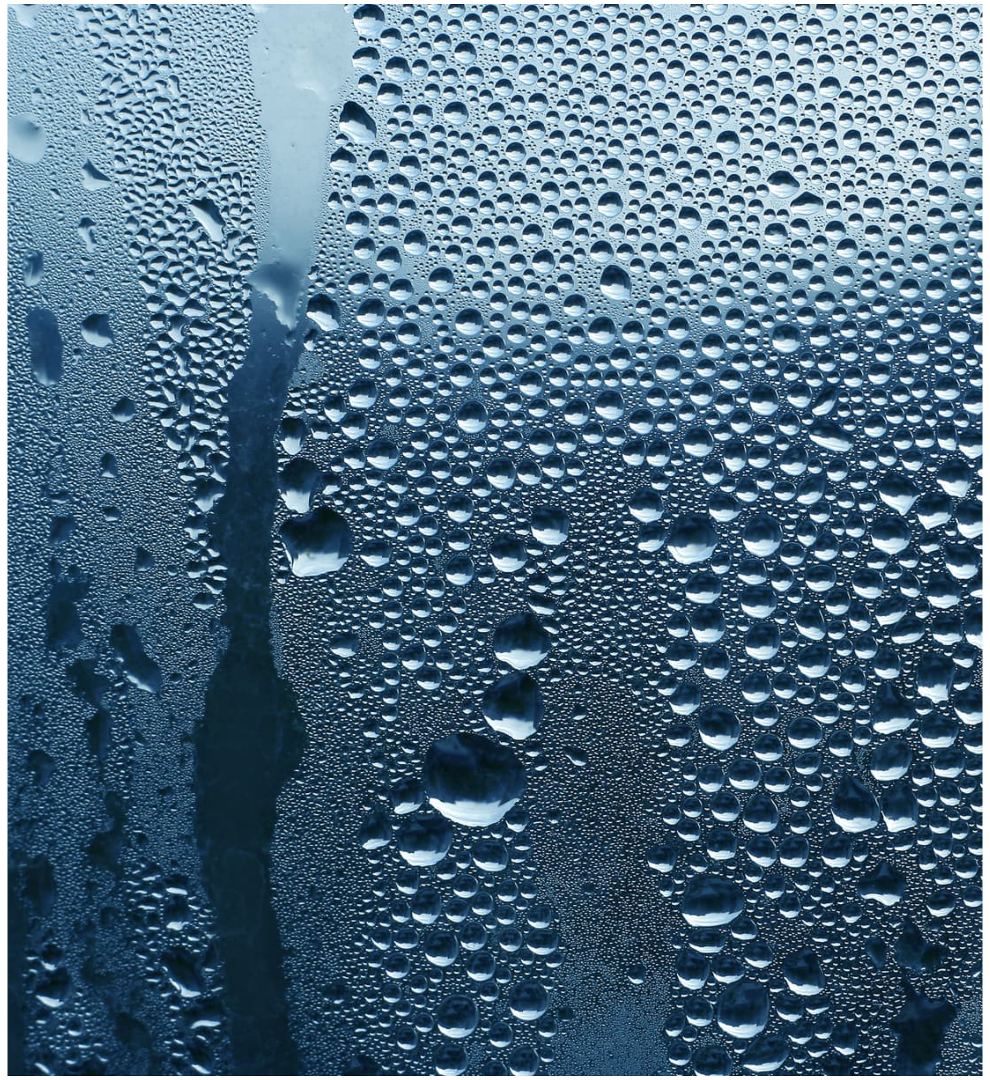
Session 6
Phase diagrams and phase transitions

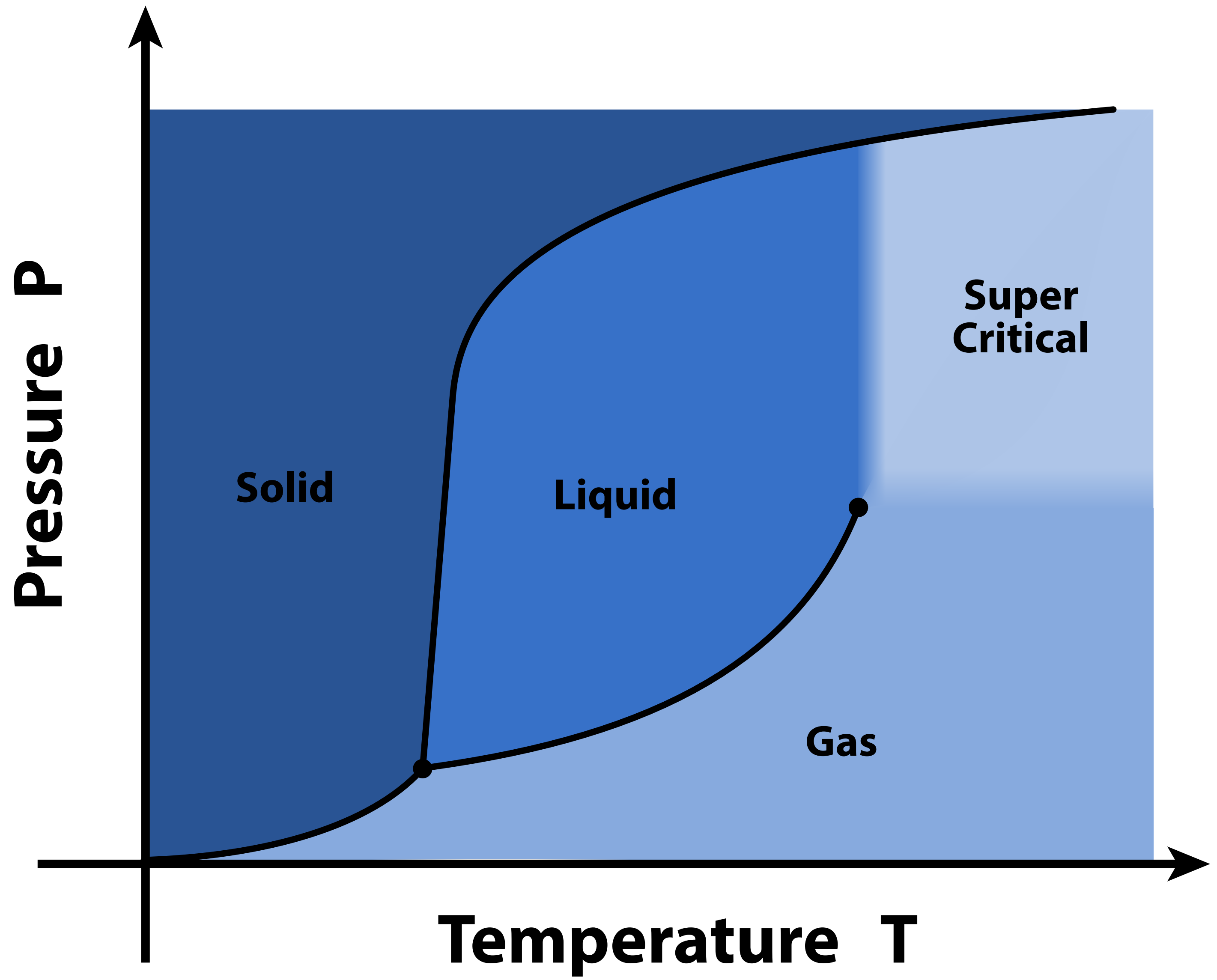
Introduction

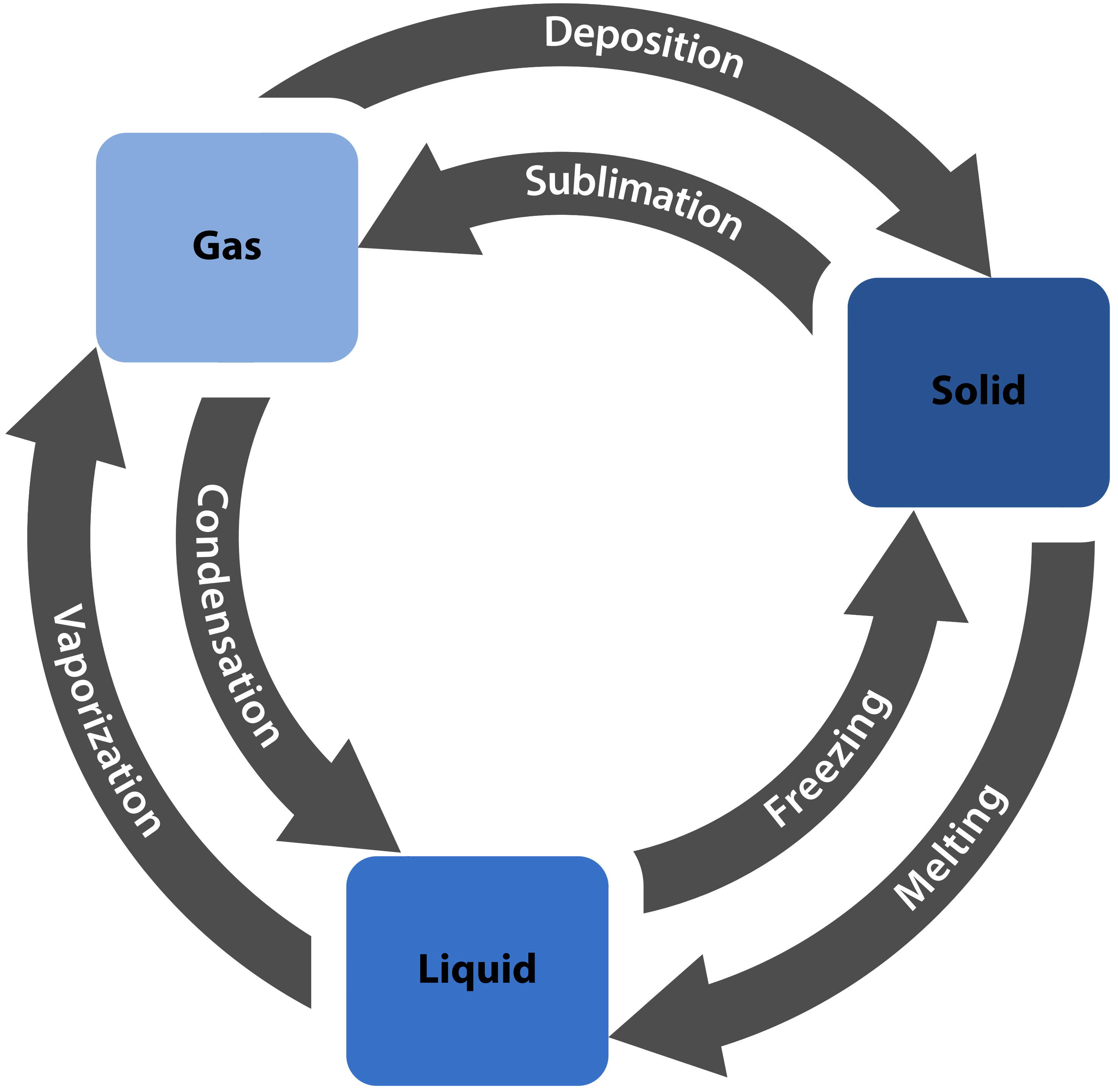
Phase transitions

Phase transitions are changes in the state of the matter. They are qualitative transformations in the appearance and behavior of a substance that are triggered by a change in the external conditions (such as temperature or pressure).

