# Constructing the phase diagram for $CO_2$

We can use the Clapeyron and Clausius-Clapeyron equations to calculate a phase diagram.

For example, we can begin with the $CO_2$ diagram shown above.
The triple point for $CO_2$ is P = 5.11 atm and T = 216.15 K.
The critical point for for $CO_2$ is P = 72.85 atm and T = 304.2 K.

We also have the following data

| **Transition** | **$\Delta_{trs}H^0$ (kJ/mol)** | **$T_{trs}$ (K)** |
|---|---|---|
| **Fusion** | 8.3 | 217.0 |
| **Sublimation** | 25.2 | 194.6 |

Note that we can calculate the enthalpy of sublimation from
$\Delta_{vap}H^o = \Delta_{sub}H^o - \Delta_{fus}H^o = 16.9$ kJ/mol.

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| Transition | $\Delta_{trs}H^0$ (kJ/mol) | $T_{trs}$ (K) |
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| Vaporization | 16.90 | 215.5 |
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$\rho_{solid}$ = 1.53 g/cm$^3$ and $\rho_{liquid}$ = 0.78 g/cm$^3$, respectively.

The density $\rho$ = m/V = nM/V so the molar volume is

$V_m$ = V/n = M/$\rho$ where M is the molar mass.

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$\rho_{solid}$ = 1.53 g/cm$^3$ and $\rho_{liquid}$ = 0.78 g/cm$^3$, respectively.

$$\Delta V_m = \frac{M_m}{\rho_2} - \frac{M_m}{\rho_1} = \frac{44}{0.78} - \frac{44}{1.53} = 27.7\ \frac{cm^3}{mol}$$

# Liquid-vapor coexistence for $CO_2$

Starting with the triple point we use the Clausius-Clapeyron equation to calculate the liquid-vapor coexistence curve.

$$ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_{vap}H_m}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

which we write in a form solving for $P_2$

$$P_2 = P_1 exp\left\{\frac{\Delta_{vap}H_m}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right\}$$

where the ratio

$$\frac{\Delta_{vap}H_m}{R} = \frac{16900\ J/mol}{8.31\ J/molK} = 2034\ K$$

# Liquid-vapor coexistence for $CO_2$

Starting from the triplet point the equation is:

$$P_2 = 5.11\, exp\left\{2034\left(\frac{1}{216.15} - \frac{1}{T_2}\right)\right\}$$

Notice that if we were to calculate the critical pressure using this formula we would obtain 77.3 atm which is about 5 atm larger than the experimental number. There are several sources of inaccuracy including mainly our neglect of the temperature dependence of the enthalpy. We can also begin at the critical point:

$$P_2 = 72.8\, exp\left\{2034\left(\frac{1}{304.2} - \frac{1}{T_2}\right)\right\}$$

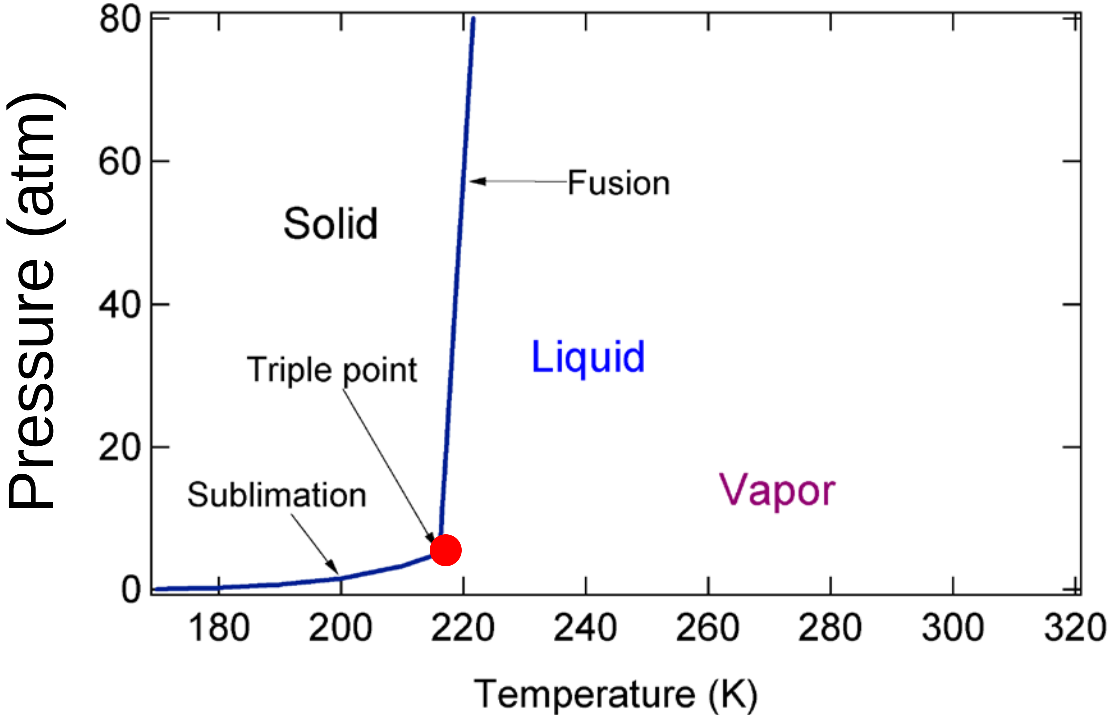
and meet in the middle.

# Constructing the liquid-vapor curve

$$P_2 = 5.11\, exp\left\{2034\left(\frac{1}{216.15} - \frac{1}{T_2}\right)\right\}$$

