The Second Law of Thermodynamics (Chapter 4)

First Law: Energy of universe is constant:

\[ \Delta E_{\text{system}} = - \Delta E_{\text{surroundings}} \]

Second Law: New variable, \( S \), entropy. Changes in \( S, \Delta S \), tell us which processes made possible by first law actually occur spontaneously.
Entropy: Statistical Definition

What is the entropy change for gas to go from $V_1$ to $V_2$?

Start with 1 atom:

After removing barrier:

- Probability of finding atom in $V_2 = 1$
- Probability of finding atom in $V_1 = 1/2$
Entropy: Statistical Definition

N atoms:

Probability of finding all N atoms in $V_1 = (1/2)^N$

Call this probability $W$: $W = (1/2)^N$

What is probability of finding $N = 100$ atoms all in half the container?

$W = (1/2)^{100} = 8 \times 10^{-31}$
Entropy: Statistical Definition

$S$, entropy is a measure of probability, $W$.

Want $S$ to be extensive, like $U$ and $H$.

Is $W$ extensive? **No**: In our example, $W = (1/2)^N$, so $W$ is not proportional to $N$ (amount of material).

Define entropy:  

$$S = k_B \ln W$$

Boltzmann’s constant:  

$$k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$$

Entropy extensive:  

$$S = k_B \ln W = k_B \ln (1/2)^N = N k_B \ln (1/2)$$

With this definition $S$ is proportional to $N$. 
Entropy: Statistical Definition

Example: $\Delta S = S_2 - S_1$ for isothermal expansion from $V_1$ to $V_2$.

$$S_1 = k_B \ln W_1 \quad \quad S_2 = k_B \ln W_2$$

$$\Delta S = S_2 - S_1 = k_B (\ln W_2 - \ln W_1) = k_B \ln \frac{W_2}{W_1}$$

We know:

$$W_1 = (c V_1)^N$$
$$W_2 = (c V_2)^N$$

$$\Delta S = k_B \ln \frac{W_2}{W_1} = k_B \ln (\frac{V_2}{V_1})^N = k_B N \ln (\frac{V_2}{V_1})$$

$$\Delta S = N k_B \ln (\frac{V_2}{V_1}) = n R \ln (\frac{V_2}{V_1})$$
Entropy: Statistical Definition

\[ \Delta S = N k_B \ln \left( \frac{V_2}{V_1} \right) = n R \ln \left( \frac{V_2}{V_1} \right) \]

Example:

- Calculate \( \Delta S \) when 2.0 moles of ideal gas expand isothermally from 1.5 L to 2.4 L.

- What is the probability that it spontaneously contracts back to 1.5 L?
Entropy: Thermodynamic Definition

Consider isothermal, reversible expansion of ideal gas.

First law: \[ \Delta U = q + w. \]

For ideal gas, if \( T \) is constant \( \Delta U = 0. \)

\[ w_{rev} = - n R T \ln (V_2 / V_1) = -q_{rev} \quad (\Delta U = 0, \text{ so } w = -q) \]

Then: \[ q_{rev} = n R T \ln (V_2 / V_1) = T \Delta S \]

\[ \Delta S = \frac{q_{rev}}{T} \]

Entropy change = \frac{\text{heat absorbed in reversible process}}{\text{temperature at which process occurs}}
Entropy: Thermodynamic Definition

\[ \Delta S = \frac{q_{\text{rev}}}{T} \]

Entropy change = \( \frac{\text{heat absorbed in reversible process}}{\text{temperature at which process occurs}} \)

We have focused on system. What about surroundings?