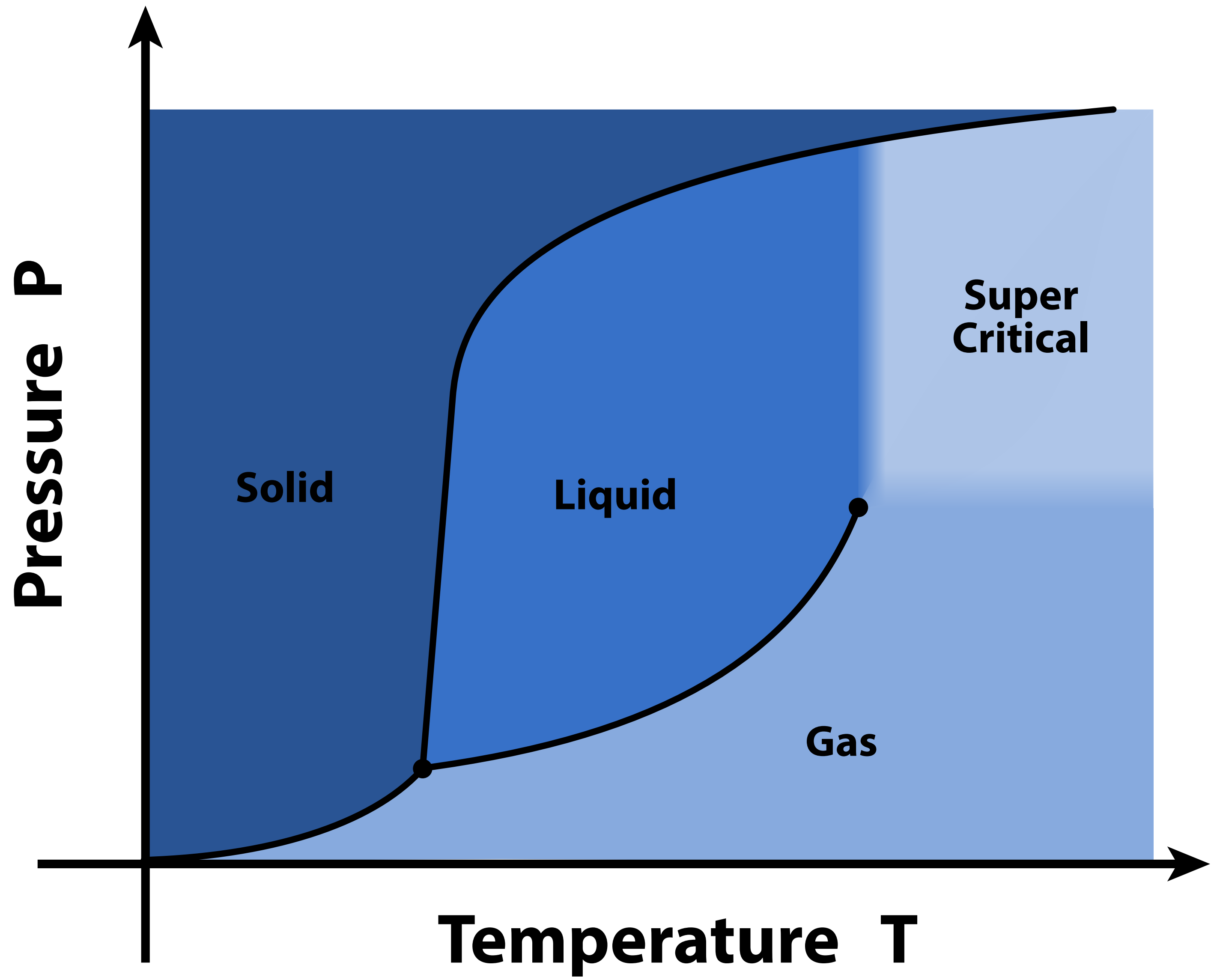




Solid - Liquid - Gas phase transitions



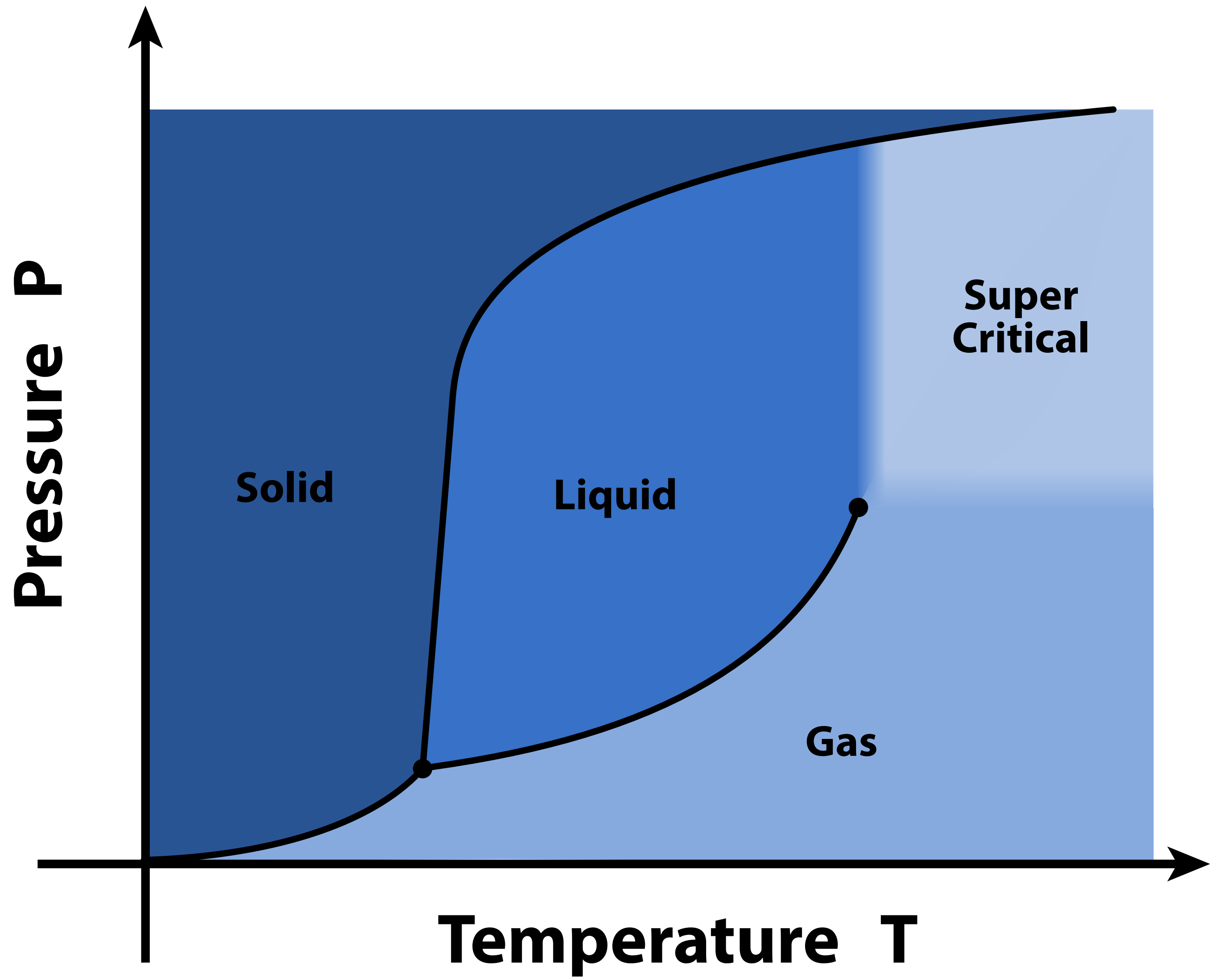


Phase diagrams



Phase diagram are charts that indicate the conditions (i.e. pressure, temper-ature, volume, ...) at which the differ-ent phases occur.

Phase diagrams



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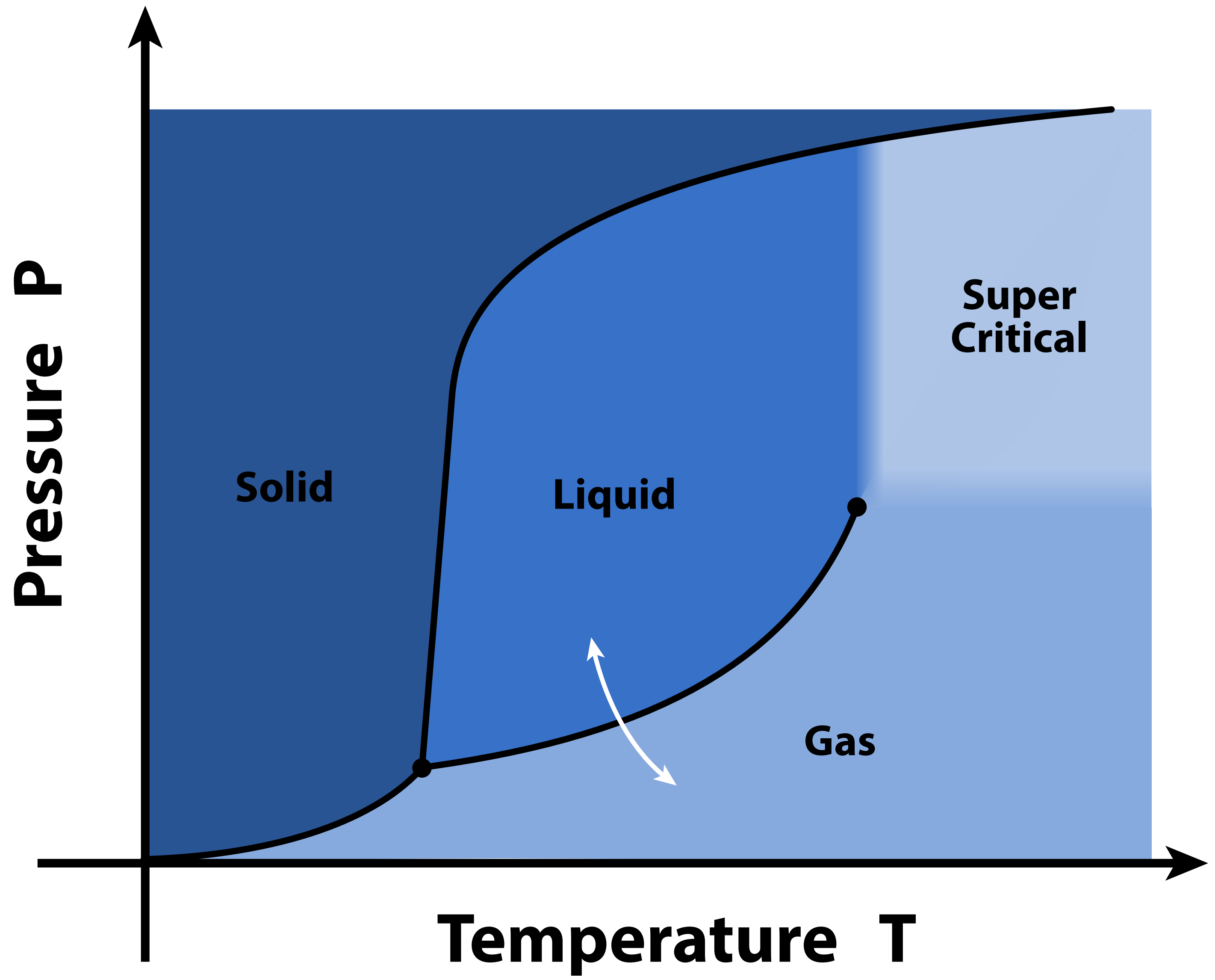
At the boundary between two regions, i.e. along a phase equilibrium curve, two phases can coexist at equilibrium.