Liquid-vapor

| P (atm) | T (K) |
|---|---|
| 5.11 | 216.15 |

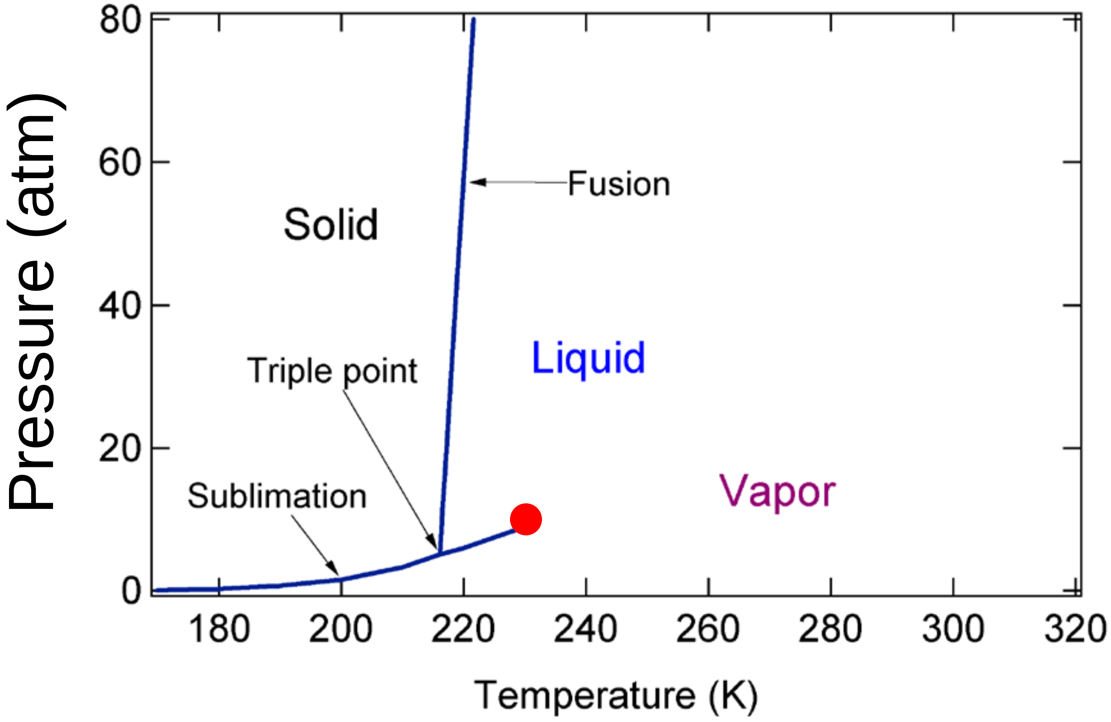


# Constructing the liquid-vapor curve

$$P_2 = 5.11\, exp\left\{2034\left(\frac{1}{216.15} - \frac{1}{T_2}\right)\right\}$$

Liquid-vapor

| P (atm) | T (K) |
|---|---|
| 5.11 | 216.15 |
| 6.03 | 220 |
| 9.0 | 230 |

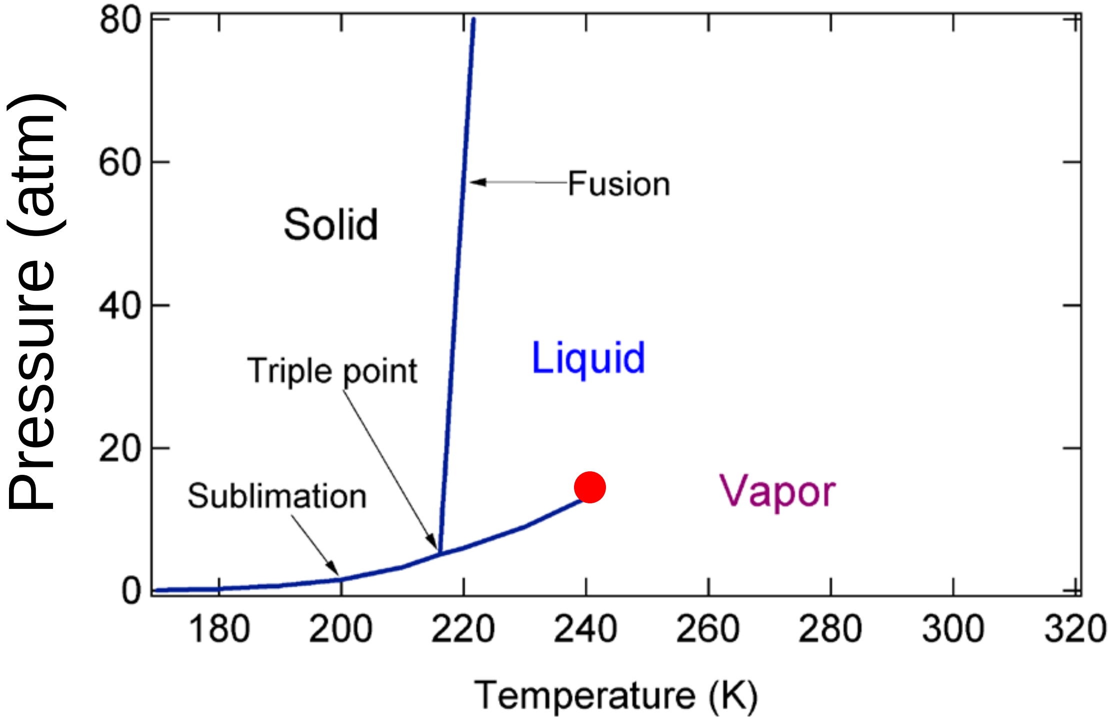


# Constructing the liquid-vapor curve

$$P_2 = 5.11\, exp\left\{2034\left(\frac{1}{216.15} - \frac{1}{T_2}\right)\right\}$$

Liquid-vapor

| P (atm) | T (K) |
|---|---|
| 5.11 | 216.15 |
| 6.03 | 220 |
| 9.0 | 230 |
| 13.0 | 240 |

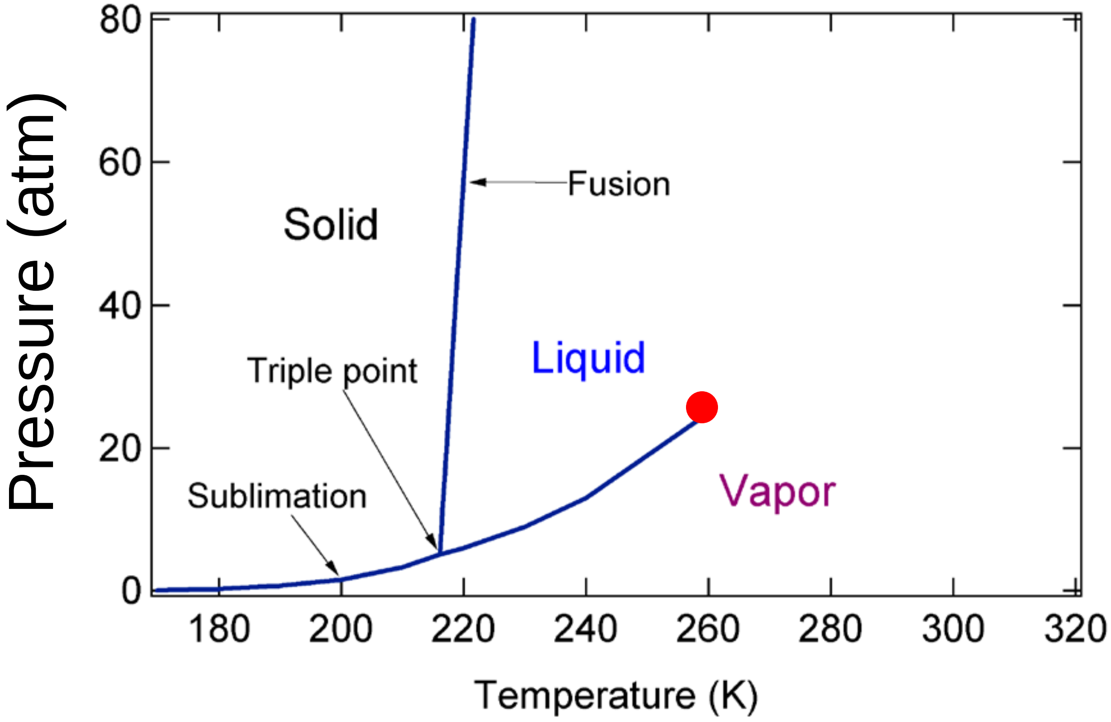


# Constructing the liquid-vapor curve

$$P_2 = 5.11\, exp\left\{2034\left(\frac{1}{216.15} - \frac{1}{T_2}\right)\right\}$$

