

Chemistry 2000 Slide Set 13: Phase diagrams

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Phases

A **phase** is a mechanically separable component of a system.

Example: a solid can be separated from a liquid by filtration.

Example: oil can be separated from water using a separatory funnel.



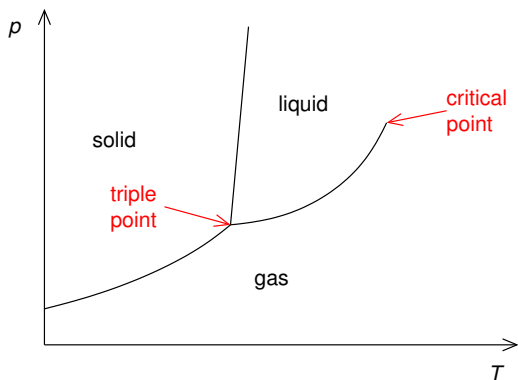
Nalgene series 4301
separatory funnel

Phase diagrams

A **phase diagram** shows the most thermodynamically stable phases under different conditions.

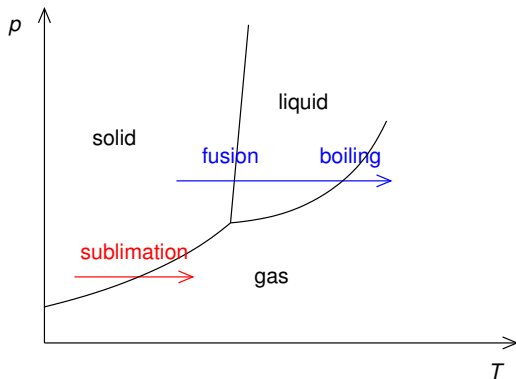
- For pure substances, temperature-pressure phase diagrams are common.

A typical phase diagram

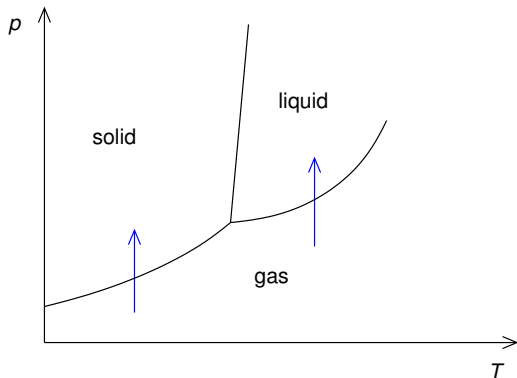


- On each curve in the phase diagram, two phases are in equilibrium.

Heating at constant pressure



Isothermal compression



- The gas condenses, either to a solid or to a liquid, as the pressure is increased.
- If the pressure on the liquid is made sufficiently large, it will eventually solidify.

Triple point

- The solid-gas and liquid-gas coexistence (vapor pressure) curves intersect at the **triple point**.
- At this point, the solid is in equilibrium with the gas and the liquid is in equilibrium with the gas, therefore the solid is also in equilibrium with the liquid.
- The solid-liquid equilibrium curve must therefore also start at this point.

Solid-liquid coexistence curve

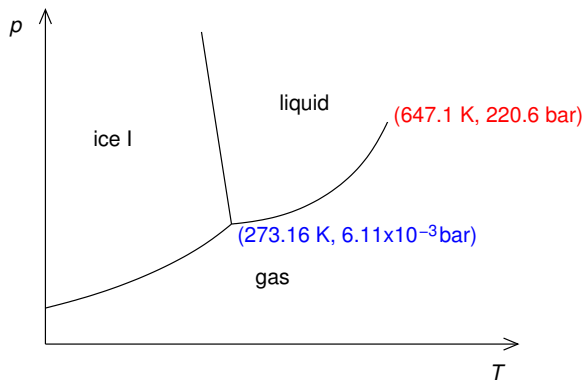
- The solid-liquid coexistence curve satisfies

$$\text{slope} = \Delta_{\text{fus}} S_m / \Delta_{\text{fus}} V_m \quad (\text{Clapeyron})$$