Phase diagrams

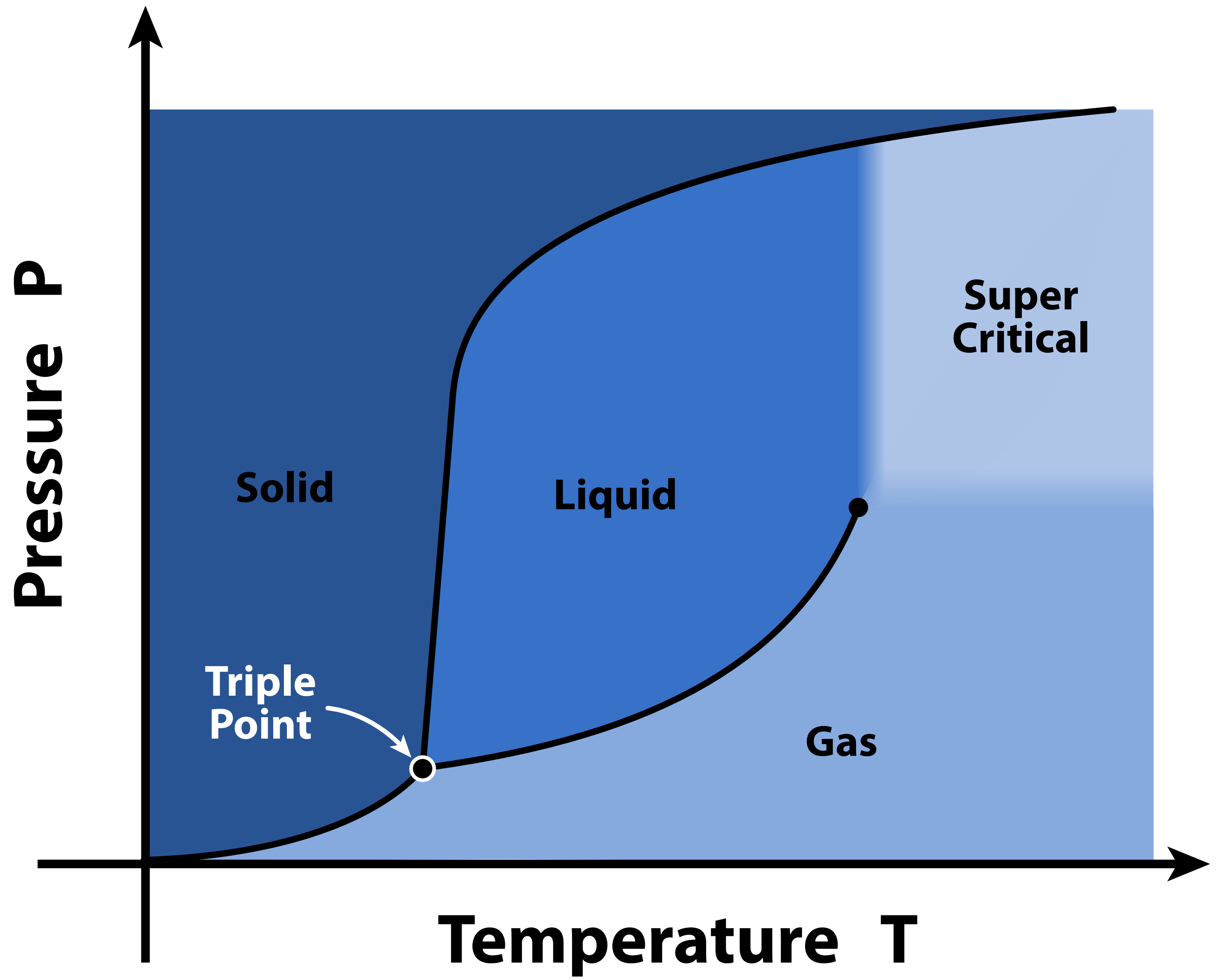


Phase diagram are charts that indicate the conditions (i.e. pressure, temperature, volume, ...) at which the different phases occur.

At the boundary between two regions, i.e. along a phase equilibrium curve, two phases can coexist at equilibrium.

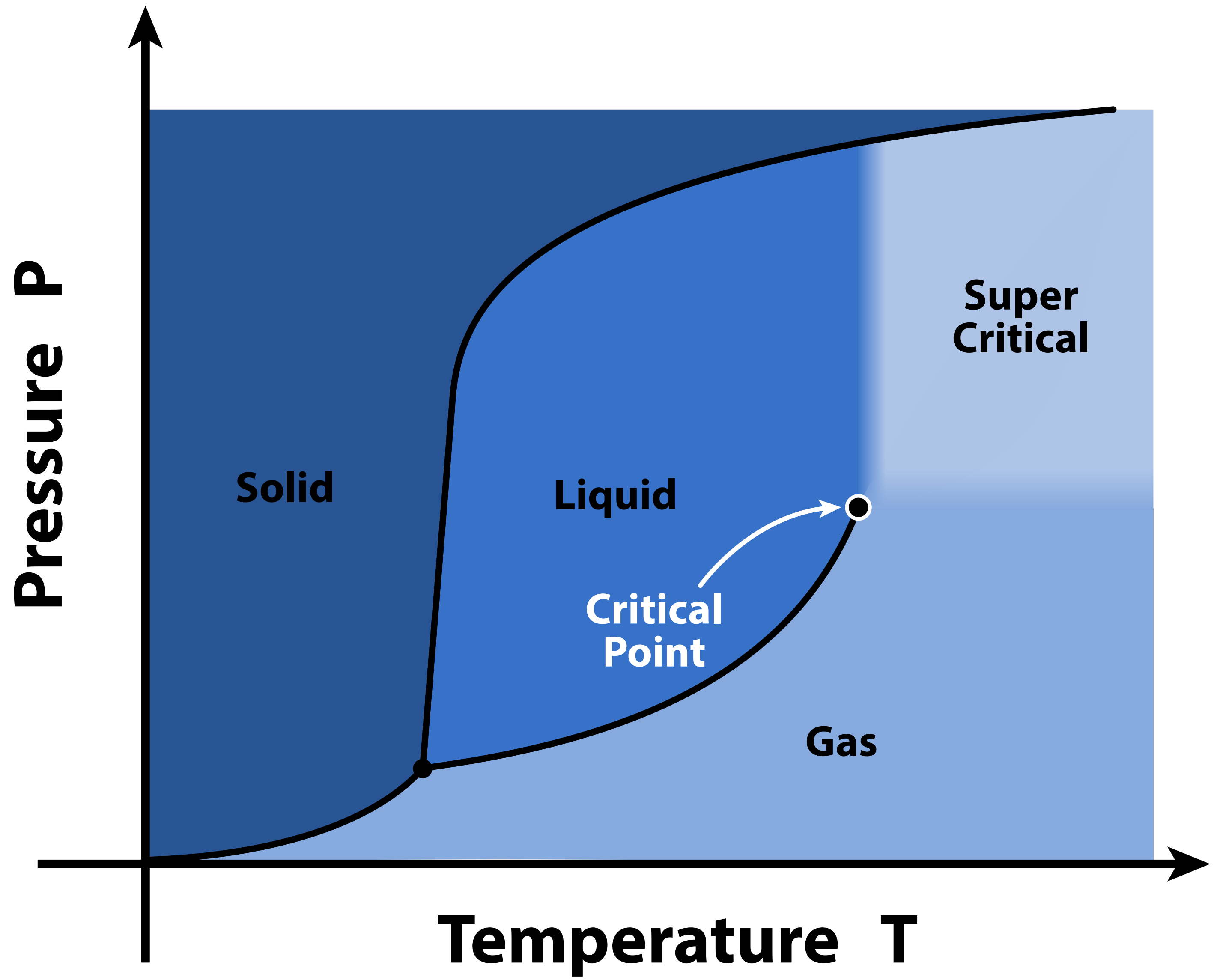
When the conditions change such that a phase equilibrium curve is crossed, the transition is triggered.

The concept of triple point



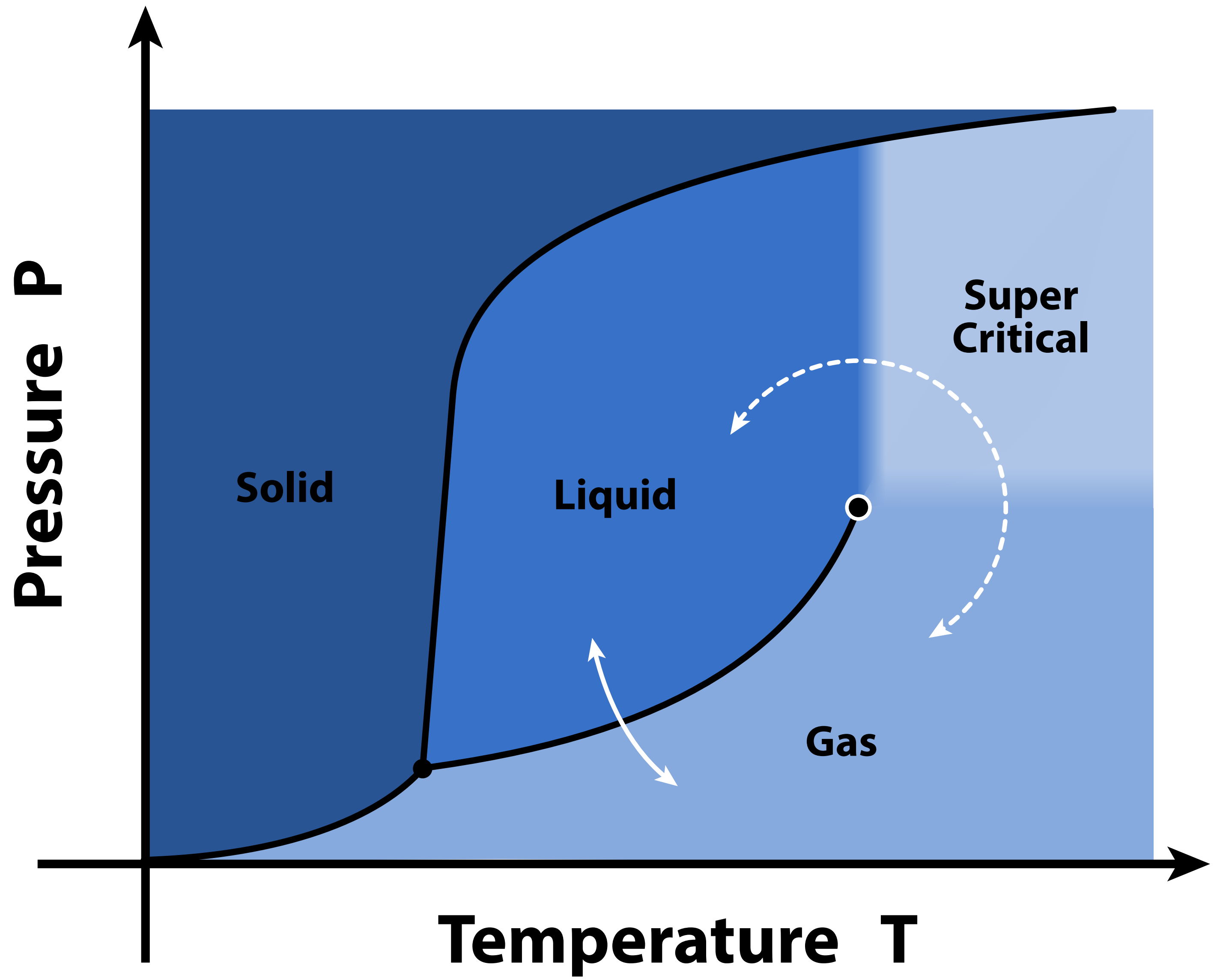
For a given substance, the triple point corresponds to the temperature and pressure at which the <u>three phases</u> (gas, liquid, and solid) coexist in thermodynamic equilibrium.

The concept of critical point



For a given substance, the critical point corresponds to the temperature and pressure of the end point of a phase equilibrium curve.

The concept of critical point



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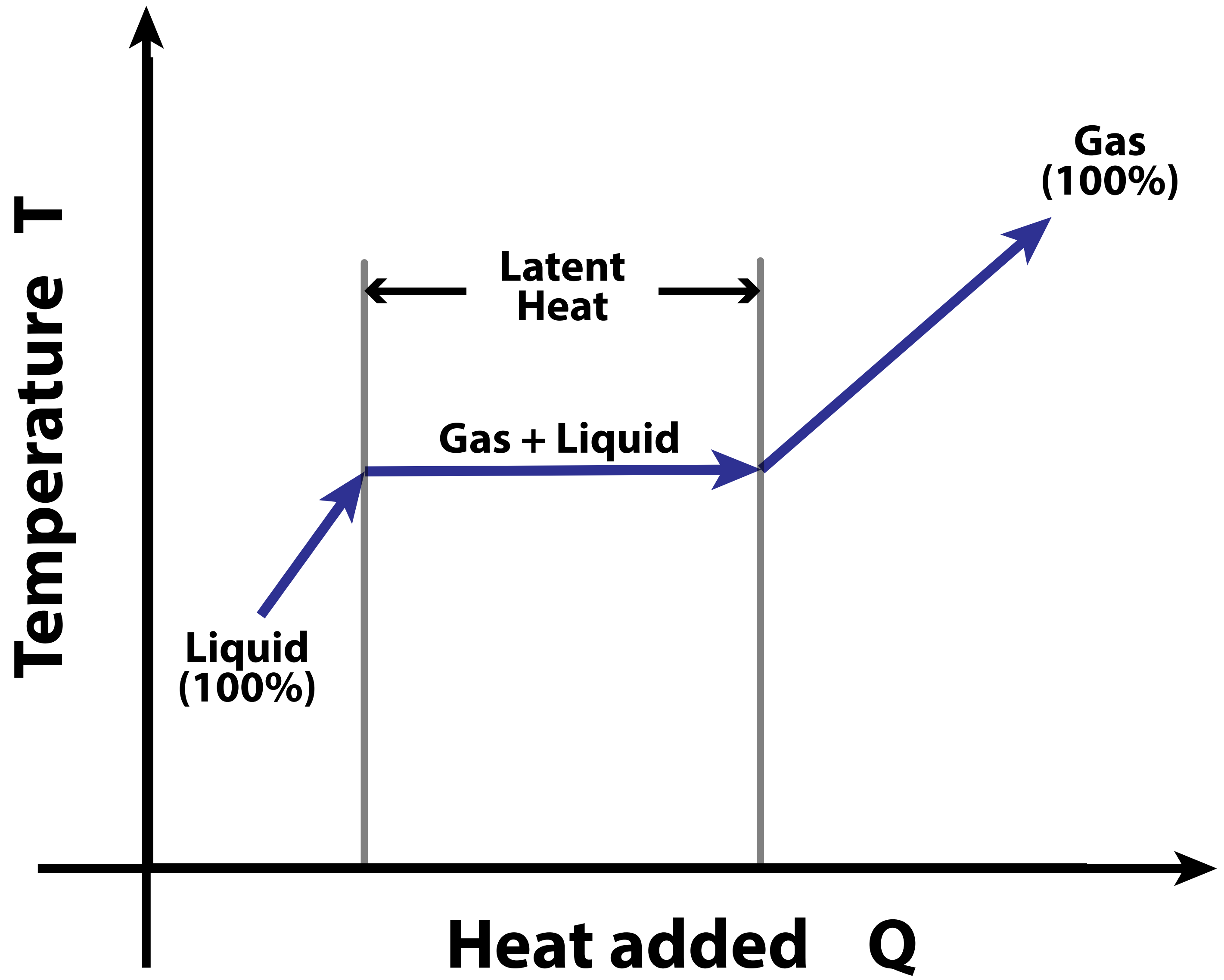
Beyond the critical point phase boundaries vanish: the transition between the two phases happens smoothly.