Surroundings (rest of universe) are VERY large; any change to surroundings is reversible:

\[ q_{\text{surr}} \approx (q_{\text{surr}})_{\text{rev}} \]

\[ \Delta S_{\text{surr}} = \text{change of entropy of surroundings} = \frac{q_{\text{surr}}}{T} \]
Entropy Change of Universe

\[ \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \]

\[ \Delta S_{\text{surr}} = \text{change of entropy of surroundings} = \frac{q_{\text{surr}}}{T} \]

\[ \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \]

- Reversible, isothermal expansion:

\[ \Delta S_{\text{sys}} = \frac{q_{\text{sys}}}{T} \]

Also: heat emitted by system = heat absorbed by surroundings

\[ q_{\text{sys}} = -q_{\text{surr}} \]

\[ \Delta S_{\text{univ}} = \frac{q_{\text{sys}}}{T} + \frac{q_{\text{surr}}}{T} = -\frac{q_{\text{surr}}}{T} + \frac{q_{\text{surr}}}{T} = 0 \]
Entropy Change of Universe

- Reversible, isothermal expansion:
  \[ \Delta S_{\text{univ}} = 0 \]

- Irreversible, isothermal expansion:
  \[ \Delta S_{\text{sys}} > q_{\text{sys}} / T \]

Because \( q_{\text{sys}} = -w_{\text{sys}} \), and system does less work if process is irreversible.

\[ \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \]
\[ = \Delta S_{\text{sys}} + q_{\text{surr}} / T \]
\[ = \Delta S_{\text{sys}} - q_{\text{sys}} / T > 0 \]
Entropy Change of Universe

• Reversible, isothermal expansion:

\[ \Delta S_{\text{univ}} = 0 \]

• Irreversible, isothermal expansion:

\[ \Delta S_{\text{univ}} > 0 \]

Second law of thermodynamics: Entropy of universe (or isolated system) increases in an irreversible, spontaneous process and remains unchanged in a reversible process.
Example: 0.50 moles of ideal gas at 20 °C expands isothermally against a constant pressure of 2.0 atm from 1.0 L to 5.0 L. Calculate the change in entropy of the system, surroundings and universe. Is the process spontaneous?
Entropy changes

We saw that for isothermal expansion of ideal gas:

\[ \Delta S = n R \ln \left( \frac{V_2}{V_1} \right) \]

What is the entropy change for:

1. Mixing gases?
2. Phase transition?
3. Heating?
4. Chemical reaction?

1. Entropy change due to mixing of ideal gases.

\[ n \quad V \]

\[ n_a, V_a \quad P, T \quad n_b, V_b \quad P, T \]

\[ n = n_a + n_b \quad V = V_a + V_b \]
1. Entropy change due to mixing of ideal gases.

For gas A: \[ \Delta S_A = n_A R \ln \left( \frac{(V_A + V_B)}{V_A} \right) \]

For gas B: \[ \Delta S_B = n_B R \ln \left( \frac{(V_A + V_B)}{V_B} \right) \]

Entropy of mixing: \[ \Delta_{\text{mix}} S = \Delta S_A + \Delta S_B \]

Recall: \[ V \propto n \] (constant T, p) \hspace{1cm} \text{Avogadro's Law}

For gas A: \[ \Delta S_A = n_A R \ln \left( \frac{(n_A + n_B)}{n_A} \right) = -n_A R \ln \left( \frac{n_A}{n_A + n_B} \right) \]

\[ \Delta S_A = -n_A R \ln x_A \]

\( x_A = \) mole fraction A
1. Entropy change due to mixing of ideal gases.

Entropy of mixing: \[ \Delta_{\text{mix}} S = \Delta S_A + \Delta S_B \]

\[ \Delta S_A = -n_A R \ln x_A \]
\[ x_A = \text{mole fraction } A \]

\[ \Delta S_B = -n_B R \ln x_B \]
\[ x_B = \text{mole fraction } B \]

\[ \Delta_{\text{mix}} S = -n_A R \ln x_A - n_B R \ln x_B \]

\[ \Delta_{\text{mix}} S > 0 \quad (x_A, x_B < 1) \quad \text{Spontaneous process} \]
2. Entropy change due to phase transition.

At 0 °C and 1 atm, ice and water are in equilibrium. If we start with ice, heat is absorbed to form water.

Enthalpy change: \[ \Delta H = q_p \]

Heat of fusion (melting): \[ \Delta_{\text{fus}} H = q_p \]

Entropy of fusion: \[ \Delta_{\text{fus}} S = q_p / T_f = \Delta_{\text{fus}} H / T_f \]

(melting at equilibrium is reversible, so \( \Delta S = q_p / T \))

\( T_f = \) fusion or melting point = 273 K for water at 1 atm.