Liquid-vapor

| P (atm) | T (K) |
|---|---|
| 5.11 | 216.15 |
| 6.03 | 220 |
| 9.0 | 230 |
| 13.0 | 240 |
| 24.9 | 260 |

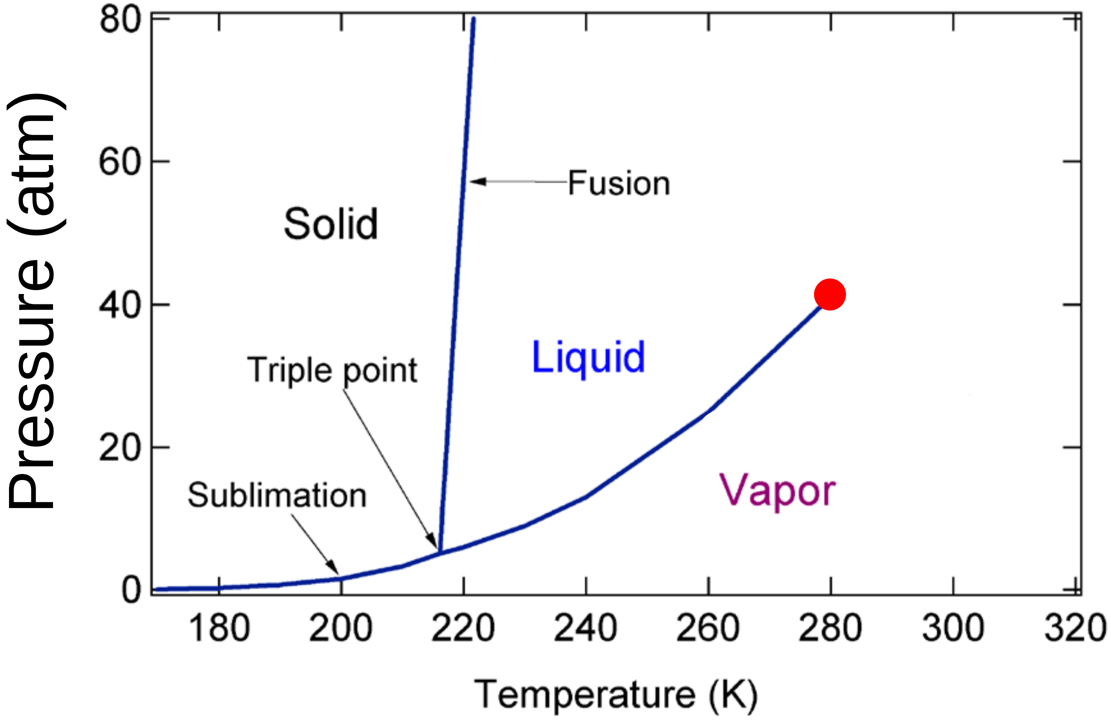


# Constructing the liquid-vapor curve

$$P_2 = 5.11\, exp\left\{2034\left(\frac{1}{216.15} - \frac{1}{T_2}\right)\right\}$$

Liquid-vapor

| P (atm) | T (K) |
|---|---|
| 5.11 | 216.15 |
| 6.03 | 220 |
| 9.0 | 230 |
| 13.0 | 240 |
| 24.9 | 260 |
| 41.0 | 280 |

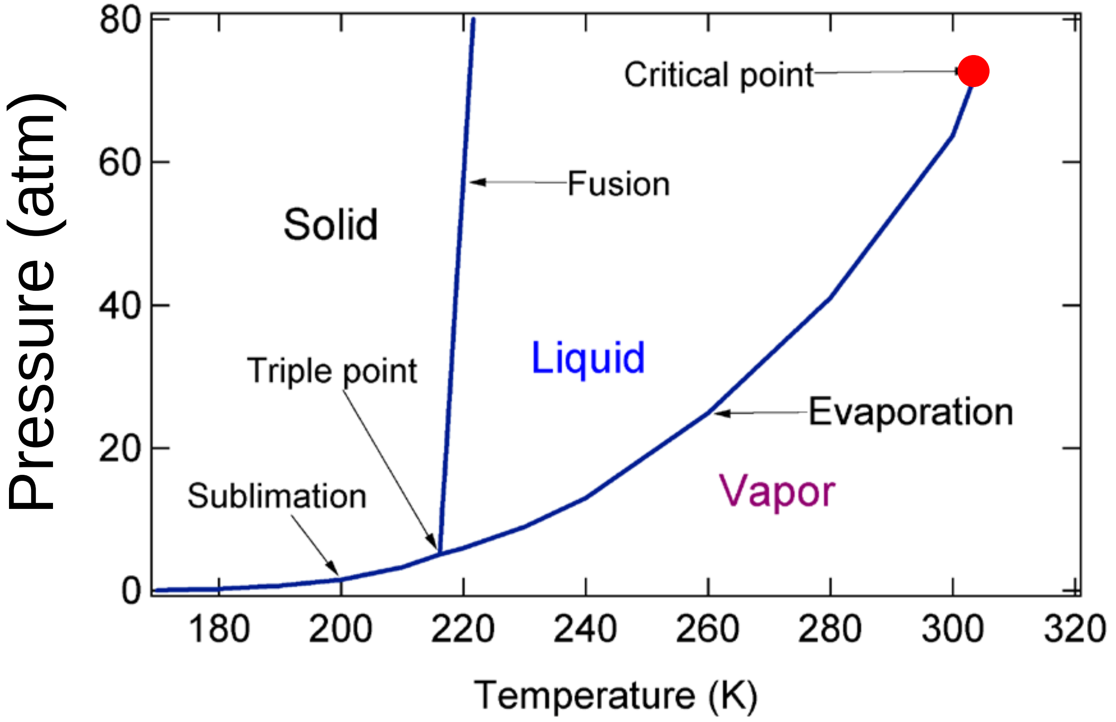


# Constructing the liquid-vapor curve

$$P_2 = 72.8\, exp\left\{2034\left(\frac{1}{304.2} - \frac{1}{T_2}\right)\right\}$$

Liquid-vapor

| P (atm) | T (K) |
|---|---|
| 5.11 | 216.15 |
| 6.03 | 220 |
| 9.0 | 230 |
| 13.0 | 240 |
| 24.9 | 260 |
| 41.0 | 280 |
| 63.7 | 300 |
| 72.8 | 304 |



# Constructing the solid-vapor curve

Starting again at the triple point we can calculate to lower temperature. We still use the Clausius-Clapeyron equation but we replace the enthalpy of vaporization with the enthalpy of sublimation:

$$P_2 = P_1 exp\left\{\frac{\Delta_{sub}H_m}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right\}$$