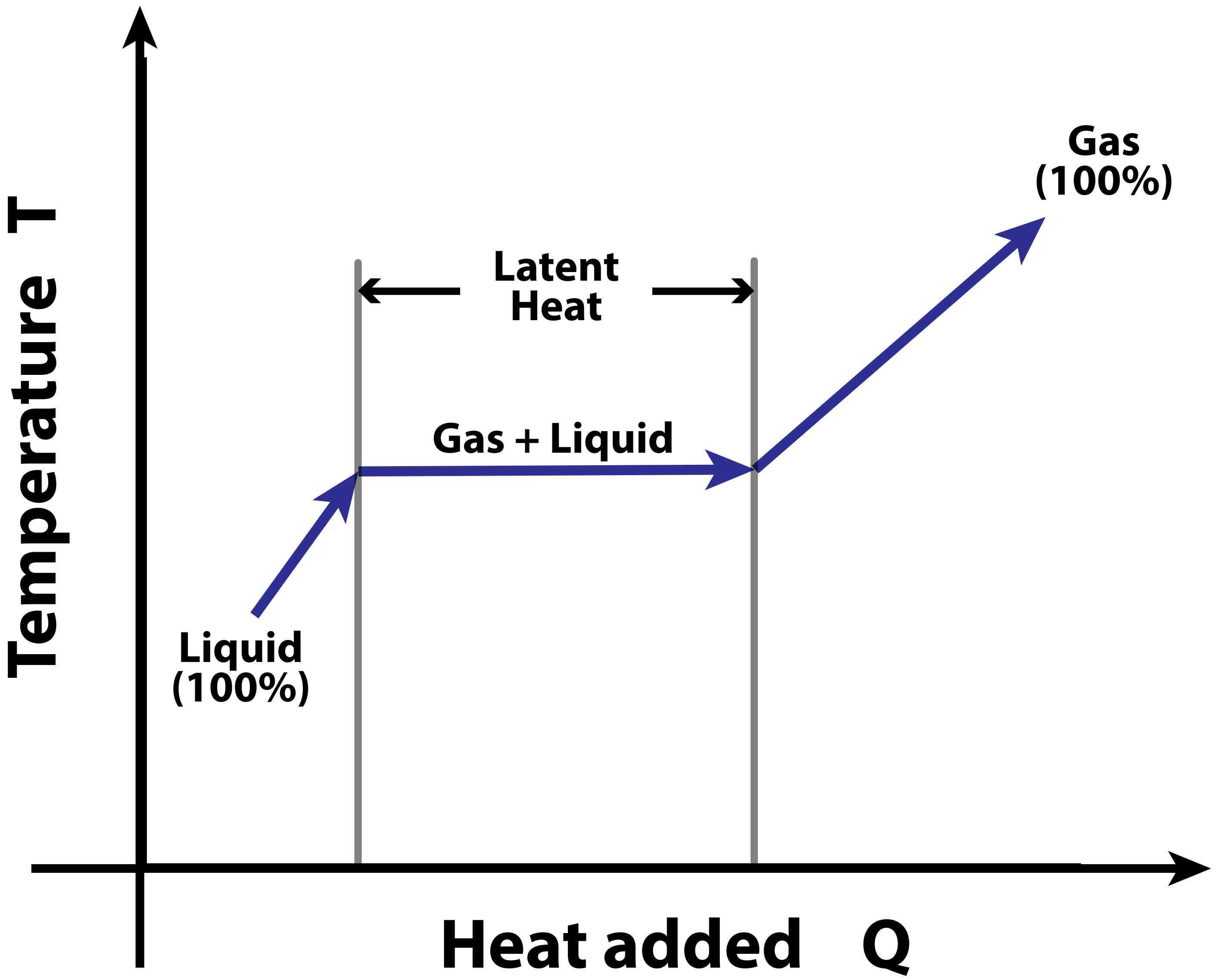
The concept of latent heat



Latent heat is energy that is supplied to or released by a substance during a phase transition while its temperature remains constant.

In other words is the energy difference between the two phases when both their temperatures are equal to the transition temperature.

The concept of latent heat



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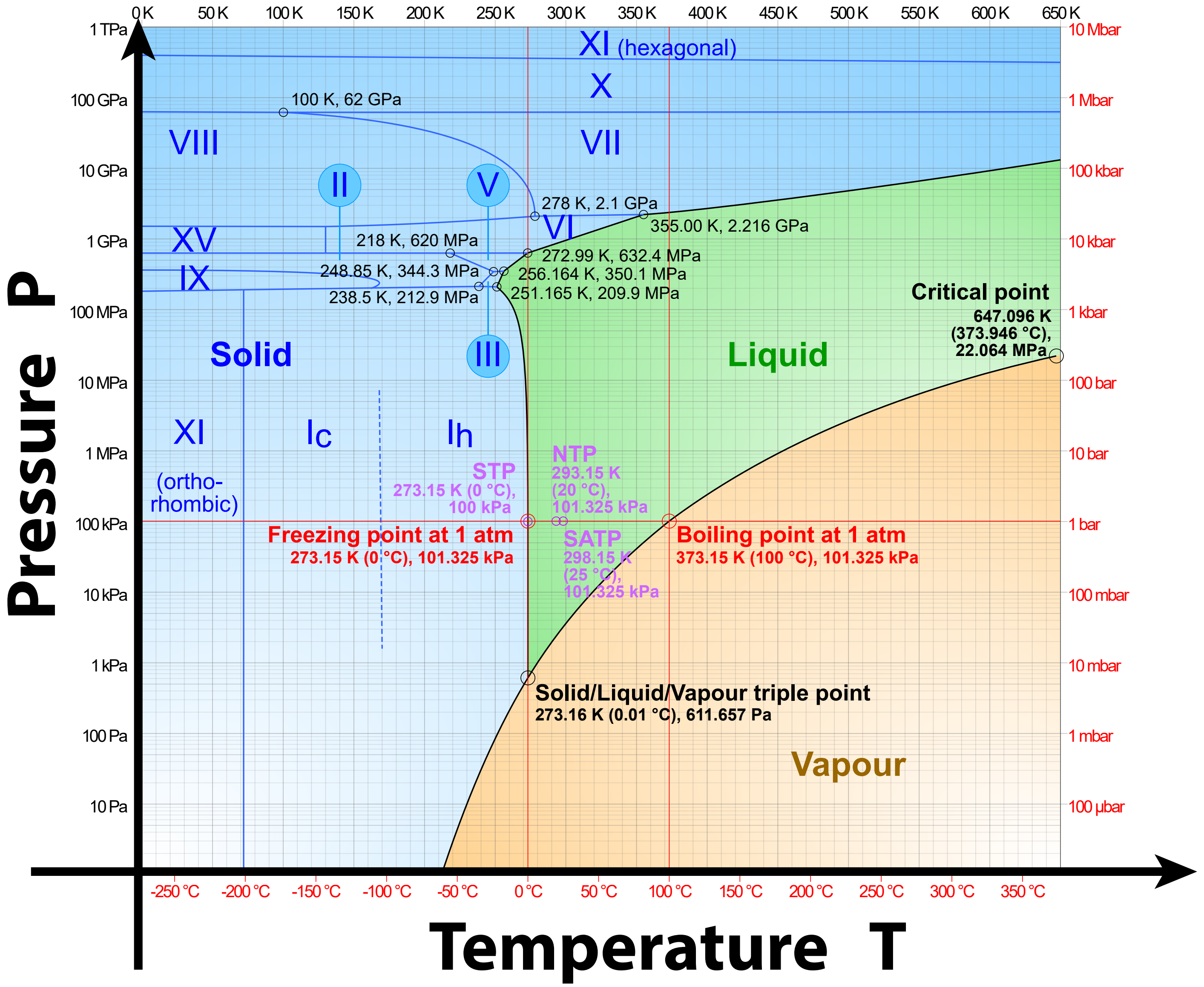
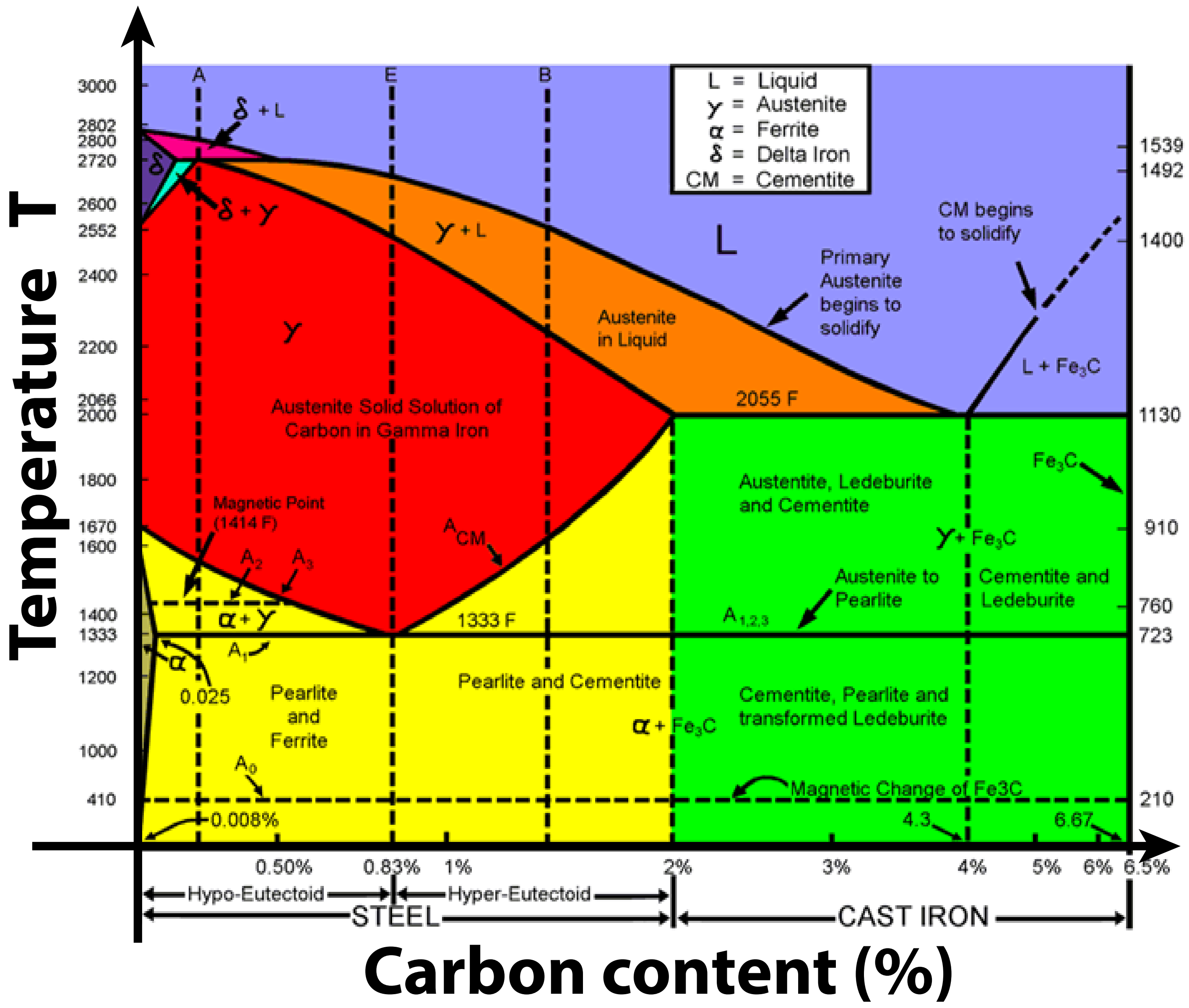
Specific latent heat: latent heat per unit of mass.