Similarly, for boiling: \[ \Delta_{\text{vap}} S = \Delta_{\text{vap}} H / T_b \]

\( T_b = \) boiling point = 373 K for water at 1 atm.
2. Entropy change due to phase transition.

Example: Given \( \Delta_{\text{fus}} H (H_2O) = 6.01 \text{ kJ mol}^{-1} \)

\[ \Delta_{\text{fus}} H (H_2O) = 6.01 \text{ kJ mol}^{-1} \]

\[ \Delta_{\text{vap}} H (H_2O) = 40.79 \text{ kJ mol}^{-1} \]

What are \( \Delta_{\text{fus}} S \) and \( \Delta_{\text{vap}} S \) for 1 mole \( H_2O \) at normal melting and boiling points?
3. Entropy change due to heating.

Consider heating system at constant p, $T_1 \rightarrow T_2$.

Entropy change:

\[ dS = \frac{dH}{T} = \frac{C_p}{T} dT \]

Integrate from $T_1$ to $T_2$:

\[ \int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} \frac{C_p}{T} dT = C_p \int_{T_1}^{T_2} \frac{dT}{T} \]

(We are assuming $C_p$ does not vary with T.)

Then:

\[ \Delta S = S_2 - S_1 = C_p \ln \left( \frac{T_2}{T_1} \right) = nC_p \ln \left( \frac{T_2}{T_1} \right) \]
3. Entropy change due to heating.

Example:

200 g $\text{H}_2\text{O}$ is heated from 10 °C to 20 °C at constant p. Given $\overline{C}_p(\text{H}_2\text{O}) = 75.3$ J K$^{-1}$ mol$^{-1}$ at these temperatures, what is $\Delta S$?
Third law of thermodynamics: Every substance has a finite, positive entropy, but at absolute zero, entropy may be zero, as for a perfect crystalline substance.

At \( T = 0 \) K, crystal usually in only 1 state \( \implies W(\text{crystal}) = 1 \).

(Recall: \( W = \text{probability for system to be in a state} \).)

\[ S = k_B \ln W = k_B \ln (1) = 0 \text{ for perfect crystal at } T = 0 \text{ K.} \]

Absolute \( U, H \) cannot be determined, only \( \Delta U \) and \( \Delta H \).

Absolute \( S \) can be determined, since \( S = 0 \) at \( T = 0 \) K.

At other temperatures we calculate:

\[ S = \int_0^T C_p \frac{dT}{T} \]
Third law of thermodynamics: Every substance has a finite, positive entropy, but at absolute zero, entropy may be zero, as for a perfect crystalline substance.

At temperature, $T$, we calculate:

$$ S = \int_{0}^{T} C_{p} \frac{dT}{T} $$

Entropy as function of $T$ for a particular substance:

Measure $C_{p}$ as function of $T$, then find $S$ using:

$$ S = \int_{0}^{T} C_{p} \frac{dT}{T} $$
4. Entropy change due to chemical reaction.

\[ \Delta_r S^\circ = \sum \nu \overline{S}^\circ(\text{products}) - \sum \nu \overline{S}^\circ(\text{reactants}) \]

\( \overline{S}^\circ = \) standard molar entropy \((J \text{ mol}^{-1} \text{ K}^{-1})\)

\( \nu = \) stoichiometric coefficient (no units)

Example: Standard molar entropy change at 298 K for

\[ \text{H}_2(g) + (1/2)\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \]
Gibbs and Helmholtz Energy

We would like to decide if a process occurs spontaneously by focusing on the system.

**Spontaneous:**

\[ \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \]

\[ = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} > 0 \]

\[ = \Delta S_{\text{sys}} - \frac{q_{\text{sys}}}{T} > 0 \]

(Now only system variables!)

At constant P: \[ q_{\text{sys}} = \Delta H_{\text{sys}} \]

At constant V: \[ q_{\text{sys}} = \Delta U_{\text{sys}} \]

At constant P, T: \[ \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \]

Spontaneous process
**Gibbs Energy**

At constant P, T: \[ \Delta S_{sys} - \Delta H_{sys} / T \] > 0

Spontaneous process

All variables are system variables: we can drop “sys” subscript.