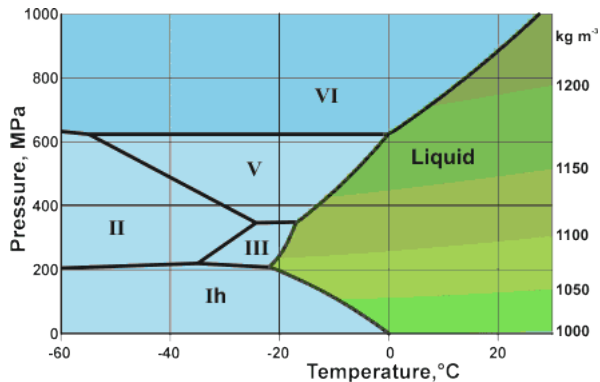
- $\Delta_{\text{fus}} S_m > 0$ (Why?)
- $\Delta_{\text{fus}} V_m$ is **usually** also positive.
- Therefore, the solid-liquid coexistence curve **usually** has a positive slope.
- Le Chatelier's principle predicts the correct slope:
 - Increasing the pressure applies a stress which should favor the denser phase.
 - This is usually the solid, so the range of temperatures over which the solid is stable should broaden as p increases.
 - The slope of the solid-liquid coexistence curve should therefore **usually** be positive.

The phase diagram of water

Phases seen near ambient conditions



More of the phase diagram of water



From: *Water Structure and Science* by Martin Chaplin,
http://www1.lsbu.ac.uk/water/water_phase_diagram.html

The Kelvin

- As of November 2018, the value of Boltzmann's constant is **fixed** to $1.380\,649 \times 10^{-23}$ J/K.

New definition of the Kelvin: A change in temperature of 1 K causes a change in thermal energy of $1.380\,649 \times 10^{-23}$ J.

- This is based on a “thermal energy” of $k_B T$.
- A practical method for measuring the temperature (i.e. for defining the Kelvin given a fixed k_B) is to make speed of sound measurements.

$$c = \sqrt{\gamma k_B T / m}$$

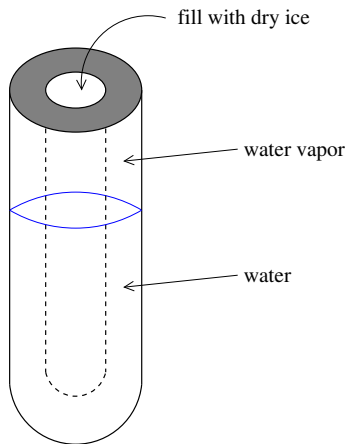
where m is the mass of one gas molecule, and γ is a constant that depends on the gas.

In particular, $\gamma = 5/3$ for an ideal monatomic gas.

The triple point and thermometry

- Speed of sound measurements are not a basis for practical laboratory thermometers, or for routine calibration of thermometers.
- On a day-to-day basis, thermometers are calibrated using physico-chemical processes that occur at reproducible temperatures.
- Boiling points can't be used because the boiling temperature varies with pressure, and pressure regulation introduces uncertainty in the calibration.
- A triple point only occurs at one particular temperature and pressure, which makes it ideal for thermometer calibration.
- Freezing points can also be used because of the steep slope of the p vs T solid-liquid coexistence curve, although not as accurately.

Triple-point cell



Practical temperature scales

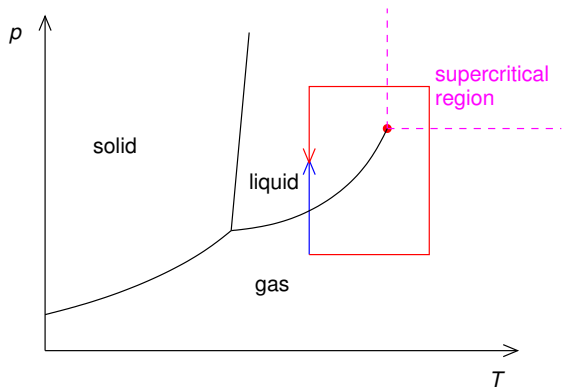
- It is difficult to use a single point to calibrate thermometers, so practical temperature scales are defined in terms of several reference points.
 - **ITS-90** (International Temperature Scale of 1990) is an international standard defining a practical temperature scale with many calibration points covering a wide range of temperatures.
- At very low temperatures, there are no usable fixed points, so the vapor pressure of helium is used as a thermometric standard.