Other examples of phase transitions and phase diagrams

Phase diagram of water

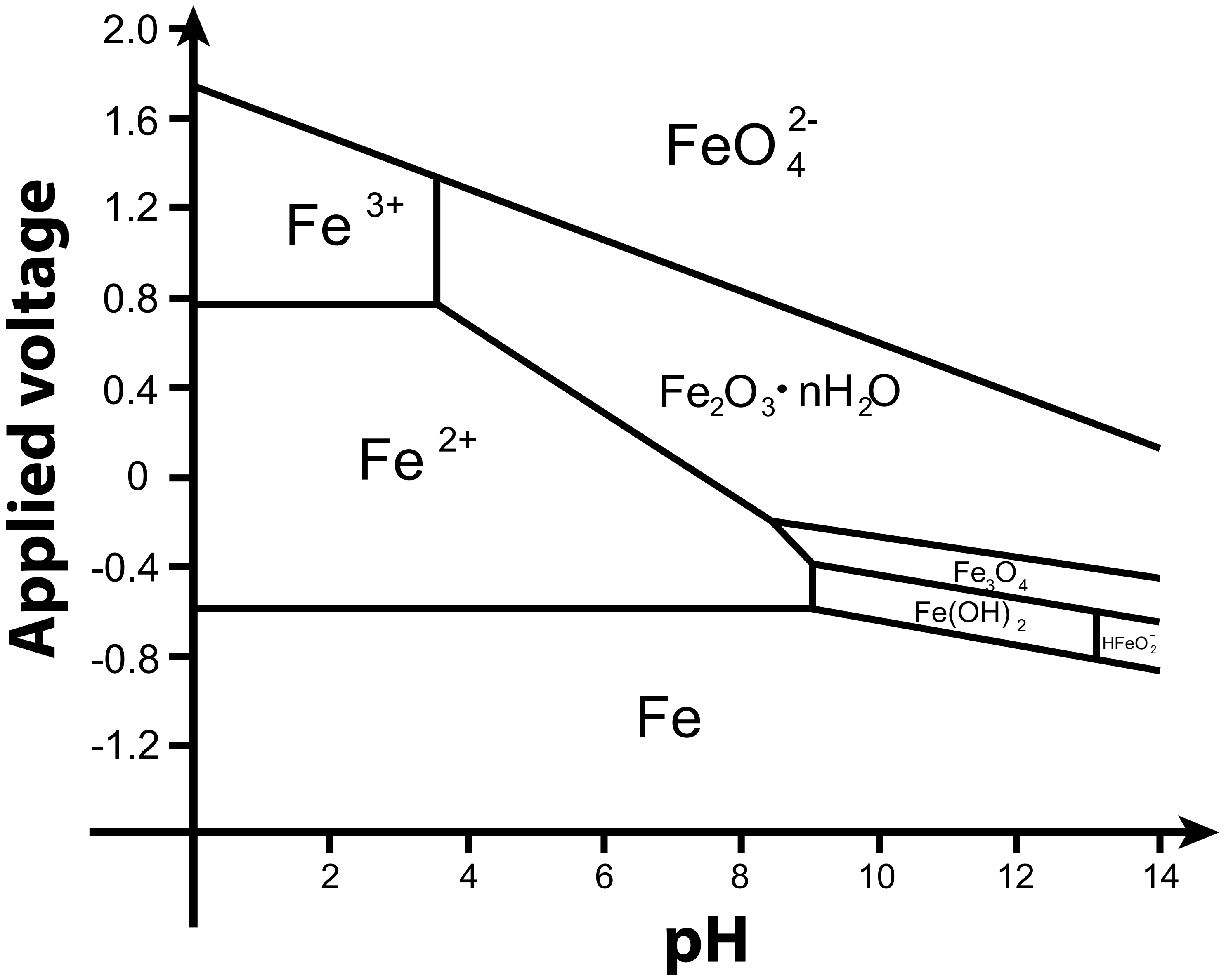


Phase diagram of iron/carbon

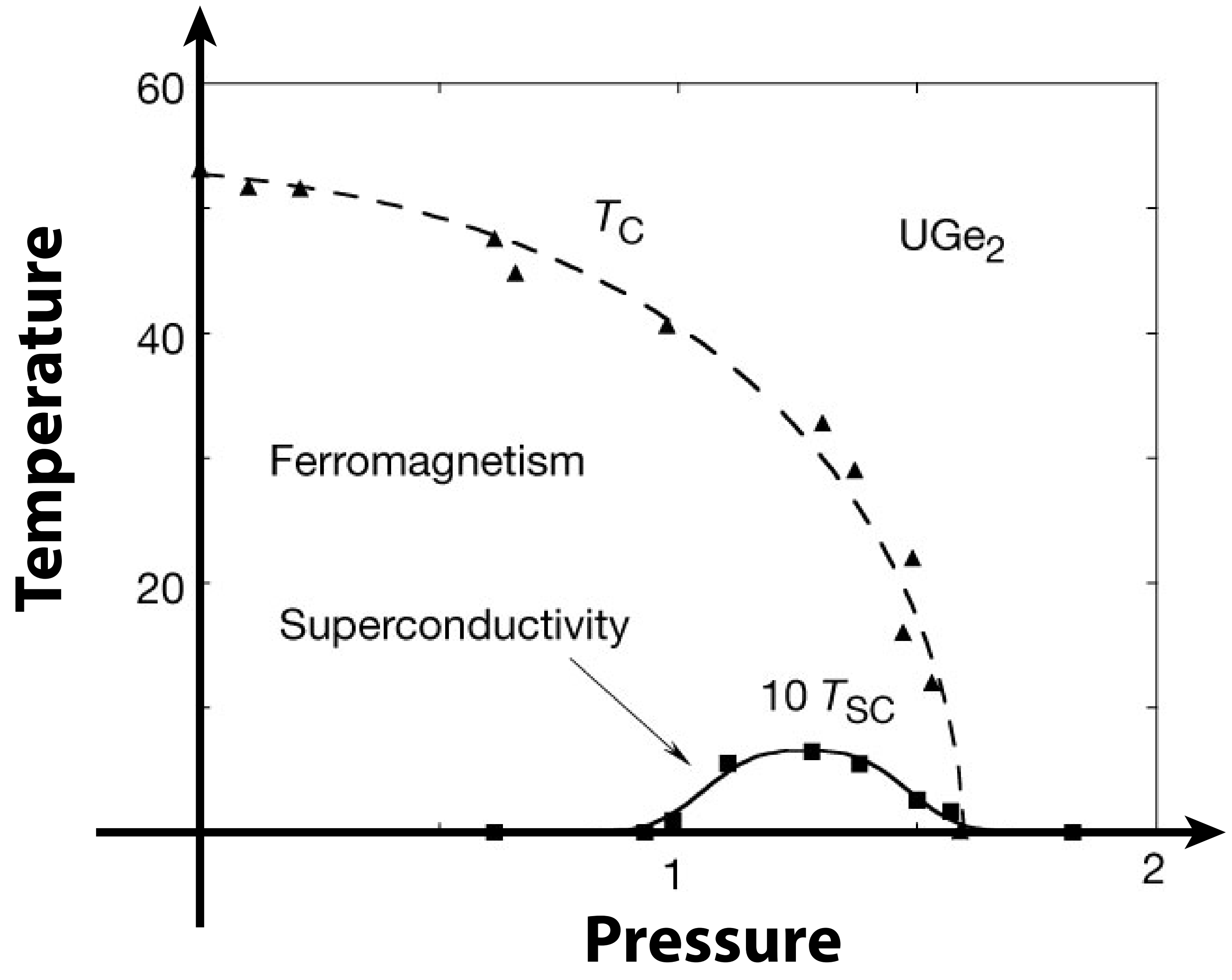


Other examples of phase transitions and phase diagrams

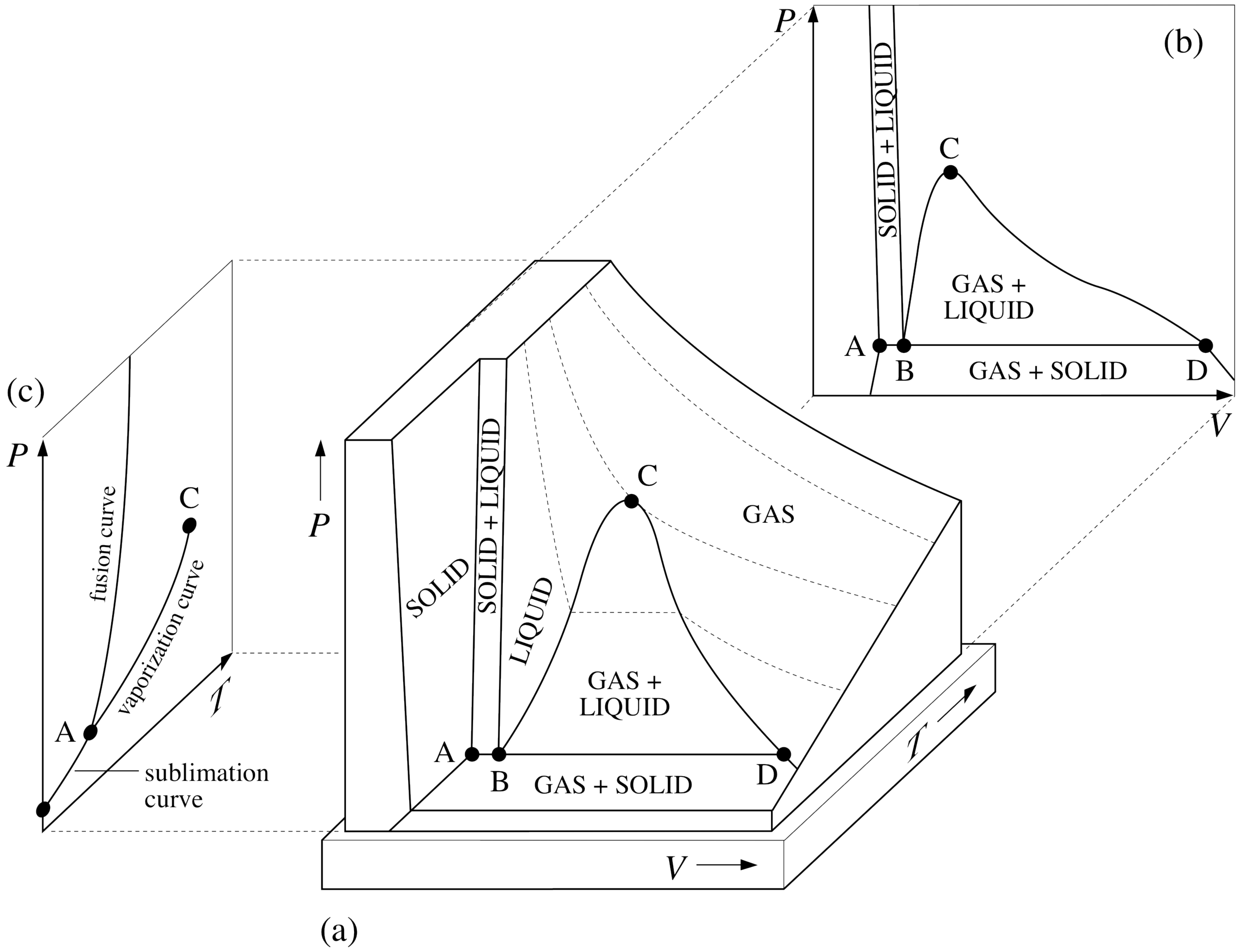
Pourbaix diagram of iron



Phase diagram of UGe2

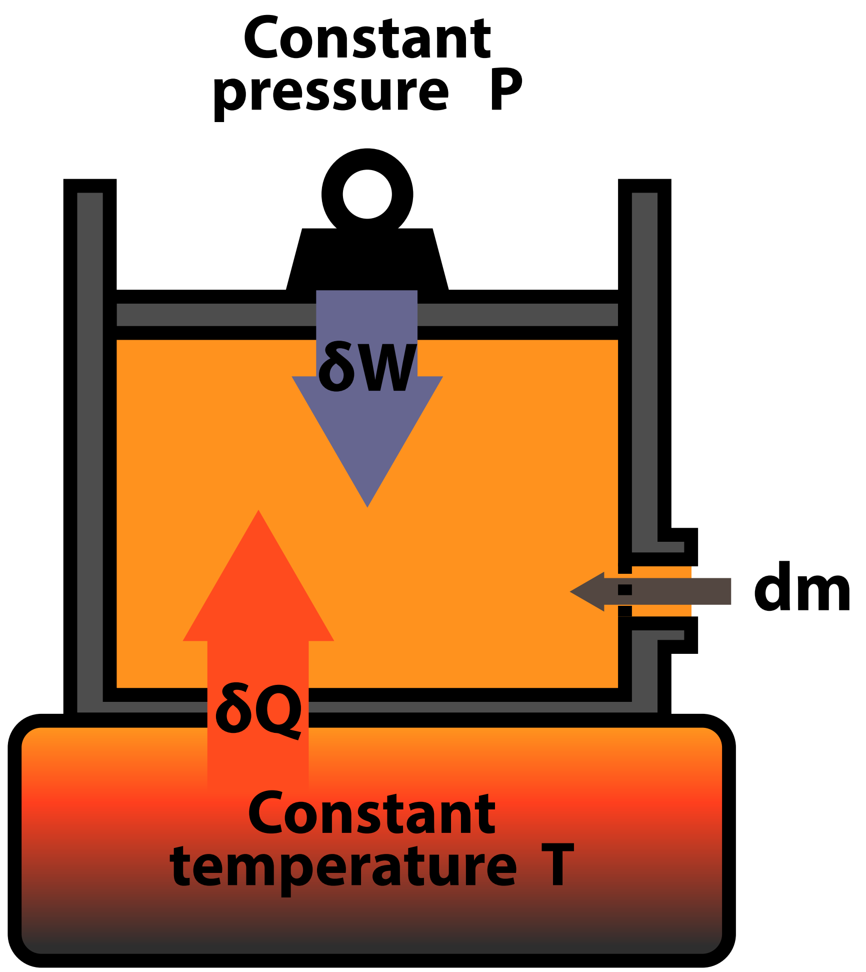


P-V-T phase diagram



Gibbs Energy and Chemical Potential