Where the ratio in the exponential is:

$$\frac{\Delta H_m}{R} = \frac{25200\ J/mol}{8.31\ J/molK} = 3032\ K$$

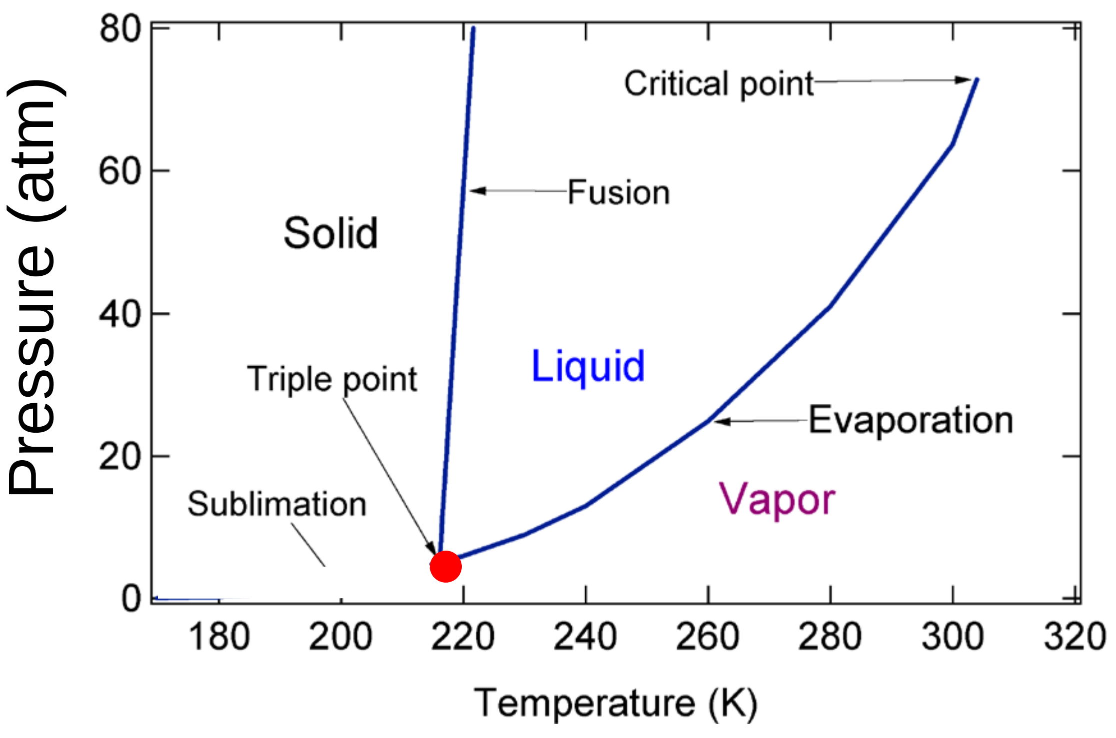
# Constructing the solid-vapor curve

Starting again at the triple point

$$P_2 = 5.11\, exp\left\{3032\left(\frac{1}{216.15} - \frac{1}{T_2}\right)\right\}$$

Solid-vapor

| P (atm) | T (K) |
| --- | --- |
| 5.11 | 216.15 |



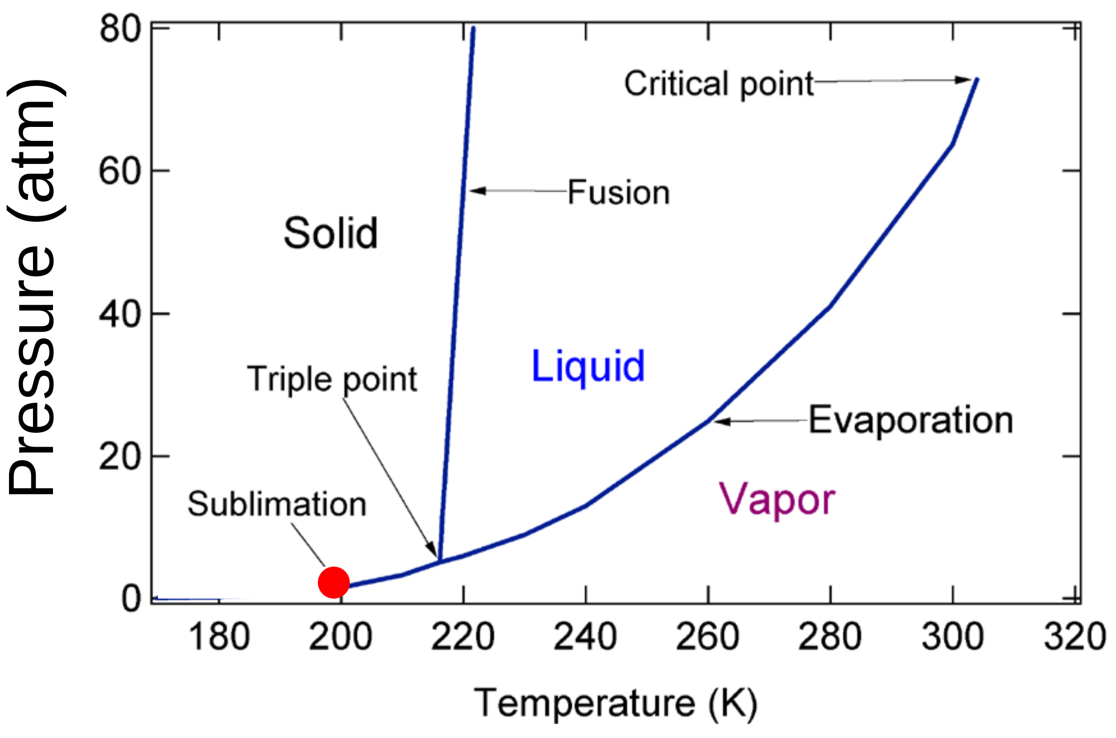
# Constructing the solid-vapor curve

Starting again at the triple point

$$P_2 = 5.11\, exp\left\{3032\left(\frac{1}{216.15} - \frac{1}{T_2}\right)\right\}$$