**Gibbs energy, G:**

\[ G = H - TS \]

Isothermal process: \[ \Delta G = \Delta H - T \Delta S \]

Therefore: \[ \Delta G < 0 \] spontaneous \[ dG = 0 \] equilibrium

\( G \) is a state function (like \( H \) and \( S \))
Helmholtz Energy

\[ \Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{q_{\text{sys}}}{T} \quad > 0 \]

At constant V: \[ q_{\text{sys}} = \Delta U_{\text{sys}} \]

At constant V, T: \[ \Delta S_{\text{sys}} - \frac{\Delta U_{\text{sys}}}{T} \quad > 0 \]

Spontaneous process

Helmholtz energy, A:

\[ A = U - TS \]

Isothermal process:

\[ \Delta A = \Delta U - T\Delta S \]

Therefore:

\[ \Delta A < 0 \quad \text{spontaneous} \quad dA = 0 \quad \text{equilibrium} \]

A is a state function (like U and S)
Helmholtz Energy

Interesting relation between $\Delta A$ and maximum possible work

Isothermal process: $\Delta A = \Delta U - T \Delta S$

Maximum work attained during reversible process, where $T \Delta S = q_{\text{rev}}$

Then: $\Delta A = \Delta U - q_{\text{rev}} = (q_{\text{rev}} + w_{\text{rev}}) - q_{\text{rev}}$

(Note: $\Delta U = q_{\text{rev}} + w_{\text{rev}}$)

Therefore: $\Delta A = w_{\text{rev}}$, which is the maximum possible work the system can do.
Example: \( \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \)

T = 25 °C, what is maximum possible work \((\Delta_r A)\) ?

Assume:

\( \Delta_r U^\circ = \Delta_r H^\circ = -2801.3 \text{ kJ/mol} \) (we found this earlier)
Chemical Reactions:

If reaction is studied at constant p (usual case), then we compute Gibbs energy of reaction, $\Delta_r G^\circ$, to decide if the reaction is spontaneous.

$$\Delta_r G^\circ = \sum \nu \Delta_f G^\circ \text{(products)} - \sum \nu \Delta_f G^\circ \text{(reactants)}$$

$\Delta_f G^\circ =$ standard molar Gibbs energy of formation (kJ mol$^{-1}$)
$\nu =$ stoichiometric coefficient (no units)

$\Delta_f G^\circ$ listed for many compounds in Appendix 2.

How are values of $\Delta_f G^\circ$ measured?
Chemical Reactions:

$\Delta_f G^\circ \text{ listed for many compounds in Appendix 2.}$

How are values of $\Delta_f G^\circ$ measured?

Example: $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$

$\Delta_r G^\circ = \sum \nu \Delta_f G^\circ(\text{products}) - \sum \nu \Delta_f G^\circ(\text{reactants})$

$\Delta_r G^\circ = \Delta_f G^\circ(CO_2(g)) - \Delta_f G^\circ(C(\text{graphite})) - \Delta_f G^\circ(O_2(g))$

Convention:

$\Delta_f G^\circ(C(\text{graphite})) = \Delta_f G^\circ(O_2(g)) = \Delta_f G^\circ(\text{most stable form}) = 0$

$\Delta_r G^\circ = \Delta_f G^\circ(CO_2(g))$

How do we measure $\Delta_r G^\circ$? $\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$
Chemical Reactions:

$\Delta_f G^\circ$ listed for many compounds in Appendix 2.

How are values of $\Delta_f G^\circ$ measured?

Example: $C$(graphite) + $O_2$(g) $\rightarrow$ $CO_2$(g)

How do we measure $\Delta_r G^\circ$? 