Open system at constant T and P, with mass transfer dm. The mass enters with specific enthalpy h, and specific entropy s.



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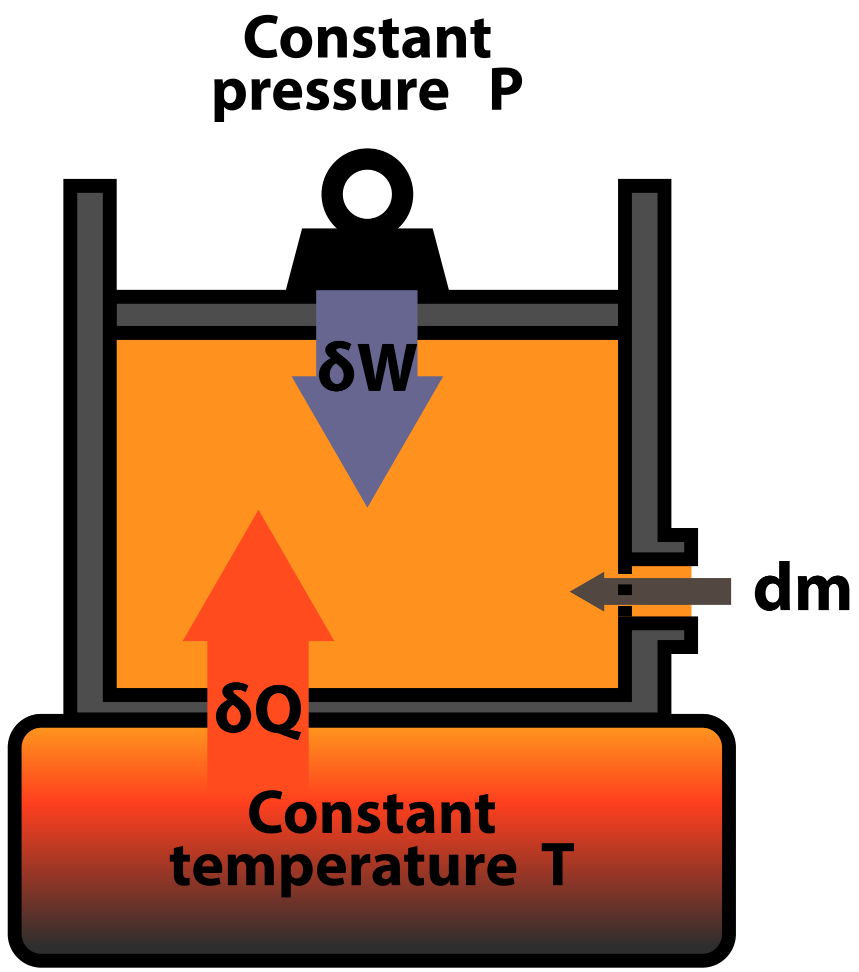
$$dU = \delta Q + \delta W + h\, dm$$



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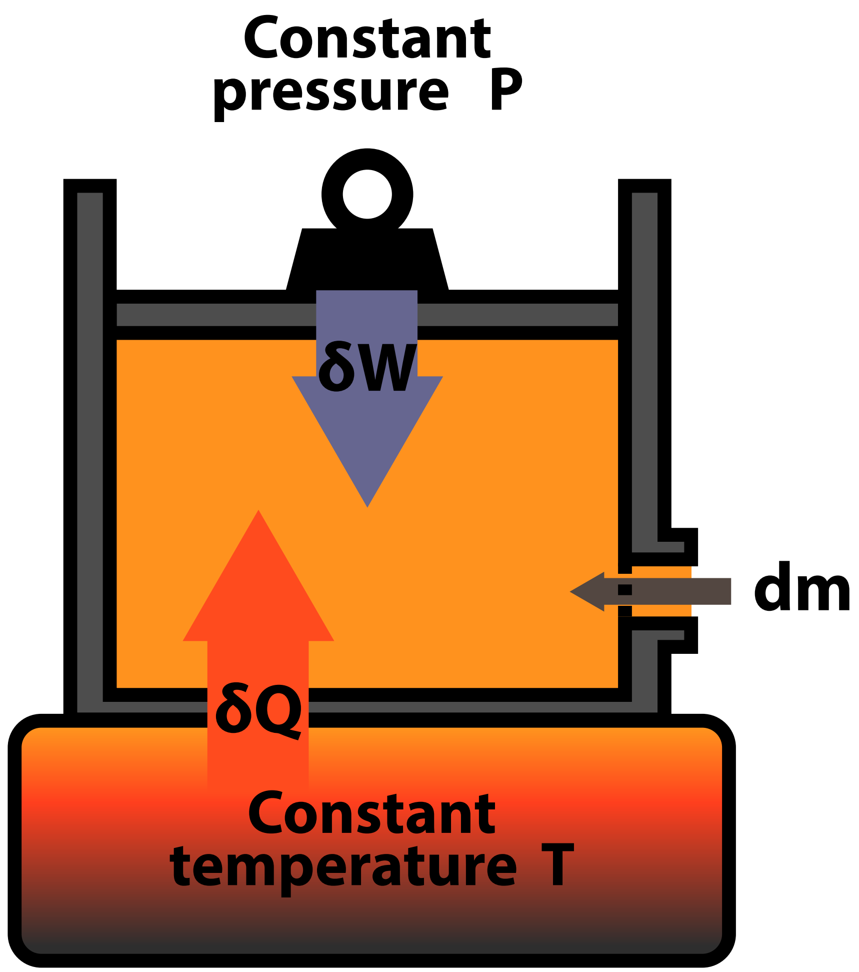
$$dS = \frac{\delta Q}{T} + s\, dm$$



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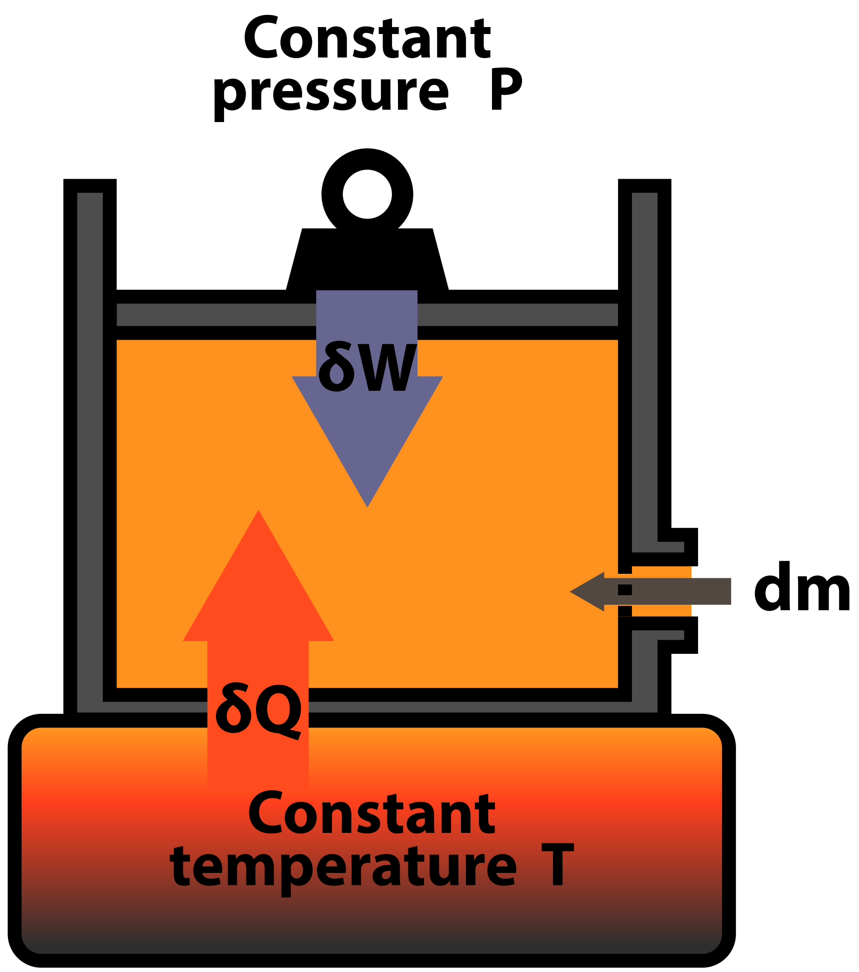
$$dS = \frac{\delta Q}{T} + s\,dm \;\Rightarrow\; \delta Q = T dS - T s\,dm$$