Solid-vapor

| P (atm) | T (K) |
|---|---|
| 5.11 | 216.15 |
| 3.38 | 210 |
| 1.64 | 200 |



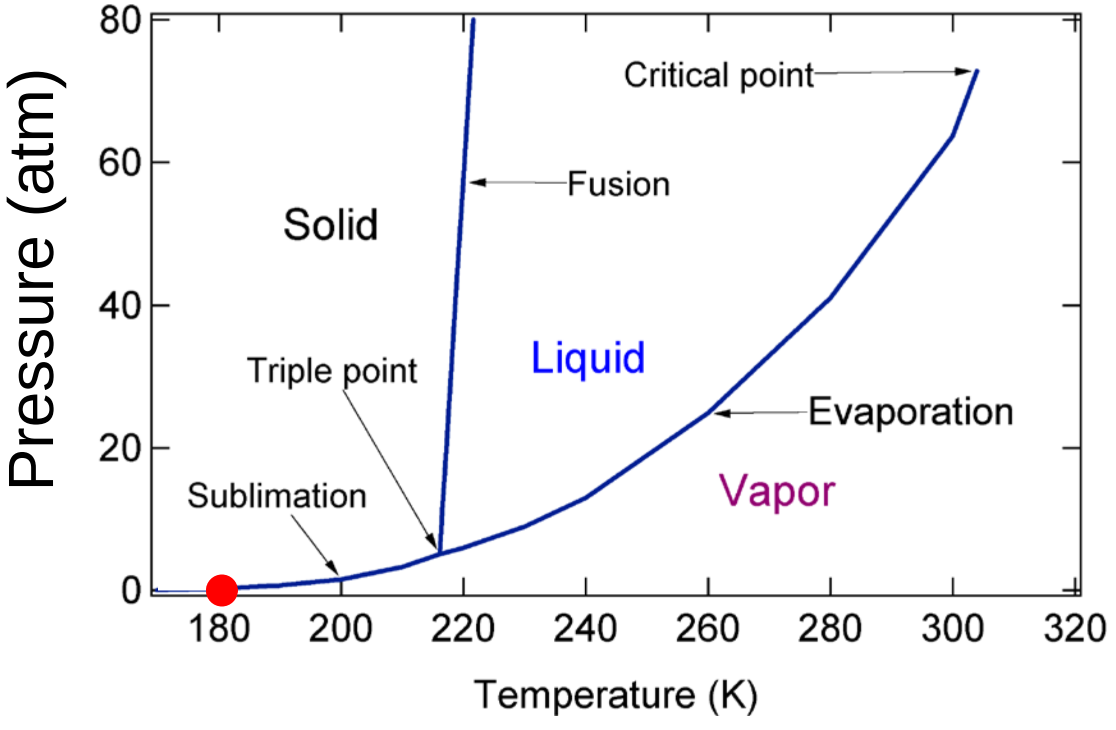
# Constructing the solid-vapor curve

Starting again at the triple point

$$P_2 = 5.11\, exp\left\{3032\left(\frac{1}{216.15} - \frac{1}{T_2}\right)\right\}$$

Solid-vapor

| P (atm) | T (K) |
|---|---|
| 5.11 | 216.15 |
| 3.38 | 210 |
| 1.64 | 200 |
| 0.725 | 190 |
| 0.298 | 180 |



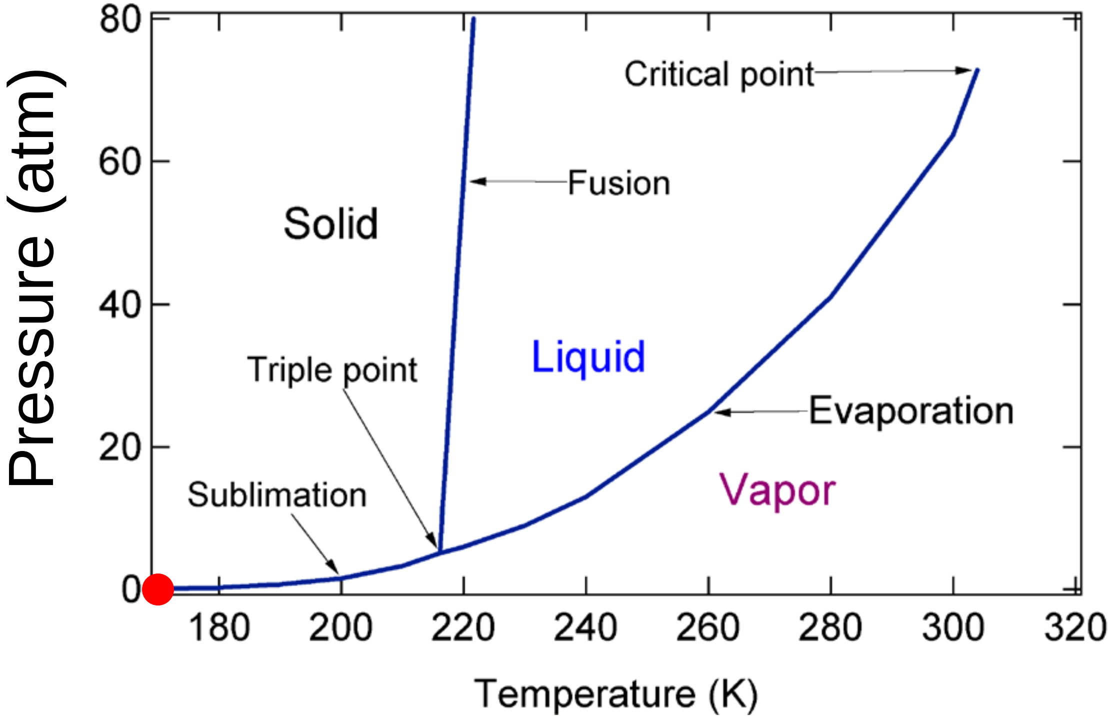
# Constructing the solid-vapor curve

Starting again at the triple point

$$P_2 = 5.11\, exp\left\{3032\left(\frac{1}{216.15} - \frac{1}{T_2}\right)\right\}$$

Solid-vapor

| P (atm) | T (K) |
|---|---|
| 5.11 | 216.15 |
| 3.38 | 210 |
| 1.64 | 200 |
| 0.725 | 190 |
| 0.298 | 180 |
| 0.111 | 170 |



# Constructing the solid-liquid curve

Using the Clapeyron equation

$$P_2 = P_1 + \frac{\Delta H_m}{\Delta V_m} ln\left(\frac{T_2}{T_1}\right)$$

we need to calculate:

$$\frac{\Delta H_m}{\Delta V_m} = \frac{8{,}300\ J/mol}{2.77\ x\ 10^{-5}\ m^3/mol} = 2.99\ x\ 10^8\ Pa$$

which can be expressed in units of atm.

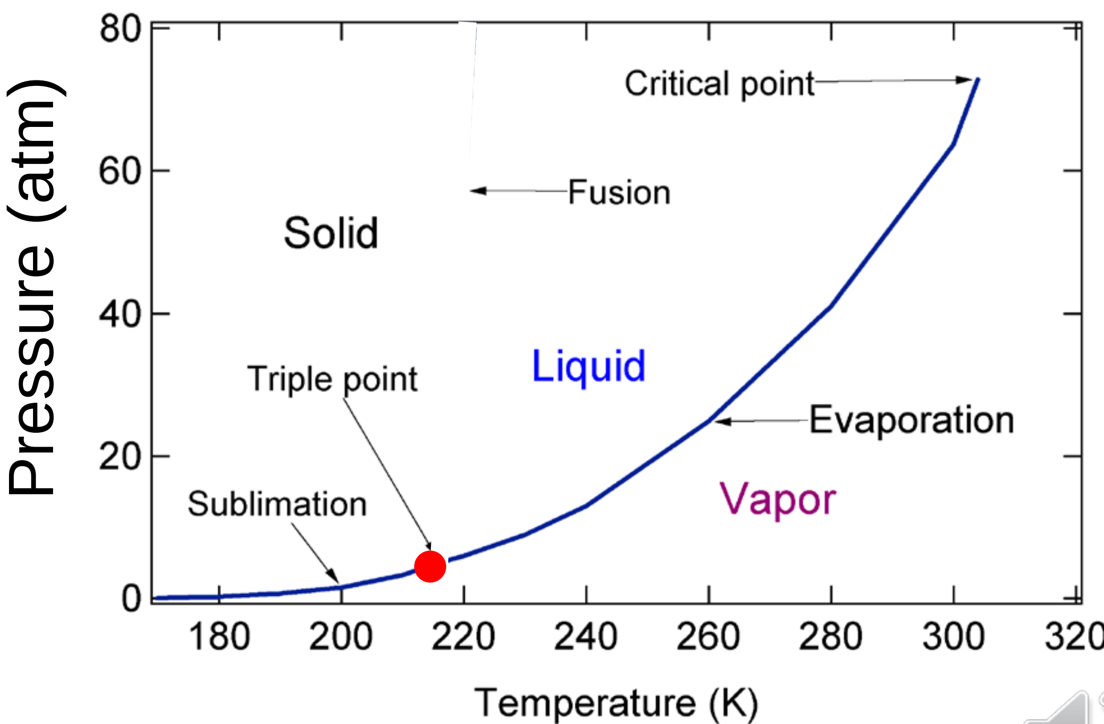
$$\frac{\Delta H_m}{\Delta V_m} = 2.99\ x\ 10^8\ Pa = 2990\ bar = 2950\ atm$$

