys energy

# Penguins

How do penguins stop themselves freezing on ice?

Figure: Rockhopper penguin. pc: `oceanwide-expeditions.com`

# Ice on blocks

I have a large chunk of steel and a large chunk of styrofoam, and place two identical ice cubes one upon each.

- Which ice cube melts faster?
- Which block feels colder?

# Radiation

- Electromagnetic radiation is emitted by a hot thing, example?
- **Black body**: absorbs everything and emits radiation
- **Silver body**: reflects everything, emits nothing
- Stefan-Boltzmann law: power emitted per unit surface area of BB

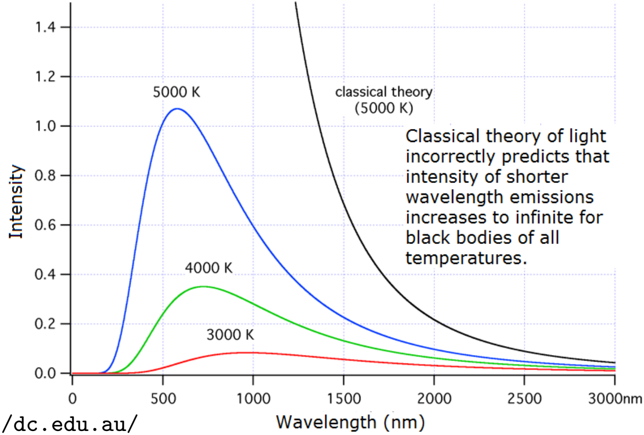
$$I = \epsilon \sigma T^4$$

$\epsilon =$ emissivity ($= 1$ for ideal), $\sigma =$ Stefan-Boltzmann constant

Units of $\sigma$? What is the emissivity of a solar hot water system?

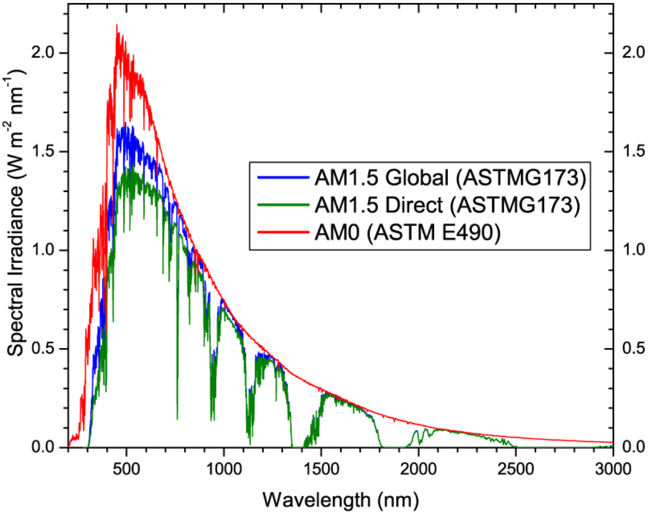
# Radiation

- As toaster heats up, toaster elements change colour.
- As wavelength of radiation decreases, energy increases
- **Ultraviolet catastrophe**: classical theory predicts that BBs emit at all wavelengths $\rightarrow$ INFINITE ENERGY!
- Infinite energy bad, data disagrees, classical theory is wrong.




`https://dc.edu.au/`

# Solar spectrum




http://www.pveducation.org/

# Boltzmann factor

- The **Boltzmann factor** is the probability ratio (probability of being in state 1 / probability of being in state 2) is $\exp\left(-(E_1 - E_2)/kT\right)$
- If we have a lot of particles (average over a lot of systems), this gives the fraction of particles in different energy states of the system.
- Absolute probability (**Boltzmann distribution**):

$$\Pr\left(\text{state } i\right) = \frac{e^{-E_i/kT}}{\sum_j e^{-E_j/kT}}$$

- Sum over all states of interest
- Amazingly broad reach, statistical mechanics

# Black body again

- **Planck's law**: spectral radiance is

$$B(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda}\frac{1}{kT}} - 1}$$

- Energy $= hc/\lambda$. Looks a lot like a Boltzmann factor in the denominator...
- *Planck got this by finding thermal equilibrium for a BB in a box*
- Turns out this is a feature of the Bose-Einstein distribution – quantum mechanics!
- You don't need to "know" this, but it is a very important bit of physics