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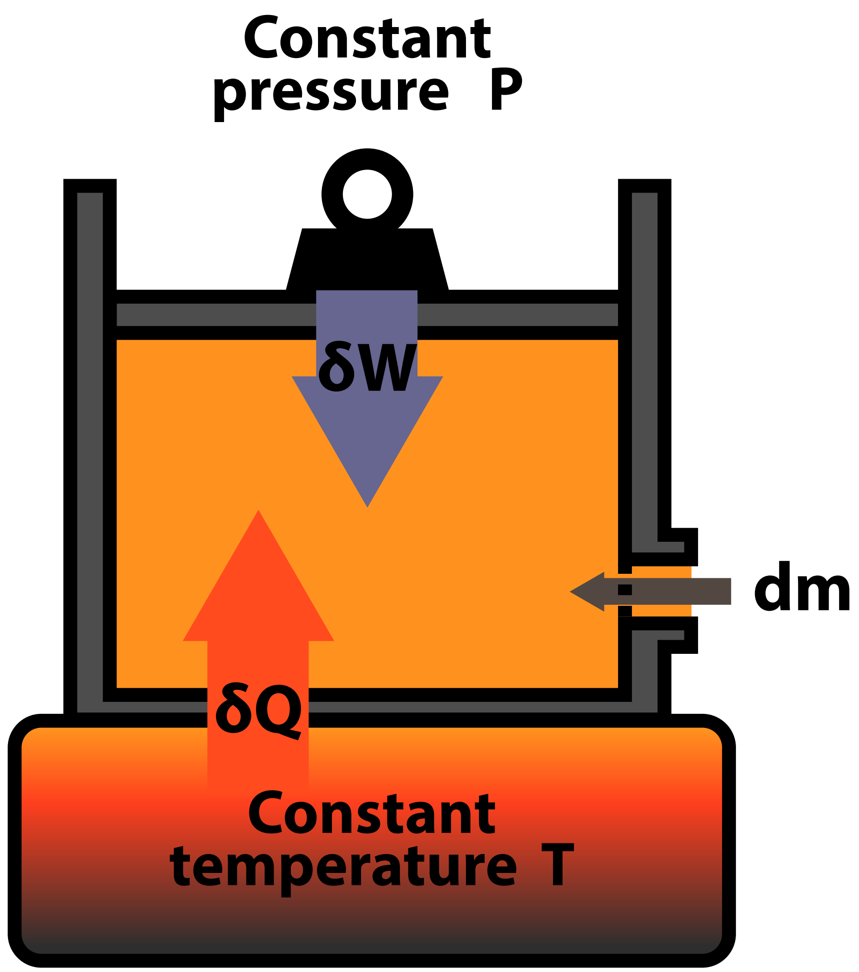

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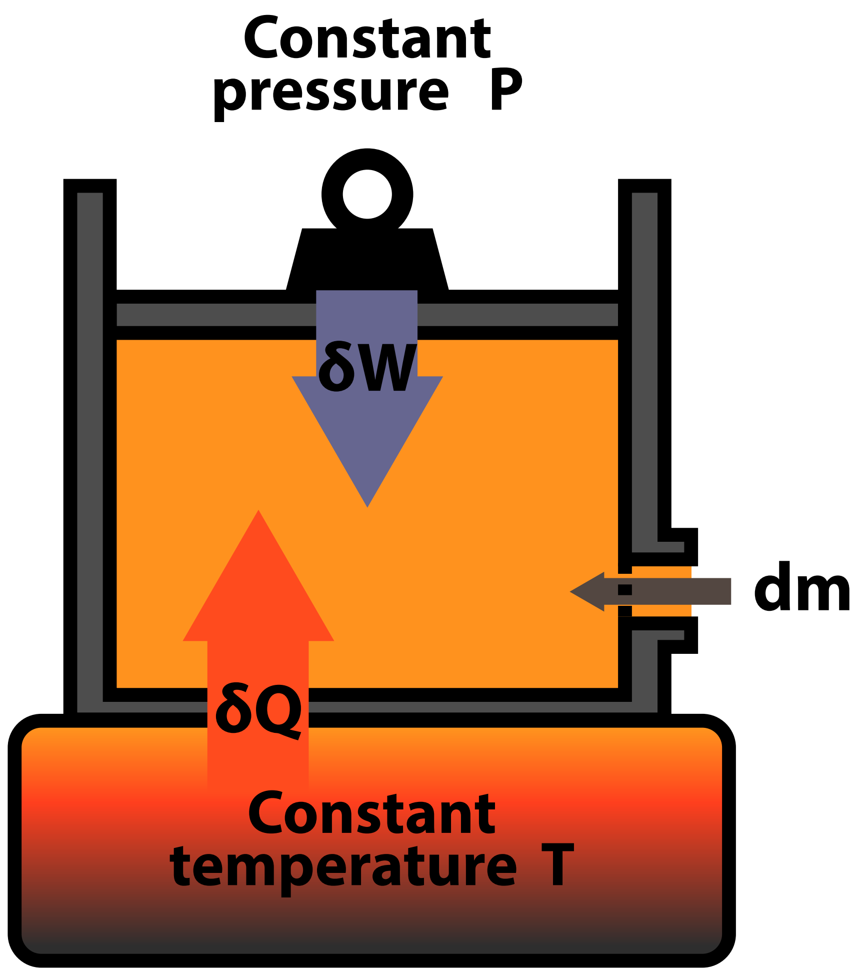

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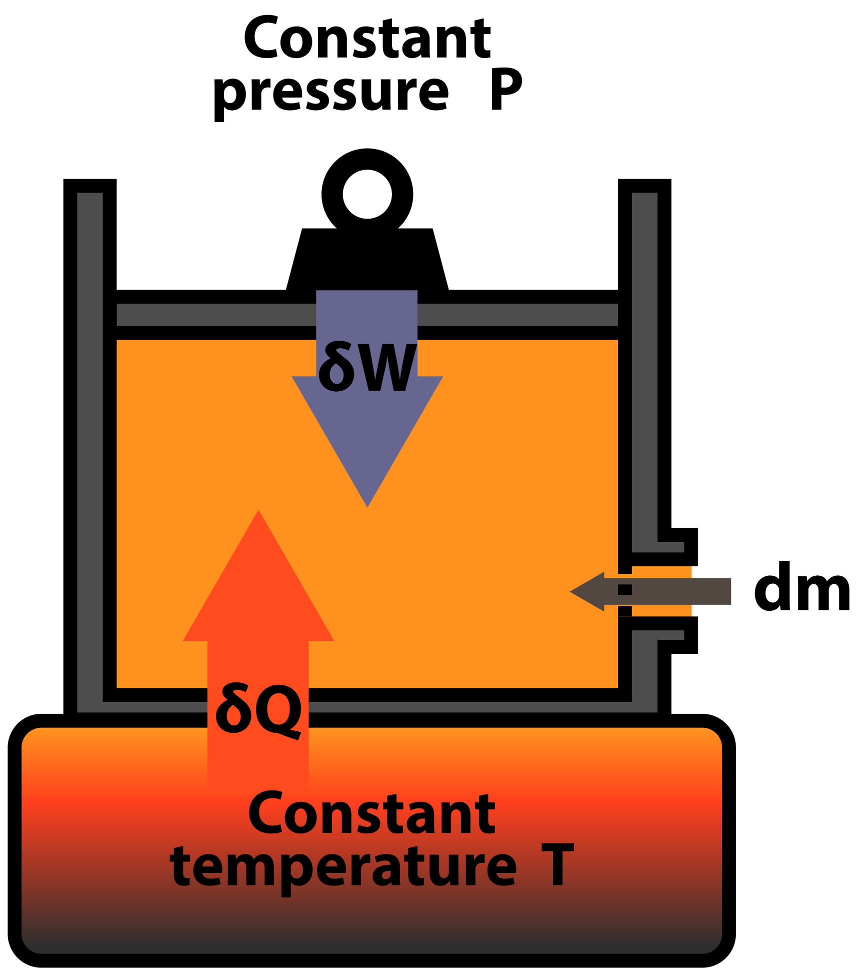
We introduce the Gibbs energy *G*, and the specific Gibbs energy *g* = *G*/*m*, (also known as chemical potential):

$$G = H - TS \quad \Rightarrow \quad g = \frac{G}{m} = h - Ts$$

Gibbs Energy and Chemical Potential



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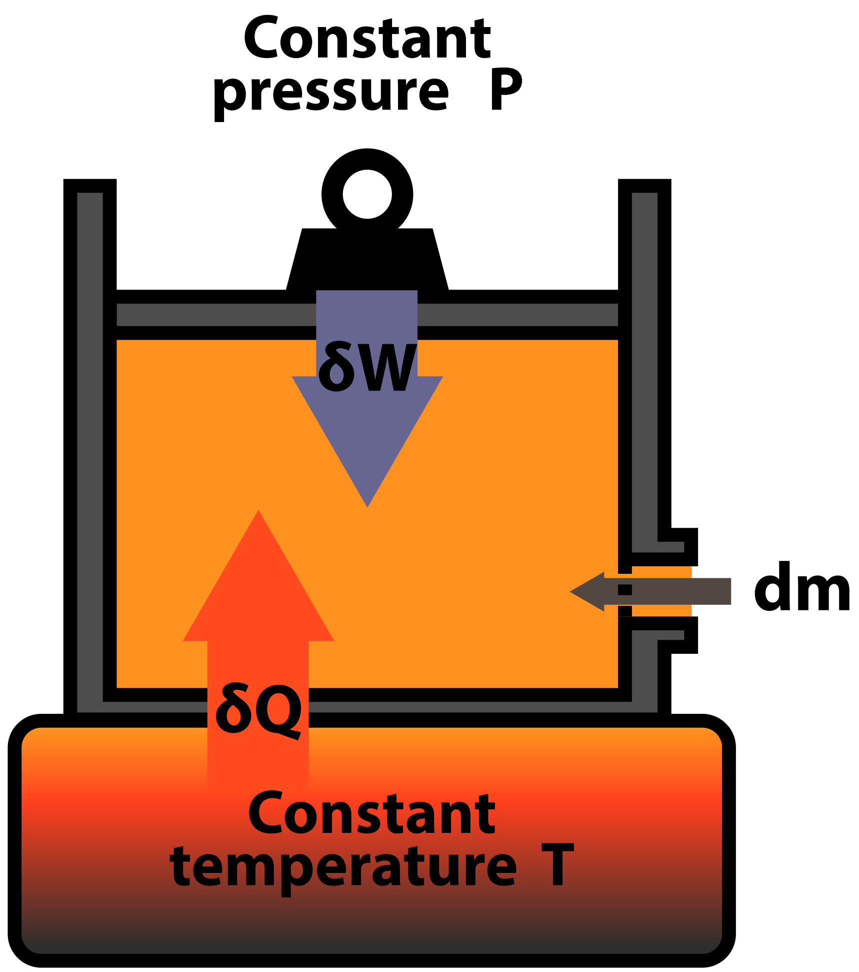

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rearranging:

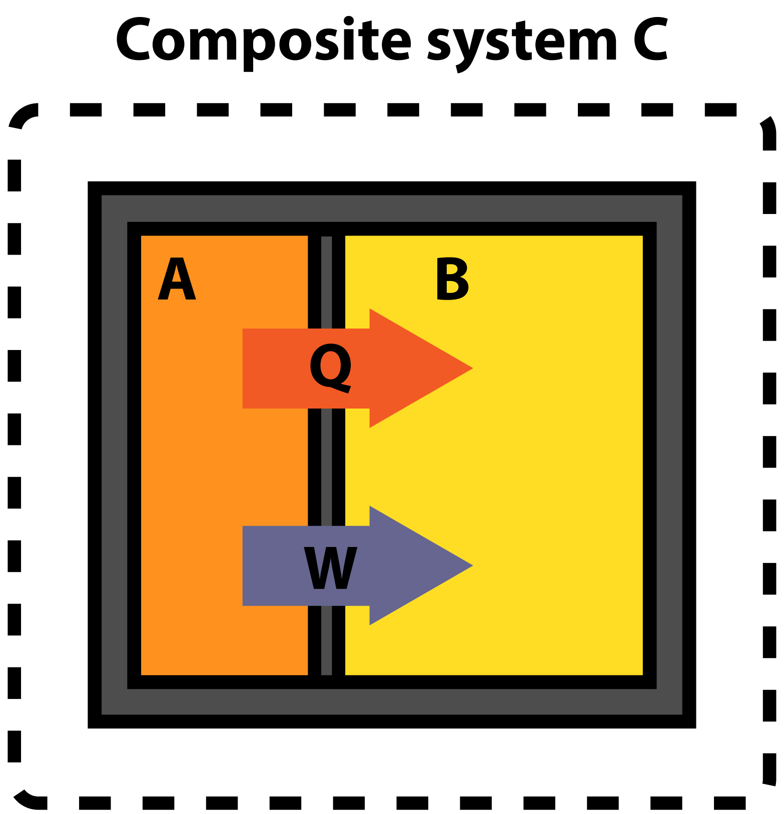
$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{g}{T}dm$$