Some examples of the calibration points of ITS-90:

Reference point	T/K
Triple point of H ₂	13.8033
Triple point of O ₂	54.3584
Triple point of Hg	234.3156
Triple point of water	273.16
Melting point of Ga	302.9146
Freezing point of In	429.7485
Freezing point of Al	933.473
Freezing point of Cu	1357.77

The critical point

- Normally, if we compress a gas, liquefaction is observed by the presence of a meniscus separating the two phases.
- As we increase the **pressure** on a gas, its density **increases**.
- As we increase the **temperature** of a liquid, its density **decreases**.
- The liquid-gas coexistence curve has a positive slope.
- If we follow this curve, at sufficiently high T and p , we may encounter a point where the liquid and gas phase densities become equal.
- This point is the **critical point**.
- There is no distinction between liquids and gases beyond this point so we describe the state in this region as a **supercritical fluid**.



Critical pressures and temperatures

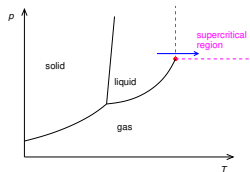
Substance	T_c /K	P_c /bar
He	5.3	2.29
H ₂	33.2	12.97
N ₂	126.0	33.9
CO ₂	304.16	73.9
HCl	325	82.7
C ₆ H ₁₄	507.4	30.3
H ₂ O	647.1	220.6

The transition to a supercritical fluid in CO₂

Atkins, Jones and Laverman, *Chemical Principles*, 7th ed. Freeman: New York, 2016, p. 361.

- (a) Liquid CO₂ dyed with a rhodium compound in equilibrium with CO₂ gas
- (b) Temperature increased near T_c . Density difference decreases. Meniscus less distinct.
- (c) Supercritical CO₂

The transition to a supercritical fluid in CO₂



Atkins, Jones and Laverman, *Chemical Principles*, 7th ed. Freeman: New York, 2016, p. 361.

- Note: no single “phase transition event”, just a gradual merging of the properties of the two phases

Applications of supercritical fluids

Solvents: Supercritical CO₂ is an excellent solvent that can dissolve many non-polar molecules.

This is a **green** technology because CO₂ is nontoxic.

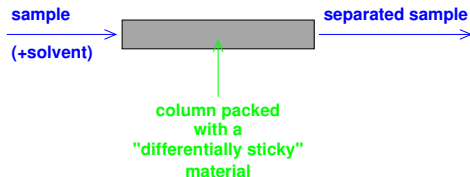
Separating CO₂ from solutes is as simple as releasing the pressure.

Examples:

- Decaffeination of coffee
- Paint solvent

Applications of supercritical fluids

Chromatography:



Molecules that “stick” better to the material in the column stay in the column longer.

Supercritical fluid chromatography (SFC): Supercritical fluids have low viscosities and surface tensions (like gases) but can dissolve solutes (like liquids).

This allows high flow rates in chromatography equipment (like in gas chromatography) while allowing the handling of materials that can't be vaporized (like in liquid chromatography).

Applications of supercritical fluids

“Working fluid” in a turbine generator:

- The efficiency of electricity generation by a turbine depends on the range of temperatures over which the “working fluid” cycles.
(We know this from the thermodynamic theory of heat engines!)
- CO₂ can be cycled between sub- and super-critical regimes relatively easily, spanning a large range of temperatures in the process at reasonable pressures.
- A higher-density fluid can carry more energy to the turbine in a smaller volume, allowing for smaller turbines (cheaper, easier to deploy).
- Supercritical CO₂ has roughly twice the density of steam at the same pressure.

Applications of supercritical fluids

“Working fluid” in a turbine generator: (continued)

- A turbine with a rotor 1.4 m long and 18 cm in diameter weighing just 70 kg using supercritical CO₂ as its working fluid should generate about 10 MW of electricity (enough to power about 10 000 homes).