# Constructing the solid-liquid curve

Using the Clapeyron equation we calculate:

Solid-liquid

| P (atm) | T (K) |
| --- | --- |
| 5.11 | 216.15 |



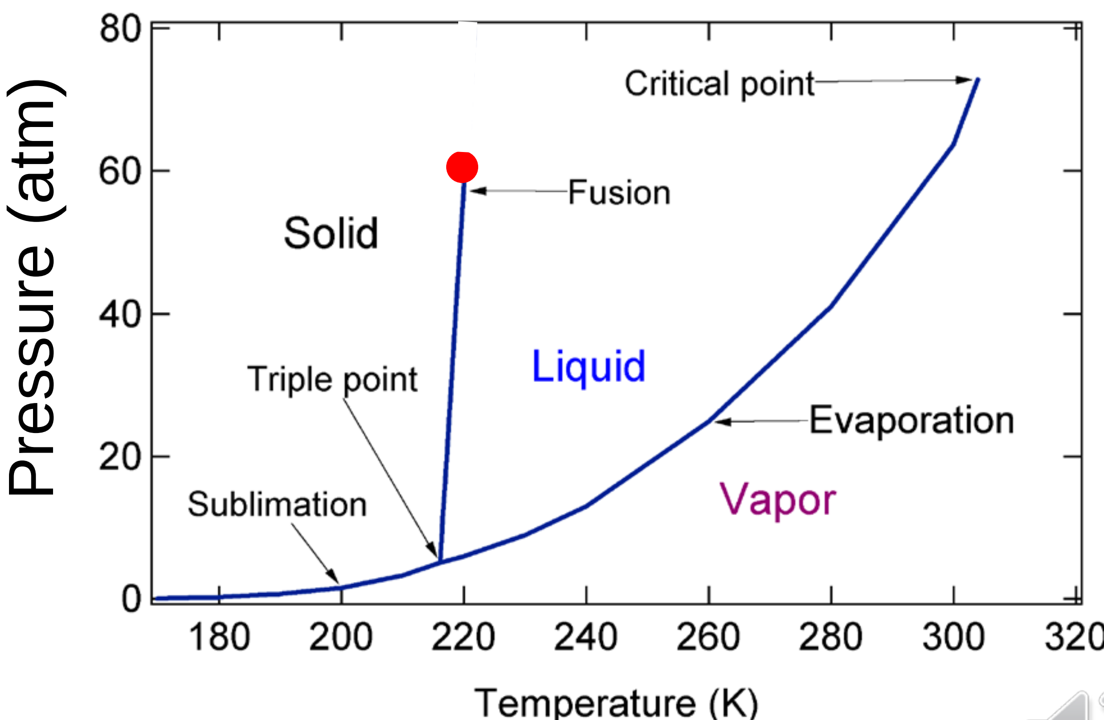
# Constructing the solid-liquid curve

Using the Clapeyron equation we calculate:

$$P_2 = 5.11 + 2950\, ln\left(\frac{T_2}{216.15}\right)$$

Solid-liquid

| P (atm) | T (K) |
|---|---|
| 5.11 | 216.15 |
| 58.0 | 220 |



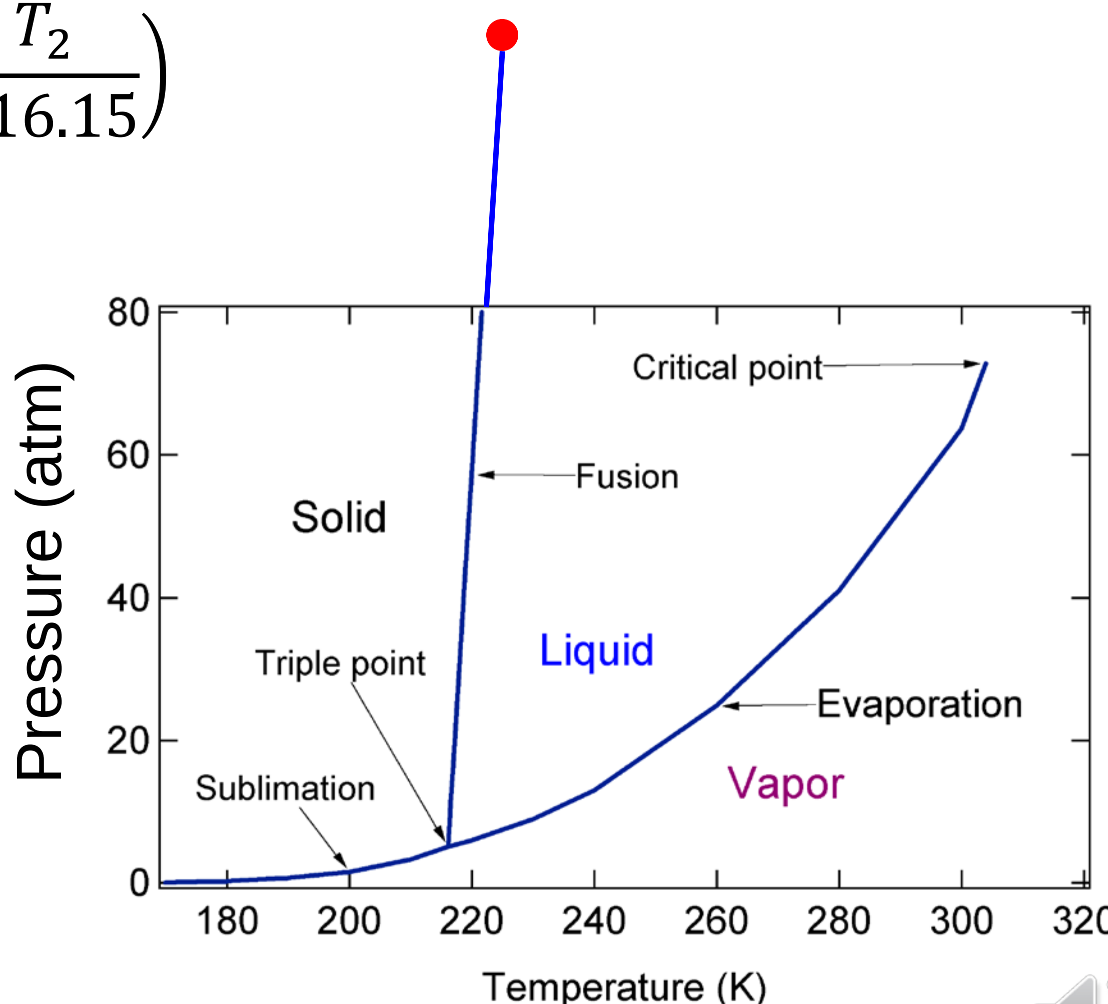
# Constructing the solid-liquid curve

Using the Clapeyron equation we calculate:

$$P_2 = 5.11 + 2950\, ln\left(\frac{T_2}{216.15}\right)$$

Solid-liquid

| P (atm) | T (K) |
|---|---|
| 5.11 | 216.15 |
| 58.0 | 220 |
| 124.2 | 230 |



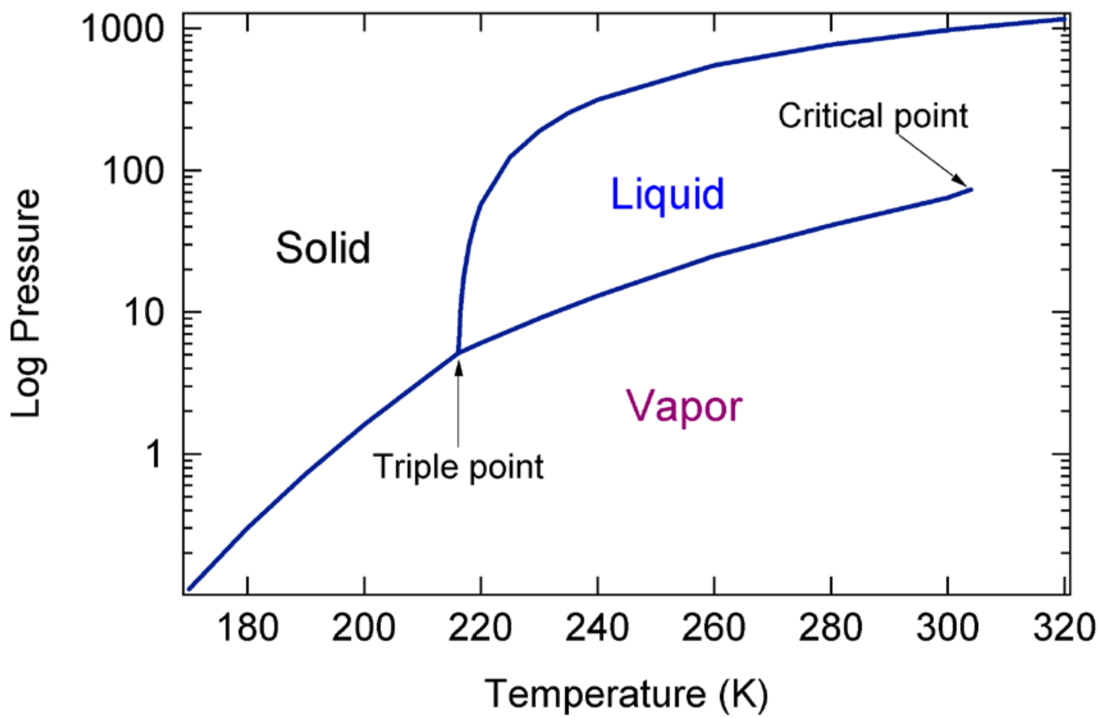
# Constructing the solid-liquid curve

Using the Clapeyron equation we calculate:

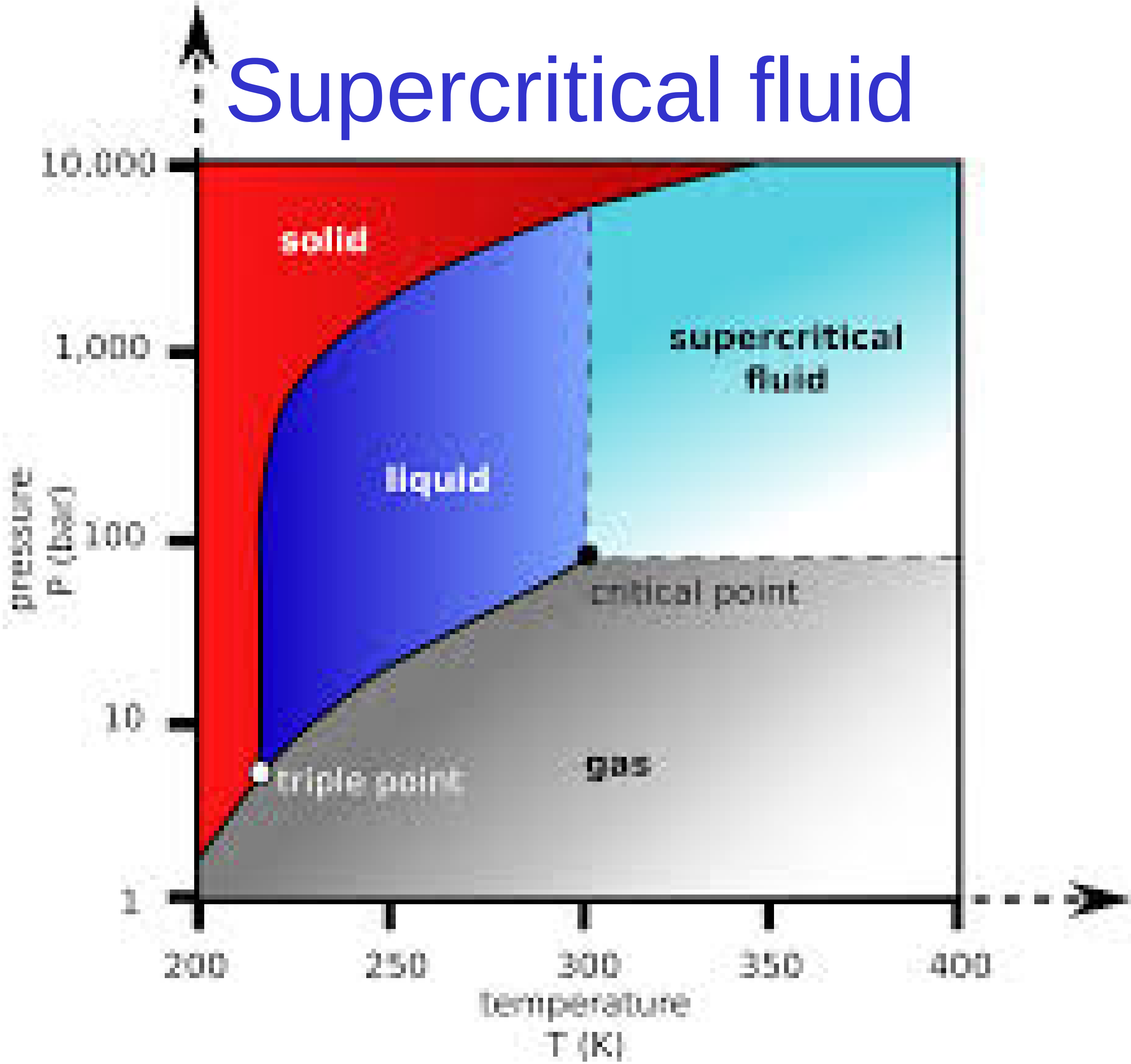
$$P_2 = 5.11 + 2950\ ln\left(\frac{T_2}{216.15}\right)$$