Gibbs equation

Equilibrium with mass transfer

As we have seen in the previous lecture, for two systems A and B that can exchange work and heat, the entropy variation of the composite system C is given by:

$$dS_C = \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right) dV_A$$



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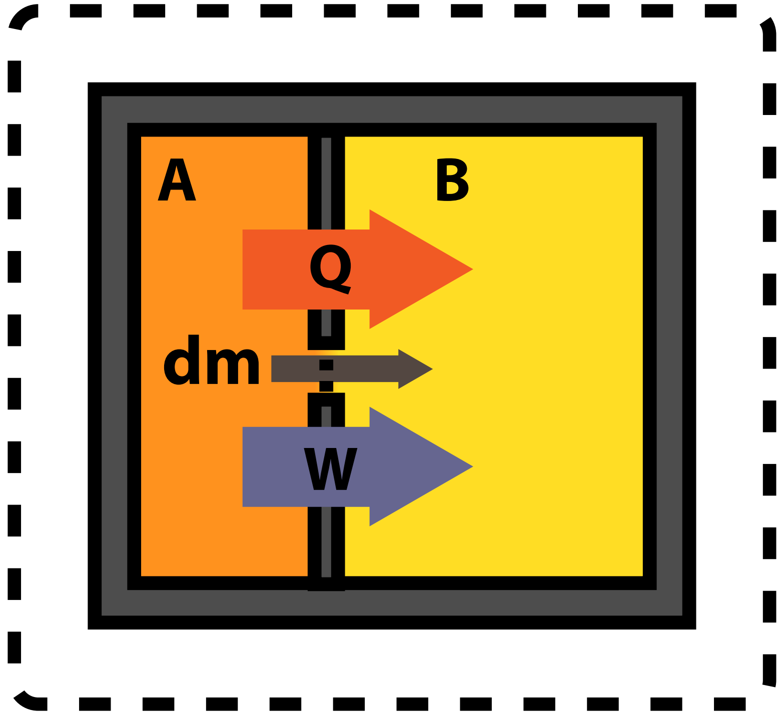
Composite system C



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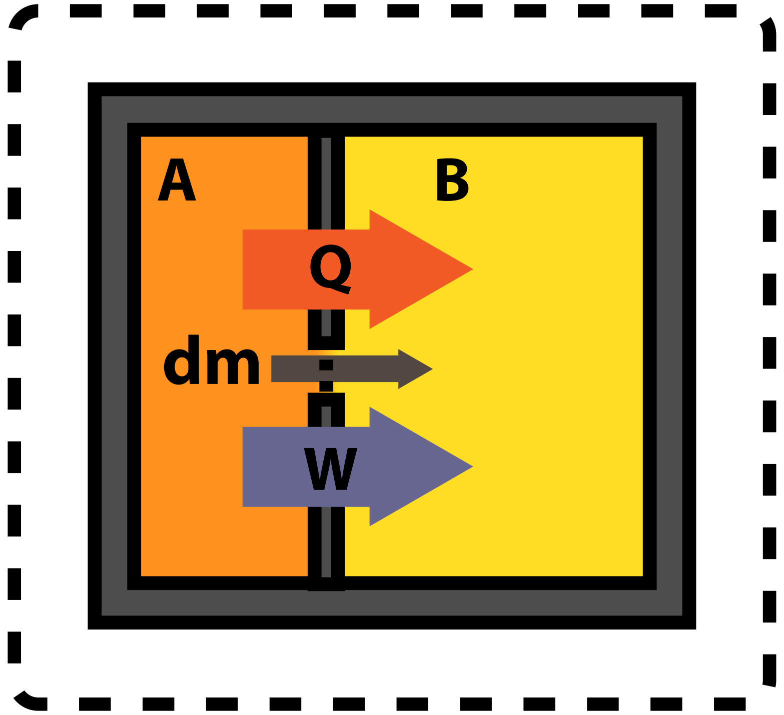

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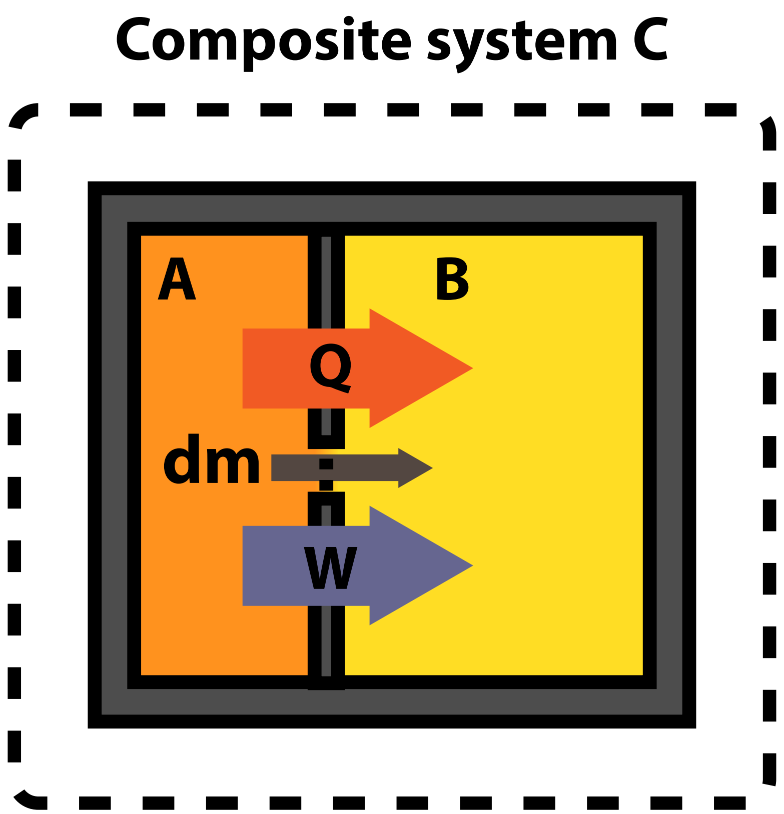

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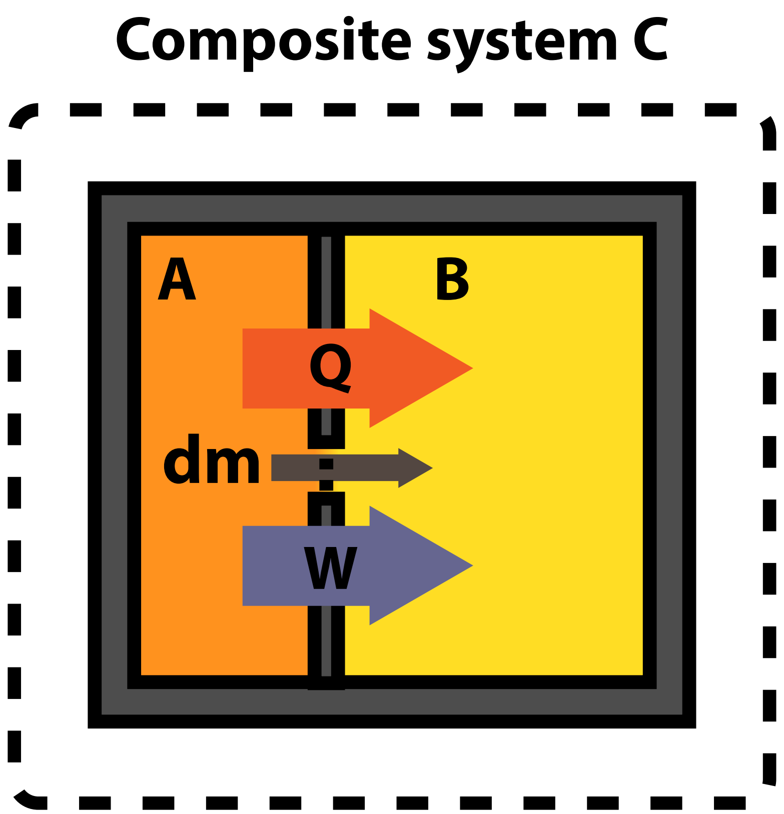

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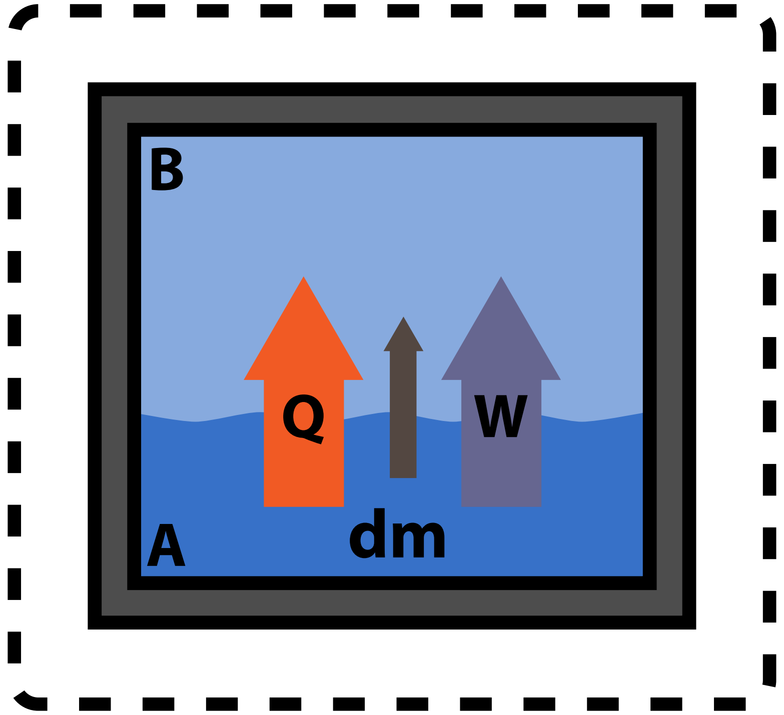
In the same way that T determines the direction of heat transfer and P of work transfer, the chemical potential g determines the direction of mass transfer, i.e. from higher chemical potential to lower chemical potential.

Phase Equilibrium

We can apply the same argument to two phases that are in contact such that they can exchange heat, work, and mass.

Composite system C



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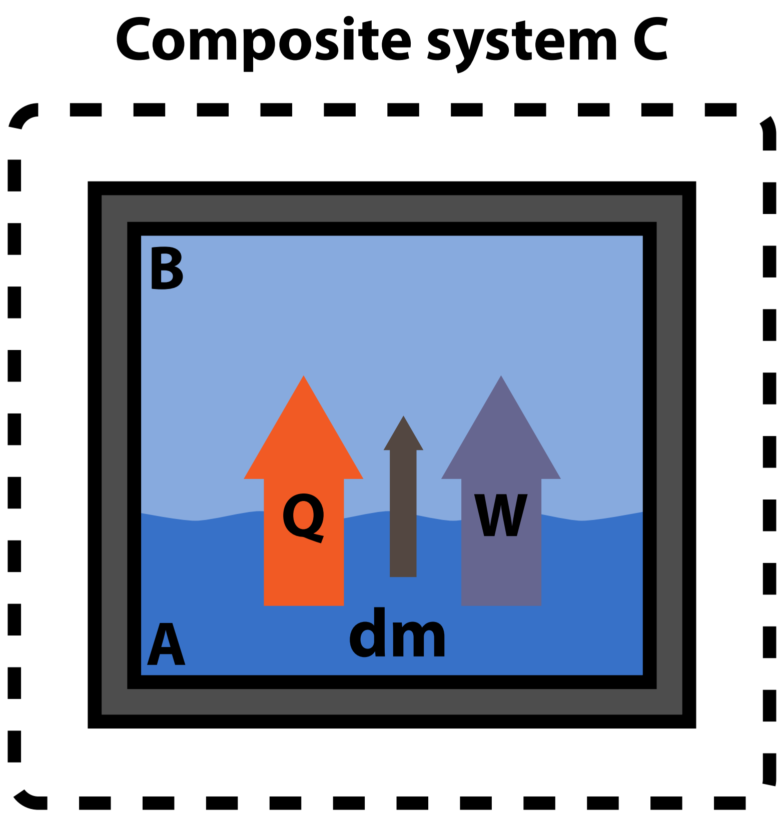

We can apply the same argument to two phases that are in contact such that they can exchange heat, work, and mass. The mass exchange between the two phases corresponds to a *phase transition*. The equilibrium between the two phases is called *phase equilibrium*.

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