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$

$\Delta_r H^\circ = -393.5$ kJ mol$^{-1}$ (measure with calorimeter)

$\Delta_r S^\circ = S^\circ(CO_2(g)) - S^\circ(C$(graphite$)) - S^\circ(O_2(g))$

$$= (213.6 - 5.7 - 205.0) \text{ J K}^{-1} \text{ mol}^{-1} = 2.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$\Delta_f G^\circ = \Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$

$$= -393.5 \text{ kJ mol}^{-1} - (298 \text{ K})(2.9 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})$$

$$= -394.4 \text{ kJ mol}^{-1}$$

Direct method to find $\Delta_f G^\circ(CO_2(g))$
Dependence of Gibbs energy on T and p:

Some thermodynamic relations:

\[ G = H - TS \quad \rightarrow \quad dG = dH - TdS - SdT \]
\[ H = U + pV \quad \rightarrow \quad dH = dU + pdV + Vdp \]
\[ dU = dq + dw, \quad dq = TdS, \quad dw = -pdV \]

Putting together: \[ dH = TdS - pdV + pdV + Vdp \]
\[ dG = Vdp - SdT \]

Constant p, variable T: \[ dp = 0 \quad \rightarrow \quad dG = -SdT \]

\[ \left( \frac{\partial G}{\partial T} \right)_p = -S \]

\( S > 0 \), so \( G \) decreases with increasing \( T \) at constant \( p \).
Dependence of Gibbs energy on $T$ and $p$:

\[ dG = V dp - S dT \]

**Constant $p$, variable $T$:**
\[
\left( \frac{\partial G}{\partial T} \right)_p = -S \\
S > 0, \text{ so } G \text{ decreases with increasing } T \text{ at constant } p.
\]

**Constant $T$, variable $p$:**
\[
\left( \frac{\partial G}{\partial p} \right)_T = V \\
V > 0, \text{ so } G \text{ increases with increasing } p \text{ at constant } T.
\]

Consider ideal gas at constant $T$:
\[ dG = V dp \]
\[
\int_{G_1}^{G_2} dG = \int_{p_1}^{p_2} V dp = nRT \int_{p_1}^{p_2} \frac{dp}{p} \quad \rightarrow \quad \Delta G = nRT \ln \left( \frac{p_2}{p_1} \right)
\]
Dependence of Gibbs energy on T and p:

Consider ideal gas at constant T:

\[ dG = Vdp \]

\[
\int_{G_1}^{G_2} dG = \int_{p_1}^{p_2} Vdp = nRT \int_{p_1}^{p_2} \frac{dp}{p} \quad \Rightarrow \quad \Delta G = nRT \ln \left( \frac{p_2}{p_1} \right)
\]

Example: 0.590 mol ideal gas at 300 K and 1.5 bar is compressed to 6.9 bar. What is \( \Delta G \)?
Gibbs Energy and Phase Equilibria

At some T and p it’s possible that for a substance 2 phases can coexist. The condition for this is:

\[ G_\alpha = G_\beta \]

\( \alpha \) = phase (such as solid), \( \beta \) = different phase

If T or p changes so \( G_\text{solid} > G_\text{liquid} \) some solid melts to liquid, lowering \( G \) of the substance. This helps us understand phase diagrams.

At given p, T:
\( G_\alpha \) is lowest for phase indicated.
How does molar Gibbs energy of solid, liquid or vapor depend on p and T?

Consider T: \( \left( \frac{\partial G}{\partial T} \right)_p = -\bar{S} < 0 \) for any phase.

\[
\left( \frac{\partial G_{\text{solid}}}{\partial T} \right)_p = -\bar{S}_{\text{solid}} \quad \left( \frac{\partial G_{\text{liquid}}}{\partial T} \right)_p = -\bar{S}_{\text{liquid}} \quad \left( \frac{\partial G_{\text{vapor}}}{\partial T} \right)_p = -\bar{S}_{\text{vapor}}
\]

\( \bar{G} \) decreases with increasing T at constant p, for any phase.

In general:

\( \bar{S}_{\text{vap}} \gg \bar{S}_{\text{liquid}} > \bar{S}_{\text{solid}} \)
How does molar Gibbs energy of solid, liquid or vapor depend on $p$ and $T$?

Consider $p$: 

$$\left(\frac{\partial \bar{G}}{\partial p}\right)_T = \bar{V} > 0 \text{ for any phase.}$$

$ar{G}$ increases with increasing $p$ at constant $T$, for any phase.

