

Lecture 37 - Latent heat and specific heat

What's important:

- latent heat at a phase change
- specific heat of gases

Demonstrations:

- cooling curve for tin

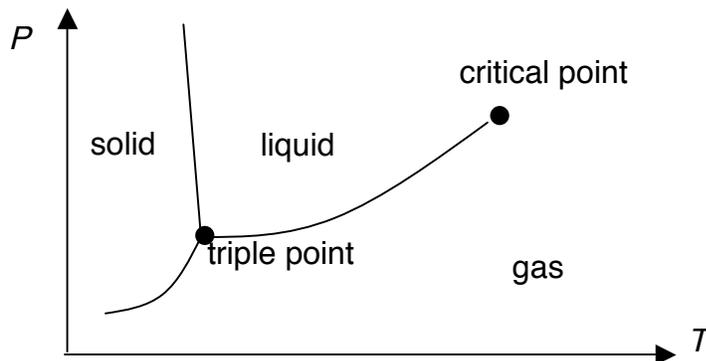
Phase changes

Fluids and solids have distinct mechanical properties: although both phases of matter resist compression, only a solid has a resistance to shear. Within the category of fluids, we also distinguish between liquids and gases:

- liquids: high compression modulus, well-defined boundary
- gases: low compression modulus, no boundary

However, under some conditions, one cannot distinguish between liquids and gases.

The mechanical properties of a pure system can be determined at a given pressure P and temperature T , and the system can be assigned a phase according to the criteria above. **However**, for some P, T combinations there may be more than one phase present (e.g. water and water vapour or ice and water vapour). This leads us to construct a *phase diagram* by specifying the phase(s) observed at particular P, T combinations:



Some notes:

- all three phases coexist at the triple point
- one can go from a liquid to a gas without passing through a phase change beyond the critical point
- in this diagram, a solid turns to a liquid under pressure (like a skate on ice); such behavior is not common.

There are other phases, like liquid crystals, that we will not discuss here; also, there are mixed systems like solutions or colloids.

To move around the phase diagram involves the addition or release of heat. We introduced the heat capacity C (describes the entire system) and the specific heat c (describes a specific amount of material like a kg or mole).

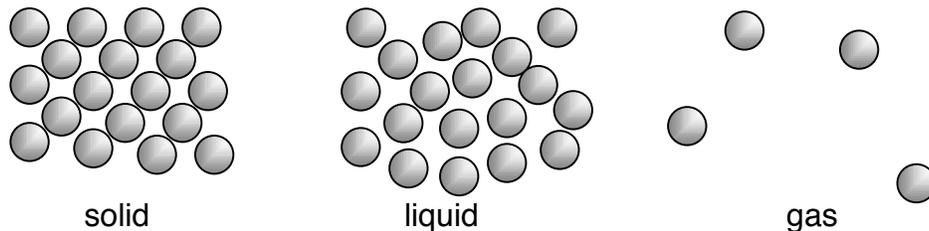
If the heat capacity is independent of temperature, the "heat flow" Q within a given phase region is given by

$$Q = C \Delta T.$$

Some examples at atmospheric pressure

phase	c (J/ K·kg)
ice	2051
water	4186
water vapour	2009 (constant pressure)

In addition, there is a *latent heat* associated with crossing a phase boundary. This is caused by the change in ordering of molecules.



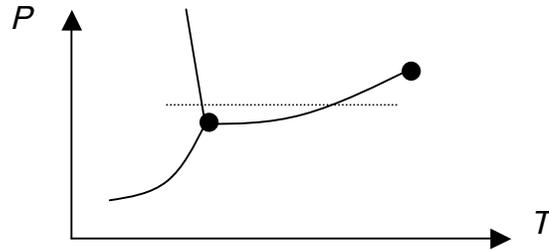
- Melting a solid requires an input of energy (at constant temperature) to loosen up the molecular or atomic bonds
- Vaporizing a liquid involves an input of energy to increase the separation between molecules. Here, the latent heat involves a change in internal energy, plus work in expanding the volume.

Examples of latent heats:

material	fusion, L_f (J / kg)	vaporization, L_v (J / kg)
water	33.5×10^4	22.6×10^5
ethyl alcohol	10.8×10^4	8.55×10^5
lead	2.32×10^4	8.59×10^5

Example:

Find the energy required to heat 1 kg of H₂O from -8 C to + 108 C at $P = 1$ atm.



Break up the path into parts:

$$\text{-8 to 0 C} \quad Q = m c \Delta t = 1 \cdot 2051 \cdot 8 = 0.16 \times 10^5 \text{ J}$$

$$\text{melting at 0 C} \quad Q = m l_f = 1 \cdot 33.5 \times 10^4 = 3.35 \times 10^5 \text{ J}$$

$$\text{0 to 100 C} \quad Q = m c \Delta t = 1 \cdot 4186 \cdot 100 = 4.186 \times 10^5 \text{ J}$$

$$\text{boiling at 0 C} \quad Q = m l_v = 1 \cdot 22.6 \times 10^5 = 22.6 \times 10^5 \text{ J}$$

$$\text{100 to 108 C} \quad Q = m c \Delta t = 1 \cdot 2009 \cdot 8 = 0.16 \times 10^5 \text{ J.}$$

Kinetic theory and molar heats

The specific heats at constant volume or constant pressure can be calculated within the kinetic theory of gases. We treat the case of structureless atoms (no rotational motion, just linear).

First, we evaluate the kinetic energy of the atoms. For N atoms, we showed previously that the average kinetic energy at temperature T is

$$E = N(3k_B T/2) = (3/2) nRT \quad (n = N/N_0 = \text{number of moles})$$

Then, at constant volume, there is no PV work, and the heat Q_v required is

$$Q_v = E_2 - E_1 = (3/2) nR(T_2 - T_1)$$

Normalizing this per mole ($n = 1$), we have

$$C_v = Q_v / (T_2 - T_1) = (3/2)R$$

The calculation may be repeated at constant pressure but we must include the work:

$$\begin{aligned} Q_p &= E_2 - E_1 + P(V_2 - V_1) \\ &= (3/2) nR(T_2 - T_1) + nR(T_2 - T_1) \\ &= (5/2) nR(T_2 - T_1) \end{aligned}$$

Again, setting $n = 1$ and dividing by $(T_2 - T_1)$:

$$C_p = Q_p / (T_2 - T_1) = (5/2)R.$$

This kind of approach may be applied to solids as well, although the motion now is 3 vibrational modes for every atom in the solid. Each vibration has $k_B T/2$ for the kinetic energy (v^2) and $k_B T/2$ for potential energy (x^2). Then,

$$\text{energy per atom} = 3 \cdot 2 \cdot k_B T/2 = 3k_B T$$

$$C_v = 3R = 25 \text{ J / K}\cdot\text{mole}$$

This result is called the Dulong-Petit value.