Solid-liquid

| P (atm) | T (K) |
|---|---|
| 5.11 | 216.15 |
| 58.0 | 220 |
| 124.2 | 230 |
| 319 | 240 |
| 559 | 260 |
| 780 | 280 |
| 987 | 300 |
| 1180 | 320 |



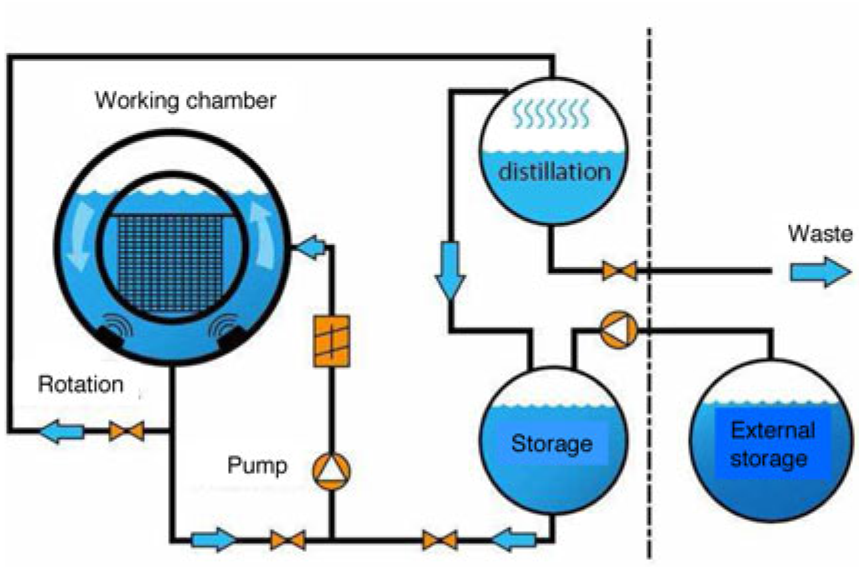
# Supercritical fluid



# Supercritical $CO_2$ dyeing process


DyeCoo uses supercritical $CO_2$ gas rather than water to infuse fabric with color. Netherlands-based company.
Read more: http://www.dexigner.com/news/25160

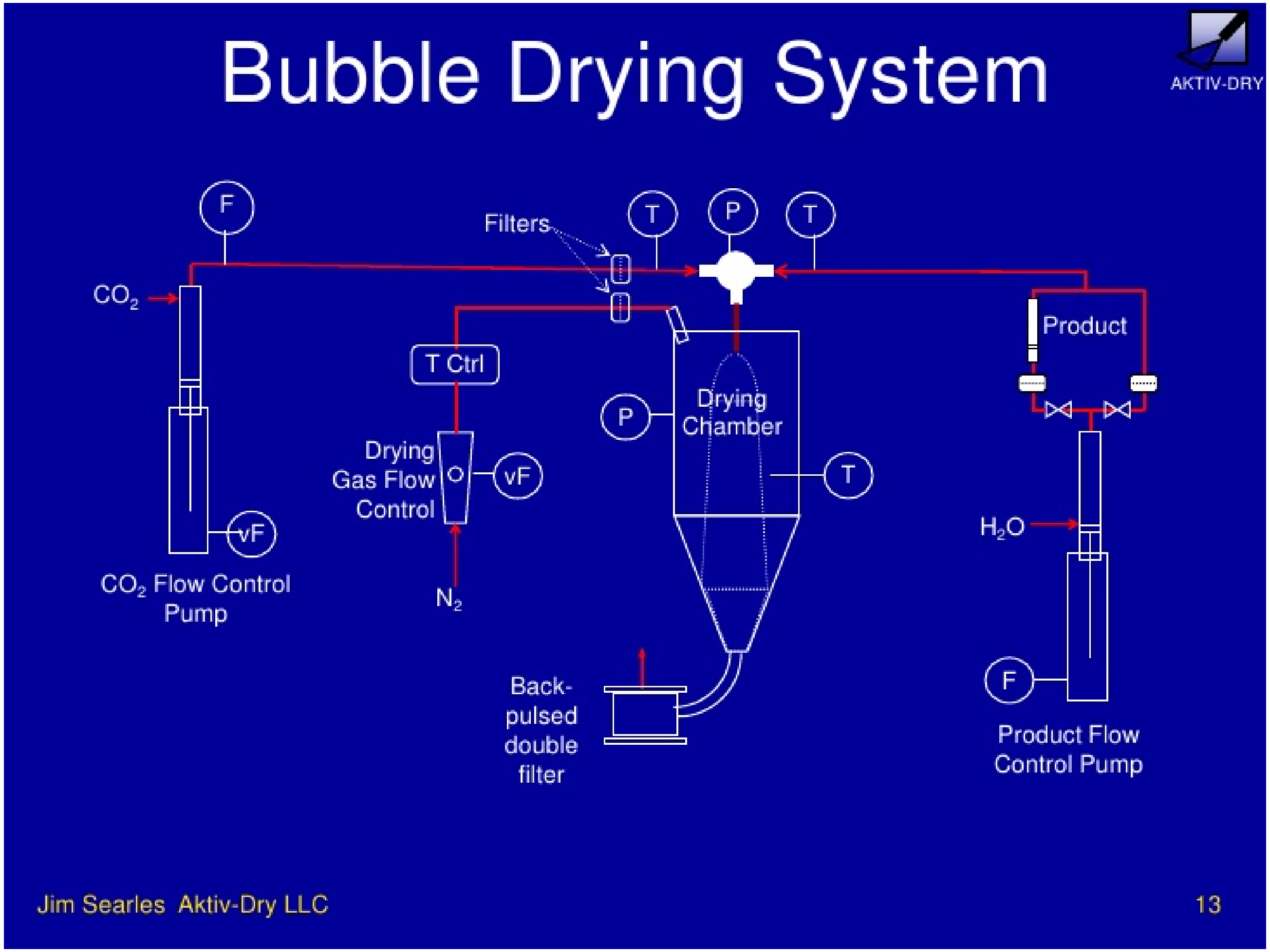
# Supercritical $CO_2$ cleaning





Unitech Annemasse is a French company that uses $CO_2$ for machine cleaning. The environmental impact of the process is negligable as there are no solvents, pollutants are removed without additives.

# $CO_2$ alternative to lyophilization




Aktiv Dry is a Boulder, Colorado company.

AKTIV-DRY

# Bubble Dried Particles