In general:

$\bar{V}_{\text{vap}} \gg \bar{V}_{\text{liquid}}, \bar{V}_{\text{solid}}$

Usually:

$\bar{V}_{\text{liquid}} > \bar{V}_{\text{solid}}$

(not $H_2O$!)

\[p_2 > p_1\]
\[T_f' > T_f\]
\[T_b' > T_b\]
More quantitatively: *Clausius-Clapeyron Equation*

Consider 2 phases, \( \alpha \) and \( \beta \). At equilibrium, \( \overline{G}_\alpha = \overline{G}_\beta \), \( d\overline{G}_\alpha = d\overline{G}_\beta \).

Recall: \[ \begin{align*} 
d\overline{G}_\alpha &= \overline{V}_\alpha dp - \overline{S}_\alpha dT \\
d\overline{G}_\beta &= \overline{V}_\beta dp - \overline{S}_\beta dT \end{align*} \]

Then: \[ \left( \overline{S}_\beta - \overline{S}_\alpha \right) dT = \left( \overline{V}_\beta - \overline{V}_\alpha \right) dp \]

Or: \[ \frac{dp}{dT} = \frac{\Delta \overline{S}}{\Delta \overline{V}} = \frac{\text{Change in molar entropy for } \alpha \rightarrow \beta}{\text{Change in molar volume for } \alpha \rightarrow \beta} \]

At equilibrium: \[ \Delta \overline{S} = \frac{\Delta \overline{H}}{T} \rightarrow \frac{dp}{dT} = \frac{\Delta \overline{H}}{T \Delta \overline{V}} \]

\( T \) = phase transition temperature, such as \( T_f \) or \( T_b \).

Clapeyron Equation gives slope of phase equilibria.
More quantitatively: Clausius-Clapeyron Equation

\[
\frac{dp}{dT} = \frac{\Delta H}{T \Delta V}
\]

Clapeyron Equation

\( T \) = phase transition temperature, such as \( T_f \) or \( T_b \).

Clapeyron Equation gives slope of phase equilibria.

Example: Calculate slope of solid-liquid equilibrium curve, \( dp/dT \), at \( T = 273.15 \text{ K} \) in atm K\(^{-1} \) for \( \text{H}_2\text{O} \), given:

\[
\Delta_{\text{fus}} \overline{H} = 6.01 \text{ kJ/mol} \quad \overline{V}_L = 0.0180 \text{ L/mol} \quad \overline{V}_S = 0.0196 \text{ L/mol}
\]
More quantitatively: Clausius-Clapeyron Equation

Calculation of $dp/dT$ easier for liquid $\rightarrow$ vapor, solid $\rightarrow$ vapor transition:

$$\Delta_{vap} \bar{V} = \bar{V}_{vapor} - \bar{V}_{condensed} \approx \bar{V}_{vapor} = RT / p \quad \text{ (ideal gas)}$$

$$\frac{dp}{dT} = \frac{\Delta_{vap} \bar{H}}{T \Delta_{vap} \bar{V}} \approx \frac{\Delta_{vap} \bar{H}}{T \bar{V}_{vap}} \approx \frac{\Delta_{vap} \bar{H}}{T(RT / p)} = p \frac{\Delta_{vap} \bar{H}}{RT^2}$$

Note: Everything on the right is $> 0$, so $dp/dT > 0$.

Rearrange and integrate:

$$\int_{p_1}^{p_2} \frac{dp}{p} = \int_{T_1}^{T_2} \frac{\Delta_{vap} \bar{H}}{R T^2} dT \quad \Rightarrow \quad \ln\left(\frac{p_2}{p_1}\right) = - \frac{\Delta_{vap} \bar{H}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Clausius-Clapeyron Equation
Phase diagram of water:

Critical point: L-V no longer distinguishable
Phase diagram of \( \text{CO}_2 \):

Critical point: L-V no longer distinguishable

Liquid unstable for \( p < 5 \text{ atm} \). At \( p = 1 \text{ atm} \), only solid, vapor
Phase Rule: Gibbs derived phase rule: \[ f = c - p + 2 \]

\( c \) = number of components

\( p \) = number of phases present

\( f \) = degrees of freedom (number of intensive variables, such as \( T \), \( p \), composition, that can be changed independently without disturbing number of phases in equilibrium)

Example: What is \( f \) for pure water

(a) in vapor phase?

(b) along phase boundary?

(c) at triple point?